Understanding Our Protoplanetary Disk by
Chemical Analysis of Components in Meteorites

Luke Daly

This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University

March 2017
DECLARATION OF AUTHORSHIP

I, Luke Daly, declare that to the best of my knowledge that this thesis entitled, ‘Understanding Our Protoplanetary Disk by Chemical Analysis of Components in Meteorites’ contains no material previously published by any other person except where due acknowledgement has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works. I warrant that I have obtained, where necessary, permission from the copyright owners to use any third-party copyright material reproduced in the thesis (e.g. questionnaires, artwork, unpublished letters), or to use any of my own published work (e.g. journal articles) in which the copyright is held by another party (e.g. publisher, co-author).

Luke Daly

Date

20/02/17
ABSTRACT

Understanding how our Solar System formed is one of the primary aims of planetary science. Primitive meteorites and the components within them are the only surviving remnants from the birth of our Solar System. As such, they preserve a record of early Solar System processes; from mineral formation in the protoplanetary disk, to the accretion of planet sized objects. Detailed analysis of meteoritic components provide clues to the conditions present when these grains formed.

Refractory metal nuggets (RMNs) are sub-micrometre alloys composed of highly siderophile elements and are thought to be among the first phases to condense in the protoplanetary disk. The highly siderophile and refractory nature of RMNs makes them resistant to subsequent alteration during nebula and parent body processes, while their high formation temperatures suggest they may have formed even before Ca-Al-rich Inclusions (CAIs), the oldest materials found in primitive meteorites. Therefore, through analysis of RMNs we can determine the processes which were prevalent when the first solid objects formed in the protoplanetary disk, and potentially some processes that occurred prior to Solar System formation.

The work contained within this thesis used a suite of novel techniques to extract detailed information relating to the composition, crystallography, and isotopic make up of RMNs. These analyses have informed our understanding about how this phase formed and was affected during processing in the protoplanetary disk and parent body.

The small size of RMNs had made them difficult to analyse in large numbers.
This work derived an approach that combined synchrotron radiation and Feature mapping to rapidly identify RMNs \textit{in situ} within meteorite thin sections. This approach identified >100 RMNs, revealing that they are not only found in CAIs but in all meteoritic components.

Geochemical analysis of these RMNs combined with those already reported in the literature revealed a diverse range of compositions. These were compared to predicted RMN compositions from established formation mechanisms such as condensation in the nebula, crystallisation from a melt, and parent body alteration. While many RMN compositions can be reconciled by these processes there remains a population of RMNs in these analyses that are inconsistent with any of the proposed mechanisms. The data suggest that the protoplanetary disk may have inherited a diverse RMN population from the giant molecular cloud fragment, which collapsed to form our Solar System. This chemical heterogeneity was not completely overprinted during processing in the protoplanetary disk.

Crystallographic analysis of RMNs using the transmission Kikuchi diffraction crystallographic mapping technique, revealed textures which had not been reported previously. These included annealing twins which have the potential to be used as a coarse thermometer for nebula heating events. Crystallographic observations of both RMNs and their host indicate that some RMNs may form during sulphidation of metal grains, as Ir and Pt are preferentially concentrated in the metal, which could constrain the sulphur fugacity of the nebula. Other observations of RMNs indicate that they can also act as nucleation sites for other phases during crystallisation of CAIs. Several RMNs had textures which imply they existed prior to their host phase.

Trace element geochemistry using atom probe microscopy revealed some
RMNs contain sulphur which, coupled with electron back scatter diffraction of the host inclusion of the RMNs, imply that the S was entrained into the RMN while the RMN was ‘free floating’ in the protoplanetary disk. Sulphidation and RMN formation are thought to occur in different regions of the protoplanetary disk. This requires RMNs and other refractory materials to migrate rapidly between a region close to the proto-sun and 1.5 AU early in the lifetime of the protoplanetary disk before the cessation of CAI formation, likely to be in the order of 100 kyr.

Finally, isotopic data was extracted from RMNs by atom probe microscopy. Isotopic analysis using atom probe had only been reported in four publications prior to this work. This work constrained the current sensitivity of the atom probe technique for isotopic analysis of highly siderophile elements and proposed a current best practice for the extraction of isotopic information from atom probe data. This procedure was able to robustly reproduce isotopic abundances from synthetic pure Re and Os and a complex alloy containing several of the highly siderophile elements which had known isotopic abundances from thermal ionisation mass spectrometry. Reducing the RMN data sets using this methodology indicated that most RMNs have solar isotopic abundances within the current sensitivity of the atom probe technique. Re-Os geochronology of five RMNs hosted within refractory inclusions plot on a line consistent with the Solar System isochron indicating these RMNs were well equilibrated with the protoplanetary disk and likely formed in the Solar System. However, three RMNs were anomalous; two had anomalously high $^{187}\text{Os}/^{189}\text{Os}$, while the third RMN hosted within a sulphide rim had $^{187}\text{Os}/^{189}\text{Os}$ below that of the initial Solar System value. The RMN with low $^{187}\text{Os}/^{189}\text{Os}$ as well as a very low Re content yield a minimum Re-depletion model age of 5.5 Ga and is therefore pre-solar and the oldest material dated so far.
Gentlemen, I would rather believe that two Yankee professors would lie than believe that stones fall from heaven

-President Thomas Jefferson

The most exciting phrase to hear in science, the one that heralds new discoveries, is not ‘Eureka!’ (I’ve found it), but ‘That’s funny…’

-Isaac Asimov

Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained

-Marie Curie

We look at science as something very elite, which only a few people can learn. That’s just not true. You just have to start early and give kids a foundation. Kids live up, or down, to expectations.

-Mae Jemison
This thesis is dedicated to my loving grandparents
Evelyn Singleton, P. W. ‘Mick’ Singleton, Philomena ‘Phyllis’ Daly and Patrick Daly
R.I.P.
ACKNOWLEDGEMENTS

The work presented in this thesis was funded by the Australian Research Council as part of the Australian Laureate Fellowship scheme and carried out at the Department of Applied Geology at Curtin University. I would also like to acknowledge the support and resources provided by the Australian Synchrotron, Melbourne; The Australian Centre for Microscopy and Microanalysis, The University of Sydney; The Centre for Microscopy, Characterisation and Analysis, The University of Western Australia; The John de Laeter Centre, and The Advanced Resource Characterisation Facility, at Curtin University.

I also wish to acknowledge the support and guidance I have received from colleagues, friends and family throughout my PhD, without which this thesis would not have been possible and without whom I would not have become the academic, researcher and person I am today. You have my eternal gratitude.

- **My primary supervisor Professor Phil Bland** Thank you so much for allowing me to be a small part of this incredible research project in this beautiful country. I’m so, so grateful for the opportunities you provided which were above and beyond anything I could have imagined. Your guidance, patience, trust, advice and pep-talks (where you seemed to know innately the right moment to encourage and also the right moment to give me a kick in the right direction), have all helped me develop the skills I’ll need as an independent researcher in academia. You took my spark of curiosity and fanned it into an inferno. You’ve been so much more than my boss, you’ve also been my mentor, my inspiration and my friend. I cannot thank you enough!
Acknowledgements

- My associate supervisors Professor Gretchen Benedix, Dr. Kathryn Dyl and Dr. Nicholas Timms – Thanks so much for all your help and support thought my PhD project. Katie thanks so much for all your advice and training at the start of my project which set me up well for the rest of my PhD. Gretchen thanks for training us in meteorite characterisation and trusting us to work on such valuable samples found by the desert fireball network. Nick thanks for all your advice and support particularly in the last few weeks leading up to submission. I will always remember the adventures we had during Metsoc. 2014.

- My collaborators around the world It has been an honour to work with so many wonderful people. Thanks for putting up with my visits and opening the door to how fun collaborative research can be. I hope to continue working with all of you in the future. It’s been a blast!

- My colleague Lucy Forman Thanks for always being there for me through everything. For all the tea, coffee, cakes, hugs, emotional support and stimulating chats. I would not have been able to do this without you.

- The Desert Fireball Network team It has been amazing to work with such a great bunch of people from so many different disciplines that all meld together to make this beautiful project work. I will treasure all the adventures we had in the field.
Acknowledgements

- **My family and friends** – To all my family and friends around the world thanks for all your support and belief in me. Particularly my Mum Dad and Brother for always supporting me and being the rock I can always count on wherever I am. To my auntie, Angie thanks for the mutual support as we both completed our PhDs. Thanks to my friends and colleagues in the DFN and fireballs in the sky for providing a creative outlet which is also full of fun science and the feeling of being part of something bigger than myself. Thanks to my office buddies over time for keeping me sane and putting up with me particularly Mary, Jen and Sarah, and all the other great friends in applied geology especially Charlotte for all the doughnuts and coffee. To everyone back in the UK for forgiving me for moving to the other side of the world. To all my friends in Perth, from Rugby, Lindy Hop, Rhythmos, Musical Theatre, and Abby and Sharni for all the great times which made my life in Perth so rich and wonderful. Last but not least ‘The Gang’, you know why! Molly, Em and Kim just never change from exactly as you are.
 CONTENTS

Declaration of Authorship iii
Abstract v
Acknowledgements xiii
Contents xvii
List of Publications xxvii
List of Additional Publications xxxi
List of Figures xxxvii
List of Tables lv
List of Symbols lix

1 Introduction 1
  1.1 The importance of meteorites .......................... 5
    1.1.1 Chondrites ........................................... 5
    1.1.2 Carbonaceous chondrites ............................. 8
  1.2 Ca-Al-Rich Inclusions (CAIs) ........................... 9
  1.3 Refractory Metal Nuggets ................................. 12
    1.3.1 Formation mechanisms ............................... 13
    1.3.2 Compositional heterogeneity ......................... 15
# Table of Contents

1.3.3 Analytical techniques ........................................ 16
1.3.4 Research prospects ............................................ 17

1.4 Research Design .................................................. 18
1.4.1 Micrometre-scale characterisation .............................. 20
1.4.2 Nanometre scale characterisation ............................... 28
1.4.3 Atomic scale characterisation .................................. 31

1.5 Research outcomes ............................................... 36
1.5.1 Chapter 2 - In situ analysis of Refractory Metal Nuggets in carbonaceous chondrites ........................................ 36
1.5.2 Chapter 3 - Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach ........................................ 38
1.5.3 Chapter 4 - Nebula sulphidation and migration of ‘free floating’ refractory metal nuggets revealed by atom probe microscopy ........................................ 39
1.5.4 Chapter 5 - Isotopic analysis of Refractory Metal Nuggets with atom probe microscopy ........................................ 40

1.6 References ......................................................... 41

2 Paper 1 – In situ analysis of Refractory Metal Nuggets in carbonaceous chondrites .......................... 63
2.1 Introduction ......................................................... 66
2.2 Method .............................................................. 71
2.2.1 X-Ray Fluorescence Microscopy ................................ 71
2.2.2 Scanning Electron Microscopy .................................. 72
2.2.3 Condensation model and precipitation proxy ................. 76
2.3 Results .............................................................. 77
2.3.1 Synchrotron ....................................................... 77

xviii
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.2 Synchrotron to SEM</td>
<td>78</td>
</tr>
<tr>
<td>2.4 Discussion</td>
<td>88</td>
</tr>
<tr>
<td>2.4.1 Evaluation of the database</td>
<td>88</td>
</tr>
<tr>
<td>2.4.2 RMNs within CAIs, chondrules and matrix</td>
<td>90</td>
</tr>
<tr>
<td>2.4.3 RMN compositional diversity</td>
<td>91</td>
</tr>
<tr>
<td>2.5 Conclusions</td>
<td>109</td>
</tr>
<tr>
<td>2.6 Acknowledgements</td>
<td>110</td>
</tr>
<tr>
<td>2.7 Appendix A. Supplementary data</td>
<td>111</td>
</tr>
<tr>
<td>2.8 References</td>
<td>111</td>
</tr>
<tr>
<td>3 Paper 2 – Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach</td>
<td>119</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>122</td>
</tr>
<tr>
<td>3.2 Methods</td>
<td>127</td>
</tr>
<tr>
<td>3.2.1 EBSD</td>
<td>127</td>
</tr>
<tr>
<td>3.2.2 Focused Ion Beam</td>
<td>128</td>
</tr>
<tr>
<td>3.2.3 TKD</td>
<td>128</td>
</tr>
<tr>
<td>3.2.4 Data reduction</td>
<td>128</td>
</tr>
<tr>
<td>3.2.5 TEM</td>
<td>130</td>
</tr>
<tr>
<td>3.3 Results</td>
<td>130</td>
</tr>
<tr>
<td>3.3.1 Allende - region A1</td>
<td>130</td>
</tr>
<tr>
<td>3.3.2 Allende - region A2</td>
<td>134</td>
</tr>
<tr>
<td>3.3.3 Allende - region A3</td>
<td>136</td>
</tr>
<tr>
<td>3.3.4 ALH 77307 - region ALH1</td>
<td>136</td>
</tr>
<tr>
<td>3.3.5 Vigarano - region V1</td>
<td>138</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>3.3.6</td>
<td>Vigarano - region V2</td>
</tr>
<tr>
<td>3.4</td>
<td>Discussion</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Allende - region A1</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Allende - region A2</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Allende - region A3</td>
</tr>
<tr>
<td>3.4.4</td>
<td>ALH 77307 - region ALH1</td>
</tr>
<tr>
<td>3.4.5</td>
<td>Vigarano - region V1 and V2</td>
</tr>
<tr>
<td>3.4.6</td>
<td>Summary</td>
</tr>
<tr>
<td>3.5</td>
<td>Conclusions</td>
</tr>
<tr>
<td>3.6</td>
<td>Acknowledgements</td>
</tr>
<tr>
<td>3.7</td>
<td>Supplementary material for Chapter 3</td>
</tr>
<tr>
<td>3.7.1</td>
<td>Supplementary material A</td>
</tr>
<tr>
<td>3.7.2</td>
<td>Supplementary material B</td>
</tr>
<tr>
<td>3.7.3</td>
<td>Supplementary material C</td>
</tr>
<tr>
<td>3.8</td>
<td>References</td>
</tr>
<tr>
<td>4</td>
<td>Paper 3 – Nebula sulfidation and evidence for migration of ‘free floating’ refractory metal nuggets revealed by atom probe microscopy</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>4.2</td>
<td>Methodology</td>
</tr>
<tr>
<td>4.3</td>
<td>Results</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Ultrarefractory Inclusion</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Refractory Metal Nuggets</td>
</tr>
<tr>
<td>4.4</td>
<td>Discussion</td>
</tr>
<tr>
<td>4.5</td>
<td>Conclusions</td>
</tr>
</tbody>
</table>
4.6 Acknowledgements .................................................. 196
4.7 Supplementary material for Chapter 4 ............................ 197
  4.7.1 Supplementary material A .................................. 197
  4.7.2 Supplementary material B .................................. 198
  4.7.3 Supplementary material C .................................. 199
  4.7.4 Supplementary material D .................................. 200
  4.7.5 Supplementary material E .................................. 201
4.8 References .............................................................. 201

5 Paper 4 – Isotopic analysis of Refractory Metal Nuggets using atom
probe microscopy ....................................................... 209
  5.1 Introduction .......................................................... 212
  5.2 Methods .............................................................. 218
    5.2.1 Samples ......................................................... 218
    5.2.2 Sample preparation .......................................... 218
    5.2.3 Atom probe microscopy (APM) ............................ 223
    5.2.4 Thermal ionisation mass spectrometry (TIMS) .......... 228
  5.3 Theoretical constraints on the technique ......................... 230
    5.3.1 Counting statistical uncertainty .......................... 230
    5.3.2 Theoretical sensitivity of isotopic abundance
          measurements .................................................. 232
  5.4 Evaluation of data reduction methods
      using pure Re and Os metals ................................... 234
    5.4.1 The effect of peak ranging methods ...................... 236
    5.4.2 The effect of elevated background ......................... 242
    5.4.3 The effect of ionic species ................................. 242

xxi
Table of Contents

L. Daly

5.4.4 Hydride formation .................................................. 245

5.5 Evaluation of data reduction methods from complex HSE alloys .................................................. 246

5.5.1 Deconvolution of peak overlaps .................................. 246

5.5.2 Reproducibility .......................................................... 252

5.5.3 Comparison with TIMS .................................................. 253

5.5.4 Recommended data reduction sequence for isotopic analysis using APM ............................................. 254

5.6 Isotopic analysis of RMNs with APM .................................. 256

5.6.1 Osmium isotopes .......................................................... 260

5.6.2 Iridium isotopes .......................................................... 262

5.6.3 Tungsten isotopes ......................................................... 262

5.6.4 Discussion ................................................................. 266

5.6.5 Re-Os geochronology ..................................................... 268

5.7 Conclusions ................................................................. 274

5.8 Acknowledgements ........................................................ 277

5.9 References ................................................................. 278

6 Thesis Conclusions .......................................................... 289

6.1 Future work ................................................................. 293

6.2 References ................................................................. 295

Appendices ................................................................. 300

A First Author Journal Publications ........................................ 301

A.1 Paper 1 – In situ analysis of Refractory Metal Nuggets in carbonaceous chondrites ........................................ 301
### A.2 Paper 2 – Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach ............................. 335

### A.3 Paper 3 – Nebula sulfidation and evidence for migration of ‘free floating’ refractory metal nuggets revealed by atom probe microscopy ......................... 365

### A.4 Paper 4 – Isotopic analysis of Refractory Metal Nuggets with atom probe. .................................................. 373

### B Co-Author journal publications and conference abstracts 381

#### B.1 Co-authored Paper A – Hidden Secrets of deformation: Impact-induced compaction within a CV chondrite. ................................. 381

#### B.2 Co-authored Paper B – Catching a falling star (or meteorite) - Fireball camera networks in the 21st Century. ............................. 397

#### B.3 Conference abstract A – Atom probe tomography of refractory metal nuggets .......................................................... 403

#### B.4 Conference abstract B – Composition of refractory metal nuggets implications for their origins. ................................. 411

#### B.5 Conference abstract C – Atom probe tomography and its application to refractory metal nuggets .......................................... 419

#### B.6 Conference abstract D – In situ analysis of refractory metal nuggets crystallography providing clues to early solar system events ........................................ 427

#### B.7 Conference abstract E – Crystallography of refractory metal nuggets identified within Ca-Al-rich inclusions, chondrules, and matrix of carbonaceous chondrites .................................................. 435
B.8 Conference abstract F — Transmission kikuchi diffraction applied to primitive grains in meteorites. ........................................ 441

B.9 Conference abstract G — In situ analysis of refractory metal alloys in carbonaceous chondrites: implications for early solar system processes. ........................................ 447

B.10 Conference abstract H — Early solar system events revealed by analysis of tiny nuggets. ........................................ 453

B.11 Conference abstract I — High resolution of tiny nuggets of platinum group elements in carbonaceous chondrites. ........................................ 461

B.12 Co-Authored Conference abstract A — Defining the crystallographic fingerprint of extraterrestrial treasures ........................................ 467

B.13 Co-Authored Conference abstract B — Recovering the primordial impact history of chondrites in unprecedented detail using massive EBSD datasets ........................................ 473

B.14 Co-Authored Conference abstract C — Constraining the Compositional Variety of Impactors at 1 AU Over the last 3.5 Ga: In Situ Identification and Analysis of 200 Meteoritic Grains in Lunar Soil ........................................ 479

B.15 Co-Authored Conference abstract D — Mineralogy and Petrology of the Murrili Meteorite ........................................ 485

Bibliography 491
LIST OF PUBLICATIONS INCLUDED AS PART OF THIS THESIS

This thesis compiles a collection of research papers that were either published, under review, submitted or in preparation at the time of writing this document. The relationship between the manuscripts are described in the introductory chapter. All papers have statement of co-authorships in Appendix A, alongside reprints of published papers.

The research papers contained within this thesis are listed below.


The formatting of each chapter within this thesis may appear to vary, and
may differ to the published form based on the requirements and formatting guidelines of each individual journal and this thesis. Due to the nature of this thesis as a composite of peer-reviewed manuscripts, there is a degree of repetition in the introductory sections of each chapter.
Several papers and conference abstracts were published during the research period but either not as a principal author or not peer-reviewed and so do not form part of the main thesis. These may be found in Appendix B.

The publications are listed below, including justification for their inclusion.


**Reason for inclusion** — I assisted in the collection of the electron backscatter diffraction and transmission Kikuchi diffraction data further demonstrating the potential of the technique described in Chapter 3.


**Reason for inclusion** — I assisted in the construction of the camera network and in the revision and editing of the manuscript.

Reason for inclusion – This work was presented as an invited oral presentation at an international conference and outlined the work in Chapter 4.


Reason for inclusion – This work was presented as an oral presentation at an international conference and outlined the work in Chapter 2.


Reason for inclusion – This work was presented as an oral presentation at an international conference and outlined the work in Chapter 4.

Reason for inclusion – This work was presented as an oral presentation at an international conference and outlined the work in Chapter 3.


Reason for inclusion – This work was presented as an oral presentation at an international conference and outlined the work in Chapter 3.


Reason for inclusion – This work was presented as a poster presentation at an international conference and outlined the work in Chapter 3.

Reason for inclusion – This work was presented as a poster presentation at an international conference and outlined the work in Chapter 2.


Reason for inclusion – This work was presented as an oral presentation at a domestic conference and outlined the work in Chapter 3.

Reason for inclusion — This work was presented as an oral presentation at a domestic conference and outlined the work in Chapter 2.


Reason for inclusion — I was a co-author of this work which was presented as an oral presentation at an international conference.


Reason for inclusion — I was a co-author of this work which was presented as an oral presentation at an international conference.

Reason for inclusion — I was a co-author of this work which was presented as an oral presentation at an international conference.


Reason for inclusion — I was a co-author of this work which was presented as an oral presentation at an international conference.
LIST OF FIGURES

1.1 Protoplanetary disk around HL Tau, a 1 Myr old star imaged by the Atacama Large Millimetre/submillimetre Array (ALMA). Credit: ALMA (NRAO/ESO/NAOJ), published in Yen et al. (2016). 2

1.2 Chondritic vs solar abundances of the elements indicating that chondrites are a close approximation to the bulk chemical composition of the Solar System and have not experienced extensive processing post-accretion. From Hutchison (2004), with data from Anders and Grevesse (1989). 7

1.3 XRF synchrotron RGB element map of a fluffy type A CAI from Vigarano CV3; Ca (red), Ni (green), Fe (blue). 10

1.4 Schematic diagram of processes relating to dust formation and migration, which are thought to occur within the protoplanetary disk, from Scott and Krot (2005). 12

1.5 SEM image of a RMN extracted from an acid residue from Berg et al. (2009). 14

1.6 Schematic diagram of the Local Electrode Atom Probe from Gault et al. (2012). 32

2.1 Bulk Synchrotron spectrum from Allende; with the raw data depicted by the bold line and the fit calculated by GeoPIXETM indicated by the dashed line. The solid and thinner black line signifies the background contribution to the spectra. Taking into account contributions such as the large iron peak and secondary pile up peak, along with the Compton scatter region, the detection limits are highlighted by the greyscale gradient map. The location of the Lα peaks for Os, Ir and Pt are highlighted in red and sit in the region of highest sensitivity and lowest detection limits. Image adapted after Dyl et al. (2014). 73
2.2 Synchrotron element maps (left hand side) and corresponding SEM back scattered electron (BSE) images (right hand side) of the same regions in meteorites, indicating how elemental hotspots of PGEs in Synchrotron maps can be used to find RMNs on the surface of meteorite samples. Hotspots of the PGEs in synchrotron data (Ir in red and Os in green) relate to RMN localities on the surface of the thin section (bright points). The upper images were from the ALH 77307 meteorite and revealed RMNs within a Sc-Zr-rich CAI-like inclusion, and the lower images were from the Vigarano meteorite and revealed a single RMN within a zoned 'fluffy' type A CAI. ........................................ 79

2.3 SEM backscatter images of RMNs in all meteoritic components a) RMN hosted in matrix from ALH 77307 in the vicinity of a CAI b) RMN hosted in a ákermanite (Ak) and perovskite (Per)-rich CAI in ALH 77307, c) RMN hosted in a chondrule in Allende within forsterite (Fo) d) RMNs hosted within a (Fe-Ni)S rim around a chondrule in Allende. ........................................ 80

2.4 At. % abundances of Fe, Ni and PGE elements vs the wt. % total pre-normalisation of the RMN component in the EDS spectra for all samples from this study. The line in each graph represents a line of best fit through the data. These show relatively shallow trends which are significantly smaller than the overall compositional variability in at. % for each element. Therefore, it is unlikely that our re-normalisation calculations have introduced any significant bias to our dataset. ........................................ 89

2.5 RMN compositions from this study (orange), the average RMN from this study (red) and RMNs from our literature database (greyscale). PGEs have been plotted in order of increasing volatility and have been normalised to Ru then CI (top), or Pt then CI (bottom). These RMNs show a wide range of individual RMN compositions. However, the average RMN from this study has approximately CI chondrite relative abundance for these elements. 92

2.6 Total PGE vs Fe and total PGE vs Ni plots by host phase (this study and the literature) indicating a well defined Fe-mixing trend (black polygon) a more dispersive Ni-mixing trend (red polygon) and a low PGE cluster (green triangle), which is dominated by sulphide phases. ........................................ 93
2.7 A comparison of Fe, Ni and PGE abundance in wt. % vs calculated equilibrium condensation temperature at $10^{-4}$ bar for RMNs from this study (green), and the literature (red). The data are plotted in the same format as Berg et al. (2009). RMN compositions exhibit good correlations with Fe and Mo but very poor correlations with Ni, Ru, Rh, Ir and Pt.  

2.8 Total PGE vs Fe abundance in at. %. These show all RMNs from this study and the literature are indicated by blue diamonds. The RMNs which match predicted equilibrium condensation compositions at $10^{-4}$ bar to within 5 at. % (top graph), and 15 at. % (bottom graph) are indicated with red diamonds.  

2.9 Total PGEs vs Fe abundance in at. % for RMNs detailed in this study (red) and the literature (black) as well as pre-solar RMNs from Croat et al. (2013) (blue), synthetic RMNs produced by precipitation from Schwander et al. (2015a) (green), and our condensation model calculated at $10^{-4}$ bar.  

2.10 Elemental ratio plots of each PGE vs Ru comparing RMNs from this study and the literature (blue) with precipitation derived RMNs from Schwander et al. (2015a) (red) and our equilibrium condensation model at $10^{-4}$ bar (purple curve). These graphs show very weak or absent correlations of observed RMNs with predicted condensation model curves or synthetic RMNs formed by precipitation.  

2.11 Variability of total PGE vs Fe abundances (at. %) of RMNs in this study and the literature from the meteorites Allende, ALH 77307, Murchison, Leoville, Orgueil, Ornans, Vigarano, Acfer 094, Adelaide and those found in cosmic spherules.  

2.12 RMN average compositions by host phase and meteorite from this study (Table 2.4). PGEs have been plotted in order of increasing volatility and have been normalised to Ru then CI (top), or Pt then CI (bottom). The average compositions of each meteorite exhibit approximately CI trends. Allende exhibits a slight depletion in Mo and W, while Vigarano shows a large W enrichment.  

2.13 Ir/Os (left) and Ir/Pt (right) plots of RMNS from this study with respect to their host phase. These plots reveal that sulphide CAI and chondrule hosted RMNs have a similar spread of PGE abundance ratios.
3.1 Characteristics of Allende - region A1: EBSD analyses of 3 RMNs are contained within a chondrule-hosted sulphide nodule. a) A low magnification back scatter electron (BSE) image of region A1, indicating the wider context of the chondrule host with associated sulphide nodules, b) A BSE image of the RMNs hosted within a sulphide, with a nearby forsterite grain (Fo) as well as associated Cr-spinel (Chr) inclusions. The numbers indicate where the EDS measurements were taken from in Table 3.1, c) An EBSD phase map overlain on a band contrast image indicating RMNs (yellow), troilite (blue) Cr-Spinel (red) and forsterite (green), the pentlandite sulphide did not index well and is located within the black area, d) An EBSD Euler image overlain on a band contrast image indicating crystallographic orientations of each phase, e) A lower hemisphere stereographic projection of RMN crystallographic axes (100), (110), and (111). The crystallographic orientations of the RMNs revealed all RMNs have the same crystallographic alignment, f) A lower hemisphere stereographic projection of the orientation of the forsterite crystallographic axes (100), (010), and (001). The red square, circle and hexagon on stereographic projections e) and f) indicate that the RMNs and the forsterite share a [100] axis. . . . . . . . . . . 132
3.2 Characteristics of Allende - region A1: TKD analyses from a FIB-produced TEM lamellae containing an RMN bearing sulphide nodule hosted in a chondrule. a) A BSE image of the RMNs in context prior to extraction. The TEM lamellae was extracted as indicated by the red rectangle. Associated minerals are forsterite (Fo), Cr-spinel (Chr) and sulphide, b) A TKD fore-scatter detector (FSD) image of the TEM lamellae RMNs and associated minerals are labelled forsterite (Fo), mackinawite (Mk), Cr-spinel (Chr), pentlandite (Pn) and troilite (Tro), c) TKD phase map, revealing five more RMNs (yellow) which were buried beneath the surface of the sample, the numbers relate to EDS measurements detailed in Table 3.2, d) TKD Euler map showing crystallographic orientations of each phase in the section, e) Lower hemisphere stereographic projection of crystallographic orientations of the RMNs revealed a consistent crystallographic orientation for all RMNs, f) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite confirming a shared [100] axis between the RMNs and forsterite observed in Figure 3.1, denoted by the red circle square and hexagon, g) Lower hemisphere stereographic projection of crystallographic orientations of pentlandite, indicating no COR between the RMN and the pentlandite h) Lower hemisphere stereographic projection of crystallographic orientations of the troilite, indicating no COR between the RMN and the troilite.
3.3 Characteristics of Allende region A2: TKD analyses from a FIB-produced TEM lamellae of an RMN-bearing forsterite inclusion hosted in a CAI. a) A low magnification BSE image of region A2 indicating the wider context of the CAI host, b) A BSE image of the RMNs (bright spots) in context prior to extraction. The TEM lamellae was extracted as indicated by the red rectangle. RMNs and associated minerals were labelled forsterite (Fo), pentlandite (Pn), and spinel (Spl), c) A FSD image of the TEM lamellae indicating the RMN bearing region at the top and revealing the surrounding spinel has $120^\circ$ grain boundary intersections and $2 \sim 5 \mu m$ grain size. RMNs and associated minerals are labelled forsterite (Fo), pentlandite (Pn), molybdenite (Mo), and spinel (Spl), d) TKD phase map, revealing a large RMN associated with molybdenite and smaller spherical RMNs suspended in forsterite. The numbers relate to EDS measurements in Table 3.2. The whole inclusion is encapsulated by spinel, e) Lower hemisphere stereographic projection of crystallographic orientations of the small RMN spheres revealing random crystallographic orientations for each RMN relative to each other, f) Lower hemisphere stereographic projection of crystallographic orientations of the spinel, g) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite, h) Lower hemisphere stereographic projection of crystallographic orientations of the pentlandite, i) Lower hemisphere stereographic projection of crystallographic orientations of the large RMN, j) Lower hemisphere stereographic projection of crystallographic orientations of molybdenite. The molybdenite and the large RMN are crystallographically aligned parallel to one another as the indicated by the red circles in i) and j).
3.4 Characteristics of Allende - region A3: EBSD analyses of a forsterite hosted RMN from a CAI. a) A low magnification FSD image of region A3 (red box) indicating the context of the RMN within the CAI, b) FSD image of Region A3 indicating where the EBSD dataset was acquired (red box), associated minerals are labelled forsterite (Fo), spinel (Spl) and diopside (Di), c) EBSD phase map indicating an RMN hosted within a forsterite grain, the number indicates the EDS measurement taken from that point detailed in Table 3.4, d) Euler map indicating crystallographic orientations, e) Lower hemisphere stereographic projection of crystallographic orientations of the RMN, f) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite. Comparing the projections reveals the RMN have a COR with the forsterite sharing their (110) axis (red circle).

3.5 Characteristics of ALH 77307 - region ALH1: TKD analyses from a FIB-produced TEM lamellae of an RMN bearing melilite crystal within a Type B-like CAI. a) A BSE image of the RMN in situ, prior to FIB extraction, hosted within a Type B-like CAI. Associated minerals are melilite (Mel) and perovskite (Prv), b) TKD band contrast image of the RMN and associated unknown phase. The labels indicate where EDS spectra from TKD and TEM were taken in Table 3.5, c) TEM image of the RMN and associated unknown phase indicating the RMN has several dislocation planes, d) TEM zoomed image of the unknown phase indicating the phase is heavily dislocated, exhibiting oriented bladed crystal morphologies, e) TKD phase map indicating a euhedral RMN (yellow), its associated unknown phase (blue), and the melilite host (red). The RMN is observed to be euhedral and the unknown phase adopts a pseudomorph texture with the RMN, f) TEM spot diffraction patterns taken from each phase. These spot diffraction patterns are overlain which revealed a shared <c> crystal axis between the RMN and the unknown phase within 6°. The RMN [002] axis is shared with the [201] axis of the melilite host.
3.6 Characteristics of Vigarano - region V1: TKD analyses of a large RMN associated with spinel and a cluster of twinned RMNs in a void. These RMNs are hosted in anorthite contained within the altered mantle of a fluffy-type A CAI. a) A lower magnification BSE image showing the wider context of region V1 within the CAI, b) A BSE image of region V1 prior to sample extraction indicating two RMNs (bright spots). The red rectangle indicates the orientation of the extracted TEM section. The RMNs here are associated with anorthite (An), c) TKD phase map indicating RMNs in yellow. The large RMN to the left of the section is associated with spinel (red). The number indicated the EDS measurement in Table 3.6. The RMN cluster to the right is within a void encapsulated by anorthite (blue), d) TKD Euler image of the section indicating crystallographic orientations. Grain boundaries are noted by black lines and twin planes are noted in red. The anorthite exhibits twins rotating at 180° around the twin plane, e) Stereographic projection plotting the poles to the crystal face for a twinned RMN indicating a rotation about the [111] axis of 60°, f) A TKD euler image magnified at the right-hand side RMN cluster revealing twin planes (red lines) within the RMNs. The numbers indicate the location of EDS measurements detailed in Table 3.5. 141
3.7 Characteristics of Vigaranò - region V2. TKD analyses of RMNs and associated HSE alteration phases. These RMNs are hosted in spinel contained within the altered mantle of a fluffy type A CAI. a) Low magnification BSE image of region V2 in the wider context of the CAI; also showing a nearby matrix region and chondrule (Chond), b) A BSE image of the RMN (bright spot) in context, before extraction. The red rectangle indicates the orientation of the TEM section, the RMN here is associated with spinel (Spl), c) A TKD phase map of the section indicating the RMN (green) powellite (red) and awaruite (blue) assemblage hosted in a spinel (yellow). The labels indicate where EDS spectra were taken in Table 3.7, d) A TKD euler map indicating crystallographic orientations of all the phases. Twin planes are shown as red lines indicating the awaruite phase is twinned, e) Lower hemisphere stereographic projection of crystallographic orientations of the awaruite, indicating a rotation about the [111] axis of 60°, f) Lower hemisphere stereographic projection of crystallographic orientations of the powellite, g) Lower hemisphere stereographic projection of crystallographic orientations of the two largest RMN grains with a shared pole in the [110] axis, h) Lower hemisphere stereographic projection of crystallographic orientations of the spinel. There are no systematic CORs observed between any of the phases.

3A.1 Backscatter electron (BSE) images of the wider context of region A1 within the Allende CV3 meteorite. Mineral labels are defined as Fo=forsterite Pn=pentlandite. a) A BSE image of the wider context of the porphyritic olivine (PO) chondrule bearing abundant Pn nodules and a Pn-rich rim where the RMNs are located. Fo within the chondrule has a Fo_{0.87-0.53} content. b) A BSE image at higher magnification showing Pn nodules within the PO chondrule rim where the RMNs are located. c) A forescatter detector (FSD) image of the Pn nodule within the PO chondrule which is RMN bearing d) A higher magnification FSD image of the Pn nodule, RMNs are now observable within the red box (bright spots) where the A1 analyses in the manuscript are detailed. The red boxes indicate the field of view of the subsequent image.
3A.2 Backscatter electron (BSE) images of the wider context of region A2 and A3 within the Allende CV3 meteorite. Mineral labels are defined as Fo=forsterite, Spl=spinel, Di=diopside, Grs=grossular, Sdl=sodalite RMN=refractory metal nugget.  
a) A BSE image of the wider context of the Type-B CAI which hosts the RMNs in region A2 and A3 within the thin section.  
b) A EBSD phase map of the CAI mineralogy which is Spl-, Di-rich with a rim of Fo and minor components of Sdl, Fo and Grs.  
c) A BSE image of the CAI showing the bulk mineralogy of Spl, and Di with small Fo enclaves bearing RMNs.  
d) A BSE image region A2 showing the RMN in the Fo enclave surrounded by Mg-rich Spl and associated Di. The Spl here is Fe-bearing with a hercynite (Hc) content of Hc_{0.27} while Di is Mg-Ca-rich with minor amounts of Fe and Ti with wollastonite (Wo) content of Wo_{0.54}.  
e) FSD image of the wider context of region A3 showing the small Fo enclave bearing an RMN hosted by Di associated with Spl. The Fo is Mg-rich with Fo_{0.83}, the Di has Wo_{0.53} and the Spl is Mg-rich with minor Fe: Hc_{0.18}. The red boxes indicate the field of view of the subsequent image, the labels within the image indicate the orientation of the subsequent image.  

3A.3 Backscatter electron (BSE) images of the wider context of region ALH1 ALH 77307 CO3.0 meteorite. Mineral labels are defined as Mel=melilit, Prv=perovskite and Cpx=clinopyroxene  
a) A BSE image of the wider context of the Type-B CAI which hosts the RMN in region ALH1. The Mel is gehlenite (Gh)-rich Gh_{0.99}. The red boxes indicate the field of view of the region ALH1 within the manuscript.  

3A.4 Backscatter electron (BSE) images of the wider context of regions V1 and V2 from Vigarano CV3 meteorite. Mineral labels are defined as Spl=spinel, An=anorthite  
a) A BSE image of the wider context of the ‘fluffy’ type-A CAI within the Vigarano thin section which hosts the RMNs in region V1 and V2.  
b) A red green blue EDS map showing the distribution of Ca (red) Na (green) and Fe (blue) within the CAI  
c) A higher magnification BSE image of region of the CAI containing V2 and associated Spl and An.  
d) Zoom in BSE image of the region containing V1 and associated Spl and An. The red boxes indicate the field of view of the region V1 and V2.  

xlvi
4.1 Electron backscatter diffraction (EBSD) and energy dispersive X-Ray spectroscopy (EDS) analyses of the region of interest from ALH 77307 CO3.0 meteorite (from Allan Hills, Antarctica). A: Backscattered electron image of the ultra-refractory inclusion (URI) indicating mineral phases; RMN – refractory metal nugget, Spl – spinel, Kan – kangite, Cpx – clinopyroxene, and Prv – perovskite. Extraction site locations of atom probe microscopy (APM) specimens RMN1–RMN5, kan1, and cpx1 are indicated by red circles, as well as RMN6 which did not run in atom probe but indicates typical euhedral crystal habit typical of these RMNs (Appendix 3E). Cpx forms a rim around most of the inclusion. Most phases exhibit 120° grain boundary intersections. Red box indicates area of EDS and EBSD maps in B and C. B: EDS red-green-blue map of S, Os, and Sc reveals position of RMNs and associated S enrichment. C: Band contrast map overlaid with phase map indicating Prv, Spl, and Kan rimmed by Cpx; no RMNs were indexed. 187

4.2 Atom probe microscopy (APM) analyses of a typical refractory metal nugget RMN3. A: In-beam secondary electron image of RMN3 after focussed-ion beam (FIB) preparation. Red box indicates where APM data were obtained. B: APM atom cloud of RMN3 indicating distribution of S (blue spheres) against background of Ir (red dots). Each coloured dot represents a single detected atom. C: Vertical concentration profile indicating variation in S concentration through RMN3. Slight S enrichment at apex of RMN3 is understood as a transient artifact due to changes in mass peak tails at start of data acquisition. URI – ultrarefractory inclusion; Pt – platinum. 189

4.3 Graph detailing composition of refractory metal nuggets RMN1–RMN5. Elements are ordered by increasing volatility; left axis indicates RMN1–RMN5 compositions in at. % and right axis depicts elemental abundance of RMN1–RMN5 normalized to a chondrite (CI: Lodders 2003). Ratios of highly siderophile elements (HSEs: Re, Os, W, Ir Mo, Ru)/CI have a flat trend with no depletions in W and Mo. HSE and S abundances vary between RMNs. 190

4.4 Typical mass-to-charge state ratio spectrum of 30–36 and 90–115 Da regions of refractory metal nuggets RMN1. S and SH ions are observed in 30 – 36 Da region and (HSE)-sulfur complexes are observed in between Ru peaks and 105 – 115 Da region. 191
4B.1 Images indicating how the refractory metal nugget (RMN) analysed in this study was prepared for lift out using the FIB. A) BSE image of the RMN (bright phase). B) Pt is deposited using the gas-injection system (GIS) in a small button over the RMN using the electron beam. C) A thicker layer of Pt is deposited with the GIS in a 2 x 7 µm rectangle using the Ga⁺ beam. . . . . . . . . . 199

4E.1 A-G) In-beam secondary electron images of the final atom probe tips of RMN1 – 5, kan1 and cpx1 respectively, the red box indicates the region that atom probe data was acquired from the tip. URI = ultra-refractory inclusion, cpx = clinopyroxene. H) In-beam secondary electron images of the final atom probe tip of RMN6 that did not run in the atom probe but reveals the euhedral crystal habit typical of these RMNs. . . . . . . . . . . . . . . . 201

5.1 Backscattered electron (BSE) images of the standard samples A) Pure Os wafer. B) Zoom in of APT lift out site (blue box) C) Pure Re wire. D) Zoom in APM lift out site of Re wire (blue box). E) Multi-HSE alloy from Schwander et al. (2015b). D) A Higher magnification image of the multi-HSE alloy. . . . . . . . . . . . . . . . 219

5.2 Images RMN7 and its wider context within the Allende CV3 meteorite. AOA=amoeboid olivine aggregate, Di=diopside, Fo=forsterite, Ilm=ilmenite, Mag=magnetite, Prv=perovskite and RMN=refractory metal nugget. A) A BSE image of the wider context of the AOA in the Allende CV3 meteorite. The yellow box indicates the field of view of image B). B) BSE image of the AOA containing RMN7 (red circle) and associated ilmenite, magnetite and perovskite encapsulated in diopside which is in turn encapsulated in forsterite. C) Close up BSE image of RMN7 indicating it is polyphase with a euhedral portion from which RMN7 was extracted and an associated complex texture which may be related to exsolution. D) In-beam secondary electron images of the final polished APM RMN7. The red box indicates the region sampled during APM. E) Atom cloud of RMN7, each sphere represents a single detected atom. Distributions of Os (red) and Re (blue). . . . . . . . . . . . . . . . . . . . . . 220
5.3 Images RMN8 and its wider context within the Murchison CM2 meteorite. URI=ultra-refractory inclusion, Spl=spinel, Dav=davisite clinopyroxene (Ma and Rossman, 2009) Pan=panguite (Ma et al., 2012), and RMN=refractory metal nugget. A) A BSE image of the wider context of the ultra-refractory inclusion within the Murchison CM2 meteorite. The red box represents the area of image B). B) BSE image of the ultra-refractory inclusion containing RMNs, RMN8 was extracted from the davisite rim of the inclusion (red circle). C) In-beam secondary electron images of the final polished APM tip for RMN8. The red box indicates the area sampled during APM. D) Atom cloud of RMN8, each sphere represents a single detected atom. Distributions of Os (red) and Re (blue)...221

5.4 Images of RMN9 and its wider context within the Allende CV3 meteorite. Pn=pentlandite, Ol=olivine, Ap=apatite, RMN=refractory metal nugget. A) A BSE image of the wider context of the chondrule from which RMN9 was extracted within the Allende CV3 section indicating the chondrule which hosted RMN9 is attached to a much larger sulphide rich chondrule. B) A BSE image of the porphyritic olivine chondrule and associated sulphide-, apatite-rich rim from which RMN9 was extracted. C) close up BSE image of the pentlandite-apatite-olivine-rich rim, with RMN9 clearly visible encapsulated with pentlandite. D) In-beam secondary electron images of the final polished APM RMN9. The red box indicates the area sampled during APM E) Atom cloud of RMN9, each sphere represents a single detected atom. Distributions of Os (red) and Re (blue)...222

5.5 A-C) In-beam secondary electron images of the final polished APM specimens from the Re wire (Re1 and Re2), and the Os wafer (Os1), respectively. The red boxes indicate the regions sampled by APM. D-E) Atom clouds of the APM data from specimens Re1 and Re2, respectively. The distribution of $^{185}\text{Re}$ is shown by the red spheres and $^{187}\text{Re}$ is shown by the green spheres. F) Atom cloud of the APM data from specimen Os1. The distribution of $^{187}\text{Os}$ is shown by the red spheres and $^{189}\text{Os}$ is shown by the green spheres...224
5.6 A-B) In-beam secondary electron images of the final polished APM specimens from the multi-HSE alloy (HSE1 and HSE2) respectively. The red boxes indicate the regions sampled by APM. C-D) Atom clouds of the APM data from specimens HSE1 and HSE2, respectively. Distributions of Os is shown by the red spheres and Re is shown by the blue spheres. 225

5.7 A-E) In-beam secondary electron images of the final polished APM specimens from RMN1 through RMN5 respectively. The red boxes indicate the regions sampled by APM. F-J) Atom clouds of the APM data from the specimens from RMNs1 – 5 respectively. Distributions of Os are shown by the red spheres and Re is shown by the blue spheres. Adapted from Chapter 4. 226

5.8 A graph depicting the change in % uncertainty $\sigma_A$ with increasing counts as defined by the power law in Equation 5.2 (orange). The effect of incorporating a background count of 100 into the uncertainty calculation (blue). An elevated uncertainty is calculated where total counts are less than an order of magnitude above background counts. 233

5.9 Graph depicting the variation in the calculated uncertainty in APM measurements of element $X$ expressed in $\epsilon$ notation assuming equal abundance of the two isotopes $^1X$ and $^2X$ calculated using Equation 5.4. The orange shaded area of the plot represents the uncertainty in $+\ve \epsilon$ and the blue shaded area represents the uncertainty in $-\ve \epsilon$. 235

5.10 Mass to charge state ratio ($m/q$) spectrum for Os$^+$ in the 90 – 100 Da range where Os$^{++}$ ions are present. These Os peaks are ranged using the full width method. 237

5.11 Mass to charge state ratio ($m/q$) spectrum for Os$^+$ in the 90 – 100 Da range where Os$^{++}$ ions are present. These Os peaks are ranged using the consistent width method. Each peak range was set to 0.25 Da. There is a slight peak at 95.5 Da from a small abundance of Os-hydride complexes. 239

5.12 Mass to charge state ratio ($m/q$) spectrum for Re$^+$ in the 90 – 100 Da range where Re$^{++}$ ions are present. These Re peaks are ranged using the consistent width method. Each peak range was set to 0.35 Da. There are slight peaks at 83 and 84 Da from a small abundance of Re-hydride complexes. 240
5.13 Graph depicting the relative abundance of the stable Os isotopes compared to terrestrial values from de Laeter et al. (2003). The consistent width method produces abundances marginally closer to the true isotopic values than the full width method. . . . . . . . . . 241

5.14 Graph depicting the relative abundance of the stable Os isotopes compared to terrestrial values from de Laeter et al. (2003). The IVAS background correction produces abundances closer overall to the expected terrestrial abundances. . . . . . . . . . . . . . . . 243

5.15 The $^{187}\text{Re}/^{185}\text{Re}$ of Re1 – 2 relative to the total counts for Re$^{++}$, and Re$^{+++}$ ions. There is no isotopic fractionation of isotopes between charge states, and both samples produce the expected terrestrial isotopic ratios consistent with TIMS measurements (shaded grey region). . . . . . . . . . . . . . . . . . . . . . . . . . 244

5.16 Isotopic abundances of Os$^{++}$ from HSE1 relative to terrestrial isotopic abundances (de Laeter et al., 2003) using different isobaric interference correction methods shown to 2σ uncertainties. Deconvolutions using $^{189}$Os, with and without a Pt correction are shown in black and purple, respectively. $^{184}$Os and $^{186}$Os abundances calculated by assuming terrestrial $^{182}$W and $^{183}$W are shown in red and blue, respectively. The graph on the left-hand side shows the large anomalies produced through the W deconvolutions of the lighter Os isotopes. The graph on the right-hand side is cropped to show detail in the heavier Os isotopes as the $^{184}$Os and $^{186}$Os relative abundances from the W deconvolution were large. . . . . . . . . . . . . . . . . . . . . . . . . . 249

5.17 Isotopic abundances of Os$^{++}$ from HSE1 relative to terrestrial (de Laeter et al., 2003). The effect of using different isotopes of Os ($^{188}$Os (red), $^{189}$Os (black), $^{190}$Os (blue), and $^{192}$Os (purple)) to deconvolve the isobaric interference by different isobaric interference correction methods is shown. . . . . . . . . . . . . . . . . . . . . . . 250

5.18 Os isotope relative abundances from HSE1 – 2 compared to terrestrial abundances (de Laeter et al., 2003). This reveals consistent isotopic measurements within the uncertainty of the counting statistics between the two APM specimens, indicating that APM isotopic analyses are reproducible. . . . . . . . . . . . . . . . . . . . . . . . . . 252
5.19 Images of APM samples SYN1 and SYN2. A) BSE image of the multi-phase alloy derived from the run products of the experiments detailed in Schwander et al. (2015a). The locations of APM samples SYN1 and SYN2 are given by the red circles. B) In-beam SEM image of the final polished APM specimen for SYN1 C) In-beam SEM image of the final polished APM specimen for SYN2.

5.20 An example mass spectrum from RMN4 indicating the added complexity in the 90 Da region due to isobaric interferences between isotopes of Os, W, Ir, Re, Pt and Ru. A similar pattern is also observed in the mass spectra of HSE1 – 2.

5.21 Bulk geochemistry of RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 in order of increasing volatility from Table 5.1. The synthetic HSE alloy is a good approximation of the average RMN in this study. RMN9 is unusual as it does not contain W, Mo, V or Rh but contains Pd which has not previously been reported in RMNs.

5.22 Isotopic abundances, to 2σ uncertainty of Os for RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 relative to a solar standard (Lodders, 2003). RMNs largely have a Solar System trend for Os, consistent with the HSE standards. RMN1 through RMN5, RMN7 through RMN9 have enrichments in the radiogenic isotope 187 Os. RMN9 has a large 187 Os depletion.

5.23 Isotopic abundances, to 2σ uncertainty, of Ir for RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 relative to a solar standard (Lodders, 2003). RMNs largely have a Solar System trend for Ir. However, RMN9 is enriched in the light Ir isotope 191 Ir.

5.24 Isotopic abundances of W for RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 relative to a solar standard (Lodders, 2003). The RMNs exhibit a different pattern than the HSE standards with highly variable 184 W contents. These are likely to be due to the presence of an isobaric interference with 92 Mo+.
5.25 RMN2 Os isotopic relative abundances compared to solar abundances with and without a Mo correction based on the difference between measured $^{184}$W and its expected abundance based on solar $^{184}$W/$^{183}$W. This correction produces Os isotopic abundances which are more consistent with expected solar ratios. The $^{184}$Os and $^{186}$Os have been corrected assuming Solar abundances of $^{189}$Os. The location of Mo$^{+}$ isobaric interference are labelled by the red boxes. ................................................................. 265

5.26 Re-Os plot of RMN1 through RMN5, RMN7 through RMN9. RMN1 through RMN4 and RMN8 plot on the 4.56 Ga Solar System isochron, however, RMN5 and RMN7 plot above the line, while RMN9 has a $^{187}$Os/$^{189}$Os below that of the initial value of the Solar System (Lodders, 2003; Anders and Grevesse, 1989). 275

5.27 Os vs age plot of HSE1 – 2 and RMN9. Showing Re depletion ages and Re model ages for the samples. Os1 is shown also but due to its supra-chondritic values a model age cannot be calculated. RMN9 has pre-solar $T_{RD}$ and $T_{MD}$ ages assuming chondritic evolution. HSE1 – 2 are slightly depleted in $^{187}$Os/$^{189}$Os relative to the TIMS measurement. .................................................. 276
LIST OF TABLES

2.1 The number of PGE hotspots in each type of inclusion (CAI, chondrule, and matrix) observed within the Acfer 094, Adelaide, ALH 77307, Kaidun, Renazzo, and Vigarano meteorites, identified using the synchrotron XRF beamline. 78

2.2 The abundance of RMNs in each type of inclusion (chondrule, matrix, sulphide and CAIs) observed within the Adelaide, ALH 77307, Allende, Murchison, and Vigarano meteorites. These RMNs were found by SEM and EDS analyses using the image overlay of synchrotron maps with PGE hotspots, and supplemented with RMNs identified using the INCA feature mapping software. 78

2.3 RMN compositions from EDS in at. %, indicating the meteorite, inclusion, and host mineral phase. The data is also available in Supplementary Appendix 1. 82

2.4 Average RMN compositions in at. %, for each meteorite analysed in this study and for each inclusion type. 88

3.1 RMN compositions from EDS analysis from Figure 3.1. The RMN number relates to the numbered regions of Figure 3.1b. b.d. = below detection. 131

3.2 RMN compositions from EDS analysis from Figure 3.2. The RMN number relates to the numbered regions of Figure 3.2c. b.d. = below detection. 131

3.3 RMN compositions from EDS analyses from the TEM lamellae detailed in Figure 3.3. The RMN number relates to the numbered regions of Figure 3.3c. b.d. = below detection. 134

3.4 RMN compositions from EDS analyses from Figure 3.4. The RMN number relates to the numbered regions of Figure 3.4c. b.d. = below detection. 136
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>EDS measurements taken from Region ALH1, comparing TEM with TKD analyses. This label corresponds to the label in Figure 3.5b. b.d. = below detection.</td>
</tr>
<tr>
<td>3.6</td>
<td>EDS measurements taken from region V1. The RMN number corresponds to the numbered regions of Figures 3.6c and e. b.d. = below detection.</td>
</tr>
<tr>
<td>3.7</td>
<td>EDS measurements taken from region V2. The label corresponds to the label regions of Figure 3.7c. b.d. = below detection. The powellite composition was derived using calculated oxygen contents of powellite, not the measured abundances from the EDS measurement</td>
</tr>
<tr>
<td>3B.1</td>
<td>A comparison of the EDS and APM measurements on the ReIrOs nugget in at. %</td>
</tr>
<tr>
<td>3C.1</td>
<td>Supplementary Material C raw EDS data.</td>
</tr>
<tr>
<td>4.1</td>
<td>Composition of RMN1–RMN5, kan1 and cpx1 measured by atom probe microscopy (with uncertainty of 2σ).</td>
</tr>
<tr>
<td>4C.1</td>
<td>Operating conditions of the Geoscience Atom Probe at Curtin University for atom probe samples RMN1 through RMN5, kan1 and cpx1, where hits relate to the number of ionic species detected during the analyses, T relates to the temperature the specimen was held at in K, Laser E is the energy of the pulsing laser in pJ, pulse frequency is the number of laser pulses per minute given in kHz, and the DR % is the detection rate of laser pulses that result in the field emission of an ion leading to a detection event as a percentage.</td>
</tr>
<tr>
<td>5.1</td>
<td>Composition of RMN1–5 and RMN7–9 and HSE1–2 measured by atom probe microscopy in at. % (with uncertainty of 2σ)</td>
</tr>
<tr>
<td>5.2</td>
<td>Operating conditions of the Geoscience Atom Probe at Curtin University for reference material Os1, Re1, Re2, HSE1 and HSE2, where hits relate to the number of ion detections during the analyses, T relates to the temperature the specimen was held at in K, Laser E is the energy of the pulsing laser in pJ, pulse frequency is the number of laser pulses per minute given in kHz, and the DR % is the detection rate of laser pulses that result in the field emission of an ion leading to a detection event as a percentage.</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5.3</td>
<td>Operating conditions of the Sydney Atom Probe for RMN7 through RMN9, where hits relate to the number of ion detections during the analyses, T relates to the temperature the specimen was held at in K, Laser E is the energy of the pulsing laser in pJ, pulse frequency is the number of laser pulses per minute given in kHz, and the DR % is the percentage of laser pulses that result in the field emission of an ion leading to a detection event.</td>
</tr>
<tr>
<td>5.4</td>
<td>Os and Re isotopic abundances and calculated ages for all samples analysed by AM using data reduction methods established above ± 2σ. Relative isotopic abundances of Os are given atomic %</td>
</tr>
<tr>
<td>5.5</td>
<td>Ir, W and PT isotopic abundances for all samples analysed by AM using data reduction methods established above ± 2σ. Relative isotopic abundances of Os are given atomic %</td>
</tr>
</tbody>
</table>
# List of Terms and Abbreviations Used in This Thesis

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACMM</td>
<td>Australian Centre for Microscopy and Microanalysis</td>
</tr>
<tr>
<td>AGB</td>
<td>Asymptotic Giant Branch Star</td>
</tr>
<tr>
<td>ALMA</td>
<td>Atacama Large Millimetre/submillimetre Array</td>
</tr>
<tr>
<td>Ak</td>
<td>Åkermanite</td>
</tr>
<tr>
<td>An</td>
<td>Anorthite</td>
</tr>
<tr>
<td>AOA</td>
<td>Amoeboid Olivine Aggregate</td>
</tr>
<tr>
<td>Ap</td>
<td>Apatite</td>
</tr>
<tr>
<td>APM</td>
<td>Atom Probe Microscopy</td>
</tr>
<tr>
<td>appm</td>
<td>Parts Per Million Atomic</td>
</tr>
<tr>
<td>AS</td>
<td>Australian Synchrotron</td>
</tr>
<tr>
<td>bcc</td>
<td>Body Centred Cubic</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electron</td>
</tr>
<tr>
<td>CAI</td>
<td>Ca-Al-Rich Inclusion</td>
</tr>
<tr>
<td>CB</td>
<td>Carbonaceous Type Bencubbin</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CH</td>
<td>Carbonaceous Type High metal</td>
</tr>
<tr>
<td>CHILI</td>
<td>Chicago Instrument for Laser Ionisation</td>
</tr>
<tr>
<td>Chr</td>
<td>Chromite</td>
</tr>
<tr>
<td>CI</td>
<td>Carbonaceous Type Ivuna</td>
</tr>
<tr>
<td>CK</td>
<td>Carbonaceous Type Karoonda</td>
</tr>
<tr>
<td>CM</td>
<td>Carbonaceous Type Mighei</td>
</tr>
<tr>
<td>CMCA</td>
<td>Centre for Microscopy, Characterisation and Analysis</td>
</tr>
<tr>
<td>CO</td>
<td>Carbonaceous Type Ornans</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>COR</td>
<td>Crystallographic Orientation Relationship</td>
</tr>
<tr>
<td>Cpx</td>
<td>Clinopyroxene</td>
</tr>
<tr>
<td>CR</td>
<td>Carbonaceous Type Renazzo</td>
</tr>
<tr>
<td>CV</td>
<td>Carbonaceous Type Vigarano</td>
</tr>
<tr>
<td>Dav</td>
<td>Davisite</td>
</tr>
<tr>
<td>Di</td>
<td>Diopside</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscatter Diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>fcc</td>
<td>Face Centred Cubic</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>Fo</td>
<td>Forsterite</td>
</tr>
<tr>
<td>FSD</td>
<td>Forescatter Detector</td>
</tr>
<tr>
<td>GAP</td>
<td>Geoscience Atom Probe</td>
</tr>
<tr>
<td>GDMS</td>
<td>Glow Discharge Mass Spectrometry</td>
</tr>
<tr>
<td>Gh</td>
<td>Gehlenite</td>
</tr>
<tr>
<td>GIS</td>
<td>Gas Injection System</td>
</tr>
<tr>
<td>GMC</td>
<td>Giant Molecular Cloud</td>
</tr>
<tr>
<td>Grs</td>
<td>Grossular</td>
</tr>
<tr>
<td>Hc</td>
<td>Hercynite</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal Close Packed</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HSE</td>
<td>Highly Siderophile Element</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>Ilm</td>
<td>Ilmenite</td>
</tr>
<tr>
<td>IVAS</td>
<td>Integrated Visualisation and Analysis Software</td>
</tr>
<tr>
<td>JdLC</td>
<td>John De Laeter Centre</td>
</tr>
<tr>
<td>Kan</td>
<td>Kangite</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser Ablation Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>LIMS</td>
<td>Laser Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>m/q</td>
<td>Mass to Charge Ratio</td>
</tr>
<tr>
<td>Mag</td>
<td>Magnetite</td>
</tr>
<tr>
<td>MCSR</td>
<td>Mass-to-Charge-State-Ratio</td>
</tr>
<tr>
<td>Mel</td>
<td>Meilite</td>
</tr>
<tr>
<td>Mk</td>
<td>Mackinawite</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenite</td>
</tr>
<tr>
<td>N-TIMS</td>
<td>Negative Ion Thermal Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>OA</td>
<td>Opaque Assemblage</td>
</tr>
<tr>
<td>Ol</td>
<td>Olivine</td>
</tr>
<tr>
<td>Pan</td>
<td>Panguite</td>
</tr>
<tr>
<td>PGE</td>
<td>Platinum Group Element</td>
</tr>
<tr>
<td>Pn</td>
<td>Pentlandite</td>
</tr>
<tr>
<td>PO</td>
<td>Porphyritic Olivine</td>
</tr>
<tr>
<td>Prv</td>
<td>Perovskite</td>
</tr>
<tr>
<td>RIMS</td>
<td>Resonance Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>RMN</td>
<td>Refractory Metal Nugget</td>
</tr>
<tr>
<td>SDD</td>
<td>Silicon Drift Detector</td>
</tr>
<tr>
<td>Sdl</td>
<td>Sodalite</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SHRIMP</td>
<td>Sensitive High-Resolution Ion Microprobe</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SNMS</td>
<td>Sputtered Neutral Mass Spectrometry</td>
</tr>
<tr>
<td>Spl</td>
<td>Spinel</td>
</tr>
<tr>
<td>SSMS</td>
<td>Spark Source Mass Spectrometry</td>
</tr>
<tr>
<td>Term</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>t-EBSD</td>
<td>Transmission Electron Backscatter Diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TIMS</td>
<td>Thermal Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>TKD</td>
<td>Transmission Kikuchi Diffraction</td>
</tr>
<tr>
<td>TMA</td>
<td>Re-Os Model Age</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-Of-Flight</td>
</tr>
<tr>
<td>TRD</td>
<td>Re depletion age</td>
</tr>
<tr>
<td>Tro</td>
<td>Troilite</td>
</tr>
<tr>
<td>URI</td>
<td>Ultra-Refractory Inclusion</td>
</tr>
<tr>
<td>VP-FESEM</td>
<td>Variable Pressure Field Emission Scanning Electron Microscope</td>
</tr>
<tr>
<td>WDS</td>
<td>Wavelength Dispersive X-Ray Spectrometry</td>
</tr>
<tr>
<td>Wo</td>
<td>Wollastonite</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence Microscopy</td>
</tr>
<tr>
<td>Z</td>
<td>Atomic Number</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

Our Solar System is thought to have formed from the gravitational collapse of a Giant Molecular Cloud (GMC) fragment (Nuth et al., 2006; Boss and Goswami, 2006; Shu et al., 1987; Miyama et al., 1984; Mac Low and Klessen, 2004). The conservation of angular momentum from the net rotation of this cloud caused it to collapse to form a disk structure around the early sun, known as the protoplanetary disk (Boss and Goswami, 2006; Shu et al., 1987; Yen et al., 2016) (Figure 1.1). Dust grains inherited from the GMC (Messenger et al., 2006; Brownlee, 1994; Anders and Zinner, 1993) and new grains that formed within the protoplanetary disk through condensation, irradiation, oxidation, reduction, and transient heating events (Stolper and Paque, 1986; Clayton et al., 1988; Hewins and Radomsky, 1990; Hewins, 1997; Lodders, 2003; MacPherson et al., 2005; Connolly Jr et al., 2006; Grady and Wright, 2006), were subsequently accreted into larger objects such as planetesimals, where they experienced thermal and aqueous metamorphism (Sears et al., 1980; Grimm and Mcsween, 1989; Browning et al., 1996; Nakamura, 2005; Grady and Wright, 2006). This was followed by further growth through impacts and heating causing differentiation
and core formation, producing planet sized objects (Malvin et al., 1984; Narayan and Goldstein, 1985; Keil et al., 1997; Gilmour et al., 2000; Scott, 2002; Grady and Wright, 2006). These planets have subsequently been modified through impacts, endogenic geological process and in some cases completely destroyed to eventually produce the Solar System we observe today (Grady and Wright, 2006; Weidenschilling and Cuzzi, 2006).

![Figure 1.1: Protoplanetary disk around HL Tau, a 1 Myr old star imaged by the Atacama Large Millimetre/submillimetre Array (ALMA). Credit: ALMA (NRAO/ESO/NAOJ), published in Yen et al. (2016).](image)

Primitive meteorites are the only surviving material from this time and contain minerals that formed at the dawn of our Solar System (MacPherson et al., 2005). They are an aggregate of diverse components (Hutchison, 2004) that preserve a record of early Solar System processes, and the conditions within the protoplanetary disk, prior to the accretion of planets and asteroids (e.g. Ebel 2006; Davis 2006 and Connolly Jr et al. 2006).

Analyses of components within primitive meteorites can improve our understanding of the early Solar System. However, several of the most interesting
types of grain are commonly small (<1 \( \mu \)m) in diameter. Examples of these are some types of pre-solar grain (i.e. diamonds, and refractory carbides in pre-solar graphite) (Amari et al., 1994; Croat et al., 2013; Zinner, 2003; Clayton and Nittler, 2004; Anders and Zinner, 1993; Hoppe and Zinner, 2000) and refractory metal nuggets (RMNs) (Wark and Lovering, 1976; Palme and Wlotzka, 1976). Pre-solar grains are so called because they exhibit isotopic signatures that are different to that of our Solar System, and are consistent with stellar nucleosynthesis (Anders and Zinner, 1993; Bernatowicz et al., 2006; Meyer and Zinner, 2006). Therefore, these grains are interpreted as having a pre-solar origin and preserve a record of galactic events and stellar evolution (Anders and Zinner, 1993; Nittler, 2003; Nittler and Dauphas, 2006). RMNs are isolated sub-micrometre metal alloys that are rich in the highly siderophile elements (HSEs) (Wark and Lovering, 1976; Palme and Wlotzka, 1976; Berg et al., 2009; Schwander et al., 2015b). Since their simultaneous discovery by Wark and Lovering (1976) and Palme and Wlotzka (1976) RMNs have generally been interpreted as primary nebula condensates as the compositions of some RMN were consistent with equilibrium condensation models (Palme and Wlotzka, 1976; Berg et al., 2009) however other mechanisms have also been proposed (e.g. Schwander et al. 2015b). The high condensation temperatures for RMNs would place them among the first solid objects to condense in the protoplanetary disk (Lodders, 2003; Campbell et al., 2001; Wark and Lovering, 1976; Berg et al., 2009), and as such are an important phase for study in primitive meteorites.

Both RMNs and pre-solar grains are rare in primitive meteorites (usually at concentration levels of less than a few hundred parts per million (Anders and Zinner, 1993; Meyer and Zinner, 2006; Lodders, 2003; Anders and Grevesse, 1989)); therefore, finding them \textit{in situ} is difficult and time consuming. Analysing these grains has previously been undertaken using a concentration step. For
example, both pre-solar grains and RMNs are resistant to acids; utilising strong acids to leach away the majority of meteoritic components concentrates pre-solar grains and RMNs in the residue (Amari et al., 1994). This approach has enabled the analysis of several hundred RMNs from Murchison CM (Berg et al., 2009; Harries et al., 2012) and Leoville CV and Allende CV (Schwander et al., 2014). However, the interpretation of the origin of RMNs from these acid residues is limited because the petrographic context of the grain within the meteorite is lost. To accurately interpret the origins of these small rare phases requires in situ analysis to retain their petrographic context.

The work contained in this thesis focuses on the identification and analysis of RMNs in situ to better understand their origins. A series of novel high resolution analyses such as synchrotron X-ray fluorescence microscopy (XRF) element mapping (Dyl et al., 2014; Ryan et al., 2010), and ‘Feature’ mapping (grain identification and Energy Dispersive X-ray Spectroscopy (EDS) analyses based on contrast in back scattered electron images) using Oxford Instrument’s INCA suite (Oxford-Instruments, 2006) was used to develop an approach for the rapid identification of a large number of RMNs in situ.

The RMNs were analysed using established techniques to extract geochemical and crystallographic information. These included EDS, Electron Backscatter Diffraction (EBSD) on polished thin sections, and Transmission Electron Microscopy (TEM) on foils extracted by Focussed-Ion Beam (FIB) milling in a scanning electron microscope (SEM). Recently, new high-resolution techniques have been developed such as Transmission Kikuchi Diffraction (TKD) and Atom Probe Microscopy (APM) which push the bounds of the minimum grain size that can be precisely measured to extract crystallographic, geochemical and isotopic information. These techniques were applied to RMNs; TKD was used to obtain high-resolution crystallographic maps of TEM samples (Trimby, 2012;
Trimby et al., 2014; Sneddon et al., 2016), and Atom Probe Microscopy (APM) (Kelly and Larson, 2012; Gault et al., 2012) was used to determine nanometre-scale geochemical and isotopic signatures of RMNs. The results of TKD and APM analyses combined with established in situ techniques served to improve our understanding of how RMNs formed in the protoplanetary disk, and the processes that have subsequently affected them.

1.1. THE IMPORTANCE OF METEORITES

Meteorites are extraterrestrial rock samples that have fallen to Earth (Hutchison, 2004). They are derived from planets, asteroids, moons and potentially comets (Shearer et al., 1998; Grady and Wright, 2006; Hutchison, 2004). Meteorites are subdivided into three broad categories: Iron, stony-irons and stony (Krot et al., 2003; Dodd, 1981; Hutchison, 2004; Sears and Dodd, 1988; Weisberg et al., 2006). The stony meteorites are further subdivided into chondrites and achondrites (Krot et al., 2003; Hutchison, 2004).

1.1.1. CHONDRITES

Chondrites are a bimodal assemblage comprised of a porous fine-grained matrix and larger millimetre-sized objects such as chondrules (spherical glassy inclusions composed mainly of silicates, from which chondrites derive their name (Hutchison, 2004; Hewins, 1997; Scott and Krot, 2003; Scott, 2007)). Chondrites have similar bulk compositions to the solar photosphere and are therefore regarded as the most primitive of all meteorite classes (Hutchison, 2004; Anders and Grevesse, 1989) (Figure 1.2). They are thought to be remnants of the first
bodies that accreted in the Solar System (Scott, 2007; Hutchison, 2004). All chondrites are classified by their petrologic type, which reflects exposure to aqueous or thermal metamorphism on their parent body on a scale of $1 - 6$ (Van Schmus and Wood, 1967). Types $2 - 1$ exhibit textures and mineralogy consistent with an increasing degree of aqueous alteration, such as the presence of hydrous phyllosilicate minerals (Rubin et al., 2007; Van Schmus and Wood, 1967). Types $4 - 6$ exhibit textures and mineralogy consistent with increasing thermal metamorphism including a coarsening of matrix grains, chondrule-matrix boundaries becoming poorly defined, recrystallisation of mesostasis and equilibration of mineral chemistry (Van Schmus and Wood, 1967; Sears and Dodd, 1988; Brearley and Jones, 1998; Hutchison, 2004). Type 3 chondrites exhibit few features relating to thermal metamorphism or aqueous alteration (Van Schmus and Wood, 1967). These type 3 chondrites represent the most unaltered and unequilibrated meteorites (Van Schmus and Wood, 1967). Petrologic type 3 chondrites are further subdivided from 3.0 – 3.9 based on thermoluminescence measurements that reflect minor degrees of thermal alteration (Sears, 1980). Meteorites of petrologic type 3.0 have undergone the least alteration, meaning that these rare samples contain pristine minerals that have remained largely unchanged since their formation in the protoplanetary disk (Van Schmus and Wood, 1967; Weisberg et al., 2006). Type 3 chondrites also contain the highest abundance of pre-solar grains (Zinner, 1998; Bernatowicz et al., 2006; Huss and Lewis, 1995), which are readily destroyed during aqueous or thermal alteration (Trigo-Rodriguez and Blum, 2009; Huss and Lewis, 1995) supporting the notion that type 3 chondrites are primitive. However, type 3 chondrites still record evidence of parent body alteration and asteroidal processing (i.e. Krot et al. 2004, 1998, 1995) so care must be taken when inferring a nebular origin for these materials.
Figure 1.2: Chondritic vs solar abundances of the elements indicating that chondrites are a close approximation to the bulk chemical composition of the Solar System and have not experienced extensive processing post-accretion. From Hutchison (2004), with data from Anders and Grevesse (1989).
Chondrites are further subdivided into ordinary chondrites, enstatite chondrites, K-group, R-group, and carbonaceous chondrites based on their texture, composition, oxygen isotope ratios and size and abundance of inclusions (Krot et al., 2003; Weisberg et al., 2006; Hutchison, 2004).

1.1.2. **Carbonaceous chondrites**

Carbonaceous chondrites are distinguished from other chondrite types by their high matrix abundance that is rich in volatiles, particularly carbon (Scott and Krot, 2003; Scott, 2007; Krot et al., 2003), as well as high Mg/Si ratios and elevated refractory lithophile element contents (Grossman, 1996). Furthermore, as well as chondrules and interstitial matrix grains, carbonaceous chondrites also contain abundant refractory inclusions such as amoeboid olivine aggregates (AOAs) and Ca-Al-rich inclusions (CAIs) (Scott and Krot, 2003; Hutchison, 2004) which are thought to form at high temperatures (MacPherson et al., 2005; Grossman and Steele, 1976). The carbonaceous chondrites are further subdivided into eight groups named after a type meteorite: carbonaceous type Ivuna (CI), carbonaceous type Vigarano (CV), carbonaceous type Mighei (CM), carbonaceous type Ornans (CO), carbonaceous type Karoonda (CK), carbonaceous type Renazzo (CR), carbonaceous type Bencubbin (CB) and carbonaceous type high metal (CH) (Weisberg et al., 2006). These subdivisions are based on major element ratios such as Al/Si, Ca/Si, Mg/Si, as well as oxygen isotope ratios and the prevalence and size of inclusions (i.e. chondrules, CAIs and AOAs) (Krot et al., 2003; Scott and Krot, 2003; Hutchison, 2004). CIs are the most aqueously altered meteorite and are almost entirely comprised of matrix with rare altered chondrules, CMs are also aqueously altered but contain chondrules and rare but small CAIs, CVs contain abundant large CAIs, while COs contain smaller
refractory inclusions but these are enriched in ultra-refractory elements such as Zr and Sc (Scott and Krot, 2003). Most carbonaceous chondrites are of petrologic types 1 – 3 so have not experienced significant thermal metamorphism (Van Schmus and Wood, 1967). The carbonaceous chondrites are therefore the most primitive of the chondrite meteorites (Clayton and Mayeda, 1999; Anders and Grevesse, 1989).

Analysing components of carbonaceous chondrites such as CAIs can reveal information about the accretionary and pre-accretionary history of the meteorite (Hutchison, 2004), as well as the conditions present in the protoplanetary disk (e.g. Grossman et al. 2000; Petaev and Wood 2005 and MacPherson et al. 2005).

1.2. CA-AL-RICH INCLUSIONS (CAIs)

CAIs are irregular shaped objects usually <1 mm in size, but can be as large as 2 – 3 cm (MacPherson et al., 2005). They are composed of refractory oxides and silicates that are Al-, Ti- and Ca-rich (Hutchison, 2004). CAIs are predominantly found within carbonaceous chondrites, but can be observed in other chondrite types (Hutchison, 2004). They are characterised based on their petrology and mineral assemblages and are initially divided into coarse-grained (>10 µm) and fine-grained inclusions (Grossman, 1975). The coarse-grained CAIs are further subdivided into Type A (melilite-rich), Type B (pyroxene-, spinel-, plagioclase- and melilite-rich) (Grossman, 1975), and Type C (anorthite-rich) (Wark, 1987). Type A inclusions are also split into ‘fluffy’ (Figure 1.3) and ‘compact’ types (MacPherson and Grossman, 1979).

Although CAIs make up <5 % of the of the mass fraction of most carbonaceous chondrites (MacPherson et al., 2005) (CVs and COs can have up to 13
Figure 1.3: XRF synchrotron RGB element map of a fluffy type A CAI from Vigarano CV3; Ca (red), Ni (green), Fe (blue).
% ; Scott and Krot 2003), they have received a significant amount of attention due to their unusual characteristics. Firstly, they are the oldest solid objects because they yield ages of 4.568 Ga that are widely interpreted as the age of our Solar System (Connelly et al., 2012; Amelin et al., 2002; Bouvier and Wadhwa, 2010). Secondly, they are composed of minerals that form at high temperatures through condensation and subsequent re-melting (MacPherson et al., 2005; Grossman et al., 2000). Some CAIs have mineral assemblages that are consistent with equilibrium condensation calculations from a solar gas (Grossman, 1973). However, most have also experienced reprocessing such as complete or partial melting (MacPherson and Grossman, 1979; MacPherson et al., 2005) and evaporation (Grossman et al., 2000).

CAIs also exhibit oxygen isotope anomalies, which were originally thought to be due to the incorporation of a pre-solar component of pure \(^{16}\)O from a supernova (Clayton et al., 1973), but are now thought to be due to mass independent fractionation caused by photodissociation (Clayton, 2002; Navon and Wasserburg, 1985; Lyons and Young, 2005; Thiemens, 1996). The refractory nature of CAIs implies a high temperature origin and \(^{10}\)Be abundances suggest an origin close to the proto-sun (McKeegan et al., 2000; MacPherson et al., 2005; Chaussidon and Gounelle, 2006; Dauphas and Chaussidon, 2011). However, CAIs have recently been observed in cometary material from the Stardust mission to Wild 2 (Brownlee et al., 2006; Zolensky et al., 2006; McKeegan et al., 2006; Messenger et al., 2008). Comets are thought to form at >20 AU (Brownlee et al., 2006) which requires a mechanism to migrate CAIs from their formation region close to the proto-sun (MacPherson et al., 2005) out to the comet forming region (Ciesla, 2010). Thus, the study of CAIs can also inform our understanding of dust migration in the protoplanetary disk (Ciesla, 2007; Shu et al., 1997; Bai, 2014; Ciesla, 2010) (Figure 1.4).
CAIs and the phases within them can reveal information pertaining to the conditions and processes that occurred at the dawn of the Solar System. One particular phase within CAIs, and the main focus of this work, is refractory metal nuggets (RMNs), which are thought to represent the first condensates in the protoplanetary disk (Wark and Lovering, 1976; Berg et al., 2009).

1.3. **Refactory Metal Nuggets**

Refactory Metal Nuggets (RMNs) are predominantly found within CAIs (Eisenhour and Buseck, 1992; Schwander et al., 2014, 2015a), but they have also been observed in chondrules and matrix but were interpreted as CAI fragments (Wang et al., 2007; Schwander et al., 2015a). RMNs are sub-micrometre sized metallic alloys composed of the highly siderophile elements (HSEs) such as W, Re, Os, Ir, Pt, Mo, Ru, and Rh, as well as Fe and Ni (Palme and Wlotzka, 1976;
Wark and Lovering, 1976) (Figure 1.5). These elements, with the exception of Fe and Ni, are also highly refractory; equilibrium condensation models for a solar gas predict that 50% of these elements will have condensed between 1392 K and 1821 K (Lodders, 2003).

There are two types of HSE-rich phase present in carbonaceous chondrites: isolated sub-micrometre metal alloys (RMNs), and opaque assemblages (OAs) that are large >1000 µm assemblages of HSE bearing metals, sulphides and oxides (El Goresy et al., 1977). The larger inclusions used to be termed ‘fremdlinge’ (translated from German as ‘foreigners’) due to their non-solar elemental ratios that suggest an extra-solar origin (El Goresy et al., 1977, 1978). However, it has since been shown that these ‘fremdlinge’ do not have nucleosynthetic anomalies (Hutcheon et al., 1987) and have been affected by oxidation and sulphidation (Blum et al., 1989). They are therefore likely to be of nebula origin hence they are now termed opaque assemblages (OAs) (Blum et al., 1989). Since the simultaneous discovery of RMNs by Palme and Wlotzka (1976) and Wark and Lovering (1976), there has been considerable debate as to how these grains formed.

1.3.1. Formation mechanisms

The high condensation temperatures and association with CAIs has led some authors to conclude that RMNs represent the first nebula condensates (Berg et al., 2009; Eisenhour and Buseck, 1992; Harries et al., 2012; Palme and Wlotzka, 1976; Sylvester et al., 1990). As such, RMNs would be the first solid objects to form in the inner protoplanetary disk and could constrain not only the temperature, but also the cooling rate of the protoplanetary disk (Berg et al., 2009). However, other authors have suggested it may be possible to produce
RMNs via crystallisation of dissolved HSEs from a silicate melt (Schwander et al., 2015b; Rudraswami et al., 2014), which is supported by experiment (Schwander et al., 2015a). Other authors concluded that RMNs might not be primary phases at all, indicating that some had experienced oxidation and sulphidation after their formation, either in the nebula or on the parent body (Blum et al., 1988; Bischoff and Palme, 1987). Other authors have also suggested that some RMNs may have a pre-solar origin (El Goresy et al., 1978, 1977) and some small (<50 nm) RMNs have been observed as inclusions within demonstrably pre-solar graphite obtained from acid residues of Orgueil (RMNs were Os-, Ru-, Fe-, Ir- and Mo-rich) and Murchison (RMNs were Os-, Ru-rich) (Croat et al., 2013).

Figure 1.5: SEM image of a RMN extracted from an acid residue from Berg et al. (2009).
1.3.2. COMPOSITIONAL HETEROGENEITY

The chemistry of RMNs is complex, with large chemical heterogeneities within the RMN population (Schwander et al., 2015b). This is the main reason why a single unifying formation mechanism cannot be agreed upon, as no model can adequately reproduce all RMN compositions. Condensation models indicate RMN compositions should follow a systematic trend (Schwander et al., 2014; Tanaka et al., 2002). However, the calculation to compare RMN compositions to predicted compositions from equilibrium condensation models used a least squares fit (i.e. Berg et al. 2009). This generates good correlations with condensation models for abundant elements in RMNs, but less abundant elements exhibit a wide scatter (see Schwander et al. 2014). Crystallisation of dissolved HSEs is also unlikely to generate such heterogeneous RMN compositions. Variable migration speeds of certain HSEs during crystallisation were suggested by Schwander et al. (2015a) to generate the observed heterogeneity. However, this mechanism does not seem plausible, as completely dissolved HSEs would intuitively crystallise RMNs with homogeneous compositions within an inclusion. Alteration of RMNs on the parent body would result in depletions in W and Mo that are readily mobilised during sulphidation or oxidation (Palme et al., 1998). However, not all RMNs exhibit this trend with most exhibiting relative elemental abundances consistent with the Solar System (Eisenhour and Buseck, 1992; Schwander et al., 2015b; Daly et al., 2017). Finally, a pre-solar origin cannot be demonstrated or excluded without accurate isotopic analysis of RMNs.
1.3.3. Analytical Techniques

The small size of RMNs (0.09 – 1.2 µm) (Berg et al., 2009) makes them difficult to analyse in sufficient numbers to produce a statistically robust dataset in order to evaluate the suggested mechanisms. Previous studies have described only a small number of RMNs (<20 per study) (e.g. Wark and Lovering 1976; Palme and Wlotzka 1976; Eisenhour and Buseck 1992 and El Goresy et al. 1977, 1978). This is insufficient to make any universal interpretations. Acid leachates of meteorites were found to contain enrichments of HSEs (Anders et al., 1975). These elements were contained within RMNs that were resistant to the leaching process (Berg et al., 2009). This permitted the analysis of several hundred RMNs (Berg et al., 2009; Harries et al., 2012; Schwander et al., 2014). However, the petrographical context of the RMN is lost during the leaching process, limiting the interpretation of RMNs and forcing the authors to assume all the RMNs were derived from CAIs.

Bulk analysis of other meteoritic material such as chondrules, matrix and sulphides indicates that these components also contain HSEs (Horan et al., 2009, 2003). This raises some questions: are RMNs really unique to CAIs or can they also be found in other components? If not what is the host phase for HSEs within these components? There is already some indication that RMNs are not unique to CAIs e.g. some RMNs were identified within chondrules (Wang et al., 2007), cosmic spherules (Rudraswami et al., 2014) and matrix (Schwander et al., 2015b). However, these authors could not rule out the possibility that these RMNs were derived from CAI fragments that were assimilated into chondrules, or comminuted and dispersed throughout the matrix.
1.3.4. Research prospects

RMNs represent a rich prospect for research as there are so many testable hypotheses regarding their formation and each would provide constraints on early nebula processes. For example, if RMNs formed through condensation, it may be possible to determine the nebula cooling rate (i.e. Berg et al. 2009). Alternatively, if some RMNs do have a pre-solar origin they may preserve signatures of galactic processes and stellar evolution similar to other pre-solar grains.

The main limiting steps in the interpretation of RMNs is the ability to find and analyse a statistically significant dataset of in situ RMNs, retaining their petrographic context, and once found, undertake detailed high resolution analyses of several RMNs. The difficulty arises from the small size and rarity of RMNs (Berg et al., 2009). Particularly lacking are detailed crystallographic studies of RMNs and their relationships with surrounding phases. The only TEM studies to date are found within Eisenhour and Buseck (1992) and Harries et al. (2012). Furthermore, if a technique can be applied that could derive accurate isotopic abundances for RMNs it would be possible to determine whether some RMNs do indeed have a pre-solar origin. However, because RMNs are so small, it has been impossible to measure their isotopic composition with sufficient accuracy to reveal any pre-solar signatures.

Two papers and one conference abstract prior to this work have reported the isotopic composition of RMNs. Hutcheon et al. (1987) analysed the isotopic compositions of Mg, Fe, Mo, Ru and W within an OA and an isolated Os, Ir-Ru-rich RMN as well as some OAs using the PANURGE ion microprobe, but found no isotopic anomalies >1 % in any of the measured elements. A second study by Berg et al. (2009) analysed two RMNs using secondary ion mass spectrome-
try revealing solar $^{189}\text{Os}/^{192}\text{Os}$ and $^{190}\text{Os}/^{192}\text{Os}$ isotopic ratios. However, the resolution of the technique was insufficient to be able to distinguish an r-process RMN from a solar RMN (Berg et al., 2009). A third abstract by Fischer-Gödde et al. (2014) analysed the Ru isotopes of a bulk sample of separated RMNs using a ThermoScientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer. Small r-process deficits were observed in the aliquot but were not sufficiently large to be consistent with a nucleosynthetic origin (Fischer-Gödde et al., 2014). It is possible that because a bulk sample containing several RMNs was analysed, any nucleosynthetic signatures from pre-solar RMNs may be diluted by RMNs with solar abundance ratios. Pre-solar RMNs should exist as they have been observed within pre-solar graphite grains (Croat et al., 2013). Therefore, if a sufficiently high-resolution technique can be applied to extract isotopic information, it may be possible to demonstrate that some RMNs have a pre-solar origin.

1.4. Research Design

Identification of rare sub-micrometre grains such as RMNs in situ currently requires a significant investment in time and resources. Finding these phases is further hampered by human biases. The identification of RMNs currently requires an individual researcher to search through thin section specimens, and consequently several factors can bias datasets, including: focusing on mineral phases or inclusions known to host the mineral of interest (i.e. Schwander et al. 2015b), incomplete or inconsistent searching, overlooking particles and fatigue. These factors result in biased and incomplete datasets.

An ideal solution is to devise a systematic, automated method that searches
an entire thin section with the required resolution to be able to identify particles in the size range typical for RMNs, and consequently provide more objective, representative and accurate statistics for the abundance of sub-micrometre phases, as well as efficiently locating all examples of the phase of interest without expending large numbers of human hours.

The work contained within this thesis utilised synchrotron radiation and Feature mapping to devise a methodology that can be applied to whole meteorite thin sections in order to rapidly and accurately locate RMNs in situ (Chapter 2).

Once sufficient RMNs were found, a series of new and established techniques capable of measurements at progressively higher resolution, from the micrometre scale through to the atomic scale were applied to RMNs. These techniques included Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) (Chapter 2), Electron Backscatter Diffraction (EBSD), Transmission Electron Microscopy (TEM), Transmission Kikuchi Diffraction (TKD) (Chapter 3), and Atom Probe Microscopy (APM) (Chapter 4 and Chapter 5). These techniques were used to extract geochemical, crystallographic and isotopic information from these RMNs to better understand the processes that formed them. The following section describes these methods and techniques utilised in this work. The specific instruments used in this work are outlined in the chapters and are therefore not repeated here.
1.4.1. Micrometre-scale characterisation

1.4.1.1. X-ray fluorescence microscopy (XRF) from synchrotron radiation

X-Ray fluorescence microscopy (XRF), is a technique that uses synchrotron radiation to generate high-energy X-rays (Van Grieken and Markowicz, 2001; Ryan et al., 2010). These are focussed into a 2 µm beam (Paterson et al., 2007; Ryan et al., 2010). The high-energy of the beam (18.5 keV) allows X-rays to penetrate up to 100 µm into the sample, which can reveal structures, as well as detect rare sub-micrometre phases at depth (Dyl et al., 2014). The XRF beamline at the Australian synchrotron is further combined with the Maia detector, a custom made 384 Si-diode detector (Ryan et al., 2010). X-rays produced in the synchrotron interact with the sample generating X-rays that are diagnostic of particular elements within the 4 – 18 keV range (Van Grieken and Markowicz, 2001; Ryan et al., 2010). This technique allows thirty key elements to be mapped, including Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, and Bi (Dyl et al., 2014). The combination of the Maia detector and a high-powered X-ray source results in a high sensitivity to certain elements. The detection limits for Os, Ir and Pt are particularly low in synchrotron XRF (on the order of 50 – 100 ppm), which is particularly useful for searching for RMNs (Cleverley et al., 2012). Synchrotron-based Maia XRF can generate quantifiable element maps (Dyl et al., 2014) for entire thin sections at a spatial resolution of 2 µm/pixel (Ryan et al., 2010) over the course of a few hours (see Figure 1.3). The raw XRF data are processed and visualised as maps by the GeoPIXE™ software using a dynamic analysis matrix to deconvolve individual element peaks (Ryan et al., 1995).
One potential issue is that the 2 µm resolution of synchrotron XRF is coarser than the diameter of most RMNs (0.09 – 1.2 µm) (Berg et al., 2009; Schwander et al., 2015b). However, RMNs will be revealed as bright hotspots in the synchrotron XRF element maps because they are rich in elements such as Os, Ir and Pt (Wark and Lovering, 1976; Palme and Wlotzka, 1976) and the detection limits of this XRF technique are sufficiently low to detect them (Cleverley et al., 2012). This makes XRF an ideal technique to rapidly identify concentrations of platinum group elements (PGEs) within meteorite samples. Subsequently ‘hotspots’ of elements associated with RMNs can then be investigated further with SEM techniques. A further complication is the large penetration depth (100 nm (Dyl et al., 2014)) of synchrotron XRF mapping, as most RMNs are sub-micrometre in size (Berg et al., 2009) many elemental ‘hotspots’ will be detected from RMNs below the samples surface, making them difficult to locate using SEM techniques.

1.4.1.2. Scanning electron microscopy

SEM provides a means of verifying the presence of RMNs at the sample surface that have been detected by synchrotron XRF.

SEM analysis uses a focussed beam of electrons that can be scanned over the sample (Joy, 2006; Lyman et al., 2012). The electron beam interacts with the sample and produces several types of emission as well as reflected electrons, such as secondary electrons (SE), backscattered electrons (BSE) characteristic X-rays, auger electrons and photons of various energies (Goldstein et al., 2012). These signals can be measured to produce various images (commonly grey-scale showing the intensity of the detected signal), which reveal different properties of the sample.
BSEs are generated from the reflection of the incident electron beam (Joy, 2006). The incident electron is scattered through an angle $\sim 90^\circ$ thereby leaving the sample (Joy, 2006). The yield of BSEs is known to be highly sensitive to the average atomic number, $Z$, of the sample beneath the incident electron beam; more BSE electrons are reflected from high $Z$ regions (Joy, 2006; Lyman et al., 1990, 2012). Within complex geological samples such as meteorites the contrast within a BSE image will reflect the variability of average $Z$ across the sample and between minerals: brighter regions will represent high $Z$ phases rich in elements such as Fe, Os, Ir, Pt whereas, darker areas will represent low $Z$ regions, rich in elements such as S, O, Si, or C. Therefore, BSE imaging is useful to broadly characterise a sample qualitatively and readily identify high average $Z$ regions for further analysis (Joy, 2006; Lyman et al., 1990, 2012). However, the yield of BSEs is also sensitive to the topography of the sample (Joy, 2006). Therefore, it is important to ensure that the sample is polished flat so the BSE image contrast purely relates to $Z$ and not sample topography. Crystallographic orientation of mineral phases can also affect BSE signal due to electron channelling along lattice planes (Joy, 2006). However, this effect is not significant for electrons that are backscattered at high angles to the sample surface.

1.4.1.3. Energy dispersive X-ray spectroscopy (EDS) mapping

The SEM electron beam also results in the emission of diagnostic X-Rays (Shindo and Oikawa, 2002). These X-rays are produced as the electron beam interacts with electrons from the inner shell of atoms within the sample (Shindo and Oikawa, 2002). The electrons are excited by the incident electron beam raising them to a higher energy level (Shindo and Oikawa, 2002). Excited electrons are
unstable in this higher energy state and return to their original position in the atomic structure by emitting diagnostic X-rays (Shindo and Oikawa, 2002). The energy of these emitted X-rays is specific to the element that was affected by the electron, meaning the identity of the element can be determined by evaluating the resulting energy spectrum (Shindo and Oikawa, 2002). The energy of the emitted X-rays is dependent on which electron in the atomic structure is excited, there are three main types K, L and M, which relate to the electron shell which was excited from the inner shell to the outer shell respectively (Shindo and Oikawa, 2002). Each of these emissions are subdivided into α, and β emission (L and M have a further subdivision: γ), which relate to the specific electron in the shell which was excited by the incident electron, and the energy level it was excited too (Shindo and Oikawa, 2002). These X-rays can be analysed through EDS or Wavelength Dispersive X-ray Spectrometry (WDS). WDS only analyse a single small energy range at a time and requires prior knowledge of the samples composition, whereas EDS detects X-rays of all energy levels resulting in a histogram (or energy spectrum) of counts vs X-ray energy with peaks relating to X-rays emitted by the major elements in the specimen (Shindo and Oikawa, 2002). The AZtec data acquisition software package from Oxford Instruments facilitates the analysis of this energy spectrum to identify and integrate peaks to calculate quantitative elemental abundances to rapidly determine the major element composition of the sample.

EDS analyses on the SEM can also be used to produce quantitative element maps of a sample (Shindo and Oikawa, 2002), meaning EDS is useful for obtaining a broad understanding of the mineral assemblage within meteorites. However, for the analysis of sub-micrometre phases, care must be taken to account for contributions from X-rays emitted by surrounding phases (i.e. Schwander et al. 2015b). This is due to the interaction volume of the electron
The interaction volume is the volume of the sample that is affected by the properties of the incident electron beam and the material (Shimizu and Murata, 1971; Cosslett and Thomas, 1965; Goldstein, 2012; Lloyd, 1987). It is usually teardrop-shaped for incident beams at high angles to the samples surface, and its size is dependent on the beam accelerating voltage, beam diameter (controlled primarily by the beam source type, such as W-filament, LAB6, or field emission), and the Z of the material being analysed (Shimizu and Murata, 1971; Cosslett and Thomas, 1965; Goldstein, 2012; Lloyd, 1987). For example, the interaction volumes for EDS using a W-filament SEM at 15 – 20kV are typically >1 µm³ (Goldstein, 2012) which is larger than many RMNs (<1 µm³) (Berg et al., 2009) or indeed any sub-micrometre sized particles. This means that X-rays will also be generated from the surrounding phases. Therefore, EDS spectra from typical SEM analyses of RMNs also contain signal from surrounding phases, and the spectra must be corrected for this in order to characterise RMN composition (Lyman et al., 1990; Schwander et al., 2015b).

1.4.1.4. ‘Feature’ mapping

One issue with identification of RMNs using synchrotron Maia XRF is that the large penetration depth of this technique (which incorporates ~ 100 µm of the sample thickness) can result in the detection of elemental hotspots relating to RMNs that are not exposed at the polished sample surface. Element detection is also somewhat user-dependant because it relies on subjective processing of the XRF data. To establish a more systematic method for RMN identification, a SEM-based technique was applied known as ‘Feature’ mapping, which is an additional proprietary software package for the INCA and AZtec software.
suites (Oxford-Instruments, 2006).

‘Feature’ mapping is a grain detection algorithm that systematically collects and montages BSE images for large areas (whole thin sections are possible), and then searches for and analyses every grain within a user-defined BSE brightness range via EDS (Oxford-Instruments, 2006). Given that RMNs have a high mean atomic number because they are comprised of HSEs (Wark and Lovering, 1976; Palme and Wlotzka, 1976), they are some of the brightest phases in meteorites, in BSE images. The ‘Feature’ mapping software can be calibrated to target only these bright phases for analysis (Oxford-Instruments, 2006).

The spatial resolution of field emission SEMs is generally better than 50 nm meaning SEMs are able to resolve features of \( \sim 50 \) nm (Trimby et al., 2014), which is the ideal size bracket in which to search for RMNs (0.09 – 1.2 \( \mu m \)) (Berg et al., 2009). The ‘Feature’ mapping technique is automated and systematically searches whole thin section(s) over reasonable time scales (overnight) (Oxford-Instruments, 2006). This means theoretically every particle larger than the step size used (in this case 100 nm) will be found and analysed. This technique could be applied to any phase which has a specific average \( Z \), meaning this technique can be used to find a multitude of phases in thin sections, not just RMNs.

1.4.1.5. Electron Backscatter Diffraction (EBSD) Mapping

Electron backscatter diffraction (EBSD) is a SEM crystallographic mapping technique for the characterisation and identification of crystal structures and their orientation in space. This is possible due to the interaction of the incident electron beam of the SEM on a tilted (70°), flat, polished, crystalline sample. The SEM electron beam at a given point interacts with crystalline materials such that electrons are diffracted by the crystal lattice within the top 10 – 50 nm, and
backscattered. Electron diffraction controlled by the crystalline lattice produces electron backscatter diffraction patterns (Nowell et al., 2005), which comprise diffraction bands, known as Kikuchi bands, of different widths, strengths and orientations that correspond to lattice planes in the analysed material. These patterns are directly related to the crystal structure and their 3D orientation relative to the plane of the section, and can be indexed in terms of mineral phase and crystallographic orientation by the detection of Kikuchi bands and a comparison (indexing) with a theoretical solution (Humphreys, 2001).

In SEM, EBSD patterns are collected by an EBSD detector, which is comprised of a phosphor screen, lens and a charge coupled device (CCD) camera to produce an image of the Kikuchi bands. These bands are detected using a Hough transform and sorted according to their widths and intensities (Schwartz et al., 2009). The angles between 5 – 10 of the most intense bands are evaluated and compared with theoretical solutions, or match units, to determine the crystal system and 3D orientation of the mineral (Schwartz et al., 2009). The more Kikuchi bands that match a particular solution the more likely this solution is correct. The accuracy of the solution is given by the Mean Angular Deviation (MAD), in degrees, which is a measure of the difference between the measured and calculated angles between Kikuchi bands; MAD values <1° are considered a good fit. There are several challenges with indexing phases particularly in multi-phase samples such as meteorites. Firstly, several minerals have the same crystal structures; for example, end member phases which form solid-solutions, such as olivine are indistinguishable with EBSD (Schwartz et al., 2009). This can be minimised with simultaneous EDS analyses to determine the chemistry of the phase to select the appropriate mineral match. Secondly, crystal lattices with lower symmetry have a continuous spectrum of inter-band angles, which increases the likelihood of an EBSD pattern matching multiple phases or
orientations, potentially resulting in misindexing. Furthermore, EBSD patterns across grains result in a mixed pattern, which can result in either non-indexing or misindexing (Schwartz et al., 2009). Largely, non-indexed and misindexed points can be minimised by adequate sample preparation, and ensuring the EBSD detector is as close as possible to the sample to increase the strength of EBSD patterns and thus improve band detection (Schwartz et al., 2009).

To acquire high quality EBSD patterns requires careful sample preparation because, the diffraction patterns are sourced from the top 10 – 50 nm (Nowell et al., 2005). Therefore, surface damage from mechanical polishing and even small variations in the topography of the sample are detrimental to the quality of the patterns produced (Nowell et al., 2005). The sample must be adequately polished to ensure that mechanical polish damage is removed and a flat surface is achieved prior to analysis. This process usually involves polishing using SiC grinding papers with progressively finer grit sizes, combined with diamond suspensions in the 1 – 0.25 µm range and a final chemical/mechanical polish using colloidal silica (0.05 µm) in NaOH to achieve the required surface for EBSD analysis (Nowell et al., 2005).

Sample preparation for EBSD is particularly challenging for the analysis of sub-micrometre phases. There is a risk that during polishing the grain may be plucked out of the sample or polished away completely. To mitigate this possibility, the sample was polished for 30 minutes, by hand, using the colloidal silica suspension. This resulted in a polish that still had remnants of damage from previous mechanical polishing stages (and consequently yielded EBSD patterns but with generally low pattern quality), while retaining the mineral phases of interest.

The EBSD data are interpreted using AZtec and Channel 5 software from
Oxford instruments. This allows us to readily observe the micro-structures within a mineral, such as twinning and internal deformation, as well as crystallographic relationships with surrounding minerals revealed by the EBSD patterns (Humphreys, 2001).

The resolution possible with EBSD varies between instruments but a spatial resolution as low as 20 – 50 nm is achievable (Chen et al., 2011; Dingley, 2004; Humphreys, 2004). However, EBSD is most useful to characterise the crystallography of minerals with grains sizes on the order of micrometres (Dingley, 2004; Schwartz et al., 2009). Sub-micrometre phases can be characterised using EBSD, however, the accuracy of the measurements is strongly dependant on the sample polish and the size of the grain (Humphreys, 2004). Therefore, in many cases, higher resolution analyses are required to accurately observe sub-micrometre scale structures within these grains.

1.4.2. Nanometre scale characterisation

The techniques described above could only characterise RMNs at the micrometre scale. Higher resolution analyses are required to acquire accurate geochemical and crystallographic data from RMNs. Several RMNs were analysed using TEM and TKD techniques.

1.4.2.1. Focused ion beam (FIB) sample preparation

To prepare RMN samples for TEM and TKD analyses they must first be extracted from the thin section. This involves the use of Focussed-Ion Beam (FIB) extraction techniques (see Li et al. 2006 and references therein). The region of interest is first covered in a layer of Pt from the Gas Injection System (GIS) using
secondary electrons in a 20 x 2 µm ‘bar’ over the region of interest to protect it from the Ga ion beam. A second thicker layer of Pt is then deposited using Ga ions. A wedge of material is milled away on both sides of the protective layer using the Ga ion beam. The sample is then attached to a Kleindiek micro-manipulator via a Pt weld and cut free from the sample using the Ga beam. The lamella is then attached to a Cu TEM grid via two Pt welds where it is thinned using a low energy Ga beam to ~ 100 nm or until the lamella becomes electron transparent.

1.4.2.2. Transmission electron microscopy (TEM)

TEM utilises a focussed beam of electrons between 60 – 150 keV that is transmitted through the sample (Reimer, 2013). TEM analyses can achieve a spatial resolution between 0.2 – 0.5 nm (Reimer, 2013), which is significantly higher than SEM techniques (20 – 50 nm) (Chen et al., 2011; Dingley, 2004; Humphreys, 2004; Sneddon et al., 2016). This increased spatial resolution reveals nano-scale features of the sample that are not observable in the SEM. The electron beam interacts with the sample to produce diagnostic X-rays in the same manner as EDS, allowing compositional data to be extracted from TEM analyses (Reimer, 2013).

The interaction of the electron beam with crystalline samples produces spot diffraction patterns that relate to the mineral crystal structure and orientation within the sample (Zaefferer, 2011). This allows for the observation of nano-scale crystallographic defects. However, determining the crystallographic orientation of a phase and the crystal structure with TEM requires a double tilt holder to rotate the specimen to align any of the crystallographic axes with the beam (i.e. Liu 1995). The amount of holder tilting is limited by the sample thickness and
specimen chamber dimensions, therefore, with some samples it may not be possible to rotate the crystal into the correct alignment.

Recent advances in Scanning TEM (STEM) now enabled imaging and EDS mapping of the entire TEM lamella (Nellist, 2007), while precession electron diffraction can produce automated orientation maps crystalline materials contained within the TEM lamellae. However, the angular resolution and accuracy of mineral indexing in precession electron diffraction is surpassed by EBSD (Sneddon et al., 2016).

1.4.2.3. **Transmission Kikuchi diffraction (TKD)**

Transmission Kikuchi Diffraction (TKD) utilises the transmission capabilities of the SEM to analyse TEM lamellae in the SEM (Trimby, 2012; Trimby et al., 2014). TKD analysis is very similar to EBSD and utilises the same Oxford Instruments software to interpret the data (Trimby, 2012; Trimby et al., 2014).

For TKD analysis, the electron transparent TEM lamellae are mounted in the SEM perpendicular to the electron beam (Sneddon et al., 2016). As the beam interacts with the sample, diagnostic X-rays are produced which can be analysed using EDS. Diffraction patterns are produced from the bottom surface of the sample, and coupled with the smaller diffraction source volume, result in an improved spatial resolution compared to EBSD (Sneddon et al., 2016). Furthermore, crystal orientation maps produced by TKD have an improved angular resolution (<0.5° Trimby et al. 2014) when compared to TEM (0.5 – 2° Zaefferer 2011) (Sneddon et al., 2016). Therefore, TKD may be the ideal tool to accurately map the crystallography and chemistry of meteoritic materials at the nano-scale.
1.4.3. ATOMIC SCALE CHARACTERISATION

TEM and TKD provide high-resolution analyses (Sneddon et al., 2016), however, these are not the highest resolution possible and cannot discern some fine textures, such as, chemical migration along grain boundaries, twin boundaries and other crystal defects, as well as to determine the trace element chemistry and isotopic abundances of sub-micrometre phases; These require sub-nanometre resolution. Atom Probe Microscopy (APM) is capable of atomic-scale resolution; i.e., detecting individual atoms (Gault et al., 2012; Kelly and Larson, 2012). APM also has the ability to reconstruct the positions of individual atoms within a sample to 0.3 nm in three dimensions (Kelly and Larson, 2012). APM has been applied extensively in the material science discipline (see Gault et al. 2012 and references therein), but has only recently been applied to geological materials (i.e. Valley et al. 2014; Piazolo et al. 2016).

1.4.3.1. ATOM PROBE MICROSCOPY (APM)

The Atom Probe Microscopy (APM) technique is described in detail in Kelly and Larson (2012) and Gault et al. (2012). The following is therefore a brief overview of the technique. Specimens analysed by APM are needle-like with a 100 nm diameter tip and a half shank angle <10° (Kelly and Larson, 2012). APM specimens are prepared using FIB techniques to mill out a sample wedge that is 2 µm wide. Two µm² wedges are attached to a pre-grown Si post with a Pt weld. The sample is then milled using an annular mask to produce a needle 1 – 5 µm tall with a tip diameter of 50 – 100 nm (Kelly and Larson, 2012). Finally, the sample is cleaned using a low kV polish to remove the top 30 nm where Ga ions may be emplaced during the shaping process (Thompson et al., 2006). The
specimen is placed in the atom probe near an annular electrode (Parman et al., 2015). The specimen is subjected to a high voltage (>1000 V) by the electrode (Parman et al., 2015). At high voltage, atoms are field evaporated from the specimen (Parman et al., 2015). These ions are accelerated across a potential difference where they impact a position sensitive detector (Parman et al., 2015) (Figure 1.6). The atom probe can also be set up in laser mode whereby the specimen is held just below the ionisation voltage (Parman et al., 2015). The specimen is then subject to a high frequency laser (100 – 250 kHz) that has sufficient energy to ionise a single atom (Parman et al., 2015) (Figure 1.6). The time of flight of the atom, as well as the x, y coordinates on the position sensitive detector, allow the 3D atomic structure of the specimen to be reconstructed (Parman et al., 2015). Ideally all atoms emitted from the specimen are detected. However, this is limited by the available space on the detector surface resulting in a detection efficiency of approximately 50 – 65 % (Parman et al., 2015).

**FIGURE 1.6:** Schematic diagram of the Local Electrode Atom Probe from Gault et al. (2012)
1.4.3.2. **Sample preparation**

APM has largely focussed on material science applications in which the exact location of the specimen in the sample is irrelevant. However, for the analysis of meteorite samples, knowledge of the exact location from which the tip was extracted is important, if not integral. The major benefit of APM is that it can analyse phases that are too small for other techniques. This complicates sample preparation because the grain of interest may be smaller than the wedge that is extracted via FIB (as is the case with RMNs, which in many cases are only 100 nm in diameter (Berg et al., 2009)). Therefore, it is important to know at all times during FIB extraction the location of the particle or grain boundary of interest. To counter this, a new approach was devised in this work for FIB preparation to ensure that RMNs were not lost or milled away during the sharpening of the APM specimen. This methodology utilised the deposition of a Pt button atop the region of interest that was then observable during milling to ensure accurate targeting of the annular mask, to taper the specimen to a needle-like shape with the RMN at the apex.

1.4.3.3. **Trace element geochemistry**

The APM technique is extremely sensitive and can detect elemental abundances at the 10 appm level provided sufficient counts are detected (Kelly and Larson, 2012). This means it can be utilised to analyse the trace element chemistry of mineral phases. Furthermore, the 3D reconstruction of the atomic positions and the size of the sample mean that it is possible to ensure only atoms emitted from the phase of interest are included in the spectrum. This means an accurate bulk chemistry of the phase of interest can be derived. This is ideal for analysing
the composition of RMNs and other sub-micrometre phases for which the trace element chemistry cannot be obtained through conventional techniques or where the phase of interest is contaminated by contributions from surrounding phases.

1.4.3.4. ISO Topic Analysis

APM measures the mass to charge state ratio (m/q) of each atom that is detected (Kelly and Larson, 2012). Furthermore, the APM has a mass resolution sufficient to discern between isotopes (Kelly, 2011). Therefore, it should be possible to extract isotopic information from the m/q spectrum. The small sample volumes that can be analysed as well as 3D atomic distribution combined with the total ionisation of the specimen that results in no mass fractionation of the sample (Parman et al., 2015) gives APM an advantage over other techniques such as the Sensitive High-Resolution Ion Microprobe (SHRIMP) or Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (i.e. Liu et al. 2008). APM can become a powerful tool for isotopic analysis. In particular, APM has the potential to accurately measure the isotopic abundances of sub-micrometre grains. The Chicago Instrument for Laser Ionisation (CHILI) instrument in Chicago has the potential to be able to conduct comparable analyses of RMNs (Kööp et al., 2016; Stephan et al., 2016) as could nano secondary ion mass spectroscopy (nanoSIMS) (Hoppe et al., 2013) pending the development of a suitable standard. Isotopic analysis from APM has only been reported in four studies prior to this work: Valley et al. (2014); Parman et al. (2015); Stadermann et al. (2011) and Heck et al. (2014), and a consistent methodology for extracting accurate isotopic information using APM has not been established. Several factors can affect the isotopic measurements of APM such as, background cor-
reactions, charge state, peak ranging methods, hydride contributions, complex ion formation, isobaric interferences and associated peak deconvolution methods as well as unique run specific effects such as temperature, voltage, and tip shape. Therefore, it is imperative that a standardised approach be established to deal with these factors as consistently as possible, which can be verified by established techniques for isotopic analysis such as Thermal Ionisation Mass Spectrometry (TIMS).

1.4.3.5. Thermal ionisation mass spectrometry (TIMS)

Thermal Ionisation Mass Spectrometry (TIMS) analysis is described in detail in Birck et al. (1997) and Aggarwal (2016), and produces precise isotopic measurements (Aggarwal, 2016). TIMS involves the chemical separation of elements within a specimen to produce several pure elemental samples to avoid contamination of the mass spectra and any potential isobaric interferences (Aggarwal, 2016). These samples loaded and dried onto a filament where they are heated to vaporise and ionise the atoms (Aggarwal, 2016). The filaments used typically must have a high melting point and work function in order to generate positive or negative ions from the sample (Aggarwal, 2016), negative ions are typically used for Os analysis (Birck et al., 1997). The ions are then focussed by electrostatic lenses before being separated by an electromagnet into beams which are determined by their mass/charge (m/q) ratio. These ions are collected and measured in a multi-faraday cup detector system (Aggarwal, 2016), or for samples with particularly low concentrations a secondary electron multiplier is used. A complication in TIMS analysis is systematic mass fractionation generated during ionisation, as lighter isotopes have a lower ionisation potential and are more easily ionised. The size of the mass fractionation is specimen
dependant and is therefore variable between samples and contribute to the analytical uncertainty of the technique (Aggarwal, 2016). Mass fractionation can be accounted for through several approaches: 1) Internal normalisation, if the isotope of interest has four or more isotopes and two stable isotopes with a known abundance, these can be used to correct the effects of mass fractionation; 2) External addition of a pre-calibrated double spike with a known isotopic ratio; 3) Total evaporation, where the entire sample is evaporated thus negating the effect of mass fractionation during the run (Aggarwal, 2016). Using these methods, precise (0.05 – 0.01 % uncertainty for isotope ratios Aggarwal 2016) isotopic data can be obtained for Re and Os (Tessalina et al., 2008) even for samples containing as little as 1 pg g$^{-1}$ Os (Birck et al., 1997).

1.5. RESEARCH OUTCOMES

The following section comprises a breakdown of the main research outcomes contained within each chapter of this thesis.

1.5.1. CHAPTER 2 - IN SITU ANALYSIS OF REFRACTORY METAL NUGGETS IN CARBONACEOUS CHONDRITES

This chapter describes the devised methodology for the identification of RMNs in situ, using a combination of XRF and Feature mapping. This resulted in the identification of over 100 RMNs within eight carbonaceous chondrites. This methodology produced one of the largest datasets of RMN compositions currently in existence. Other large datasets such as those of Berg et al. (2009) are limited as they are derived from acid residues where the petrographic context of
the RMN is lost. Furthermore, the leaching process may also affect the chemistry of RMNs (Daly et al., 2017). The only comparable in situ dataset is published in Schwander et al. (2015b). However, that dataset may be biased, as only CAIs, some chondrules, and their immediate surroundings were investigated for RMNs. This results of Chapter 2 reveal that RMNs are present within every meteoritic component, refuting the widely-held assumption that RMNs are unique to CAIs (e.g. Berg et al. 2009).

Retaining the petrographic context of RMNs, as well as being able to find and compare over one hundred examples enhances the ability to interpret their origins. The RMNs found in this work using the synchrotron XRF and Feature mapping techniques were analysed using EDS to obtain bulk compositions. These were compared to bulk compositions for RMNs reported in the literature in order to evaluate the various suggested formation mechanisms. The mechanisms compared included equilibrium condensation in the solar nebula (Berg et al., 2009), crystallisation from a silicate, or CAI melt (Schwander et al., 2015b), secondary process within the parent body (Blum et al., 1988) and a pre-solar origin (El Goresy et al., 1978). It was found that the diverse chemical heterogeneity within RMNs cannot be readily explained by any single nebula or parent body processes, or combinations thereof. The heterogeneous compositions suggest that RMNs either experienced a complex thermal history with successive episodes of condensation, melting and evaporation similar to cosmic spherules (Rudraswami et al., 2014), this is unlikely given the petrographic context of many RMNs precludes such an origin, or the solar nebula was initially seeded with an inherently diverse population of RMNs from the GMC and this heterogeneity was not overprinted or reset during nebula and parent body processing. The main implication of the latter explanation is that pre-solar RMNs may have survived nebula processing and can be found within
primitive meteorites. These findings are detailed in Chapter 2 and published in *Geochimica et Cosmochimica Acta* (Appendix A).

### 1.5.2. Chapter 3 - Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach

Several TEM lamellae containing RMNs and their associated host phases were extracted using FIB techniques from three carbonaceous chondrites: Allende CV3, Vigarano CV3 and ALH 77307 CO3. This included RMNs from several meteorite inclusions, including CAIs and sulphides. These RMNs were analysed using TKD and TEM to determine their crystallography and chemistry. Single phase RMNs from the same inclusion had different compositions which suggested that crystallisation from a silicate or CAI melt is not a dominant RMN forming process, as this mechanism would produce identical RMN compositions within the same inclusion. Crystallographic analyses of RMNs using TKD revealed textures which had not previously been observed. These include annealing twins in RMNs, which could constrain temperatures experienced during transient heating events. Other RMNs were crystallographically aligned with each other and hosted in sulphides. These RMNs are interpreted to form through the migration of HSEs away from the sulphidation reaction front, formed during the inclusions exposure to an S-rich gas during nebula sulphidation (Lauretta et al., 1996), and therefore could be used to constrain sulphur fugacity in the nebula. Some RMNs had crystallographic orientation relationships with their surrounding host phase, sharing a major crystal axis. This is interpreted as a nucleation texture which imply that some RMNs formed prior to their host phase which used the RMN as a nucleation site. The variety of
textures observed in RMNs indicate that they have a complex formation history. These findings are detailed in Chapter 3 and have been accepted for publication in *Geochimica et Cosmochimica Acta*.

**1.5.3. Chapter 4 - Nebula sulphidation and migration of ‘free floating’ refractory metal nuggets revealed by atom probe microscopy**

Atom probe microscopy (APM) was utilised to determine the major, minor and trace element composition of RMNs from an ultra-refractory inclusion (an inclusion composed of Zr-, and Sc-rich minerals (Ma et al., 2014)) in the ALH 77307 CO 3.0 meteorite in conjunction with textural observations using EBSD and EDS. Analysis revealed that some RMNs are not only composed of HSEs as had been previously thought, but also contain S. Sulphur is a volatile element, whereas HSEs are refractory (Lodders, 2003). The textures and mineral associations within the ultra-refractory inclusion are inconsistent with exposure to a S-rich gas (Lauretta et al., 1996; Lehner et al., 2013). This suggests that these RMNs were originally ‘free floating’ in the nebula when they incorporated S. The location of S condensation in the protoplanetary disk is between 0.5 – 1.5 AU (Ciesla, 2015), whereas the formation of RMNs is expected to occur near the proto-sun in the CAI forming region (<0.5 AU) (MacPherson et al., 2005). This requires either efficient mixing of material in the protoplanetary disk, as supported by several models of disk dynamics (i.e. Ciesla 2007), or the CAI forming region contained abundant S in the gas which diffused into these ‘free floating’ RMNs. These analyses show that the resolution possible with APM, and its ability to detect trace element abundances can inform our understanding of disk processes. These findings are detailed in Chapter 4 and are currently
under review in *Geology*.

### 1.5.4. Chapter 5 - Isotopic analysis of Refractory Metal Nuggets with Atom Probe Microscopy

In this chapter it is demonstrated that APM can accurately reproduce isotopic abundances for a number of HSEs through progressively more complex samples. These results are consistent with TIMS measurements. This suggests that isotopic information extracted by APM reflects real isotopic abundances. Therefore, for analysis of HSE materials that cannot be corroborated with TIMS, such as RMNs, the measured isotopic abundances from APM are robust. We constrain the current the current analytical sensitivity of APM for isotopic analysis of Re and Os using our approach is $\pm 1\%$ with significant grounds for improvement. This is not sufficient to detect nucleosynthetic anomalies (Yokoyama and Walker, 2016); none of the RMNs measured here exhibited nucleosynthetic anomalies.

RMNs and the standard materials analysed by APM contain abundant Os and Re. The $^{187}$Re-$^{187}$Os radiometric isotope system was used to calculate a model age for these samples. Five of the RMNs in this study were found to plot on an isochron consistent with the age of the Solar System (4.5 Ga), which is to be expected for RMNs of nebula origin (Amelin et al., 2002). However, the uncertainties associated with the isochron are large ($>5$ Ga). Single grain model ages were also calculated, which corroborate the solar age for these five RMNs, albeit with significantly lower uncertainties ($<1$ Ga). Interestingly, three RMNs did not plot on the solar isochron. The calculated single grain ages for two of these RMNs were older than the Solar System by 1 Ga and 0.2 Ga accounting for the uncertainty derived from the counting statistics. The other RMN had a lower
\(^{187}\text{Os}/^{189}\text{Os}\) ratio than the Solar System initial value. This RMN is pre-solar and has calculated Re-depletion and model ages that are \(>5.5\) Ga; the oldest material ever dated. These RMNs preserve a pre-solar age but do not exhibit an associated nucleosynthetic anomaly. These old RMNs may therefore represent a new type of pre-solar grain that do not exhibit nucleosynthetic anomalies. Osmium isotopes are well mixed in the protoplanetary disk (Brandon et al., 2005; Yokoyama et al., 2007; Walker, 2012; Reisberg et al., 2009; Yokoyama et al., 2010), but anomalies in Os isotope ratios have been observed on a granular level within acid residues (Reisberg et al., 2009; Yokoyama et al., 2010). The anomalous Os isotopes here are direct evidence for a pre-solar component some RMNs. APM can therefore, inform our understanding of stellar evolution, and the initial isotopic structure of the protoplanetary disk. This work is detailed in Chapter 5.

1.6. References


CHAPTER 2

PAPER 1 – IN SITU ANALYSIS OF REFRACTORY METAL NUGGETS IN CARBONACEOUS CHONDRITES

Luke Daly\textsuperscript{a}, Philip A. Bland\textsuperscript{a}, Kathryn A. Dyl\textsuperscript{a}, Lucy V. Forman\textsuperscript{a}, Katy A. Evans\textsuperscript{a}, Patrick W. Trimby\textsuperscript{b}, Steve Moody\textsuperscript{b}, Limei Yang\textsuperscript{b}, Hongwei Liu\textsuperscript{b}, Simon P. Ringer\textsuperscript{c}, Christopher G. Ryan\textsuperscript{d}, and Martin Saunders\textsuperscript{e}

\textsuperscript{a}Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

\textsuperscript{b}Australian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW 2006, Australia.

\textsuperscript{c}Australian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW, 2006, Australia.
CSIRO Earth Sciences and Resource Engineering, 26 Dick Perry Avenue, Kensington, Perth, WA 6151, Australia.

Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, WA 6009, Australia.

This article is published in Geochimica et Cosmochimica Acta, v. 216, p. 61 – 81
doi: 10.1016/j.gca.2016.11.030 and reprinted with permission in Appendix A.
ABSTRACT

Micrometre to sub-micrometre-scale alloys of platinum group elements (PGEs) known as refractory metal nuggets (RMNs) have been observed in primitive meteorites. The Australian Synchrotron X-ray Fluorescence (XRF) beamline, in tandem with the Maia detector, allows rapid detection of PGEs in concentrations as low as 50-100 ppm at 2 µm resolution. Corroborating these analyses with traditional electron microscopy techniques, RMNs can be rapidly identified in situ within carbonaceous chondrites. These results dispute the assumption of most previous studies: that RMNs are unique to Ca-Al-rich inclusions (CAIs). We find that RMNs are, in fact, observed within all components of carbonaceous chondrites, such as the matrix, chondrules (consistent with observations from Schwander et al. (2015b) and Wang et al. (2007)), and sulphides; though the majority of RMNs are still found in CAIs. The chemistry of RMNs reveals a complex diversity of compositions, which nevertheless averages to CI chondrite abundance ratios. This implies that RMNs are the dominant, if not sole host phase for PGEs. One hundred and thirteen RMNs from this study are combined with reported compositions in the literature, and compared to condensation model compositions similar to Berg et al. (2009), RMNs derived experimentally by precipitation (Schwander et al., 2015a), host phase and host meteorite. Comparisons reveal only weak correlations between parent body processes (sulphidation) and nebular processes (condensation and precipitation) with RMN compositions. It appears that none of these processes acting in isolation or in tandem can explain the diversity observed in the RMN population. Our interpretation is that the Solar Nebula inherited an initially compositionally diverse population of RMNs from the Giant Molecular Cloud; that a variety of Solar System processes have acted on that population; but none have com-
pletely homogenised it. Most RMNs have experienced disk and asteroidal processing, but some may have retained a primordial composition. RMNs have been identified in pre-solar graphite grains (Croat et al., 2013). We anticipate that pre-solar RMNs will be present elsewhere in primitive meteorites.

2.1. INTRODUCTION

Ca-Al-rich inclusions (CAIs) are the oldest solids to have formed in the Solar System, with an age of $4567.30 \pm 0.16$ Ma (Connelly et al., 2012). CAIs have been interpreted as primary high-temperature condensates which formed close to the protosun during the initial stages of the Solar Nebula, although some inclusions have experienced some degree of remelting (MacPherson et al., 2005). Analyses of CAIs indicate a significant enrichment in the platinum group elements (PGEs) W, Re, Os, Ir, Ru and Pt of between 22.8-11.9 times the elemental abundance observed in carbonaceous Ivuna-type (CI) chondrites (Grossman, 1973; Wänke et al., 1974). This enrichment was predicted to manifest itself in the form of refractory metal nuggets (RMNs) within these early condensates (Grossman and Ganapathy, 1976). This was confirmed by the observation of PGE-rich metal grains within CAIs in Allende (Palme and Wlotzka, 1976; Wark and Lovering, 1976).

Since this discovery, there has been ongoing debate over how RMNs formed. Initially Palme and Wlotzka (1976) found the composition of the RMN contained within a 20 µm CAI-hosted sulphide from Allende, plotted onto an ideal condensation curve for a nebular gas. These authors demonstrated that this RMN could form as a homogeneous primary condensate in the Solar Nebula, noting the high 50 % condensation temperatures of the PGEs within the RMN
would imply that these alloys should condense first. The RMN contained CI abundance ratios of the PGEs which indicated an equilibrium condensation temperature slightly higher than that of Fe. They also calculated that the expected abundance of RMN nucleation centres in the nebular would be sufficient, although this has been disputed by later studies (Petaev and Wood, 2005). However, subsequent studies have shown that these RMNs described by Palme and Wlotzka (1976) and Wark and Lovering (1976) had also been affected by secondary alteration on the parent body, including oxidation, sulphurisation, and exsolution (Bischoff and Palme, 1987; Blum et al., 1988; Palme and Wlotzka, 1976). These RMNs, therefore, cannot be considered primary nebular condensates (Bischoff and Palme, 1987; Blum et al., 1988).

To ascertain whether such grains could be produced from condensation in the Solar Nebula, Grossman (1973) calculated the chemical composition of the solid phases that would condense from a cooling solar gas. This work has been developed and refined with more recent calculations for condensation in the Solar Nebula by Fegley and Palme (1985) and Lodders (2003). These studies indicated that the PGEs should condense between $1392 \text{ K}$ and $1821 \text{ K}$ at $10^{-4}$ bar. However, it should be noted that local variability in the nebula dust component may cause these predicted condensation temperatures to vary (Petaev and Wood, 2005). RMNs appear to be the host for these elements in primitive carbonaceous chondrites. These predictions were supported by observations of sub-μm RMNs hosted within unaltered ‘fluffy’ type A CAIs from Allende. These RMNs had compositions consistent with a condensation origin, particularly, the presence of elements such as Mo and W, which are easily lost with even minor degrees of alteration (Palme et al., 1998). These RMNs also exhibited none of the secondary alteration textures observed in previous studies (Blander et al., 1980; Eisenhour and Buseck, 1992). Individual
RMNs with compositions consistent with condensation origin have also been described by Eisenhour and Buseck (1992).

Further analysis of RMNs divided them into two distinct families within CAIs (El Goresy et al., 1978): large 1-1000 µm multiphase inclusions containing micrometre-sized grains of RMNs (Blum et al., 1988), and isolated micrometre to sub-micrometre RMNs (Wark, 1986). Studies by El Goresy et al. (1977) and El Goresy et al. (1978) suggested that RMNs in multiphase inclusions had non-solar abundance ratios of PGEs and that isolated RMNs had solar abundance ratios. This indicated, alongside the condensation sequence of minerals which hosted the multiphase inclusions, that they could have had a pre-solar origin and conversely isolated grains may have had a nebular origin. However, such an origin for the multiphase inclusions is unlikely as these samples yielded solar isotopic ratios for Mg, Fe, Mo, Ru and W (Hutcheon et al., 1987). A pre-solar origin for RMNs has also been suggested by Wark and Lovering (1976) for non-solar PGE abundance ratios within isolated RMNs. Recent work has observed RMNs within pre-solar graphite (Croat et al., 2013) and a possible mechanism for the formation pre-solar-RMNs in asymptotic giant branch stars was discussed in Schwander et al. (2014b). These are the only RMNs that can be interpreted as having a pre-solar origin with relative certainty, though due to their small size, isotopic analyses have not been possible.

The analysis of RMNs has been limited by the difficulty of finding sufficient numbers due to their small size. This has meant that the contextual work on RMNs has been restricted to CAIs. Anders et al. (1975) noted that PGEs were enriched in residue samples of Allende (CV3oxA) that have been dissolved with strong acids. This observation prompted Berg et al. (2009) to study similar residues from the Murchison (CM2) meteorite using an acid digestion technique devised by Amari et al. (1994). This procedure concentrated RMNs and
permitted the analysis of several hundred grains rather than the <20 analysed in situ in CAIs from previous studies. Following earlier work, Berg et al. (2009) proceeded with the assumption that RMNs in their residues had previously been associated with CAIs. The compositions of RMNs contained within these residues from energy-dispersive X-ray spectroscopy (EDS) were in agreement with theoretical equilibrium condensation calculations for similar grains (Campbell et al., 2001). This led Berg et al. (2009) to conclude that all the analysed grains were nebula condensates. However, later work by Schwander et al. (2014a), who used an extra density separation to further concentrate RMNs, from Murchison, Allende and Leoville residues, showed that some, but not all RMNs from these residues have been affected by metamorphic oxidation and sulphidation on the parent body which resulted in the loss of W and Mo.

The abundant grains found in acid residues have significantly expanded the number of analyses of RMNs, but the loss of contextual information during acid dissolution of the bulk sample severely limits interpretation of the data. The assumption that has arisen in prior studies is that RMNs are unique to CAIs (Berg et al., 2009; Bischoff and Palme, 1987; Blander et al., 1980; Eisenhour and Buseck, 1992; El Goresy et al., 1978; Fegley and Kormacki, 1984; Grossman et al., 1977; Palme and Wlotzka, 1976; Palme et al., 1982; Sylvester et al., 1990; Wark, 1986; Wark and Lovering, 1976). However, recent work by Wang et al. (2007) described RMNs within chondrules. Schwander et al. (2015b) analysed over 200 RMNs in situ including the observation of RMNs within the matrix. This study suggests that the compositions of RMNs and their petrological context are inconsistent with a simple condensation model and that precipitation is a more likely mechanism for RMN formation, whereby the PGEs are dissolved into a silicate, or CAI melt. On quenching of this melt spherical RMNs are precipitated. This theory is supported by experimentally derived RMN-like
A diversity of terms can be found in the literature applied to these materials. In this study we will adopt the following terminology: RMNs will refer to any micrometre-sub-micrometre metal alloy grain that contains >1 atomic percent (at. %) of any PGE (Re, Os, Ir, Pt, Ru, Rh, Pd, W or Mo). If there is sufficient evidence to suggest a mechanism for how the RMN formed, a suitable precursor shall be attached to the start of the word i.e. pre-solar-RMN for an RMN with a demonstrably pre-solar origin similar to the naming scheme adopted by Croat et al. (2013). This can be extended to any process, e.g. sulphidation would produce sulphidation-RMNs, and primary nebular condensates would be designated condensation-RMNs, etc.

This paper presents a multidisciplinary study using the Australian Synchrotron (AS) X-ray Fluorescence (XRF) beamline alongside scanning electron microscopy (SEM) with EDS to facilitate rapid identification of RMNs in situ. The applications of these techniques allow rapid non-destructive quantification and determination at sub-micrometre scales whilst preserving context. The results of these analyses call into question the assumption that RMNs are unique to CAIs: we observe them in all chondritic components; reiterating and expanding upon observations made by Schwander et al. (2015b) and Wang et al. (2007). Comparing RMN compositions to equilibrium condensation models revealed a significant inconsistency. This suggests condensation in the nebular environment is unlikely for a large fraction of RMNs.
2.2. Method

The samples analysed in this study are thin and thick sections from the primitive carbonaceous chondrites: C2-ungrouped Acfer 094, C2-ungrouped Adelaide, CO3.0 ALH77307, CV3 Allende, CR2 Kaidun, CR2 Renazzo, and Murchison CM2, and CV3 Vigarano. Each thin section has an area of approximately 1 – 4 cm².

2.2.1. X-Ray Fluorescence Microscopy

The samples were analysed using the XRF beamline at the AS, combined with the Maia detector; a custom made 384 Si-diode detector (Ryan et al., 2010) with a dwell time of 0.488 msec per pixel. A more detailed discussion of the technique and its application to meteorites can be found in Dyl et al. (2014). This technique allows for rapid data collection over large areas with a resolution of 2 µm. The detector can analyse elements between the 4-18 keV range (Ryan et al., 2010). A particularly useful detail for this study is that PGE Lα, β, and γ energy peaks for Os, Ir and Pt lie in the most sensitive region of the spectrum (Figure 2.1), with L-α peaks at 8.910, 9.174 and 9.441 keV, respectively (Dyl et al., 2014). This permits detection down to 50-100 ppm for these elements (Cleverley et al., 2012).

The data collected was interpreted using the GeoPIXE software, which uses a dynamic analysis matrix to deconvolve peaks of each individual element to generate elemental distribution maps (Ryan et al., 1995). The element maps are used to identify pixel-sized hotspots of PGEs as likely candidates for the location of RMNs with slight adjustments to contrast and brightness to make
the most abundant regions stand out from the background.

The sample of Acfer 094 had been gold-coated for previous studies, and although this has been largely removed, a small residue remains. This generated a slight problem as the gold peak is in the same region of the spectrum as the Os, Ir, and Pt energy peaks. This interfered with the spectrum, and generated false positives. In the case of this sample, the problem was countered by analysing each spectrum on an individual basis to ensure true RMNs were observed rather than a residual gold particle.

Due to the penetrating nature of the X-ray beam employed (18.5 keV), fluorescence X-rays from elements are received from up to 100 µm depth into the sample (Dyl et al., 2014). This generates a problem when trying to corroborate PGE hotspots with established techniques such as SEM and EDS, which only have penetration depths of ~ 1 µm. This, coupled with the size of the RMNs, which tend to be 90 nm-1.2 µm (Berg et al., 2009) means that any one PGE hotspot identified with the synchrotron has a 99 % chance of being buried beneath the surface of the sample. However, this is also a benefit as a larger number of in situ grains are observed.

2.2.2. Scanning Electron Microscopy

The samples were analysed using two instruments: the Zeiss 1555 VP-FESEM at the Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia, and the Zeiss EVO50 LaB6 at the Australian Centre for Microscopy and Microanalysis (ACMM), the University of Sydney. Both instruments are equipped with 80 mm² high count rate silicon drift detector (SDD) EDS detectors. In both cases an accelerating voltage of 25 kV was used. Element maps derived from the AS data were geo-referenced with the live
FIGURE 2.1: Bulk Synchrotron spectrum from Allende; with the raw data depicted by the bold line and the fit calculated by GeoPIXE™ indicated by the dashed line. The solid and thinner black line signifies the background contribution to the spectra. Taking into account contributions such as the large iron peak and secondary pile up peak, along with the Compton scatter region, the detection limits are highlighted by the greyscale gradient map. The location of the Lα peaks for Os, Ir and Pt are highlighted in red and sit in the region of highest sensitivity and lowest detection limits. Image adapted after Dyl et al. (2014).
SEM image using the image overlay feature in Oxford Instrument’s AZtec software. This method allowed rapid searching for RMNs present at the surface of the sample with high accuracy. This process was augmented by the feature mapping software in the Inca suite, which allowed whole thin section searches based on contrast bands. As RMNs are one of the densest phases in meteorites and backscatter microscopy reveals density differences in mineral phases; the brightest spots were refractory metal grains. This allowed us to analyse every metal grain at the surface of a sample. This method detected all the RMNs that were found using the combined synchrotron and EDS geo-referencing technique described above, along with a few others that were missed. The composition of the grains was derived using standardless quantitative analysis, using the standard database embedded within the Aztec software. Although a total of 145 RMNs were measured, the EDS spectra obtained through the feature mapping technique did not permit quantitative compositional measurements. 113 RMNs were relocated in the sample and a second EDS measurement was taken with a longer live time and with a process time of 5, enabling better energy resolution and detection limits. Elemental abundances for Ru, Mo, W, Re, Os, Ir and Pt were derived using the L-α X-ray lines in the spectra which are better separated than the M lines. Fe and Ni abundances were calculated using the K X-ray lines. Detection limits for elements within RMNs were <2 at. % for small RMNs and <1 at. % for larger RMNs. The relative uncertainty in these measurements is approximately ± 10 % providing sufficient accuracy to detect major and minor elements and draw comparisons between measured RMN compositions in different meteoritic components.

As the interaction volume of the EDS measurements is significantly larger than the RMN, we would expect some contribution from the surrounding phases in the spectra. Therefore, we have corrected and renormalised our data
using the same methodology as Schwander et al. (2015b); removing elements present in the surrounding host phase such as Mg, Ca, O, Al, Si, etc, and only retaining elements present in RMNs: Fe, Ni, Ru, Rh, Mo, W, Re, Os, Ir, and Pt (Harries et al., 2012). As Schwander et al. (2015b) described, it should be noted that Fe may be slightly overestimated in some samples due to small amounts of Fe in the surrounding phases, increasing the Fe signal. Also Ni and Fe are likely to be elevated in RMNs found in Fe-Ni sulphides due to the contribution of Fe and Ni in the host. RMN compositions were converted to atomic percent (at. %) and renormalised.

Some RMNs were extracted from the sample using a Focused Ion Beam (FIB) technique using the Zeiss Auriga FIB-SEM at the ACMM, the University of Sydney. A thin protective layer of Pt was deposited using secondary electrons followed by a much thicker Pt layer deposited using Ga ions. The sample was then cut out using the Ga beam and extracted using a Kleindiek micromanipulator and welded to a Cu transmission electron microscopy mount by depositing more Pt. The sample was thinned down to 100 nm using a fine Ga beam. The samples were analysed using transmission Kikuchi diffraction (TKD) on a Zeiss ULTRA Plus FEG SEM at the ACMM, the University of Sydney. EDS data from the RMNs in each section were collected with an X-Max 20 mm² SDD EDS detector using an acceleration voltage of 30 kV. The same X-ray lines used to calculate elemental abundances, and the detection limits and uncertainty are similar to those described above. As Pt was used as a protective layer it is likely that we could observe an enrichment in the Pt signal from fluorescence in the chamber. Samples prepared in this way are denoted by a ‘*’ in Table 2.3.
2.2.3. Condensation model and precipitation proxy

An exhaustive literature search was conducted in an attempt to produce a library of all previous RMN compositional data (Berg et al., 2009; Bischoff and Palme, 1987; Blander et al., 1980; Wark and Lovering, 1976; Wark, 1986; Palme et al., 1982; Croat et al., 2013; Schwander et al., 2014a; Palme et al., 1994; Wark and Lovering, 1978; Harries et al., 2012; Schwander et al., 2015b). We also include compositions of synthetic RMNs thought to be derived from precipitation processes (Schwander et al., 2015a), as well as RMNs observed in cosmic spherules (Rudraswami et al., 2014). These analyses were plotted alongside observed RMN compositions from this study.

Compositions for hypothetical RMN condensates were calculated using the approach described in Palme and Wlotzka (1976) with slight modification. A set of ten non-linear equations were specified for the elements Fe, Ni, Ru, Pt, Rh, Mo, Ir, Os, Re and W, each of the form of Palme and Wlotzka (1976) equation [6]. Values for the cosmic abundances were taken from Lodders (2003). The equations were solved using a non-linear equation solver embedded in the Mathematica™ package at $10^{-3}$ and $10^{-4}$ bars for temperatures from 1200 to 1700 K with 10 K increments to produce a set of alloy compositions, $calc$, where $calc$ is a $1 \times 10$ matrix consisting of the mole fractions of the ten specified elements. Residuals, $\Sigma (obs_i - calc_{i,T})^2$, were calculated where $i$ represents each of the 10 elements, $obs$ is the $1 \times 10$ matrix of the analysed alloy compositions for the 10 elements, $obs_i$ is the mole fraction of element $i$ in the alloy of interest, and $calc_{i,T}$ is the mole fraction of element $i$ in the calculated alloy at specified temperature $T$. Residuals were calculated at each temperature for each alloy, and the temperature with the minimum residual for each alloy was chosen as the best guess of the temperature at which that alloy equilibrated with the
fractionated solar nebula. Pressures of $10^{-4}$ bar provided smaller residuals and compositions calculated at this pressure were therefore used. Oxide compounds of W and Mo were excluded from the model, and all activity coefficients were set to 1, in accordance with other condensation models (Berg et al., 2009; Harries et al., 2012). Temperatures were calculated for analysed RMNs using the same methodology as Berg et al. (2009): using a least squares fit for each RMN composition to the predicted composition as a function of temperature for pressures $10^{-3}$ bar and $10^{-4}$ bar. The results of Harries et al. (2012) were used as a check for the method and were found to be generally consistent with the results obtained in this model.

2.3. RESULTS

2.3.1. SYNCHROTRON

In depth analyses of the element maps derived from the AS were used to target and identify hotspots of PGEs. The vast majority of observed hotspots are pixel-sized, indicating grains are $<2 \mu m$. Each carbonaceous chondrite section analysed yielded an average of 10 hotspots per sample, with a maximum of 71 in Vigarano and a minimum of two in Adelaide and Acfer 094. The proximity of the K$\alpha$ and L$\alpha$ peaks of the PGEs to each other and major elements such as Zn, combined with the penetration depth, make it difficult to deconvolve the spectrum into individual element peaks. This means that the spectrum’s shape is defined by the most abundant element in that energy range. Great care was taken in analysing the spectra to avoid misidentification due to peak overlaps; removing false positives. Most observed hotspots are located within CAIs as
expected, however a number are observed within chondrules, sulphides, and matrix (Table 2.1). Kaidun and Renazzo seem to be dominated by matrix RMNs, although as these meteorites are brecciated and contain only rare small CAIs this may explain this preferred matrix association for RMNs in these meteorites.

**Table 2.1:** The number of PGE hotspots in each type of inclusion (CAI, chondrule, and matrix) observed within the Acfer 094, Adelaide, ALH 77307, Kaidun, Renazzo, and Vigarano meteorites, identified using the synchrotron XRF beamline.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Total RMNs</th>
<th>CAI</th>
<th>Host Chondrule</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acfer 094</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Adelaide</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>17</td>
<td>12</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Kaidun</td>
<td>9</td>
<td>0</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Renazzo</td>
<td>6</td>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Vigarano</td>
<td>71</td>
<td>69</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

**2.3.2. SYNCHROTRON TO SEM**

**Table 2.2:** The abundance of RMNs in each type of inclusion (chondrule, matrix, sulphide and CAIs) observed within the Adelaide, ALH 77307, Allende, Murchison, and Vigarano meteorites. These RMNs were found by SEM and EDS analyses using the image overlay of synchrotron maps with PGE hotspots, and supplemented with RMNs identified using the INCA feature mapping software.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Total RMNs</th>
<th>Chondrule</th>
<th>Host Matrix</th>
<th>Sulphide</th>
<th>CAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adelaide</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>16</td>
<td>0</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Allende</td>
<td>86</td>
<td>4</td>
<td>6</td>
<td>53</td>
<td>23</td>
</tr>
<tr>
<td>Murchison</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Vigarano</td>
<td>37</td>
<td>1</td>
<td>0</td>
<td>19</td>
<td>17</td>
</tr>
</tbody>
</table>
Figure 2.2: Synchrotron element maps (left hand side) and corresponding SEM back scattered electron (BSE) images (right hand side) of the same regions in meteorites, indicating how elemental hotspots of PGEs in Synchrotron maps can be used to find RMNs on the surface of meteorite samples. Hotspots of the PGEs in synchrotron data (Ir in red and Os in green) relate to RMN localities on the surface of the thin section (bright points). The upper images were from the ALH 77307 meteorite and revealed RMNs within a Sc-Zr-rich CAI-like inclusion, and the lower images were from the Vigarano meteorite and revealed a single RMN within a zoned ‘fluffy’ type A CAI.
Figure 2.3: SEM backscatter images of RMNs in all meteoritic components
a) RMN hosted in matrix from ALH 77307 in the vicinity of a CAI b) RMN hosted in a åkermanite (Ak) and perovskite (Per)-rich CAI in ALH 77307, c) RMN hosted in a chondrule in Allende within forsterite (Fo) d) RMNs hosted within a (Fe-Ni)S rim around a chondrule in Allende.
Not all Synchrotron PGE hotspots yielded an RMN present on the surface of the sample in the SEM. This is expected due to the large penetration depth of synchrotron radiation. However, some hotspots revealed more than one RMN (Figure 2.2). The feature mapping technique also increased the number of observed RMNs substantially, revealing several RMNs that the synchrotron data had not identified. Therefore, despite the low probability of observing RMNs at the surface with synchrotron radiation, the combination of these techniques, particularly the utilisation of the INCA feature mapping technique, identified 145 RMNs. These RMNs vary in size from 0.1 µm to 9.71 µm with an average of 1.2 µm, and a median of 0.88 µm. With the exception of two anomalously large (>5 µm) RMNs the vast majority are consistent with the size ranges described in other studies (Berg et al., 2009; Schwander et al., 2015b). These RMNs were found across several meteorite samples; 2 in Adelaide, 86 in Allende, 37 in Vigarano, and 16 in ALH 77307. Most RMNs are found in CAIs (51) or sulphides which are hosted within CAIs, chondrules, and chondrule rims (79), but a number are observed within the matrix (9) and chondrules (6) of these meteorites (Figure 2.3) (Table 2.2). Of the 145 RMNs identified 113 have reliable EDS chemical analyses. The composition of the RMNs derived from EDS varies greatly between host and samples; Re and Rh were below detection limits for most RMNs analysed. The compositions of RMNs with reliable EDS data from this study are summarised in Table 2.3 and average compositions of RMNs for each inclusion and meteorite are detailed in Table 2.4.
Table 2.3: RMN compositions from EDS in at. %, indicating the meteorite, inclusion, and host mineral phase. The data is also available in Supplementary Appendix 1.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Inclusion</th>
<th>Host</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Rh</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adelaide</td>
<td>CAI</td>
<td>anorthite</td>
<td>66.9</td>
<td>7.7</td>
<td>7.0</td>
<td>b.d.</td>
<td>14.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Adelaide</td>
<td>Chondrule</td>
<td>melilitc</td>
<td>91.8</td>
<td>2.6</td>
<td>2.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.3</td>
<td>0.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>ALH 77307</td>
<td>CAI</td>
<td>ScZr-spinel</td>
<td>25.9</td>
<td>2.1</td>
<td>13.7</td>
<td>b.d.</td>
<td>21.0</td>
<td>2.6</td>
<td>b.d.</td>
<td>14.2</td>
<td>20.5</td>
<td>b.d.</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>CAI</td>
<td>ScZr-spinel</td>
<td>43.0</td>
<td>3.4</td>
<td>13.9</td>
<td>b.d.</td>
<td>16.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>9.5</td>
<td>13.5</td>
<td>b.d.</td>
</tr>
<tr>
<td>ALH 77307*</td>
<td>CAI</td>
<td>akermanite</td>
<td>46.3</td>
<td>6.7</td>
<td>13.1</td>
<td>3.2</td>
<td>14.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.6</td>
<td>2.9</td>
<td>8.3</td>
</tr>
<tr>
<td>ALH 77307*</td>
<td>CAI</td>
<td>akermanite</td>
<td>40.0</td>
<td>3.8</td>
<td>9.1</td>
<td>b.d.</td>
<td>38.8</td>
<td>2.0</td>
<td>b.d.</td>
<td>2.8</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>anorthite</td>
<td>58.5</td>
<td>2.7</td>
<td>10.9</td>
<td>b.d.</td>
<td>17.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.3</td>
<td>6.2</td>
<td>b.d.</td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>anorthite</td>
<td>46.4</td>
<td>13.6</td>
<td>15.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.7</td>
<td>12.9</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>anorthite</td>
<td>16.1</td>
<td>29.2</td>
<td>14.4</td>
<td>b.d.</td>
<td>24.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>5.0</td>
<td>5.8</td>
<td>5.3</td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>forsterite</td>
<td>18.1</td>
<td>b.d.</td>
<td>44.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>22.6</td>
<td>14.8</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>forsterite</td>
<td>21.3</td>
<td>5.4</td>
<td>41.0</td>
<td>b.d.</td>
<td>6.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>12.4</td>
<td>13.9</td>
<td>b.d.</td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>forsterite</td>
<td>30.3</td>
<td>12.0</td>
<td>31.1</td>
<td>b.d.</td>
<td>2.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>10.2</td>
<td>13.6</td>
<td>b.d.</td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>forsterite</td>
<td>62.0</td>
<td>b.d.</td>
<td>19.1</td>
<td>b.d.</td>
<td>2.4</td>
<td>b.d.</td>
<td>9.0</td>
<td>7.5</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>21.5</td>
<td>9.7</td>
<td>38.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>16.4</td>
<td>13.7</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>30.9</td>
<td>24.9</td>
<td>22.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>10.8</td>
<td>10.5</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>37.5</td>
<td>49.5</td>
<td>4.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.5</td>
<td>7.4</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>29.8</td>
<td>20.5</td>
<td>28.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>10.6</td>
<td>10.8</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>34.0</td>
<td>31.6</td>
<td>16.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.2</td>
<td>10.3</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>30.6</td>
<td>1.9</td>
<td>64.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>2.3</td>
<td>b.d.</td>
<td></td>
</tr>
</tbody>
</table>

b.d. = below detection limit.
<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Inclusion</th>
<th>Host</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Rh</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>39.7</td>
<td>42.7</td>
<td>5.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.8</td>
<td>7.1</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>melilite</td>
<td>33.7</td>
<td>59.5</td>
<td>b.d.</td>
<td>1.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.2</td>
<td>0.9</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>perovskite</td>
<td>44.5</td>
<td>b.d.</td>
<td>13.4</td>
<td>b.d.</td>
<td>22.8</td>
<td>b.d.</td>
<td>9.1</td>
<td>10.2</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>perovskite</td>
<td>79.3</td>
<td>b.d.</td>
<td>20.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>pyroxene</td>
<td>35.3</td>
<td>5.5</td>
<td>26.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>18.8</td>
<td>14.2</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>pyroxene</td>
<td>21.7</td>
<td>1.3</td>
<td>43.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>16.9</td>
<td>16.9</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>pyroxene</td>
<td>20.3</td>
<td>b.d.</td>
<td>45.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>16.5</td>
<td>17.6</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>pyroxene</td>
<td>54.3</td>
<td>6.4</td>
<td>17.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>10.5</td>
<td>11.1</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>spinel</td>
<td>27.0</td>
<td>2.9</td>
<td>31.4</td>
<td>b.d.</td>
<td>17.0</td>
<td>b.d.</td>
<td>11.4</td>
<td>10.4</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>spinel</td>
<td>49.4</td>
<td>3.6</td>
<td>15.6</td>
<td>b.d.</td>
<td>16.2</td>
<td>b.d.</td>
<td>7.1</td>
<td>8.1</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>forsterite</td>
<td>32.4</td>
<td>64.4</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.6</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>forsterite</td>
<td>34.6</td>
<td>62.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>forsterite</td>
<td>29.7</td>
<td>32.7</td>
<td>28.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>6.4</td>
<td>1.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim forsterite</td>
<td>32.5</td>
<td>61.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni)S</td>
<td>68.9</td>
<td>28.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni)S</td>
<td>71.5</td>
<td>27.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni)S</td>
<td>65.9</td>
<td>29.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.8</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni)S</td>
<td>71.2</td>
<td>26.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.2</td>
<td>0.3</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni)S</td>
<td>70.0</td>
<td>25.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni)S</td>
<td>71.8</td>
<td>26.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Meteorite</td>
<td>Inclusion</td>
<td>Host</td>
<td>Fe</td>
<td>Ni</td>
<td>Ru</td>
<td>Rh</td>
<td>Mo</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------</td>
<td>---------------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>84.2</td>
<td>11.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>66.3</td>
<td>30.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>70.9</td>
<td>28.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>68.7</td>
<td>28.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>68.5</td>
<td>28.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.2</td>
<td>0.5</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>69.8</td>
<td>28.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>67.4</td>
<td>30.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>70.7</td>
<td>29.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>44.1</td>
<td>3.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>49.1</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>44.1</td>
<td>40.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>6.0</td>
<td>9.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>57.8</td>
<td>35.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.1</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>60.1</td>
<td>34.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.6</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>63.5</td>
<td>29.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>5.8</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>42.8</td>
<td>41.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.2</td>
<td>13.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>49.1</td>
<td>48.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.8</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>49.3</td>
<td>37.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>11.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>46.2</td>
<td>40.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.6</td>
<td>10.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>49.6</td>
<td>31.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.3</td>
<td>16.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>39.1</td>
<td>46.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.3</td>
<td>10.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meteorite</td>
<td>Inclusion</td>
<td>Host</td>
<td>Fe</td>
<td>Ni</td>
<td>Ru</td>
<td>Rh</td>
<td>Mo</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>---------------------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>51.0</td>
<td>33.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.5</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>62.6</td>
<td>34.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.3</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>71.3</td>
<td>23.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.9</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>47.1</td>
<td>39.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.7</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>58.4</td>
<td>32.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.0</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>66.3</td>
<td>32.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>61.3</td>
<td>32.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>54.6</td>
<td>39.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>46.2</td>
<td>39.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.7</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim Sulphide</td>
<td>(Fe,Ni)S</td>
<td>56.7</td>
<td>36.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.5</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>47.9</td>
<td>37.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>59.5</td>
<td>31.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>5.2</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>67.7</td>
<td>27.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>5.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide</td>
<td>(Fe,Ni)S</td>
<td>47.8</td>
<td>35.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>9.1</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>62.4</td>
<td>27.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.0</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>61.3</td>
<td>32.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>62.2</td>
<td>30.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>6.1</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>38.3</td>
<td>4.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.9</td>
<td>52.8</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>65.5</td>
<td>28.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.6</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>53.3</td>
<td>36.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.2</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3 – continued from previous page

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Inclusion</th>
<th>Host</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Rh</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>67.1</td>
<td>21.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>9.3</td>
<td>1.8</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule sulphide</td>
<td>(Fe,Ni)S</td>
<td>54.1</td>
<td>34.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.9</td>
<td>7.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Matrix</td>
<td>melilitte</td>
<td>51.4</td>
<td>46.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.7</td>
<td>b.d.</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Matrix</td>
<td>melilitte</td>
<td>40.6</td>
<td>58.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Matrix</td>
<td>melilitte</td>
<td>48.9</td>
<td>47.2</td>
<td>1.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>0.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Matrix</td>
<td>melilitte</td>
<td>74.5</td>
<td>21.4</td>
<td>1.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.6</td>
<td>1.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Matrix</td>
<td>melilitte</td>
<td>60.7</td>
<td>38.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Matrix</td>
<td>melilitte</td>
<td>66.3</td>
<td>33.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Allende*</td>
<td>Chondrule sulphide</td>
<td>pentlandite</td>
<td>45.2</td>
<td>33.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.8</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td>Allende*</td>
<td>Chondrule sulphide</td>
<td>pentlandite</td>
<td>45.4</td>
<td>32.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.7</td>
<td>4.8</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>Allende*</td>
<td>Chondrule sulphide</td>
<td>pentlandite</td>
<td>51.9</td>
<td>31.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>6.7</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Allende*</td>
<td>Chondrule sulphide</td>
<td>pentlandite</td>
<td>29.0</td>
<td>63.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.4</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Allende*</td>
<td>Chondrule sulphide</td>
<td>pentlandite &amp; troilite</td>
<td>43.5</td>
<td>34.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>6.0</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>Murchison</td>
<td>CAI</td>
<td>forsterite</td>
<td>77.5</td>
<td>4.7</td>
<td>7.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.2</td>
<td>3.3</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Murchison</td>
<td>CAI</td>
<td>perovskite</td>
<td>57.3</td>
<td>5.1</td>
<td>5.3</td>
<td>b.d.</td>
<td>24.3</td>
<td>1.6</td>
<td>3.6</td>
<td>1.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Murchison</td>
<td>CAI sulphide</td>
<td>(Fe,Ni)S</td>
<td>47.0</td>
<td>29.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>15.7</td>
<td>7.2</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Murchison</td>
<td>Matrix sulphide</td>
<td>(Fe,Ni)S</td>
<td>40.8</td>
<td>35.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.5</td>
<td>3.8</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>anorthrite</td>
<td>53.0</td>
<td>40.8</td>
<td>4.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>anorthrite</td>
<td>55.8</td>
<td>40.6</td>
<td>2.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>melilitte</td>
<td>67.3</td>
<td>30.1</td>
<td>1.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Meteorite</td>
<td>Inclusion</td>
<td>Host</td>
<td>Fe</td>
<td>Ni</td>
<td>Ru</td>
<td>Rh</td>
<td>Mo</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>------------</td>
<td>------</td>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>pyroxene</td>
<td>72.2</td>
<td>1.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.5</td>
<td>4.6</td>
<td>b.d.</td>
<td>9.5</td>
<td>4.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>pyroxene</td>
<td>61.1</td>
<td>34.2</td>
<td>2.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>pyroxene</td>
<td>63.9</td>
<td>31.0</td>
<td>1.9</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.6</td>
<td>0.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>pyroxene</td>
<td>67.5</td>
<td>28.2</td>
<td>1.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Vigarano</td>
<td>CAI</td>
<td>spinel</td>
<td>50.5</td>
<td>15.5</td>
<td>15.3</td>
<td>b.d.</td>
<td>11.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.1</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>62.9</td>
<td>29.5</td>
<td>5.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>0.9</td>
<td>b.d.</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>67.4</td>
<td>15.5</td>
<td>11.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.6</td>
<td>2.8</td>
<td>b.d.</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>61.5</td>
<td>30.1</td>
<td>4.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.0</td>
<td>2.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>65.7</td>
<td>14.1</td>
<td>14.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.4</td>
<td>3.7</td>
<td>b.d.</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>55.4</td>
<td>39.2</td>
<td>2.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.7</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>57.0</td>
<td>36.4</td>
<td>3.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>anorthite</td>
<td>64.4</td>
<td>17.7</td>
<td>10.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.4</td>
<td>3.7</td>
<td>b.d.</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>spinel</td>
<td>38.3</td>
<td>14.5</td>
<td>23.2</td>
<td>b.d.</td>
<td>13.1</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.8</td>
<td>3.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Vigarano*</td>
<td>CAI</td>
<td>spinel &amp; anorthite</td>
<td>48.8</td>
<td>48.6</td>
<td>1.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.4</td>
<td>b.d.</td>
<td>0.5</td>
</tr>
</tbody>
</table>

b.d. Element was below detection limits for this RMN

*RMNs prepared using FIB techniques
Table 2.4: Average RMN compositions in at. %, for each meteorite analysed in this study and for each inclusion type.

<table>
<thead>
<tr>
<th>Average RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Rh</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>All RMN</td>
<td>39.1</td>
<td>20.9</td>
<td>11.9</td>
<td>1.6</td>
<td>10.9</td>
<td>1.6</td>
<td>1.8</td>
<td>5.3</td>
<td>3.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Adelaide</td>
<td>73.4</td>
<td>4.7</td>
<td>4.4</td>
<td>b.d.</td>
<td>13.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.2</td>
<td>0.9</td>
<td>2.4</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>36.6</td>
<td>3.7</td>
<td>11.7</td>
<td>3.0</td>
<td>21.5</td>
<td>2.2</td>
<td>b.d.</td>
<td>7.3</td>
<td>9.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Allende</td>
<td>36.3</td>
<td>21.6</td>
<td>16.5</td>
<td>0.7</td>
<td>8.8</td>
<td>0.2</td>
<td>2.2</td>
<td>6.4</td>
<td>3.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Murchison</td>
<td>45.4</td>
<td>15.2</td>
<td>5.4</td>
<td>b.d.</td>
<td>19.8</td>
<td>1.3</td>
<td>b.d.</td>
<td>4.9</td>
<td>3.2</td>
<td>4.9</td>
</tr>
<tr>
<td>Vigarano</td>
<td>51.4</td>
<td>23.7</td>
<td>5.8</td>
<td>b.d.</td>
<td>9.3</td>
<td>4.0</td>
<td>0.9</td>
<td>1.9</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>CAI</td>
<td>38.7</td>
<td>16.1</td>
<td>13.7</td>
<td>1.7</td>
<td>13.1</td>
<td>2.2</td>
<td>0.9</td>
<td>5.5</td>
<td>5.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Chondrule</td>
<td>41.5</td>
<td>42.0</td>
<td>9.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.6</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulphide</td>
<td>49.5</td>
<td>27.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.1</td>
<td>b.d.</td>
<td>2.7</td>
<td>9.3</td>
<td>3.2</td>
<td>5.0</td>
</tr>
<tr>
<td>Matrix</td>
<td>56.2</td>
<td>40.2</td>
<td>1.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

b.d. Element was below detection limits for this RMN

2.4. Discussion

2.4.1. Evaluation of the Database

The detection of elements such as Al, Ca, Mg, and O (which were present in the host phase and not from the RMN), from the RMN EDS measurement, resulted in small wt. % totals. To evaluate whether this deduction and subsequent renormalisation process has introduced any inherent biases or compound errors, each renormalised element was plotted in relation to the initial wt. % total of PGEs + Fe + Ni before re-normalisation (Figure 2.4). If the normalisation process was producing a systematic error, steep trends from small wt. % totals to high wt. % totals would be observed. However, these graphs had very shallow to flat trends indicating normalisation has not introduced significant bias.
FIGURE 2.4: At. % abundances of Fe, Ni and PGE elements vs the wt. % total pre-normalisation of the RMN component in the EDS spectra for all samples from this study. The line in each graph represents a line of best fit through the data. These show relatively shallow trends which are significantly smaller than the overall compositional variability in at. % for each element. Therefore, it is unlikely that our re-normalisation calculations have introduced any significant bias to our dataset.
2.4.2. RMNs within CAIs, chondrules and matrix

This study reveals that RMNs can be found within all components of carbonaceous chondrites. Current theories surrounding the origin of RMNs are tied to their assumed unique occurrence within CAIs e.g. Berg et al. (2009). CAIs are thought to form initially as high temperature condensates (Grossman and Ganapathy, 1976; Wänke et al., 1974) (although most have experienced further processes such as remelting (MacPherson, 2005)). Therefore, the assumed model of formation for RMNs has been that they condensed at high temperatures in the same location and environment as CAIs (Grossman and Ganapathy, 1976). However, this single condensation event model is hard to reconcile with the myriad of compositions observed within RMNs (Grossman et al., 1977; Schwander et al., 2015b). In addition, it should be borne in mind that CAIs affect the bulk composition of meteorites by enhancing refractory abundance above CI, indicating that CAIs were added to an approximately solar bulk ‘background’ composition. But in chemical analysis of matrix, or (CAI-absent) CI chondrite, we still observe PGEs. What then is the host phase of these elements? One possibility is finely comminuted CAI. However, if this were true, we would observe an enhancement in all refractory elements such as Ca and Al, which is not the case. Therefore RMNs in the matrix are unlikely to be broken fragments of CAIs as stipulated by Schwander et al. (2015a) and are likely to have their own formation history. The chondrules that host the RMNs in this study do not appear to contain fragments of CAIs and the RMNs are contained within forsterite (Figure 2.3), so similarly a CAI initial source for these chondrule-hosted RMNs is unlikely. The fact that we have now observed RMNs within matrix and chondrules demonstrates that CAIs are not a necessary factor in their formation. Indeed, their presence in chondritic components which formed at temperatures far below CAIs raises several new possibilities for RMN formation.
2.4.3. RMN compositional diversity

RMN PGE abundances compared to CI chondrite defined by (Lodders, 2003) (Figure 2.5) show large enrichments and depletions relative to CI. Most RMNs are equally enriched or depleted in all refractory elements, however, some RMNs have significant relative depletions in Mo and W. The RMNs associated with this trend are principally hosted within sulphides, supporting the idea that sulphidation mobilises Mo and W (Palme et al., 1998). Nevertheless, the average RMN composition approximately follows a CI chondrite trend indicating that these refractory elements are primarily hosted within RMNs in meteorites. This expands the observation of Schwander et al. (2015b): that the average composition of RMNs matches that of the PGE content of the bulk CAI to encompass the whole meteorite.

2.4.3.1. RMN compositional diversity between inclusions

The total PGE contents of RMNs when compared with Fe and Ni (Figure 2.6) reveal three main trends in the dataset: a ‘Fe mixing line’ between 100 at. % PGE and 100 at. % Fe (black polygon); a ‘Ni mixing line’ from 90 at. % PGE, 0 at. % Fe to 20 at. % PGE, 40 at. % Fe (red polygon); and a ‘low PGE region’ PGE <30 at. % and 20 – 80 at. % Fe (green triangle). RMNs from acid residue studies were exclusively found within the high PGE portion of the Fe mixing line. These RMNs were significantly more PGE-rich and Fe and Ni-poor than most RMNs analysed in situ. RMNs in residues should contain RMNs from all meteoritic components which would include RMNs with high Ni and Fe contents. As this is not what we observe then it is likely that the process of concentrating RMNs in acid residues leaches RMNs of their Ni and Fe content. The low PGE
Figure 2.5: RMN compositions from this study (orange), the average RMN from this study (red) and RMNs from our literature database (greyscale). PGEs have been plotted in order of increasing volatility and have been normalised to Ru then CI (top), or Pt then CI (bottom). These RMNs show a wide range of individual RMN compositions. However, the average RMN from this study has approximately CI chondrite relative abundance for these elements.
Figure 2.6: Total PGE vs Fe and total PGE vs Ni plots by host phase (this study and the literature) indicating a well defined Fe-mixing trend (black polygon) a more dispersive Ni-mixing trend (red polygon) and a low PGE cluster (green triangle), which is dominated by sulphide phases.
region is primarily composed of matrix, chondrule and sulphide-hosted RMNs. CAI-hosted RMNs are evenly spread across all regions. The universal presence of CAI-hosted RMNs in all regions suggests that no single process equilibrated the composition of RMNs within CAIs.

Furthermore, the average chemical composition of RMNs within each host phase is significantly different (Table 2.4). Sulphide, matrix and chondrule hosted RMNs are depleted in most PGEs relative to CAI-hosted RMNs, and W and Mo are completely absent or in extremely low concentrations. There is a large range of RMN compositions observed within the dataset. We compared the observed spread of RMN compositions to the compositional distribution expected to be produced by proposed RMN forming processes, specifically: condensation, precipitation and sulphidation acting in isolation or in tandem.

2.4.3.2. SULPHIDATION AS A RMN FORMING PROCESS

The high abundance of Fe-Ni-sulphide hosted RMNs contained within the low PGE region (Figure 2.6) potentially allows us to interpret RMNs within this region as derived from, or affected by, sulphidation. If we assume that sulphide hosted RMNs were formed or had their composition modified by sulphidation, then either these RMNs have been affected by exposure to a S-rich gas in the nebula (Lauretta et al., 1996), and/or a parent body process has imposed a compositional fingerprint on these grains. The RMNs from this study are hosted in Fe-Ni sulphides and are therefore likely to be affected by parent body processes altering the chemistry of the sulphides from stochiometric troilite. It has been suggested that the presence of W and Mo could be used as an indicator for primitive RMNs as even low degrees of alteration would remobilise these two elements (Eisenhour and Buseck, 1992). Therefore, the fact that no W or
Mo is observed in sulphide-hosted RMNs may be taken as evidence that these grains have been altered. We also do not observe any associated Mo or W dominated sulphide phases with these RMNs. We therefore expect that as the Fe-Ni-sulphide is significantly larger than the RMNs, the mobilised W and Mo become disseminated throughout the host sulphide during sulphidation, replacing Fe or Ni.

The fact that matrix, CAI and chondrule RMNs are also found within this region, that are not associated with sulphides suggests that this region is not a unique expression of sulphidation and other processes can produce RMNs with low PGE abundances. Therefore the compositional variance in the whole region cannot be explained completely by sulphidation.

### 2.4.3.3. Condensation as a RMN forming process

Calculated RMN condensation temperatures show a reasonable agreement with condensation models for some elements, particularly Fe. However, other elements, such as Ru, Ir, Pt, and particularly Ni deviate substantially from the expected curve (Figure 2.7).

To evaluate how closely the measured compositions of RMNs agree with modelled compositions, RMNs were grouped where every element is within 5 or 15 at. % agreement of the best fit calculated condensation composition (Figure 2.8). As the tolerance is raised from 5 – 15 at. %, the number of RMNs consistent with condensation models increases from 5 % to 50 %. These RMNs are clustered exclusively along the Fe-mixing line. However, a significant portion of RMNs within the Fe-mixing line do not conform to the condensation model even at high tolerance levels. This indicates that condensation is not exclusively responsible for RMNs within the Fe mixing line. The abundance
**Figure 2.7**: A comparison of Fe, Ni and PGE abundance in wt. % vs calculated equilibrium condensation temperature at $10^{-4}$ bar for RMNs from this study (green), and the literature (red). The data are plotted in the same format as Berg et al. (2009). RMN compositions exhibit good correlations with Fe and Mo but very poor correlations with Ni, Ru, Rh, Ir and Pt.
of RMNs consistent with our equilibrium condensation model in this study is similar to the abundance calculated in Schwander et al. (2014a) in which only 4 out of 123 RMNs were consistent with an equilibrium condensation model. Interestingly, the 5% of RMNs that are consistent with condensation are hosted within opaque assemblages from Palme et al. (1994), cosmic spherules from Rudraswami et al. (2014), several CAIs with melting textures from Schwander et al. (2015a), as well as a RMN from a chondrule rim sulphide (this study), all of which do not have textures consistent with condensation.

It is clear that predicted RMN compositions from current equilibrium condensation models cannot be reconciled with observations. Alternative condensation models, namely non-equilibrium condensation, fractional condensation and the effect of the activity coefficient will now be considered.

Previous equilibrium condensation models have assumed that the activity coefficients for each element are 1 (Berg et al., 2009). Schwander et al. (2014a), noted that varying the activity coefficient would result in a migration of the condensation curve for each element. However, the systematic trend in RMN compositions would be maintained and therefore cannot account for the spread of observed RMN compositions.

Fractional condensation would result from successive periods of condensation followed by removal of RMNs from the reservoir, depleting it in the elements that had already condensed. The expected observations of this process would depend on the mechanism for isolating the RMNs from the condensing gas. If the RMNs were removed by encapsulation within other condensing phases, we would expect to observe a mineralogical association with RMNs enriched in certain PGEs. For example, high temperature phases such as hibonite and corundum would be expected to bear RMNs enriched in the more refractory
Figure 2.8: Total PGE vs Fe abundance in at. %. These show all RMNs from this study and the literature are indicated by blue diamonds. The RMNs which match predicted equilibrium condensation compositions at $10^{-4}$ bar to within 5 at. % (top graph), and 15 at. % (bottom graph) are indicated with red diamonds.
PGEs such as Os, Re, and W, while lower temperature phases such as Mg-spinel and anorthite would contain RMNs enriched in the more volatile PGEs such as Pt. Schwander et al. (2015b) demonstrated that there is no systematic variability of RMN compositions with host phase. Therefore, this mechanism is unlikely. If the RMNs are physically removed from the reservoir we may expect to observe a chemically distinct RMN population within different host inclusions such as chondrules and CAIs. Figure 2.6 revealed that the abundance of Fe and Ni in CAI hosted RMNs encompass the whole range of chemical compositions, including those occupied by sulphides, chondrules and matrix. This indicates that this mechanism for fractional condensation is also unlikely. We would also expect to observe clusters of RMNs with similar compositions which relate to the temperature they were fractionated from the condensing gas. However, no such such clustering of RMN compositions is observed (see Figure 2.6).

Non-equilibrium condensation, similar to other condensation models, is expected to produce a systematic trend in RMN compositions. The non-equilibrium condensation model produced by Tanaka et al. (2002) revealed that although the condensation temperatures for certain PGEs may vary significantly, the overall condensation sequence for the elements within RMNs remains the same as that predicted for equilibrium condensation. Furthermore, we may expect to observe zonation in RMNs that condensed in this manner. However, zoning has not been reported in previous transmission electron microscopy studies of RMNs (Harries et al., 2012; Eisenhour and Buseck, 1992).

It is apparent that more complex nebular condensation models still result in RMNs with a systematic compositional trend. This cannot be reconciled with the large spread in the compositional data reported for RMNs. Therefore, nebular condensation is unlikely to be a dominant process in RMN formation.
2.4.3.4. Precipitation as a potential RMN forming process

Some RMNs have been demonstrably attributed to precipitation processes, where an RMN has crystallised from a melt; either in experimental studies (Schwander et al., 2015a), or observed in cosmic spherules (Rudraswami et al., 2014). Although as cosmic spherules have a complex history of evaporation and remelting it is unclear whether these RMN compositions are derived from a pure precipitation process. When the synthetic RMNs are superimposed over RMNs analysed in this study and the literature (Figure 2.9), precipitation RMNs fall along the Fe-mixing line in a similar trend to the condensation model curve. Therefore, even if we assume that the Fe-mixing line can be reconciled by a combination of condensation and precipitation processes there is still the Ni-mixing line which is inconsistent with all the processes we have described.

Considering each element in isolation, overlaying precipitation derived RMNs and our equilibrium condensation model curve over observed RMNs, from this study and the literature (Figure 2.10), we reveal a further disparity. The spread of RMN compositions cannot be fully explained by precipitation Mo/Ru, W/Ru, Pt/Ru and Ir/Ru ratios for example do not match synthetic precipitates. Os/Ru at low Os concentrations does approximately follow a trend defined by synthetic precipitation derived RMNs, however there is also a population with very high Os abundances which is not consistent. Furthermore these RMN elemental ratios do not exhibit any association with the equilibrium condensation curve, except for a weak association in Os and Ir. Precipitation encounters the same problem as condensation; whilst it can produce compositions consistent with some RMN observations, it cannot explain them all. Furthermore, the population of RMNs that are consistent with condensation and precipitation are not complementary, and therefore cannot be an expression
of both processes acting in tandem.

The synthetic RMNs derived from precipitation in Schwander et al. (2015a) represent a single experiment, which naturally may not perfectly match nebula conditions. It is possible that precipitation could explain all RMN compositions if the experiments were carried out under different conditions. However, there is a significant logical problem with the model. If all the PGEs are dissolved into a silicate or CAI-like melt, over time these elements will naturally become homogeneously distributed. Upon quenching the RMNs that do form should have homogeneous compositions within each inclusion. Heterogeneous RMNs would form only if PGEs are still heterogeneously distributed within the inclusion and were not molten for sufficient time to equilibrate. Therefore heterogeneous RMNs within remelted inclusions may not derive their heterogeneity from precipitation, but from an inherited heterogeneous distribution of the PGEs within the inclusion that did not equilibrate.

2.4.3.5. Other parent body processes

To ascertain if there is any variation between RMNs from different parent bodies, RMNs were separated according to meteorite (Figure 2.11). Allende seems to encompass the whole range of RMN compositions. However, other meteorites cluster into certain regions. Murchison, Leoville, Orgueil, ALH 77307 and Adelaide represent certain portions of the Fe-mixing line. Ornans follows the Ni-mixing line into the low PGE region, and Vigarano contains RMNs from the low PGE region and the mid-section of the Fe-mixing line.

It is possible that this spread is due to a small dataset for some meteorites. However, the methodology used in this study would find most, if not all RMNs in a thin section, and all observed RMNs were analysed. Therefore it is possible
Figure 2.9: Total PGEs vs Fe abundance in at. % for RMNs detailed in this study (red) and the literature (black) as well as pre-solar RMNs from Croat et al. (2013) (blue), synthetic RMNs produced by precipitation from Schwander et al. (2015a) (green), and our condensation model calculated at $10^{-4}$ bar.
Figure 2.10: Elemental ratio plots of each PGE vs Ru comparing RMNs from this study and the literature (blue) with precipitation derived RMNs from Schwander et al. (2015a) (red) and our equilibrium condensation model at $10^{-4}$ bar (purple curve). These graphs show very weak or absent correlations of observed RMNs with predicted condensation model curves or synthetic RMNs formed by precipitation.
that RMN populations may vary between parent bodies. In particular, the clustering of RMNs within Vigarano suggests this may be the case as several RMNs are observed and yet the spread of RMNs remains constrained.

![Diagram](image)

**Figure 2.11:** Variability of total PGE vs Fe abundances (at. %) of RMNs in this study and the literature from the meteorites Allende, ALH 77307, Murchison, Leoville, Orgueil, Ornans, Vigarano, Acfer 094, Adelaide and those found in cosmic spherules.

Average abundances of PGEs in RMNs between meteorites have approximately chondritic trends (Figure 2.12). Vigarano exhibits an enrichment in W, whereas Allende exhibits a depletion in W and Mo. This may be interpreted as a real compositional difference related to the formation history and oxidation state of the meteorite. However, as very few RMNs contain Mo or W these anomalies are therefore likely to be caused primarily by the averaging of a few W-rich RMNs in the case of Vigarano and a few Mo and W-poor RMNs in Allende.
Chapter 2

Figure 2.12: RMN average compositions by host phase and meteorite from this study (Table 2.4). PGEs have been plotted in order of increasing volatility and have been normalised to Ru then CI (top), or Pt then CI (bottom). The average compositions of each meteorite exhibit approximately CI trends. Allende exhibits a slight depletion in Mo and W, while Vigarano shows a large W enrichment.
PGEs are predominantly siderophile and generally unreactive, with the exception of W and Mo which have been shown to be mobile under low degrees of alteration (Palme et al., 1998). It has been shown by experiment that Pt, Mo and W will mobilise under reducing conditions at 1600 K before Os and Ir (Schwander et al., 2015a). Therefore, to alter the entire PGE content in RMNs on the parent body would require significantly higher temperatures than all carbonaceous chondrite parent bodies have experienced. The heterogeneity in the PGE content of RMNs must therefore be present prior to accretion. Therefore, a parent body process producing heterogeneous RMNs is unlikely.

2.4.3.6. Petrological context

Finally, the context of the RMN is taken into account. RMNs have been shown to occur throughout carbonaceous chondrites. The methodology described in this study retains their context and mineralogical association. Therefore, we can check if the formation process implied by evaluation of the chemical data is plausible. Indeed, it is the case that some RMNs with compositions consistent with a condensation origin are located within a mineral assemblage that has an igneous history, such as the RMNs in cosmic spherules from Rudraswami et al. (2014). Cosmic spherules are thought to experience a very complex succession of heating, melting, and evaporation (Brownlee et al., 1997; Taylor et al., 2000; Genge et al., 2008) and therefore cannot have a condensation origin. Furthermore, although precipitation is thought to produce a diversity of chemical compositions in RMNs Schwander et al. (2015a), not all inclusions in meteorites have an igneous history. Therefore, some RMNs cannot have formed via this process.
2.4.3.7. A COMBINATION OF SOLAR SYSTEM PROCESSES

No single process is responsible for the RMN variability we observe. However, it may be possible to produce this diversity through a combination of these processes. Indeed RMNs within cosmic spherules (Rudraswami et al., 2014) which do have a complex thermal history including heating, melting, and evaporation (Brownlee et al., 1997; Taylor et al., 2000; Genge et al., 2008), nearly cover the whole range of observed RMN compositions (Figure 2.11). However, RMNs hosted within different meteoritic inclusions have a similar diversity of Ir/Os and Ir/Pt ratios (Figure 2.13). The overlap of sulphide hosted RMNs in particular indicates that sulphidation does not significantly alter the original elemental ratio. Therefore the diversity of RMN compositions cannot be related to precipitation or condensation derived RMNs being sulphidised. We have already discussed how equilibrium condensation is not capable of producing the diversity of RMNs observed, and precipitation is unlikely to generate the observed diversity. Synthetic RMN compositions from precipitates and equilibrium condensation RMN compositions are not complementary. Therefore even a combination of these proposed formation mechanisms will not result in the suite of compositions we observe. This leaves three possibilities. Firstly, it
may be possible to imagine a complex sequence of condensation, re-melting, evaporation, vaporisation, sulphidation, and oxidation that could produce a single RMN composition. However, the diversity of RMN compositions we observe would require almost every single RMN to experience a unique but complex formation history similar to cosmic spherules. This is inconsistent with textual observations of some RMN hosts, such as the RMN in a fluffy type A CAI in (Palme et al., 1998) and RMNs within a ‘fluffy’ type A CAI from Vigarano in this study (Figure 2.2). These RMNs do not have compositions consistent with a single event equilibrium condensation model and yet are contained within a ‘pristine’ inclusion and therefore are unlikely to have been significantly altered by subsequent processes. It is also inconsistent with RMNs with variable compositions within the same inclusions Schwander et al. (2015b). Secondly there may be a nebula or parent body process which has not yet been identified which is capable of producing the observed heterogeneity within RMNs either individually, or in tandem with the previously discussed processes. Finally, there is a possibility that this diversity of RMN compositions could be produced by inheriting an initially heterogeneous assemblage of pre-solar RMNs which were never completely equilibrated by subsequent nebular processing.

2.4.3.8. A pre-solar initial origin?

We have to accept that neither condensation (primary nebula), precipitation (secondary nebula), nor sulphidation (secondary asteroidal) and parent body processes can produce individually or in tandem the myriad of compositions of RMNs we observe in meteorites. We cannot currently produce the diversity of RMNs via a combination of known nebular and/or parent body processes, therefore we are required to look elsewhere.
The Solar System formed from a Giant Molecular Cloud fragment which would have included refractory metals from a variety of stellar sources. These are likely to be hosted in metal alloys. The resulting diversity of RMN compositions represents the initial condition of the protoplanetary disk. Our data indicate that while RMNs have been affected by condensation, precipitation, sulphidation and (possibly other) parent body processes, none of these processes are dominant, and together, they have not homogenised or equilibrated the RMN population and removed that initial compositional diversity. If this interpretation is correct, a prediction would be that pre-solar RMNs are present as discrete grains within primitive chondrites and IDPs, rather than solely hosted in pre-solar graphite (Croat et al., 2013). Therefore, some of the grains analysed in the course of this study belong to that pre-solar population. The most likely candidates for this are those RMNs found within the Ni-mixing line which is not readily explained by any process discussed in this study. Isotopic analysis is required to support this.

2.5. CONCLUSIONS

Observing RMNs in multiple components in meteorites, not just in CAIs, directly contradicts the assumption made by many studies that RMNs are unique to CAIs. Each RMN host has its own characteristic RMN compositional suite. However, the average RMN composition across all minerals averages to the bulk Solar System and CI chondrite implying that PGEs are primarily, if not uniquely, hosted within RMNs. Condensation models, experimentally derived RMNs from precipitation, and parent body processes such as sulphidation are unable to produce the suite of RMN compositions observed, either in isolation or in tandem. It may be possible to derive the suite of RMN compositions
through complex sequences of condensation evaporation and remelting as we observe a similar diversity in cosmic spherules. However, such a complex thermal sequence is not plausible for all meteoritic components. The Solar Nebula inherited a vast diversity of RMN compositions from a variety of stellar sources. Our data suggests that this initial RMN population was never fully homogenised. While some RMNs have been modified by nebular and asteroidal processes, the compositional diversity of the RMN population observed in this study indicates that the original pre-solar signature was never completely erased. If this assumption is correct, some RMNs may have escaped Nebula processing and will retain their pre-solar composition. Therefore, we should observe some demonstrably pre-solar RMNs not just within pre-solar graphite, but in other components as well. These conclusions could only be drawn by analysis of RMNs in situ highlighting the importance of retaining context and petrological associations.

2.6. ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council via their Australian Laureate Fellowship program. This research was undertaken on the XFM beamline at the Australian Synchrotron, Victoria, Australia. The authors acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the Australian Centre for Microscopy and Microanalysis, the University of Sydney and the Centre for Microscopy, Characterisation and Analysis, University of Western Australia. The authors would also like to thank the rest of the Desert Fireball Network research group as well as Mr Timmons Erikson, Mr Mark Daly, Ms Mary Munroe, Ms Sarah Hayes and Ms Jennifer Porter for their assistance. Finally the authors
would like to thank the three reviewers, as well as associate editor Nicolas Dauphas for their constructive comments and suggestions which significantly improved this manuscript.

2.7. Appendix A. Supplementary Data

Supplementary Data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.11.030

2.8. References


CHAPTER 3

PAPER 2 – CRYSTALLOGRAPHY OF REFRACTORY METAL NUGGETS IN CARBONACEOUS CHONDRITES: A TRANSMISSION KIKUCHI DIFFRACTION APPROACH.

Luke Daly\textsuperscript{a}, Philip A. Bland\textsuperscript{a}, Kathryn A. Dyl\textsuperscript{a}, Lucy V. Forman\textsuperscript{a}, David W. Saxey\textsuperscript{b}, Steven M. Reddy\textsuperscript{a,b}, Denis Fougerouse\textsuperscript{a,b}, William D. A. Rickard\textsuperscript{b} Patrick W. Trimby\textsuperscript{c}, Steve Moody\textsuperscript{c}, Limei Yang\textsuperscript{c}, Hongwei Liu\textsuperscript{c}, Simon P. Ringer\textsuperscript{d}, Martin Saunders\textsuperscript{e}, Sandra Piazolo\textsuperscript{f}

\textsuperscript{a}Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

\textsuperscript{b}Geoscience Atom Probe Facility, Advanced Resource Characterisation Facility, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA, Australia.
Section 3.0

Australian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW 2006, Australia.

Australian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW, 2006, Australia.

Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, WA 6009, Australia.


This article is published in Geochimica et Cosmochimica Acta, v. 216, p. 42 – 60
doi: 10.1016/j.gca.2017.03.037 and reprinted with permission in Appendix A.
ABSTRACT

Transmission Kikuchi diffraction (TKD) is a relatively new technique that is currently being developed for geological sample analysis. This technique utilises the transmission capabilities of a scanning electron microscope (SEM) to rapidly and accurately map the crystallographic and geochemical features of an electron transparent sample. TKD uses a similar methodology to traditional electron backscatter diffraction (EBSD), but is capable of achieving a much higher spatial resolution (5-10 nm) (Trimby, 2012; Trimby et al., 2014). Here we apply TKD to refractory metal nuggets (RMNs) which are micrometre to sub-micrometre metal alloys composed of highly siderophile elements (HSEs) found in primitive carbonaceous chondrite meteorites. TKD allows us to analyse RMNs in situ, enabling the characterisation of nanometre-scale variations in chemistry and crystallography, whilst preserving their spatial and crystallographic context. This provides a complete representation of each RMN, permitting detailed interpretation of their formation history.

We present TKD analysis of five transmission electron microscopy (TEM) lamellae containing RMNs coupled with EBSD and TEM analyses. These analyses revealed textures and relationships not previously observed in RMNs. These textures indicate some RMNs experienced annealing, forming twins. RMNs also acted as nucleation centres, and formed immiscible metal-silicate fluids. In fact, each RMN analysed in this study had different crystallographic textures. These RMNs also had heterogeneous compositions, even between RMNs contained within the same inclusion, host phase and even separated by only a few nanometres. RMNs are also affected by secondary processes at low temperature causing exsolution of molybdenite. However, most RMNs had crystallographic textures indicating that the RMN formed prior to their host
inclusion. TKD analyses reveal most RMNs have been affected by processing in the protoplanetary disk. Despite this alteration, RMNs still preserve primary crystallographic textures and heterogeneous chemical signatures. This heterogeneity in crystallographic relationships, which mostly suggest that RMNs pre-date their host, is consistent with the idea that there is not a dominant RMN forming process. Each RMN has experienced a complex history, supporting the suggestion of Daly et al. (2017), that RMNs may preserve a diverse pre-solar chemical signature inherited from the Giant Molecular Cloud.

3.1. INTRODUCTION

There are two main hosts for highly siderophile elements (HSEs) in primitive carbonaceous chondrite meteorites: refractory metal nuggets (RMNs) and opaque assemblages (OAs). OAs are larger (>10 µm) multi-phase alloys (El Goresy et al., 1977), whereas RMNs are single phase alloys. OAs originally were termed fremdlinge due to their proposed pre-solar origin (El Goresy et al., 1977). However, isotopic analysis of fremdlinge by Hutcheon et al. (1987) indicate that they have solar isotopic ratios and so were named OAs by Palme et al. (1994) to reflect their solar origin.

To avoid confusion between the two objects here we define RMNs as any micrometre-sub-micrometre homogeneous (Harries et al., 2012) metal alloy within carbonaceous chondrite meteorites which contain >1 atomic percent (at. %) HSEs (Re, Os, Ir, Pt, Ru, Rh, W or Mo), in line with the definition in Daly et al. (2017).

Since the co-discovery of RMNs by Palme and Wlotzka (1976) and Wark and Lovering (1976), it had been assumed that they are only found in Ca-Al
rich inclusions (CAIs) (Blander et al., 1980; Berg et al., 2009; Harries et al., 2012; Hewins et al., 2014). However, observations of RMNs in chondrules (Wang et al., 2007), matrix (Schwander et al., 2015b), an unusual xenolith from Allende, likely to be a dark inclusion (Palme et al., 1989), as well as recent X-ray fluorescence microscopy (XRF) synchrotron data, have revealed that this is not the case. Daly et al. (2017) showed that RMNs are found within all components of carbonaceous chondrites. The refractory nature of RMNs which contain only elements with 50% condensation temperatures above Fe and Ni (Lodders, 2003) lead to the conclusion that RMNs are primary condensates (Berg et al., 2009; Fegley and Palme, 1985; Grossman, 1973; Harries et al., 2012; Lodders, 2003; Palme and Wlotzka, 1976). This is consistent with the assumption that RMNs were hosted solely within CAIs (Berg et al., 2009; Harries et al., 2012; Hewins et al., 2014; Blander et al., 1980) which also form at high temperatures (MacPherson et al., 2005; Grossman et al., 2000) and are thought to form initially as condensates (Grossman, 1973). Thus, formation mechanisms for RMNs were only considered within the context of CAIs.

Recent work by Schwander et al. (2015b) and Rudraswami et al. (2014) respectively has shown that this is not necessarily the case: an alternative mechanism may be crystallisation of RMNs from a silicate melt, CAI melt, or during the formation of cosmic spherules. Furthermore, RMNs have, in some cases, been subjected to secondary processes as implied by sulphidation and oxidation textures (Bischoff and Palme, 1987; Blum et al., 1988; Palme and Wlotzka, 1976). However, other studies have suggested that RMNs may have a pre-solar origin (El Goresy et al., 1977, 1978; Wark and Lovering, 1976). This was confirmed by recent observations of 20 – 50 nm RMNs hosted within pre-solar graphite (Croat et al., 2013).

A combination of 113 in situ energy-dispersive X-ray spectroscopy (EDS)
measurements of RMNs and the database of RMNs reported in the literature over the last 40 years, revealed a large range of RMN compositions which cannot be reconciled by a single Solar System process (Daly et al., 2017). Our interpretation is that an inherently diverse population of RMNs was incorporated into the protoplanetary disk. These RMNs were altered by subsequent disk processing, but the primordial diversity was never overprinted (Daly et al., 2017).

The crystallography of RMNs can offer important insights into their origin and formation. For example, the three phase condensation model of Sylvester et al. (1990) predicted that RMNs should be found in three main crystal systems: body centred cubic (bcc) composed predominantly of W, Mo, and Cr; hexagonal close packed (hcp) composed predominantly of Re, Os, and Ru; and a face centred cubic (fcc) structure composed of Ir, Pt, Rh, Co, Ni, Fe, and Au. This assertion was proposed to reconcile RMN compositions that do not fit a single-phase condensation model. However, the observed crystallography of RMNs using transmission electron microscopy (TEM) spot diffraction patterns indicate that they are largely monocrystalline, homogeneous, subhedral-euhedral hcp crystals (Eisenhour and Buseck, 1992; Harries et al., 2012; Croat et al., 2013). This observation does not support the three phase condensation model, and reinforces the idea of a single phase equilibrium condensation origin for RMNs, in agreement with calculations by Campbell et al. (2001) and Wark and Lovering (1976). However, the chemical heterogeneity of RMNs is still not fully understood.

Previous work has either been limited to analysis of a few grains in situ (Blum et al., 1988; El Goresy et al., 1978; Palme and Wlotzka, 1976; Wark, 1986; Wark and Lovering, 1976), or analysis of many grains using acid residues (Berg et al., 2009; Harries et al., 2012; Schwander et al., 2014) where the original context
of the RMN was lost. Two studies have analysed large quantities of RMNs in situ: Daly et al. (2017) and Schwander et al. (2015a). Schwander et al. (2015a) demonstrated that the condensation temperature of the host mineral phase did not correlate with appropriate RMN compositions assuming RMNs formed as condensates, implying that condensation was an unlikely formation mechanism for RMNs in that study.

Analyses of inclusion-host systems in terrestrial rocks using large electron backscatter diffraction (EBSD) datasets, and the documentation of crystallographic orientation relationships (CORs) between mineral phases by Griffiths et al. (2016) revealed variable CORs between mineral inclusions and their host phase relate to changing metamorphic conditions. The context of the RMN is integral to the accurate interpretation and discernment of mineral formation mechanisms, as the formation history of the host itself will influence the interpretation. For example, RMNs hosted within chondrules which are not thought to have a condensation history, may indicate that these RMNs formed via a different mechanism. Also, any secondary alteration events experienced by the host phase would necessarily affect the RMN and may influence its crystallography and composition.

To determine which processes have affected RMNs since their formation, high resolution in situ analyses are required. Ma et al. (2014) demonstrated that combining chemical and crystallographic data through EBSD can be used to determine the origins of refractory grains such as RMNs, interpreting two new mineral phases, allendeite and hexamolybdenum, as primary nebular condensates. In this work we will apply transmission Kikuchi diffraction (TKD); a relatively new technique for which the applications to geological (Jacob et al., 2016; Piazolo et al., 2016) and meteoritical samples (Forman et al., 2016) are beginning to be explored. TKD is also referred to as transmission
EBSD (t-EBSD) (Keller and Geiss, 2012). The technique allows the elemental and crystallographic mapping of a TEM lamella in a scanning electron microscope (SEM). It uses the same software and techniques as EBSD, but with an order of magnitude improvement in the resolution attainable (Trimby, 2012; Trimby et al., 2014; Sneddon et al., 2016). This approach allows us to observe RMNs in context, preserving any CORs with associated host phases, and rapidly map the crystallography of these grains at ~ 5 nm resolution. It therefore provides a completely new window on the crystallography, orientation, and deformation history of these materials that has not been accessible before. TKD analysis can facilitate better interpretation of the sequence of events that may have affected each RMN since formation, and how these processes may have affected the RMNs crystallography and chemistry.

The only other study utilising TKD on meteoritic materials by Forman et al. (2016) demonstrated that TKD can be used to highlight the differences in how matrix and chondrules are affected by temperature and stress during impact induced compaction in the matrix of Allende near a chondrule. Here we will further demonstrate the potential of this technique in the analysis of RMNs. We will show and explore the possible observable effects on the crystallography and chemistry, produced by primary nebula processes, i.e. condensation and crystallisation; secondary nebular processes, i.e. transient heating events; and secondary asteroidal processes, i.e. sulphidation. TKD observations are supplemented with the utilisation of established techniques, such as EBSD and TEM.
3.2. METHODS

To identify RMNs in situ, a combination of Synchrotron XRF analyses corroborated with SEM observations using map overlay and feature mapping software packages was used. A full description of the procedure can be found in Daly et al. (2017). Several RMN bearing regions were identified for analysis in this study: Region A1, a sulphide nodule hosted within a porphyritic olivine (PO) chondrule in Allende; A2 and A3 were found within different forsterite enclaves within the same spinel-diopside-rich Type B CAI in Allende; ALH1, was extracted from a type B-like CAI in ALH 77307; and V1 and V2 from the reheated portion of a ‘fluffy’ type A CAI in Vigarano. Backscattered electron maps relating to the wider petrographic context of each RMN in this study is provided in Supplementary material A. Regions A1 and A3 were analysed using EBSD techniques. Ideally all regions would have been analysed by EBSD, however, these were the only regions where a sufficient polish was achieved to undertake EBSD. Regions A1, A2, ALH1, V1, and V2 were extracted and analysed using TKD, and region ALH1 was also analysed using TEM.

3.2.1. EBSD

The samples were prepared for EBSD by hand polishing for 30 minutes using 0.01 µm colloidal silica in NaOH solution. This reduces the risk of polishing away the micrometre sized RMNs identified on the surface whilst achieving the polish required for EBSD. The samples were then coated with 10 nm of carbon. EDS and EBSD data were collected using the Zeiss ULTRA Plus Field emission gun (FEG) SEM at the Australian Centre for Microscopy and Microanalysis (ACMM), The University of Sydney, with an X-Max 20mm$^2$ SDD EDS detector.
at an accelerating voltage of 20 kV, and probe current of 4 – 20 nA.

### 3.2.2. Focussed Ion Beam

The samples A1, A2, ALH1, V1, and V2 were extracted and prepared for TEM and TKD using a focussed ion beam (FIB) on the Zeiss Auriga FIB-SEM at the ACMM, The University of Sydney. The regions of interest were initially covered with a protective strip of Pt using secondary electrons, followed by a thicker layer deposited using the Ga beam. This procedure is to protect the sample during milling, and thinning, while also adding structural support to the lamellae. The section was extracted using a Kleindiek micromanipulator, and welded to a Cu TEM grid with further Pt deposition. The sample was then thinned to approximately 100 nm thickness to allow the transmission of electrons.

### 3.2.3. TKD

The samples A1, A2, ALH1, V1, and V2 were analysed using TKD on the Zeiss ULTRA Plus FEG SEM at the ACMM, The University of Sydney. TKD mapping was performed using a Nordlys-NANO EBSD detector, and EDS maps were collected with an X-Max 20 mm$^2$ SDD EDS detector using an acceleration voltage of 30 kV as described in Trimby (2012) and Trimby et al. (2014).

### 3.2.4. Data Reduction

The EDS, EBSD and TKD maps were collected and interpreted using the Oxford instruments AZtec and Channel 5 software packages. Grain boundaries were
defined by >10 degree misorientation. Element abundances were derived from
the EDS maps using standardless quantitative methods embedded in the Aztec
software. EDS measurements of RMNs were taken with a process time of 5.
This allows for better energy resolution and detection limits. The L-alpha X-Ray
lines were used to calculate elemental abundances for Ru, Mo, W, Re, Os, Ir and
Pt, as these are better separated than the M lines. K X-ray lines were used to
calculate Fe and Ni abundances. Detection limits for elements within RMNs
were approximately <1 at. %. The relative uncertainty in these measurements is
approximately ± 10 %. We also assessed the accuracy of the EDS measurement
by comparing EDS and atom probe microscopy measurements from a 1 mm
RuIrOs nugget from a placer deposit in Tasmania, Australia. All elements were
consistent between EDS and atom probe within the 10 % relative uncertainty
except for Ir which was within 13 % (see Supplementary Material B for a full de-
scription). This provides sufficient precision to detect major and minor elements
and draw comparisons between measured RMN compositions in different me-
teoritic components. All other elements present in the spectra such as Mg, Al,
Ca, Cu etc; were ignored following the methodology of Schwander et al. (2015a)
and Daly et al. (2017), as they are likely to be generated by fluorescence in the
SEM chamber from elements in the surrounding phases, or the sample mount.
We do not expect these elements to be present in RMNs, but for completeness
the full compositions calculated for each analysis including the contaminating
elements is included in Supplementary Material C.

Not all expected HSEs were detected in every EDS analysis. For example,
Rh was only detected in one RMN which may be due to its low abundance
(Lodders, 2003). Other HSEs may be present in the RMNs in concentrations
below the detection limits of the EDS.

RMNs were mostly characterised by a fcc awaruite or a hcp rutheniridosmine
crystal structure from the EBSD database as the phase that best described most RMNs observed.

3.2.5. TEM

The FIB lamella taken from ALH 77307 (region ALH1) was also analysed using the JEOL2200 TEM, ACMM, the University of Sydney and the FEI Titan G280 – 200 TEM/STEM, Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia at an accelerating voltage of 200 kV. The sample was mounted on a double-tilt sample holder allowing the sample to be tilted in two directions. This allows greater flexibility to find and identify crystallographic axes. High resolution EDS maps, spot diffraction patterns and high resolution TEM (HRTEM) images were collected.

3.3. RESULTS

3.3.1. ALLENDE - REGION A1

This region revealed RMNs hosted within a pentlandite nodule. The pentlandite nodule is hosted in the rim of a sulphide-rich PO chondrule. Three RMNs were observed on the surface in the EBSD dataset (Figure 3.1), while a further five RMNs were revealed during the TKD analyses that were previously buried beneath the surface of the sample (Figure 3.2). The RMNs varied in size from 0.1 µm to 1 µm, and form anhedral-subhedral fcc single crystals. The RMNs had identical CORs relative to each other (Figures 3.1 and 3.2). The RMNs have no COR with the pentlandite host phase, however, they do share a [100] axis with
the nearby forsterite crystal (Figure 3.1 and 3.2). Three RMNs from the EBSD dataset (Table 3.1) and four from the TKD dataset (Table 3.2) were large enough to generate good EDS spectra. The composition of the RMNs indicated that in most cases Fe and Ni are relatively homogeneous between RMNs, with the exception of entry # 3 in Table 3.2. Fe and Ni were overestimated in the EBSD dataset as the interaction volume of the EDS measurement was larger than the RMN. This means that there was a contribution to the EDS spectra from the surrounding pentlandite. The abundances of Ir and Pt vary between RMNs (Tables 3.1 and 3.2). The Pt should be interpreted with caution as there was likely to be some contribution of Pt from the fluorescence of the Pt protective layer deposited during FIB sample preparation in the EDS spectra in Table 3.2. However, the EDS spectra from the EBSD dataset (Table 3.1) confirms that Pt is present and variable. Mo and W are completely absent in all RMNs in this region and Os is only observed in RMN 2 in Table 3.2).

**Table 3.1:** RMN compositions from EDS analysis from Figure 3.1. The RMN number relates to the numbered regions of Figure 3.1b. b.d. = below detection.

<table>
<thead>
<tr>
<th>RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62.2</td>
<td>30.8</td>
<td>6.1</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>61.3</td>
<td>32.9</td>
<td>b.d.</td>
<td>5.8</td>
</tr>
<tr>
<td>3</td>
<td>62.4</td>
<td>27.8</td>
<td>2.0</td>
<td>7.8</td>
</tr>
</tbody>
</table>

**Table 3.2:** RMN compositions from EDS analysis from Figure 3.2. The RMN number relates to the numbered regions of Figure 3.2c. b.d. = below detection.

<table>
<thead>
<tr>
<th>RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.2</td>
<td>33.5</td>
<td>b.d.</td>
<td>1.8</td>
<td>19.6</td>
</tr>
<tr>
<td>2</td>
<td>45.4</td>
<td>32.3</td>
<td>0.7</td>
<td>4.8</td>
<td>16.8</td>
</tr>
<tr>
<td>3</td>
<td>29.0</td>
<td>63.6</td>
<td>b.d.</td>
<td>7.4</td>
<td>b.d.</td>
</tr>
<tr>
<td>4</td>
<td>51.9</td>
<td>31.8</td>
<td>b.d.</td>
<td>6.7</td>
<td>9.7</td>
</tr>
</tbody>
</table>
FIGURE 3.1: Characteristics of Allende - region A1: EBSD analyses of 3 RMNs are contained within a chondrule-hosted sulphide nodule. a) A low magnification back scatter electron (BSE) image of region A1, indicating the wider context of the chondrule host with associated sulphide nodules, b) A BSE image of the RMNs hosted within a sulphide, with a nearby forsterite grain (Fo) as well as associated Cr-spinel (Chr) inclusions. The numbers indicate where the EDS measurements were taken from in Table 3.1, c) An EBSD phase map overlain on a band contrast image indicating RMNs (yellow), troilite (blue) Cr-Spinel (red) and forsterite (green), the pentlandite sulphide did not index well and is located within the black area, d) An EBSD Euler image overlain on a band contrast image indicating crystallographic orientations of each phase, e) A lower hemisphere stereographic projection of RMN crystallographic axes (100), (110), and (111). The crystallographic orientations of the RMNs revealed all RMNs have the same crystallographic alignment, f) A lower hemisphere stereographic projection of the orientation of the forsterite crystallographic axes (100), (010), and (001). The red square, circle and hexagon on stereographic projections e) and f) indicate that the RMNs and the forsterite share a [100] axis.
Figure 3.2: Characteristics of Allende - region A1: TKD analyses from a FIB-produced TEM lamellae containing an RMN bearing sulphide nodule hosted in a chondrule. a) A BSE image of the RMNs in context prior to extraction. The TEM lamellae was extracted as indicated by the red rectangle. Associated minerals are forsterite (Fo), Cr-spinel (Chr) and sulphide, b) A TKD fore-scatter detector (FSD) image of the TEM lamellae RMNs and associated minerals are labelled forsterite (Fo), mackinawite (Mk), Cr-spinel (Chr), pentlandite (Pn) and troilite (Tro), c) TKD phase map, revealing five more RMNs (yellow) which were buried beneath the surface of the sample, the numbers relate to EDS measurements detailed in Table 3.2, d) TKD Euler map showing crystallographic orientations of each phase in the section, e) Lower hemisphere stereographic projection of crystallographic orientations of the RMNs revealed a consistent crystallographic orientation for all RMNs, f) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite confirming a shared [100] axis between the RMNs and forsterite observed in Figure 3.1, denoted by the red circle square and hexagon, g) Lower hemisphere stereographic projection of crystallographic orientations of pentlandite, indicating no COR between the RMN and the pentlandite h) Lower hemisphere stereographic projection of crystallographic orientations of the troilite, indicating no COR between the RMN and the troilite.
3.3.2. Allende - region A2

This RMN was extracted from a forsterite enclave within a spinel and diopside-rich Type-B CAI in the Allende CV3 meteorite. TKD revealed a cluster of RMNs with two distinct morphologies. The first was a large polycrystalline RMN associated with molybdenite. The second was several smaller spherical isolated RMNs (20 – 100 nm) hosted in forsterite. The whole inclusion was surrounded by spinel (Figure 3.3). There is no COR between the spinel and the inclusion. All RMNs here had a hcp structure and uniform chemistry in relation to Ru, Ir and Pt. They were also completely devoid of Mo which was situated in the molybdenite (Table 3.3). The molybdenite and the larger polycrystalline RMN are crystallographically aligned with each other. They also exhibit a higher misorientation density, whereas the forsterite and smaller RMNs are uniform single crystals. The surrounding spinel is equigranular (2 – 5 µm) with 120° grain boundary intersections.

**Table 3.3**: RMN compositions from EDS analyses from the TEM lamellae detailed in Figure 3.3. The RMN number relates to the numbered regions of Figure 3.3c. b.d. = below detection.

<table>
<thead>
<tr>
<th>Spectrum Label</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Ru</th>
<th>Os</th>
<th>Ir</th>
<th>S</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>b.d.</td>
<td>2.6</td>
<td>34.0</td>
<td>32.8</td>
<td>26.1</td>
<td>b.d.</td>
<td>39.2</td>
</tr>
<tr>
<td>2</td>
<td>4.6</td>
<td>b.d.</td>
<td>1.8</td>
<td>33.9</td>
<td>34.0</td>
<td>25.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>31.4</td>
<td>37.6</td>
<td>25.2</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>29.5</td>
<td>36.2</td>
<td>29.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>30.6</td>
<td>36.6</td>
<td>28.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>28.5</td>
<td>39.1</td>
<td>26.0</td>
<td>b.d.</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.3: Characteristics of Allende region A2: TKD analyses from a FIB-produced TEM lamellae of an RMN-bearing forsterite inclusion hosted in a CAI. a) A low magnification BSE image of region A2 indicating the wider context of the CAI host, b) A BSE image of the RMNs (bright spots) in context prior to extraction. The TEM lamellae was extracted as indicated by the red rectangle. RMNs and associated minerals were labelled forsterite (Fo), pentlandite (Pn), and spinel (Spl), c) A FSD image of the TEM lamellae indicating the RMN bearing region at the top and revealing the surrounding spinel has 120° grain boundary intersections and 2 – 5 µm grain size. RMNs and associated minerals are labelled forsterite (Fo), pentlandite (Pn), molybdenite (Mo), and spinel (Spl), d) TKD phase map, revealing a large RMN associated with molybdenite and smaller spherical RMNs suspended in forsterite. The numbers relate to EDS measurements in Table 3.2. The whole inclusion is encapsulated by spinel, e) Lower hemisphere stereographic projection of crystallographic orientations of the small RMN spheres revealing random crystallographic orientations for each RMN relative to each other, f) Lower hemisphere stereographic projection of crystallographic orientations of the spinel, g) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite, h) Lower hemisphere stereographic projection of crystallographic orientations of the pentlandite, i) Lower hemisphere stereographic projection of crystallographic orientations of the large RMN, j) Lower hemisphere stereographic projection of crystallographic orientations of molybdenite. The molybdenite and the large RMN are crystallographically aligned parallel to one another as the indicated by the red circles in i) and j).
3.3.3. **Allende - region A3**

This RMN was hosted within another forsterite enclave within the same spinel-, diopside-rich Type-B CAI as A2. EBSD analyses revealed that the RMN has a COR with forsterite, sharing the [110] axis (Figure 3.4).

**Table 3.4:** RMN compositions from EDS analyses from Figure 3.4. The RMN number relates to the numbered regions of Figure 3.4c. b.d. = below detection.

<table>
<thead>
<tr>
<th>RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Mo</th>
<th>Os</th>
<th>Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.5</td>
<td>5.3</td>
<td>50.4</td>
<td>3.8</td>
<td>4.5</td>
<td>14.6</td>
</tr>
</tbody>
</table>

3.3.4. **ALH 77307 - region ALH1**

ALH1 is an RMN extracted from a perovskite bearing melilite rich type B-like CAI rimmed with diopside in ALH 77307 CO3.0. TKD and TEM analysis revealed a single RMN hosted within melilite. The RMN is polyphase with a fcc region and a trigonal region. The trigonal crystal system is an unknown configuration in RMNs. We will refer to this trigonal region henceforth as the unknown phase, to distinguish it from the regular fcc RMN. As the unknown phase had not previously been documented, no mineral EBSD data were available to index it. Therefore, a proxy of Fe_7W_6 with space group 166 and \(a = b = 0.4731\) nm and \(c = 2.57\) nm was used. The trigonal crystal structure of the unknown phase had a very long c axis relative to the a and b axes. Using this proxy and TEM spot diffraction, this phase was revealed to be closely related (mean angular deviation of 0.79) to the trigonal Fe_7W_6 proxy with \(a = b = 0.46\) nm \(c = 2.55\) nm with space group R-3m (166), and a simplified chemical formula \((\text{Fe, Ni})_6(\text{Mo, Ru, W, Os, Ir})_7\). The ionic radii of all elements are very similar so an empirical formula based on 13 atoms would be \((\text{Fe}_{5.2}\text{Ni}_{0.5}\text{Mo}_{5.0}\text{Ru}_{1.2}\text{W}_{0.5}\text{Os}_{0.4}\text{Ir}_{0.2}\text{Pt}_{0.3})\).
Figure 3.4: Characteristics of Allende - region A3: EBSD analyses of a forsterite hosted RMN from a CAI. a) A low magnification FSD image of region A3 (red box) indicating the context of the RMN within the CAI, b) FSD image of Region A3 indicating where the EBSD dataset was acquired (red box), associated minerals are labelled forsterite (Fo), spinel (Spl) and diopside (Di), c) EBSD phase map indicating an RMN hosted within a forsterite grain, the number indicates the EDS measurement taken from that point detailed in Table 3.4, d) Euler map indicating crystallographic orientations, e) Lower hemisphere stereographic projection of crystallographic orientations of the RMN, f) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite. Comparing the projections reveals the RMN have a COR with the forsterite sharing their (110) axis (red circle).
The fcc RMN is euhedral. The unknown phase follows the grain boundary defined by the RMN and the melilite host. Which is consistent with a pseudomorph texture (Figure 3.5). This unknown phase was heavily deformed with elongate bladed crystal growths (Figure 3.5). TKD supported by TEM analyses indicated that the RMN was crystallographically aligned with the melilite host, as the [002] axis of the RMN was oriented parallel to the [201] axis of the melilite phase. The RMN was also crystallographically related to the unknown phase, sharing the same <c> axis to within 6° (Figure 3.5). The RMN and the unknown phase had similar abundances of Fe, Ni, Ru, Os and Ir. However, Mo was enriched within the unknown phase relative to the RMN, and W was present in the unknown phase but absent from the RMN. Comparing EDS measurements with TKD and TEM indicate that TEM is largely unaffected by Pt fluorescence unlike the TKD measurements. This implies that Pt was only present in the RMN and not in the unknown phase (Table 3.5).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mineral</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>TEM</td>
<td>RMN</td>
<td>55.5</td>
</tr>
<tr>
<td>TKD</td>
<td></td>
<td>48.7</td>
</tr>
<tr>
<td>TEM</td>
<td>unknown phase</td>
<td>50.9</td>
</tr>
<tr>
<td>TKD</td>
<td></td>
<td>40.0</td>
</tr>
</tbody>
</table>

3.3.5. Vigarano - Region V1

TKD analyses of Vigarano - region V1 revealed a large anhedral 1 μm RMN with a fcc structure associated with an isolated spinel grain to the left of the section. To the right of the section, there was a cluster of 7 RMNs between 0.5 – 0.1 μm
**Figure 3.5:** Characteristics of ALH 77307 - region ALH1: TKD analyses from a FIB-produced TEM lamellae of an RMN bearing melilite crystal within a Type B-like CAI. a) A BSE image of the RMN in situ, prior to FIB extraction, hosted within a Type B-like CAI. Associated minerals are melilite (Mel) and perovskite (Prv), b) TKD band contrast image of the RMN and associated unknown phase. The labels indicate where EDS spectra from TKD and TEM were taken in Table 3.5, c) TEM image of the RMN and associated unknown phase indicating the RMN has several dislocation planes, d) TEM zoomed image of the unknown phase indicating the phase is heavily dislocated, exhibiting oriented bladed crystal morphologies, e) TKD phase map indicating a euhedral RMN (yellow), its associated unknown phase (blue), and the melilite host (red). The RMN is observed to be euhedral and the unknown phase adopts a pseudomorph texture with the RMN, f) TEM spot diffraction patterns taken from each phase. These spot diffraction patterns are overlain which revealed a shared $<c>$ crystal axis between the RMN and the unknown phase within 6°. The RMN [002] axis is shared with the [201] axis of the melilite host.
The cluster of RMNs were euhedral fcc crystals with twinning planes which rotated approximately 60° around the [111] axis with a 20 – 130 nm spacing between twin planes (Figure 3.6). The host phase of the RMNs was anorthite feldspar which was also twinned with a 180° rotation around the twin plane (Figure 3.6). Each RMN had a different composition, with variations observed across all elements despite being located in the same inclusion of the same meteorite, and even between the cluster of 7 RMNs exhibiting twinning (Table 3.6).

### Table 3.6: EDS measurements taken from region V1. The RMN number corresponds to the numbered regions of Figures 3.6c and e. b.d. = below detection.

<table>
<thead>
<tr>
<th>RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Mo</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.7</td>
<td>48.6</td>
<td>1.8</td>
<td>b.d.</td>
<td>0.4</td>
<td>b.d.</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>67.4</td>
<td>15.5</td>
<td>11.8</td>
<td>b.d.</td>
<td>2.5</td>
<td>2.8</td>
<td>b.d.</td>
</tr>
<tr>
<td>3</td>
<td>62.9</td>
<td>29.4</td>
<td>5.6</td>
<td>b.d.</td>
<td>1.1</td>
<td>0.9</td>
<td>b.d.</td>
</tr>
<tr>
<td>4</td>
<td>65.6</td>
<td>14.2</td>
<td>14.2</td>
<td>b.d.</td>
<td>2.4</td>
<td>3.6</td>
<td>b.d.</td>
</tr>
<tr>
<td>5</td>
<td>61.4</td>
<td>30.1</td>
<td>4.6</td>
<td>b.d.</td>
<td>1.0</td>
<td>1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>6</td>
<td>55.3</td>
<td>39.2</td>
<td>2.5</td>
<td>b.d.</td>
<td>0.7</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>7</td>
<td>57.0</td>
<td>36.4</td>
<td>3.5</td>
<td>b.d.</td>
<td>1.1</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>64.3</td>
<td>17.8</td>
<td>10.7</td>
<td>b.d.</td>
<td>3.3</td>
<td>3.8</td>
<td>b.d.</td>
</tr>
</tbody>
</table>

### 3.3.6. Vigarano - region V2

TKD analyses of Vigarano - region V2 revealed a RMN and associated metal and oxide phases hosted within a spinel grain. The boundary with the spinel and the assemblage exhibited straight edges. The assemblage was subdivided into three phases: a RMN hcp phase, powellite, and awaruite. Each phase had a different composition. Mo only found in the powellite. The awaruite exhibited twinning with a rotation about the [111] axis of 60° (Figure 3.7). Os
Figure 3.6: Characteristics of Vigarano - region V1: TKD analyses of a large RMN associated with spinel and a cluster of twinned RMNs in a void. These RMNs are hosted in anorthite contained within the altered mantle of a fluffy-type A CAI. a) A lower magnification BSE image showing the wider context of region V1 within the CAI, b) A BSE image of region V1 prior to sample extraction indicating two RMNs (bright spots). The red rectangle indicates the orientation of the extracted TEM section. The RMNs here are associated with anorthite (An), c) TKD phase map indicating RMNs in yellow. The large RMN to the left of the section is associated with spinel (red). The number indicated the EDS measurement in Table 3.6. The RMN cluster to the right is within a void encapsulated by anorthite (blue), d) TKD Euler image of the section indicating crystallographic orientations. Grain boundaries are noted by black lines and twin planes are noted in red. The anorthite exhibits twins rotating at 180° around the twin plane, e) Stereographic projection plotting the poles to the crystal face for a twinned RMN indicating a rotation about the [111] axis of 60°, f) A TKD euler image magnified at the right-hand side RMN cluster revealing twin planes (red lines) within the RMNs. The numbers indicate the location of EDS measurements detailed in Table 3.5.
only occurred in the RMN phase which was also enriched in Ru and depleted in Ni relative to the awaruite (Table 3.7).

Table 3.7: EDS measurements taken from region V2. The label corresponds to the label regions of Figure 3.7c. b.d. = below detection. The powellite composition was derived using calculated oxygen contents of powellite, not the measured abundances from the EDS measurement.

<table>
<thead>
<tr>
<th>RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Mo</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powellite 1</td>
<td>1.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>17.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.4</td>
<td>13.8</td>
<td>66.7</td>
</tr>
<tr>
<td>Powellite 2</td>
<td>1.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td>18.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>14.2</td>
<td>66.7</td>
</tr>
<tr>
<td>Awaruite</td>
<td>42.3</td>
<td>41.8</td>
<td>8.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.9</td>
<td>3.6</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>RMN</td>
<td>45.2</td>
<td>8.4</td>
<td>35.1</td>
<td>b.d.</td>
<td>6.8</td>
<td>3.3</td>
<td>1.2</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
</tbody>
</table>

3.4. DISCUSSION

Previous studies of RMNs have mostly lacked high resolution in situ crystallographic measurements, and instead focussed on the compositional variability between RMNs and mineralogical associations to inform interpretations. This new high resolution data provided by TKD may provide us with the key to accurately interpret the formation history of individual RMNs and any subsequent alteration, based on a synthesis of their petrographic context, morphology, chemistry, and CORs with host phases.

Similar analyses have been applied successfully to other phases (e.g. Jacob et al. 2016 and references there in). However, there is limited experimental work regarding the crystallography, CORs, and phase relationships between micrometre HSE nuggets such as RMNs and their associated minerals. Therefore, the following interpretations and discussions relating to the observed textures in RMNs serve only to demonstrate the potential of high resolution crystallo-
Figure 3.7: Characteristics of Vigarano - region V2. TKD analyses of RMNs and associated HSE alteration phases. These RMNs are hosted in spinel contained within the altered mantle of a fluffy type A CAI. a) Low magnification BSE image of region V2 in the wider context of the CAI; also showing a nearby matrix region and chondrule (Chond), b) A BSE image of the RMN (bright spot) in context, before extraction. The red rectangle indicates the orientation of the TEM section, the RMN here is associated with spinel (Spl), c) A TKD phase map of the section indicating the RMN (green) powellite (red) and awaruite (blue) assemblage hosted in a spinel (yellow). The labels indicate where EDS spectra were taken in Table 3.7, d) A TKD euler map indicating crystallographic orientations of all the phases. Twin planes are shown as red lines indicating the awaruite phase is twinned, e) Lower hemisphere stereographic projection of crystallographic orientations of the awaruite, indicating a rotation about the [111] axis of 60°, f) Lower hemisphere stereographic projection of crystallographic orientations of the powellite, g) Lower hemisphere stereographic projection of crystallographic orientations of the two largest RMN grains with a shared pole in the [110] axis, h) Lower hemisphere stereographic projection of crystallographic orientations of the spinel. There are no systematic CORs observed between any of the phases.
graphic analysis as a tool to extract information pertaining to the formation history meteoritic components and inclusions. To quantify these processes precisely would require further experimental petrography which is beyond the scope of the present study.

3.4.1. Allende - Region A1

RMNs are mostly interpreted as a primary phase (Berg et al., 2009; Schwander et al., 2015a; Palme and Wlotzka, 1976). However, if the RMNs observed here represent preserved primary phases they must survive chondrule formation, and subsequent sulphidation either in the nebula (Lauretta et al., 1996) or during metasomatism on the CV parent body (Blum et al., 1989) to arrive in their current petrographic context (Figure 3.1a). The shared COR between RMNs suggests that these RMNs are genetically related. Furthermore, these RMNs are depleted in W, Mo and Os which are readily mobilised during oxidation and sulphidation of RMNs (Fegley and Palme, 1985; Hewins et al., 1996; Palme et al., 1998). These observations suggest that these RMNs were affected if not formed by secondary processes either in the nebula or on the CV parent body. Therefore, a primordial origin for these RMNs is unlikely.

Deriving RMNs through secondary processes within chondrules requires a concentration mechanism for the HSEs due to their low abundances (measurements of bulk chondrules of the Allende meteorite indicate that they are depleted relative to bulk CV in siderophile elements such as Ir although coarse grained rims may be enriched or consistent with bulk CV (Rubin and Wasson, 1987; Grossman et al., 1988; Lodders, 2003)), a mechanism which produces and preserves the COR between RMNs and forsterite (Figure 3.2), and generates heterogeneous Ir and Pt compositions (Table 3.2).
HSE are soluble in sulphide (Makovicky et al., 1986, 1988, 1990). However, as RMNs are present the environmental conditions must have promoted the exsolution or preservation of metal. HSE alloys have been shown to exsolve from HSE-saturated sulphides during cooling as the solubility of HSE in sulphide decreases at low temperatures (Makovicky et al., 1986, 1988). HSE alloys can also be formed by S-loss from the system (Peregoedova et al., 2004) due to a reduction in the solubility of HSEs at low oxygen fugacity (Ballhaus and Ulmer, 1995) even at trace levels of HSE (Peregoedova et al., 2004). If these RMNs were exsolution products during cooling of the sulphide we might expect to observe a COR with the host sulphide (Feinberg et al., 2004; Fleet et al., 1980) which is not the case here.

The sulphide nodules within the chondrule are all rounded blebs which is consistent with the formation of a metal-silicate immiscible fluid during chondrule formation and melting (Grossman and Wasson, 1982). This would also have the effect of concentrating the HSEs in the metal phase due to their high partition coefficients ($D_{metal/silicate}^metal$, of approximately $10^4$ (Grossman, 2010; Borisov and Palme, 1995, 1997)). Some of the sulphide blebs exhibit rim structures which are consistent with the expected textures produced by nebula sulphidation (Lauretta et al., 1996) and implies that these blebs were once originally pure metal. However, this appears to be the only sulphide bleb to contain RMNs in the chondrule. This suggests that the HSEs were not initially evenly distributed throughout the chondrule, as in that case all or none of the sulphide blebs should contain RMNs. This suggests that the HSEs were pre-concentrated, likely in an RMN, which was assimilated into a single metal bleb. Thus, enriching this bleb in HSEs.

During sulphidation of the chondrule (Lauretta et al., 1996) the sulphur fugacity of the vapour was insufficient to promote the incorporation of Pt and
Ir into the sulphide causing it to be retained in the metal. These RMNs are then the product of the migration of HSEs which are more compatible with the metal phase (Ir, Pt) away from the sulphidation front. Experimental work by Peregoedova et al. (2004) suggest that this may occur at sulphur fugacity between $f_{S_2} \sim 6.9$ and $\sim 0.9$. If these could be constrained further, we could determine the maximum $f_{S_2}$ experienced during nebula sulphidation. The heterogeneous chemistry is generated by either heterogeneous distribution of HSEs in the nodule, which is unlikely due to the affinity of HSE to metal (Borisov and Palme, 1995, 1997; Grossman, 2010), or heterogeneities in local mineral chemistry - proximity to forsterite or proximity to troilite etc, or variable sizes of the ‘catchment area’ from which the HSEs were delivered to the RMN.

The COR between the forsterite grains and RMNs by way of a shared [100] axis may originate during the initial crystallisation of the chondrule, where forsterite crystallised around the Fe-metal bleb. Subsequent crystallisation of the Fe-metal would produce a COR by way of minimising the interfacial energy (Frondel, 1940), see also reaction fabric (Lauder, 1961)). Therefore, these RMNs preserve the initial alignment of the original Fe-metal bleb. There is no possibility of producing the observed alignment by compaction or through magnetic susceptibility. Furthermore, these RMNs are not connected in a 3D worm-like structure but are isolated grains, so the original alignment is preserved despite the isolation of these RMNs. This orientation relationship is preserved during sulphidation (Lauretta et al., 1996), and throughout any subsequent metasomatic alteration of the CV3 parent body (Blum et al., 1989).

In summary, the most likely sequence of events that occurred to produce the RMNs in Allende - region A1 is as follows: during chondrule formation an immiscible metal-silicate melt formed (Grossman and Wasson, 1982). One of these metal nodules incorporated an HSE enriched particle. On cooling the
Chapter 3
L. Daly

forsterite crystallised first around the still molten metal nodule. Further cooling crystallised the metal nodule with a COR with forsterite through minimising the interfacial energy (Frondel, 1940; Lauder, 1961). The chondrule was then exposed to a sulphur-rich gas which sulpidised the metal grain (Lauretta et al., 1996). The sulphur fugacity was such that Pt and Ir were above the saturation point for the sulphide (Peregoedova et al., 2004) causing them to preferentially remain in the metal. Tungsten, Mo and Os which have higher affinities for sulphide remained in the sulphide (Fegley and Palme, 1985) or perhaps were stripped during metasomatic alteration on the parent body (Blum et al., 1989).

3.4.2. ALLENDE - REGION A2

The RMNs here are hosted within a forsterite enclave, encapsulated by euhedral spinel associated with diopside within a Type-B CAI. The CAI had textures consistent with melting - a sub-rounded morphology and euhedral spinel laths, as well as recrystallisation due to annealing which produced the equigranular texture of the surrounding spinel with 120° grain boundary intersections (Smith, 1948; Komatsu et al., 2001), typical for this type of inclusion (MacPherson et al., 2005; Grossman et al., 2000).

The RMNs in this section are separated into two morphologies: a large RMN associated with molybdenite and smaller spherical RMNs hosted within the forsterite. The spherical morphology of these RMNs suggests that they were once molten as an immiscible metal-silicate fluid (Grossman and Wasson, 1982). The spherical morphology was maintained during crystallisation by the surface tension between the fluids, which prevented the RMN adopting its preferred cubic habit.

The melting point of RMN alloys is not well constrained, although the
melting point of pure element phases such as Os under normal atmospheric conditions is known to be very high (3127 °C) (Griffith, 2009), even for mixed alloys - the Ru-Ir-Os system has a melting temperature >3000 °C (Bird and Bassett, 1980). However, the melting point of PGE alloys in oxide and silicate melts may be lower (Bai et al., 2000). For example, the Ir-Si and Ru-Si system have a eutectic at ~ 1500 °C (Massalski et al., 1990; Allevato and Vining, 1993; Ivanenko et al., 2002). Finally, the melting point of an RMN under vacuum would also decrease. The triple point of forsterite under nebular conditions is approximately 1890 °C (Nagahara et al., 1994). However, within the spinel-forsterite system forsterite melts at ~ 1700 °C (Milholland and Presnall, 1998) and within the diopside-forsterite system forsterite melts at ~ 1300 °C (Presnall et al., 1978). Therefore, it may be possible to have forsterite and RMN melts coexisting to produce the rounded blebs (Grossman and Wasson, 1982).

Spherical RMNs have been observed by Schwander et al. (2015a). These authors concluded that such RMNs were derived from the crystallisation of dissolved HSEs into metal grains from a CAI melt. They suggested crystallisation would produce RMNs with spherical morphologies through a minimisation of the surface energy at the RMN grain boundary and the surrounding liquid. The RMNs here also have homogeneous chemistries consistent with this origin (Daly et al., 2017). However, in this case the abundance of HSEs is too high to completely dissolve in the forsterite melt due to the high metal-silicate partition coefficients (Grossman, 2010; Borisov and Palme, 1995) and the low volume of the forsterite.

Alternatively, this inclusion may represent a small OA (Blum et al., 1989; Palme et al., 1994). These are thought to be incorporated into CAIs as homogeneous alloys and subsequently separate into a number of phases during subsequent alteration of the CAI. The COR between the larger RMN and the
molybdenite and the ‘interfingering’ texture of the two phases is consistent with a reaction texture caused during exsolution of the two phases under oxidising conditions (Fegley and Palme, 1985). Therefore, this assemblage and the associated RMNs may represent exsolution products during the phase separation of the initially homogeneous alloy at lower temperatures under variable oxygen fugacity (Palme et al., 1994; Blum et al., 1988, 1989). If this is the case, some isolated RMNs may be derived from disrupted OAs (Blum et al., 1989). However, exsolution textures are usually associated with CORs with the host (Feinberg et al., 2004; Fleet et al., 1980) which are not observed within the small spherical RMNs. This implies a low temperature exsolution origin is less likely for these RMNs.

In summary, the most likely sequence of events experienced by this section is that a small OA was incorporated into a CAI pre-cursor (Blum et al., 1989, 1988; Palme et al., 1994). On melting and subsequent crystallisation of the CAI the OA was sequestered as an inclusion within spinel (Blum et al., 1989). During a subsequent high temperature event which melted the OA an immiscible metal-silicate fluid formed which cooled producing randomly oriented small spherical RMNs within forsterite. During low temperature alteration at high oxygen fugacity the larger RMN exsolved into molybdenite and a metallic phase (Blum et al., 1989).

### 3.4.3. **Allende - Region A3**

This RMN was hosted in the core of a forsterite enclave surrounded by diopside with associated euhedral spinel laths from the same Type-B CAI from region A2.

The RMN share a [110] axis with the forsterite. This is similar to the observed
COR between RMNs and forsterite in region A1 where the [100] is shared. Here the RMN is situated in the core of the forsterite inclusion. The COR may have formed due to the minimisation of interfacial energy between the RMN and the forsterite, as was the case for the original metal nodule in region A1. However, in this case as the RMN is likely to crystallise at higher temperatures than the forsterite (Bird and Bassett, 1980; Presnall et al., 1978) and is situated at the core of the forsterite grain, it is possible that this RMN also acted as a nucleation site.

There are two types of nucleation: homogeneous and heterogeneous. Homogeneous nucleation occurs when the crystal nucleates from a newly formed embryo of similar material, whereas, heterogeneous nucleation occurs when a crystal nucleates off a pre-existing nuclei or pre-existing mineral (Herlach, 1994). Homogeneous nucleation occurs at lower temperatures and slower cooling rates as the embryos require time to form (Herlach, 1994). Conversely, heterogeneous nucleation occurs at initially high temperatures followed by subsequent rapid cooling (Herlach, 1994). Homogeneous nucleation would not generate CORs between the forsterite and the RMN. Therefore, the forsterite may have nucleated heterogeneously around the RMN. This confines the initial temperature to above that of forsterite nuclei embryo formation, followed by rapid cooling.

3.4.4. ALH 77307 - REGION ALH1

The RMN in this section is euhedral and hosted within a type B-like CAI. The texture of the CAI with euhedral perovskite laths indicates it was once molten, and 120° grain boundary intersections of the melilite indicate that it was subsequently annealed (Smith, 1948; Komatsu et al., 2001), consistent with this type of inclusion (MacPherson et al., 2005; Grossman et al., 2000) The
RMN is associated with an unknown phase which adopted a pseudomorph texture with the RMN. For metal grains in meteorites a euhedral morphology is interpreted as mineral growth in an unconstrained environment within a vapour or melt (Rubin, 1994), although it is plausible that euhedral metal laths could grow during metamorphism none have been reported (Rubin, 1994). Therefore, euhedral RMNs are interpreted to have grown in an unconstrained environment.

The unknown phase was likely to be a secondary phase formed by alteration of the RMN, separating Mo and W into the unknown phase due to their increased mobility during alteration events (Fegley and Palme, 1985; Palme et al., 1998). The pseudomorph texture indicated that the secondary alteration must have occurred whilst the RMN was within the CAI post-crystallisation. The process that caused this phase separation must have occurred at temperatures lower than the melting point of the melilite host (1410 – 1510 °C (Mendybaev et al., 2006; Stolper, 1982)). If this was not the case the unknown phase would have been able to grow unconstrained, and would not exhibit the observed deformation features, or conform to the original RMN grain boundary (Rubin, 1994). There are two possible alteration sites: alteration on the parent body, or alteration in the nebula. ALH 77307 is one of the most primitive meteorites in the collection, with a maximum parent body temperature of 203 °C (Cody et al., 2008).

The observed textures within the unknown phase exhibit a high dislocation density. The TKD data indicate these dislocations have various orientation changes between grains of the unknown phase while maintaining a COR with the RMN to within 6°. This could form through either crystal plastic deformation or rapid formation. Crystal plastic deformation requires an induced stress field, which is unlikely in an asteroidal environment and therefore this grain
likely formed rapidly. We suggest this unknown phase formed by solid state recrystallisation of the RMN during a transient heating event in the protoplanetary disk, prior to the incorporation of the CAI into the parent body. If the conditions required for this phase transformation were known, it would be possible to constrain this event.

The RMN shares a minor axis with the melilite host. This COR with the melilite mineral may indicate that the melilite crystal nucleated around the RMN. This is interpreted along a similar line of reasoning to region A3.

These observations indicate that during crystallisation this CAI experienced rapid cooling which caused heterogeneous nucleation of melilite around the RMN. This was followed by a second transient heating event below 1410 °C (Mendybaev et al., 2006; Stolper, 1982) that exsolved the unknown phase from the RMN and produced the pseudomorph texture and the observed crystallographic alignments, as well as annealing the CAI. This is consistent with our understanding of CAI formation (MacPherson et al., 2005; Grossman et al., 2000).

3.4.5. Vigarano - region V1 and V2

The CAI bearing the V1 and V2 regions has a zoned texture with a relatively unaltered core. There is potentially re-heated material surrounding the core, and Wark Lovering rims around the edge of the CAI. The region is interpreted as ‘re-heated’ due to the presence of annealing textures such as 180° mirror twins within the anorthite (Figure 3.6) and 120° grain-boundary-intersection spinel grains (Figure 3.7) (Smith, 1948; Komatsu et al., 2001). The RMNs were extracted from this re-heated portion of the CAI, and are hosted within an anorthite grain (Region V1) and a spinel grain (Region V2).
The RMNs in V1 had two distinct morphologies: an anhedral RMN associated with spinel, and several euhedral twinned RMNs with straight grain boundaries (Figure 3.6). The euhedral RMNs likely formed in an unconstrained environment in the presence of a fluid or gas (Rubin, 1994). Their accumulation in a void space indicates that they may have originally been free floating in the nebula gas, or were initially suspended in a mineral which has since been removed. The chemistry of each RMN in V1 are different from each other, and none have chondritic relative elemental ratios even though these grains are hosted within the same CAI, and in some places are situated adjacent to each other. However, an ‘average’ RMN derived from the mean HSE abundance of these RMNs is consistent with chondritic elemental ratios. None contain detectable Mo suggesting these elements may have been remobilised (Fegley and Palme, 1985). There is no transfer or re-equilibration of HSEs, even between RMNs separated by only a few nanometres. The RMN associated with the spinel in V1 together form a spherical inclusion. There is a slight curvature of the RMN grain boundary towards the bottom of the inclusion (Figure 3.6). This curvature could be interpreted as the meniscus between two fluids which suggests that the RMN and the spinel were both molten forming an immiscible silicate-metal melt.

The region V2 contains a complex HSE-rich inclusion and is unlike any previously described RMN in this study. The RMN has separated into three phases: a Mo-rich powellite, a Ni-rich twinned awaruite and an Os, Ru-enriched RMN. These textures are consistent with an OA (El Goresy et al., 1977; Blum et al., 1988) (Figure 3.7). This inclusion contains two metal phases: awaruite and the RMN, which exhibit a complementary depletion or enrichment in Ru and an enrichment or depletion in Ni, respectively. The powellite is the only phase present to contain Mo. The redox state of Mo implies the event that mobilised
the Mo was oxidising (Fegley and Palme, 1985) and likely occurred within the CAI which provided the Ca component. This containment in the CAI inhibited the escape of Mo. All of the phases exhibit deviations from chondritic relative abundances consistent with a OA (El Goresy et al., 1977; Palme et al., 1994).

The crystal twins observed within RMNs in Vigarano in both the euhedral RMNs in V1 (Figure 3.6) and the awaruite in V2 (Figure 3.7) have not previously been reported in RMNs despite numerous and detailed SEM (Sylvester et al., 1990; Schwander et al., 2015a; Wark and Lovering, 1976) and TEM studies (Harries et al., 2012; Croat et al., 2013). This demonstrates the value of TKD and its ability to map the crystallography and chemistry of a lamella rapidly, in comparison to established techniques such as TEM. Twinning can be produced via a number of different mechanisms, such as growth, annealing and deformation (Cahn, 1954).

The pressure and strain rate required for the onset of shock twinning for micrometre alloys of HSEs such as RMNS is not well constrained. The Vigarano meteorite has undergone very little processing in terms of deformation and shock (Scott et al., 1992). Vigarano is classified as shock stage S1 (Komatsu et al., 2001; Scott et al., 1992) implying it experienced <5 GPa (Stöffler and Keil, 1991). Neumann lines in kamacite are generated by shock in iron meteorites at ~ 1 GPa (Bischoff and Stoeffler, 1992). Vigarano contains kamacite, but such textures have not been reported within these metal inclusions in Vigarano (Mcsween, 1977). Furthermore, shock twinning is dependent on both grain size, where smaller grains are more resistant to shock twinning (Meyers et al., 1995). Therefore, if RMNs are comparable to kamacite metals in Vigarano and the fact that a second RMN within the same TEM lamellae does not exhibit twinning it is reasonable to assume that these twins are not derived from shock related processes.
This leaves two possibilities: growth twins and annealing twins. If the observed twins were growth twins formed from nucleation these would be observed as simple penetration twins. This would result in clear crystal faces with changes in the morphology of the RMN which are coincident with the twin boundary. This is not observed within the sample as the crystal faces are well formed and continuous across the twin boundary. We would also expect this to be a much more common observation in RMNs if they formed growth twins.

Annealing twins form at high temperatures with relatively little stress. In fcc crystals they classically form along the [111] axis with a 60° misorientation (Brandon, 1966), which is consistent with the observed RMN twins in Vigarano (Figure 3.6). This implies that the twinning observed is probably formed by annealing. TEM experiments by Dai et al. (2001) observed annealing twin formation in FePt nanoparticles. This study indicated that while heating under vacuum for one hour, annealing twins began to form at 450 °C, and were completely annealed by 530 °C. The nanoparticles studied coalesced into larger grains at 600 – 700 °C. The RMNs observed in Vigarano, however, have not coalesced. The specific grains in the aforementioned study are compositionally different to RMNs observed in our research, so only limited comparisons can be made. However, the temperature dependence of the onset of annealing twinning (Dai et al., 2001) indicates that by constraining their formation temperature by experiment for RMN alloy compositions, annealing twins could be used as a coarse thermometer for early Solar System processes.

These annealing twins could form either as a result of thermal metamorphism on the CV parent body, or pre-accretion in the nebula either as free floating RMNs or subsequent to RMN incorporation into the CAI.
The CAI here did contain nepheline and sodalite which are evidence for parent body alteration (Krot et al., 1997). The highest estimates place the maximum parent body temperatures experienced by Vigarano at 415 °C (Cody et al., 2008), and most estimates for Vigarano peak temperatures are much lower than this (<330 °C) (e.g. Bonal et al. 2006, 2007). If RMNs anneal in this temperature range we could further constrain parent body temperatures. The twinning present in the awaruite in V2 may be of this nature as awaruite is a low temperature phase which forms at <500 °C (Reuter et al., 1989) associated with parent body alteration (Müller et al., 1995).

These RMNs are hosted in anorthite and spinel which do not exhibit textures consistent with melting. These phases melt at 1250 °C and 1550 °C respectively (Stolper, 1982) so therefore, if RMNs form annealing twins between 400 – 1200 °C (the maximum Vigarano parent body temperature and the temperature that anorthite melts in CAIs (Bonal et al., 2006; Cody et al., 2008; Stolper, 1982)) this would allow us to determine the temperature of transient heating events in the nebula.

Annealing RMNs in the nebula environment prior to incorporation into the host may be unlikely as CAIs also form at high temperatures (MacPherson et al., 2005) close to the formation temperatures of RMNs (Berg et al., 2009) which would leave only a narrow window for the formation of annealing twins, which may then be overprinted by subsequent re-heating within the CAI.

The temperature dependence of the onset of annealing twin formation and complete recrystallisation (Dai et al., 2001) means that if the temperature range of RMN annealing were constrained, annealing textures could be used as a low-resolution thermometer for pre-accretion heating events, or parent body heating.
3.4.6. Summary

RMNs are a complicated group of alloy minerals in meteorites. It is apparent that each individual RMN preserves a history of Solar System events and possibly even pre-solar events.

The morphology of RMNs may indicate the processes and environment the RMN formed in, e.g., euhedral RMNs are expected to form in unconstrained environments such as growth in a fluid or gas phase (Rubin, 1994). If this growth is impeded or the RMN is subsequently altered, we would expect to observe anhedral-subhedral RMNs. Spherical RMNs have previously been interpreted as forming through crystallisation from a silicate melt (Schwander et al., 2015a). However, the spherical RMNs observed here are more likely to represent the formation of immiscible metal-silicate melt at high temperatures.

The analyses of RMNs using TKD have revealed several crystallographic textures that had not been documented previously. These observations provide evidence for, and could provide constraints on, several Solar System processes. CORs between RMNs and their host and petrological data can be used to demonstrate that in some cases RMNs acted as a heterogeneous nucleation site for the host phase during crystallisation. The presence of annealing twins within RMNs which are temperature dependant (Dai et al., 2001) means that RMNs could be used as a coarse thermometer for parent body or nebula heating events. The context of the RMN in relation to its host phase and inclusion can also indicate when and where the RMN was altered and under what conditions.

Several RMNs when analysed by TKD revealed that they were in fact polyphase inclusions similar to OAs, although these are much smaller than those described previously (El Goresy et al., 1977; Blum et al., 1989). It is not
clear if this reflects a property of HSE-rich alloys in meteorites to separate into phases during low temperature alteration (Blum et al., 1988, 1989; Palme et al., 1994) or a genetic link between OAs and RMNs. In any case, it appears that OAs can exsolve RMN like inclusions while RMN sized objects can be internally complex.

The relative chemical abundances of HSEs in RMNs are variable with the exception of the small spherical RMNs in A2 which have uniform chemistry with near chondritic relative elemental abundances. This may be due to a separation of immiscible metal-silicate fluids during melting of an OA. These RMNs are also situated next to a RMN which appears to preserve dislocations and a reaction texture which is consisted with exsolution at lower temperatures and higher oxygen fugacity (Blum et al., 1989), signifying it formed before the melting event. RMNs in A1 appear to be able to form by migration of HSEs during sulphidation of metal nodules. In all other RMNs in this study, including altered RMNs, we still observe non-chondritic relative abundances of at least two HSEs. HSE elements Os, Ir, Pt and Ru are observed to be largely unaffected by most asteroidal processes. Os can be mobilised in transient heating events at high oxygen fugacity. Tungsten and Mo are mobilised by low levels of alteration in either a high oxygen fugacity environment or in the presence of sulphur (Fegley and Palme, 1985). Isolated RMN-bearing inclusions can preserve Mo and W where they are encapsulated within an impermeable host. The immobility of most HSEs is evident even in RMNs in the same inclusion, same host mineral and even in some separated by a few nanometres of void space. This suggests that RMNs are resistant to re-equilibration, and individual RMNs can be approximated to a closed system during the majority of Solar System processes with regard to these elements. Therefore, the refractory component of RMNs may preserve a primary or even pre-solar signature.
Combining these observations provides evidence that supports the suggestion of Daly et al. (2017); RMNs that have not been homogenised during melting, preserve a primordial signature that is inconsistent with condensation and is likely to have originated as part of an inherently diverse population of RMNs distributed throughout the Giant Molecular Cloud. Isotopic analyses of individual RMNs would provide a clear answer to this hypothesis.

3.5. CONCLUSIONS

TKD and other high resolution in situ analyses are integral to the interpretation of RMNs, enabling us to evaluate the sequence of events that may have affected RMN chemistry and relations to host inclusions since the formation of the RMN. Every section analysed in this study could not be fully interpreted without the incorporation of every facet of information provided by TKD analyses. The relationships between RMN chemistry, morphology, CORs and mineral associations observed in this study combine to form a powerful dataset that can begin to build a framework from which RMN formation and alteration can be determined. Previous work on RMNs showed that they exhibit heterogeneous chemical compositions, inconsistent with a single formation model (Daly et al., 2017). TKD of RMNs reveal a suite of crystallographic features such as twinning - interpreted here as annealing twins, CORs, randomly oriented spherical nano-RMNs, reaction textures, nucleation centres and fluid immiscibility textures. This indicates that RMNs experienced a diversity of formation histories even between RMNs within the same meteorite, inclusion, and even separated by a few nanometres. In cases where the RMN had been altered we still observe chemical heterogeneities between RMNs. The variety of crystallographic textures observed indicate each individual RMN has a complex formation history.
These observations are consistent with the suggestion of Daly et al. (2017), that some RMNs have survived Solar System formation and preserve an inherited heterogeneity from the Giant Molecular Cloud.

3.6. ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council via their Australian Laureate Fellowship program. This research was undertaken on the XRF beamline at the Australian Synchrotron, Victoria, Australia. The authors acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the Australian Centre for Microscopy and Microanalysis, the University of Sydney and the Centre for Microscopy, Characterisation and Analysis, University of Western Australia. This work was conducted within the Geoscience Atom Probe Facility at Curtin University, which is part of the Advanced Resource Characterisation Facility (ARCF). The Advanced Resource Characterisation Facility is being developed under the auspices of the National Resource Sciences Precinct - a collaboration between CSIRO, Curtin University and The University of Western Australia - and is supported by the Science and Industry Endowment Fund (SIEF RI13−01). SMR acknowledges support from the ARC Core to Crust Fluid System COE (CE11E0070) The authors would also like to thank guest editor Prof. Chi Ma, as well as reviews from Prof. Herbert Palme and Prof. Alexander Krot and one anonymous reviewer for their invaluable comments which improved the manuscript substantially, as well as Prof. Amy Riches for arranging and organising the HSE special issue and ensuring it was published in good time. The authors would finally like to thank the rest of the Desert Fireball Network research group as well as, Mr Mark Daly, and Ms Jennifer Porter for their
assistance and support.

3.7. SUPPLEMENTARY MATERIAL FOR CHAPTER 3

3.7.1. SUPPLEMENTARY MATERIAL A

Supplementary material A contains figures pertaining to the petrological context of the RMNs in this study.
Figure 3A.1: Backscatter electron (BSE) images of the wider context of region A1 within the Allende CV3 meteorite. Mineral labels are defined as Fo=forsterite Pn=pentlandite. a) A BSE image of the wider context of the porphyritic olivine (PO) chondrule bearing abundant Pn nodules and a Pn-rich rim where the RMNs are located. Fo within the chondrule has a $\text{Fo}_{0.87-0.53}$ content. b) A BSE image at higher magnification showing Pn nodules within the PO chondrule rim where the RMNs are located. c) A forescatter detector (FSD) image of the Pn nodule within the PO chondrule which is RMN bearing d) A higher magnification FSD image of the Pn nodule, RMNs are now observable within the red box (bright spots) where the A1 analyses in the manuscript are detailed. The red boxes indicate the field of view of the subsequent image.
Figure 3A.2: Backscatter electron (BSE) images of the wider context of region A2 and A3 within the Allende CV3 meteorite. Mineral labels are defined as Fo=forsterite, Spl=spinel, Di=diopside, Grs=grossular, Sdl=sodalite, RMN=refractory metal nugget. a) A BSE image of the wider context of the Type-B CAI which hosts the RMNs in region A2 and A3 within the thin section. b) A EBSD phase map of the CAI mineralogy which is Spl-, Di-rich with a rim of Fo and minor components of Sdl, Fo and Grs. c) A BSE image of the CAI showing the bulk mineralogy of Spl, and Di with small Fo enclaves bearing RMNs. d) A BSE image region A2 showing the RMN in the Fo enclave surrounded by Mg-rich Spl and associated Di. The Spl here is Fe-bearing with a hercynite (Hc) content of Hc$_{0.27}$ while Di is Mg-Ca-rich with minor amounts of Fe and Ti with wollastonite (Wo) content of Wo$_{0.54}$. e) FSD image of the wider context of region A3 showing the small Fo enclave bearing an RMN hosted by Di associated with Spl. The Fo is Mg-rich with Fo$_{0.83}$, the Di has Wo$_{0.53}$ and the Spl is Mg-rich with minor Fe: Hc$_{0.18}$. The red boxes indicate the field of view of the subsequent image, the labels within the image indicate the orientation of the subsequent image.
Figure 3A.3: Backscatter electron (BSE) images of the wider context of region ALH1 ALH 77307 CO3.0 meteorite. Mineral labels are defined as Mel=melilitie, Prv=perovskite and Cpx=clinopyroxene a) A BSE image of the wider context of the Type-B CAI which hosts the RMN in region ALH1. The Mel is gehlenite (Gh)-rich Gh0.99. The red boxes indicate the field of view of the region ALH1 within the manuscript.
FIGURE 3A.4: Backscatter electron (BSE) images of the wider context of regions V1 and V2 from Vigarano CV3 meteorite. Mineral labels are defined as Spl=spinel, An=anorthite a) A BSE image of the wider context of the ‘fluffy’ type-A CAI within the Vigarano thin section which hosts the RMNs in region V1 and V2. b) A red green blue EDS map showing the distribution of Ca (red) Na (green) and Fe (blue) within the CAI c) A higher magnification BSE image of region of the CAI containing V2 and associated Spl and An. d) Zoom in BSE image of the region containing V1 and associated Spl and An. The red boxes indicate the field of view of the region V1 and V2.
3.7.2. **Supplementary Material B**

Supplementary material B contains a brief description of the atom probe microscopy technique used to assess the accuracy of the EDS data.

### 3.7.2.1. Atom Probe Microscopy

Atom probe microscopy (APM) combines high spatial resolution with chemical/isotopic sensitivity down to 10 appm (Gault et al., 2012; Kelly and Larson, 2012; Miller and Forbes, 2014). The technique has been widely used in materials science and engineering over the past 50 years, and is known to produce accurate, quantitative chemical analysis of small samples, giving results consistent with other techniques, particularly in the case of metal alloys (Miller et al., 1996; Miller, 2000).

### 3.7.2.2. Sample and Preparation

A 1 mm RuIrOs nugget from a placer deposit in Tasmania, Australia was analysed by both APM and EDS. The EDS methodology is already described in detail in the manuscript and so will not be repeated here. After EDS measurements were taken on the RuIrOs nugget, atom probe specimens were prepared by extracting a wedge of material from the nugget using a focussed-ion beam. This wedge was attached to a Si post and milled using an annular mask to produce a needle-like specimen with a 100 nm diameter tip, following the methodology of (Thompson et al., 2007).

The resulting specimen needle was analysed in laser mode using a Cameca
LEAP 4000X HR atom probe microscope at, the Advanced Resource Characterisation Facility, housed within the John de Laeter Centre, Curtin University.

The resulting mass-to-charge-state-ratio spectra was analysed with the IVAS 3.6.14 software package, using the full width of the element peaks to determine the bulk chemistry of the sample. These data were compared to the EDS measurements (Table 3B.1). For all elements detected by EDS, the two datasets are in agreement, within the 10 % relative uncertainty associated with the EDS measurements. This result provides confirmation that the EDS data reported here are reliable and quantitative, within the relative uncertainty.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Fe at.%</th>
<th>Ni at.%</th>
<th>Ru at.%</th>
<th>Rh at.%</th>
<th>Mo at.%</th>
<th>W at.%</th>
<th>Os at.%</th>
<th>Ir at.%</th>
<th>Pt at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom probe</td>
<td>2.42</td>
<td>0.48</td>
<td>15.8</td>
<td>0.48</td>
<td>b.d.</td>
<td>43.9</td>
<td>35.9</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>EDS</td>
<td>2.6 b.d.</td>
<td>15.6 b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>41.9</td>
<td>39.8</td>
<td>b.d.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.7.3. Supplementary Material C
Table 3C.1: Supplementary Material C raw EDS data.

<table>
<thead>
<tr>
<th>Spectrum label</th>
<th>Region A2</th>
<th>Region A1 TKD</th>
<th>Region A1 EBSD</th>
<th>Region A3 EBSD</th>
<th>Region V2 TKD</th>
<th>Region V1 TKD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe Ni Ru Rh Mo W Os Ir Pt O Mg Al Si S Cr Zn Ca Zr Er C Cu F Ge Ga Y Co H</td>
<td>Fe Ni Ru Rh Mo W Os Ir Pt O Mg Al Si S Cr Zn Ca Zr Er C Cu F Ge Ga Y Co H</td>
<td>Fe Ni Ru Rh Mo W Os Ir Pt O Mg Al Si S Cr Zn Ca Zr Er C Cu F Ge Ga Y Co H</td>
<td>Fe Ni Ru Rh Mo W Os Ir Pt O Mg Al Si S Cr Zn Ca Zr Er C Cu F Ge Ga Y Co H</td>
<td>Fe Ni Ru Rh Mo W Os Ir Pt O Mg Al Si S Cr Zn Ca Zr Er C Cu F Ge Ga Y Co H</td>
<td></td>
</tr>
<tr>
<td>Molybdenite</td>
<td>0.9 56.5 2.9 2.7 37.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.3 32.1 2.4 2.1 2.4 11.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.0 31.9 1.7 32.0 23.5 2.4 3.0 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.2 28.6 3.4 22.9 4.5 17.2 2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4.9 28.6 3.4 26.3 4.2 13.8 2.8 1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.5 28.6 3.4 26.1 3.2 0.9 2.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.6 25.5 3.4 23.2 5.7 17.2 2.4 1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe Ni Ru Rh Mo W Os Ir Pt O Mg Al Si S Cr Zn Ca Zr Er C Cu F Ge Ga Y Co H</td>
<td>1 5.6 4.2 0.2 2.4 10.2 5.5 0.6 0.1 67.2 4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7.0 5.0 0.1 0.7 2.6 6.7 0.9 0.1 72.1 4.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.5 7.8 0.9 0.0 7.0 2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.4 3.9 0.8 1.2 6.7 6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM RMN</td>
<td>55.5 9.4 7.5 6.7 7.0 4.0 9.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TKD RMN</td>
<td>9.8 1.7 2.4 0.6 2.8 0.4 0.6 2.0 14.3 9.7 0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM Unknown Phase</td>
<td>50.9 4.2 6.3 26.6 6.7 14.0 8.9 27.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TKD Unknown Phase</td>
<td>7.3 0.7 1.7 7.1 0.4 0.5 0.3 0.4 16.4 8.9 0.1 0.2 0.5 49.2 6.3 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM Unknown Phase</td>
<td>5.3 1.0 4.1 0.8 0.4 0.1 15.0 12.0 5.0 0.1 0.2 49.0 17.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powellite 1</td>
<td>0.2 2.0 0.0 47.2 12.0 1.5 38.9 9.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powellite 2</td>
<td>0.2 2.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Awaruite</td>
<td>3.8 3.8 0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMN</td>
<td>5.3 1.0 4.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM RMN</td>
<td>55.5 9.4 7.5 6.7 7.0 4.0 9.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TKD RMN</td>
<td>9.8 1.7 2.4 0.6 2.8 0.4 0.6 2.0 14.3 9.7 0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM Unknown Phase</td>
<td>50.9 4.2 6.3 26.6 6.7 14.0 8.9 27.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TKD Unknown Phase</td>
<td>7.3 0.7 1.7 7.1 0.4 0.5 0.3 0.4 16.4 8.9 0.1 0.2 0.5 49.2 6.3 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM Unknown Phase</td>
<td>5.3 1.0 4.1 0.8 0.4 0.1 15.0 12.0 5.0 0.1 0.2 49.0 17.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powellite 1</td>
<td>0.2 2.0 0.0 47.2 12.0 1.5 38.9 9.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powellite 2</td>
<td>0.2 2.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Awaruite</td>
<td>3.8 3.8 0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMN</td>
<td>5.3 1.0 4.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At.

Region A2
Region A1 TKD
Region A1 EBSD
Region A3 EBSD
Region V2 TKD
Region V1 TKD

Table 3C.1: Supplementary Material C raw EDS data.
3.8. REFERENCES


CHAPTER 4

PAPER 3 — NEBULA SULFIDATION AND
EVIDENCE FOR MIGRATION OF ‘FREE
FLOATING’ REFRUCTORY METAL NUGGETS
REVEALED BY ATOM PROBE MICROSCOPY.

Luke Daly\textsuperscript{a}, Philip A. Bland\textsuperscript{a}, David W. Saxey\textsuperscript{b}, Steven M. Reddy\textsuperscript{ab}, Denis Fougerouse\textsuperscript{ab}, William D. A. Rickard\textsuperscript{b}, and Lucy V. Forman\textsuperscript{a}

\textsuperscript{a}Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA, Australia.

\textsuperscript{b}Geoscience Atom Probe Facility, Advanced Resource Characterisation Facility, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA, Australia.

This article is published in Geology, v. 45, no. 9, p. 847 — 850
doi: 10.1130/G39075.1 and reprinted with permission in Appendix A.
ABSTRACT

Disk models have been proposed which imply particles migrate rapidly in the protoplanetary disk. However, the only physical constraints on this process from meteorites are observations of refractory inclusions in cometary material from the NASA Stardust mission. Atom probe microscopy (APM) of sub-micrometer refractory metal nuggets (RMNs) contained within a Sc-Zr-rich ultra-refractory inclusion (URI) from the ALH 77307 carbonaceous Ornans (CO) 3.0 meteorite revealed the presence of sulfur at 0.06 – 1.00 atomic percent (at. %) abundances within RMNs. The mineralogical assemblage, petrographic texture and flat chondrite-normalized highly siderophile element ratios indicate S exposure was unlikely to have occurred after the RMNs were incorporated into the URI. APM analyses suggest these RMNs were likely ‘free floating’ when they were exposed to a S-condensing gas. This requires early, rapid migration of RMNs to cooler regions of the disk to incorporate S and then cycling back to the Ca-Al-rich inclusion (CAI)-forming region for incorporation in the URI, or conditions in the CAI-forming region that promote the incorporation of S into RMNs.

4.1. INTRODUCTION

Refractory metal nuggets (RMNs) are micrometer to sub-micrometer metal alloys composed of the highly siderophile elements (HSEs) Os, Ir, Pt, W, Mo, Ru, Rh, Fe and Ni, and they are found in primitive meteorites (Palme and Wlotzka, 1976; Wark and Lovering, 1976). They are thought to form early, at high temperatures (Berg et al., 2009) alongside other refractory inclusions such
as Ca-Al-rich inclusions (CAIs) and their associated phases, close to the proto-
sun (MacPherson et al., 2005). These refractory materials are found within
carbonaceous chondrite meteorites and within cometary material returned
from the NASA *Stardust* mission (Brownlee et al., 2006; Zolensky et al., 2006;
McKeegan et al., 2006).

This observations require a mechanism for materials to migrate from prox-
imal to distal heliocentric distances >30 astronomical units (AU). Several mech-
anism have been suggested that can distribute material throughout a proto-
planetary disk within reasonable time scales; i.e., $10^5$ yr (Ciesla, 2010) relative
to the lifetime of the nebula ($10^6$ yr; Russell et al. 2006). Principally, these sug-
gested mechanisms are the X-wind model (Shu et al., 1997), diffusion along
the disk’s midplane (Ciesla, 2007; Bockelée-Morvan et al., 2002; Hughes and
Armitage, 2010), and disk winds (Bai, 2014). The only physical constraints on
these models is the presence of CAIs in comets. However, RMNs, as one of
the first phases to form in a protoplanetary disk (Berg et al., 2009), preserve
geochemical information pertaining to the initial conditions of our solar system
and therefore may be an ideal phase in which to observe evidence of particle
migration in the disk. However, establishing the exact compositions of RMNs
is difficult due to their sub-micrometer size (Schwander et al., 2015).

To address this issue, we use a focused-ion beam (FIB) for site-specific sam-
pling of a suite of RMNs to recover RMN samples for atom probe microscopy
(APM). APM is a novel technique that allows subnanometer-resolution quanti-
tative three-dimensional (3-D) elemental mapping of ion distributions down
to 10 appm (atomic parts per million) concentrations in very small samples
(Kelly and Larson, 2012; Gault et al., 2012), and we use it to provide quantitative
bulk chemistry data from a suite of submicrometer RMNs. These data reveal
trace abundances of sulfur, which have not previously been observed in RMNs.
Our results therefore provide further constraints on early solar system material transport and disk processes.

4.2. METHODOLOGY

An Sc-Zr-rich ultrarefractory inclusion (URI) bearing abundant RMNs was identified in the ALH 77307 CO3.0 meteorite (from Allan Hills, Antarctica). ALH 77307 CO3.0 was chosen because it is one of the most primitive meteorites and experienced minimal parent body processing (Grossman and Brearley, 2005). The URI was characterized using simultaneous electron backscatter diffraction (EBSD) and energy dispersive X-ray spectroscopy (EDS) mapping on the TESCAN MIRA3 variable pressure-field emission scanning electron microscope (VP-FESEM), at the John de Laeter Centre (JdLC), Curtin University, Perth, Australia (see Appendix 3A). Six RMNs (RMN1–RMN6) between 900 and 300 nm and a portion of the interior and rim of the URI (kan1 and cpx1, respectively) were extracted from the sample and milled to needle-like shapes using the TESCAN LYRA3 FIB scanning electron microscope (SEM) at JdLC, using a modified version of Thompson et al. (2007)’s methodology for site-specific targeting of submicron features (Figure 4.1 and Figure 4.2; Appendix 3B). The resulting specimens were analysed on the local electrode atom probe (LEAP; 4000X HR Geoscience Atom Probe), part of the Advanced Resource Characterisation Facility at JdLC (Appendix 3C). The numbers of ionic species detected by APM from each specimen were 2.4, 17.0, 8.0, 5.6, 14.7, 7.3, and $0.6 \times 10^6$ for the RMN1–RMN5, kan1 and cpx1 specimens, respectively; RMN6 did not run (Appendix 3E). Elemental abundances in each specimen were calculated using the IVAS 3.6.14 software package (Appendix 3D).
The chemistry and structure of the RMNs and adjacent phases was analyzed prior to lift out for APM analyses by EDS and EBSD, respectively. EDS data were used to aid in the interpretation of the APM mass spectra for major elements, and EBSD data were used to identify the mineral phases by their crystal structure and thereby constrain the oxide content. Because the phase and therefore oxygen abundance were known, this allowed corrections to be made for any oxygen stoichiometry errors in the APM compositional quantification (Karahka et al., 2015; Gault et al., 2016; Amirifar et al., 2015; Devaraj et al., 2013).

4.3. RESULTS

4.3.1. ULTRAREFRACTORY INCLUSION

EDS and EBSD analyses revealed that the URI was dominated by Zr- and Sc-rich oxide phases: perovskite, spinel and kangite (Ma et al., 2013). The URI was largely encapsulated by a rim of clinopyroxene (Figure 4.1). The oxide minerals were equigranular, with some grain and phase boundaries interlocking at 120°. All phases exhibited minimal internal deformation; internal misorientations of individual grains were <1°.

The compositions of APM specimens extracted from the kangite (kan1) and the clinopyroxene rim (cpx1) are summarized in Table 4.1.

4.3.2. REFRACTORY METAL NUGGETS

RMNs were found throughout the URI. Euhedral RMNs were observed by SEM, exhibiting straight crystal facets (Appendix 3E). APM from RMN1–RMN5
Figure 4.1: Electron backscatter diffraction (EBSD) and energy dispersive X-Ray spectroscopy (EDS) analyses of the region of interest from ALH 77307 CO3.0 meteorite (from Allan Hills, Antarctica). A: Backscattered electron image of the ultra-refractory inclusion (URI) indicating mineral phases; RMN – refractory metal nugget, Spl – spinel, Kan – kangiite, Cpx – clinopyroxene, and Prv – perovskite. Extraction site locations of atom probe microscopy (APM) specimens RMN1–RMN5, kan1, and cpx1 are indicated by red circles, as well as RMN6 which did not run in atom probe but indicates typical euhedral crystal habit typical of these RMNs (Appendix 3E). Cpx forms a rim around most of the inclusion. Most phases exhibit 120° grain boundary intersections. Red box indicates area of EDS and EBSD maps in B and C. B: EDS red-green-blue map of S, Os, and Sc reveals position of RMNs and associated S enrichment. C: Band contrast map overlaid with phase map indicating Prv, Spl, and Kan rimmed by Cpx; no RMNs were indexed.
revealed they were composed of the HSEs Re, Os, W, Ir, Mo, Ru, V, Pt, Rh, Ni, Co, Fe and Cr, as expected (Table 4.1 and Figure 4.3). However, they also contained 0.06 – 1.00 at. % S; which is a relatively volatile element (50% condensation temperature of 664 K (Lodders, 2003), i.e., the temperature at which 50% of the element would have condensed from a gas of solar composition) not previously observed within RMNs (Figure 4.1B, Figure 4.3 and Figure 4.4). All elements were uniformly distributed throughout the specimens with the exception of S (Figure 4.2). For the most part, this heterogeneity appears to be an artefact due to initial specimen shaping (Figure 4.2).
Figure 4.2: Atom probe microscopy (APM) analyses of a typical refractory metal nugget RMN3. A: In-beam secondary electron image of RMN3 after focussed-ion beam (FIB) preparation. Red box indicates where APM data were obtained. B: APM atom cloud of RMN3 indicating distribution of S (blue spheres) against background of Ir (red dots). Each coloured dot represents a single detected atom. C: Vertical concentration profile indicating variation in S concentration through RMN3. Slight S enrichment at apex of RMN3 is understood as a transient artifact due to changes in mass peak tails at start of data acquisition. URI – ultrarefractory inclusion; Pt – platinum.
FIGURE 4.3: Graph detailing composition of refractory metal nuggets RMN1–RMN5. Elements are ordered by increasing volatility; left axis indicates RMN1–RMN5 compositions in at. % and right axis depicts elemental abundance of RMN1–RMN5 normalized to a chondrite (CI: Lodders 2003). Ratios of highly siderophile elements (HSEs: Re, Os, W, Ir Mo, Ru)/CI have a flat trend with no depletions in W and Mo. HSE and S abundances vary between RMNs.
FIGURE 4.4: Typical mass-to-charge state ratio spectrum of 30 – 36 and 90 – 115 Da regions of refractory metal nuggets RMN1. S and SH ions are observed in 30 – 36 Da region and (HSE)-sulfur complexes are observed in between Ru peaks and 105 – 115 Da region.
Table 4.1: Composition of RMN1–RMN5, kan1 and cpx1 measured by atom probe microscopy (with uncertainty of 2σ).

<table>
<thead>
<tr>
<th>APM specimen</th>
<th>Re</th>
<th>Os</th>
<th>W</th>
<th>Ir</th>
<th>Mo</th>
<th>Ru</th>
<th>V</th>
<th>Pt</th>
<th>Rh</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Cr</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMN1</td>
<td>1.28</td>
<td>12.48</td>
<td>2.47</td>
<td>14.65</td>
<td>31.73</td>
<td>15.79</td>
<td>0.17</td>
<td>0.34</td>
<td>0.02</td>
<td>2.66</td>
<td>0.06</td>
<td>17.33</td>
<td>0.03</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>±0.016</td>
<td>±0.048</td>
<td>±0.017</td>
<td>±0.054</td>
<td>±0.079</td>
<td>±0.056</td>
<td>±0.006</td>
<td>±0.009</td>
<td>±0.003</td>
<td>±0.023</td>
<td>±0.004</td>
<td>±0.059</td>
<td>±0.003</td>
<td>±0.008</td>
</tr>
<tr>
<td>RMN2</td>
<td>1.09</td>
<td>11.49</td>
<td>1.99</td>
<td>13.17</td>
<td>31.02</td>
<td>18.43</td>
<td>0.21</td>
<td>0.21</td>
<td>0.01</td>
<td>3.02</td>
<td>0.04</td>
<td>19.16</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>±0.005</td>
<td>±0.017</td>
<td>±0.006</td>
<td>±0.018</td>
<td>±0.028</td>
<td>±0.022</td>
<td>±0.002</td>
<td>±0.003</td>
<td>±0.001</td>
<td>±0.009</td>
<td>±0.001</td>
<td>±0.022</td>
<td>±0.001</td>
<td>±0.001</td>
</tr>
<tr>
<td>RMN3</td>
<td>1.33</td>
<td>13.65</td>
<td>2.68</td>
<td>16.19</td>
<td>29.55</td>
<td>14.03</td>
<td>0.26</td>
<td>0.48</td>
<td>0.03</td>
<td>2.29</td>
<td>0.05</td>
<td>19.40</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>±0.009</td>
<td>±0.027</td>
<td>±0.010</td>
<td>±0.031</td>
<td>±0.041</td>
<td>±0.029</td>
<td>±0.004</td>
<td>±0.006</td>
<td>±0.002</td>
<td>±0.012</td>
<td>±0.002</td>
<td>±0.034</td>
<td>±0.002</td>
<td>±0.001</td>
</tr>
<tr>
<td>RMN4</td>
<td>1.41</td>
<td>13.85</td>
<td>3.13</td>
<td>15.45</td>
<td>22.92</td>
<td>9.01</td>
<td>0.35</td>
<td>0.64</td>
<td>0.07</td>
<td>3.72</td>
<td>0.12</td>
<td>29.06</td>
<td>0.07</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>±0.011</td>
<td>±0.033</td>
<td>±0.011</td>
<td>±0.036</td>
<td>±0.044</td>
<td>±0.028</td>
<td>±0.005</td>
<td>±0.008</td>
<td>±0.003</td>
<td>±0.018</td>
<td>±0.003</td>
<td>±0.050</td>
<td>±0.003</td>
<td>±0.002</td>
</tr>
<tr>
<td>RMN5</td>
<td>0.86</td>
<td>8.67</td>
<td>1.60</td>
<td>10.52</td>
<td>23.73</td>
<td>11.21</td>
<td>0.17</td>
<td>0.12</td>
<td>0.03</td>
<td>5.58</td>
<td>0.19</td>
<td>37.16</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>±0.006</td>
<td>±0.017</td>
<td>±0.007</td>
<td>±0.019</td>
<td>±0.029</td>
<td>±0.020</td>
<td>±0.002</td>
<td>±0.004</td>
<td>±0.002</td>
<td>±0.015</td>
<td>±0.003</td>
<td>±0.036</td>
<td>±0.002</td>
<td>±0.001</td>
</tr>
<tr>
<td>kan1</td>
<td>59.23</td>
<td>16.27</td>
<td>0.40</td>
<td>5.30</td>
<td>5.90</td>
<td>5.87</td>
<td>2.84</td>
<td>3.03</td>
<td>0.26</td>
<td>5.04</td>
<td>0.34</td>
<td>18.63</td>
<td>0.18</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>±0.332</td>
<td>±0.092</td>
<td>±0.008</td>
<td>±0.042</td>
<td>±0.022</td>
<td>±0.037</td>
<td>±0.029</td>
<td>±0.026</td>
<td>±0.016</td>
<td>±0.004</td>
<td>±0.007</td>
<td>±0.017</td>
<td>±0.004</td>
<td>±0.017</td>
</tr>
<tr>
<td>cpx1</td>
<td>60.00</td>
<td>12.31</td>
<td>3.28</td>
<td>15.70</td>
<td>1.29</td>
<td>2.09</td>
<td>0.07</td>
<td>2.89</td>
<td>0.21</td>
<td>3.23</td>
<td>0.05</td>
<td>0.17</td>
<td>0.05</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>±0.728</td>
<td>±0.138</td>
<td>±0.067</td>
<td>±0.184</td>
<td>±0.052</td>
<td>±0.100</td>
<td>±0.019</td>
<td>±0.067</td>
<td>±0.072</td>
<td>±0.015</td>
<td>±0.011</td>
<td>±0.013</td>
<td>±0.008</td>
<td>±0.011</td>
</tr>
</tbody>
</table>

Note: APM—atom probe microscopy; RMN—refractory metal nugget; kan1 and cpx1 are the interior and rim of the ultrarefractory inclusion, respectively.
4.4. DISCUSSION

Some of the minerals within the URI exhibit $120^\circ$ grain boundary intersections (Figure 4.1). These textures are indicative of annealing (Komatsu et al., 2001; Smith, 1948). The rim surrounding the URI also penetrates into the inclusion along grain boundaries, and crystal edges in contact with the rim are rounded, consistent with partial melting (Bulau et al., 1979). This indicates that the URI experienced elevated temperatures after it formed.

RMNs are assumed to be pure metallic alloys (i.e., Daly et al. 2017; Schwander et al. 2015) composed of HSEs with 50% condensation temperatures of 1821 – 1408 K (Lodders, 2003). APM of RMNs revealed this is not always the case; these RMNs contain $0.06 - 1.00$ at. % abundances of S (Table 4.1, and Figure 4.3 and Figure 4.4). Sulfur content in RMN1–RMN5 were variable, but no relationship was observed between the S content and the host mineral, proximity to the edge of the URI, or RMN size.

Sulfidation of metals phases in meteorites is thought to occur either on the parent body (Blum et al., 1989) or in the nebula through exposure to H$_2$S gas, where Fe metal reacts with H$_2$S to produce sulfides such as troilite (Lauretta et al., 1996). ALH 77307 CO3.0 is one of the most primitive meteorites (Grossman and Brearley, 2005), so parent-body alteration is unlikely; sulfidation of these RMNs likely occurred in the nebula.

Sulfur is volatile with a 50% condensation temperature of 664 K (Lodders, 2003); the 50% condensation temperature of HSEs is $\sim 1000$ K higher than S (Lodders, 2003). The presence of S in RMNs is inconsistent with our current understanding of RMN formation, which requires high temperatures that prohibit the condensation of S (Berg et al., 2009). There is also a spatial inconsistency be-
cause RMNs, CAIs and URIs are expected to form close to a proto-sun (<0.5 AU; MacPherson et al. 2005), where temperatures are high (Ciesla, 2009), whereas Fe-sulfidation is thought to occur rapidly (<1000 yr), early in nebular evolution, and at low temperatures (~ 500 – 700 K) between 0.5 and 1.5 AU (Lauretta et al., 1996; Ciesla, 2015).

Disk mechanics are capable of transporting grains to the outer portions of the disk (Shu et al., 1997; Ciesla, 2007; Bai, 2014) over short timescales, i.e., $10^5$ yr (Ciesla, 2010). This could emplace the URI into the region of the disk where sulfidation is predicted to occur (0.5 – 1.5 AU; Ciesla 2015). However, the URI did not exhibit the expected textures and mineralogy associated with sulfidation, such as silicate enrichment in Fe, Mn, and Na, and depletion in Mg, with associated abundant sulfide phases such as niningherite and oldhamite (Lehner et al., 2013). The RMNs are euhedral (Appendix 3E), have no relationship between S abundance and the location of the RMNs within the URI and did not exhibit depletions in Mo and W (Figure 4.3), which are readily mobilized under oxidizing conditions (Fegley and Palme, 1985). Therefore, it is unlikely that the RMNs were sulfidized within the URI.

The S-bearing RMNs here were most likely exposed to an S-condensing gas while ‘free floating’ in the nebula prior to incorporation into the URI. This requires outward migration of RMNs to colder regions of the disk (0.5 – 1.5 AU; Ciesla 2015) to incorporate S, followed by inward migration back to the CAI-forming region to be incorporated into the URI. Heterogeneous distribution of S between RMNs implies that incorporation into and partial melting of the URI did not overprint this primary composition and may provide further evidence for migration; each migrating RMN may follow a different path and incorporate more or less S as a consequence.
Disk models suggest even small 5 µm particles could be delivered to the region where sulfidation is predicted to occur (0.5 – 1.5 AU; Ciesla 2015), over ~ $10^5$ yr (Ciesla, 2009). These sulfidized RMNs would then be radially transported back towards the protosun. This is possible through turbulent mixing of particles or gas-drag migration (Cuzzi and Weidenschilling, 2006). If these time scales are reasonable, dust particles may experience several cycles of outward and inward migration during disk evolution. However, such efficient mixing would also result in the migration of primordial dust from the outer portions of the disk (Brownlee, 1994) into the CAI-forming region, which would become entrained in CAIs. This is inconsistent with CAI mineralogy, which is refractory in nature (MacPherson et al., 2005). Therefore, any mechanism for particle migration within the disk may include an early period or region where only refractory materials are cycling from their formation region into, and out of, an environment that permits the incorporation of S into RMNs. This requires a barrier to particle migration from the outer portions of the disk. Alternatively, H$_2$S was likely present in the gas in the CAI-forming region (Antonelli et al., 2014), and the HSE component of RNs may permit a small amount of S to be incorporated into RMNs at higher temperatures than for pure Fe, negating the need for particle migration. However, this interpretation requires all RMNs to be S-bearing, which is inconsistent with all prior RMN analyses.

The presence of S in RMNs, as revealed here by APM, indicates that some RMNs spend a significant period ‘free floating’ in the nebula prior to incorporation in inclusions. They may also migrate rapidly early in the disk’s lifetime and be exposed to an environment that permits the incorporation of S before returning to the CAI-forming region to be incorporated in a URI.
4.5. CONCLUSIONS

Atom probe microscopy provides the resolution and dynamic range required for geochemical analysis of primitive submicrometer grains in meteorites. The high sensitivity of APM allows us to accurately analyse the bulk- and trace-element composition of grains that are too small for conventional techniques. APM has revealed trace abundances of S within RMNs, which indicates that some RMNs reacted with an S gas prior to incorporation into their host URI while they were ‘free floating’. This requires either a high-temperature H$_2$S-RMN reaction in the CAI-forming region or rapid, early migration of RMNs to cooler regions of the disk followed by inward migration back to the CAI-forming region for incorporation into the URI.

The results from this study reveal that APM analyses of primordial dust grains provide information regarding the spatial and temporal temperature and chemical variations in a protoplanetary disk. APM represents a new tool in the analysis of sub-micrometer grains in meteorites to extract information pertaining to the evolution of the disk from every grain in meteorites. APM can therefore assist in the calibration of disk evolution models.

4.6. ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council via their Australian Laureate Fellowship program to Bland. This work was conducted within the Geoscience Atom Probe Facility at Curtin University, Perth, Australia, which is part of the Advanced Resource Characterization Facility (ARCF). The ARCF is being developed under the auspices of the National Resource Sciences Precinct
– a collaboration between the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Curtin University, and The University of Western Australia – and it is supported by the Science and Industry Endowment Fund (SIEF RI13 – 01). We acknowledge the use of Curtin University’s Microscopy and Microanalysis Facility, for which instrumentation has been partially funded by Curtin University, state and commonwealth governments. Reddy acknowledges support from the Australian Research Council Centre of Excellence for Core to Crust Fluid Systems (CE11E0070). We also thank Porter as well as three anonymous reviewers, and editor J. Totman Parrish.

4.7. Supplementary Material for Chapter 4

4.7.1. Supplementary Material A

The sample was hand polished using 0.01 µm colloidal silica in a NaOH solution for 30 minutes to reduce the potential of polishing away the inclusions while still achieving sufficient polish for EBSD analysis. The sample was coated with 10 nm of carbon. The inclusion was characterised using EBSD and EDS on the TESCAN MIRA VP-FESEM, at the John de Laeter Centre, Curtin University. The sample was tilted to 70° and an accelerating voltage of 30 kV was used. EDS spectra were collected using an X-Max 150 mm² Silicon Drift detector and a process time of 5 selected from the AZtec software was used. EBSD patterns were collected using a Nordlys Nano high resolution detector with a step size of 0.13 µm. The data were interpreted using the Oxford Instruments AZtec 3.0 and Channel 5 software packages.
4.7.2. Supplementary Material B

The samples were prepared from ALH 77307 using the TESCAN LYRA 3 FIB-SEM at the Advanced Resource Characterisation Facility (ARCF), John de Laeter Centre, Curtin University. The FIB was operated with an accelerating voltage of 30 kV. The methodology used here has been previously described in detail (Thompson et al., 2007), however, we have adapted it slightly. The following is therefore a brief explanation of the specific additions we made to the targeting and lift-out procedure. To improve the targeting of sub-micron crystals, a small (50 nm diameter) ‘button’ (topographical feature) of Pt was initially deposited with the SEM electron beam over the target grain. This was followed by the ion beam deposition of a larger (2.5 x 10 µm) protective layer of Pt. The Pt button was still visible after the deposition of the protective layer, indicating the location of the region of interest (Figure 4B.1). The material located underneath the Pt layer was then milled using the FIB to form a wedge ~ 10 x 2.5 x 2.5 µm each on 3 sides. The wedge was then attached to a Smartact nanomanipulator by a small Pt weld and cut free from the sample. Portions (2.5 x 2.5 µm) of the wedge were then attached with Pt to prefabricated Si posts on a 22 post Si coupon wafer from Cameca Instruments. The wedge segments were then milled into a needle shape using annular masks until the tip of the sample was ~ 100 nm in diameter with a ~ 5° half shank angle. The Pt button bulging under the protective layer was used to guide the position of the annular masks and thus allows the accurate targeting of the RMN which was usually <<0.5 µm. Finally a 5 kV accelerating voltage annular milling routine was used to remove the damaged/Ga implanted layer.
Figure 4B.1: Images indicating how the refractory metal nugget (RMN) analysed in this study was prepared for lift out using the FIB. A) BSE image of the RMN (bright phase). B) Pt is deposited using the gas-injection system (GIS) in a small button over the RMN using the electron beam. C) A thicker layer of Pt is deposited with the GIS in a 2 x 7 µm rectangle using the Ga⁺ beam.

4.7.3. Supplementary material C

Atom probe microscopy can determine the chemical composition, as well as any compositional heterogeneity at the sub-nanometre scale, in 3 dimensions within a small volume, up to 1 µm in size. Atom probe microscopes employing a pulsed laser have allowed analysis of non-conducting materials, and have recently been applied to geological samples; including zircons (Valley et al., 2014; Reddy et al., 2016; Peterman et al., 2016; Piazolo et al., 2016), sulphides (Fougerouse et al., 2016), carbonates and barite (Pérez-Huerta et al., 2016; Weber et al., 2016). The local electrode atom probe (LEAP), used in this study has been described in detail (Kelly and Larson, 2012; Gault et al., 2012).

The Cameca LEAP 4000X HR Geoscience Atom Probe (GAP), Curtin University, is currently the only atom probe facility established for dedicated analysis of geological materials. Laser energy, pulse rate, specimen temperation and evaporation rate parameters are detailed in Table 4C.1.
TABLE 4C.1: Operating conditions of the Geoscience Atom Probe at Curtin University for atom probe samples RMN1 through RMN5, kan1 and cpx1, where hits relate to the number of ionic species detected during the analyses, T relates to the temperature the specimen was held at in K, Laser E is the energy of the pulsing laser in pJ, pulse frequency is the number of laser pulses per minute given in kHz, and the DR % is the detection rate of laser pulses that result in the field emission of an ion leading to a detection event as a percentage.

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Hits</th>
<th>T (K)</th>
<th>Laser E (pJ)</th>
<th>Pulse Frequency (kHz)</th>
<th>DR %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMN1</td>
<td>2,400,000</td>
<td>80</td>
<td>250</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>RMN2</td>
<td>17,000,000</td>
<td>60</td>
<td>300</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>RMN3</td>
<td>8,000,000</td>
<td>60</td>
<td>300</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>RMN4</td>
<td>5,600,000</td>
<td>60</td>
<td>300</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>RMN5</td>
<td>14,700,000</td>
<td>70</td>
<td>300</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>kan1</td>
<td>7,300,000</td>
<td>60</td>
<td>300</td>
<td>200</td>
<td>0.5</td>
</tr>
<tr>
<td>cpx1</td>
<td>600,000</td>
<td>60</td>
<td>300</td>
<td>125</td>
<td>0.5</td>
</tr>
</tbody>
</table>

4.7.4. SUPPLEMENTARY MATERIAL D

The resulting mass to charge state ratio spectrum produced by each sample must be individually evaluated due to the detection of not only individual ions but also molecular ions, particularly oxides in the case of kan1 and opx1 and sulphide complexes in the case of RMN1 – 5. The spectra were all binned to 0.01 Da. Individual peaks were ranged using the IVAS software package. Peaks were ranged from the position of initial increase above the background level to the point where the peak returns to the background level. RMN1 – 5 contained S peaks and also HSE-sulphur complexes (Figure 4.4). EDS measurements of the region were used to inform the spectrum ranging. cpx7 was known from EDS and EBSD to have a clinopyroxene structure. However, significantly more O was detected than is possible in the clinopyroxene structure. The difficulty of accurately quantifying O has been reported elsewhere in the atom probe literature (Gault et al., 2016; Karahka et al., 2015; Pérez-Huerta et al., 2016). Therefore, the bulk composition was renormalised to the oxygen stoichiometry.
of clinopyroxene based on the EBSD data. Uncertainty in the at. % totals for each element was calculated as two standard deviations ($\sigma$) where:

$$\sigma = \sqrt{A + B} \quad (\text{Larson et al., 2013})$$ (4.1)

$A$ is the total ions detected and $B$ is the total background.

### 4.7.5. Supplementary Material E

![Figure 4E.1: A-G) In-beam secondary electron images of the final atom probe tips of RMN1 – 5, kan1 and cpx1 respectively, the red box indicates the region that atom probe data was acquired from the tip. URI = ultra-refractory inclusion, cpx = clinopyroxene. H) In-beam secondary electron images of the final atom probe tip of RMN6 that did not run in the atom probe but reveals the euhedral crystal habit typical of these RMNs.](image)

### 4.8. References


CHAPTER 5

PAPER 4 – ISOTOPIC ANALYSIS OF
REFRACTORY METAL NUGGETS USING
ATOM PROBE MICROSCOPY

Luke Daly\textsuperscript{a}, Philip A. Bland\textsuperscript{a}, Svetlana Tessalina\textsuperscript{c}, David W. Saxey\textsuperscript{b}, Steven M. Reddy\textsuperscript{ab}, Denis Fougerouse\textsuperscript{ab}, William D. A. Rickard\textsuperscript{b}, and Lucy V. Forman\textsuperscript{a}, Patrick W. Trimby\textsuperscript{d}, Limei Yang\textsuperscript{d}, Alex, La Fontaine\textsuperscript{d}, Julie Cairney\textsuperscript{d}, Simon P. Ringer\textsuperscript{e}, and Bruce F. Schaefer\textsuperscript{f}

\textsuperscript{a}Department of Applied Geology, Curtin University, GPO Box U1987, Bentley, Perth, WA 6845, Australia

\textsuperscript{b}Geoscience Atom Probe, Advanced Resource Characterisation Facility, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA, Australia.

\textsuperscript{c}John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA, Australia.
dAustralian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW 2006, Australia.

eAustralian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW, 2006, Australia.

fDepartment of Earth and Planetary Sciences, Macquarie University NSW, 2109, Australia.

This article is in preparation for publication.
ABSTRACT

Atom probe microscopy (APM) has the potential to extract isotopic information from nano-materials which cannot be analysed by other techniques. However, constraints on the sensitivity and precision of isotopic measurements with APM have not been quantified, and a robust methodology for data reduction has not been established.

To rectify this the theoretical sensitivity of the APM technique to measure isotopic ratios based on counting statistics of a hypothetical dataset of $>10^6$ atoms is calculated as $\pm 40\epsilon$ (0.5 %). Isotopic information from pure Os and Re metals was used to evaluate data reduction techniques in order to produce a robust data reduction methodology. APM can reproduce isotopic abundances of Re and Os which are consistent with measurements obtained using thermal ionisation mass spectrometry (TIMS). Applying this methodology to a synthetic multi-element alloy, comparable in composition to an average RMN we were able to extract Re and Os isotopic abundances consistent with those obtained with TIMS. In particular, $^{187}$Os/$^{188}$Os measurements for both the pure and complex alloys were accurate within the calculated uncertainty. We determined that our current methodology allows us to constrain the relative isotopic abundances for Os and Re to within 1 %.

We applied this technique to refractory metal nuggets (RMNs) in primitive carbonaceous chondrite meteorites to obtain isotopic information in order to test the hypothesis that some RMNs had a pre-solar origin. The 1 % relative uncertainty of our current approach could distinguish an s-process pre-solar grain but is insufficient to distinguish an r-process pre-solar nucleosynthetic anomaly from solar isotopic abundances for Re and Os and further work is
required to hone these analyses. However, variations in radiogenic $^{187}$Os can be detected and the good agreement of $^{187}$Os/$^{189}$Os ratios obtained using both TIMS and APM measurements serves as confirmation that APM can extract robust isotopic abundances to calculate accurate model ages from the Re-Os system.

Calculated model ages obtained from the RMNs revealed that seven grains plot on the Solar System $^{187}$Os/$^{189}$Os $^{187}$Re/$^{189}$Os isochron. This suggests the grains were equilibrated during the formation of the Solar System. However, one RMN exhibits an anomaly in $^{187}$Os/$^{189}$Os. While we cannot categorically rule out an unknown artefact in the APM datasets, previous APM analyses of standard materials indicate that this anomaly is real suggesting this RMN grains may have formed in a pre-solar environment.

The anomalous RMN exhibits an $^{187}$Os/$^{185}$Os ratio which is lower than the initial value of the Solar System. Re depletion and model ages indicate that this RMN has a minimum age of 5.5 Ga (Re-depletion model age: $7.9 \pm 2.3$ Ga) and is likely to be older assuming the galactic evolution of Re-Os is comparable to chondritic. This RMN is therefore the oldest material dated so far, and is demonstrably pre-solar. This RMN also provides evidence for a granular level heterogeneities in Os that did not equilibrate with the protoplanetary disk.

5.1. INTRODUCTION

Refractory metal nuggets (RMNs) are a sub-micrometre metal alloy found in primitive carbonaceous chondrite meteorites and are composed of highly siderophile elements (HSEs) (Berg et al., 2009; Schwander et al., 2015b; Wark and Lovering, 1976; Palme and Wlotzka, 1976). Although most RMNs are
likely to have formed, or were affected by processes in the protoplanetary disk (Daly et al., 2017) (Chapter 2 and Chapter 3), some may have a pre-solar origin (El Goresy et al., 1978, 1977; Daly et al., 2017). RMNs have also been observed in demonstrably pre-solar graphite (Croat et al., 2013) and may have formed through condensation in the circumstellar environment around asymptotic giant branch (AGB) star (Schwander et al., 2014). However, to demonstrate a grain is pre-solar, isotopic anomalies must be observed which are different to solar isotopic abundances and are consistent with a nucleosynthetic process (Anders and Zinner, 1993; Bernatowicz et al., 2006; Meyer and Zinner, 2006).

The Big Bang produced the universe’s quota of H, He + trace Li Be and B (Meyer and Zinner, 2006). All elements heavier than these were synthesised subsequently. Hoyle (1946) proposed the location for nucleosynthesis of the heavy elements to be inside stars. This was confirmed by observations of short lived radionuclide of Tc within S-stars (Merrill, 1952). The seminal paper of Burbidge et al. (1957) commonly known as B2FH, as well as Hoyle (1954) and Cameron (1957) laid the foundation for the mechanics of stellar nucleosynthesis for the elements. Elements heavier than Fe are formed by neutron capture through the r-process (rapid neutron capture) and the s-process (slow neutron capture) (Burbidge et al., 1957; Meyer and Zinner, 2006). The s-process is thought to occur in He shell of AGB stars where neutron flux is low compared to $\beta$ decay which allows unstable isotopes to decay between neutron captures (Meyer and Zinner, 2006). The s-process isotopes are mixed up into the outer layers of the star during the third dredge up (Meyer and Zinner, 2006). Conversely the r-process forms heavier nuclei where neutron flux is much greater than the $\beta$ decay rate, which rapidly builds up heavy nuclei (Meyer and Zinner, 2006). A stellar source for the r-process is likely to be in supernova explosions however, this has yet to be conclusively observed (Meyer and Zinner, 2006). Observations
of old metal poor stars reveal that they have r-process abundances consistent with the Solar System indicating that r-process may dominate the s-process in the early galaxy (Sneden et al., 1996). Enrichments and depletions or r- and s-process isotopes are observed in pre-solar grains in meteorites (Meyer and Zinner, 2006; Bernatowicz et al., 2006; Anders and Zinner, 1993; Zinner, 1998; Hoppe and Zinner, 2000; Nittler, 2003; Clayton and Nittler, 2004). These isotopic trends are likely to be observed in any pre-solar RMNs.

The small size of RMNs has precluded isotopic analysis and only four RMNs have been measured to date. Two RMNs were analysed by Berg et al. (2009) using secondary ion mass spectrometry (SIMS), which revealed solar $^{189}$Os/$^{192}$Os and $^{190}$Os/$^{192}$Os isotopic ratios. However, the sensitivity of the measurement was insufficient to distinguish solar isotopic proportions from r-process nucleosynthesis (Berg et al., 2009). Similarly, isotopic analysis of opaque assemblages and an RMN by Hutcheon et al. (1987) did not detect isotopic anomalies consistent with a pre-solar origin - the isotopic abundances were consistent with solar abundances. Isotopic analysis of Ru on a bulk RMN sample by Fischer-Gödde et al. (2014) revealed small r-process depletions but these were too small to be consistent with stellar nucleosynthesis. These few isotopic studies imply that RMNs originate in the Solar System, however, the analytical sensitivity of the techniques used by these authors were not sufficient to conclusively rule out an r-process nucleosynthetic site ($\pm 1\%$ Berg et al. 2009), though a Solar origin is still the most likely interpretation. Further isotopic analyses of several more RMNs should be undertaken to evaluate the possibility that some RMNs have a pre-solar origin.

Atom probe microscopy (APM) is a high-resolution technique capable of analysing small cylindrical volumes (up to approximately 100 x 100 x 1000 nm) with a spatial resolution of 0.3 nm in three dimensions (Kelly and Larson,
APM can also determine the chemical composition of a sample and nanometre scale heterogeneities within (Kelly and Larson, 2012). APM has a high sensitivity and can detect trace abundances of elements down to the 10 ppm level for sample volumes over $10^6$ nm$^3$ (Kelly and Larson, 2012). Therefore, APM can provide the sensitivity required for accurate isotopic analysis of RMNs.

Data collected by APM record the mass to charge state ratio ($m/q$) of individual atoms (Kelly, 2011). The mass resolving power ($m/\Delta m$ where $m$ is mass and $\Delta m$ is the variation in mass between atoms) of the atom probe is better than 200 (Kelly, 2011). Therefore, APM is capable of discerning peaks separated by 0.15 daltons (Da) (Kelly, 2011). This is sufficient to discern isotopic peaks from ions of different charge states (i.e. $^{94}$Mo$^{+++}$ and $^{63}$Cr$^{++}$), but is currently insufficient to determine the mass difference between ions that have the same mass (i.e. $^{54}$Cr$^{++}$ and $^{54}$Fe$^{++}$) (Kelly, 2011). $^{54}$Cr$^{++}$ and $^{54}$Fe$^{++}$ have a difference in mass of 0.0005 Da which requires a mass resolving power $>1.5\times10^5$ (Kelly, 2011) to distinguish these ionic species. These isobaric interferences are beyond the mass resolving power of any technique currently available (Kelly, 2011) and require peak deconvolution calculations to estimate the contribution of each isotope to the total peak.

The mass resolving power of APM suggests that isotopic analysis of most materials is possible. Several papers have reported isotopic abundances using APM (i.e. Thuvander et al. 2011; Mukherjee et al. 2015, 2016; Shimizu et al. 2013 and Shimizu et al. 2009), but only a few have attempted to demonstrate that these abundances are quantitative (i.e. Valley et al. 2014; Parman et al. 2015; Stadermann et al. 2011 and Heck et al. 2014).

Valley et al. (2014) reported Pb isotopic abundances extracted from a Hadean
zircon. Valley et al. (2014) demonstrated that the $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic abundances measured using APM recorded an age consistent with measurements of the same zircon using secondary ion mass spectrometry (SIMS). This suggests that isotopic analysis with APM is possible and capable of reliably reproducing the results of other more established high precision techniques.

Stadermann et al. (2011) and Heck et al. (2014) reported APM data for C isotopic ratios for nanodiamonds within meteorites, which indicate that the $^{12}\text{C}/^{13}\text{C}$ ratio is anomalous relative to Solar System $^{12}\text{C}/^{13}\text{C}$ ratios. However, these anomalous isotopic ratios may instead reflect contributions of $^{12}\text{C}$-hydrides to the $^{13}\text{C}$ peak (Stadermann et al., 2011; Heck et al., 2014) and possible under-representation of the $^{12}\text{C}$ peak due to molecular ion formation and detector dead times (Thuvander et al., 2011). Further work is required to validate these ratios. If these data can be corrected robustly for C-H molecules, APM can resolve isotopic variations with sufficient accuracy to determine if any nano-diamonds in meteorites have a pre-solar origin (Stadermann et al., 2011).

Parman et al. (2015) demonstrated that isotopic abundances of a NIST standard of isoferroplatinum Pt$_3$Fe, can be reproduced using APM. Of 25 isotopic abundances of Pt, Fe, Ir, Ni, Cu, and Ru measured in Parman et al. (2015) 20 were within 5 % of the NIST values (Parman et al., 2015). The isotope abundances which were >5 % of the NIST values contained isotopes that had extremely low abundances, <0.1 wt. % i.e. $^{190}\text{Pt}$ (Parman et al., 2015). The level of accuracy presented in Parman et al. (2015), using only minor corrections due to hydride formation, suggests that further evaluation of the methodology will serve to improve the accuracy of isotopic abundances measured using APM.

Field evaporation during APM analysis is ideal for isotopic analysis as the whole sample is ionised, and it is assumed that there is no bias in the detection
of elements or between isotopes; i.e., all species are ionised and detected equally (Kingham, 1982; Straub et al., 1999). However, unique factors in each analysis, such as voltage, tip shape and temperature are not constant between analyses and their effect on the resulting mass spectrum is not quantified and potentially not quantifiable (Parman et al., 2015; Reddy et al., 2016). Furthermore, the benefit of APM is its ability to analyse samples, such as RMNs, that are prohibitively small for other techniques. Consequently, results are difficult to corroborate across differing analytical techniques. However, it is possible to assess whether the APM analytical protocols that are applied to RMNs are robust, by comparing APM analysis of standard materials such as pure elements and alloys with similar compositions to the unknown material, that are large enough to be corroborated by other techniques.

This study will build on the work of Parman et al. (2015) to quantify the isotopic resolution possible with APM and evaluate and correct any sources of uncertainty. Here we analyse large >1 mm alloys of standard material using APM to calculate the isotopic relative abundances which can be confirmed by thermal ionisation mass spectrometry (TIMS). The samples included simple, single element alloys through to complex multi-HSE alloys with comparable compositions to average RMNs (Schwander et al., 2015a). These APM analyses will be used to devise a methodology to reliably reproduce isotopic abundances of known samples. This methodology will then be applied to RMNs analyses.
5.2. METHODS

5.2.1. SAMPLES

The standard reference materials analysed in this study were a pure Re wire, a pure Os wafer, and a synthetic multi-HSE alloy with a composition consistent with an average RMN from Schwander et al. (2015a) (Figure 5.1). Three further RMNs were extracted (RMN7 through RMN9). RMN7 was extracted from an perovskite-diopside-rich region of an amoeboid olivine aggregate (AOA) from the Allende CV3 meteorite (Figure 5.2). RMN8 was extracted from the davisite rim (Ma and Rossman, 2009) around an ultra-refractory inclusion comprised of spinel, and panguite (Ma et al., 2012) from the Murchison CM2 meteorite (Figure 5.3). RMN9 was extracted from a pentlandite and apatite rich rim around a porphyritic olivine (PO) chondrule in the Allende CV3 meteorite (Figure 5.4). These RMNs were identified using the methodology detailed in Chapter 2. These RMNs were added to the APM datasets RMN1 through RMN5, already collected from ALH 77307 CO3.0 in Chapter 4.

5.2.2. SAMPLE PREPARATION

Initially a piece of the standard materials listed in Section 5.1.2 were removed from the main mass for TIMS analysis. APM specimens were prepared from the remaining Re wire (Re1 and Re2), Os wafer (Os1) (Figure 5.5), and multi-HSE alloy (HSE1 and HSE2) (Figure 5.6) using a focussed-ion beam (FIB). The methodology is described in Chapter 4.

RMN7 through RMN9 (Figure 5.2, 5.3 and 5.4) were prepared for APM on
Figure 5.1: Backscattered electron (BSE) images of the standard samples A) Pure Os wafer. B) Zoom in of APT lift out site (blue box) C) Pure Re wire. D) Zoom in APM lift out site of Re wire (blue box). E) Multi-HSE alloy from Schwander et al. (2015b). F) A Higher magnification image of the multi-HSE alloy.
Figure 5.2: Images RMN7 and its wider context within the Allende CV3 meteorite. AOA=amoeboid olivine aggregate, Di=diopside, Fo=forsterite, Ilm=ilmenite, Mag=magnetite, Prv=perovskite and RMN=refractory metal nugget. A) A BSE image of the wider context of the AOA in the Allende CV3 meteorite. The yellow box indicates the field of view of image B). B) BSE image of the AOA containing RMN7 (red circle) and associated ilmenite, magnetite and perovskite encapsulated in diopside which is in turn encapsulated in forsterite. C) Close up BSE image of RMN7 indicating it is polyphase with a euhedral portion from which RMN7 was extracted and an associated complex texture which may be related to exsolution. D) In-beam secondary electron images of the final polished APM RMN7. The red box indicates the region sampled during APM. E) Atom cloud of RMN7, each sphere represents a single detected atom. Distributions of Os (red) and Re (blue).
Figure 5.3: Images RMN8 and its wider context within the Murchison CM2 meteorite. URI=ultra-refractory inclusion, Spl=spinel, Dav=davisite clinopyroxene (Ma and Rossman, 2009) Pan=panguite (Ma et al., 2012), and RMN=refractory metal nugget. A) A BSE image of the wider context of the ultra-refractory inclusion within the Murchison CM2 meteorite. The red box represents the area of image B). B) BSE image of the ultra-refractory inclusion containing RMNs, RMN8 was extracted from the davisite rim of the inclusion (red circle). C) In-beam secondary electron images of the final polished APM tip for RMN8. The red box indicates the area sampled during APM. D) Atom cloud of RMN8, each sphere represents a single detected atom. Distributions of Os (red) and Re (blue).
FIGURE 5.4: Images of RMN9 and its wider context within the Allende CV3 meteorite. Pn=pentlandite, Ol=olivine, Ap=apatite, RMN=refractory metal nugget. A) A BSE image of the wider context of the chondrule from which RMN9 was extracted within the Allende CV3 section indicating the chondrule which hosted RMN9 is attached to a much larger sulphide rich chondrule. B) A BSE image of the porphyritic olivine chondrule and associated sulphide-, apatite-rich rim from which RMN9 was extracted. C) close up BSE image of the pentlandite-apatite-olivine-rich rim, with RMN9 clearly visible encapsulated with pentlandite. D) In-beam secondary electron images of the final polished APM RMN9. The red box indicates the area sampled during APM E) Atom cloud of RMN9, each sphere represents a single detected atom. Distributions of Os (red) and Re (blue).
the Zeiss Auriga FIB at the Australian Centre for Microscopy and Microanalysis, at The University of Sydney, using the same methodology detailed in Chapter 4. These supplemented the APM samples RMN1 through RMN5 already extracted from ALH 77307 CO3.0 in Chapter 4 (Figure 5.7). Their bulk chemistry as well as the compositions of HSE1 and HSE2 are detailed in Table 5.1.

<table>
<thead>
<tr>
<th>APM sample</th>
<th>Re</th>
<th>Os</th>
<th>W</th>
<th>Ir</th>
<th>Mo</th>
<th>Ru</th>
<th>V</th>
<th>At. % abundance</th>
<th>Pr</th>
<th>Rh</th>
<th>Ru</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSE1</td>
<td>3.004 ± 0.009</td>
<td>9.660 ± 0.014</td>
<td>7.643 ± 0.014</td>
<td>8.211 ± 0.015</td>
<td>7.455 ± 0.014</td>
<td>25.956 ± 0.025</td>
<td>2.020 ± 0.006</td>
<td>7.296 ± 0.001</td>
<td>0.002 ± 0.001</td>
<td>13.624 ± 0.019</td>
<td>± 0.004 ± 0.004</td>
<td></td>
</tr>
<tr>
<td>HSE2</td>
<td>2.569 ± 0.007</td>
<td>9.563 ± 0.013</td>
<td>7.376 ± 0.012</td>
<td>8.198 ± 0.012</td>
<td>29.003 ± 0.023</td>
<td>23.675 ± 0.023</td>
<td>2.166 ± 0.007</td>
<td>7.196 ± 0.001</td>
<td>0.002 ± 0.001</td>
<td>13.647 ± 0.003</td>
<td>± 0.008 ± 0.008</td>
<td></td>
</tr>
<tr>
<td>RMN1</td>
<td>1.279 ± 0.016</td>
<td>12.484 ± 0.048</td>
<td>2.473 ± 0.017</td>
<td>14.666 ± 0.054</td>
<td>31.730 ± 0.079</td>
<td>31.789 ± 0.066</td>
<td>0.168 ± 0.006</td>
<td>0.009 ± 0.001</td>
<td>0.006 ± 0.001</td>
<td>0.003 ± 0.001</td>
<td>± 0.016 ± 0.077</td>
<td></td>
</tr>
<tr>
<td>RMN2</td>
<td>1.406 ± 0.011</td>
<td>13.161 ± 0.033</td>
<td>3.022 ± 0.011</td>
<td>15.421 ± 0.036</td>
<td>22.915 ± 0.044</td>
<td>22.915 ± 0.050</td>
<td>0.156 ± 0.006</td>
<td>0.009 ± 0.001</td>
<td>0.003 ± 0.001</td>
<td>0.003 ± 0.001</td>
<td>± 0.003 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>RMN3</td>
<td>1.330 ± 0.009</td>
<td>13.645 ± 0.027</td>
<td>2.679 ± 0.010</td>
<td>16.187 ± 0.031</td>
<td>29.547 ± 0.046</td>
<td>14.034 ± 0.026</td>
<td>0.477 ± 0.027</td>
<td>0.029 ± 0.001</td>
<td>0.040 ± 0.001</td>
<td>0.022 ± 0.001</td>
<td>± 0.017 ± 0.047</td>
<td></td>
</tr>
<tr>
<td>RMN4</td>
<td>1.092 ± 0.005</td>
<td>11.491 ± 0.017</td>
<td>1.986 ± 0.013</td>
<td>13.166 ± 0.018</td>
<td>31.619 ± 0.018</td>
<td>18.481 ± 0.022</td>
<td>0.213 ± 0.027</td>
<td>0.010 ± 0.001</td>
<td>0.024 ± 0.001</td>
<td>0.042 ± 0.012</td>
<td>± 0.001 ± 0.121</td>
<td></td>
</tr>
<tr>
<td>RMN5</td>
<td>0.859 ± 0.005</td>
<td>8.671 ± 0.017</td>
<td>1.597 ± 0.019</td>
<td>10.523 ± 0.019</td>
<td>23.730 ± 0.020</td>
<td>11.215 ± 0.024</td>
<td>0.110 ± 0.023</td>
<td>0.018 ± 0.001</td>
<td>0.029 ± 0.001</td>
<td>0.034 ± 0.001</td>
<td>± 0.010 ± 0.062</td>
<td></td>
</tr>
<tr>
<td>RMN6</td>
<td>2.259 ± 0.027</td>
<td>22.922 ± 0.062</td>
<td>4.023 ± 0.037</td>
<td>11.489 ± 0.059</td>
<td>27.854 ± 0.069</td>
<td>12.174 ± 0.066</td>
<td>0.147 ± 0.014</td>
<td>0.004 ± 0.001</td>
<td>0.018 ± 0.001</td>
<td>0.030 ± 0.001</td>
<td>± 0.010 ± 0.035</td>
<td></td>
</tr>
<tr>
<td>RMN7</td>
<td>0.865 ± 0.010</td>
<td>8.136 ± 0.028</td>
<td>2.267 ± 0.041</td>
<td>12.327 ± 0.041</td>
<td>18.268 ± 0.044</td>
<td>6.752 ± 0.074</td>
<td>0.064 ± 0.014</td>
<td>0.008 ± 0.001</td>
<td>0.021 ± 0.001</td>
<td>0.046 ± 0.001</td>
<td>± 0.011 ± 0.046</td>
<td></td>
</tr>
<tr>
<td>RMN8</td>
<td>0.023 ± 0.001</td>
<td>0.544 ± 0.007</td>
<td>0.186 ± 0.012</td>
<td>6.426 ± 0.018</td>
<td>5.842 ± 0.020</td>
<td>35.866 ± 0.001</td>
<td>49.657 ± 0.000</td>
<td>0.088 ± 0.006</td>
<td>0.065 ± 0.001</td>
<td>± 0.002 ± 0.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: Composition of RMN1 – 5 and RMN7 – 9 and HSE1 – 2 measured by atom probe microscopy in at. % (with uncertainty of 2σ)

5.2.3. Atom probe microscopy (APM)

APM specimens Os1, Re1, Re2, HSE1, HSE2 and RMNs1 through RMN5 were analysed in the Geoscience Atom Probe, at the Advanced Resource Characterisation Facility housed at the John de Laeter Centre, Curtin University, by holding the sample at high voltage and firing a high frequency ultra-violet laser at the apex of the specimen to facilitate field evaporation of a single atom. The operating conditions and counts measured are detailed in Table 5.2.

The APM samples RMN7 – 9 from Allende CV3 were analysed on the Cameca LEAP 4000X Si at the Australian Centre for Microscopy and Microanalysis, The University of Sydney. The operating conditions and total counts measured are detailed in Table 5.3.
Figure 5.5: A-C) In-beam secondary electron images of the final polished APM specimens from the Re wire (Re₁ and Re₂), and the Os wafer (Os₁), respectively. The red boxes indicate the regions sampled by APM. D-E) Atom clouds of the APM data from specimens Re₁ and Re₂, respectively. The distribution of $^{185}\text{Re}$ is shown by the red spheres and $^{187}\text{Re}$ is shown by the green spheres. F) Atom cloud of the APM data from specimen Os₁. The distribution of $^{187}\text{Os}$ is shown by the red spheres and $^{189}\text{Os}$ is shown by the green spheres.
Figure 5.6: A-B) In-beam secondary electron images of the final polished APM specimens from the multi-HSE alloy (HSE1 and HSE2) respectively. The red boxes indicate the regions sampled by APM. C-D) Atom clouds of the APM data from specimens HSE1 and HSE2, respectively. Distributions of Os is shown by the red spheres and Re is shown by the blue spheres.
FIGURE 5.7: A-E) In-beam secondary electron images of the final polished APM specimens from RMN1 through RMN5 respectively. The red boxes indicate the regions sampled by APM. F-J) Atom clouds of the APM data from the specimens from RMNs1 – 5 respectively. Distributions of Os are shown by the red spheres and Re is shown by the blue spheres. Adapted from Chapter 4.
**TABLE 5.2:** Operating conditions of the Geoscience Atom Probe at Curtin University for reference material Os1, Re1, Re2, HSE1 and HSE2, where hits relate to the number of ion detections during the analyses, T relates to the temperature the specimen was held at in K, Laser E is the energy of the pulsing laser in pJ, pulse frequency is the number of laser pulses per minute given in kHz, and the DR % is the detection rate of laser pulses that result in the field emission of an ion leading to a detection event as a percentage.

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Hits</th>
<th>T (K)</th>
<th>Laser E (pJ)</th>
<th>Pulse Frequency (kHz)</th>
<th>DR %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os1</td>
<td>5294379</td>
<td>70</td>
<td>200</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>Re1</td>
<td>2710619</td>
<td>70</td>
<td>150</td>
<td>200</td>
<td>0.5</td>
</tr>
<tr>
<td>Re2</td>
<td>2756837</td>
<td>70</td>
<td>100</td>
<td>200</td>
<td>0.5</td>
</tr>
<tr>
<td>HSE1</td>
<td>1827218</td>
<td>60</td>
<td>100</td>
<td>200</td>
<td>0.5</td>
</tr>
<tr>
<td>HSE2</td>
<td>38250642</td>
<td>60</td>
<td>100</td>
<td>200</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**TABLE 5.3:** Operating conditions of the Sydney Atom Probe for RMN7 through RMN9, where hits relate to the number of ion detections during the analyses, T relates to the temperature the specimen was held at in K, Laser E is the energy of the pulsing laser in pJ, pulse frequency is the number of laser pulses per minute given in kHz, and the DR % is the percentage of laser pulses that result in the field emission of an ion leading to a detection event.

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Hits</th>
<th>T (K)</th>
<th>Laser E (pJ)</th>
<th>Pulse Frequency (kHz)</th>
<th>DR %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMN7</td>
<td>1787026</td>
<td>50</td>
<td>80</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>RMN8</td>
<td>13618621</td>
<td>50</td>
<td>60–450</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>RMN9</td>
<td>14198895</td>
<td>50</td>
<td>100</td>
<td>250</td>
<td>0.5</td>
</tr>
</tbody>
</table>
5.2.4. THERMAL IONISATION MASS SPECTROMETRY (TIMS)

TIMS is a highly sensitive technique for isotopic analysis (0.05 – 0.01 % uncertainty for isotope ratios Aggarwal 2016), it is particularly useful for geochronology as it can distinguish between the Re and Os components which allows a direct measurement of the $^{187}\text{Os}/^{188}\text{Os}$ ratio without the isobaric interference of $^{187}\text{Re}$. TIMS analysis of RMNs is not possible due to their small size and therefore low total mass of Re and Os < 100 attograms, and four orders of magnitude lower than has previously been measured by TIMS (Birck et al., 1997). However, the material used here as standard materials were sufficiently large to contain sufficient Re and Os for TIMS analysis. A small portion of the Re wire, Os wafer, and multi-HSE alloy were separated from the main mass using pliers, or a diamond wire saw, respectively.

The Os isotopic composition of each standard sample was analysed in the John de Laeter Centre for Mass-Spectrometry at Curtin University (Perth, WA). In order to achieve a complete digestion of the pure Os metal and the multi-HSE alloy, we applied the Carius tube digestion method (Shirey and Walker, 1995). Approximately 5 mg of Os metal and multi-HSE alloy were consumed. The acid digestion was done using concentrated acids (1 mL of purged double-distilled HNO$_3$ and 3 mL of triple-distilled HCl). This mixture was chilled and sealed in previously cleaned Pyrex borosilicate Carius Tubes (CT) and heated up to 220 °C for 60 hrs. Osmium was extracted from the acid solution by chloroform solvent extraction (Cohen and Waters, 1996), then back-extracted into HBr, followed by purification via microdistillation (Birck et al., 1997). The purified Os fraction of each sample was loaded onto two separate Pt filaments, and measured using Negative Ion-TIMS (N-TIMS) on a ThermoFisher Triton® mass spectrometer using Faraday cup collectors at the John de Laeter Centre, Curtin
University. The measured isotopic ratios were corrected for mass fractionation using $^{192}\text{Os}/^{188}\text{Os} = 3.092016$.

The internal precision of the measured $^{187}\text{Os}/^{188}\text{Os}$ in all samples was better than 0.15 % ($2\sigma$ standard deviation). The pure Os metal was analysed six times (3 times on each filament), giving the average of 0.1417 with an external reproducibility of 0.14 % ($0.0002 \times 2\sigma$ standard deviation). The multi-HSE alloy was analysed five times for both filaments, giving an average of 0.10696 ± 0.0003 with an external reproducibility of 0.3 % ($0.0003 \times 2\sigma$ standard deviation). The pure Re metal used for the atom probe experiment represents an in-house Re standard made from zone refined Re filament. Its $^{185}\text{Re}/^{187}\text{Re}$ ratio is estimated at $0.5987 \pm 0.0008$ ($n = 12, 2\sigma$ standard deviation).

To monitor long-term TIMS instrument reproducibility for Os, an AB–2 Os standard (University of Alberta) was analysed that is the lab protocol for this instrument. The AB–2 Os standard yielded $0.10687 \pm 0.00012$ ($2\sigma$ standard deviation) during the period of the measurements, which is consistent with those reported by Selby and Creaser (2003) ($0.106838 \pm 0.00004$). The total procedural blank for Os was 0.50 pg, its contribution is insignificant for the samples studied. The $^{187}\text{Os}/^{188}\text{Os}$ ratios for the blank was $0.201 \pm 0.020$.

The Os ratios were recalculated for $^{189}$ Os to be consistent with the atom probe analysis using the $^{188}\text{Os}/^{189}\text{Os}$ ratio detailed in de Laeter et al. (2003).
5.3. **THEORETICAL CONSTRAINTS ON THE TECHNIQUE**

During APM analysis it is assumed that every atom within a specimen tip is ionised with an equal likelihood, and every ion has an equal chance of detection regardless of elemental species or atomic weight (Kelly and Larson, 2012). Other time of flight (TOF) techniques where there is incomplete ionisation must be corrected for isotopic mass fractionation (Guillong and Günther, 2002). These effects are not expected to occur in APM (Parman et al., 2015).

In an ideal APM sample the only source of uncertainty is derived from the chance of detection for an individual atom, which can be described by standard counting statistics (Larson et al., 2013). In this section we explain how the precision of APM datasets varies with counts and determine the theoretical precision possible with the technique, and the size of isotopic anomalies that may be detected.

5.3.1. **COUNTING STATISTICAL UNCERTAINTY**

Uncertainties in APM measurements can be calculated using three methods: counting statistics (Larson et al., 2013), comparing the APM measurements of a known standard (i.e. Parman et al. 2015), or comparing APM measurements to another technique (i.e. Valley et al. 2014). Here we use a combination of all three methods.

The calculated uncertainty from the counting statistics in APM measurements is expressed as the standard deviation ($\sigma$) described by Equation 5.1 from Larson et al. (2013).
\[ \sigma = \sqrt{A + B} \quad (5.1) \]

Where \( A \) is the total counts detected from a single ranged peak and \( B \) is the average background counts across the range of the peak form which ‘signal’ counts \( A \) are counted. For all data presented in this section we propagated the \( 2\sigma \) calculated uncertainty for the measurements.

The precision of the APM measurement improves with the number of counts detected and the relative uncertainty decreases. This relationship can be expressed as a power law (Equation 5.2).

\[ 2\sigma_A = 200 \frac{1}{\sqrt{A}} \quad (5.2) \]

Where \( A \) is the total counts detected, and \( \sigma_A \) is the % uncertainty of the counts. The uncertainties associated with low counts (<10^3), for a single m/q peak are large (>± 10 %), but improve with higher counts (Figure 5.8). Counts >10^6 from a single m/q peak have an associated uncertainty <± 0.2 % and counts >± 10^8 from a single m/q peak have associated uncertainties <0.02 % (Figure 5.8), however, for most geological samples the number of counts detected from a single m/q peak are unlikely to be >10^7. Theoretically, if the only source of uncertainty in APM measurements was derived from counting statistics, at high counts (>10^6) the precision of APM for a single m/q peak is more precise than some ionisation methods, such as spark source mass spectrometry (SSMS), laser ionisation mass spectrometry (LIMS) and resonance ionisation mass spectrometry (RIMS) which have associated uncertainties of ± 3 – 5 % for single ion collectors and ± 1 % for multi-collectors (Becker, 2002). The theoretical sensitivity of APM at high counts is comparable to secondary
ion mass spectrometry (SIMS), sputtered neutral mass spectrometry (SNMS), TIMS, glow discharge mass spectrometry (GDMS) and inductively coupled plasma mass spectrometry (ICP-MS), which have associated uncertainties of ± 0.02 – 1 % for single ion collectors (Becker, 2002).

Equation 5.2 does not take into account the background counts in the spectrum as well as other systematic sources of uncertainty in the APM acquisition such as detector dead times or ‘ringing effects’, subtle peak overlaps, interferences, etc; therefore, the true uncertainties will be higher. Background levels are variable between specimens and peaks within the mass-to-charge-state-ratio (MCSR) spectrum but are generally small (<10 counts per bin, of width 0.001 Da Parman et al. 2015). The average background counts in APM datasets over a 0.2 Da peak range width from this study were <100 counts. The background contribution to the calculated uncertainty where \( A > 10B \) trends rapidly towards 0 (Figure 5.8). Where \( A \leq B \) the relative uncertainty is higher than predicted by Equation 5.2 (Figure 5.8). Therefore, Equation 5.2 is only valid where measured counts in the peak are larger than the background counts by one order of magnitude (Figure 5.8).

### 5.3.2. Theoretical sensitivity of isotopic abundance measurements

The relationship between counts and their uncertainties calculated from Equation 5.1 and Equation 5.2 can be used to estimate the size of isotopic anomaly it is possible to detect with APM, for an ideal case. Let us consider a hypothetical element \( X \), which has two isotopes \(^1X\) and \(^2X\). The variability in isotopic abundances of a material is usually recorded in epsilon notation (\( \epsilon \)) which describes the isotopic variation in a sample relative to a standard reference (i.e.
Figure 5.8: A graph depicting the change in % uncertainty $\sigma_A$ with increasing counts as defined by the power law in Equation 5.2 (orange). The effect of incorporating a background count of 100 into the uncertainty calculation (blue). An elevated uncertainty is calculated where total counts are less than an order of magnitude above background counts.
CI chondrite) in parts per 10000 and is described by Equation 5.3 (Yokoyama and Walker, 2016; Schaefer, 2016):

$$\epsilon = \left[ \frac{(1X)_{\text{sample}}}{(1X)_{\text{standard}}} - 1 \right] \times 10000 \quad (5.3)$$

This can be expanded to form a general case whereby the uncertainty of an APM measurement of element X can be expressed in $\epsilon$ notation.

$$\epsilon = \left[ \frac{(1X+2\sigma_1X)}{(1X+2\sigma_2X)}_{\text{sample}} - 1 \right] \times 10000 \quad (5.4)$$

If $^1X$ and $^2X$ have the same relative abundance whereby $^1X/^2X = 1$ we can apply Equation 5.4 to visualise the sensitivity of the technique with increasing counts (see Figure 5.9). Low counts ($<10^3$) result in large uncertainties ($\epsilon > 1000$), whereas high count rates ($>10^6$) are more precise and could discern isotopic anomalies of $>\epsilon 40$ (Figure 5.9). Some isotopic anomalies observed in meteoritic components are of comparable size (See Yokoyama and Walker 2016), and isotopic anomalies in pre-solar grains are greater still (Anders and Zinner, 1993; Nittler, 2003; Zinner, 2003). Therefore, the sensitivity of the APM technique has the potential to detect these isotopic anomalies.

5.4. EVALUATION OF DATA REDUCTION METHODS USING PURE RE AND OS METALS

The constraints calculated above are for an idealised case for a simple sample. Meteorite samples are more complex and contain several elements in major
Figure 5.9: Graph depicting the variation in the calculated uncertainty in APM measurements of element X expressed in $\epsilon$ notation assuming equal abundance of the two isotopes $^{1}X$ and $^{2}X$ calculated using Equation 5.4. The orange shaded area of the plot represents the uncertainty in $+ve \epsilon$ and the blue shaded area represents the uncertainty in $-ve \epsilon$.

minor and trace abundances which populate the m/q spectrum with several peaks. The APM technique also produces elemental ions with multiple charge states (Parman et al., 2015), hydride ions (Parman et al., 2015), molecular ions (Thuvander et al., 2011; Heck et al., 2014; Stadermann et al., 2011), and isobaric interferences (Kelly, 2011) which affect the m/q spectrum and must be identified, quantified, and corrected. Furthermore, using the integrated visualisation and analysis software (IVAS) from CAMECA, data reduction methods, such as peak ranging, and background corrections may introduce artefacts into the datasets. Pure Re (Re1 and Re2) and pure Os (Os1) APM specimens were reduced in order to assess the effect of the background correction, peak ranging, hydride formation and multiple charge states on the measured isotopic abundances. This allows us to determine which data-reduction methods accurately reproduce isotopic measurements as measured by TIMS.
5.4.1. The effect of peak ranging methods

To calculate the abundance of counts under a peak the limits of the peak must be established or ‘ranged’ using the IVAS software. Peaks can be ranged using multiple methods. Several methods have already been evaluated by Hudson et al. (2011). Here we will describe and discuss the advantages and limitations of two methods: the full width method (R6 in Hudson et al. 2011), and the consistent width method (an expansion of R5 in Hudson et al. 2011).

5.4.1.1. The full width method

For the full width method, peaks are ranged from where they first emerge above the background level to where they descend below the background (Hudson et al., 2011) (Figure 5.10). This method is advantageous as it includes all the counts beneath the peak. However, it will also include contributions from neighbouring peaks and peak tails which may result in an overestimation of the contribution of the species of interest to the measured peak.

5.4.1.2. The consistent width method

The consistent width method is an expansion of the max bin method used in Hudson et al. (2011). In the method used here, the smallest peak of the element is identified and ranged so the entire range is above background when centred over the peak apex. The remaining isotope peaks are ranged using the same width centred over the apex of the peak (Figure 5.11 and 5.12) (Os1 = 0.25 Da whilst Re1 = 0.35 Da and Re2 = 0.20 Da). This method neglects counts present on the limbs of each peak, resulting in lower total counts and higher calculated
Figure 5.10: Mass to charge state ratio (m/q) spectrum for OsI in the 90 – 100 Da range where Os^{++} ions are present. These Os peaks are ranged using the full width method.
uncertainties than the full width method. However, the contribution from neighbouring peaks is reduced. Furthermore, because the range is consistent (although we do assume the peak shapes within the range are the same which is not unreasonable), the peak shapes beyond the range width are ignored: each peak is treated the same way thus removing the bias introduced when higher peaks are ranged with a larger width. This is advantageous as the consistent width method is then not affected by variations in the peak shape beyond defined range, such as peak broadening at elevated counts, or long peak tails. These factors can cause overestimations using any methodology which treats each peak individually, such as the full width method, but also any full width half maximum ranging methods (Hudson et al., 2011). Our consistent width method is more desirable than the max bin method as it incorporates more counts, reducing our calculated uncertainties. Generally, the consistent width method produces abundances that are more representative of true relative abundances.

5.4.1.3. Evaluation of ranging methods

Os1 was reduced using both ranging methods (Figure 5.10 and 5.11). The relative abundance of the stable Os isotopes was calculated and compared to expected terrestrial abundances (de Laeter et al., 2003) (Figure 5.13). Both methods produce the expected Os isotopic abundances to <0.5 %. This is within the calculated uncertainties and is consistent with TIMS measurements (Figure 5.13). However, the consistent width method is generally more accurate (Figure 5.13).
FIGURE 5.11: Mass to charge state ratio (m/q) spectrum for Os1 in the 90 – 100 Da range where Os^{++} ions are present. These Os peaks are ranged using the consistent width method. Each peak range was set to 0.25 Da. There is a slight peak at 95.5 Da from a small abundance of Os-hydride complexes.
Figure 5.12: Mass to charge state ratio (m/q) spectrum for Re I in the 90 – 100 Da range where Re$^{++}$ ions are present. These Re peaks are ranged using the consistent width method. Each peak range was set to 0.35 Da. There are slight peaks at 83 and 84 Da from a small abundance of Re-hydride complexes.
Figure 5.13: Graph depicting the relative abundance of the stable Os isotopes compared to terrestrial values from de Laeter et al. (2003). The consistent width method produces abundances marginally closer to the true isotopic values than the full width method.
5.4.2. The effect of elevated background

Background counts between different APM measurements are variable; with some datasets indicating an elevated background within a ‘forest’ of peaks (Figure 5.12). IVAS performs a background correction based on the local background levels in the mass range just below the peak range. However, the white-noise background should remain essentially constant in the time-of-flight (TOF) spectrum, which corresponds to a decaying global background in the m/q spectrum (Parman et al., 2015; Hudson et al., 2011). Therefore, elevated background counts may represent real atom detections from specific isotopes or from neighbouring peak tails. The ion counts for the Os isotopes in Os1 (ranged using the consistent width method) were calculated assuming a constant background of 150 counts over the width of the peak range (0.25 Da) calculated by ranging portion of background of the same width just prior to the onset of the peak of interest. This was then subtracted from the total counts detected over that same range. The ion counts were also calculated using the IVAS background correction. The resulting isotopic relative abundances for the stable Os isotopes from both corrections were compared in Figure 5.14.

Both methods produce the expected isotopic abundances within the calculated uncertainty. The isotopic abundances derived from the IVAS background correction are closer to the expected terrestrial isotopic abundances.

5.4.3. The effect of ionic species

Atom ionisation occurs during field evaporation using APM. The ionic charge of an atom can be variable causing emission of atoms in several charge states (+), (++) or (+++). This is due to the difference in the field strength required
Figure 5.14: Graph depicting the relative abundance of the stable Os isotopes compared to terrestrial values from de Laeter et al. (2003). The IVAS background correction produces abundances closer overall to the expected terrestrial abundances.
for single and multiple ionisation of each element (Tsong, 1978). The Re1 and Re2 datasets contain Re ions in the (++) charge state; (+) ions are not observed. The data were reduced using the consistent width method, and the IVAS background correction for Re++ and Re+++. The $^{187}\text{Re}/^{185}\text{Re}$ ratios were consistent with the expected terrestrial ratios and TIMS measurements, within calculated uncertainties (Figure 5.15). Although uncertainties associated with the (+++) ions are larger due to smaller count totals, isotopic fractionation between charge states is not observed. Therefore, multiple charge states do not need to be taken into account to measure true isotopic abundances and regions of the spectrum can be chosen that contain charge states for elements where there are fewer isobaric interferences.

![Figure 5.15: The $^{187}\text{Re}/^{185}\text{Re}$ of Re1 – 2 relative to the total counts for Re++, and Re+++. There is no isotopic fractionation of isotopes between charge states, and both samples produce the expected terrestrial isotopic ratios consistent with TIMS measurements (shaded grey region).](image)
5.4.4. HYDRIDE FORMATION

Previous experiments using APM have reported the formation of hydride molecules (i.e. Parman et al. 2015). These are thought to arise from H present in the ultra-high vacuum environment (Kelly, 2011). Some elements form hydride complexes more readily than others (Heck et al., 2014; Parman et al., 2015), but the cause of this is unknown. If hydrides are present hydrides combined with lighter isotopes will contribute to the peaks of heavier isotopes causing an apparent over abundances of heavier isotopes relative to lighter isotopes which biases the data. (Parman et al., 2015) reported contributions from hydrides of Pt of ~ 0.4 % for each peak. These contributions are significant and may affect some APM data.

The m/q spectra of Os1, Re1 and Re2 do contain small peaks of Os-H or Re-H 0.5 Da above the heaviest isotopes (Figure 5.11 and 5.12). The peaks associated with hydride complexes for the ++ charge states of each element were ranged using the full width method due to their small size, and after an IVAS background correction was calculated, the hydride peaks were found to contain < 100 counts. Assuming every isotope of an element has an equal chance of forming a hydride ion, which does not seem unreasonable given how the complexes are thought to form (Kelly, 2011), we can compare the size of the hydride peaks to the size of the single ion peak. This suggests that for Re and Os, < 0.02 % of each isotope form hydride complexes which is less than the calculated uncertainty of the measurement.
5.5. EVALUATION OF DATA REDUCTION METHODS
FROM COMPLEX HSE ALLOYS

5.5.1. DECONVOLUTION OF PEAK OVERLAPS

One challenge with isotopic analysis of m/q spectra is the presence of isobaric interferences between isotopes of different elements which have the same m/q ratio. This is particularly challenging in geological samples which contain several major, minor and trace elements; several isobaric interferences may be present in the APM m/q spectra (Valley et al., 2014; Reddy et al., 2016; Peterman et al., 2016; Piazolo et al., 2016; Fougerouse et al., 2016; Pérez-Huerta et al., 2016; Weber et al., 2016). These isobaric interferences can be deconvolved using Equation 5.5 if the relative abundances of one of the isotopes for the overlapping peaks is known or can be assumed.

\[ i_X = i_A - \left( \frac{i_{Y_A}}{i_{Y_{standard}}} \right) Y_{standard} \]  \hspace{1cm} (5.5)

\( i_X \) is the total counts in an m/q peak containing counts of overlapping isotopes from elements X and Y of mass \( i \). \( j \) is another isotope of element Y which does not have an associated isobaric interference. \( i_{Y_{standard}} \) is the known relative abundance of \( jY \) and \( iY \) in at. %. \( i_{Y_A} \) is the total counts from the m/q peak of isotope \( j \) from element Y. This calculation can only be performed if the isotopic abundances are known. Therefore, it is not possible to calculate radiogenic daughter products, or samples which exhibit isotopic fractionation using Equation 5.5. Also the isotope used in the correction cannot also be affected by an isobaric interference of its own.
In this section we reduced the HSE1 and HSE2 APM datasets using the IVAS background correction and the consistent width method. Hydride contributions to the spectrum were comparable to those calculated above and were ignored. These data contain a number of isobaric interferences which were corrected to evaluate the effect that the choice of isotope, the choice of element, and contributions from ‘hidden’ overlaps had on the accuracy of isobaric interference deconvolution. We focused on the 90 – 102 Da region of the m/q spectra which contained Os++. This will establish a current ‘best practice’ methodology for the deconvolution of isobaric interferences in APM.

5.5.1.1. THE CHOICE OF ELEMENT: THE KNOWN KNOWNS

In this section we examine the effect of each element used to deconvolve isobaric interferences. Osmium has several known isobaric interferences with other HSEs: $^{190}$Os and $^{192}$Os overlap with $^{190}$Pt and $^{192}$Pt, while $^{184}$Os and $^{186}$Os overlap with $^{184}$W and $^{186}$W and $^{187}$Os overlaps with $^{187}$Re. Using HSE1, the $^{184}$Os, $^{186}$Os-$^{184}$W, $^{186}$W overlaps were deconvolved, first assuming terrestrial abundances of $^{189}$Os, and then assuming terrestrial abundances of $^{183}$W and $^{184}$W (Figure 5.16). The W correction produces large anomalies for $^{184}$Os and $^{186}$Os, including an impossible negative abundance (Figure 5.16). The Os correction forces the $^{184}$Os and $^{186}$Os to be in agreement with terrestrial values. The large anomalies in the W deconvolution are caused by the high abundance of $^{184}$W and $^{186}$W relative to $^{184}$Os and $^{186}$Os (de Laeter et al., 2003). Therefore, the isotope with the lowest expected peak contribution should be chosen to perform the deconvolution. However, if isotopic anomalies are present in the sample this information will be lost from the element used in the correction. Consequently, the abundances of the other isotope in the isobaric interference will represent the sum of the
anomalies present in both isotopes.

Following this method $^{190}\text{Os}$ and $^{192}\text{Os}$ using $^{190}\text{Pt}$ and $^{192}\text{Pt}$ were deconvolved assuming a terrestrial abundance for $^{195}\text{Pt}$ (de Laeter et al., 2003). Since Pt is less abundant in the sample, and $^{190}\text{Pt}$ and $^{192}\text{Pt}$ have low abundances relative to $^{195}\text{Pt}$ the interferences with $^{190}\text{Os}$ and $^{192}\text{Os}$ will be small but easy to estimate. These factors will result in a low contribution to the overall interference peak. $^{195}\text{Pt}$ was chosen as opposed to other Pt isotopes as it is an odd-numbered isotope which is advantageous for the reasons outlined in Section 5.5.1.3. This deconvolution, unlike the Os deconvolution above, has the benefit of producing ‘real’ values of $^{190}\text{Os}$ and $^{192}\text{Os}$. However, this correction drives Os isotopic relative abundances away from terrestrial values (Figure 5.16). This could be due to a number of factors; an isobaric interference in the $^{195}\text{Pt}$ peak will overestimate $^{190}\text{Pt}$ and $^{192}\text{Pt}$ and consequentially underestimate $^{190}\text{Os}$ and $^{192}\text{Os}$. Additionally, Os isotopes may have isobaric interferences causing them to appear enriched. However, even with these simple corrections the Os isotopes are within 1% of the relative difference from the expected isotopic abundances and within the calculated uncertainties. Therefore, any other contributions from other sources are likely to be small.

Utilising the least abundant isotope is not appropriate in all cases, for example the $^{187}\text{Re}$-$^{187}\text{Os}$ overlap. $^{187}\text{Os}$ is the radiogenic daughter product of $^{187}\text{Re}$ (Schaefer, 2016; Selby et al., 2007), so for geological samples $^{187}\text{Os}$ will be variable and contingent on the $^{187}\text{Re}$ concentration. As these concentrations are used in radiometric dating (Schaefer, 2016; Selby et al., 2007), they, cannot be assumed to have standard values. Re isotopic relative abundances are constant across a range of rock types, including meteorites (Lodders, 2003; Walczyk and Heumann, 1993; de Laeter et al., 2003; Anders and Grevesse, 1989; Luck et al., 1980), so although $^{187}\text{Os}$ is less abundant than $^{187}\text{Re}$, $^{185}\text{Re}$ and $^{187}\text{Re}$ should be
used to deconvolve the isobaric interference to produce a ‘real’ abundance of $^{187}$Os. The relative abundance of $^{187}$Os in HSE1 and HSE2 is significantly lower (1.3 %) than present day un-fractionated $^{187}$Os (1.9 %) (de Laeter et al., 2003) (Table 5.4).

**Figure 5.16:** Isotopic abundances of Os$^{++}$ from HSE1 relative to terrestrial isotopic abundances (de Laeter et al., 2003) using different isobaric interference correction methods shown to $2\sigma$ uncertainties. Deconvolutions using $^{189}$Os, with and without a Pt correction are shown in black and purple, respectively. $^{184}$Os and $^{186}$Os abundances calculated by assuming terrestrial $^{182}$W and $^{183}$W are shown in red and blue, respectively. The graph on the left-hand side shows the large anomalies produced through the W deconvolutions of the lighter Os isotopes. The graph on the right-hand side is cropped to show detail in the heavier Os isotopes as the $^{184}$Os and $^{186}$Os relative abundances from the W deconvolution were large.

5.5.1.2. THE CHOICE OF ISOPTOE, THE KNOWN UNKNOWNS

Some elements have several isotopes which could be used in the deconvolution of isobaric interferences; Os has seven (Lodders, 2003; de Laeter et al., 2003). We deconvolved $^{184}$Os, $^{186}$Os-$^{184}$W, $^{186}$W using $^{188}$Os, $^{189}$Os, $^{190}$Os, and $^{192}$Os to determine how the choice of isotope affects the calculated isotopic abundances (Figure 5.17). The $^{189}$Os deconvolution is closest to the expected terrestrial isotopic abundances for $^{184}$Os, and $^{186}$Os. However, the other more abundant
Os isotopes; i.e., $^{190}$Os, produce more counts and therefore are more precise. These isotopes should theoretically be closer to terrestrial values. However, this is not the case as isobaric interferences associated with these isotopes may not be accounted for.

![Graph](image)

**Figure 5.17:** Isotopic abundances of Os$^{++}$ from HSE1 relative to terrestrial (de Laeter et al., 2003). The effect of using different isotopes of Os ($^{188}$Os (red), $^{189}$Os (black), $^{190}$Os (blue), and $^{192}$Os (purple)) to deconvolve the isobaric interference by different isobaric interference correction methods is shown.

### 5.5.1.3. Other Overlapping Ions, The Unknown Unknowns

It is plausible that there may be elements of different charge states or molecular ions, other than Os, Re, W and Pt, present in this region of the m/q spectrum which have not been accounted for. The 90 – 100 Da range in the m/q spectrum may contain contributions from Mo$^+$ and Ru$^+$ isotopes. If these are present
they will cause overestimations in $^{184}\text{Os}$, $^{188}\text{Os}$, $^{190}\text{Os}$, and $^{192}\text{Os}$. In the case of Ru$^+$, several peaks should not overlap; i.e., $^{100,101,102,104}\text{Ru}$, so their contributions can be calculated using the method described in Section 5.5.1. However, for Mo$^+$, all isotopes in this region of the spectrum overlap with other isotopes.

Peak overlaps may also be caused by complex ions such as Mo$_2^{++}$ etc. In fact, there is a large number of combinations and charge states which can produce a wide range of mass charge values. However, only a finite number of these are realistic. From the pure samples Os1, Re1 and Re2 a $(^{++})$ charge state is the dominant emission with minor contributions from $(^{+++})$ ions in the m/q spectra; $(^+)$ ions are not observed. This, coupled with the good correlation between the Os and terrestrial isotopic abundances for these samples suggests that if these contributions are present they are small. However, there are slight enrichments ($<0.4\%$) of $^{188}\text{Os}$ and $^{190}\text{Os}$ in HSE1 (Figure 5.16 and 5.17). These are discussed in more detail in Section 5.6.3.

If Mo$^+$ ions are present to even a small degree, it is possible to eliminate interference as $^{189}\text{Os}$ does not have an isobaric overlap. This is because $^{189}\text{Os}$ in the $(^{++})$ charge state is at 94.5 Da in the m/q spectra; therefore, no ion in the $(^+)$ or $(^{+++})$ charge state can overlap. The only possible overlaps for these peaks are generated by a molecular ion with a mass of 189 in the $(^{++})$ state, or a mass of 378 in the $(^{+++})$ charge state. There are only a few element combinations possible from those present in the sample, and none of these are detected here. Therefore, the species that should be used to separate overlapping isotope peaks are odd numbered isotopes in the $(^{++})$ charge state, as they have a reduced chance of being affected by isobaric interferences.
5.5.2. Reproducibility

APM analysis of multi-element samples from the same material may produce different peaks in the m/q spectra over separate analyses. This may be the result of subtle variations in the analytical conditions. Os isotopic data was reduced using the methods described in Sections 5.4 – 5.5 for HSE1 and HSE2 (Figure 5.18). These reveal that within the calculated uncertainty the Os measurements of both samples are the same, and consistent with expected terrestrial values. This implies that APM consistently detects isotopic abundances for materials from the same sample. The only significant variations are within the bounds of the calculated uncertainty of the measurements.

Figure 5.18: Os isotope relative abundances from HSE1 – 2 compared to terrestrial abundances (de Laeter et al., 2003). This reveals consistent isotopic measurements within the uncertainty of the counting statistics between the two APM specimens, indicating that APM isotopic analyses are reproducible.
5.5.3. Comparison with TIMS

The $^{187}\text{Os}/^{189}\text{Os}$ ratio of the bulk HSE alloy, recalculated from the $^{187}\text{Os}/^{188}\text{Os}$ measurement from the TIMS data is within the calculated uncertainty of HSE1, however, HSE2 is slightly lower and outside the calculated uncertainty. Varying the width of the peak range and also performing a uniform background correction all return this same depleted ratio. HSE1 and HSE2 overlap each other within the calculated uncertainty. There are three possibilities which could account for this: a systematic depletion caused by the peak deconvolution of $^{187}\text{Re}-^{187}\text{Os}$, contamination of the sample post extraction from the resin block prior to TIMS analysis, or in-homogeneous distribution of $^{187}\text{Os}/^{189}\text{Os}$ within the standard. The pure elements accurately reproduce the Re and Os isotopic measurements between TIMS and APM therefore the peak deconvolution should not have a significant effect. It is possible the diamond wire saw used to cut the alloy may have introduced contamination however, due to the abundance of Os in the alloy this contamination would have to be large which is unlikely. The alloy itself was produced synthetically by Schwander et al. (2015a) through melting pure elements together in an electric arc furnace. The final product is poly-phase (Figure 5.1). It is possible that the other HSE metals, particularly Re, may have contained impurities of Os with variable $^{187}\text{Os}/^{189}\text{Os}$ which were not homogenised during the formation and quenching of the alloy. As TIMS measures the bulk sample and APM only samples a small region it is possible that TIMS represents an average $^{187}\text{Os}/^{189}\text{Os}$ for the sample while APM sampled a depleted phase in an isotopically in-homogeneous alloy. The final run products of Schwander et al. (2015a) were re-heated to $>1600{^\circ}\text{C}$ which may have homogenised any isotopic heterogeneity. These run products were also analysed by APM (SYN1 and SYN2) (Figure 5.19). These were not initially included in this work as the experiment formed an Si-HSE
alloy, which complicated the APM m/q spectra. However, deconvolving only the $^{185}$Re, $^{187}$Os and $^{189}$Os mass peaks from these data produced $^{187}$Os/$^{189}$Os ratios of $0.88 \pm 0.006$ and $0.085 \pm 0.015$ respectively which are both consistent with the TIMS measurements. This suggests the original alloy was isotopically heterogeneous and HSE2 sampled a low $^{187}$Os/$^{189}$Os region relative to the bulk alloy as measured by TIMS. These all suggest that APM is reliably reproducing Re-Os isotopic abundances and can detect isotopic heterogeneities within bulk samples.

5.5.4. **Recommended data reduction sequence for isotopic analysis using APM**

Through evaluation of the above standards we have demonstrated that the isotopic abundances of elements in APM datasets can be affected by a number of variables. We have evaluated several of these and corrected for them to reliably reproduce isotopic abundances of Os and Re for several standard materials. Based on the discussion above, the following is proposed as a general best practice for the reduction of isotopic data from APM:

1. Use a consistent width method for ranging isotopic peaks.

2. Use the IVAS background correction.

3. Analyse simple materials to observe how they behave in the APM, usual charge states and complex ions.

4. Evaluate hydride formation and correct if significant.

5. Choose the least abundant isotope and element in the system to correct isobaric interferences.
Figure 5.19: Images of APM samples SYN1 and SYN2. A) BSE image of the multi-phase alloy derived from the run products of the experiments detailed in Schwander et al. (2015a). The locations of APM samples SYN1 and SYN2 are given by the red circles. B) In-beam SEM image of the final polished APM specimen for SYN1. C) In-beam SEM image of the final polished APM specimen for SYN2.
6. Evaluate the possibility of hidden overlaps in the spectrum

7. Corroborate results on suitable standard materials with techniques such as TIMS.

5.6. ISOTOPIC ANALYSIS OF RMNs WITH APM

The agreement between the isotopic measurements obtained with APM and TIMS for both pure elements and complex synthetic alloys suggests that isotopic analysis using the methodology outlined above is robust for alloys comprised of Re and Os and possibly other HSEs. The bulk compositions of RMN1 through RMN5 and RMN7 through RMN8 are similar to HSE1 and HSE2 (Figure 5.21 and Figure 5.20). One exception is the presence of small amounts of S and V in the RMNs. Therefore, APM analyses for both materials should produce similar m/q spectra. We can apply our methodology to the RMN APM datasets to extract isotopic information. The resulting relative abundances of the isotopes of Ir, W and Os within RMN1 through RMN5 and RMN7 through RMN9 are outlined in Figure 5.22, 5.23 and 5.24 and summarised in Table 5.4.

The bulk chemistry of RMN9 is different to the other datasets as it does not contain W or Mo. RMN9 is also enriched in Pt and contains Pd, which has not been previously reported for RMNs. This is likely related to is provenance in a sulphide inclusion in the rim of a chondrule whereas the other RMNs are from refractory inclusions.
Figure 5.20: An example mass spectrum from RMN4 indicating the added complexity in the 90 Da region due to isobaric interferences between isotopes of Os, W, Ir, Re, Pt and Ru. A similar pattern is also observed in the mass spectra of HSE1 – 2.
Figure 5.21: Bulk geochemistry of RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 in order of increasing volatility from Table 5.1. The synthetic HSE alloy is a good approximation of the average RMN in this study. RMN9 is unusual as it does not contain W, Mo, V or Rh but contains Pd which has not previously been reported in RMNs.
Table 5.4: Os and Re isotopic abundances and calculated ages for all samples analysed by AM using data reduction methods established above $\pm 2\sigma$.
Relative isotopic abundances of Os are given atomic %

<table>
<thead>
<tr>
<th>APM samples</th>
<th>$^{184}$Os</th>
<th>$^{186}$Os</th>
<th>$^{187}$Os</th>
<th>$^{188}$Os</th>
<th>$^{189}$Os</th>
<th>$^{190}$Os</th>
<th>$^{192}$Os</th>
<th>$^{187}$Re/$^{189}$Os</th>
<th>$^{187}$Re/$^{185}$Re</th>
<th>Age (Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.665</td>
</tr>
<tr>
<td>Re2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.672</td>
</tr>
<tr>
<td>N-TIMS Re</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.6740</td>
</tr>
<tr>
<td>Os1</td>
<td>1.616</td>
<td>1.870</td>
<td>13.196</td>
<td>16.079</td>
<td>26.341</td>
<td>40.899</td>
<td>0.116</td>
<td>-</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>N-TIMS Os</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0010</td>
</tr>
<tr>
<td>HSE1</td>
<td>0.020</td>
<td>1.604</td>
<td>1.350</td>
<td>13.432</td>
<td>26.558</td>
<td>40.738</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
<td>3.6</td>
</tr>
<tr>
<td>HSE2</td>
<td>0.020</td>
<td>1.600</td>
<td>1.288</td>
<td>13.392</td>
<td>26.614</td>
<td>40.832</td>
<td>0.079</td>
<td>-</td>
<td>-</td>
<td>4.3</td>
</tr>
<tr>
<td>SYN1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>SYN2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>N-TIMS HSE</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0875</td>
</tr>
<tr>
<td>RMN1</td>
<td>0.020</td>
<td>1.603</td>
<td>1.713</td>
<td>13.475</td>
<td>16.306</td>
<td>26.532</td>
<td>40.372</td>
<td>0.105</td>
<td>0.361</td>
<td>4.32</td>
</tr>
<tr>
<td>RMN2*</td>
<td>0.020</td>
<td>1.568</td>
<td>1.743</td>
<td>13.406</td>
<td>16.234</td>
<td>26.744</td>
<td>40.279</td>
<td>0.107</td>
<td>0.380</td>
<td>4.45</td>
</tr>
<tr>
<td>RMN3</td>
<td>0.020</td>
<td>1.582</td>
<td>1.671</td>
<td>13.378</td>
<td>16.098</td>
<td>26.585</td>
<td>40.686</td>
<td>0.104</td>
<td>0.344</td>
<td>4.31</td>
</tr>
<tr>
<td>RMN4</td>
<td>0.020</td>
<td>1.593</td>
<td>1.674</td>
<td>13.311</td>
<td>16.207</td>
<td>26.571</td>
<td>40.644</td>
<td>0.103</td>
<td>0.327</td>
<td>4.45</td>
</tr>
<tr>
<td>RMN5</td>
<td>0.020</td>
<td>1.595</td>
<td>1.752</td>
<td>13.329</td>
<td>16.231</td>
<td>26.431</td>
<td>40.661</td>
<td>0.108</td>
<td>0.323</td>
<td>5.30</td>
</tr>
<tr>
<td>RMN7</td>
<td>0.020</td>
<td>1.576</td>
<td>1.947</td>
<td>13.738</td>
<td>16.039</td>
<td>26.605</td>
<td>40.995</td>
<td>0.121</td>
<td>0.433</td>
<td>5.71</td>
</tr>
<tr>
<td>RMN8</td>
<td>0.020</td>
<td>1.621</td>
<td>1.946</td>
<td>13.450</td>
<td>16.488</td>
<td>26.665</td>
<td>39.830</td>
<td>0.118</td>
<td>0.384</td>
<td>5.92</td>
</tr>
<tr>
<td>RMN9</td>
<td>0.020</td>
<td>1.590</td>
<td>1.960</td>
<td>13.240</td>
<td>16.150</td>
<td>26.280</td>
<td>40.780</td>
<td>0.121</td>
<td>0.301</td>
<td>1.674</td>
</tr>
<tr>
<td>Terrestrial</td>
<td>0.000</td>
<td>0.016</td>
<td>0.016</td>
<td>0.133</td>
<td>0.162</td>
<td>0.263</td>
<td>0.409</td>
<td>0.101</td>
<td>0.301</td>
<td>x</td>
</tr>
</tbody>
</table>

*Corrected for Mo*
TABLE 5.5: Ir, W and Pt isotopic abundances for all samples analysed by AM using data reduction methods established above ± 2σ. Relative isotopic abundances of Os are given atomic %

<table>
<thead>
<tr>
<th>APM sample</th>
<th>191Ir</th>
<th>193Ir</th>
<th>182W</th>
<th>183W</th>
<th>184W</th>
<th>186W</th>
<th>190Pt</th>
<th>192Pt</th>
<th>194Pt</th>
<th>195Pt</th>
<th>196Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSE1</td>
<td>0.999</td>
<td>1.001</td>
<td>1.015</td>
<td>0.993</td>
<td>1.004</td>
<td>0.986</td>
<td>1.152</td>
<td>1.015</td>
<td>0.984</td>
<td>1.015</td>
<td>1.000</td>
</tr>
<tr>
<td>± 0.026</td>
<td>± 0.004</td>
<td>± 0.008</td>
<td>± 0.007</td>
<td>± 0.005</td>
<td>± 0.008</td>
<td>± 32.298</td>
<td>± 0.625</td>
<td>± 0.014</td>
<td>± 0.010</td>
<td>± 0.015</td>
<td>± 0.023</td>
</tr>
<tr>
<td>HSE2</td>
<td>1.000</td>
<td>1.000</td>
<td>1.002</td>
<td>1.000</td>
<td>1.002</td>
<td>0.966</td>
<td>1.009</td>
<td>1.009</td>
<td>0.969</td>
<td>1.009</td>
<td>0.966</td>
</tr>
<tr>
<td>± 0.006</td>
<td>± 0.004</td>
<td>± 0.007</td>
<td>± 0.004</td>
<td>± 0.008</td>
<td>± 23.345</td>
<td>± 0.520</td>
<td>± 0.013</td>
<td>± 0.009</td>
<td>± 0.015</td>
<td>± 0.023</td>
<td></td>
</tr>
<tr>
<td>RMN1</td>
<td>1.003</td>
<td>0.998</td>
<td>1.002</td>
<td>1.012</td>
<td>1.018</td>
<td>0.972</td>
<td>1.195</td>
<td>1.053</td>
<td>1.292</td>
<td>1.054</td>
<td>1.596</td>
</tr>
<tr>
<td>± 0.008</td>
<td>± 0.006</td>
<td>± 0.003</td>
<td>± 0.024</td>
<td>± 0.031</td>
<td>± 1348.158</td>
<td>± 25.949</td>
<td>± 0.076</td>
<td>± 0.133</td>
<td>± 0.646</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMN2</td>
<td>1.004</td>
<td>0.998</td>
<td>0.968</td>
<td>0.935</td>
<td>1.137</td>
<td>0.915</td>
<td>0.965</td>
<td>0.850</td>
<td>1.628</td>
<td>2.704</td>
<td>1.019</td>
</tr>
<tr>
<td>± 0.007</td>
<td>± 0.005</td>
<td>± 0.018</td>
<td>± 0.023</td>
<td>± 0.017</td>
<td>± 0.021</td>
<td>± 370.908</td>
<td>± 10.988</td>
<td>± 0.034</td>
<td>± 0.083</td>
<td>± 0.322</td>
<td></td>
</tr>
<tr>
<td>RMN3</td>
<td>1.003</td>
<td>0.998</td>
<td>1.000</td>
<td>0.972</td>
<td>1.067</td>
<td>0.941</td>
<td>0.643</td>
<td>0.566</td>
<td>0.938</td>
<td>1.162</td>
<td>1.181</td>
</tr>
<tr>
<td>± 0.006</td>
<td>± 0.004</td>
<td>± 0.014</td>
<td>± 0.018</td>
<td>± 0.013</td>
<td>± 0.017</td>
<td>± 412.373</td>
<td>± 7.950</td>
<td>± 0.022</td>
<td>± 0.050</td>
<td>± 0.219</td>
<td></td>
</tr>
<tr>
<td>RMN4</td>
<td>1.004</td>
<td>0.988</td>
<td>1.005</td>
<td>0.982</td>
<td>1.031</td>
<td>0.971</td>
<td>0.609</td>
<td>0.536</td>
<td>0.948</td>
<td>1.472</td>
<td>1.791</td>
</tr>
<tr>
<td>± 0.006</td>
<td>± 0.004</td>
<td>± 0.012</td>
<td>± 0.014</td>
<td>± 0.010</td>
<td>± 0.014</td>
<td>± 546.551</td>
<td>± 10.572</td>
<td>± 0.026</td>
<td>± 0.053</td>
<td>± 0.282</td>
<td></td>
</tr>
<tr>
<td>RMN5</td>
<td>1.001</td>
<td>1.000</td>
<td>1.011</td>
<td>0.991</td>
<td>1.001</td>
<td>0.993</td>
<td>0.893</td>
<td>0.786</td>
<td>1.170</td>
<td>0.797</td>
<td>1.228</td>
</tr>
<tr>
<td>± 0.006</td>
<td>± 0.004</td>
<td>± 0.013</td>
<td>± 0.017</td>
<td>± 0.011</td>
<td>± 0.015</td>
<td>± 1148.794</td>
<td>± 22.104</td>
<td>± 0.078</td>
<td>± 0.096</td>
<td>± 0.286</td>
<td></td>
</tr>
<tr>
<td>RMN7</td>
<td>1.011</td>
<td>0.993</td>
<td>1.099</td>
<td>0.975</td>
<td>0.992</td>
<td>0.928</td>
<td>1.136</td>
<td>1.001</td>
<td>0.926</td>
<td>1.002</td>
<td>1.052</td>
</tr>
<tr>
<td>± 0.011</td>
<td>± 0.008</td>
<td>± 0.044</td>
<td>± 0.066</td>
<td>± 0.044</td>
<td>± 0.064</td>
<td>± 524.685</td>
<td>± 9.068</td>
<td>± 0.051</td>
<td>± 0.044</td>
<td>± 0.103</td>
<td></td>
</tr>
<tr>
<td>RMN8</td>
<td>1.003</td>
<td>0.998</td>
<td>1.093</td>
<td>0.987</td>
<td>0.958</td>
<td>0.966</td>
<td>0.442</td>
<td>0.390</td>
<td>0.380</td>
<td>0.784</td>
<td>14.440</td>
</tr>
<tr>
<td>± 0.007</td>
<td>± 0.005</td>
<td>± 0.020</td>
<td>± 0.029</td>
<td>± 0.019</td>
<td>± 0.023</td>
<td>± 681.580</td>
<td>± 13.299</td>
<td>± 0.055</td>
<td>± 0.085</td>
<td>± 0.438</td>
<td></td>
</tr>
<tr>
<td>RMN9</td>
<td>1.041</td>
<td>0.976</td>
<td>1.152</td>
<td>1.015</td>
<td>0.977</td>
<td>1.016</td>
<td>0.990</td>
<td>1.062</td>
<td>4.084</td>
<td>0.113</td>
<td>0.014</td>
</tr>
<tr>
<td>± 0.008</td>
<td>± 0.003</td>
<td>± 0.020</td>
<td>± 0.019</td>
<td>± 0.014</td>
<td>± 0.010</td>
<td>± 0.015</td>
<td>± 0.023</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.6.1. Osmium isotopes

Isotopic abundances of Os for RMN1 through RMN5 and RMN7 through RMN8 were in broad agreement with HSE1 and HSE2 and the expected Solar System abundances (Lodders, 2003) (Figure 5.22). Some RMNs exhibited a slight enrichment in 188Os and 190Os which is likely caused by an isobaric interference with Mo+ isotopes. However, the contribution of Mo+ does not affect the spectrum significantly as the Os isotopes are still solar within 0.5%. Most RMNs also exhibit an enrichment in 187Os relative to solar abundances (Figure 5.22). This is due to the radiogenic nature of 187Os and the variable Re/Os contents of the RMNs (Figure 5.21). RMN9 is depleted in 187Os relative to solar (Figure 5.22) but also has lower Re contents.
Figure 5.22: Isotopic abundances, to 2σ uncertainty of Os for RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 relative to a solar standard (Lodders, 2003). RMNs largely have a Solar system trend for Os, consistent with the HSE standards. RMN1 through RMN5, RMN7 through RMN9 have enrichments in the radiogenic isotope $^{187}$Os. RMN9 has a large $^{187}$Os depletion.
5.6.2. Iridium Isotopes

Isotopic abundances of Ir for RMN1 – 5 and RMN7 – 8 were also in broad agreement with HSE1 – 2 and the expected Solar System abundances (Lodders, 2003) (Figure 5.23 and Table 5.5) to within 0.5%. However, some RMNs were slightly enriched in the lighter $^{191}$Ir. This was most pronounced in RMN7 and RMN9. This is unlikely to be a real anomaly as Ir isotopic abundances are relatively constant (Lodders, 2003; Walczyk and Heumann, 1993; Anders and Grevesse, 1989; de Laeter et al., 2003). The cause of this in the case of RMN7 is likely to be the low total counts recorded during the analysis. RMN9 on the other hand was a large dataset. However, its bulk chemistry is different from the other RMNs and HSE1 and HSE2 and therefore, there may be other species in the m/q spectrum causing this enrichment. Alternatively, the observed depletions of W and Os may reduce the background counts in this region of the m/q spectrum, artificially elevating the counts compared to $^{193}$Ir.

5.6.3. Tungsten Isotopes

Isotopic abundances of $^{182}$W, $^{183}$W and $^{186}$W for RMNs1 – 5 had similar relative abundance trends to HSE1 – 2 (Figure 5.24 and Table 5.5). RMN7 – 8 had elevated $^{182}$W and RMN9 did not contain W. $^{184}$W was variable in all RMNs. This is almost certainly caused by isobaric interferences with Mo$^+$ ions. The W m/q spectra are affected to a greater extent than the Os, as Os is more abundant in these RMNs than W. This may dilute the effect of the Mo$^+$ overlaps on the Os isotopes. The size of the Mo$^+$ contribution is unlikely to be related to Mo abundance. It is more likely to be caused by subtle differences in the analysis conditions and unique properties of the sample, such as tip shape.
Figure 5.23: Isotopic abundances, to 2σ uncertainty, of Ir for RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 relative to a solar standard (Lodders, 2003). RMNs largely have a Solar System trend for Ir. However, RMN9 is enriched in the light Ir isotope $^{191}$Ir.
This means a broad Mo correction for all datasets cannot be calculated and the Mo\(^+\) contribution must be calculated for each dataset individually. We calculated the \(^{92}\text{Mo}^+\) contribution present in RMN2, (which exhibits the largest anomaly) to be \(\sim 3000\) counts (\(\sim 17\%\) of the peak), assuming a solar \(^{184}\text{W}/^{183}\text{W}\) ratio. The presence of Mo\(^+\) here will also affect the Os isotopes which have isobaric interferences with Mo\(^+\) (Figure 5.25). However, most RMN datasets do not exhibit a significant enrichment in \(^{184}\text{W}\) so this correction only needs to be undertaken for certain analyses.

**Figure 5.24:** Isotopic abundances of W for RMN1 through RMN5, RMN7 through RMN9, HSE1 and HSE2 relative to a solar standard (Lodders, 2003). The RMNs exhibit a different pattern than the HSE standards with highly variable \(^{184}\text{W}\) contents. These are likely to be due to the presence of an isobaric interference with \(^{92}\text{Mo}^+\).
Figure 5.25: RMN2 Os isotopic relative abundances compared to solar abundances with and without a Mo correction based on the difference between measured $^{184}\text{W}$ and its expected abundance based on solar $^{184}\text{W}/^{183}\text{W}$. This correction produces Os isotopic abundances which are more consistent with expected solar ratios. The $^{184}\text{Os}$ and $^{186}\text{Os}$ have been corrected assuming Solar abundances of $^{189}\text{Os}$. The location of Mo$^+$ isobaric interference are labelled by the red boxes.
5.6.4. DISCUSSION

The isotopes discussed in the above sections contain anomalies for some isotopes in RMN1 through RMN8, which although they are small (<0.5 %) are still outside the calculated uncertainty of the APM technique. The main source of these anomalies is likely to be features present in the m/q spectra which have not been accounted for such as Mo\(^+\) ions. We have only accounted for some of the most predictable overlaps. However, these anomalies are larger in the RMN samples compared to the HSE standards which are close to their expected terrestrial values (Figure 5.22, 5.23 and 5.24). RMN9 contains larger anomalies in Ir and Os (2 – 4 %)

If the anomaly in RMN9 is real, several mechanisms exist to fractionate isotopes: mass-dependant fractionation, mass-independent fractionation and fractionation during nucleosynthesis (Yokoyama and Walker, 2016). Mass-dependent fractionation of HSEs is likely to be insignificant due the small relative difference between the mass of the isotopes (Schaefer, 2016) and none of the observed isotopic systems exhibit trends consistent with this. Mass-independent fractionation is usually driven by factors such as bond strength, and vibrational frequency and usually associated with photochemical reactions (Thiemens et al., 2012) however, such anomalies, if present, will also be small (Epov et al., 2011).

There are two main nucleosynthetic anomalies observed in pre-solar grains which are related to r- and s- process nucleosynthesis, proposed to occur during supernovae and the death of AGB stars, respectively (Meyer and Zinner, 2006; Anders and Zinner, 1993; Clayton and Nittler, 2004; Nittler, 2003). Most RMNs samples are depleted in \(^{192}\)Os and to a lesser extent \(^{186}\)W which are predominantly r-process isotopes (Yokoyama and Walker, 2016), however there
is no corresponding depletion in $^{189}$Os which is also predominantly produced through the $r$-process (Yokoyama and Walker, 2016). Therefore, these anomalies are inconsistent with stellar nucleosynthesis.

These anomalies may not be real and could be explained by small contributions from another species formed during APM analysis. The depletions in $^{192}$Os are much harder to reconcile, however, as they require an isobaric interference which affects all other Os isotopes, or a mechanism which results in the peak being under-represented. The latter may be the case here. The $^{192}$Os is located between the two isotopes of Ir, in this region of the $m/q$ spectrum. The background associated with the $^{192}$Os peak is higher than the other Os isotopes in the spectra. This may result in a larger amount of $^{192}$Os counts being removed as background during the IVAS correction resulting in lower final counts. Therefore, although the IVAS background correction in many cases produces reliable results in some specific cases may underestimate or overestimate an isotope in proximity to a highly abundant isotope.

An ideal solution to this is to produce a peak modelling algorithm which models the peak shape including peak tails. Peaks for single ions are largely symmetrical though they can be skewed towards high $m/q$ due to late emissions from the sample due to residual heat from the pulsing laser (Parman et al., 2015). The main peak can be approximated to a Gaussian function while any peak tail can be approximated to an exponential decay function. Combining these equations would allow the accurate determination of total counts produced by every peak to produce the $m/q$ spectra. This would demonstrate if the $^{192}$Os depletion and others are an artefact of the data reduction, while also increasing the accuracy of the APM measurement. This is currently limiting isotopic analysis by APM from reaching its theoretical potential, and future work will aim to model develop this algorithm. However, the methods employed here
produce isotopic abundances for Os Ir and W isotopes which are within 1 % of the expected terrestrial and solar abundances, and in many cases are much lower. This represents an 80 % improvement in precision over the results of Parman et al. (2015). Despite this progress our methodology is not currently sensitive enough to observe nucleosynthetic anomalies, and much more can be done to improve the sensitivity and accuracy of these measurements.

5.6.5. RE-Os GEOCHRONOLOGY

Radiogenic isotopic systems exhibit much greater variations which are discernible using our current data reduction methodology. The samples analysed with APM contain Re and Os. $^{187}$Re decays to $^{187}$Os by $\beta$ decay with a half life of 41.6 Ga (Selby et al., 2007). Isotopic measurements for Re and Os are consistent with TIMS analyses of the multi-HSE alloy within the calculated uncertainty, as well as with the pure Re and Os metals. Traditional Re-Os geochronology uses $^{188}$Os or $^{186}$Os to normalise the radiogenic nuclides. However, due to the potential overlap with Mo$^{+}$ ions, we used $^{189}$Os, as it does not have a overlap with Mo$^{+}$ and it is also an odd-numbered isotope, and is therefore less likely to have any other associated isobaric interferences. All the isotopes used to extract isotopic abundances for Re-Os geochronology ($^{185}$Re, $^{187}$Re, $^{187}$Os, and $^{189}$Os) are also of this nature.

The standards used are of terrestrial origin and are either pure Os or synthetic samples. Therefore, the current Re/Os will have no relationship to the age. We can therefore calculate a Re depletion age for these samples based on the $^{187}$Os/$^{189}$Os ratio of the sample and chondrite (Equation 5.6).
HSE1 and HSE2 have Re depletion ages of $3.6 \pm 0.9$ Ga and $4.2 \pm 0.7$ Ga respectively. Os1 has a supra chondritic $^{187}\text{Os}/^{189}\text{Os}$ ratio. A Re depletion age therefore, cannot be calculated as Os1 evolved with elevated Re/Os prior to refinement into the pure alloy and its initial Re/Os ratio is not known. In the case of the RMNs, data obtained by APM both $^{187}\text{Re}/^{189}\text{Os}$ and $^{187}\text{Os}/^{189}\text{Os}$ were plotted in Re-Os space (Figure 5.26). RMN1 through RMN4 plot on a line consistent with the 4.56 Ga Solar System isochron. RMN7 is also consistent with this within the analytical uncertainty. However, RMN5 and RMN7 are above this line within the calculated uncertainty of the measurement whereas RMN9 plots below the initial $^{187}\text{Os}/^{189}\text{Os}$ value. The calculated age from the ‘isochron’ between RMN1 through RMN4 is reasonable at 4.2 Ga with a MSWD of 0.080. However, due to the size of the calculated uncertainties in these measurements the corresponding resultant uncertainties associated with this age are large ($\pm 5.6$ Ga).

If we assume these RMNs had an solar initial $^{187}\text{Os}/^{189}\text{Os}$ ratio, it is possible to calculate an individual grain age using Equation 5.7 (Table 5.4).

$$t = \frac{1}{\lambda} \ln \left( \left( \frac{\frac{^{187}\text{Os}}{^{189}\text{Os}}_{\text{sample}}}{\frac{^{187}\text{Os}}{^{189}\text{Os}}_{\text{chondrite}}} - \frac{^{187}\text{Os}}{^{189}\text{Os}}_{\text{initial}} \right) + 1 \right)$$  (5.7)

The ages calculated with Equation 5.7 have smaller calculated uncertainties of $1.2 - 0.4$ Ga. This demonstrates the potential of APM analysis as applied to radiometric dating of grains which otherwise could not be dated. However, even with these large uncertainties RMN5 and RMN8 appear to be older than
the Solar System; \(5.3 \pm 0.7\) Ga and \(5.9 \pm 1.1\) Ga respectively.

An age for RMN9 cannot be calculated using Equation 5.7 as it has a lower than chondritic \(^{187}\text{Os} / ^{189}\text{Os}\) ratio. However, sub chondritic \(^{187}\text{Os} / ^{189}\text{Os}\) values indicate this RMN must be pre-solar. If we can assume a chonditic \(^{187}\text{Os} / ^{189}\text{Os}\) evolution prior to the formation of the Solar System we can calculate a Re-depletion age \((T_{RD})\) using Equation 5.6. This estimates an age of \(7.9 \pm 2.3\) Ga. This is older than the Solar System by \(3.3 \pm 2.3\) Ga i.e. it is beyond analytical uncertainty by 1 Ga. As there is still Re in the RMN this should be considered a minimum age due to subsequent radioactive decay. To account for this Re a model age \((T_{MA})\) was calculated with an estimated age of \(13.4 \pm 5.2\) Ga (Figure 5.27). These ages are very old and older than the Solar system and comparable to the age of the galaxy (Luck et al., 1980). However, these are only accurate if the galactic chemical evolution of \(^{187}\text{Os} / ^{189}\text{Os}\) follows a chondritic trend which is unlikely to be the case.

Could these old ages be introduced during data reduction? This may be the case for RMN5 and RMN8 that are only inconsistent with a Solar age by \(0.2 - 0.4\) Ga. These RMN show an enrichment in \(^{187}\text{Os}\). This could be caused by an elevated \(^{187}\text{Re-Os}\) peak, due to isobaric interferences. However, this effect is not observed in other RMN and HSE specimens which have similar geochemistry. Furthermore, because the \(^{187}\text{Re-Os}\) peak is odd-numbered, the possible causes of an isobaric interference are limited. Any interference must also only affect the \(^{187}\text{Re-Os}\) peak as all other isotopes appear to have solar relative abundances. Another possible explanation for the old ages is the \(^{185}\text{Re}\) peak used to calculate the \(^{187}\text{Re}\) contribution may be depleted. However, as discussed previously depletions in APM datasets are difficult to produce. The Re1 and Re2 data suggest that \(^{185}\text{Re}\) is, if anything, slightly enriched which would result in a \(^{187}\text{Os}\) depletion relative to the TIMS data as was the case for
HSE1 and HSE2. As only a small change in our approach could result in these RMN being Solar within analytical uncertainty we cannot convincingly make a case for these being true pre-solar grains. RMN9 however does contain large $^{187}$Os anomalies that would require more than a slight interference correction.

While we cannot categorically rule out the possibility that this ‘old’ RMN9 is also produced as an artefact in the APM, all other analysis both of RMNs and standards, are inconsistent with that interpretation. We have shown that other RMNs fall on the Solar System Re-Os isochron and our analysis of standard materials produce results consistent with TIMS analyses. Therefore, from the APM analyses conducted so far it appears that APM can robustly measure these isotopes. Therefore, it is likely that this ‘old’ ages or at least depleted $^{187}$Os signature is a real feature. If the age is correct, these grains are pre-solar and also, to the best of our knowledge, the oldest solid objects ever dated. However, pre-solar grains are defined by the presence of nucleosynthetic anomalies (Meyer and Zinner, 2006; Anders and Zinner, 1993; Clayton and Nittler, 2004; Nittler, 2003) which are not detected in these RMNs. Although the precision in the APM measurements using our methodology for data reduction may not be sufficient to detect an r-process signature.

If this age is real, RMN9 represent a new type of pre-solar grain, which originated from a stellar source where nucleosynthesis was not occurring. Furthermore, if this RMN is pre-solar our assumption for the initial $^{187}$Os/$^{189}$Os value used to calculate the age is invalid. In fact, $^{187}$Os/$^{189}$Os ratios prior to the formation of the Solar System would be lower as less $^{187}$Re will have decayed to $^{187}$Os (Luck et al., 1980; Clayton et al., 1973) which would increase the age further.

Additionally, if real, this age is unlikely to represent a formation age of the
RMN as grain survival times in the interstellar medium are short (<4x10^8 yr) (Jones et al., 1994). However, this study focussed on silicate and carbonaceous materials, it is possible that metallic alloys such as RMNs may be more robust to grain destruction mechanisms and may be able to survive for longer timescales in the interstellar medium (Mouri and Taniguchi, 2000). This is at least partially supported by the observation of older cosmic-ray exposure ages associated with iron meteorites vs chondritic meteorites which is in part due to the greater mechanical strength of iron meteorites (Hartmann et al., 1999). However, for RMNs to survive from formation to insertion into the protoplanetary disk would require metal grain survival times to be an order of magnitude longer than silicates. Therefore, assuming that RMNs cannot survive intact they must be derived from stars. The parent star of these RMN can be approximated as a closed system relative to galactic chemical evolution that preserves the initial Re/Os present when the star formed. These ages may represent the formation age of the parent star and also the average galactic 187 Os/189 Os at the time it formed. The absence of a nucleosynthetic anomaly in these RMNs require them to originate from stars which have not begun or will not begin nucleosynthesis. Possible sources include mass loss from low mass stars which produce planetary nebulae or mass ejections from AGB stars prior to the third dredge up where freshly synthesised s-process nuclides are mixed into the outer shell of the star (Vassiliadis and Wood, 1993; Weymann, 1963). Based on the ages of 1 – 2 Ga we can postulate the size of the star that created the RMNs to be between 2 – 3 solar masses (Prialnik, 2000). This would represent the main sequence lifetimes for this star (Prialnik, 2000).

Alternatively, the elevated 187 Os/189 Os may not represent an old age but an initially heterogeneous protoplanetary disk with respect to 187 Os/189 Os. RMN9 has a lower 187 Os/189 Os ratio than the initial value for the bulk Solar System.
despite the ongoing decay of $^{187}$Re during the intervening time period. However, this may be due to the low Re/Os ratio of RMN9. RMN9 unlike the others is hosted in the sulphide rim of a chondrule not an ultra-refractory inclusion. Chondrules are thought to form for a longer duration than CAIs (Connelly et al., 2012) and may form at larger heliocentric distances than CAIs (Scott and Krot, 2005). RMN9 also contains Pd which should not be present in RMNs derived through condensation as it has a lower 50% condensation temperature than that of Fe (Lodders, 2003), and has been assumed to form in solid solution with the condensation of Fe metal (Palme, 2008). The presence of Pd is likely to be produced by remobilisation of Pd. This is supported by the lack of W and Mo which are removed during oxidation (Fegley and Palme, 1985). However, here the conditions promoted the mobilisation of Pd into the metal. Despite this alteration, we still observe a depletion in $^{187}$Os/$^{189}$Os. Therefore, this sulphide grain must have formed in an $^{187}$Os/$^{189}$Os depleted reservoir or incorporated a HSE rich particle with sub-solar $^{187}$Os/$^{189}$Os ratios. Therefore, RMN9 may not be a pre-solar grain as its formation from its petrological context and chemistry imply at least some nebular processing but is comprised of ‘old’ pre-solar Os.

Measurements of Ru and W isotopes suggest that the protoplanetary disk may have been isotopically heterogeneous (Fischer-Gödde et al., 2015; Holst et al., 2015). Conversely, isotopic measurements of Os show it is well mixed in the protoplanetary disk (Brandon et al., 2005; Yokoyama et al., 2007; Walker, 2012). However, within acid residues of primitive meteorites Os isotopes exhibit diverse isotopic abundances (Reisberg et al., 2009; Yokoyama et al., 2010). This suggests that although Os is well mixed the carrier phases of Os were not equilibrated therefore individual grains may preserve isotopic anomalies.

Previously, RMNs were thought to form at high temperatures close to the proto-sun through condensation or crystallisation (Berg et al., 2009; Schwan-
These processes homogenise the isotopic heterogeneity and produce a solar trend consistent with that seen in RMN1 through RMN4 and RMN5 through RMN8. Conversely, \(^{187}\text{Os}/^{189}\text{Os}\) ratios of RMN9 are not equilibrated and therefore must have formed elsewhere or at least ‘old’ isotopic Os was inherited by this RMN. However, disk models suggest that only the inner Solar System experiences temperatures high enough to form RMNs (Lecar et al., 2006; Ciesla, 2009; Berg et al., 2009). This means the isotopic diversity observed RMNs is unlikely to be due to RMNs forming at various heliocentric distances in distinct isotopic reservoirs determined by disk dynamics. Isotopic heterogeneity must have been inherited from a population of RMNs which were already present in the giant molecular cloud (GMC) derived from a variety of stellar environments consistent with the predictions of Daly et al. (2017).

In either case it would appear there are at least two main RMN populations, one where the \(^{187}\text{Os}/^{189}\text{Os}\) isotopes have been equilibrated during high temperature processing in the inner disk and one which preserves a heterogeneous \(^{187}\text{Os}/^{189}\text{Os}\) signature inherited from the GMC and survived nebula processing. Further isotopic analyses of RMNs using APM may reveal a variety of isotopic signatures.

5.7. CONCLUSIONS

Real APM datasets contain several sources of uncertainty beyond simple counting statistics. Here, we present a methodology to extract isotopic information from samples using APM, specifically for those containing Re and Os. Our methodology of measuring isotopic abundances is robust to within 1% for pure elements and complex alloys. These measurements have been corroborated
Figure 5.26: Re-Os plot of RMN1 through RMN5, RMN7 through RMN9. RMN1 through RMN4 and RMN8 plot on the 4.56 Ga Solar System isochron, however, RMN5 and RMN7 plot above the line, while RMN9 has a $^{187}\text{Os}/^{189}\text{Os}$ below that of the initial value of the Solar System (Lodders, 2003; Anders and Grevesse, 1989).
Figure 5.27: Os vs age plot of HSE1 – 2 and RMN9. Showing Re depletion ages and Re model ages for the samples. Os1 is shown also but due to its supra-chondritic values a model age cannot be calculated. RMN9 has pre-solar $T_{RD}$ and $T_{MD}$ ages assuming chondritic evolution. HSE1 – 2 are slightly depleted in $^{187}$Os/$^{189}$Os relative to the TIMS measurement.
by those obtained with TIMS. Therefore, the Re-Os isotopic compositions of RMNs are able to be analysed by APM. Solar isotopic abundances of W, Re, Os and Ir exist within all RMNs of this study. The accuracy of APM is sufficient to utilise Re-Os radiometric dating. Seven RMNs plot on the 4.56 Ga Solar system isochron, however one RMN has a lower $^{187}$Os/$^{189}$Os value than the initial value for the Solar System. While the presence of unknown artefacts in the APM m/q spectra cannot be categorically ruled out, these are not present in other APM datasets from RMNs and also standard materials which have been corroborated with TIMS, therefore this anomaly is likely to be real. Calculated model ages for this grain is pre-solar substantially outside of the analytical uncertainty and has a minimum age of $7.9 \pm 2.3$ Ga assuming a galactic Re-Os evolution trend similar to that of chondrites which makes this RMN the oldest material dates so far to the best of our knowledge, and demonstrates that this RMN is demonstrably pre-solar. Pre-solar model ages for RMNs are consistent with the prediction of Daly et al. (2017) for the existence of a surviving population of pre-solar RMNs that are inherited from the GMC. These include RMNs which record the oldest ages yet reported.

5.8. ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council via their Australian Laureate Fellowship program. This work was conducted within the Geoscience Atom Probe Facility at Curtin University, which is part of the Advanced Resource Characterization Facility (ARCF). The Advanced Resource Characterisation Facility is being developed under the auspices of the National Resource Sciences Precinct – a collaboration between CSIRO, Curtin University and The University of Western Australia – and is supported by the Science and Indus-
try Endowment Fund (SIEF RI13 – 01). The authors acknowledge the use of Curtin University’s Microscopy and Microanalysis Facility, whose instrumentation has been partially funded by the University, State and Commonwealth Governments, SMR acknowledges support from the ARC Core to Crust Fluid System COE (CE11E0070). The authors would also like to thank Dr. Daniel Schwander for providing the multi-HSE alloy and experimental run products used as standard materials in this work, and Ms Jennifer Porter for her support.

5.9. REFERENCES


Holst, J. C., Paton, C., Wielandt, D., and Bizzarro, M. (2015). Tungsten isotopes in bulk meteorites and their inclusions—Implications for processing of presolar...


Chapter 5


Mukherjee, S., Givan, U., Senz, S., Bergeron, A., Francoeur, S., De La Mata, M.,


CHAPTER 6

Thesis Conclusions

Detailed analysis of meteoritic components improve our understanding of the processes which formed our Solar System. Refractory metal nuggets (RMNs) are a sub-micrometre phase which are thought to form at the very beginning of our Solar System (Berg et al., 2009; Wark and Lovering, 1976; Palme and Wlotzka, 1976; Lodders, 2003) and perhaps even before (Croat et al., 2013; El Goresy et al., 1978). In this work a combination of novel and established techniques were applied that facilitated the identification and high resolution analysis of refractory metal nuggets (RMNs) in situ. The information extracted during these analysis calls into question the current consensus for the origin on RMNs.

One challenge for the analysis of refractory metal nuggets (RMNs), is identifying them in situ within meteorite samples. This work devised an approach which rapidly identifies RMNs in situ using a combination of X-ray fluorescence microscopy at the Australian Synchrotron and Feature mapping software in the INCA suite from Oxford Instruments. This approach was used to identify >100 RMNs in situ across eight carbonaceous chondrite meteorites. RMNs were
observed in all components of carbonaceous chondrites, not only CAIs as had been widely assumed previously (i.e. Berg et al. 2009; Bischoff and Palme 1987; Blander et al. 1980; Eisenhour and Buseck 1992; El Goresy et al. 1978; Fegley and Kornacki 1984; Grossman et al. 1977; Palme and Wlotzka 1976; Palme et al. 1982; Sylvester et al. 1990; Wark 1986 and Wark and Lovering 1976). These RMNs were analysed further using high resolution techniques such as transmission Kikuchi diffraction (TKD) and atom probe microscopy (APM). In situ analyses of RMNs using these novel high resolution techniques have increased our understanding of how these grains might form, with implications for Solar System processes, disk dynamics and the pre-solar component inherited by our Solar System from the Giant Molecular Cloud (GMC).

Chemical analysis of RMNs in situ using energy dispersive X-ray spectroscopy revealed a range of compositions. This compositional diversity present in the RMN population cannot be explained by any of the established mechanisms such as equilibrium condensation in the nebula environment (Berg et al., 2009), crystallisation from a silicate, or CAI melt (Schwander et al., 2015b), or sulphidation (Blum et al., 1988), in isolation or in tandem. These data suggest that the compositional heterogeneity of RMNs could be reconciled if the protoplanetary disk inherited a diverse population of RMNs from the GMC (Chapter 2).

Crystallographic analysis of RMNs using TKD revealed textures which had not been reported before in RMNs. One cluster of RMNs exhibited annealing twins which form at high temperatures (Dai et al., 2001). If the formation temperatures of annealing twins could be constrained for alloys with similar compositions to RMNs, these textures could be used as a coarse thermometer to measure the temperatures reached during transient heating events in the protoplanetary disk. Other RMNs had textures which imply that they formed
through replacement of metal with sulphide (Lauretta et al., 1996) and could be used to constrain sulphur fugacity in the nebula. Some RMNs exhibited nucleation textures and crystallographic relationships with their host, suggesting that the host formed subsequent to the RMNs. The variety of textures observed in RMNs through TKD suggest they have a complex formation history (Chapter 3).

APM revealed some RMNs are S-bearing. The associated textures of these RMNs and their host inclusion suggests that these RMNs were initially ‘free floating’ in the protoplanetary disk prior to incorporation into their host. The location of RMN formation, as well as other refractory inclusions, is thought to occur close to the proto-sun where temperatures are high (\(>1400\) K) (MacPherson et al., 2005; Ciesla, 2010), while sulphidation is thought to occur between 0.5 – 1.5 AU where temperatures are lower (500 – 700 K) (Lauretta et al., 1996; Ciesla, 2015). These data suggest there was an early period of rapid migration of refractory materials in the inner protoplanetary disk that allowed RMNs, and other refractory materials to migrate away from the proto-sun (Shu et al., 1997; Ciesla, 2007, 2010; Bai, 2014), into the sulphidation region (Lauretta et al., 1996; Ciesla, 2015), before being returned (Cuzzi and Weidenschilling, 2006) and incorporated into their refractory inclusion (Chapter 4).

APM is capable of measuring isotopic abundances. The theoretical sensitivity of the atom probe for the detection of isotopic anomalies at counts \(>10^6\) was calculated to be \(>\epsilon 40\). Data reduction methods were evaluated to devise a approach to extract isotopic information from the dataset that account for the background correction, ranging method, hydride formation and isobaric interferences. APM analysis was compared to thermal ionization mass spectrometry (TIMS) on progressively more complex terrestrial samples from pure elemental Re and Os, through to synthetic highly siderophile element (HSE) alloys analogous to RMNs (Schwander et al., 2015a). APM isotopic abundances
derived from the standards were in agreement with the TIMS data within the limits of uncertainty of the APM measurements and within 1% of expected relative terrestrial abundances (de Laeter et al., 2003). Therefore, robust isotopic analysis of RMNs using APM is possible. RMNs here appear to have solar isotopic abundance ratios for all elements within the sensitivity of the technique suggesting a Solar System origin for these RMNs (Chapter 5).

The Re-Os radiometric dating system was applied to RMNs. This revealed that five RMNs plot on an isochron consistent with the age of the Solar System, however the associated uncertainties are large. Assuming a solar initial $^{187}\text{Os}/^{188}\text{Os}$ ratio individual RMN ages were calculated which were also consistent with the age of the Solar System with reduced associated uncertainties. However, two other RMNs produced individual grain ages that are older than the Solar System by at least 0.2 Ga, while another unusual RMN had an $^{187}\text{Os}/^{189}\text{Os}$ ratio below the Solar System initial value (Lodders, 2003), which strongly implies this RMN is pre-solar. Re depletion and Re model ages for the RMN with the sub-solar $^{187}\text{Os}/^{189}\text{Os}$ ratio generate ages $>5.5$ Ga, which is the oldest age calculated from any material. Brandon et al. (2005); Yokoyama et al. (2007); Walker (2012); Reisberg et al. (2009) and Yokoyama et al. (2010) have shown that Os is well mixed in bulk meteorite samples, however, on a granular level Os isotopic heterogeneity is preserved (Reisberg et al., 2009; Yokoyama et al., 2010), indicating the initial Os isotopic diversity was not equilibrated in the protoplanetary disk. These old RMNs are direct evidence for this heterogeneity, and show that some RMNs preserve a pre-solar component consistent with the predictions made in Daly et al. (2017) and Chapter 2.
6.1. FUTURE WORK

The results obtained in this work have opened several avenues for further research. The grain identification approach combining Feature mapping and XRF synchrotron element mapping to identify RMNs (Chapter 2) could be applied to search for other sub-micrometre phases \textit{in situ}. The approach could be applied to search for HSE-rich phases in terrestrial samples (O’Driscoll and González-Jiménez, 2016). Analyses of large numbers of HSE-rich phases in a variety of lithologies may inform our understanding of HSE ore genesis.

The textures revealed in RMNs using TKD and their interpretations would benefit significantly from confirmation by experiment. For example, it would be worthwhile demonstrating that the HSEs do migrate into isolated metal alloys during sulphidation of HSE bearing metal grains in the nebula environment (Chapter 3). Furthermore, the temperature sensitive formation of annealing twins has the potential to act as a coarse thermometer. This thermometer could be calibrated by experiment by heating similar synthetic alloys to observe the onset of annealing. This would allow us to quantify the maximum temperature reached during transient heating events in the protoplanetary disk (Chapter 3). It would also be useful to calculate the abundance of S that can diffuse into an RMN from a nebula gas to evaluate whether RMN cycling in the disk is necessary to incorporate S into their structure (Chapter 4).

The constraints on the precision of HSE isotopic abundance measurements obtained using APM and corroboration with TIMS (Chapter 5) could be expanded to encompass all elements. It may be possible to improve on the data reduction methods detailed in this work by applying peak modelling algorithms rather than ranging methods within the IVAS software. The IVAS ranging
method neglects counts from the peak tails which under-lap subsequent peaks. If these peaks, including their tails, could be accurately modelled, the total contribution of each isotope could be calculated and accounted for. This may be the reason why some isotopes are anomalous within the uncertainty of the APM measurement, as they may be underestimated or overestimated slightly due to under-lapping peak tails.

Re-Os geochronology of RMNs indicate that most record a Solar System age, however, some appear to be older. RMNs from extracted from a variety of meteoritic components should be analysed by APM under the same conditions to confirm this observation, as well as several RMNs from the same inclusion to increase the precision of the Solar System isochron. Furthermore, it may be beneficial to corroborate the result using another technique to ensure that the old RMNs described here do not represent an unidentified analytical artefact in APM. An ideal candidate would be the Chicago Instrument for Laser Ionization (CHILI) which is capable of analysing grains of similar size to RMNs, whilst separating three elements during ionisation and removing the isobaric interferences (Kööp et al., 2016; Stephan et al., 2016). This trait would be particularly useful to separate the isobaric interference of the $^{187}$Os and $^{187}$Re isotopes.

The Re-Os geochronology through atom probe tomography could also be applied to other Os bearing micro-alloys such as those observed in cosmic spherules (Rudraswami et al., 2014), in Martian meteorites (Lorand et al., 2012, 2014), or terrestrial HSE-alloys such as those observed in ophiolitic peridotites (Augé, 1988) or chromites (O’Driscoll and González-Jiménez, 2016). The ability to date individual sub-micrometre alloys from these types of samples provided by APM could shed light on the timing and nature of HSE mineralisation on Mars and on Earth.
6.2. REFERENCES


APPENDIX A

FIRST AUTHOR JOURNAL PUBLICATIONS

A.1. PAPER 1 — IN SITU ANALYSIS OF REFRACTORY METAL NUGGETS IN CARBONACEOUS CHONDRITES


REPRINTED WITH PERMISSION OF ELSEVIER:
INTRODUCTION
1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightlink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS
2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
   "Reprinted from Publication title, Vol / edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

**LIMITED LICENSE**

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at [http://www.sciencedirect.com/science/journal/xxxxx](http://www.sciencedirect.com/science/journal/xxxxx) or the Elsevier homepage for books at [http://www.elsevier.com](http://www.elsevier.com); Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at [http://www.elsevier.com](http://www.elsevier.com). All content posted to the web site must maintain the copyright information line on the bottom of each image.

**Posting licensed content on Electronic reserve:** In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

**Preprints:**

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

**Accepted Author Manuscripts:** An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-
incorporated changes suggested during submission, peer review and editor-author communications. Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

**Published journal article (JPA):** A published journal article (JPA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment. Policies for sharing publishing journal articles differ for subscription and gold open access articles:

**Subscription Articles:** If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded JPAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect. If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

**Gold Open Access Articles:** May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository. 19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded JPAs as part of
the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated. The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:
- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
STATEMENT OF AUTHORSHIP

TITLE OF PAPER: In situ analysis of Refractory Metal Nuggets in carbonaceous chondrites.

PUBLICATION STATUS: Accepted

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript for this publication.

Overall Percentage: 69%

Signature: {signature} Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Paper: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: {signature} Date: 20/02/17
Name of Co-Author: Kathryn A. Dyl

Contribution to the Paper: Helped in Synchrotron data reduction and editing and revision of the manuscript.

Overall Percentage: 2%

Signature: Kathryn A. Dyl Date: 2/22/17

Name of Co-Author: Lucy V. Forman

Contribution to the Paper: Helped in the final review of the manuscript.

Overall Percentage: 2%

Signature: Lucy V. Forman Date: 2/2/17

Name of Co-Author: Katy A. Evans

Contribution to the Paper: Developed the condensation model helped in the final review of the manuscript.

Overall Percentage: 5%

Signature: Katy A. Evans Date: 2/2/17

Name of Co-Author: Patrick W. Trimby

Contribution to the Paper: Helped in feature mapping TKD and the final review of the manuscript.

Overall Percentage: 5%

Signature: Patrick W. Trimby Date: 2/2/17

Name of Co-Author: Steve Moody


Overall Percentage: 1%

Signature: Steve Moody Date: 2/2/17
Appendix A

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)

Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Hongwei Liu

Contribution to the Paper: Helped with TEM analysis.
Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Simon P. Ringer

Contribution to the Paper: Helped in the final review of the manuscript.
Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Christopher G. Ryan

Contribution to the Paper: Helped with Synchrotron analyses and GeoPIXE data reduction.
Overall Percentage: 2%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Martin Saunders.

Contribution to the Paper: Helped with TEM analysis.
Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17
In situ analysis of Refractory Metal Nuggets in carbonaceous chondrites

Luke Daly a,⇑, Phil A. Bland a, Kathryn A. Dyl a, Lucy V. Forman a, Katy A. Evans a, Patrick W. Trimby b, Steve Moody b, Limei Yang b, Hongwei Liu b, Simon P. Ringer c, Christopher G. Ryan d, Martin Saunders e

a Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
b Australian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW 2006, Australia
c Australian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW 2006, Australia
d CSIRO Earth Sciences and Resource Engineering, 26 Dick Perry Avenue, Kensington, Perth, WA 6151, Australia
e Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, WA 6009, Australia

Accepted for publication 17 November 2016; available online 25 November 2016

Abstract

Micrometre to sub-micrometre-scale alloys of platinum group elements (PGEs) known as Refractory Metal Nuggets (RMNs) have been observed in primitive meteorites. The Australian Synchrotron X-ray Fluorescence (XRF) beamline, in tandem with the Maia detector, allows rapid detection of PGEs in concentrations as low as 50–100 ppm at 2 μm resolution. Corroborating these analyses with traditional electron microscopy techniques, RMNs can be rapidly identified in situ within carbonaceous chondrites. These results dispute the assumption of most previous studies: that RMNs are unique to Ca–Al-rich inclusions (CAIs). We find that RMNs are, in fact, observed within all components of carbonaceous chondrites, such as the matrix, chondrules (consistent with observations from Schwander et al. (2015b) and Wang et al. (2007)), and sulphides; though the majority of RMNs are still found in CAIs. The chemistry of RMNs reveals a complex diversity of compositions, which nevertheless averages to CI chondrite abundance ratios. This implies that RMNs are the dominant, if not sole host phase for PGEs. One hundred and thirteen RMNs from this study are combined with reported compositions in the literature, and compared to condensation model compositions similar to Berg et al. (2009), RMNs derived experimentally by precipitation (Schwander et al., 2015a), host phase and host meteorite. Comparisons reveal only weak correlations between parent body processes (sulphidation) and nebular processes (condensation and precipitation) with RMN compositions. It appears that none of these processes acting in isolation or in tandem can explain the diversity observed in the RMN population. Our interpretation is that the Solar Nebula inherited an initially compositionally diverse population of RMNs from the Giant Molecular Cloud; that a variety of Solar System processes have acted on that population; but none have completely homogenised it. Most RMNs have experienced disk and asteroidal processing, but some may have retained a primordial composition. RMNs have been identified in pre-solar graphite grains (Croat et al., 2013). We anticipate that pre-solar RMNs will be present elsewhere in primitive meteorites.

Keywords: Refractory Metal Nuggets; Solar Nebula; Solar System; Origin; Meteorites; Carbonaceous chondrites

⇑ Corresponding author.
E-mail address: luke.daly@postgrad.curtin.edu.au (L. Daly).

http://dx.doi.org/10.1016/j.gca.2016.11.030
0016-7037/© 2016 Elsevier Ltd. All rights reserved.
1. INTRODUCTION

Ca–Al-rich inclusions (CAIs) are the oldest solids to have formed in the Solar System, with an age of 4567.30 ± 0.16 Ma (Connolly et al., 2012). CAIs have been interpreted as primary high-temperature condensates which formed close to the protosun during the initial stages of the Solar Nebula, although some inclusions have experienced some degree of remelting (MacPherson et al., 2005). Analyses of CAIs indicate a significant enrichment in the platinum group elements (PGEs) W, Re, Os, Ir, Ru and Pt of between 22.8 and 11.9 times the elemental abundance observed in carbonaceous Ivuna-type (CI) chondrules (Grossman, 1973; Wänke et al., 1974). This enrichment is predicted to manifest itself in the form of Refractory Metal Nuggets (RMNs) within these early condensates (Grossman and Ganapathy, 1976). This was confirmed by the observation of PGE-rich metal grains within CAIs in Allende (Palme and Wlotzka, 1976; Wark and Lovering, 1976).

Since this discovery, there has been ongoing debate over how RMNs formed. Initially Palme and Wlotzka (1976) found the composition of the RMN contained within a 20 µm CAI-hosted sulphide from Allende, plotted onto an ideal condensation curve for a nebular gas. These authors demonstrated that this RMN could form as a homogeneous primary condensate in the Solar Nebula, noting the high 50% condensation temperatures of the PGEs within the RMN would imply that these alloys should condense first. The RMN contained CI abundance ratios of the PGEs which indicated an equilibrium condensation temperature slightly higher than that of Fe. They also calculated that the expected abundance of RMN nucleation centres in the nebular would be sufficient, although this has been disputed by later studies (Petaev and Wood, 2005). However, subsequent studies have shown that these RMNs described by Palme and Wlotzka (1976) and Wark and Lovering (1976) had also been affected by secondary alteration on the parent body, including oxidation, sulphurisation, and exsolution (Bischoff and Palme, 1987; Blum et al., 1988; Palme and Wlotzka, 1976). These RMNs, therefore, cannot be considered primary nebular condensates (Bischoff and Palme, 1987; Blum et al., 1988).

To ascertain whether such grains could be produced from condensation in the Solar Nebula, Grossman (1973) calculated the chemical composition of the solid phases that would condense from a cooling solar gas. This work has been developed and refined with more recent calculations for condensation in the Solar Nebula by Fegley and Palme (1983) and Lodders (2003). These studies indicated that the PGEs should condense between 1392 K and 1821 K at 10⁻⁴ bar. However, it should be noted that local variability in the nebula dust component may cause these predicted condensation temperatures to vary (Petaev and Wood, 2005). RMNs appear to be the host for these elements in primitive carbonaceous chondrules. These predictions were supported by observations of sub-µm RMNs hosted within unaltered ‘fluffy’ type A CAIs from Allende. These RMNs had compositions consistent with a condensation origin, particularly, the presence of elements such as Mo and W, which are easily lost with even minor degrees of alteration (Palme et al., 1998). These RMNs also exhibited none of the secondary alteration textures observed in previous studies (Blander et al., 1980; Eisenhour and Buseck, 1992). Individual RMNs with compositions consistent with condensation origin have also been described by Eisenhour and Buseck (1992).

Further analysis of RMNs divided them into two distinct families within CAIs (El Goresy et al., 1978): large 1–1000 µm multiphase inclusions containing micrometre-sized grains of RMNs (Blum et al., 1988), and isolated micrometre to sub-micrometre RMNs (Wark, 1986). Studies by El Goresy et al. (1977) and El Goresy et al. (1978) suggested that RMNs in multiphase inclusions had non-solar abundance ratios of PGEs and that isolated RMNs had solar abundance ratios. This indicated, alongside the condensation sequence of minerals which hosted the multiphase inclusions, that they could have had a pre-solar origin and conversely isolated grains may have had a nebular origin. However, such an origin for the multiphase inclusions is unlikely as these samples yielded solar isotopic ratios for Mg, Fe, Mo, Ru and W (Hutcheon et al., 1987). A pre-solar origin for RMNs has also been suggested by Wark and Lovering (1976) for non-solar PGE abundance ratios within isolated RMNs. Recent work has observed RMNs within pre-solar graphite (Croat et al., 2013) and a possible mechanism for the formation pre-solar-RMNs in asymptotic giant branch stars was discussed in Schwander et al. (2014). These are the only RMNs that can be interpreted as having a pre-solar origin with relative certainty, though due to their small size, isotopic analyses have not been possible.

The analysis of RMNs has been limited by the difficulty of finding sufficient numbers due to their small size. This has meant that the contextual work on RMNs has been restricted to CAIs. Anders et al. (1975) noted that PGEs were enriched in residue samples of Allende (CV3oxA) that have been dissolved with strong acids. This observation prompted Berg et al. (2009) to study similar residues from the Murchison (CM2) meteorite using an acid digestion technique devised by Amari et al. (1994). This procedure concentrated RMNs and permitted the analysis of several hundred grains rather than the <20 analysed in situ in CAIs from previous studies. Following earlier work, Berg et al. (2009) proceeded with the assumption that RMNs in their residues had previously been associated with CAIs. The compositions of RMNs contained within these residues from energy-dispersive X-ray spectroscopy (EDS) were in agreement with theoretical equilibrium condensation calculations for similar grains (Campbell et al., 2001). This led Berg et al. (2009) to conclude that all the analysed grains were nebula condensates. However, later work by Schwander et al. (2014), who used an extra density separation to further concentrate RMNs, from Murchison, Allende and Leoville residues, showed that some, but not all RMNs from these residues have been affected by metamorphic oxidation and sulphidation on the parent body which resulted in the loss of W and Mo.
The abundant grains found in acid residues have significantly expanded the number of analyses of RMNs, but the loss of contextual information during acid dissolution of the bulk sample severely limits interpretation of the data. The assumption that has arisen in prior studies is that RMNs are unique to CAIs (Berg et al., 2009; Bischoff and Palme, 1987; Blander et al., 1980; Eisenhour and Buseck, 1992; El Goresy et al., 1978; Fegley and Kornacki, 1984; Grossman et al., 1977; Palme and Wlotzka, 1976; Palme et al., 1982; Sylvester et al., 1990; Wark, 1986; Wark and Lovering, 1976). However, recent work by Wang et al. (2007) described RMNs within chondrules. Schwander et al. (2015) analysed over 200 RMNs in situ including the observation of RMNs within the matrix. This study suggests that the compositions of RMNs and their petrological context are inconsistent with a simple condensation model and that precipitation is a more likely mechanism for RMN formation, whereby the PGEs are dissolved into a silicate, or CAI melt. On quenching of this melt spherical RMNs are precipitated. This theory is supported by experimentally derived RMN-like precipitates from CAI melts in Schwander et al. (2015).

A diversity of terms can be found in the literature applied to these materials. In this study we will adopt the following terminology: RMNs will refer to any micrometre – sub-micrometre metal alloy grain that contains >1 atomic percent (at.%) of any PGE (Re, Os, Ir, Pt, Ru, Rh, Pd, W or Mo). If there is sufficient evidence to suggest a mechanism for how the RMN formed, a suitable precursor shall be attached to the start of the word i.e. pre-solar-RMN for an RMN with a demonstrably pre-solar origin similar to the naming scheme adopted by Croat et al. (2013). This can be extended to any process, e.g. sulphidation would produce sulphidation-RMNs, and primary nebular condensates would be designated condensation-RMNs, etc.

This paper presents a multidisciplinary study using the Australian Synchrotron (AS) X-ray Fluorescence (XRF) beamline alongside scanning electron microscopy (SEM) with EDS to facilitate rapid identification of RMNs in situ. The applications of these techniques allow rapid non-destructive quantification and determination at sub-micrometre scales whilst preserving context. The results of these analyses call into question the assumption that RMNs are unique to CAIs: we observe them in all chondritic components; reiterating and expanding upon observations made by Schwander et al. (2015) and Wang et al. (2007). Comparing RMN compositions to equilibrium condensation models revealed a significant inconsistency. This suggests condensation in the nebular environment is unlikely for a large fraction of RMNs.

2. METHOD

The samples analysed in this study are thin and thick sections from the primitive carbonaceous chondrites: C2-ungrouped Acfer 094, C2-ungrouped Adelaide, CO3.0 ALH77307, CV3 Allende, CR2 Kaidun, CR2 Renazzo, and Murchison CM2, and CV3 Vigaran. Each thin sections has an area of approximately 1–4 cm².

2.1. X-ray fluorescence microscopy

The samples were analysed using the XRF beamline at the AS, combined with the Maia Si-detector (Ryan et al., 2010) with a dwell time of 0.488 ms per pixel. A more detailed discussion of the technique and its application to meteorites can be found in Dyl et al. (2014). This technique allows for rapid data collection over large areas with a resolution of 2 μm. The detector can analyse elements between the 4 and 18 keV range (Ryan et al., 2010). A particularly useful detail for this study is that PGE Lα, β, and γ energy peaks for Os, Ir and Pt lie in the most sensitive region of the spectrum (Fig. 1), with L-β peaks at 8.910, 9.174 and 9.441 keV, respectively (Dyl et al., 2014). This permits detection down to 50–100 ppm for these elements (Cleverley et al., 2012).

The data collected was interpreted using the GeoPIXE software, which uses a dynamic analysis matrix to deconvolve peaks of each individual element to generate elemental distribution maps (Ryan et al., 1995). The element maps are used to identify pixel-sized hotspots of PGEs as likely candidates for the location of RMNs with slight adjustments to contrast and brightness to make the most abundant regions stand out from the background.

The sample of Acfer 094 had been gold-coated for previous studies, and although this has been largely removed, a small residue remains. This generated a slight problem as the gold peak is in the same region of the spectrum as the Os, Ir, and Pt energy peaks. This interfered with the spectrum, and generated false positives. In the case of this sample, the problem was countered by analysing each spectrum on an individual basis to ensure true RMNs were observed rather than a residual gold particle.

Due to the penetrating nature of the X-ray beam employed (18.5 keV), fluorescence X-rays from elements are received from up to 100 μm depth into the sample (Dyl et al., 2014). This generates a problem when trying...
to corroborate PGE hotspots with established techniques such as SEM and EDS, which only have penetration depths of ~1 μm. This, coupled with the size of the RMNs, which tend to be 90 nm–1.2 μm (Berg et al., 2009) means that any one PGE hotspot identified with the synchrotron has a 99% chance of being buried beneath the surface of the sample. However, this is also a benefit as a larger number of in situ grains are observed.

2.2. Scanning electron microscopy

The samples were analysed using two instruments: the Zeiss 1555 VP-FESEM at the Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia, and the Zeiss EVO50 LaB6 at the Australian Centre for Microscopy and Microanalysis (ACMM), the University of Sydney. Both instruments are equipped with 80 mm² high count rate silicon drift detector (SDD) EDS detectors. In both cases an accelerating voltage of 25 kV was used. Element maps derived from the AS data were geo-referenced with the live SEM image using the image overlay feature in Oxford Instrument’s AZtec software. This method allowed rapid searching for RMNs present at the surface of the sample with high accuracy. This process was augmented by the feature mapping software in the Inca suite, which allowed whole thin section searches based on contrast bands. As RMNs are one of the densest phases in meteorites and backscatter microscopy reveals density differences in mineral phases; the brightest spots were refractory metal grains. This allowed us to analyse every metal grain at the surface of a sample. This method detected all the RMNs that were found using the combined synchrotron and EDS geo-referencing technique described above, along with a few others that were missed. The composition of the grains was derived using standardless quantitative analysis, using the standard database embedded within the AZtec software. Although a total of 145 RMNs were measured, the EDS spectra obtained through the feature mapping technique did not permit quantitative compositional measurements. 113 RMNs were relocated in the chamber. Samples prepared in this way are denoted one PGE hotspot identified with the synchrotron has a 99% chance of being buried beneath the surface of the sample. However, this is also a benefit as a larger number of in situ grains are observed.

As Schwander et al. (2015) described, it should be noted that Fe may be slightly overestimated in some samples due to small amounts of Fe in the surrounding phases, increasing the Fe signal. Also Ni and Fe are likely to be elevated in RMNs found in Fe-Ni sulphides due to the contribution of Fe and Ni in the host. RMN compositions were converted to atomic percent (at. %) and renormalised.

Some RMNs were extracted from the sample using a Focussed Ion Beam (FIB) technique using the Zeiss Auriga FIB-SEM at the ACMM, the University of Sydney. A thin protective layer of Pt was deposited using secondary electrons followed by a much thicker Pt layer deposited using Ga ions. The sample was then cut out using the Ga beam and extracted using a Kleindiek micromanipulator and welded to a Cu transmission electron microscopy mount by depositing more Pt. The sample was thinned down to 100 nm using a fine Ga beam. The samples were analysed using transmission Kikuchi diffraction (TKD) on a Zeiss ULTRA 60 Plus FEG SEM at the ACM, the University of Sydney. EDS data from the RMNs in each section were collected with an X-Max 20 mm² SDD EDS detector using an acceleration voltage of 30 kV. The same X-ray lines used to calculate elemental abundances, and the detection limits and uncertainty are similar to those described above. As Pt was used as a protective layer it is likely that we could observe an enrichment in the Pt signal from fluorescence in the chamber. Samples prepared in this way are denoted by a superscript note 1 in Table 3.

2.3. Condensation model and precipitation proxy

An exhaustive literature search was conducted in an attempt to produce a library of all previous RMN compositional data (Berg et al., 2009; Bischoff and Palme, 1987; Blander et al., 1980; Wark and Lovering, 1976; Wark, 1986; Palme et al., 1982; Croat et al., 2013; Schwander et al., 2014; Palme et al., 1994; Wark and Lovering, 1978; Harries et al., 2012; Schwander et al., 2015). We also include compositions of synthetic RMNs thought to be derived from precipitation processes (Schwander et al., 2015), as well as RMNs observed in cosmic spherules (Rudraswami et al., 2014). These analyses were plotted alongside observed RMN compositions from this study.

Compositions for hypothetical RMN condensates were calculated using the approach described in Palme and Wlotzka (1976) with slight modification. A set of ten non-linear equations were specified for the elements Fe, Ni, Ru, Pt, Rh, Mo, Ir, Os, Re and W, each of the form of Palme and Wlotzka (1976), equation [6]. Values for the cosmic abundances were taken from Lodders (2003). The equations were solved using a non-linear equation solver embedded in the Mathematica package at 10⁵ and 10•4 bars for temperatures from 1200 to 1700 K with 10 K increments to produce a set of alloy compositions, calc, where calc is a 1 × 10 matrix consisting of the mole fractions of the ten specified elements. Residuals, Σᵢ(obsᵢ − calcᵢ)², were calculated where i represents each of the 10 elements, obs is the 1 × 10 matrix of the analysed
3. RESULTS

3.1. Synchrotron

In depth analyses of the element maps derived from the AS were used to target and identify hotspots of PGEs. The vast majority of observed hotspots are pixel-sized, indicating grains are <2 μm. Each carbonaceous chondrite section analysed yielded an average of 10 hotspots per sample, with a maximum of 71 in Vigarano and a minimum of two in Adelaide and Acfer 094. The proximity of the Kα and Lα peaks of the PGEs to each other and major elements such as Zn, combined with the penetration depth, make it difficult to deconvolve the spectrum into individual element peaks. This means that the spectrum’s shape is defined by the most abundant element in that energy range. Great care was taken in analysing the spectra to avoid misidentification due to peak overlaps; removing false positives. Most RMNs were identified within chondrules, chondrule rims (79), but a number are observed within the matrix (9) and chondrules (6) of these meteorites (Fig. 3), Table 2. Of the 145 RMNs identified 113 have reliable EDS chemical analyses. The composition of the RMNs derived from EDS varies greatly between host and samples; Re and Rh were below detection limits for most RMNs analysed. The compositions of RMNs with reliable EDS data from this study are summarised in Table 3 and average compositions of RMNs for each inclusion and matrix are detailed in Table 4.

4. DISCUSSION

4.1. Evaluation of the database

The deduction of elements such as Al, Ca, Mg, and O (which were present in the host phase and not from the RMN), from the RMN EDS measurement, resulted in small wt% totals. To evaluate whether this deduction and subsequent re-normalisation process has introduced any inherent biases or compound errors, each re-normalised element was plotted in relation to the initial wt% total of PGEs + Fe + Ni before re-normalisation (Fig. 4). The reversal of the normalisation process was plotted in relation to the initial wt% total of PGEs + Fe + Ni before re-normalisation (Fig. 4). If the normalisation process was producing a systematic error, steep trends from small wt% totals to high wt% totals would be observed. However, these graphs had very shallow to flat trends indicating normalisation has not introduced significant bias.

4.2. RMNs within CAIs, chondrules and matrix

This study reveals that RMNs can be found within all components of carbonaceous chondrites. Current theories surrounding the origin of RMNs are tied to their assumed unique occurrence within CAIs e.g. Berg et al. (2009). CAIs

Table 1

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Total RMNs</th>
<th>Host</th>
<th>CAI</th>
<th>Chondrule</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acfer 094</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Adelaide</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>17</td>
<td>12</td>
<td>0</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Kaidun</td>
<td>9</td>
<td>0</td>
<td>1</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Renazzo</td>
<td>6</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Vigarano</td>
<td>71</td>
<td>69</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

this may explain this preferred matrix association for RMNs in these meteorites.
are thought to form initially as high temperature condensates (Grossman and Ganapathy, 1976; Wänke et al., 1974) (although most have experienced further processes such as remelting (MacPherson, 2005)). Therefore, the assumed model of formation for RMNs has been that they condensed at high temperatures in the same location and environment as CAIs (Grossman and Ganapathy, 1976). However, this single condensation event model is hard to reconcile with the myriad of compositions observed within RMNs (Grossman et al., 1977; Schwander et al., 2015). In addition, it should be borne in mind that CAIs affect the bulk composition of meteorites by enhancing refractory abundance above CI, indicating that CAIs were added to an approximately solar bulk ‘background’ composition. But in chemical analysis of matrix, or (CAI-absent) CI chondrite, we still observe PGEs. What then is the host phase of these elements? One possibility is finely comminuted CAI. However, if this were true, we would observe an enhancement in all refractory elements such as Ca and Al, which is not the case. Therefore RMNs in the matrix are unlikely to be broken fragments of CAIs as stipulated by Schwander et al. (2015) and are likely to have their own formation history. The chondrules that host the RMNs in this study do not appear to contain fragments of CAIs and the RMNs are contained within forsterite (Fig. 3), so similarly a CAI initial source for these chondrule-hosted RMNs is unlikely. The fact that we have now observed RMNs within matrix and chondrules demonstrates that CAIs are not a necessary factor in their formation. Indeed, their presence in chondritic components which formed at temperatures far below CAIs raises several new possibilities for RMN formation.

4.3. RMN compositional diversity

RMN PGE abundances compared to CI chondrite defined by (Lodders, 2003) (Fig. 5) show large enrichments and depletions relative to CI. Most RMNs are equally enriched or depleted in all refractory elements, however, some RMNs have significant relative depletions in Mo and W. The RMNs associated with this trend are principally hosted within sulphides, supporting the idea that sulphurisation mobilises Mo and W (Palme et al., 1998). Nevertheless, the average RMN composition approximately follows a CI chondrite trend indicating that these refractory elements are primarily hosted within RMNs in meteorites. This expands the observation of Schwander et al. (2015): that the average composition of RMNs matches that of the PGE content of the bulk CAI to encompass the whole meteorite.
4.3.1. RMN compositional diversity between inclusions

The total PGE contents of RMNs when compared with Fe and Ni (Fig. 6) reveal three main trends in the dataset: a Fe mixing line between 100 at.% PGE and 100 at.% Fe (black polygon); a Ni mixing line from 90 at.% PGE, 0 at.% Fe to 20 at.% PGE, 40 at.% Fe (red polygon); and a 'low PGE region' PGE < 30 at.% and 20–80 at.% Fe (green triangle). RMNs from acid residue studies were exclusively found within the high PGE portion of the Fe mixing line. These RMNs were significantly more PGE-rich and Fe and Ni-poor than most RMNs analysed in situ. RMNs in residues should contain RMNs from all meteoritic components which would include RMNs with high Ni and Fe contents. As this is not what we observe then it is likely that the process of concentrating RMNs in acid residues leaches RMNs of their Ni and Fe content. The low PGE region is primarily composed of matrix, chondrule and sulphide-hosted RMNs. CAI-hosted RMNs are evenly spread across all regions. The universal presence of CAI-hosted RMNs in all regions suggests that no single process equilibrated the composition of RMNs within CAs.

Furthermore, the average chemical composition of RMNs within each host phase is significantly different (Table 4). Sulphide, matrix and chondrule hosted RMNs are depleted in most PGEs relative to CAI-hosted RMNs, and W and Mo are completely absent or in extremely low concentrations. There is a large range of RMN compositions observed within the dataset. We compared the observed spread of RMN compositions to the compositional distribution expected to be produced by proposed RMN forming processes, specifically: condensation, precipitation and sulphidation acting in isolation or in tandem.

Table 2
The abundance of RMNs in each type of inclusion (chondrule, matrix, sulphide and CAs) observed within the Adelaide, ALH 77307, Allende, Murchison, and Vigarano meteorites. These RMNs were found by SEM and EDS analyses using the image overlay of synchrotron maps with PGE hotspots, and supplemented with RMNs identified using the INCA feature mapping software.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Total RMNs</th>
<th>Chondrule</th>
<th>Matrix</th>
<th>Sulphide</th>
<th>CAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adelaide</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>16</td>
<td>0</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Allende</td>
<td>86</td>
<td>4</td>
<td>6</td>
<td>53</td>
<td>23</td>
</tr>
<tr>
<td>Murchison</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Vigarano</td>
<td>37</td>
<td>1</td>
<td>0</td>
<td>19</td>
<td>17</td>
</tr>
</tbody>
</table>

4.3.1. RMN compositional diversity between inclusions

Fig. 3. SEM backscatter images of RMNs in all meteoritic components (a) RMN hosted in matrix from ALH 77307 in the vicinity of a CAI (b) RMN hosted in a akermanite (Ak) and perovskite (Per)-rich CAI in ALH 77307, (c) RMN hosted in a chondrule in Allende within forsterite (Fo) (d) RMNs hosted within a (Fe-Ni) S rim around a chondrule in Allende.
Table 3
RMN compositions from EDS in at.%, indicating the meteorite, inclusion, and host mineral phase. The data is also available in Supplementary Appendix 1.

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Inclusion</th>
<th>Host</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Rh</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adelaide</td>
<td>CAI</td>
<td>Anorthite</td>
<td>66.9</td>
<td>7.7</td>
<td>7.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>14.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.3</td>
</tr>
<tr>
<td>Adelaide</td>
<td>Chondrule</td>
<td>Melilite</td>
<td>91.8</td>
<td>2.6</td>
<td>2.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>21.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.3</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>CAI</td>
<td>ScZr-spinel</td>
<td>25.9</td>
<td>2.1</td>
<td>13.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>14.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.3</td>
</tr>
<tr>
<td>ALH 77307</td>
<td>CAI</td>
<td>AKermanite</td>
<td>46.3</td>
<td>6.7</td>
<td>13.3</td>
<td>3.2</td>
<td>14.8</td>
<td>b.d.</td>
<td>4.6</td>
<td>2.9</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>ALH 77307*</td>
<td>CAI</td>
<td>Forsterite</td>
<td>41.0</td>
<td>3.8</td>
<td>9.1</td>
<td>b.d.</td>
<td>38.8</td>
<td>b.d.</td>
<td>9.5</td>
<td>14.2</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Anorthite</td>
<td>46.4</td>
<td>13.6</td>
<td>15.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.3</td>
<td>14.2</td>
<td>9.5</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Anorthite</td>
<td>16.1</td>
<td>29.2</td>
<td>14.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>5.0</td>
<td>14.2</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Forsterite</td>
<td>21.3</td>
<td>5.4</td>
<td>41.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>12.4</td>
<td>14.2</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Forsterite</td>
<td>30.3</td>
<td>12.0</td>
<td>31.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>10.8</td>
<td>10.5</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Melilite</td>
<td>30.6</td>
<td>1.9</td>
<td>64.7</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.5</td>
<td>2.3</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Melilite</td>
<td>39.7</td>
<td>42.7</td>
<td>5.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.8</td>
<td>1.7</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Perovskite</td>
<td>44.5</td>
<td>13.4</td>
<td>22.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>9.1</td>
<td>10.2</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Pyroxene</td>
<td>79.3</td>
<td>20.7</td>
<td>2.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>16.5</td>
<td>17.6</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Spinel</td>
<td>27.0</td>
<td>10.5</td>
<td>17.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>11.4</td>
<td>10.4</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>CAI</td>
<td>Spinel</td>
<td>49.4</td>
<td>3.6</td>
<td>15.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.1</td>
<td>8.3</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>32.4</td>
<td>64.4</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>0.6</td>
<td>2.2</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>34.6</td>
<td>62.6</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>1.8</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>29.7</td>
<td>32.7</td>
<td>26.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.6</td>
<td>1.8</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>32.5</td>
<td>61.5</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>68.9</td>
<td>28.6</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>71.5</td>
<td>27.7</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>65.9</td>
<td>29.2</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>71.2</td>
<td>26.7</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>70.0</td>
<td>25.5</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>71.8</td>
<td>26.6</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>84.2</td>
<td>11.1</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>66.3</td>
<td>30.6</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>70.9</td>
<td>28.6</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>68.7</td>
<td>28.2</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>68.5</td>
<td>28.3</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>69.8</td>
<td>28.9</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>67.4</td>
<td>30.4</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>73.5</td>
<td>26.1</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>70.7</td>
<td>29.0</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.1</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>44.1</td>
<td>3.1</td>
<td>14.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>44.1</td>
<td>40.8</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>57.8</td>
<td>35.3</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>60.1</td>
<td>34.9</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>63.5</td>
<td>29.9</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>42.8</td>
<td>41.5</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>49.1</td>
<td>48.2</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>49.3</td>
<td>37.5</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>46.2</td>
<td>40.5</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>49.6</td>
<td>31.4</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>39.1</td>
<td>46.7</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule</td>
<td>Forsterite</td>
<td>51.0</td>
<td>33.8</td>
<td>0.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.4</td>
<td>4.9</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.2. Sulphidation as a RMN forming process

The high abundance of Fe–Ni-sulphide hosted RMNs contained within the low PGE region (Fig. 6) potentially allows us to interpret RMNs within this region as derived from, or affected by, sulphidation. If we assume that sulphide hosted RMNs were formed or had their composition modified by sulphidation, then either these RMNs have been affected by exposure to a S-rich gas in the nebula (Lauretta et al., 1996), and/or a parent body process has imposed a compositional fingerprint on these grains. The Table 3 (continued)

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Inclusion Host</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Rh</th>
<th>Mo</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>62.6</td>
<td>34.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.3</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>71.3</td>
<td>23.3</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.9</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>47.1</td>
<td>39.1</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>7.7</td>
<td>6.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>58.4</td>
<td>32.6</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.0</td>
<td>7.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>66.3</td>
<td>32.5</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>6.3</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>61.3</td>
<td>32.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>2.5</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>54.6</td>
<td>39.0</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.1</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>46.2</td>
<td>39.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>3.7</td>
<td>10.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>48.6</td>
<td>30.8</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.7</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>Chondrule rim sulphide (Fe,Ni) S</td>
<td>47.8</td>
<td>35.4</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1.2</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*RMNs prepared using FIB techniques.

Appendix A

L. Daly et al. / Geochimica et Cosmochimica Acta 216 (2017) 61–81 69
RMNs from this study are hosted in Fe-Ni sulphides and are therefore likely to be affected by parent body processes altering the chemistry of the sulphides from stochiometric troilite. It has been suggested that the presence of W and Mo could be used as an indicator for primitive RMNs as even low degrees of alteration would remobilise these two elements (Eisenhour and Buseck, 1992). Therefore, the fact that no W or Mo is observed in sulphide-hosted RMNs may be taken as evidence that these grains have been altered. We also do not observe any associated Mo or W dominated sulphide phases with these RMNs. We therefore expect that as the Fe-Ni-sulphide is significantly larger than the RMNs, the mobilised W and Mo become disseminated throughout the host sulphide during sulphidation, replacing Fe or Ni.

The fact that matrix, CAI and chondrule RMNs are also found within this region, that are not associated with sulphides suggests that this region is not a unique expression of sulphidation and other processes can produce RMNs with low PGE abundances. Therefore the compositional variance in the whole region cannot be explained completely by sulphidation.

Table 4

<table>
<thead>
<tr>
<th>Average RMNs compositions in at.%, for each meteorite analysed in this study and for each inclusion type.</th>
</tr>
</thead>
<tbody>
<tr>
<td>All RMN</td>
</tr>
<tr>
<td>Adelaide</td>
</tr>
<tr>
<td>ALH 77307</td>
</tr>
<tr>
<td>Allende</td>
</tr>
<tr>
<td>Murchison</td>
</tr>
<tr>
<td>Vigarano</td>
</tr>
<tr>
<td>CAI</td>
</tr>
<tr>
<td>Chondrule</td>
</tr>
<tr>
<td>Sulphide</td>
</tr>
<tr>
<td>Matrix</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>39.1</td>
</tr>
<tr>
<td>73.4</td>
</tr>
<tr>
<td>36.6</td>
</tr>
<tr>
<td>36.3</td>
</tr>
<tr>
<td>45.4</td>
</tr>
<tr>
<td>51.4</td>
</tr>
<tr>
<td>38.7</td>
</tr>
<tr>
<td>41.5</td>
</tr>
<tr>
<td>49.5</td>
</tr>
<tr>
<td>56.2</td>
</tr>
</tbody>
</table>

b.d., element was below detection limits for this RMN.

Fig. 4. At.% abundances of Fe, Ni and PGE elements vs the wt.% total pre-normalisation of the RMN component in the EDS spectra for all samples from this study. The line in each graph represents a line of best fit through the data. These show relatively shallow trends which are significantly smaller than the overall compositional variability in at.% for each element. Therefore, it is unlikely that our re-normalisation calculations have introduced any significant bias to our dataset.
4.3.3. Condensation as a RMN forming process

Calculated RMN condensation temperatures show a reasonable agreement with condensation models for some elements, particularly Fe. However, other elements, such as Ru, Ir, Pt, and particularly Ni deviate substantially from the expected curve (Fig. 7).

To evaluate how closely the measured compositions of RMNs agree with modelled compositions, RMNs were grouped where every element is within 5 or 15 at.% agreement of the best fit calculated condensation composition (Fig. 8). As the tolerance is raised from 5 to 15 at.%, the number of RMNs consistent with condensation models increases from 5% to 50%. These RMNs are clustered exclusively along the Fe-mixing line. However, a significant portion of RMNs within the Fe-mixing line do not conform to the condensation model even at high tolerance levels. This indicates that condensation is not exclusively responsible for RMNs within the Fe mixing line. The abundance of RMNs consistent with our equilibrium condensation model in this study is similar to the abundance calculated in Schwander et al. (2014) in which only 4 out of 123 RMNs were consistent with CI chondrite relative abundance for these elements.

Fig. 5. RMN compositions from this study (orange), the average RMN from this study (red) and RMNs from our literature database (grayscale). PGEs have been plotted in order of increasing volatility and have been normalised to Ru then CI (top), or Pt then CI (bottom). These RMNs show a wide range of individual RMN compositions. However, the average RMN from this study has approximately CI chondrite relative abundance for these elements.
an equilibrium condensation model. Interestingly, the 5% of RMNs that are consistent with condensation are hosted within opaque assemblages from Palme et al. (1994), cosmic spherules from Rudraswami et al. (2014), several CAIs with melting textures from Schwander et al. (2015), as well as a RMN from a chondrule rim sulphide (this study), all of which do not have textures consistent with condensation.

It is clear that predicted RMN compositions from current equilibrium condensation models cannot be reconciled with observations. Alternative condensation models, namely non-equilibrium condensation, fractional condensation and the effect of the activity coefficient will now be considered.

Previous equilibrium condensation models have assumed that the activity coefficients for each element are 1 (Berg et al., 2009). Schwander et al. (2014), noted that varying the activity coefficient would result in a migration of the condensation curve for each element. However, the systematic trend in RMN compositions would be maintained and therefore cannot account for the spread of observed RMN compositions.

Fractional condensation would result from successive periods of condensation followed by removal of RMNs from the reservoir, depleting it in the elements that had already condensed. The expected observations of this process would depend on the mechanism for isolating the RMNs from the condensing gas. If the RMNs were

Fig. 6. Total PGE vs Fe and total PGE vs Ni plots by host phase (this study and the literature) indicating a well defined Fe-mixing trend (black polygon) a more dispersive Ni-mixing trend (red polygon) and a low PGE cluster (green triangle), which is dominated by sulphide phases.
Fig. 7. A comparison of Fe, Ni and PGE abundance in wt% vs calculated equilibrium condensation temperature at 10^{-4} bar for RMNs from this study (green), and the literature (red). The data are plotted in the same format as Berg et al. (2009). RMN compositions exhibit good correlations with Fe and Mo but very poor correlations with Ni, Ru, Rh, Ir and Pt.
removed by encapsulation within other condensing phases, we would expect to observe a mineralogical association with RMNs enriched in certain PGEs. For example, high temperature phases such as hibonite and corundum would be expected to bear RMNs enriched in the more refractory PGEs such as Os, Re, and W, while lower temperature phases such as Mg-spinel and anorthite would contain RMNs enriched in the more volatile PGEs such as Pt. Schwander et al., 2015 demonstrated that there is no systematic variability of RMN compositions with host phase. Therefore, this mechanism is unlikely. If the RMNs are physically removed from the reservoir we may expect to observe a chemically distinct RMN population within different host inclusions such as chondrules and CAIs. Schwander et al., 2015 demonstrated that there is no systematic variability of RMN compositions with host phase. Therefore, this mechanism is unlikely. If the RMNs are physically removed from the reservoir we may expect to observe a chemically distinct RMN population within different host inclusions such as chondrules and CAIs.

Fig. 6 revealed that the abundance of Fe and Ni in CAI hosted RMNs encompass the whole range of chemical compositions, including those occupied by sulphides, chondrules and matrix. This indicates that this mechanism for fractional condensation is also unlikely. We would also expect to observe clusters of RMNs with similar compositions which relate to the temperature they were fractionated from the condensing gas. However, no such clustering of RMN compositions is observed (see Fig. 6).

Non-equilibrium condensation, similar to other condensation models, is expected to produce a systematic trend in RMN compositions. The non-equilibrium condensation model produced by Tanaka et al. (2002) revealed that although the condensation temperatures...
for certain PGEs may vary significantly, the overall condensation sequence for the elements within RMNs remains the same as that predicted for equilibrium condensation. Furthermore, we may expect to observe zonation in RMNs that condensed in this manner. However, zoning has not been reported in previous transmission electron microscopy studies of RMNs (Harries et al., 2012; Eisenhour and Buseck, 1992).

It is apparent that more complex nebular condensation models still result in RMNs with a systematic compositional trend. This cannot be reconciled with the large spread in the compositional data reported for RMNs. Therefore, nebular condensation is unlikely to be a dominant process in RMN formation.

4.3.4. Precipitation as a potential RMN forming process

Some RMNs have been demonstrably attributed to precipitation processes, where an RMN has crystallised from a melt; either in experimental studies (Schwander et al., 2015), or observed in cosmic spherules (Rudraswami et al., 2014). Although as cosmic spherules have a complex history of evaporation and remelting it is unclear whether these RMN compositions are derived from a pure precipitation process. When the synthetic RMNs are superim-

Fig. 9. Total PGEs vs Fe abundance in at.% for RMNs detailed in this study (red) and the literature (black) as well as pre-solar RMNs from Croat et al. (2013) (blue), synthetic RMNs produced by precipitation from Schwander et al. (2015) (green), and our condensation model calculated at 10^-4 bar.
posed over RMNs analysed in this study and the literature (Fig. 9), precipitation RMNs fall along the Fe-mixing line in a similar trend to the condensation model curve. Therefore, even if we assume that the Fe-mixing line can be reconciled by a combination of condensation and precipitation processes there is still the Ni-mixing line which is inconsistent with all the processes we have described.

Considering each element in isolation, overlaying precipitation derived RMNs and our equilibrium condensation model curve over observed RMNs, from this study and the literature (Fig. 10), we reveal a further disparity. The spread of RMN compositions cannot be fully explained by precipitation Mo/Ru, W/Ru, Pt/Ru and Ir/Ru ratios for example do not match synthetic precipitates. Os/Ru at low Os concentrations does approximately follow a trend defined by synthetic precipitation derived RMNs, however there is also a population with very high Os abundances which is not consistent. Furthermore these RMN elemental ratios do not exhibit any association with the equilibrium condensation curve, except for a weak association in Os and Ir. Precipitation encounters the same problem as condensation; whilst it can produce compositions consistent with some RMN observations, it cannot explain them all. Furthermore, the population of RMNs that are consistent with condensation and precipitation are not complementary, and therefore cannot be an expression of both processes acting in tandem.

The synthetic RMNs derived from precipitation in Schwander et al. (2015) represent a single experiment, which naturally may not perfectly match nebula conditions. It is possible that precipitation could explain all RMN compositions if the experiments were carried out under different conditions.
conditions. However, there is a significant logical problem with the model. If all the PGEs are dissolved into a silicate or CAI-like melt, over time these elements will naturally become homogeneously distributed. Upon quenching the RMNs that do form should have homogeneous compositions within each inclusion. Heterogeneous RMNs would form only if PGEs are still heterogeneously distributed within the inclusion and were not molten for sufficient time to equilibrate. Therefore heterogeneous RMNs within remelted inclusions may not derive their heterogeneity from precipitation, but from an inherited heterogeneous distribution of the PGEs within the inclusion that did not equilibrate.

4.3.5. Other parent body processes

To ascertain if there is any variation between RMNs from different parent bodies, RMNs were separated according to meteorite (Fig. 11). Allende seems to encompass the whole range of RMN compositions. However, other meteorites cluster into certain regions. Murchison, Leoville, Orgueil, ALH 77307 and Adelaide represent certain portions of the Fe-mixing line. Ornans follows the Ni-mixing line into the low PGE region, and Vigarano contains RMNs from the low PGE region and the mid-section of the Fe-mixing line.

It is possible that this spread is due to a small dataset for some meteorites. However, the methodology used in this study would find most, if not all RMNs in a thin section, and all observed RMNs were analysed. Therefore it is possible that RMN populations may vary between parent bodies. In particular, the clustering of RMNs within Vigarano suggests this may be the case as several RMNs are observed and yet the spread of RMNs remains constrained.

4.3.6. Petrological context

Finally, the context of the RMN is taken into account. RMNs have been shown to occur throughout carbonaceous chondrites. The methodology described in this study retains their context and mineralogical association. Therefore, we can check if the formation process implied by evaluation of the chemical data is plausible. Indeed, it is the case that some RMNs with compositions consistent with a condensation origin are located within a mineral assemblage that has an igneous history, such as the RMNs in cosmic spherules.

Average abundances of PGEs in RMNs between meteorites have approximately chondritic trends (Fig. 12). Vigarano exhibits an enrichment in W, whereas Allende exhibits a depletion in W and Mo. This may be interpreted as a real compositional difference related to the formation history and oxidation state of the meteorite. However, as very few RMNs contain Mo or W these anomalies are therefore likely to be caused primarily by the averaging of a few W-rich RMNs in the case of Vigarano and a few Mo and W-poor RMNs in Allende.

PGEs are predominantly siderophile and generally unreactive, with the exception of W and Mo which have been shown to be mobile under low degrees of alteration (Palme et al., 1998). It has been shown by experiment that Pt, Mo and W will mobilise under reducing conditions at 1600 K before Os and Ir (Schwander et al., 2015). Therefore, to alter the entire PGE content in RMNs on the parent body would require significantly higher temperatures than all carbonaceous chondrite parent bodies have experienced. The heterogeneity in the PGE content of RMNs must therefore be present prior to accretion. Therefore, a parent body process producing heterogeneous RMNs is unlikely.
from Rudraswami et al. (2014). Cosmic spherules are thought to experience a very complex succession of heating, melting, and evaporation (Brownlee et al., 1997; Taylor et al., 2000; Genge et al., 2008) and therefore cannot have a condensation origin. Furthermore, although precipitation is thought to produce a diversity of chemical compositions in RMNs (Schwander et al., 2015), not all inclusions in meteorites have an igneous history. Therefore, some RMNs cannot have formed via this process.

4.3.7. A combination of Solar System processes

No single process is responsible for the RMN variability we observe. However, it may be possible to produce this diversity through a combination of these processes. Indeed RMNs within cosmic spherules (Rudraswami et al., 2014) which do have a complex thermal history including heating, melting, and evaporation (Brownlee et al., 1997; Taylor et al., 2000; Genge et al., 2008), nearly cover the whole range of observed RMN compositions (Fig. 11). However, RMNs hosted within different meteoritic inclusions have a similar diversity of Ir/Os and Ir/Pt ratios (Fig. 13). The overlap of sulphide hosted RMNs in particular indicates that sulphidation does not significantly alter the original elemental ratio. Therefore the diversity of RMN compositions cannot be related to precipitation or condensation derived RMNs being sulphidised. We have already dis-

Fig. 12. RMN average compositions by host phase and meteorite from this study (Table 4). PGEs have been plotted in order of increasing volatility and have been normalised to Ru then CI (top), or Pt then CI (bottom). The average compositions of each meteorite exhibit approximately CI trends. Allende exhibits a slight depletion in Mo and W, while Vigarano shows a large W enrichment.

![Diagram showing RMN average compositions by host phase and meteorite from this study](image-url)
cussed how equilibrium condensation is not capable of producing the diversity of RMNs observed, and precipitation is unlikely to generate the observed diversity. Synthetic RMN compositions from precipitates and equilibrium condensation RMN compositions are not complementary. Therefore even a combination of these proposed formation mechanisms will not result in the suite of compositions we observe. This leaves three possibilities. Firstly, it may be possible to imagine a complex sequence of condensation, remelting, evaporation, vaporisation, sulphidation, and oxidation that could produce a single RMN composition. However, the diversity of RMN compositions we observe would require almost every single RMN to experience a unique but complex formation history similar to cosmic spherules. This is inconsistent with textual observations of some RMN hosts, such as the RMN in a fluffy type A CAI in (Palme et al., 1998) and RMNs within a ‘fluffy’ type A CAI from Vigarano in this study (Fig. 2). These RMNs do not have compositions consistent with a single event equilibrium condensation model and yet are contained within a ‘pristine’ inclusion and therefore are unlikely to have been significantly altered by subsequent processes. It is also inconsistent with RMNs with variable compositions within the same inclusions Schwander et al., 2015. Secondly there may be a nebula or parent body process which has not yet been identified which is capable of producing the observed heterogeneity within RMNs either individually, or in tandem with the previously discussed processes. Finally, there is a possibility that this diversity of RMN compositions could be produced by inheriting an initially heterogeneous assemblage of pre-solar RMNs which were never completely equilibrated by subsequent nebular processing.

4.3.8. A pre-solar initial origin?

We have to accept that neither condensation (primary nebula), precipitation (secondary nebula), nor sulphidation (secondary asteroidal) and parent body processes can produce individually or in tandem the myriad of compositions of RMNs we observe in meteorites. We cannot currently produce the diversity of RMNs via a combination of known nebular and/or parent body processes, therefore we are required to look elsewhere.

The Solar System formed from a Giant Molecular Cloud fragment which would have included refractory metals from a variety of stellar sources. These are likely to be host in metal alloys. The resulting diversity of RMN compositions represents the initial condition of the protoplanetary disk. Our data indicate that while RMNs have been affected by condensation, precipitation, sulphidation and (possibly other) parent body processes, none of these processes are dominant, and together, they have not homogenised or equilibrated the RMN population and removed that initial compositional diversity. If this interpretation is correct, a prediction would be that pre-solar RMNs are present as discrete grains within primitive chondrites and IDPs, rather than solely hosted in pre-solar graphite (Croat et al., 2013). Therefore, some of the grains analysed in the course of this study belong to that pre-solar population. The most likely candidates for this are those RMNs found within the Ni-mixing line which is not readily explained by any process discussed in this study. Isotopic analysis is required to support this.

5. CONCLUSIONS

Observing RMNs in multiple components in meteorites, not just in CAIs, directly contradicts the assumption made by many studies that RMNs are unique to CAIs. Each RMN host has its own characteristic RMN compositional suite. However, the average RMN composition across all minerals averages to the bulk Solar System and CI chondrite implying that PGEs are primarily, if not uniquely, hosted within RMNs. Condensation models, experimentally derived RMNs from precipitation, and parent body processes such as sulphidation are unable to produce the suite of RMN compositions observed, either in isolation or in tandem. It may be possible to derive the suite of RMN compositions through complex sequences of condensation evaporation and remelting as we observe a similar diversity in cosmic spherules. However, such a complex thermal sequence is not plausible for all meteoritic components. The Solar Nebula inherited a vast diversity of RMN compositions from a variety of stellar sources. Our data suggests that this initial RMN population was never fully homogenised. While some RMNs have been modified by
necular and asteroidal processes, the compositional diver-
sity of the RMN population observed in this study indicates
that the original pre-solar signature was never completely
erased. If this assumption is correct, some RMNs may have
escaped Nebula processing and will retain their pre-solar
composition. Therefore, we should observe some demon-
strably pre-solar RMNs not just within pre-solar graphite,
but in other components as well. These conclusions could
only be drawn by analysis of RMNs in situ highlighting
the importance of retaining context and petrological
associations.

ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council via
their Australian Laureate Fellowship program. This research was
undertaken on the XFM beamline at the Australian Synchrotron,
Victoria, Australia. The authors acknowledge the facilities, and
the scientific and technical assistance, of the Australian Microscopy
& Microanalysis Research Facility at the Australian Centre for
Microscopy and Microanalysis, the University of Sydney and the
Centre for Microscopy, Characterisation and Analysis, University of
Western Australia. The authors would also like to thank the rest
of the Desert Fireball Network research group as well as Mr. Tim-
mons Erikson, Mr. Mark Daly, Ms. Mary Munroe, Ms. Sarah
Hayes and Ms. Jennifer Porter for their assistance. Finally the
authors would like to thank the three reviewers, as well as associate
editor Nicolas Dauphas for their constructive comments and sug-
gestions which significantly improved this manuscript.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found,
in the online version, at http://dx.doi.org/10.1016/
j.gca.2016.11.030.

REFERENCES

Amari S., Lewis R. S. and Anders E. (1994) Interstellar grains in
meteorites: I. Isolation of SiC, graphite and diamond; size
distributions of SiC and graphite. Geochimica et Cosmochimica
Acta 58, 459-470.

Anders E., Gros J., Takahashi H., Morgan J. and Higuchi H.
(1975) Extinct superheavy element in the Allende meteorite.
Science 190, 459-470.

Berg T., Mauk J., Schönense G., Marois E., Hopp P., Ott U.
and Palme H. (2009) Direct evidence for condensation in the
early solar system and implications for nebular cooling rates.

Bochoff A. and Palme H. (1987) Composition and mineralogy of
refractory-metal-rich assemblages from a Ca, Al-rich inclusion
in the Allende meteorite. Geochimica et Cosmochimica Acta 51,
2733-2748.

refractory metal particles in the Allende meteorite. Geochimica
et Cosmochimica Acta 44, 217-223.

Blum J. D., Wasserburg G., Hutchison I. D., Beckett J. R. and

Address Presented 1996 July 25, Berlin, Germany: the elemental
composition of stony cosmic spherules. Meteoritics & Planetary
Science 32, 157-175.

Campbell A. J., Humayun M., Meibom A., Krot A. N. and Keil K.

Cleverley J., Ryan C., Hough R., Bland P., Fisher L. and Dyl K.
(2012) Quantified, whole section, Maia XRF mapping of trace
elements in allende. Meteoritics and Planetary Science Supple-
ment 55, 5175.

thermal processing of solids in the solar protoplanetary disk.
Science 338, 651-655.

Croat T., Berg T., Bernatowicz T., Groopman E. and JadHAV M.
(2013) Refractory metal nuggets within presolar graphite: First
condensates from a circumstellar environment. Meteoritics &
Planetary Science 48, 466-469.

and Hough R. M. (2014) Quantified, whole section trace
element mapping of carbonaceous chondrites by Synchrotron
X-ray Fluorescence Microscopy: I. CV meteorites. Geochimica
et Cosmochimica Acta 134, 100-119.

Eisenhour D. and Buseck P. (1992) Transmission electron microscopy of RMNs: implications for single-phase condensa-
tion of the refractory siderophile elements. Meteoritics 27, 217-
218.

Fremdlinge: potential presolar material in Ca-Al-rich inclu-

El Goresy A., Nagel K., and Ramdohr P. (1978) Fremdlinge and
their noble relatives. In Lunar and Planetary Science Conference

refractory noble metals and lithophile trace elements in
refractory inclusions in carbonaceous chondrites. Earth and
planetary science letters 68, 181-197.

Fegley B. and Palme H. (1985) Evidence for oxidizing conditions in
the solar nebula from Mo and W depletions in refractory
inclusions in carbonaceous chondrites. Earth and Planetary
Science Letters 72, 311-326.

classification of micrometeorites. Meteoritics & Planetary
Science 43, 497-555.

Grossman L. (1973) Refractory trace elements in Ca-Al-rich
inclusions in the Allende meteorite. Geochimica et Cosmochimica
Acta 37, 1119-1140.

Grossman L. and Ganapathy R. (1976) Trace elements in the
Allende meteorite – I. Coarse-grained, Ca-rich inclusions.
Geochimica et Cosmochimica Acta 40, 331-344.

elements in the Allende meteorite – III. Coarse-grained inclu-
sions revisited. Geochimica et Cosmochimica Acta 41, 1647-
1664.

Structural clues to the origin of refractory metal alloys as
condensates of the solar nebula. Meteoritics & Planetary
Science 47, 2148-2159.

Isotopic studies of Mg, Fe, Mo, Ru and W in Fremdlinge from
Allende refractory inclusions. Geochimica et Cosmochimica
Acta 51, 3175-3192.

iron sulfide formation in the solar nebula. Icarus 122, 288-315.

temperatures of the elements. The Astrophysical Journal 591,
1220-1247.

Appendix A

L. Daly et al. / Geochimica et Cosmochimica Acta 216 (2017) 61–81


Associate editor: Nicolas Dauphas
A.2. **Paper 2 – Crystallography of Refractory Metal Nuggets in Carbonaceous Chondrites: A Transmission Kikuchi Diffraction Approach**


Reprinted with permission of Elsevier:
This Agreement between Luke Daly ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number 4200341458274  
License date Oct 01, 2017  
Licensed Content Publisher Elsevier  
Licensed Content Publication Geochimica et Cosmochimica Acta  
Licensed Content Title Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach  
Licensed Content Author Luke Daly, Phil A. Bland, Kathryn A. Dyl, Lucy V. Forman, David W. Saxey, Steven M. Reddy, Denis Fougerouse, William D. A. Rickard, Patrick W. Trimby, Steve Moody, Limei Yang, Hongwei Liu, Simon P. Ringer, Martin Saunders, Sandra Piazolo  
Licensed Content Date Nov 1, 2017  
Licensed Content Volume 216  
Licensed Content Issue n/a  
Licensed Content Pages 19  
Start Page 42  
End Page 60  
Type of Use reuse in a thesis/dissertation  
Intended publisher of new work other  
Portion full article  
Format both print and electronic  
Are you the author of this Elsevier article? Yes  
Will you be translating? No  
Title of your thesis/dissertation Understanding Our Protoplanetary Disk by Chemical Analysis of Components in Meteorites  
Publisher of new work Curtin University  
Author of new work Professor Phil Bland  
Expected completion date Nov 2017  
Estimated size (number of pages) 560  
Requestor Location Luke Daly  
72 Hensman Street  
South Perth, WA 6151  
Australia  
Attn: Luke Daly  
Total 0.00 GBP  

Terms and Conditions

INTRODUCTION
1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

**GENERAL TERMS**

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

   "Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment
terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. For journal authors: the following clauses are applicable in addition to the above:

Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.). Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
via their non-commercial person homepage or blog
- by updating a preprint in arXiv or RePEc with the accepted manuscript
- via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
- directly by providing copies to their students or to research collaborators for their personal use
- for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement

- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment. Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect. Please refer to Elsevier's posting policy for further information.

18. For book authors the following clauses are applicable in addition to the above:
- Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. Posting to a repository: Authors are permitted to post a summary of their chapter only in their institution's repository.

19. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third
party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

**Terms & Conditions applicable to all Open Access articles published with Elsevier:**

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated. The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

**Additional Terms & Conditions applicable to each Creative Commons user license:**

**CC BY:** The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at [http://creativecommons.org/licenses/by/4.0](http://creativecommons.org/licenses/by/4.0).

**CC BY NC SA:** The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and any new works must be made available on the same conditions. The full details of the license are available at [http://creativecommons.org/licenses/by-nc-sa/4.0](http://creativecommons.org/licenses/by-nc-sa/4.0).

**CC BY NC ND:** The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at [http://creativecommons.org/licenses/by-nc-nd/4.0](http://creativecommons.org/licenses/by-nc-nd/4.0).

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions:**

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
STATEMENT OF AUTHORSHIP

TITLE OF PAPER: Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach

PUBLICATION STATUS: Accepted

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Paper: Led all aspects of this research, Drafted and revised the manuscript for this publication.

Overall Percentage: 66%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Paper: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Kathryn A. Dyl
Contribution to the Paper: Helped in editing and revision of the manuscript.
Overall Percentage: 2%

Signature: [Signature]
Date: 2/22/17

Name of Co-Author: Lucy V. Forman
Contribution to the Paper: Helped in the final review of the manuscript.
Overall Percentage: 2%

Signature: [Signature]
Date: 2/22/17

Name of Co-Author: David W. Saxey
Overall Percentage: 1%

Signature: [Signature]
Date: 2/22/17

Name of Co-Author: Steven M. Reddy
Contribution to the Paper: Assisted with atom probe analysis
Overall Percentage: 1%

Signature: [Signature]
Date: 2/22/17

Name of Co-Author: Denis Fougerouse
Contribution to the Paper: Atom Probe FIB sample preparation.
Overall Percentage: 1%

Signature: [Signature]
Date: 2/22/17
Name of Co-Author: William D. A. Rickard
Contribution to the Paper: Atom Probe FIB sample preparation.
Overall Percentage: 1%
Signature: 
Date: 20/02/17

Name of Co-Author: Patrick W. Trimby
Contribution to the Paper: Assisted with TKD data collection and analysis and editing and revision of the manuscript.
Overall Percentage: 5%
Signature: 
Date: 20/02/17

Name of Co-Author: Steve Moody
Overall Percentage: 1%
Signature: 
Date: 20/02/17

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)
Overall Percentage: 1%
Signature: 
Date: 20/02/17

Name of Co-Author: Hongwei Liu.
Contribution to the Paper: Assisted with TEM analysis.
Overall Percentage: 1%
Signature: 
Date: 20/02/17
Name of Co-Author: Simon P. Ringer
Contribution to the Paper: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%

Signature: Simon P. Ringer  Date: 20/02/17

Name of Co-Author: Martin Saunders
Contribution to the Paper: Assisted with TEM analysis.
Overall Percentage: 2%

Signature: Martin Saunders  Date: 20/02/17

Name of Co-Author: Sandra Piazolo
Contribution to the Paper: Assisted interpretation of TKD data and editing and revision of the manuscript.
Overall Percentage: 5%

Signature: Sandra Piazolo  Date: 20/02/17
Crystallography of refractory metal nuggets in carbonaceous chondrites: A transmission Kikuchi diffraction approach

Luke Daly a,⇑, Phil A. Bland b, Kathryn A. Dyl a, Lucy V. Forman a, David W. Saxey b, Steven M. Reddy a,b, Denis Fougerouse a,b, William D.A. Rickard b, Patrick W. Trimby c, Steve Moody e, Limei Yang c, Hongwei Liu c, Simon P. Ringer d, Martin Saunders e, Sandra Piazolo f

a Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
b Geoscience Atom Probe Facility, Advanced Resource Characterisation Facility, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA, Australia
c Australian Centre for Microscopy and Microanalysis, The University of Sydney, NSW 2006, Australia
d Australian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW 2006, Australia
e Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, WA 6009, Australia
f Department of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia

Received 18 September 2016; accepted in revised form 29 March 2017; available online 5 April 2017

Abstract

Transmission Kikuchi diffraction (TKD) is a relatively new technique that is currently being developed for geological sample analysis. This technique utilises the transmission capabilities of a scanning electron microscope (SEM) to rapidly and accurately map the crystallographic and geochemical features of an electron transparent sample. TKD uses a similar methodology to traditional electron backscatter diffraction (EBSD), but is capable of achieving a much higher spatial resolution (5–10 nm) (Trimby, 2012; Trimby et al., 2014). Here we apply TKD to refractory metal nuggets (RMNs) which are micrometre to sub-micrometre metal alloys composed of highly siderophile elements (HSEs) found in primitive carbonaceous chondrite meteorites. TKD allows us to analyse RMNs in situ, enabling the characterisation of nanometre-scale variations in chemistry and crystallography, whilst preserving their spatial and crystallographic context. This provides a complete representation of each RMN, permitting detailed interpretation of their formation history.

We present TKD analysis of five transmission electron microscopy (TEM) lamellae containing RMNs coupled with EBSD and TEM analyses. These analyses revealed textures and relationships not previously observed in RMNs. These textures indicate some RMNs experienced annealing, forming twins. Some RMNs also acted as nucleation centres, and formed immiscible metal-silicate fluids. In fact, each RMN analysed in this study had different crystallographic textures. These RMNs also had heterogeneous compositions, even between RMNs contained within the same inclusion, host phase and even separated by only a few nanometres. Some RMNs are also affected by secondary processes at low temperature causing exsolution of molybdenite. However, most RMNs had crystallographic textures indicating that the RMN formed prior to their host inclusion. TKD analyses reveal most RMNs have been affected by processing in the protoplanetary disk. Despite this alteration, RMNs still preserve primary crystallographic textures and heterogeneous chemical signatures. This heterogeneity in crystallographic relationships, which mostly suggest that RMNs pre-date their host, is consistent with the idea that there is not a dominant

⇑ Corresponding author.
E-mail address: luke.daly@postgrad.curtin.edu.au (L. Daly).

http://dx.doi.org/10.1016/j.gca.2017.03.037
0016-7037/© 2017 Elsevier Ltd. All rights reserved.
RMN forming process. Each RMN has experienced a complex history, supporting the suggestion of Daly et al. (2017), that RMNs may preserve a diverse pre-solar chemical signature inherited from the Giant Molecular Cloud.

Keywords: Refractory metal nuggets; Solar nebula; Solar System; Origin; Meteorites; Carbonaceous chondrites; Crystallography; Crystallisation; Transmission Kikuchi diffraction

1. INTRODUCTION

There are two main hosts for highly siderophile elements (HSEs) in primitive carbonaceous chondrite meteorites: refractory metal nuggets (RMNs) and opaque assemblages (OAs). OAs are larger (>10 μm) multi-phase alloys (El Goresy et al., 1977), whereas RMNs are single phase alloys. OAs originally were termed fremdlinge due to their proposed pre-solar origin (El Goresy et al., 1977). However, isotopic analysis of fremdlinge by Hutcheon et al. (1987) indicate that they have solar isotopic ratios and so were named OAs by Palme et al. (1994) to reflect their solar origin.

To avoid confusion between the two objects we define RMNs in this study as any micrometre-sub-micrometre homogeneous (Harries et al., 2012) metal alloy within carbonaceous chondrite meteorites which contain 0.1 to 1 atomic percent (at.%) HSEs (Re, Os, Ir, Pt, Ru, Rh, W or Mo), in line with the definition in Daly et al. (2017).

Since the co-discovery of RMNs by Palme and Wlotzka (1976) and Wark and Lovering (1976), it has been assumed that they are only found in Ca-Al rich inclusions (CAIs) (Blander et al., 1980; Berg et al., 2009; Harries et al., 2012; Hewins et al., 2014). However, observations of RMNs in chondrules (Wang et al., 2007), matrix (Schwaner et al., 2015a), an unusual xenolith from Allende, likely to be a dark inclusion (Palme et al., 1988), as well as recent X-ray fluorescence microscopy (XRF) synchrotron data, have revealed that this is not the case. Daly et al. (2017) showed that RMNs are found within all components of carbonaceous chondrites. The refractory nature of RMNs which contain only elements with 50% condensation temperatures above Fe and Ni (Lodders, 2003) lead to the conclusion that RMNs are primary condensates (Grossman, 1973; Palme and Wlotzka, 1976; Fegley and Palme, 1985; Berg et al., 2009; Harries et al., 2012; Lodders, 2003). This is consistent with the assumption that RMNs were hosted solely within CAIs (Blander et al., 1980; Berg et al., 2009; Harries et al., 2012; Hewins et al., 2014) which also form at high temperatures (Grossman et al., 2000; MacPherson et al., 2003) and are thought to form initially as condensates (Grossman, 1973). Thus, formation mechanisms for RMNs were only considered within the context of CAIs.

Recent work by Rudraswami et al. (2014) and Schwander et al. (2015a) respectively has shown that this is not necessarily the case: an alternative mechanism may be crystallisation of RMNs from a silicate melt, CAI melt, or during the formation of cosmic spherules. Furthermore, RMNs have, in some cases, been subjected to secondary processes as implied by sulphidation and oxidation textures (Palme and Wlotzka, 1976; Bischoff and Palme, 1987; Blum et al., 1988). However, other studies have suggested that RMNs may have a pre-solar origin (Wark and Lovering, 1976; El Goresy et al., 1977; El Goresy et al., 1978). This was confirmed by recent observations of 20 – 50 nm RMNs hosted within pre-solar graphite (Croat et al., 2013).

A combination of 113 in situ energy-dispersive X-ray spectroscopy (EDS) measurements of RMNs and the database of RMNs reported in the literature over the last 40 years, revealed a large range of RMN compositions which cannot be reconciled by a single Solar System process (Daly et al., 2017). Our interpretation is that an inherently diverse population of RMNs was incorporated into the protoplanetary disk. These RMNs were altered by subsequent disk processing, but the primordial diversity was never overprinted (Daly et al., 2017).

The crystallography of RMNs can offer important insights into their origin and formation. For example, the three phase condensation model of Sylvester et al. (1990) predicted that RMNs should be found in three main crystal systems: body centred cubic (bcc) composed predominantly of W, Mo, and Cr; hexagonal close packed (hcp) composed predominantly of Re, Os, and Ru; and a face centred cubic (fcc) structure composed of Ir, Pt, Rh, Co, Ni, Fe, and Au.

This assertion was proposed to reconcile RMN compositions that do not fit a single-phase condensation model. However, the observed crystallography of RMNs using transmission electron microscopy (TEM) spot diffraction patterns indicate that they are largely monocrystalline, homogeneous, subhedral-euhedral hcp crystals (Eisenhour and Buseck, 1992; Harries et al., 2012; Croat et al., 2013). This observation does not support the three phase condensation model, and reinforces the idea of a single phase equilibrium condensation origin for RMNs, in agreement with calculations by Wark and Lovering (1976) and Campbell et al. (2001). However, the chemical heterogeneity of RMNs is still not fully understood.

Previous work has either been limited to analysis of a few grains in situ (Palme and Wlotzka, 1976; Wark and Lovering, 1976; El Goresy et al., 1978; Wark, 1986; Blum et al., 1988), or analysis of many grains using acid residues (Berg et al., 2009; Harries et al., 2012; Schwander et al., 2014) where the original context of the RMN was lost. Two studies have analysed large quantities of RMNs in situ: Schwander et al. (2015b) and Daly et al. (2017). Schwander et al. (2015b) demonstrated that the condensation temperature of the host mineral phase did not correlate with appropriate RMN compositions assuming RMNs formed as condensates, implying that condensation was an unlikely formation mechanism for RMNs in that study.
Analyses of inclusion-host systems in terrestrial rocks using large electron backscatter diffraction (EBSD) datasets, and the documentation of crystallographic orientation relationships (CORs) between mineral phases by Griffiths et al. (2016) revealed variable CORs between mineral inclusions and their host phase relate to changing metamorphic conditions. The context of the RMN is integral to the accurate interpretation and discernment of mineral formation mechanisms, as the formation history of the host itself will influence the interpretation. For example, RMNs hosted within chondrules which are not thought to have a condensation history, may indicate that these RMNs formed via a different mechanism. Also, any secondary alteration events experienced by the host phase would necessarily affect the RMN and may influence its crystallography and composition.

To determine which processes have affected RMNs since their formation, high resolution in situ analyses are required. Ma et al. (2014) demonstrated that combining chemical and crystallographic data through EBSD can be used to determine the origins of refractory grains such as RMNs, interpreting two new mineral phases, allendeite and hexamolybdenum, as primary nebular condensates. In this work we will apply transmission Kikuchi diffraction (TKD), a relatively new technique for which the applications to geological (Jacob et al., 2016; Piazolo et al., 2016) and meteoritical samples (Forman et al., 2016) are beginning to be explored. TKD is also referred to as transmission EBSD (t-EBSD) (Keller and Geiss, 2012). The technique allows the elemental and crystallographic mapping of a TEM lamella in a scanning electron microscope (SEM). It uses the same software and techniques as EBSD, but with an order of magnitude improvement in the resolution attainable (Trimbly, 2012; Trimbly et al., 2014; Snelson et al., 2016). This approach allows us to observe RMNs in context, preserving all CORs with associated host phases, and rapidly map the crystallography of these grains at ~5 nm resolution. It therefore provides a completely new window on the crystallography, orientation, and deformation history of these materials that has not been accessible before. TKD analysis can facilitate better interpretation of the sequence of events that may have affected each RMN since formation, and how these processes may have affected the RMNs crystallography and chemistry.

The only other study utilising TKD on meteoritic materials by Forman et al. (2016) demonstrated that TKD can be used to highlight the differences in how matrix and chondrules are affected by temperature and stress during impact induced compaction in the matrix of Allende near a chondrule. Here we will further demonstrate the potential of this technique in the analysis of RMNs. We will show and explore the possible observable effects on the crystallography and chemistry, produced by primary nebula processes, i.e. condensation and crystallisation; secondary nebular processes, i.e. transient heating events; and secondary asteroidal processes, i.e. sulphidation. TKD observations are supplemented with the utilisation of established techniques, such as EBSD and TEM.

2. METHODS

To identify RMNs in situ, a combination of Synchrotron XRF analyses corroborated with SEM observations using map overlay and feature mapping software packages was used. A full description of the procedure can be found in Daly et al. (2017). Several RMN bearing regions were identified for analysis in this study: Region A1, a sulphide nodule hosted within a porphyritic olivine (PO) chondrule in Allende; A2 and A3 were found within different forsterite enclaves within the same spinel-diopside-rich Type B CAI in Allende; ALH1, was extracted from a type B-like CAI in ALH 77307; and V1 and V2 from the reheated portion of a ‘fluffy’ type A CAI in Vigarano. Backscattered electron maps relating to the wider petrographic context of each RMN in this study is provided in Supplementary material A. Regions A1 and A3 were analysed using EBSD techniques. Ideally all regions would have been analysed by EBSD, however, these were the only regions where a sufficient polish was achieved to undertake EBSD. Regions A1, A2, ALH1, V1, and V2 were extracted and analysed using TKD, and region ALH1 was also analysed using TEM.

2.1. EBSD

The samples were prepared for EBSD by hand polishing for 30 min using 0.01 μm colloidal silica in NaOH solution. This reduces the risk of polishing away the micrometre sized RMNs identified on the surface whilst achieving the polish required for EBSD. The samples were then coated with 10 nm of carbon. EDS and EBSD data were collected using the Zeiss ULTRA Plus Field emission gun (FEG) SEM at the Australian Centre for Microscopy and Microanalysis (ACMM), The University of Sydney, with an X-Max 20 mm2 SDD EDS detector at an accelerating voltage of 20 kV, and probe current of 4–20 nA.

2.2. Focussed ion beam

The samples A1, A2, ALH1, V1, and V2 were extracted and prepared for TEM and TKD using a focussed ion beam (FIB) on the Zeiss Auriga FIB-SEM at the ACMM, The University of Sydney. The regions of interest were initially covered with a protective strip of Pt using secondary electrons, followed by a thicker layer deposited using the Ga beam. This procedure is to protect the sample during milling, and thinning, while also adding structural support to the lamellae. The section was extracted using a Kleindiek micromanipulator, and welded to a Cu TEM grid with further Pt deposition. The sample was then thinned to approximately 100 nm thickness to allow the transmission of electrons.

2.3. TKD

The samples A1, A2, ALH1, V1, and V2 were analysed using TKD on the Zeiss ULTRA Plus FEG SEM at the ACMM, The University of Sydney. TKD mapping was performed using a Nordlys-NANO EBSD detector, and EDS maps were collected with an X-Max 20 mm2 SDD.
EDS detector using an acceleration voltage of 30 kV as described in Trimby (2012) and Trimby et al. (2014).

2.4. Data reduction

The EDS, EBSD and TKD maps were collected and interpreted using the Oxford instruments AZtec and Channel 5 software packages. Grain boundaries were defined by >10° misorientation. Element abundances were derived from the EDS maps using standardless quantitative methods embedded in the Aztec software. EDS measurements of RMNs were taken with a process time of 5. This allows for better energy resolution and detection limits. The L-alpha X-ray lines were used to calculate elemental abundances for Ru, Mo, W, Re, Os, Ir and Pt, as these are better separated than the M lines. K X-ray lines were used to calculate Fe and Ni abundances. Detection limits for elements within RMNs were approximately <1 at.%. The relative uncertainty in these measurements is approximately ±10%. We also assessed the accuracy of the EDS measurement by comparing EDS and atom probe microscopy measurements from a 1 mm RuIrOs nugget from a placer deposit in Tasmania, Australia. All elements were consistent between EDS and atom probe within the 10% relative uncertainty except for Ir which was within 13% (see Supplementary Material B for a full description). This provides sufficient precision to detect major and minor elements and draw comparisons between measured RMN compositions in different meteoritic components. All other elements present in the spectra such as Mg, Al, Ca, Cu etc. were ignored following the methodology of Schwander et al. (2015b) and Daly et al. (2017), as they are likely to be generated by fluorescence in the SEM chamber from elements in the surrounding phases, or the sample mount. We do not expect these elements to be present in RMNs, but for completeness the full compositions calculated for each analysis including the contaminating elements is included in Supplementary Material C.

Not all expected HSEs were detected in every EDS analysis. For example, Rh was only detected in one RMN which may be due to its low abundance (Lodders, 2003). Other HSEs may be present in the RMNs in concentrations below the detection limits of the EDS.

RMNs were mostly characterised by a fcc awaruite or a hcp rutheniridosmine crystal structure from the EBSD database as the phase that best described most RMNs observed.

2.5. TEM

The FIB lamella taken from ALH 77307 (region ALH1) was also analysed using the JEOL2200 TEM, ACMM, the University of Sydney and the FEI Titan G280 – 200 TEM/STEM, Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia at an accelerating voltage of 200 kV. The sample was mounted on a double-tilt sample holder allowing the sample to be tilted in two directions. This allows greater flexibility to find and identify crystallographic axes. High resolution EDS maps, spot diffraction patterns and high resolution TEM (HRTEM) images were collected.

3. RESULTS

3.1. Allende – region A1

This region revealed RMNs hosted within a pentlandite nodule. The pentlandite nodule is hosted in the rim of a sulphide-rich PO chondrule. Three RMNs were observed on the surface in the EBSD dataset (Fig. 1), while a further five RMNs were revealed during the TKD analyses that were previously buried beneath the surface of the sample (Fig. 2). The RMNs varied in size from 0.1 μm to 1 μm, and form anhedral-subhedral faceted crystals. The RMNs had identical CORs relative to each other (Figs. 1 and 2). The RMNs have no COR with the pentlandite host phase, however, they do share a [100] axis with the nearby forsterite crystal (Figs. 1 and 2). Three RMNs from the EBSD dataset (Table 1) and four from the TKD dataset (Table 2) were large enough to generate good EDS spectra. The composition of the RMNs indicated that in most cases Fe and Ni are relatively homogeneous between RMNs, with the exception of entry # 3 in Table 2. Fe and Ni were overestimated in the EBSD dataset as the interaction volume of the EDS measurement was larger than the RMN. This means that there was a contribution to the EDS spectra from the surrounding pentlandite. The abundances of Ir and Pt vary between RMNs (Tables 1 and 2). The Pt should be interpreted with caution as there was likely to be some contribution of Pt from the fluorescence of the Pt protective layer deposited during FIB sample preparation in the EDS spectra in Table 2. However, the EDS spectra from the EBSD dataset (Table 1) confirms that Pt is present and variable. Mo and W are completely absent in all RMNs in this region and Os is only observed in RMN 2 in Table 2.

3.2. Allende – region A2

This RMN was extracted from a forsterite enclave within a spinel and diopside-rich Type-B CAI in the Allende CV3 meteorite. TKD revealed a cluster of RMNs with two distinct morphologies. The first was a large poly-crystalline RMN associated with molybdenite. The second was several smaller spherical isolated RMNs (20-100 nm) hosted in forsterite. The whole inclusion was surrounded by spinel (Fig. 3). There is no COR between the spinel and the inclusion. All RMNs here had a hcp structure and uniform chemistry in relation to Ru, Ir and Pt. They were also completely devoid of Mo which was situated in the molybdenite (Table 3). The molybdenite and the larger poly-crystalline RMN are crystallographically aligned with each other. They also exhibit a higher misorientation density, whereas the forsterite and smaller RMNs are uniform single crystals. The surrounding spinel is equigranular (2-5 μm) with 120° grain boundary intersections.

3.3. Allende – region A3

This RMN was hosted within another forsterite enclave within the same spinel-, diopside-rich Type-B CAI as A2. EBSD analyses revealed that the RMN has a COR with forsterite, sharing the [110] axis (Fig. 4).
Fig. 1. Characteristics of Allende – region A1: EBSD analyses of 3 RMNs are contained within a chondrule-hosted sulphide nodule. (a) A low magnification back scatter electron (BSE) image of region A1, indicating the wider context of the chondrule host with associated sulphide nodules. (b) A BSE image of the RMNs hosted within a sulphide, with a nearby forsterite grain (Fo) as well as associated Cr-spinel (Chr) inclusions. The numbers indicate where the EDS measurements were taken from in Table 1. (c) An EBSD phase map overlain on a band contrast image indicating RMNs (yellow), troilite (blue) Cr-Spinel (red) and forsterite (green), the pentlandite sulphide did not index well and is located within the black area. (d) An EBSD Euler image overlain on a band contrast image indicating crystallographic orientations of each phase, (e) A lower hemisphere stereographic projection of RMN crystallographic axes (100), (110), and (111). The crystallographic orientations of the RMNs revealed all RMNs have the same crystallographic alignment. (f) A lower hemisphere stereographic projection of the orientation of the forsterite crystallographic axes (100), (010), and (001). The red square, circle and hexagon on stereographic projections (e) and (f) indicate that the RMNs and the forsterite share a [100] axis.
ALH1 is an RMN extracted from a perovskite bearing melilite-rich B-like CAI rimmed with diopside in ALH 77307 CO3.0. TKD and TEM analysis revealed a single RMN hosted within melilite. The RMN is polyphase with a fcc region and a trigonal region. The trigonal crystal system is an unknown configuration in RMNs. We will refer to this trigonal region henceforth as the unknown phase, to distinguish it from the regular fcc RMN. As the unknown phase had not previously been documented, no mineral EBSD data were available to index it. Therefore, a proxy of Fe$_7$W$_6$ with space group 166 and $a = b = 0.4731$ nm and $c = 2.57$ nm was used. The trigonal crystal structure of the unknown phase had a very long $c$ axis relative to the $a$ and $b$ axes. Using this proxy and TEM spot diffraction, this phase was revealed to be closely related (mean angular deviation of $0.79^\circ$) to the trigonal Fe$_7$W$_6$ proxy with $a = b = 0.46$ nm $c = 2.55$ nm with space group R-3 m (166), and a simplified chemical formula (Fe, Ni)$_6$(Mo, Ru, W, Os, Ir)$_7$. The ionic radii of all elements are very similar so an empirical formula based on 13 atoms would be (Fe$_{5.2}$Ni$_{0.5}$Mo$_{5.0}$Ru$_{1.2}$W$_{0.3}$Os$_{0.4}$Ir$_{0.2}$Pt$_{0.3}$). The fcc RMN is euhedral. The unknown phase follows the grain boundary defined by the RMN and the melilite host. Which is consistent with a pseudomorph texture (Fig. 5). This unknown phase was heavily deformed with elongate bladed crystal growths (Fig. 5). TKD supported by TEM analyses indicated that the RMN was crystallographically aligned with the melilite host, as the [002] axis of the RMN was oriented parallel to the [201] axis of the melilite phase. The RMN was also crystallographically related to the unknown phase, sharing the same $c$ axis to within $6^\circ$ (Fig. 5). The RMN and the unknown phase had similar abundances of Fe, Ni, Ru, Os and Ir. However, Mo was enriched within the unknown phase relative to the RMN.
and W was present in the unknown phase but absent from the RMN. Comparing EDS measurements with TKD and TEM indicate that TEM is largely unaffected by Pt fluorescence unlike the TKD measurements. This implies that Pt was only present in the RMN and not in the unknown phase (Table 5).

3.5. Vigarano – region V1

TKD analyses of Vigarano – region V1 revealed a large anhedral 1 μm RMN with a fcc structure associated with an isolated spinel grain to the left of the section. To the right of the section, there was a cluster of 7 RMNs between 0.5 and
The cluster of RMNs were euhedral fcc crystals with twinning planes which rotated approximately 60° around the [111] axis of 20–130 nm spacing (Fig. 6). Each RMN had a different composition, with variations observed across all elements despite being located in the same inclusion of the same meteorite, and even between the cluster of 7 RMNs exhibiting twinning (Table 6).

### Table 3
RMN compositions from EDS analyses from the TEM lamellae detailed in Fig. 3. The RMN number relates to the numbered regions of Fig. 3c. b.d. = below detection limit: 1 at. % Ni, 0.4 at. % Ru, 0.1 at. % Os, 0.2 at. % Ir and 0.6 at. % S.

<table>
<thead>
<tr>
<th>Spectrum label</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Mo</th>
<th>Os</th>
<th>Ir</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenite</td>
<td>0.9 b.d.</td>
<td>59.9 b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.5 b.d.</td>
<td>2.6</td>
<td>34.0</td>
<td>32.8</td>
<td>26.1</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.6 b.d.</td>
<td>1.8</td>
<td>33.9</td>
<td>34.0</td>
<td>25.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.3 b.d.</td>
<td>b.d.</td>
<td>31.4</td>
<td>37.6</td>
<td>25.2</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.7 b.d.</td>
<td>b.d.</td>
<td>29.5</td>
<td>36.2</td>
<td>29.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.8 b.d.</td>
<td>b.d.</td>
<td>30.6</td>
<td>36.6</td>
<td>28.0</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.3 b.d.</td>
<td>b.d.</td>
<td>28.5</td>
<td>39.1</td>
<td>26.0</td>
<td>b.d.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RMN</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Mo</th>
<th>Os</th>
<th>Ir</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.5</td>
<td>5.3</td>
<td>50.4</td>
<td>3.8</td>
<td>4.5</td>
<td>14.6</td>
<td></td>
</tr>
</tbody>
</table>

0.1 µm (Fig. 6). The cluster of RMNs were euhedral fcc crystals with twinning planes that rotated approximately 60° around the [111] axis with a 20–130 nm spacing between twin planes (Fig. 6). The host phase of the RMNs was anorthite feldspar which was also twinned with a 180° rotation around the twin plane (Fig. 6). Each RMN had a different composition, with variations observed across all elements despite being located in the same inclusion of the same meteorite, and even between the cluster of 7 RMNs exhibiting twinning (Table 6).

3.6. Vigarano – region V2

TKD analyses of Vigarano – region V2 revealed a RMN and associated metal and oxide phases hosted within a spinel grain. The boundary with the spinel and the assemblage exhibited straight edges. The assemblage was subdivided into three phases: a RMN hcp phase, powellite, and awaruite. Each phase had a different composition. Mo only found in the powellite. The awaruite exhibited twinning with a rotation around the [111] axis of 60° (Fig. 7). Os only occurred in the RMN phase which was also enriched in Ru and depleted in Ni relative to the awaruite (Table 7).

### 4. DISCUSSION

Previous studies of RMNs have mostly lacked high resolution in situ crystallographic measurements, and instead focussed on the compositional variability between RMNs and mineralogical associations to inform interpretations. This new high resolution data provided by TKD may provide us with the key to accurately interpret the formation history of individual RMNs and any subsequent alteration, based on a synthesis of their petrographic context, morphology, chemistry, and CORs with host phases.

Similar analyses have been applied successfully to other phases (e.g. Jacob et al., 2016 and references there in). However, there is limited experimental work regarding the crystallography, CORs, and phase relationships between micrometre HSE nuggets such as RMNs and their associated minerals. Therefore, the following interpretations and discussions relating to the observed textures in RMNs serve only to demonstrate the potential of high resolution crystallographic analysis as a tool to extract information pertaining to the formation history of meteoritic components and inclusions. To quantify these processes precisely would require further experimental petrography which is beyond the scope of the present study.

### 4.1. Allende – region A1

RMNs are mostly interpreted as a primary phase (Palme and Wlotzka, 1976; Berg et al., 2009; Schwaneder et al., 2015b). However, if the RMNs observed here represent preserved primary phases they must survive chondrule formation, and subsequent sulphidation either in the nebula (Lauretta et al., 1996) or during metasomatism on the CV parent body (Blum et al., 1989) to arrive in their current petrographic context (Fig. 1a). The shared COR between RMNs suggests that these RMNs are genetically related. Furthermore, these RMNs are depleted in W, Mo and Os which are readily mobilised during oxidation and sulphidation of RMNs (Fegley and Palme, 1985; Jones and Scott, 1996; Palme et al., 1998). These observations suggest that these RMNs were affected if not formed by secondary processes either in the nebula or on the CV parent body. Therefore, a primordial origin for these RMNs is unlikely.

Deriving RMNs through secondary processes within chondrules requires a concentration mechanism for the HSEs due to their low abundances (measurements of bulk chondrules of the Allende meteorite indicate that they are depleted relative to bulk CV in siderophile elements such as Ir although coarse grained rims may be enriched or consistent with bulk CV (Rubin and Wasson, 1987; Grossman et al., 1988; Lodders, 2003)), a mechanism which produces and preserves the COR between RMNs and forsterite (Fig. 2), and generates heterogeneous Ir and Pt compositions (Table 2).

HSE are soluble in sulphide (Makovicky et al., 1986; Makovicky et al., 1988; Makovicky et al., 1990). However, as RMNs are present the environmental conditions must have promoted the exsolution or preservation of metal. HSE alloys have been shown to exsolve from HSE-saturated sulphides during cooling as the solubility of HSE in sulphide decreases at low temperatures (Makovicky et al., 1986; Makovicky et al., 1988). HSE alloys can also be formed by S-loss from the system (Peregoedova et al., 2004) due to a reduction in the solubility of HSEs at low oxygen fugacity (Ballhaus and Ulmer, 1995) even at trace levels of HSE (Peregoedova et al., 2004). If these RMNs were exsolution products during cooling of the sulphide we might expect to observe a COR with the host sulphide (Fleet et al., 1980; Feinberg et al., 2004) which is not the case here.
The sulphide nodules within the chondrule are all rounded blebs which is consistent with the formation of a metal-silicate immiscible fluid during chondrule formation and melting (Grossman and Wasson, 1982). This would also have the effect of concentrating the HSEs in the metal phase due to their high partition coefficients \(D_{metal/silicate} \approx 10^4\) (Borisov and Palme, 1995; Borisov and Palme, 1997; Grossman, 2010). Some of the sulphide blebs exhibit rim structures which are consistent with the expected textures produced by nebula sulphidation (Lauretta et al., 1996) and implies that these blebs were once originally pure metal. However, this appears to be the only sulphide bleb to contain RMNs in the chondrule. This suggests that the HSEs were not initially evenly distributed throughout the chondrule, as in that case all or none of the sulphide blebs should contain RMNs. This suggests that the HSEs were pre-concentrated, likely in an RMN, which was assimilated into a single metal bleb. Thus, enriching this bleb in HSEs.

During sulphidation of the chondrule (Lauretta et al., 1996) the sulphur fugacity of the vapour was insufficient to promote the incorporation of Pt and Ir into the sulphide causing it to be retained in the metal. These RMNs are then the product of the migration of HSEs which are more compatible with the metal phase (Ir, Pt) away from the sulphidation front. Experimental work by Peregoedova et al. (2004) suggest that this may occur at sulphur fugacity between \(f_{S_2}/C_0\) and \(-0.9\). If these could be constrained further, we could determine the maximum \(f_{S_2}\) experienced during nebula sulphidation. The heterogeneous chemistry is generated by either heterogeneous distribution of HSEs in the nodule, which is unlikely due to the affinity of HSE

---

**Fig. 4.** Characteristics of Allende – region A3: EBSD analyses of a forsterite hosted RMN from a CAI. (a) A low magnification FSD image of region A3 (red box) indicating the context of the RMN within the CAI, (b) FSD image of Region A3 indicating where the EBSD dataset was acquired (red box), associated minerals are labelled forsterite (Fo), spinel (Spl) and diopside (Di), (c) EBSD phase map indicating an RMN hosted within a forsterite grain, the number indicates the EDS measurement taken from that point detailed in Table 4, (d) Euler map indicating crystallographic orientations, (e) Lower hemisphere stereographic projection of crystallographic orientations of the RMN, (f) Lower hemisphere stereographic projection of crystallographic orientations of the forsterite. Comparing the projections reveals the RMN have a COR with the forsterite sharing their (110) axis (red circle).
to metal (Borisov and Palme, 1995; Borisov and Palme, 1997; Grossman, 2010), or heterogeneities in local mineral chemistry – proximity to forsterite or proximity to troilite etc. or variable sizes of the ‘catchment area’ from which the HSEs were delivered to the RMN.

The COR between the forsterite grains and RMNs by way of a shared [100] axis may originate during the initial crystallisation of the chondrule, where forsterite crystallised around the Fe-metal bleb. Subsequent crystallisation of the Fe-metal would produce a COR by way of minimising the

---

**Fig. 5.** Characteristics of ALH 77307 – region ALH1: TKD analyses from a FIB-produced TEM lamella of an RMN bearing melilite crystal within a Type B-like CAI. (a) A BSE image of the RMN in situ, prior to FIB extraction, hosted within a Type B-like CAI. Associated minerals are melilite (Mel) and perovskite (Prv), (b) TKD band contrast image of the RMN and associated unknown phase. The labels indicate where EDS spectra from TKD and TEM were taken in Table 5, (c) TEM image of the RMN and associated unknown phase indicating the phase is heavily dislocated, exhibiting oriented bladed crystal morphologies, (e) TKD phase map indicating a euhedral RMN (yellow), its associated unknown phase (blue), and the melilite host (red). The RMN is observed to be euhedral and the unknown phase adopts a pseudomorph texture with the RMN, (f) TEM spot diffraction patterns taken from each phase. These spot diffraction patterns are overlain which revealed a shared (c) crystal axis between the RMN and the unknown phase within 6°. The RMN [002] axis is shared with the [201] axis of the melilite host.
interfacial energy (Frondel, 1940), see also reaction fabric (Lauder, 1961). Therefore, these RMNs preserve the initial alignment of the original Fe-metal bleb. There is no possibility of producing the observed alignment by compaction or through magnetic susceptibility. Furthermore, these RMNs are not connected in a 3D worm-like structure but are isolated grains, so the original alignment is preserved despite the isolation of these RMNs. This orientation relationship is preserved during sulphidation (Lauretta et al., 1996), and throughout any subsequent metamorphic alteration of the CV3 parent body (Blum et al., 1989).

In summary, the most likely sequence of events that occurred to produce the RMNs in Allende – region A1 is as follows: during chondrule formation an immiscible metal-silicate melt formed (Grossman and Wasson, 1982). One of these metal nodules incorporated an HSE enriched particle. On cooling the forsterite crystallised first around the still molten metal nodule. Further cooling crystallised the metal nodule with a COR with forsterite through minimising the interfacial energy (Frondel, 1940). Lauder, 1961). The chondrule was then exposed to a sulphur rich gas which sulphidised the metal grain (Lauretta et al., 1996). The sulphur fugacity was such that Pt and Ir were above the saturation point for the sulphide (Peregoedova et al., 2004) causing them to preferentially remain in the metal. Tungsten, Mo and Os were also decreased. The triple point of forsterite under nebular conditions is approximately 1890°C (Nagahara et al., 1994). However, within the spinel-forsterite system forsterite melts at 1700°C (Milholland and Presnall, 1998) and within the diopside-forsterite system forsterite melts at ~1300°C (Presnall et al., 1978). Therefore, it may be possible to have forsterite and RMN melts coexisting to produce the rounded blebs (Grossman and Wasson, 1982).

Spherical RMNs have been observed by Schwander et al. (2015b). These authors concluded that such RMNs were derived from the crystallisation of dissolved HSEs into metal grains from a CAI melt. They suggested crystallisation would produce RMNs with spherical morphologies through a minimisation of the surface energy at the RMN grain boundary and the surrounding liquid. The RMNs here also have homogeneous chemistries consistent with this origin (Daly et al., 2017). However, in this case the abundance of HSEs is too high to completely dissolve in the forsterite melt due to the high metal-silicate partition coefficients (Borisov and Palme, 1995; Grossman, 2010) and the low volume of the forsterite.

Alternatively, this inclusion may represent a small OA (Blum et al., 1989; Palme et al., 1994). These are thought to be incorporated into CAIs as homogeneous alloys and subsequently separate into a number of phases during subsequent alteration of the CAI. The COR between the larger RMN and the molybdenite and the ‘interfingering’ texture of the two phases is consistent with a reaction texture caused during exsolution of the two phases under oxidising conditions (Fegley and Palme, 1988). Therefore, this assemblage and the associated RMNs may represent exsolution products during the phase separation of the initially homogeneous alloy lower temperatures under variable oxygen fugacities (Blum et al., 1988; Blum et al., 1989; Palme et al., 1994). If this is the case, some isolated RMNs may be

### Table 5

EDS measurements taken from Region ALH, comparing TEM with TKD analyses. This label corresponds to the label in Fig. 5b. b.d. = below detection limit: 0 at.% Rh, 0.4 at.% W, and 0.1 at.% Pt.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mineral</th>
<th>Fe at.%</th>
<th>Ni at.%</th>
<th>Ru at.%</th>
<th>Rh at.%</th>
<th>Mo at.%</th>
<th>W at.%</th>
<th>Os at.%</th>
<th>Ir at.%</th>
<th>Pt at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM</td>
<td>RMN</td>
<td>55.5</td>
<td>9.4</td>
<td>7.5</td>
<td>b.d.</td>
<td>6.7</td>
<td>b.d.</td>
<td>7.0</td>
<td>4.0</td>
<td>9.9</td>
</tr>
<tr>
<td>TKD</td>
<td>RMN</td>
<td>48.7</td>
<td>8.2</td>
<td>11.8</td>
<td>2.8</td>
<td>14.0</td>
<td>b.d.</td>
<td>2.0</td>
<td>2.8</td>
<td>9.8</td>
</tr>
<tr>
<td>TEM</td>
<td>unknown phase</td>
<td>50.9</td>
<td>9.4</td>
<td>6.3</td>
<td>b.d.</td>
<td>26.6</td>
<td>1.8</td>
<td>7.9</td>
<td>2.2</td>
<td>b.d.</td>
</tr>
<tr>
<td>TKD</td>
<td>unknown phase</td>
<td>40.0</td>
<td>3.7</td>
<td>9.2</td>
<td>b.d.</td>
<td>38.8</td>
<td>2.0</td>
<td>2.8</td>
<td>1.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>
derived from disrupted OAs (Blum et al., 1989). However, exsolution textures are usually associated with CORs with the host (Fleet et al., 1980; Feinberg et al., 2004) which are not observed within the small spherical RMNs. This implies a low temperature exsolution origin is less likely for these RMNs.

In summary, the most likely sequence of events experienced by this section is that a small OA was incorporated into a CAI pre-cursor (Blum et al., 1988; Blum et al., 1989; Palme et al., 1994). On melting and subsequent crystallisation of the CAI the OA was sequestered as an inclusion within spinel (Blum et al., 1989). During a subsequent
high temperature event which melted the OA an immiscible metal-silicate fluid formed which cooled producing randomly oriented small spherical RMNs within forsterite. During low temperature alteration at high oxygen fugacity the larger RMN exsolved into molybdenite and a metallic phase (Blum et al., 1989).

4.3. Allende – region A3

This RMN was hosted in the core of a forsterite enclave surrounded by diopside with associated euhedral spinel laths from the same Type-B CAI from region A2.

The RMN share a [110] axis with the forsterite. This is similar to the observed COR between RMNs and forsterite in region A1 where the [100] is shared. Here the RMN is situated in the core of the forsterite inclusion. The COR may have formed due to the minimisation of interfacial energy between the RMN and the forsterite, as was the case for the original metal nodules in region A1. However, in this case as the RMN is likely to crystallise at higher temperatures than the forsterite (Presnall et al., 1978; Bird and Bassett, 1980) and is situated at the core of the forsterite grain, it is possible that this RMN also acted as a nucleation site.

There are two types of nucleation: homogeneous and heterogeneous. Homogeneous nucleation occurs when the crystal nucleates from a newly formed embryo of similar material, whereas, heterogeneous nucleation occurs when a crystal nucleates off a pre-existing nuclei or pre-existing material, whereas, heterogeneous nucleation occurs when crystal nucleates from a newly formed embryo of similar heterogeneous. Homogeneous nucleation occurs when the nucleation site.

Grain, it is possible that this RMN also acted as a nucleation site.

Table 6

<table>
<thead>
<tr>
<th>RMN grain</th>
<th>Fe</th>
<th>Ni</th>
<th>Ru</th>
<th>Mo</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.7</td>
<td>48.6</td>
<td>1.8</td>
<td>b.d.</td>
<td>0.4</td>
<td>b.d.</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>67.4</td>
<td>15.5</td>
<td>11.8</td>
<td>b.d.</td>
<td>2.5</td>
<td>2.8</td>
<td>b.d.</td>
</tr>
<tr>
<td>3</td>
<td>62.9</td>
<td>29.4</td>
<td>5.6</td>
<td>b.d.</td>
<td>1.1</td>
<td>0.9</td>
<td>b.d.</td>
</tr>
<tr>
<td>4</td>
<td>65.6</td>
<td>14.2</td>
<td>14.2</td>
<td>b.d.</td>
<td>2.4</td>
<td>3.6</td>
<td>b.d.</td>
</tr>
<tr>
<td>5</td>
<td>62.4</td>
<td>30.1</td>
<td>4.6</td>
<td>b.d.</td>
<td>1.0</td>
<td>1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>6</td>
<td>65.3</td>
<td>39.2</td>
<td>2.5</td>
<td>b.d.</td>
<td>0.7</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>7</td>
<td>57.0</td>
<td>36.4</td>
<td>3.5</td>
<td>b.d.</td>
<td>1.1</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>64.3</td>
<td>17.8</td>
<td>10.7</td>
<td>b.d.</td>
<td>3.3</td>
<td>3.8</td>
<td>b.d.</td>
</tr>
</tbody>
</table>

The RMN at. %

perovskite laths indicate it was once molten, and 120° grain boundary intersections of the melilite indicate that is was subsequently annealed (Smith, 1948; Komatsu et al., 2001), consistent with this type of inclusion (Grossman et al., 2000; MacPherson et al., 2005) The RMN is associated with an unknown phase which adopted a pseudo-morph texture with the RMN. For metal grains in meteorites a euhedral morphology is interpreted as mineral growth in an unconstrained environment within a vapour or melt (Rubin, 1994), although it is plausible that euhedral metal laths could grow during metamorphism none have been reported (Rubin, 1994). Therefore, euhedral RMNs are interpreted to have grown in an unconstrained environment.

The unknown phase was likely to be a secondary phase formed by alteration of the RMN, separating Mo and W into the unknown phase due to their increased mobility during alteration events (Fegley and Palme, 1985; Palme et al., 1998). The pseudomorph texture indicated that the secondary alteration must have occurred whilst the RMN was within the CAI post-crystallisation. The process that caused this phase separation must have occurred at temperatures lower than the melting point of the melilite host (1410–1510 °C (Stolper, 1982; Mendybaev et al., 2006)). If this was not the case the unknown phase would have been able to grow unconstrained, and would not exhibit the observed deformation features, or conform to the original RMN grain boundary (Rubin, 1994). There are two possible alteration sites: alteration on the parent body, or alteration in the nebula. ALH 77307 is one of the most primitive meteorites in the collection, with a maximum parent body temperature of 203 °C (Cody et al., 2008).

The observed textures within the unknown phase exhibit a high dislocation density. The TKD data indicate these dislocations have various orientation changes between grains of the unknown phase while maintaining a COR with the RMN to within 6°. This could form through either crystal plastic deformation or rapid formation. Crystal plastic deformation requires an induced stress field, which is unlikely in an asteroidal environment and therefore this grain likely formed rapidly. We suggest this unknown phase formed by solid state recrystallisation of the RMN during a transient heating event in the protoplanetary disk, prior to the incorporation of the CAI into the parent body. If the conditions required for this phase transformation were known, it would be possible to constrain this event.

The RMN shares a minor axis with the melilite host. This COR with the melilite mineral may indicate that the melilite crystal nucleated around the RMN. This is interpreted along a similar line of reasoning to region A3. These observations indicate that during crystallisation this CAI experienced rapid cooling which caused heterogeneous nucleation of melilite around the RMN. This was followed by a second transient heating event below 1410 °C (Stolper, 1982; Mendybaev et al., 2006) that exsolved the unknown phase from the RMN and produced the pseudo-morph texture and the observed crystallographic alignments, as well as annealing the CAI. This is consistent with our understanding of CAI formation (Grossman et al., 2000; MacPherson et al., 2005).

4.4. ALH 77307 – region ALHI

The RMN in this section is euhedral and hosted within a type B-like CAI. The texture of the CAI with euhedral
4.5. Vigarano – region V1 and V2

The CAI bearing the V1 and V2 regions has a zoned texture with a relatively unaltered core. There is potentially reheated material surrounding the core, and Wark Lovering rims around the edge of the CAI. The region is interpreted as ‘re-heated’ due to the presence of annealing textures such as 180° mirror twins within the anorthite (Fig. 6) and 120° grain-boundary-intersection spinel grains (Smith, 1948; Komatsu et al., 2001). The RMNs were extracted from this re-heated portion of the CAI, and are hosted within an anorthite grain (Region V1) and a spinel grain (Region V2).

The RMNs in V1 had two distinct morphologies: an anhedral RMN associated with spinel, and several euhedral twinned RMNs with straight grain boundaries (Fig. 6).

Fig. 7. Characteristics of Vigarano – region V2. TKD analyses of RMNs and associated HSE alteration phases. These RMNs are hosted in spinel contained within the altered mantle of a fluffy type A CAI. (a) Low magnification BSE image of region V2 in the wider context of the CAI also showing a nearby matrix region and chondrule (Chond), (b) A BSE image of the RMN (bright spot) in context, before extraction. The red rectangle indicates the orientation of the TEM section, the RMN here is associated with spinel (Spl), (c) A TKD phase map of the section indicating the RMN (green) powellite (red) and awaruite (blue) assemblage hosted in a spinel (yellow). The labels indicate where EDS spectra were taken in Table 7, (d) A TKD euler map indicating crystallographic orientations of all the phases. Twin planes are shown as red lines indicating the awaruite phase is twinned, (e) Lower hemisphere stereographic projection of crystallographic orientations of the awaruite, indicating a rotation about the [111] axis of 60°, (f) Lower hemisphere stereographic projection of crystallographic orientations of the powellite, (g) Lower hemisphere stereographic projection of crystallographic orientations of the two largest RMN grains with a shared pole in the [110] axis, (h) Lower hemisphere stereographic projection of crystallographic orientations of the spinel. There are no systematic CORs observed between any of the phases.

4.5. Vigarno – region V1 and V2

The CAI bearing the V1 and V2 regions has a zoned texture with a relatively unaltered core. There is potentially reheated material surrounding the core, and Wark Lovering rims around the edge of the CAI. The region is interpreted as ‘re-heated’ due to the presence of annealing textures such as 180° mirror twins within the anorthite (Fig. 6) and 120° grain-boundary-intersection spinel grains (Smith, 1948; Komatsu et al., 2001). The RMNs were extracted from this re-heated portion of the CAI, and are hosted within an anorthite grain (Region V1) and a spinel grain (Region V2).

The RMNs in V1 had two distinct morphologies: an anhedral RMN associated with spinel, and several euhedral twinned RMNs with straight grain boundaries (Fig. 6).
euhedral RMNs likely formed in an unconstrained environment in the presence of a fluid or gas (Rubin, 1994). Their accumulation in a void space indicates that they may have originally been free floating in the nebula gas, or were initially suspended in a mineral which has since been removed. The chemistry of each RMN in V1 are different from each other, and none have chondritic relative elemental ratios even though these grains are hosted within the same CAI, and in some places are situated adjacent to each other. However, an ‘average’ RMN derived from the mean HSE abundances of these RMNs is consistent with chondritic elemental ratios. None contain detectable Mo suggesting these elements may have been remobilised (Fegley and Palme, 1985). There is no transfer or re-equilibration of HSEs, even between RMNs separated by only a few nanometres. The RMN associated with the spinel in V1 together form a spherical inclusion. There is a slight curvature of the RMN grain boundary towards the bottom of the inclusion (Fig. 6). This curvature could be interpreted as the meniscus between two fluids which suggests that the RMN and the spinel were both molten forming an immiscible silicate-metal melt.

The region V2 contains a complex HSE-rich inclusion and is unlike any previously described RMN in this study. The RMN has separated into three phases: a Mo-rich powellite, a Ni-rich twinned awaruite and an Os, Ru-enriched RMN. These textures are consistent with an OA (El Goresy et al., 1977; Blum et al., 1988) (Fig. 7). This inclusion contains two metal phases: awaruite and the RMN, which exhibit a complementary depletion or enrichment in Ru and an enrichment or depletion in Ni, respectively. The powellite is the only phase present to contain Mo. All of the phases exhibit deviations from chondritic relative abundances consistent with an OA (El Goresy et al., 1977; Palme et al., 1994).

The crystal twins observed within RMNs in Vigarano in both the euhedral RMNs in V1 (Fig. 6) and the awaruite in V2 (Fig. 7) have not previously been reported in RMNs despite numerous and detailed SEM (Wark and Lovering, 1976; Sylvester et al., 1990; Schwander et al., 2015b) and TEM studies (Harries et al., 2012; Crost et al., 2013). This demonstrates the value of TKD and its ability to map the crystallography and chemistry of a lamella rapidly, in comparison to established techniques such as TEM. Twinning can be produced via a number of different mechanisms, such as growth, annealing and deformation (Cahn, 1954).

The pressure and strain rate required for the onset of shock twinning for micrometre alloys of HSEs such as RMNs is not well constrained. The Vigarano meteorite has undergone very little processing in terms of deformation and shock (Scott et al., 1992). Vigarano is classified as shock stage SI (Scott et al., 1992; Komatsu et al., 2001) implying it experienced <5 GPa (Stöffler and Keil, 1991). Neumann lines in kamacite are generated by shock in iron meteorites at ~1 GPa (Bischoff and Stöffler, 1992). Vigarano contains kamacite, but such textures have not been reported within these metal inclusions in Vigarano (McSween, 1977). Furthermore, shock twinning is dependent on both grain size, where smaller grains are more resistant to shock twinning (Meyers et al., 1995). Therefore, if RMNs are comparable to kamacite metals in Vigarano and the fact that a second RMN within the same TEM lamellae does not exhibit twinning it is reasonable to assume that these twins are not derived from shock related processes.

This leaves two possibilities: growth twins and annealing twins. If the observed twins were growth twins formed from nucleation these would be observed as simple penetration twins. This would result in clear crystal faces with changes in the morphology of the RMN which are coincident with the twin boundary. This is not observed within the sample as the crystal faces are well formed and continuous across the twin boundary. We would also expect this to be a much more common observation in RMNs if they formed growth twins.

Annealing twins form at high temperatures with relatively little stress. In fcc crystals they classically form along the [111] axis with a 60° misorientation (Brandon, 1966), which is consistent with the observed RMN twins in Vigarano (Fig. 6). This implies that the twinning observed is probably formed by annealing. TEM experiments by Dai et al. (2001) observed annealing twin formation in FePt nanoparticles. This study indicated that while heating under vacuum for one hour, annealing twins began to form at 450 °C, and were completely annealed by 530 °C. The nanoparticles studied coalesced into larger grains at 600–700 °C. The RMNs observed in Vigarano, however, have not coalesced. The specific grains in the aforementioned study are compositionally different to RMNs observed in our research, so only limited caparisons can be made. However, the temperature dependence of the onset of annealing
twinning (Dai et al., 2001) indicates that by constraining their formation temperature by experiment for RMN alloy compositions, annealing twins could be used as a coarse thermometer for early Solar System processes.

These annealing twins could form either as a result of thermal metamorphism on the CV parent body, or pre-accretion in the nebula either as free floating RMNs or subsequent to RMN incorporation into the CAI.

The CAI here did contain nepheline and sodalite which are evidence for parent body alteration (Krot et al., 1997). The highest estimates place the maximum parent body temperatures experienced by Vigarano at 415 °C (Cody et al., 2008), and most estimates for Vigarano peak temperatures are much lower than this (<330 °C) (e.g. Bonal et al., 2006; Bonal et al., 2007). If RMNs anneal in this temperature range we could further constrain parent body temperatures.

The twinning present in the awaruite in V2 may be of this nature as awaruite is a low temperature phase which forms at <500 °C (Reuter et al., 1989) associated with parent body alteration (Müller et al., 1993). These RMNs are hosted in anorthite and spinel which do not exhibit textures consistent with melting. These phases melt at 1250 °C and 1550 °C respectively (Stolper, 1982) so therefore, if RMNs form annealing twins between 400 and 1200 °C (the maximum Vigarano parent body temperature and the temperature that anorthite melts in CAIs (Stolper, 1982; Bonal et al., 2006; Cody et al., 2008)) this would allow us to determine the temperature of transient heating events in the nebula.

Annealing RMNs in the nebula environment prior to incorporation into the host may be unlikely as CAIs also form at high temperatures (MacPherson et al., 2005) close to the formation temperatures of RMNs (Berg et al., 2009) which would leave only a narrow window for the formation of annealing twins, which may then be overprinted by subsequent re-heating within the CAI.

The temperature dependence of the onset of annealing twin formation and complete recrystallisation (Dai et al., 2001) means that if the temperature range of RMN annealing were constrained, annealing textures could be used as a low resolution thermometers for pre-accretion heating events, or parent body heating.

4.6. Summary

RMNs are a complicated group of alloy minerals in meteorites. It is apparent that each individual RMN preserves a history of Solar System events and possibly even pre-solar events.

The morphology of RMNs may indicate the processes and environment the RMN formed in, e.g., euhedral RMNs are expected to form in unconstrained environments such as growth in a fluid or gas phase (Rubin, 1994). If this growth is impeded or the RMN is subsequently altered, we would expect to observe anhedral-subhedral RMNs. Spherical RMNs have previously been interpreted as forming through crystallisation from a silicate melt (Schwander et al., 2015b). However, the spherical RMNs observed here are more likely to represent the formation of immiscible metal-silicate melt at high temperatures.

The analyses of RMNs using TKD have revealed several crystallographic textures that had not been documented previously. These observations provide evidence for, and could provide constraints on, several Solar System processes. CO2s between RMNs and their host and petrological data can be used to demonstrate that in some cases RMNs acted as a heterogeneous nucleation site for the host phase during crystallisation. The presence of annealing twins within RMNs which are temperature dependant (Dai et al., 2001) means that RMNs could be used as a coarse thermometer for parent body or nebula heating events. The context of the RMN in relation to its host phase and inclusion can also indicate when and where the RMN was altered and under what conditions.

Several RMNs when analysed by TKD revealed that they were in fact polyphase inclusions similar to OAs, although these are much smaller than those described previously (El Goresy et al., 1977; Blum et al., 1989). It is not clear if this reflects a property of HSE-rich alloys in meteorites to separate into phases during low temperature alteration (Blum et al., 1988; Blum et al., 1989; Palme et al., 1994) or a genetic link between OAs and RMNs. In any case, it appears that OAs can exsolve RMN like inclusions while RMN sized objects can be internally complex.

The relative chemical abundances of HSEs in RMNs are variable with the exception of the small spherical RMNs in A2 which have uniform chemistry with near chondritic relative elemental abundances. This may be due to a separation of immiscible metal-silicate fluids during melting of an OA. These RMNs are also situated next to a RMN which appears to preserve dislocations and a reaction texture which is consistent with exsolution at lower temperatures and higher oxygen fugacity (Blum et al., 1989), signifying it formed before the melting event. RMNs in A1 appear to be able to form by migration of HSEs during sulphidation of metal nodules. In all other RMNs in this study, including altered RMNs, we still observe non-chondritic relative abundances of at least two HSEs. HSE elements Os, Ir, Pt and Ru are observed to be largely unaffected by most asteroidal processes. Os can be mobilised in transient heating events at high oxygen fugacity. Tungsten and Mo are mobilised by low levels of alteration in either a high oxygen fugacity environment or in the presence of sulphur (Fegeley and Palme, 1985). Isolated RMN-bearing inclusions can preserve Mo and W where they are encapsulated within an impermeable host. The immobility of most HSEs is evident even in RMNs in the same inclusion, same host mineral and even in some separated by a few nanometres of void space. This suggests that RMNs are resistant to re-equilibration, and individual RMNs can be approximated to a closed system during the majority of Solar System processes with regard to these elements. Therefore, the refractory component of RMNs may preserve a primary or even pre-solar signature.

Combining these observations provides evidence that supports the suggestion of Daly et al. (2017); RMNs that have not been homogenised during melting, preserve a primordial signature that is inconsistent with condensation and is likely to have originated as part of an inherently diverse population of RMNs distributed throughout the
Giant Molecular Cloud. Isotopic analyses of individual RMNs would provide a clear answer to this hypothesis.

5. CONCLUSIONS

TKD and other high resolution in situ analyses are integral to the interpretation of RMNs, enabling us to evaluate the sequence of events that may have affected RMN chemistry and relations to host inclusions since the formation of the RMN. Every section analysed in this study could not be fully interpreted without the incorporation of every facet of information provided by TKD analyses. The relationships between RMN chemistry, morphology, CORs and mineral associations observed in this study combine to form a powerful dataset that can begin to build a framework from which RMN formation and alteration can be determined. Previous work on RMNs showed that they exhibit heterogeneous chemical compositions, inconsistent with a single formation model (Daly et al., 2017). TKD of RMNs reveal a suite of crystallographic features such as twinning – interpreted here as annealing twins, CORs, randomly oriented spherical nano-RMNs, reaction textures, nucleation centres and fluid immiscibility textures. This indicates that RMNs experienced a diversity of formation histories even between RMNs within the same meteorite, inclusion, and even separated by a few nanometres. In cases where the RMN had been altered we still observe chemical heterogeneities between RMNs. The variety of crystallographic textures observed indicate each individual RMN has a complex formation history. These observations are consistent with the suggestion of Daly et al. (2017), that some RMNs have survived Solar System formation and preserve an inherited heterogeneity from the Giant Molecular Cloud.

ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council via their Australian Laureate Fellowship program. This research was undertaken on the XRF beamline at the Australian Synchrotron, Victoria, Australia. The authors acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the Australian Centre for Microscopy and Microanalysis, the University of Sydney and the Centre for Microscopy, Characterisation and Analysis, University of Western Australia. This work was conducted within the Geoscience Atom Probe Facility at Curtin University, which is part of the Advanced Resource Characterisation Facility (ARCF). The Advanced Resource Characterisation Facility is being developed under the auspices of the National Research Science Precinct – a collaboration between CSIRO, Curtin University and The University of Western Australia – and is supported by the Science and Industry Endowment Fund (SIEF RI13 – 01). SMR acknowledges support from the ARC Core to Crust Fluid System COE (CE11E0070). The authors would also like to thank guest editor Dr. Chi Ma, as well as reviews from Prof. Herbert Palme and Prof. Alexander Krot and one anonymous reviewer for their invaluable comments which improved the manuscript substantially, as well as Prof. Amy Riches for arranging and organising the HSE special issue and ensuring it was published in good time. The authors would finally like to thank the rest of the Desert Fireball Network research group as well as, Mr. Mark Daly, and Ms. Jennifer Porter for their assistance and support.

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2017.03.037.

REFERENCES


Geochimica et Cosmochimica Acta 51, 3175–3192.


A.3. **Paper 3 – Nebula sulfidation and evidence for migration of ‘free floating’ refractory metal nuggets revealed by atom probe microscopy**

*Geology* (2017), v. 45, no. 9, p. 847 – 850

Special "Fair Use" permission

If you want to use a single figure, a brief paragraph, or a single table from a GSA publication, GSA considers this to be fair usage, and you need no formal permission and no fees are assessed unless you or your publisher require a formal permission letter. In that case, you should print a copy of this document and present it to your publisher.

An author has the right to use his or her article or a portion of the article in a thesis or dissertation without requesting permission from GSA, provided the bibliographic citation and the GSA copyright credit line are given on the appropriate pages.
STATEMENT OF AUTHORSHIP

TITLE OF PAPER: Nebula sulfidation and evidence for migration of ‘free floating’ refractory metal nuggets revealed by atom probe microscopy.

PUBLICATION STATUS: Accepted

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript.

Overall Percentage: 68%

Signature: [Signature]  Date: [Date]

Name of Co-Author: Philip A. Bland

Contribution to the Paper: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature]  Date: [Date]
Name of Co-Author: David W. Saxey
Contribution to the Paper: Assisted with Atom Probe data collection and data reduction editing and review of the manuscript.
Overall Percentage: 5%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Steven M. Reddy
Contribution to the Paper: Assisted with EBSD interpretation editing and review of the manuscript.
Overall Percentage: 5%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Denis Fougerouse
Contribution to the Paper: Assisted with FIB sample preparation and editing and review of the manuscript.
Overall Percentage: 5%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: William D. A. Rickard
Contribution to the Paper: Assisted with FIB sample preparation and editing and review of the manuscript.
Overall Percentage: 5%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Lucy V. Forman
Contribution to the Paper: Assisted in editing and review of manuscript.
Overall Percentage: 2%
Signature: [Signature]
Date: 22.2.17.
Nebula sulfidation and evidence for migration of “free-floating” refractory metal nuggets revealed by atom probe microscopy

Luke Daly1,2, Phil A. Bland3, David W. Saxey3, Steven M. Reddy2,3, Denis Fougerouse2,3, William D.A. Rickard3, and Lucy V. Forman2
1School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK
2Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6102, Australia
3Geoscience Atom Probe Facility, Advanced Resource Characterisation Facility, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

ABSTRACT

Disk models have been proposed that imply particles migrate rapidly in a protoplanetary disk. However, the only physical constraints on these processes from meteorites are observations of refractory inclusions in cometary material from the NASA Stardust mission. Atom probe microscopy (APM) of sub-micrometer refractory metal nuggets (RMNs) contained within a Sc-Zr-rich ultrarefractory inclusion (URI) from the ALH 77307 carbonaceous Ornans (CO) 3.0 meteorite revealed the presence of sulfur at 0.06–1.00 atomic percent (at%) abundances within RMNs. The mineralogical assemblage, petrographic texture, and flat chondrite-normalized highly siderophile element ratios indicate S exposure was unlikely to have occurred after the RMNs were incorporated into the URI. APM analyses suggest these RMNs were likely “free floating” when they were exposed to a S-condensing gas. This requires early, rapid migration of RMNs to cooler regions of the disk to incorporate S and then cycling back to the Ca-Al-rich inclusion (CAI)–forming region for incorporation in the URI, or conditions in the CAI-forming region that promote the incorporation of S into RMNs.

INTRODUCTION

Refractory metal nuggets (RMNs) are micro-meter to submicrometer metal alloys composed of highly siderophile elements (HSEs): Os, Ir, Pt, W, Mo, Ru, Rh, Fe, and Ni, and they are found in primitive meteorites (Palme and Wlotzka, 1976; Wark and Lovering, 1976). They are thought to form early, at high temperatures (Berg et al., 2009) alongside other refractory inclusions such as Ca-Al-rich inclusions (CAIs) and their associated phases, close to a protosun (MacPherson et al., 2005). These refractory materials are found within carbonaceous chondrite meteorites and within cometary material returned from the NASA Stardust mission (Brownlee et al., 2006; McKeean et al., 2006; Zolensky et al., 2006). This observation requires a mechanism for particles to migrate from proximal to distant heliocentric distances >30 astronomical units (AU). Several mechanisms have been suggested that can distribute material throughout a protoplanetary disk within reasonable time scales, i.e., 104 yr (Ciesla, 2010) relative to the lifetime of the nebula (106 yr; Russell et al., 2006). Principally, these suggested mechanisms are the X-wind model (Shu et al., 1997), diffusion along the disk’s midplane (Bockelée-Morvan et al., 2002; Ciesla, 2007; Hughes and Armitage, 2010), and disk winds (Bai, 2014). The only physical constraints on these models is the presence of CAIs in comets. However, RMNs, as one of the first phases to form in a protoplanetary disk (Berg et al., 2009), preserve geochemical information pertaining to the initial conditions of our solar system and therefore may be an ideal phase in which to observe evidence of particle migration in the disk. However, establishing the exact compositions of RMNs is difficult due to their submicrometer size (Schwander et al., 2015).

To address this issue, we use a focused-ion beam (FIB) for site-specific sampling of a suite of RMNs to recover RMN samples foratom probe microscopy (APM). APM is a novel technique that allows subnanometer-resolution quantitative three-dimensional (3-D) elemental mapping of ion distributions down to 10 appm (atomic parts per million) concentrations in very small samples (Gault et al., 2012; Kelly and Larson, 2012), and we used it to provide quantitative bulk chemistry data from a suite of submicrometer RMNs. These data reveal trace abundances of sulfur, which have not previously been observed in RMNs. Our results therefore provide further constraints on early solar system material transport and disk processes.

METHODOLOGY

A Sc-Zr-rich ultrarefractory inclusion (URI) bearing abundant RMNs was identified in the ALH 77307 CO3.0 meteorite (from Allan Hills, Antarctica). ALH 77307 CO3.0 was chosen because it is one of the most primitive meteorites and experienced minimal parent body processing (Grossman and Bredaey, 2005). The URI was characterized using simultaneous electron backscatter diffraction (EBSD) and energy dispersive X-ray spectroscopy (EDS) mapping on the TESCAN MIRA3 variable pressure–field emission scanning electron microscope (VP-FESEM) at the John de Laeter Centre (JdLC), Curtin University, Perth, Australia (see Appendix DRA in the GSA Data Repository1). Six RMNs (RMN1–RMN6) between 900 and 300 nm, and a portion of the interior and rim of the URI (kan1 and cpx1, respectively) were extracted from the sample and milled to needle-like shapes using the TESCAN LYRA3 FIB scanning electron microscope (SEM) at JdLC, using a modified version of Thompson et al.’s (2007) methodology for site-specific targeting of submicron features (Figs. 1 and 2; Appendix DRB). The resulting specimens were analyzed on the local electrode atom probe (LEAP, 4000X HR Geoscience Atom Probe), part of the Advanced Resource Characterization Facility at JdLC (Appendix DRC). The numbers of ionic species detected by APM from each specimen were 2.4, 17.0, 8.0, 5.6, 14.7, 7.3, and 0.6 × 104 for the RMN1–RMN5, kan1, and cpx1 specimens, respectively. RMN6 did not run (Appendix DRE). Elemental abundances in each specimen were calculated using the IVAS 3.6.14 software package (Appendix DRD).

The chemistry and structure of the RMNs and adjacent phases were analyzed prior to lift out for APM analyses by EDS and EBSD, respectively. EDS data were used to aid the interpretation of the APM mass spectra for major elements, and EBSD data were used to identify the mineral phases by their crystal structure and thereby constrain the oxide content. Because the phase and therefore oxygen abundance were known, this allowed corrections to be made for any oxygen stoichiometry errors in the APM compositional quantification (Devur et al., 2013; Amirifar et al., 2015; Karahkka et al., 2015; Gault et al., 2016).
EDS and EBSD analyses revealed that the URI was dominated by Zr- and Sc-rich oxide phases: perovskite, spinel, and kangite (Ma et al., 2013). The URI was largely encapsulated by a rim of clinopyroxene (Fig. 1). The oxide minerals were equigranular, with some grain and phase boundaries interlocking at 120°. All phases exhibited minimal internal deformation; internal misorientations of individual grains were <1°.

The compositions of APN specimens extracted from the kangite (kan1) and the clinopyroxene rim (cpx1) are summarized in Table 1.

DISCUSSION
Some of the minerals within the URI exhibit 120° grain boundary intersections (Fig. 1). These textures are indicative of annealing (Komatsu et al., 2001; Smith, 1948). The rim of the URI also penetrates into the inclusion along grain boundaries, and crystal edges in contact with the rim are rounded, consistent with partial melting (Bulau et al., 1979). This indicates that the URI experienced elevated temperatures after it formed.

RMNs are assumed to be pure metallic alloys (i.e., Schwander et al., 2015; Daly et al., 2017) composed of HSEs with 50% condensation temperatures of 1821–1408 K (Lodders, 2003). APM of RMNs revealed this is not always the case; these RMNs contain 0.06–1.00 at% abundances of S (Table 1; Figs. 3 and 4). Sulfur contents in RMN1–RMN5 were variable, but no relationship was observed between the S content and the host mineral, proximity to the edge of the URI or RMN size.

Sulfidation of metal phases in meteorites is thought to occur either on the parent body (Blum et al., 1989) or in the nebula through exposure to H2S gas, where Fe metal reacts with H2S to produce sulfides such as troilite (Lauretta et al., 1996). ALH 77307 CO3.0 is one of the most primitive meteorites (Grossman and Brearley, 2005), so parent-body alteration is unlikely; sulfidation of these RMNs likely occurred in the nebula.

Sulfur is volatile with a 50% condensation temperature of 664 K (Lodders, 2003); the 50% condensation temperature of HSEs is ~1000 K higher than S (Lodders, 2003). The presence of S in RMNs is inconsistent with our current understanding of RMN formation, which requires high temperatures that prohibit the condensation of S (Berg et al., 2009). There is also a spatial inconsistency because RMNs, CAIs, and URIs are expected to form close to a proto-sun (~0.5 AU; MacPherson et al., 2005), where temperatures are high (Ciesla, 2009), whereas Fe-sulfidation is thought to occur rapidly (<1000 yr), early in nebular evolution, and at low temperatures (~500–700 K) between 0.5 and 1.5 AU (Lauretta et al., 1996; Ciesla, 2015).

Disk mechanics are capable of transporting grains to the outer portions of the disk (Shu et al., 1997; Ciesla, 2007; Bai, 2014) over short time scales, i.e., 10^3 yr (Ciesla, 2010). This could emplace the URI into the region of the disk where sulfidation is predicted to occur (0.5–1.5 AU; Ciesla, 2015). However, the URI did not exhibit the expected textures and mineralogy associated with sulfidation, such as silicate enrichment in Fe, Mn, and Na, and depletion
in Mg, with associated abundant sulfide phases such as niningerhite and oldhamite (Lehner et al., 2013). The RMNs are euhedral (Appendix DRE), have no relationship between S abundance and the location of the RMNs within the URI, and did not exhibit depletions in Mo and W (Fig. 3), which are readily mobilized under oxidizing conditions (Fegley and Palme, 1985). Therefore, it is unlikely that the RMNs were sulfidized within the URI.

The S-bearing RMNs here were most likely exposed to an S-condensing gas while “free floating” in the nebula prior to incorporation into the URI. This requires outward migration of RMNs to colder regions of the disk (0.5–1.5 AU; Ciesla, 2015) to incorporate S, followed by inward migration back to the CAI-forming region to be incorporated into the URI. Heterogeneous distribution of S between RMNs implies that incorporation into and partial melting of the URI did not overprint this primary composition and may provide further evidence for migration; each migrating RMN may follow a different path and incorporate more or less S as a consequence.

Disk models suggest even small 5 μm particles could be delivered to the region where sulfidation is predicted to occur (0.5–1.5 AU; Ciesla, 2015) over ~10^7 yr (Ciesla, 2009). These sulfidized RMNs would then be radially transported back toward the protosun. This is possible through turbulent mixing of particles or gas-drag migration (Cuzzi and Weidenschilling, 2006). If these time scales are reasonable, dust particles may experience several cycles of outward and inward migration during disk evolution. However, such efficient mixing would also result in the migration of primordial dust from the outer portions of the disk (Brownlee, 1994) into the CAI-forming region, which would become entrained in CAIs. This is inconsistent with CAI mineralogy, which is refractory in nature (MacPherson et al., 2005). Therefore, any mechanism for particle migration within the disk may include an early period or region where only refractory materials are cycling from their formation region into, and out of, an environment that permits the incorporation of S into RMNs. This requires a barrier to particle migration from the outer portions of the disk. Alternatively, H2S was likely present in the gas in the CAI-forming region (Antonelli et al., 2015), and the HSE component of RMNs may permit a small amount of S to be incorporated into RMNs at higher temperatures than for pure Fe, negating the need for particle migration. However, this interpretation requires all RMNs to be S-bearing, which is inconsistent with all prior RMN analyses.

The presence of S in RMNs, as revealed here by APM, indicates that some RMNs spend a significant period “free floating” in the nebula prior to incorporation inclusions. They may also migrate rapidly early in the disk’s lifetime and be exposed to an environment that permits the incorporation of S before returning to the CAI-forming region to be incorporated in a URI.

CONCLUSIONS

Atom probe microscopy provides the resolution and dynamic range required for geochemical analysis of primitive submicrometer grains in meteorites. The high sensitivity of APM allows us to accurately analyze the bulk- and trace-element composition of grains that are too small for conventional techniques. APM has revealed trace abundances of S within RMNs, which indicates that some RMNs reacted with an S gas prior to incorporation into their host URI while they were “free floating.” This requires either a high-temperature H2S gas–RMN reaction in the CAI-forming region or rapid, early migration of RMNs to cooler regions of the disk followed by inward migration back to the CAI-forming region for incorporation into the URI.

The results from this study reveal that APM analyses of primordial dust grains provide...
information regarding the spatial and temporal temperature and chemical variations in a protoplanetary disk. APM represents a new tool in the analysis of submicrometer grains in meteorites to extract information pertaining to the evolution of the disk from every grain in meteorites. APM can therefore assist in the calibration of disk evolution models.

ACKNOWLEDGMENTS

This work was funded by the Australian Research Council via their Australian Laureate Fellowship program to Bland. This work was conducted within the Geoscience Atom Probe Facility at Curtin University, Perth, Australia, which is part of the Advanced Research Characterisation Facility (ARCF) being developed under the auspices of the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Curtin University, and The University of Western Australia—and it is supported by the Science and Industry Endowment Fund (SIEF RJ13–01). We acknowledge the use of Curtin University’s Microscopy and Microanalytical Facility, for which instrumentation has been partially funded by Curtin University and state and commonwealth governments. Reddy acknowledges support from the Australian Research Council Centre of Excellence for Core to Crust Fluid Systems—a collaboration of The University of Western Australia and The University of Arizona Press, p. 242–381.


Manuscript received 17 February 2017
Revised manuscript received 11 May 2017
Manuscript accepted 28 May 2017
Printed in USA

REFERENCES CITED


A.4. **Paper 4 – Isotopic analysis of refractory metal nuggets with atom probe.**

*(in preparation)*

Luke Daly, Philip A. Bland, Svetlana Tessalina, David W. Saxey, Steven M. Reddy, Denis Fougerouse, William D. A. Rickard, Lucy V. Forman, Patrick W. Trimby, Limei Yang, Alex, La Fontaine, Julie Cairney, Simon P. Ringer, and Bruce F. Schaefer
STATEMENT OF AUTHORSHIP

TITLE OF PAPER: Isotopic analysis of Refractory Metal Nuggets with atom probe.

PUBLICATION STATUS: In preparation

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript.

Overall Percentage: 66%

Signature: [Signature]  Date: [Date]

Name of Co-Author: Philip A. Bland

Contribution to the Paper: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature]  Date: [Date]
Name of Co-Author: Svetlana Tessalina

Contribution to the Paper: Assisted with TIMS analysis and editing and revision of the manuscript.

Overall Percentage: 5%

Signature: ___________________________ Date: 20/02/17

Name of Co-Author: David W. Saxey

Contribution to the Paper: Assisted with atom probe data collection and reduction and in the final review of the manuscript.

Overall Percentage: 5%

Signature: ___________________________ Date: 20/02/17

Name of Co-Author: Steven M. Reddy

Contribution to the Paper: Assisted in editing and revision of the manuscript.

Overall Percentage: 1%

Signature: ___________________________ Date: 20/02/17

Name of Co-Author: Denis Fougerouse


Overall Percentage: 1%

Signature: ___________________________ Date: 20/02/17

Name of Co-Author: William D. A. Rickard


Overall Percentage: 1%

Signature: ___________________________ Date: 20/02/17
Name of Co-Author: Lucy V. Forman
Contribution to the Paper: Assisted in editing and revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature]
Date: 22.2.17

Name of Co-Author: Patrick W. Trimby
Contribution to the Paper: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Steve Moody
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Alex La Fontaine.
Contribution to the Paper: Assisted with atom probe data collection and reduction.
Overall Percentage: 5%
Signature: [Signature]
Date: 20/02/17
Name of Co-Author: Julie Cairney
Contribution to the Paper: Assisted with revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17

Name of Co-Author: Simon P. Ringer
Contribution to the Paper: Assisted with revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17

Name of Co-Author: Bruce F. Schaefer
Contribution to the Paper: Assisted in interpretation of Re-Os isotopic data and editing and revision of the manuscript.
Overall Percentage: 2%
Signature: [Signature] Date: 20/02/17
APPENDIX B

CO-AUTHOR JOURNAL PUBLICATIONS
AND CONFERENCE ABSTRACTS

B.1. CO-AUTHORED PAPER A — HIDDEN SECRETS OF DEFORMATION: IMPACT-INDUCED COMPACTION WITHIN A CV CHONDRITE.


Creative Commons Attribution License (CC BY)

This article is available under the terms of the Creative Commons Attribution License (CC BY). You may copy and distribute the article, create extracts, abstracts and new works from the article, alter and revise the article, text or data mine the article and otherwise reuse the article commercially (including reuse and/or resale of the article) without permission from Elsevier. You must give appropriate credit to the original work, together with a link to the formal publication through the relevant DOI and a link to the Creative Commons user license above. You must indicate if any changes are made but not in any way that suggests the licensor endorses you or your use of the work.

Permission is not required for this type of reuse.
STATEMENT OF AUTHORSHIP

TITLE OF PAPER: Hidden Secrets of deformation: Impact-induced compaction within a CV chondrite.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, the principle author certifies the contribution made to the manuscript by Luke Daly is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Lucy V. Forman

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript for this publication.

Overall Percentage: 70%

Signature: [Signature] Date: 22.2.17

Name of Co-Author: Luke Daly

Contribution to the Paper: Assisted data collection, editing and revision of the manuscript.

Overall Percentage: 3%

Signature: [Signature] Date: 20/02/17
Hidden secrets of deformation: Impact-induced compaction within a CV chondrite


a Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
b Royal School of Mines, Department of Earth Science & Engineering, Imperial College London, Prince Consort Road, South Kensington, SW7 2BP, United Kingdom
c Department of the Geophysical Sciences, The University of Chicago, 5734 South Ellis Avenue, Chicago, IL 60637, USA
d Australian Centre for Microscopy and Microanalysis, The University of Sydney, NSW, 2006, Australia

e Australian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW, 2006, Australia

A R T I C L E   I N F O

Article history:
Received 1 October 2015
Received in revised form 27 July 2016
Accepted 27 July 2016
Available online 12 August 2016

Editors: C. Sotin

Keywords:
Allende
impact
compaction
meteorite
deformation
crystallography

A B S T R A C T

The CV3 Allende is one of the most extensively studied meteorites in worldwide collections. It is currently classified as S1—essentially unshocked—using the classification scheme of Stöffler et al. (1991), however recent modelling suggests the low porosity observed in Allende indicates the body should have undergone compaction-related deformation. In this study, we detail previously undetected evidence of impact through use of Electron Backscatter Diffraction mapping to identify deformation microstructures in chondrules, AOs and matrix grains. Our results demonstrate that forsterite-rich chondrules commonly preserve crystal-plastic microstructures (particularly at their margins); that low-angle boundaries in deformed matrix grains of olivine have a preferred orientation; and that disparities in deformation occur between chondrules, surrounding and non-adjacent matrix grains. We find heterogeneous compaction effects present throughout the matrix, consistent with a highly porous initial material. Given the spatial distribution of these crystal-plastic deformation microstructures, we suggest that this is evidence that Allende has undergone impact-induced compaction from an initially heterogeneous and porous parent body. We suggest that current shock classifications (Stöffler et al., 1991) relying upon data from chondrule interiors do not constrain the complete shock history of a sample.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Planetary systems evolve from a molecular cloud comprised of dust (condensed minerals and presolar grains) and gas, to a protoplanetary disk, where most of the mass is concentrated in the ‘mid-plane’ of that disk. Turbulence allows for gas and particle clumping and accretion of the dust into centimetre- to metre-sized bodies (Cuzzi and Weidenschilling, 2006). Interactions with the gas and collisions lead these solids to grow and accumulate into planetesimals measuring 10 s to 100 s of kilometers in diameter. As this accumulation must be relatively gentle to ensure sticking and adhesion among the components, primordial planetesimals formed in this way would preserve large pore spaces in between each component, resulting in very high porosities (>65%) (Blum, 2003; Weidenschilling and Cuzzi, 2006).

Planetary evolution from these primordial objects to the asteroids that we see today requires that porosity be greatly reduced, as evidenced by the worldwide collection of meteorites that comprises comparatively low-porosity rocks. A number of mechanisms for porosity reduction and weak fabric development have been suggested, including metamorphism and expansion/contraction cycles (Stacey et al., 1961; Zellensky et al., 1997), accretional compaction (Cain et al., 1986), gravitational compaction (Fujimura et al., 1983) and sedimentation; perhaps the two most plausible mechanisms being compaction from lithostatic overburden (Cain et al., 1986) and impacts (Scott, 2002; Sharp and DeCarli, 2006; Davison et al., 2010; Beitz et al., 2013; Bland et al., 2014). It is apparent that the gravity field of even relatively large planetesimals would be insufficient and to generate the required lithostatic pressure to cause sufficient compaction that could adequately explain the low porosities of meteorites (Weidenschilling and Cuzzi, 2006; Friedrich et al., 2014). The anisotropy of magnetic susceptibility (AMS) studies done by Cattaneo et al. (2005) conclude that dynamic compaction via impacts is the most likely mechanism for...
fabric development and therefore porosity reduction, which is also supported by a wide number of findings within meteorite collections; low (but variable) porosities throughout a given sample; heterogenous porosities within the same chondrite group; subtle mineral deformation microstructures; widespread porosity at 2 μm; and localised melt pockets within matrix (Nakamura et al., 1992; Consolmagno et al., 1998; Brenker et al., 2000; Cuzzi et al., 2008; Johansen et al., 2009). Such evidence is not unique to carbonaceous chondrites; it is also present in ordinary chondrites, in the form of high-pressure polymorphism, vitrification of silicate minerals and deformation of olivine grains (Rubin, 2004). Recent work on the CM meteorite Muschroom has also revealed porosity loss was induced by impact and predicted a pre-compaction bulk porosity of up to ~50% (Hanna et al., 2015). Further support for the occurrence of impacts on early Earth is that porous bodies is found in Housen et al.'s work (1999) regarding impact-cratering on the asteroids Mathilde; an unusual lack of blanket ejecta around prominent craters indicates the impacts that produced them occurred when the body was highly porous. Other studies also argue that impacts on such a large scale may destroy the target body if the porosity was not sufficiently high and the impact direct; the pores allow the target to sustain the impacts without being disrupted and oblique impacts lead to less ejecta and the crater morphologies present on Mathilde (Housen et al., 1999; Cheng and Barnouin-Jha, 1999; Housen and Vishniac, 2011). Impact-induced compaction is therefore discussed in depth with relation to the research outlined in this paper.

Evidence of impact shock is routinely observed in current meteorite collections and a short level is assigned to each meteorite (Stoffler et al., 1991; Scott et al., 1992; Sharp and DeCarli, 2006). The approach taken by Stoffler et al. (1991) uses published data on the impact experiment on low-porosity and homogenous terrestrial rocks, lunar rocks and single crystals, taking these materials as analogues for low-porosity, H, L and LL ordinary chondrites. A set of shock metamorphic features seen in analogue materials are used to calibrate the peak pressure experienced for that meteorite, and determine a shock level. This classification is based upon the largest of grains in any sample (Stoffler et al., 1991; Scott et al., 1992). X-Ray Fluorescence analysis, Allende, the sample of study in this paper, is identified as a 31 ± 15% shocked and is expected to have experienced no more than 6 GPa at peak shock pressure (Scott et al., 1992). The samples and procedures used in the early study may not be ideal for several reasons: meteorites are not homogeneous materials, and grain size plays an important role in determining the shock reaction of a grain, especially when pore space is considered (Davison et al., 2010). Most importantly, the experimental impact studies that underpin the Stoffler et al. (1991) and Scott et al. (1992) approach are concerned with impacts into low or zero-porosity targets and, by extension, impacts into compacted planetesimals. Therefore, this approach may not be suitable for approximating impacts into highly porous primordial objects.

Recent numerical models consider more complex scenarios, concerned with impacts into unprocessed porous planetesimals, bimodal material and mixed compositions of the target body. Davison et al. (2010) model shock propagation through homogeneous, porous planetesimals and find high porosity to be positively related to higher impact-generated temperatures on an asteroidal scale. Similar numerical simulations have highlighted the importance of pore collapse in the target body upon impact, which generates large amounts of heat, allowing the whole medium to experience elevated temperatures and potential melting (Consolmagno et al., 1998; Davison et al., 2010; 2014). Further improvements were made to these models to acknowledge the small-scale and complex material properties of primitive bodies: chondrites are essentially bimodal mixtures of porous, fine-grained matrix and large chondrules without intercrystalline porosity (Bland et al., 2011; Davison et al., 2014). In an impact compaction simulation with a bulk shock pressure of only ~1 GPa, the bulk post-shock temperature was ~425 K, but the matrix was heated to ~530 K from an initial temperature of 300 K, whereas chondrules were heated by only a few degrees (Davison et al., 2014). Heating occurs at chondrule edges adjacent to initially porous areas of matrix, and at the edges of closely spaced chondrules, and pressure distribution within chondrules is also not uniform: chondrule edges are predicted to experience higher pressures than chondrule interiors. Porosity in matrix also varies, with high-porosity regions observed in the lee of chondrules. Petrologic evidence of these features has yet to be identified, but the models give an indication of how a bimodal heterogeneous material may react upon impact.

In light of the models described above (Davison et al., 2010; Davison et al., 2014), the shock pressure aspect of Allende’s impact history may simply be absent from large, resilient chondrules. Allende is a well-studied sample that contains approximately 40% matrix (MacDade et al., 2011), and has a measured bulk porosity of ~22%. Recent fabric analysis has inferred ~50% pore volume reduction has occurred in Allende via impact (Bland et al., 2011; Hanna et al., 2015), but this is unlikely to be homogeneous throughout any sample. Assuming initial matrix porosity is >65%, this implies a pre-compaction matrix:chondrule volume ratio of > 2:1. Numerical simulations that exposed such a chondrule–matrix mixture to a ~1 GPa shock wave reproduced the observed bulk and matrix porosity in Allende, and suggest that localised heating by heterogeneous pore collapse may have been a significant process.

In this study we explore the possibility that matrix grains and chondrules responded differently to planetary compaction. We establish how the microscopic and textual study of this meteorite holds interesting implications about the evolution of the parent body of Allende.

2. Approach & methods

In this study we analysed a thin section of Allende. The initial imaging of the thin section on the Nanofocus X-Ray Fluorescence Beamline (XRF) at the Australian Synchrotron facilities in Melbourne. Here, 25 element maps were collected for the entire sample in under 10 min (Fig. 1). These were compared with the collected Energy Dispersive Spectroscopy (EDS) data for accuracy of elemental distribution throughout the sample, in addition to monitoring any instrumental drift. The Maia detector on this beamline had an energy sensitivity in the range of 13–193 keV, encompassed a number of major elements with an energy resolution of 300–400 eV, and in this case, produced maps with a spatial resolution of 2 μm per pixel. All maps were acquired in the spectrometry mode and so were not required beforehand for the imaging to occur. In addition, the Maia detector was able to detect elements at the 10–100 ppm scale commonly lower than other traditional imaging techniques (Fisher et al., 2014). Owing to the high-energy beam in use (18.5 keV), this technique sampled a larger depth than other traditional imaging techniques, and so data collected represented an average of the volume sampled (Dyl et al., 2014). Further information regarding this imaging technique can be found in the Analytical Methods section of Dyl et al. (2014). This map was used as a means of identifying areas of interest for further Secondary Electron (SE), Backscatter Electron (BSE), EDS and Electron Backscatter Diffraction (EBSD) analyses.

Ten regions encompassing chondrules, Ameboïd Olivine Aggregate (AOA) and matrix grains were mapped using a variety of imaging techniques, utilising the Tescan Mirax FESEM, at the John de Laeter centre at Curtin University, Western Australia. It is important to note that all maps were taken in the same physical...
Fig. 1. X-Ray Fluorescence Synchrotron map of a thin section of the Allende meteorite. Chondrule and matrix sites to be discussed are shown (C = chondrule/ADA, M = matrix). Note that M-1, M-3 and M-4 are proximal to a chondrule or ADA, and M-2 is in an area devoid of chondrules, ADAs and CAIs.

Table 1
EBSD and SEM imaging parameters used for imaging at each of the chondrule, ADA and matrix sites in this sample of Allende.

<table>
<thead>
<tr>
<th>Site</th>
<th>Type</th>
<th>Step size (μm)</th>
<th>Imaging threshold (μm)</th>
<th>Number of points</th>
<th>Mean Angular Deviation (MAD) (% ACC</th>
<th>Acc. Voltage (kV)</th>
<th>Furst (°)</th>
<th>Not indexed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>Chondrule</td>
<td>0.5</td>
<td>2</td>
<td>77284</td>
<td>0.38</td>
<td>20</td>
<td>82.5</td>
<td>16.0</td>
</tr>
<tr>
<td>C-2</td>
<td>Chondrule</td>
<td>2</td>
<td>8</td>
<td>172125</td>
<td>0.60</td>
<td>45.8</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>C-3</td>
<td>ADA</td>
<td>0.41</td>
<td>3.6</td>
<td>240310</td>
<td>0.53</td>
<td>36.3</td>
<td>63.2</td>
<td></td>
</tr>
<tr>
<td>M-1</td>
<td>Matrix</td>
<td>0.1</td>
<td>0.4</td>
<td>110732</td>
<td>0.68</td>
<td>49.9</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>M-2</td>
<td>Matrix</td>
<td>0.12</td>
<td>0.48</td>
<td>2154956</td>
<td>0.67</td>
<td>37.2</td>
<td>59.3</td>
<td></td>
</tr>
<tr>
<td>M-3</td>
<td>Matrix</td>
<td>0.2</td>
<td>0.8</td>
<td>122760</td>
<td>0.67</td>
<td>35.5</td>
<td>52.87</td>
<td></td>
</tr>
<tr>
<td>M-4</td>
<td>Matrix</td>
<td>0.35</td>
<td>1.4</td>
<td>15708</td>
<td>0.80</td>
<td>37.9</td>
<td>51.3</td>
<td></td>
</tr>
</tbody>
</table>

orientation in the SEM, allowing for direct and accurate comparisons of crystallographic features between sites.

Standard Secondary Electron (SE) and Back-Scattered Electron (BSE) images were collected at a voltage of 20 kV, a beam intensity of 17, an aperture size of 30 μm and a working distance between 10 and 15 mm. These images were used to define regions of interest for further analysis and image collection. Electron Backscatter Diffraction (EBSD) was the primary technique used in the study. EBSD enabled mapping of the crystallographic orientation of grains in a thin section, both in relation to crystallographic axes and neighbouring grains. Automated and simultaneous EBSD and EDS maps were generated using Oxford Instruments’ Aztec acquisition system, using a fixed x and y step size for each site in a user-defined grid, varying between 0.1 μm and 8 μm, dependent upon the grain size distribution at each particular site. This approach generated a dataset with high spatial resolution whilst also being time-efficient. Table 1 shows the conditions under which the maps were collected at each site. SE images were obtained to confirm that topographic features present in or around chondrules did not bias the EBSD data and interpretation.

Allende was found to contain abundant matrix grains at the sub-micrometre scale, and so greater spatial resolution was required for accurate analysis of the smaller grains. The Transmission Kikuchi Diffraction (TKD) technique utilized electron transparent samples in the SEM, coupled with conventional EBSD instrumentation, resulting in an order of magnitude improvement in spatial resolution compared to EBSD (sub 10 nm – Trimbly et al., 2014). A transmission electron microscope (TEM) foil was extracted containing a sectional view of a chondrule rim and adjacent matrix material. The sample was created using a focused ion beam (FIB) SEM (Carl Zeiss Auriga) at the Australian Centre for Microscopy & Microanalysis (ACMM), Sydney. To protect the sample from gallium beam damage a platinum layer was deposited and the sample lifted out using a Kleindiek micromanipulator. The section was mounted on a molybdenum grid using platinum welds and the sample was further thinned to 100 nm. The TEM foil was analysed using TKD and EDS on a Carl Zeiss Ultra Plus FEG SEM at the ACMM, Sydney. TKD and EDS data were acquired using an Oxford Instruments AZtec system with a Nordlys-Nano EBSD detector and an X-Max 20 mm² SDD EDS detector and with an accelerating voltage of 30 kV.

EBSD data were processed using the Oxford Instruments HKL software package Channel 5.12, generating crystallographic orientation maps, phase maps and pole figure plots that were compared across each site. In this process, noise reduction and data processing were done in a very similar manner to that described in Watt et al. (2006); isolated misindexed data points were removed using a wildspike correction, and all non-indexed points infilled to a six nearest-neighbour extrapolation. Grains were detected in each map based upon crystallographic orientation, and using a misori-
entation angle of at least 10° between two adjacent pixels to identify grain boundaries. Given the step size was between 10°, two adjacent pixels to identify grain boundaries. Given the step size was reduced to allow for reliable data interpretation, which also removed misindexed points. Grain orientation data for each point on each map were plotted on to a lower hemisphere, equal area projections as one point per grain to avoid grain size related bias during contouring. In this study, we focused on olivine grains to enable a direct comparison with shock-level studies. Although compositions across the olivine solid-solution can be found in Allende, there was little variation in their crystal structure. EBSD does not discriminate between olivine sub-types, and so all EBSD patterns from olivine were successfully indexed using the ‘forsterite’ match unit in the HKL database (indexing statistics are given for each region of interest in Table 1).

Low-angle boundaries (LABs) can form due to a number of mechanisms. Both orientation selective dissolution and grain growth in a vein setting may result in grains of similar orientation forming apparent low-angle sub-grain boundaries where their edges meet. Neither of these mechanisms are likely given the primitive nature of Allende. LABs can also be a geometric consequence of grain impingement between two similarly-oriented grains (Wheeler et al., 2001). Where grains preserve crystallographic variations that cannot be attributed to fractures, it was assumed that they were deformed crystal-plastically (via dislocation creep and recovery). Dislocation slip systems were then inferred assuming pure tilt boundary geometry, whereby an orthogonal relationship exists between the rotation axis of low-angle boundaries, pole to the dominant dislocation slip plane and slip direction (e.g. Purkis et al., 2001). misindexed grains were defined due to a dispersion of crystallographic poles in each grain. As the rotation axes did not lie in the plane perpendicular to the LAB trace, we can infer these boundaries formed due to tilt and did not show evidence of twist-boundary formation. Further information regarding this test can be found in the methods section of Gray (2013). LAB planes were inferred from traces in map view and contain misorientation axes. Axes of misorientation were identified based upon axes of pole dispersions in lower hemisphere plots. The related slip systems were then inferred using geometric criteria; a slip-system is composed of both a slip plane and direction; the pole to the slip plane is contained within the low-angle boundary with the misorientation axis, and the slip direction is perpendicular to that plane.

The numerical simulations described by Bland et al. (2014) provided peak and post-shock stress (pressure), temperature and porosity distributions for numerous impactor velocity and initial matrix/chondrule abundance scenarios. To compare more directly the data from our study with the simulation predictions, shear strain distribution maps were produced from the simulation outputs. The particle positions in the simulations were used to derive the second invariant of the total strain tensor using the method described by Bowling (2015). This invariant measure of shear deformation includes the net elastic plus plastic strain at the end of the simulations (i.e., the finite strains). As the elastic-plastic rheological model used in the numerical simulations to represent the chondrules and matrix incorporates a yield strength that is pressure, strain and temperature dependent, it can describe (very approximately) both brittle (low pressure) and ductile (high pressure) deformation. In reality, olivine rheology is more complex in detail, and involves anisotropic elastic and plastic properties. Furthermore, as the matrix of fine grains and interstitial pore space is treated as a uniform continuum in the simulations, we note that the strain in the matrix is the bulk strain of the grains and the pore spaces, which will be largely accommodated by grain rearrangement and pore collapse, rather than permanent deformation of individual matrix grains; i.e., ‘details’ of the strain in individual matrix grains is not resolved. Despite these limitations we expect the qualitative distribution of shear strain observed in the numerical simulations to provide an informative comparison with permanent strain derived from our crystallographic orientation analysis.

3. Results & analysis

Olivine in the chondrules in Allende was commonly Mg-rich, i.e., forsteritic, whereas matrix olivine was more Fe-rich, i.e., Fayalitic (Fig. 1). Prior studies calculate proportions of chondrule and matrix to be approximately 60% and 40% respectively (McSween, 1979; Macke et al., 2011). The chondrules, AOA and Calcium Aluminum Inclusions (CAIs) were also weakly elongate as is shown in Fig. 1. Within the 1.28 cm² sample area of our sample, we observed a large variation in matrix grain sizes (Supplementary Figs. 1–4). EBSD analyses resolved forsterite, diopside, and enstatite, which have been recorded previously (Stoffler et al., 1991). As expected, this sample was highly texturally heterogeneous, containing different chondrule types and a wide range of matrix grain shapes and sizes. We found no evidence of high-pressure polymorphs, such as ringwoodite, that would indicate high shock pressures.

3.1. Chondrules and AOA

Three chondrules and AOA sites were examined (Fig. 2), and are collectively referred to as ‘chondrule sites’ from this point forward. For each site, a ‘cumulative misorientation map’ was generated that each of which was indexed in crystallographic orientation (minimum misorientation) from a user-specified point within the grain (all sites, Fig. 2c). These maps resolved misorientations to a precision based upon the fit quality of the indexing solutions (mean angular deviation (MAD), Table 1) in each map, which were typically reliable down to approximately 0.5° for each site. Each of the chondrules showed very little or no internal deformation in their interior: up to a maximum of 1° in the central parts of the grains. However, the outer 10–30 μm of the chondrule and outermost AOA grains commonly preserved up to 6° of progressive, cumulative misorientation that did not relate to brittle fractures (all sites, Fig. 2c and Fig. 3). This relationship is visible in the local misorientation maps, where each pixel was coloured to reflect mean misorientation with the eight nearest neighbour data points (Fig. 4). Figs. 3 and 4 show that progressive crystallographic misorientations at the edges of the grains are accommodated by many relatively planar LABs, parallel to the grain edge. Fig. 3 demonstrates the deformation at C-1 is cumulative and begins in the outer 30 μm of the grain, reaching maximum deformation at the edge (7–8°). Not only were the highest degrees of strain at the grain edges at each site, but LABs were also generally concentrated at the top and bottom, and to the right of the chondrules and AOA, as indicated by the continuous, cumulative strain at the margins of chondrule C-1, for example (Figs. 2b, 2c, 3 and 4).

3.2. Matrix grains

Maps of crystallographic orientation for olivine at the four matrix sites are shown in Fig. 5. Grain size and shape maps and distribution histograms are presented in Supplementary Figs. 1–4, and matrix grains measured in the TKD section are shown in Fig. 6. It is clear a variety of grain sizes are present; between 0.1 μm and 50 μm. The grains were chiefly subhedral and lath-shaped, characterised as having an aspect ratio greater than 2:1 in 2D. A wide range of intragrain misorientation characteristics were observed at a very fine scale in matrix grains; up to 20° of internal deformation across a 20 μm grain was recorded at site M-2, with as little
Fig. 2. Chondrule/ESA sites C-1, C-2 and C-3 respectively. (a) Backscatter Electron (BSE) images, (b) Euler maps of each site, showing the orientation of each grain in terms of the three Euler angles, and (c) texture component maps showing a vast increase in deformation at grain edges when compared to grain interiors (scale bar is shown in degrees °).

Fig. 3. (a) Map of texture component for chondrule at C-1. White transect line is shown through lower outer edge of the chondrule. (b) Misorientation profile for the white transect line in (a) demonstrates the gradual increase in orientation deviation in an outwards direction from the innermost point of the transect. This confirms the outer edges of chondrules deform gradually and cumulatively from the inner to outer points along the transect.
as 2° internal deformation across a selection of grains at site M-1 (Figs. 5 and 6). Whilst a wide range of values were recorded, average internal deformation was high, with the majority of values in the 8–15° range. It is important to note that in contrast to chondrules, intragrain deformation was observed throughout the full length of the matrix grains, and the magnitude of deformation is consistently greater in all cases.

At sites M-1 and M-3, the trace of planar LAB orientations were measured relative to the map x-y reference frame plotted onto rose diagrams (Fig. 7). The rose plots reveal a dominant trend of the LABs, preferentially aligned with map y direction (i.e., circa 0° and 180° in Fig. 7). This is significant because aligned LABs indicate a relatively consistent applied stress field at the scale of the observations, such as those produced in controlled olivine deformation experiments by Kohlstedt and Goetze (1974). The spatial density of low-angle boundaries was more consistent throughout the matrix grains when compared with chondrule sites; where chondrules and AAs have a higher density of LABs at their edges, those found in matrix grains were not confined to the grain edges and were present throughout the grain area (Figs. 5 and 6). This is consistent with findings of experimentally stressed olivine crystals; undulose extinction along the grains indicates multiple, similarly oriented low-angle boundaries are present, accommodating changes in crystallographic orientation (Kohlstedt and Goetze, 1974; Pierron et al., 1999).

The matrix sites also presented a range of porosities. In some locations, grains appeared very compact with an extremely low porosity (e.g., M-2), whereas areas of M-1 and M-4 appeared more porous with lower indexing rates over the whole region. Quantification of this porosity is currently a work in progress. It is important to recall that images at each site were collected at different image resolutions, allowing for maximum efficiency and coverage whilst maintaining the high indexing ratios (Table 1). As some grains were smaller than the specified step-size for imaging each site, this may have resulted in non-indexing of those grains, making the EBSD-inferred porosity of the region incorrect. In light of this, secondary electron images were obtained (Supplementary Fig. 5) for each matrix site, and these confirmed and qualified the porosity variations implied in the EBSD maps.

### 3.3. Slip systems

Based upon the misorientation axes observed from the EBSD maps we have inferred the likely slip-systems that have contributed to the LABs in chondrules, AAs and matrix grains including those within the TKD data. C-1 and C-3 had a misorientation axis of the [100] (a-axis), while C-2 had misorientation along the [010] (b-axis) (Fig. 4). Matrix grains largely had misorientation axes of [010] (b-axis) whilst one examined grain at M-3 had a misorientation axis of [100] (c-axis). EBSD, BSE and SE images indicated that the LABs occur within grains and so it was assumed they result from intragrain plasticity, which would have required high stresses. Chondrule site C-3 (Fig. 7e) displayed evidence of two different slip systems; the misorientation axis was [100] in both cases, but one slip system comprised slip in the [001] direction along the [010] plane, and the other involved slip in the [010] direction along the [001] plane. A variety of slip systems were inferred across each of the sites; of the 9 examples found, matrix slip systems were most commonly [001][100] (slip in the [001] direction along the [100] plane), with occurrences of other common systems at each site. Chondrule grain slip systems were more widely varied and include [001][010], [011][100] and [010][100] throughout the sites.

### 3.4. Strain distribution observations

The qualitative distribution of strain observed in chondrules and matrix is consistent with numerical simulations results (Fig. 9). In the simulated chondrules, the predicted mean strain is low, but localised near their margins for 1.0 and 1.5 km/s cases (Figs. 5a and b), whereas strain is higher and distributed throughout the chondrules for the 2 km/s case (Fig. 9c). In all simulated impactor velocity scenarios, the matrix strain is always higher than within the chondrules, with an increase in mean strain with impactor velocity (Fig. 9). Strain in the matrix is typically more intensely developed immediately adjacent to the chondrules, most commonly with an eccentric distribution and asymmetric strain shadows (Fig. 9). All of the simulations predict strong gradients in matrix strain over the micrometre scale (Fig. 9).
4. Discussion

Previous work has shown that Allende has a weak but prominent fabric throughout, with an alignment of the short $<100>$ axis of fayalitic olivine grains (Watt et al., 2006). Our study confirmed the weak fabric, albeit with varying alignments (Supplementary Figs. 1–4 and 6). Chondrules, AOAs, CAIs and larger grains are elongate in the vertical orientation, indicative of a horizontal compaction orientation in the plane of the images (Fig. 1). However, we also observed a significant difference in spatial distri-
A large portion of the deformation of chondrule grain edges is concentrated at the top, bottom and to the right of the chondrules. Further to this, deformation is absent on the left and less prominent on the right of these grains when compared with the top and bottom areas. Coupled with an absence of matrix grain deformation to the left of such grains, a compressional ‘shadow’ has been generated. It is possible that compaction of pores against the boundary of the grain normal to the compacting direction generated enough heat such that these areas of the grains were compressed but show no evidence of strain. The top and bottom of the
chondrules may not have experienced the same degree of compaction and, therefore, less pore collapse and subsequent heating would have occurred (Davison et al., 2010). Here, there may not have been sufficient heat to deform these regions without strain being evident. However, the lack of evidence for melting observed at this scale indicates this may not be the case, and therefore other possibilities, such as shear heating, should be considered. Given that the presence of strain ‘shadows’ on the left side of the larger grains, it is probable that a similar shadow would be evident in the matrix as a higher porosity relative to surrounding matrix areas. Whilst the sample has lost a large portion of it’s initial porosity (~50%), the compaction process is very unlikely to generate uniformly low porosities throughout the matrix due to the bimodal grain size distribution of the material, and therefore porosity heterogeneities are to be expected.

The microstructural analysis clearly shows that deformation was spatially heterogeneous, and indicative that Allende experienced locally heterogeneous (stress, temperature) conditions. Olivine deforms crystal-plastically in response to stress at high temperatures. This is achieved by the activity of several possible dislocation slip systems, and it is well established that distinct slip systems operate in different environmental conditions (e.g. stress, temperature, H₂O activity) for terrestrially deformed olivine (Karlo et al., 2008). Operation of different slip systems produces different types of crystallographic fabrics, which can be identified by trends in clustering in lower-hemisphere, equal-area plots of the EBSD data (Karlo et al., 2008). Therefore, quantification of fabrics may be used to infer temperature and pressure conditions at the time of fabric generation. Using this approach, we can deduce that the variable slip-systems identified within the chondrules and AOA probably reflected heterogeneous stress and temperature conditions throughout the sample. Most slip systems within matrix grains are indicative of deformation under dry and low-moderate stress conditions, with some variation to higher-stress slip systems (Karlo et al., 2008). M-1 and M-2 presented a weak A-type fabric when compared with Karlo et al.’s (2008) classification system, where M-3 displayed a D-type fabric. The fabric types indicated high temperatures (~1470 K) and low stresses (0–150 MPa) at sites M-1 and M-2, and moderate temperature (1200–1470 K) and stress (>350 MPa) conditions at M-3 (Karlo et al., 2008). Sites M-1 and M-2 were situated away from chondrules, whereas M-3 was very close to and between two chondrules and so higher stresses may be expected. However, the lack of high-pressure phases and mosaicism of LABs in the sample limit the shock pressures at time of deformation to below 10 GPa (Langenhorst, 2002). There has been some speculation that the presence of pores prior to compaction allows for higher-temperature slip-systems to activate in olivine when compared with zero-porosity samples (Goetz and Poirier, 1978). Therefore, it is possible that higher-temperature slip-systems may have activated in highly porous regions of the sample.

The microstructures observed in this sample of Allende and other evidence can be used to evaluate several different models for the compaction of Allende. An early theory highlighted a static force, such as burial compaction due to gravity, as a possible source of compression (Fujimura et al., 1983). The microstructural features we have observed in this study do not indicate that this is the compaction mechanism; the asymmetry in large grain deformation
Fig. 8. Texture component maps of Chondrule/AOA site C-1, C-2 and C-3 (i). This demonstrates the degrees of rotation in Euler angles from a central, unstrained point within the presented grain. This data is plotted on lower hemisphere, equal area, stereographic projections (ii). At each site the orientation of the low-angle boundaries is shown on the equal area plots as red lines for each highlighted grain in the maps. At site C-1 and C-3, the misorientation axis is the [100] axis, and at C-2 the misorientation axis is [010]. At sites C-2 and C-3 two sets of low-angle boundaries are observed and cause a two-way dispersion in the data.

Fig. 9. Finite invariant shear strain distribution maps derived from numerical simulations for three impact speeds: a) \( v_i = 1.0 \text{ km/s} \); b) \( v_i = 1.5 \text{ km/s} \); c) \( v_i = 2.0 \text{ km/s} \), which generate bulk shock pressures of approximately 1.7 and 3 GPa, respectively. In these simulations chondrules are treated as single grains, the matrix of fine grains and pore space is treated as a continuum. Hence, while simulated strains in the chondrules are expected to be comparable to those observed inside chondrule grains, the strain distribution within the matrix is the bulk strain of both matrix grains and pore space combined and is not directly comparable to strain observed in individual matrix grains.

indicates localised compaction from one direction, not multiple directions. The slip systems that activated within the grains are widely varied, but some require heating beyond 1450 °C. In the case of lithostatic compaction, heating is expected to be continuous for the duration of the slow compaction process as pores are continuously destroyed. If temperatures of 1450 °C were achieved for any length of time, widespread melting would have occurred, which has not been observed. A lack of overprinting in the mi-
crostructures also implies all structural features were generated at the same time; comparison due to lithostatic forces would result in microstructures forming over longer time periods, and therefore we might expect to see cross-cutting deformation relationships. At a large scale, Allende microstructures are approximately preserved in its currently compressed form (Svensk et al., 1995). This strength may be surpassed in the centre of a planetary body with a radius greater than approximately 300 km and, therefore, lithostatic pressure may result in the compaction observed if Allende sampled the centre of a planetary body. However, this mechanism is un-
able to explain the asymmetry of deformation in the chondrules and distribution of porosity and crystal-plasticity in the matrix grains. Porosity reduction under these conditions should have or-
thorhomnic symmetry. Overburden-related stresses in small plane-
tary bodies are unlikely to be high enough to activate slip systems responsible for the observed fabrics in the matrix olivine in Al-
ende. Furthermore, Allende is a primitive meteorite of petrologic type 3, and if it originates from the centre of a planetary body, it would not remain in a primitive state. A number of CO, CB and CM meteorites have lower porosities than Allende (Macke et al., 2011), and so if the same principle applies to their deep ocean on their respective parent bodies, many asteroids would have been completely destroyed to create a number of meteorites in our col-
lections. The oxidised CV subclass (e.g. Allende) is significantly less compacted than the reduced CV subclass (20% porosity) compared with ∼5% porosity (Macke et al., 2011), but the oxidised sam-
ple presents significantly higher metamorphism. We would expect the inverse relationship to be evident where lithostatic overburden forces are present. Therefore, we think that their present state in our solar sys-
tem that appear to be of low bulk density when compared with their likely meteorite equivalents (Britt et al., 2002); this suggests that these bodies are still highly porous, and so a planet-wide compaction process is further unlikely. Gravitational compres-
sion forces generate gradual and continuous heating and were likely involved in the early heating of the body and initial stages of lithi-
fication. Therefore, we believe that it is improbable that lithostatic overburden could have generated the compressional microstruc-
tures, but possibly contributed to overall lithification.

Consequently, we consider that rapid and compres-
sion forces during impact events in the creation of the afore-
mentioned microstructures. The asymmetric distribution of strain (i.e., crystal-plastic deformation and porosity reduction) around chondrules and AOa grains, and highly heterogeneous stresses and temperatures inferred from operative slip systems are consistent with numerical simulations of impacts at these scales (Davison et

al., 2010, 2014; Bland et al., 2014). We observed a varied yet gen-
erally greater intensity of deformation in small matrix grains when compared with large chondrule and AOa grains; a rapid loss of pore space in compaction generates a temperature increase in the matrix which would likely experience more heat than chondrules, and consequently would be more deformed relative to the large low-porosity grains. The preferential orientation of LAB planes and crystallographically preferred orientation in the matrix grains can be readily explained by differential heating between chondrules and matrix during a single moderate-impact event, which would consequently reduce bulk porosity. Microstructural evidence also in-
dicates an instantaneous and rapid compressional force is re-
sponsible.

Allende has a lack of macrostructure shock features that previ-
ously suggested it was unaffected by impact, however as a result of porosity loss, any further impacts post-compaction are unlikely to cause substantial compression or generate compaction-related shock features (Sharp and DeCarli, 2006; Davison et al., 2010; Bland et al., 2014). Compaction via impact is a much simpler sce-
nario when compared with lithostatic overburden; it is unlikely
that a large number of asteroites were completely destroyed to
produce the samples in our vast meteorite collections, and low-
velocity collisions into small planetary bodies are much more common and easier to achieve (Housen and Holstalpe, 2011; Bland et al., 2013). At a planetary scale, samples originating closer to the asteroid surface would show more evidence of meta-
phism when compared with samples at depth on the parent body following impact processing; this is reflected in the properties of oxidised and reduced CV class meteorites, where higher porosities and significant metamorphism are observed in oxidised samples compared with reduced samples. In situ evidence of impacts into highly porous bodies has been found on C-type asteroid Mathilde; whilst CV meteorites may not originate from C-type asteroids (Bell, 1988), the principal of impacts into early, highly porous bodies is well supported by this prior research (Housen et al., 1999; Cheng and Benzouit-Jha, 1999; Housen and Weisberg, 2001). Fur-
thermore, conclusions from impact compaction studies that cor-
relate compaction pressures with overall shock stages for each carbonaceous chondrite class support our findings (Weidenschilling and Cuzzi, 2006; Bland et al., 2013).

Shock wave attenuation into a polymetallic and porous medium has been shown to induce shear heating at grain boundary con-
tacts (Gillet and Goree, 2013). We predict Allende to have experi-
enced no more than 10 GPa based on the absence of high-pressure polymorphs and mosaicism in the olivine grains. At this pressure, we expect that Allende would have begun to melt at 1600 °C, but at lower pressures heating to 1150 °C could have induced melting (Ager et al., 1995). The microstructural features presented indicate that these grains did not experience such temperatures, but shear heating may have been more pronounced at the planetary body, resulting in grain sintering, lithification and strengthening of Al-
ende. The geometry of deformation seen in the matrix does show potential evidence of shear processing (Fig. 2), whereby LABs parallel to the direction of compression have formed. Additionally, the lower edges of C-1 and C-3 (Fig. 2) appear fragmented from the rest of the surrounding material, which could indicate that shear-
induced disaggregation has occurred. Experiments examining the sintering behaviour of olivine have found that it is favoured where a fine-grained (micrometre-scale) aggregate is rapidly heated to high T: an analogous scenario to that encountered by a high porosity matrix during impact-induced compaction (Cooper and Kolsheed, 1984). Weak evidence of this can be found in Allende (Fig. 6), where grains have a higher amount of deformation at the contact margin. However, understanding the intricacies of lithifica-
tion in this sample is beyond the scope of this paper and should be examined at higher resolution in future work.

The local and regional pressure and temperature anomalies over distances of 10–100 μm can be attributed to interactions of shock waves in the bimodal, porous medium, resulting in heterogeneous deformation. The simulations described by Bland et al. (2014) re-
veal that low-velocity impacts of 2 km/s in a material of 70% matrix, 30% chondrule result in peak pressures in chondrules of ∼6.5 GPa, but with predicted post-shock heating temperatures of 370 K in chondrules, and 1100 K in the matrix. These models also yield large disparities in peak pressure between matrix and chondrules; chondrule interiors realistically experience 4-5 GPa, chondrule edges approximately up to 8 GPa, and over only 100 μm within the matrix, a pressure range of 7-18 GPa may arise (Bland et al., 2014). Whilst peak pressures cannot be directly compared with our data, comparisons with the modelled first order approxi-
imations of corresponding strain distribution are more analogous. Acknowledging the limitations of the simulations to be able to capture the complexity of olivine rheology exactly, the strain in the modelled 1.0 km/s and 1.5 km/s scarios (0.8 GPa bulk shock pressure) show the strongest similarity to the observed chondrule deformation from EBSD mapping (Figs. 3 and 4). First-order predictions of the higher intensity strain in the matrix are also
consistent with observations from EBSD mapping (Figs. 5 and 6). These outcomes suggest that the high-velocity and high-density production of the bimodal sample to compression and we infer impacts are responsible for the petrographic features described.

5. Conclusions

EBSD analysis in this study of Allende has revealed the following:

1. Crystal-plastic deformation at the margins of chondrule grains, commonly with an asymmetric distribution (in the context of all figures shown).

2. A lack of crystal-plastic deformation within chondrule interiors (c1).

3. High degrees of crystal-plastic deformation throughout matrix olivine grains (up to 20° of misorientation). This deformation was spatially heterogeneous, with asymmetric zones of intense deformation close to chondrules.

4. A dominance of LAs in matrix olivine grains with strongly preferred boundary plane orientations in the reference frame of the sample surface.

We conclude Allende has been compacted via impact processing. Planar shock shock modeling shows a low impact velocity of a few km/s into a 50% bulk porosity target material is sufficient to produce the features present. The effect of the temperature difference between the two components following impact is large and significant. Although low pressures (1–1.3 GPa, Bland et al., 2014) are unlikely to have produced petrographic shock evidence traditionally observed in chondrules. Matrix grains are the key to understanding the magnitude of the compaction-inducing impact, as they show preservation of compaction-related deformation and provide a more accurate representation of peak temperatures and stresses.

Acknowledgements

This work was funded by the Australian Research Council via their Australian Laureate Fellowship programme (FL110100074) (PAB). This research was supported by the Curtin International Postgraduate Research Scholarship awarded to LF and LD, and GKB acknowledges support from Curtin University via their Research Fellowship scheme. GSC and TMD acknowledge funding from the UK Science and Technology Facilities Council STFC grant ST/P001520/1. The authors would also like to acknowledge the technical assistance and use of facilities at John de Laeter Microscopy centre, at Curtin University; the Australian Synchrotron XFM beamline, and the University of Sydney node of the Australian Microscopy & Microanalysis Research Facility: Sydney Microscopy & Microanalysis. The authors would like to thank the handling editor and anonymous reviewer for their constructive comments in the review process.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.07.050.

References


B.2. **Co-authored Paper B – Catching a Falling Star (or meteorite) - Fireball Camera Networks in the 21st Century.**


March 7, 2017

Mr. Luke Daly  
Curtin University  
Kent Street  
Bentley WA 6102  
Australia  

Email: luke.daly@postgrad.curtin.edu.au

Dear Mr. Daly:

I received your e-mail message of 2017-03-06 requesting permission to reproduce the following article, on which you are a co-author as a member of the Desert Fireball Network, in its entirety as part of your Ph.D. thesis, *Understanding our Protoplanetary Disk by Chemical Analysis of Components in Meteorites*, submission for Curtin University:


It is with pleasure that we grant you permission to reproduce this article without cost and all subsequent editions of the work, its ancillaries, and other derivative works, in any form or medium, whether now known or hereafter developed, in all languages, for distribution throughout the world on the conditions that reference is given to the original publication of the Mineralogical Society of America.

Sincerely,

J. Alexander Speer  
Executive Director, MSA
STATEMENT OF AUTHORSHIP

Catching a falling star (or meteorite) - Fireball camera networks in the 21st Century.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, the principle author certifies the contribution made to the manuscript by Luke Daly is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Philip A. Bland

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript for this publication.

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Luke Daly

Contribution to the Paper: Assisted with the construction of the Desert Fireball Network, and outreach.

Overall Percentage: 4%

Signature: [Signature] Date: 20/02/17
Fireball over Perenjori, 260 km north of
DFN Team members: Martin Towner, Jonathan
e-mail: G.Benedix@curtin.edu.au

System processes that meteorites contain.
towards interpreting the record of early Solar
surface, only a handful of meteorites have
a million square kilometers of the Earth's
Network; McCrosky et al. 1978) and Canada
work, based in the Czech Republic, became
Camera Networks
Fireball camera networks are designed to
recover meteorites with orbits. The first
network, based in the Czech Republic, became
active in 1959 and continues to operate as part of
the European Fireball Network (Obbert et al. 1998).
In the 60s, 70s, and 80s, two other networks were operational in North America, covering parts of the US (Prairie Meteorite
Network, McCrosky et al. 1978) and Canada (Meteorite Observation and Recovery Project; Halliday et al. 1996). Despite covering over
a million square kilometers of the Earth's surface, only a handful of meteorites have been recovered. This is unfortunate because
the promise of these camera networks is great—knowing the spatial context (an
orbit) bridges the gap between meteorite and
asteroid research, with the potential to revolu-
tionize both fields. Although the methodology
employed in these earlier networks is sound,
they are limited by their location: temperate zones
where vegetation and weather conditions
are not well suited for meteorite preser-
vation or retrieval. It is hard to spot a meteorite
in a cornfield, on the tundra, or in a forest.
Moreover, meteorites weather away quite rap-
sidly on Earth (Bland et al. 1998); even brief exposure to rain will affect the primordial
record they hold (Jenniskens et al. 2012).
The Desert Fireball Network
Deserts are exceptionally suited to finding meteorites due to the lack of plant cover and
because the environmental conditions limit
degradation (Bland et al. 2009). Around 80%
of all meteorites have been found in deserts.
Could a network sited in a desert deliver
greater numbers of meteorites with orbits?
The benefit is that searching should be easier.
The major difficulty is building hardware
to survive and operate autonomously for
extended periods in a harsh environment.
To test the concept, a trial network of four film
cameras in the Nullarbor desert of Western
Australia was established in 2007 (Bland et al.
2012). Australia was considered ideally
suited for the network because of clear skies
and environmental conditions. Prior to
this project, there were no known southern
hemisphere meteorites with orbits, or indeed
any extended campaigns observing southern
hemisphere fireballs (Fig. 1). The initial Desert
Fireball Network (DFN) covered only a small
area (172,000 km²), but by 2010, two mete-
orites had already been recovered (Bunburra
Rockhole and Mason Gulley) using trajectory
information calculated from fireball images.
The images also allowed us to determine
the precise pre-atmosphere orbits for these rocks (Bland et al. 2009; Towner et al. 2011).
Bunburra Rockhole was an especially inter-
esting find—a unique basaltic achondrite with
an impact near Earth object orbit (Bland et al.
2009). This achievement has allowed us to
upgrade and expand the DFN.

Citizen Science
DFN is a natural outlet for community out-
reach/engagement because of the widespread
interest in fireballs and meteorites. Fireballs
get more and more media coverage, espe-
cially in the age of expanding use of dash-
boards and security cameras. Fireballs in the
Sky (FITS) is a citizen science project linked
to the DFN (www.fireballsinthesky.com.
au) with the goal of sharing the research and
enabling the global public. School stu-
dents and the general public are encouraged
to contribute and interact with scientists as
the team develops, essentially becoming
members of Fireballs in the Sky community.
There are a number of ways to engage with
the team: e-newsletters, a blog, Facebook (www.
facebook.com/fireballsinthesky), and Twitter
fireballsky.com.au/download-app) has been
developed so that the public can record and
share their fireball sightings with scientists,
participating in real-time research (Fig. 2).
The app works around the world, allowing
orbital data to be confirmed from anywhere
on the planet, even if no meteorite is found.
Users receive updates on the specific event
that they have witnessed, and the data they
collect is used to inform future predictions
on meteor showers throughout the year and
provides users a display directing them to the
specific location in the sky for that shower.
Finally, with technologies invented for the next generation digital observatories, we are developing an inexpensive ‘kit’ fireball camera station that would allow interested amateurs to plug in a digital camera and have their own advanced fireball observatory. A versatile interface will allow users to customize camera settings, schedule operations, and download imagers using Wi-Fi. The ability to use it for daytime photography means that the system can be adapted for multiple functions outside of fireball observations.

The goal of DFN is to increase recovery of meteorites with orbits: a growing, lasting resource for the research community. It is our hope that with the smartphone app and new home kit hardware, the public can make a real contribution to the field and participate in this research as it happens.

REFERENCES


FIGURE 2

Three screenshots illustrating the main features of the Fireballs in the Sky smartphone app. (LEFT) The menu allows a user to report a sighting, check current, upcoming meteor showers in their area, and get up-to-date news on what’s happening with the DFN research team.

(Middle) To record a sighting, the user points the phone at the start and end positions in the sky and "draws" the path of the fireball. The user then adjusts the duration, brightness, shape, and colour of the fireball before reaching a summary page. Because it is a simulation, not a video, this is done after the fireball has burned out. With multiple reports, a sighting can be confirmed and will be listed on the app for users to check.

(Right) Once a user selects a meteor shower, the app will provide data such as expected peak, zenith hourly rate, and moon phase. The app will then direct the user to the best area to look in the sky, in real time.
B.3. **Conference Abstract A — Atom Probe Tomography of Refractory Metal Nuggets**


*Presented at the 4th International Highly Siderophile Element Geochemistry Workshop, July 2016, Durham University, UK.*

Abstract published in proceedings of The 4th International Highly Siderophile Element Geochemistry Workshop.

**Reason for inclusion** — This work was presented as an oral presentation at an international conference and outlines the work detailed in Chapter 4.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Atom probe tomography of refractory metal nuggets.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and presented the results at The 4th Highly Siderophile Elements Geochemistry Workshop (2016) Durham University.

Overall Percentage: 80%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Lucy V. Forman
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature]
Date: 22.2.17.

Name of Co-Author: Steven M. Reddy
Contribution to the Abstract: Assisted with the final review of the manuscript.
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: William D. A. Rickard
Contribution to the Abstract: Assisted with FIB sample preparation.
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: David W. Saxey
Contribution to the Abstract: Assisted with atom probe analysis
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Alexandre La Fontaine
Contribution to the Abstract: Assisted with atom probe analysis.
Overall Percentage: 1%
Signature: [Signature]
Date: 20/02/17
Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)
Contribution to the Abstract: Assisted with FIB sample preparation.
Overall Percentage: 1%

Name of Co-Author: Patrick W. Trimby
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%

Name of Co-Author: Julie Cairney
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%

Name of Co-Author: Simon Ringer
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%

Name of Co-Author: Bruce F. Schaefer
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
8

Atom probe tomography of refractory metal nuggets


1Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. (luke.daly@postgrad.curtin.edu.au)
2GAP, JDLC, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.
3ACMM, University of Sydney, NSW 2006, Australia.
4AINST, & School of Aerospace, Mechanical & Mechatronic Engineering, University of Sydney, NSW 2006, Australia.
5Department of Earth and Planetary Sciences, Macquarie University NSW, 2109, Australia.

Highly siderophile elements are concentrated in micrometre to sub-micrometre metallic grains called refractory metal nuggets (RMNs) in the most primitive carbonaceous chondrite meteorites. Initially thought to be unique to Ca-Al-Rich inclusions, we used synchrotron XFM to show they are present in all meteoritic components [1].

RMNs are thought to form via nebula condensation [2], although new evidence suggests they can also be produced via crystallisation from silicate melts [3]. However, in situ analysis of 109 RMNs combined with a literature database, reveals a wide variety of compositions that no single process can adequately explain. Our interpretation is that the inherently diverse primordial population of RMNs, incorporated into the protoplanetary disk was modified, but not completely homogenised by later solar system processing. Therefore, RMNs potentially preserve pre-solar chemical and isotopic signatures [1].

To explore this idea we present the first use of atom probe tomography on RMNs. This technique provides 3D atomic resolution reconstructions of a 100 nm wide needle prepared using a focussed ion beam; capable of revealing atomic-scale variations in chemistry and isotopic composition. Preliminary results on 3 RMNs will be discussed. Initial observations reveal nanometre scale variability in chemistry, and the presence of sulphur within RMNs, potentially indicating nebular sulphidation.

B.4. Conference abstract B — Composition of refractory metal nuggets implications for their origins.


Abstract published in proceedings of The Lunar and Planetary Science Conference, no. 1903 p. 1880

Reason for inclusion — This work was presented as an oral presentation at an international conference and outlined the work detailed in Chapter 2.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Composition of refractory metal nuggets implications for their origins.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and delivered the oral presentation of the work at The 47th Lunar and Planetary Science Conference, March 2016, The Woodlands, Texas, USA.

Overall Percentage: 78%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Katy Evans

Contribution to the Abstract: Assisted with the condensation calculations and editing and revision of the manuscript.

Overall Percentage: 2%

Signature: [signature]
Date: 20/02/17

Name of Co-Author: Kathryn A. Dyl

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [signature]
Date: 2/22/17

Name of Co-Author: Lucy V. Forman

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [signature]
Date: 22/2/17

Name of Co-Author: Patrick W. Trimby

Contribution to the Abstract: Assisted with TKD analysis and the editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [signature]
Date: 20/02/17

Name of Co-Author: Steve Moody

Contribution to the Abstract: FIB sample preparation.

Overall Percentage: 1%

Signature: [signature]
Date: 20/02/17
Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)

Contribution to the Abstract: FIB sample preparation.

Overall Percentage: 1%

Signature: [Signature Image] Date: 20/02/17

Name of Co-Author: Hongwei Liu

Contribution to the Abstract: Assisted with TEM data collection and analysis, and editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature Image] Date: 20/02/17

Name of Co-Author: Alexandre La Fontaine

Contribution to the Abstract: Assisted with atom probe analysis and editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature Image] Date: 20/02/17

Name of Co-Author: Julie Cairney

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature Image] Date: 20/02/17

Name of Co-Author: Simon P. Ringer

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature Image] Date: 20/02/17
Name of Co-Author: Martin Saunders

Contribution to the Abstract: Assisted with TEM analysis and the editing, and revision of the manuscript.

Overall Percentage: 1%

Signature: M. Saunders  Date: 20/02/17
Introduction: Refractory metal nuggets (RMNs) are composed primarily of Fe, Ni, and platinum group elements (PGEs). They are thought to form by condensation in the early Solar Nebula [1]. However, it has also been suggested that RMNs can form via crystallisation from a silicate melt [2]. Here we combine in situ analysis of RMNs, RMN compositions reported in the literature, and predicted compositions from a condensation model to define populations of RMNs based on their chemistry.

Methodology: 109 RMNs were analysed in situ from Allende, Murchison, Vigarano, ALH 77307, and Adelaide, using energy dispersive X-Ray spectroscopy (EDS) at the University of Sydney, Curtin University, and the University of Western Australia. These observations were supported by analyses from EDS during Transmission Kikuchi Diffraction (TKD), and EDS obtained in transmission electron microscopes (TEMs).

Results and discussion: Plots of total PGE vs Fe (Fig 1), and total PGE vs Ni (Fig 5) show three distinct trends which can be defined by a Fe mixing line, a Ni mixing line and a cluster of low PGE concentrations (Fig 1). To check this is not an artifact of data processing, the data was plotted by original wt%, meteorite, author, technique, and inclusion type; revealing no systematic errors due to these factors.

Plotting the data in a similar vein to [1] (Fig 2) indicates that RMNs do approximately follow a condensation trend.

Figure 1: Total PGE/Fe in RMNs from this study and the literature. Showing a Fe mixing trend (black oval), a Ni mixing trend (red oval) and a low PGE region (green triangle).

An exhaustive literature search was performed in an attempt to include all published RMN compositions [1, 3-12], as well as RMNs thought to have formed via crystallisation in a silicate melt [2, 13], giving a sum total of 380 RMNs for this study.

All compositions have been converted to atomic percent and renormalised, only taking into account the elements Fe, Ni, Ru, Rh, Mo, W, Re, Os, Ir, and Pt. RMN compositions were compared to a condensation model similar to [1].

Figure 2: Composition of Os in RMNs compared to model condensation temperatures, RMNs within 5 at% of the condensation model for all elements are highlighted in black.

However, when the abundance of every element in each individual RMN was compared to the predicted composition from the condensation model, of the 380 RMNs analysed, only 29 were consistent to within 5 at% for every element. Of these 29, 22 were cosmic spherule-hosted RMNs from [13], which are thought to form by crystallisation. Of the remaining 7, only 2 had condensation temperatures >1500 K (Fig 2). In fact, when RMNs that formed via crystallisation are superimposed onto elemental plots (Fig 3) the spread is much more consistent with this mechanism of formation. Therefore, it is likely that most, if not all
RMNs formed by crystallisation, not condensation. Current condensation models cannot explain the full elemental composition of individual RMNs. This could be due to a lack of accurate activity coefficients for PGEs, this is required if we are to completely discount condensation as a possible mechanism for RMN formation.

Nevertheless, a crystallisation origin can only account for RMNs that follow the Fe mixing line (Fig 4). As such, the Fe mixing line is dominant in both RMN models. This suggests that crystallisation is a more consistent origin for RMNs than condensation. Figure 5 reveals that the low PGE cluster is dominated primarily by sulphide-hosted RMNs. Therefore, these grains are likely to have been affected by, if not formed due to sulphidation. However, the Ni mixing line remains an enigma. Fig 5 reveals the sulphide cluster is situated towards the end of the Ni mixing line. Therefore, the Ni trend and the sulphide cluster are potentially an expression of varying degrees of sulphidation of RMNs, or sulphidation of RMNs with variable compositions produced by crystallisation; with Fe being replaced by Ni, dragging the Fe mixing line down towards the Ni mixing line.

**Conclusion:** In situ analysis of RMN compositions reveals two populations of RMNs. The first follows a Fe mixing line, derived by crystallisation of RMNs from a silicate melt as described by [2]. The second follows a Ni mixing line produced by secondary sulphidation of crystallisation derived RMNs. A condensation origin for RMNs seems unlikely, but a crystallisation origin questions our current understanding of how meteoritic components form.

**References:**
B.5. **Conference Abstract C — Atom Probe Tomography and Its Application to Refractory Metal Nuggets**


*Presented at The 79th Annual Meeting of the Meteoritical Society, August 2016, Berlin, Germany.*


**Reason for inclusion** – This work was presented as an oral presentation at an international conference and outlines the work detailed in Chapter 4.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Atom probe tomography and its application to refractory metal nuggets.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and delivered the oral presentation of the work at The 79th Annual Meeting of the Meteoritical Society, August 2016, Berlin, Germany.

Overall Percentage: 80%

Signature: Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: Date: 20/02/17
Name of Co-Author: Lucy V. Forman
Contribution to the Abstract: Assisted with the final review of the manuscript.
Overall Percentage: 1%
Signature: [Signature]  
Date: 22.2.17

Name of Co-Author: Steven M. Reddy
Contribution to the Abstract: Assisted with the final review of the manuscript.
Overall Percentage: 1%
Signature: [Signature]  
Date: 20/02/17

Name of Co-Author: William D. A. Rickard
Contribution to the Abstract: Assisted with FIB sample preparation.
Overall Percentage: 1%
Signature: [Signature]  
Date: 20/02/17

Name of Co-Author: David W. Saxey
Contribution to the Abstract: Assisted with atom probe analysis.
Overall Percentage: 1%
Signature: [Signature]  
Date: 20/02/17
Name of Co-Author: Alexandre La Fontaine
Contribution to the Abstract: Assisted with atom probe analysis.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)
Contribution to the Abstract: Assisted with FIB sample preparation.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17

Name of Co-Author: Patrick W. Trimby
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17

Name of Co-Author: Julie M. Cairney
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17

Name of Co-Author: Simon P. Ringer
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: [Signature] Date: 20/02/17
Name of Co-Author: Bruce F. Schaefer

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature]

Date: 20/02/17
Atom probe tomography and its application to refractory metal nuggets.
L. Daly¹, P. A. Bland¹, L. V. Forman¹, S. M. Reddy²,³, W. D. A. Rickard⁴, D. W. Saxey⁵, A. La Fontaine⁶, L. Yang⁷, P. W. Trimby⁷, J. Cairney⁷, S. Ringer⁷ and B. F. Schaeffer.
¹Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.
Luke.daly@postgrad.curtin.edu.au, ²Geoscience Atom Probe, Advanced Resource Characterisation Facility, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. ³Australian Centre for Microscopy and Microanalysis, The University of Sydney, NSW 2006, Australia. ⁴Australian Institute for Nanoscale Science and Technology, and School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW, 2006, Australia. ⁵Department of Earth and Planetary Sciences, Macquarie University NSW, 2109, Australia.

Introduction: Refractory metal nuggets (RMNs) are sub-micron metal alloys composed of highly siderophile elements found within primitive carbonaceous chondrites. Their unique occurrence within Ca-Al-rich inclusions (CAIs), has recently been questioned using synchrotron XFM observing RMNs in all meteoritic components [1]. RMNs are thought to form by condensation in the nebula [2] and/or crystallisation from a silicate melt [3]. However, a combined data set of 109 in situ RMN compositions, combined with a literature database have revealed a large diversity of compositions that cannot be produced by any single process. Therefore, we suggest that an inherently diverse population of RMNs was incorporated into the protoplanetary disk. These RMNs have undergone some processing but the inherited compositional diversity was never completely overprinted by subsequent solar system processes. Therefore, we might expect some RMNs to preserve a pre-solar isotopic and chemical signature [1].

Method and results: Candidate RMNs were identified in CAIs in ALH 77307 and Allende. These RMNs were extracted, mounted, and shaped to a 100 nm wide needle using a Focused Ion Beam. The samples were placed into the CAMECA Local Electrode Atom Probe (LEAP) 4000X Si, Australian Centre of Microscopy and Microanalysis, Sydney University or the Geoscience Atom Probe CAMECA LEAP 4000X HR, Advanced Resource Characterisation Facility, Curtin University. Single atoms were ionised using field evaporation by high frequency laser (Curtin) pulses and accelerated towards the detector by the surrounding electric field. Time of flight measurements of ions hitting a position sensitive detector determined the elemental identity and its initial position in the tip [4]. IVAS software interpreted the data and generated a 3D reconstruction of the tip denoting the position of every detected atom. This revealed atomic scale chemical variations RMNs indicating they are not all chemically homogeneous (Figure 1). The RMN in ALH 77307 contained sulphur, a potential indicator for nebula sulphidation.

Figure 1: Allende RMN atom probe tip, indicating nanometer variations between Fe rich and Mo rich sub-volume.

B.6. **CONFERENCE ABSTRACT D — IN SITU ANALYSIS OF REFRACTORY METAL NUGGETS CRYSTALLOGRAPHY PROVIDING CLUES TO EARLY SOLAR SYSTEM EVENTS**


*Presented at The 78th Annual Meeting of the Meteoritical Society, July 2015, Berkeley, California, USA*

Abstract published in proceedings of The 78th Annual Meeting of the Meteoritical Society, July 2015, Berkeley, California, USA, no. 1856, p. 5061

**Reason for inclusion** — This work was presented as an oral presentation at an international conference and outlines the work detailed in Chapter 3.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Crystallography of refractory metal nuggets in carbonaceous chondrites.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and delivered the oral presentation for the work at The 78th Annual Meeting of the Meteoritical Society.

Overall Percentage: 79%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Lucy V. Forman

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature] Date: 22.2.17.

Name of Co-Author: Patrick, W. Trimby

Contribution to the Abstract: Assisted with TKD analysis editing and revision of the manuscript.

Overall Percentage: 5%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Steve Moody


Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)


Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Hongwei W. Liu

Contribution to the Abstract: Assisted with TEM analysis and assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Simon P. Ringer

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature of Simon P. Ringer] Date: 20/02/17

Name of Co-Author: Martin Saunders

Contribution to the Abstract: Assisted with TEM data collection and analysis and editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature of Martin Saunders] Date: 20/02/17
Introduction: Refractory metal nuggets (RMNs) are thought to be the first solids to condense from a cooling nebular gas [1]. Here we present in situ analysis of RMNs revealing new observations, which may assist in the interpretation of how they form.

Method: RMNs were extracted from samples of Allende, Vigarano, and ALH77307 in the form of a 100 nm thick TEM lamella using a Focused Ion Beam (FIB). The samples were analysed using Transmission Kikuchi Diffraction (TKD) and Transmission Electron Microscopy (TEM) techniques.

Results and discussion: Analyses of RMNs in situ revealed new textures that have not previously been documented:

Twinning in Vigarano RMNs: We observed twins in RMNs hosted within a ‘fluffy’ Type A CAI. They are most likely annealing twins due to the 60° misorientation about the [111] axis across the twin boundary. Annealing twins form under high-temperature, low-pressure conditions. No experimental data exists for the compositions of interest; in FePt nanoparticles annealing begins around ~500 °C [2]. Assuming similar or higher temperatures were required for Vigarano RMNs, we can say that this is significantly higher than estimates for Vigarano parent body metamorphism [3], and therefore that annealing must have occurred before the CAI was incorporated into the chondrite. The mineral phase hosting the RMNs also exhibits annealing textures, but the whole CAI does not. We suggest a very short-lived nebular heating event as a mechanism.

RMN alignment in Allende and ALH77307: RMNs found in ALH77307 CAIs and Allende chondrules exhibit a crystallographic relationship with their host phase. In ALH77307 the RMN [002] axis is parallel to the [201] axis in the host Åkermanite phase. The RMN <c> axis is parallel to a secondary FeMoOs phase exhibiting apparent super-cooling textures. The origin of this preferred alignment is interpreted as nucleation of forsterite about RMNs producing a shared alignment via a minimisation of surface energy. This alignment is preserved during secondary sulphidisation.

Conclusion: In situ analysis of RMNs is providing us with a detailed picture of how these most refractory materials, and their host inclusions formed and were subsequently altered.

B.7. **Conference abstract E — Crystallography of refractory metal nuggets identified within Ca-Al-rich inclusions, chondrules, and matrix of carbonaceous chondrites**


*Presented at The 77th Annual Meeting of the Meteoritical Society, September 2014, Casablanca, Morocco*


**Reason for inclusion** — This work was presented as an oral presentation at an international conference and outlines the work detailed in Chapter 3.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Crystallography of refractory metal nuggets identified within Ca-Al-rich inclusions, chondrules, and matrix of carbonaceous chondrites.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and delivered the oral presentation of the work at The 77th Annual Meeting of the Meteoritical Society, September 2014, Casablanca, Morocco.

Overall Percentage: 81%

Signature: [Signature Image] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature Image] Date: 20/02/17
Name of Co-Author: Kathryn A. Dyl
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: Date: 2/22/17

Name of Co-Author: Lucy V. Forman
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: Date: 2/22/17

Name of Co-Author: Patrick W. Trimby
Contribution to the Abstract: Assisted with TKD analysis, editing and revision of the manuscript.
Overall Percentage: 5%
Signature: Date: 2/22/17

Name of Co-Author: Steve Moody
Overall Percentage: 1%
Signature: Date: 2/22/17

Name of Co-Author: Simon P. Ringer
Contribution to the Abstract: Assisted with editing and revision of the manuscript.
Overall Percentage: 1%
Signature: Date: 2/22/17
CRYSTALLOGRAPHY OF REFRACTORY METAL NUGGETS IDENTIFIED WITHIN CA-AL-RICH INCLUSIONS, CHONDRULES AND MATRIX OF CARBONACEOUS CHONDrites,

L. Daly\(^1\), P. A. Bland\(^1\), K. A. Dyl\(^1\), L. V. Forman\(^1\), P. W. Trimby\(^1\), S. Moody\(^2\) and S. P. Ringer\(^2\)

\(^1\)Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845. E-mail: luke.daly@postgrad.curtin.edu.au. \(^2\)Australian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW 2006, Australia.

**Introduction:** Refractory metal nuggets (RMNs) as described by [1,2] are predicted to be some of the first Nebular condensates [3]. Previous work assumes these grains occur exclusively within Ca-Al-rich Inclusions (CAIs) [4]. Initial results utilising the Australian Synchrotron (AS) suggest this is not the case [5]. Here we present the combination of X-Ray Fluorescence (XRF) and scanning electron microscopy (SEM) techniques that positively identify RMNs within chondrules and matrix, as well as CAIs. We show for the first time the application of transmission Kikuchi diffraction (TKD) to a meteorite, defining nanometer-scale crystallographic and compositional variations of RMNs.

**Method:** Carbonaceous chondrites Vigarano and Allende were analysed with the AS XRF beamline and Maia detector. GeoPIXE software generated element maps, [6] identifying pixel-sized (2μm) hotspots of platinum group elements (PGEs). Analyses using electron back scatter diffraction (EBSD), and energy dispersive spectroscopy confirmed the presence of PGE alloys at the surface of the sample in the location of the hotspots. TKD analyses on focused ion beam generated sections of PGE alloys, using a 25nm step size, provided high spatial resolution data on the crystallography, orientation, and chemistry of RMNs in situ.

**Results and Discussion:** This approach has identified several RMNs in CAI material, and 6 RMNs within non-CAI material: 4 from Vigarano (3 within chondrules, and 1 within matrix), and 2 from chondrules within Allende. EBSD analysis of RMNs within Allende’s chondrules indicate that the RMNs are single crystal cubic alloys with random crystal orientations. TKD analyses of 7 RMNs, between 80-500nm, in CAIs from Vigarano are also cubic alloys with random orientations, but in several cases exhibit polysynthetic twins with 20-130nm spacing. TKD Analysis of 3 PGE alloys, between 0.7-1.1μm, found within sulphide nodules enclosed within a chondrule of Allende reveal they are also single crystal cubic alloys; however the orientations of these grains are nearly identical. This heavily implies that these grains formed through parent body processes rather than condensation in the Nebula. However their similarity in appearance to RMNs highlights the importance of analysing these grains in situ.

Identifying RMNs enclosed within matrix and chondrules as well as CAIs has significant implications for how we interpret their formation. It is our aim with further research and analyses of RMNs in situ to develop a unifying theory of RMN formation.

B.8. **Conference abstract F — Transmission Kikuchi diffraction applied to primitive grains in meteorites.**


*Presented at The 46th Lunar and Planetary Science Conference, March 2015, The Woodlands, Texas, USA.*


**Reason for inclusion** — This work was presented as an poster presentation at an international conference and outlines the work detailed in Chapter 3.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Transmission kikuchi diffraction applied to primitive grains in meteorites.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and delivered the poster presentation at The 46th Lunar and Planetary Science Conference, March 2015.

Overall Percentage: 82%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Patrick W. Trimby

Contribution to the Abstract: Assisted with TKD analysis and in editing and revision of the manuscript.

Overall Percentage: 5%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Steve Moody


Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)


Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Simon P. Ringer

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17
TRANSMISSION KIKUCHI DIFFRACTION APPLIED TO PRIMITIVE GRAINS IN METEORITES. L. Daly¹, P. A. Bland¹, P. W. Trimby², S. Moody², L. Yang² and S. P. Ringer², ¹Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA, 6845, Australia. E-mail luke.daly@postgrad.curtin.edu.au, ²Australian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW, 2006, Australia.

Introduction: Transmission Kikuchi diffraction (TKD) is a relatively new technique in electron microscopy utilizing the transmission capabilities of scanning electron microscopes (SEMs) to analyse focussed ion beam (FIB) prepared transmission electron microscope (TEM) lamellae. This technique can analyse grains in the 10nm size range, which is an increase in resolution from standard electron back scatter diffraction (EBSD) of at least an order-of-magnitude [1,2]. TKD also provides detailed information on the crystallography, orientation and composition variations across the whole section, not just in a small region as in standard TEM analysis. This is particularly useful in the analysis of matrix grains in primitive meteorites and IDPs which can often be ~100nm across. Here we illustrate its effectiveness applied to micron-scale Refractory Metal Nuggets (RMNs).

Methodology: FIB sections containing RMNs were extracted from the meteorites Allende, ALH 77307, and Vigarano using the Zeiss Auriga FIB-SEM at the
Australian Centre for Microscopy and Microanalysis (ACMM), Sydney. The RMN from Allende is hosted within a chondrule sulphide, and the RMNs from ALH 77307 and Vigarano are hosted within Ca-Al rich inclusions (CAIs). Also a section across a chondrule, the chondrule rim and the surrounding matrix was taken. The FIB lamellae were then analysed using a Zeiss ULTRA Plus FEG SEM. Energy dispersive X-ray spectroscopy (EDS) and TKD maps were collected simultaneously from each of the samples using a Nordlys-NANO EBSD detector and a X-Max 20mm² SDD EDS detector using an accelerating voltage of 30kV. The maps were processed using the Oxford Instruments Aztec and Channel 5 software.

**Results:** TKD analysis of these grains revealed some complex variations in terms of crystallography (see Figure 1) and mineralogy (see Figure 2) which were not apparent in SEM observations of the bulk sample prior to extraction; including the observation of twinning in several RMNs. The section across a chondrule, rim and matrix region indicates that the rotation axis within the forsterite olivine changes from rotation about the [001] axis in the matrix closest to the chondrule to rotation predominantly around the [100] and [010] axis further away from the chondrule (see Figure 3).

**Discussion:** TKD allows mapping of TEM lamella at 10nm resolution and, while this does not compete with the atomic scale resolution possible with a TEM, it does allow us to observe subtle variations in tiny particles which may not be observed in the TEM due to the difficulty in orienting and tilting the sample into the desired orientation. It also allows us to observe differences in the crystallographic orientation of these grains both in relation to other grains and within the grain itself which is not directly possible with a TEM. The ability to use established software packages such as Aztec and Channel 5 means that the speed of data processing and interpretation is greatly enhanced. TKD is ideal for analysing internal variations in submicron-sized grains which would not be possible to observe using conventional EBSD.

**Conclusion:** Although it is a new microscopy technique, TKD is proving to be an excellent tool for the analysis of sub-micron grains in meteorites, as our initial results from RMNs indicate. Observing nm-scale structures within micron-scale nebular and pre-solar grains would give us a new perspective on the formation and subsequent processing history of these primitive materials.


**Acknowledgements:** This work was funded by the Australian Research Council via their Australian Laureate Fellowship program. The authors acknowledge the facilities and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Australian Centre for Microscopy & Microanalysis at the University of Sydney.


Abstract published in proceedings of The Lunar and Planetary Science Conference, no. 1777, p. 2071

Reason for inclusion — This work was presented as an poster presentation at an international conference and outlines the work detailed in Chapter 2.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: In situ analysis of refractory metal alloys in carbonaceous chondrites: implications for early solar system processes.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and delivered the poster presentation at The 46th Lunar and Planetary Science Conference, March 2014.

Overall Percentage: 84%

Signature: [Signature]

Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature]

Date: 20/02/17
Name of Co-Author: Kathryn A. Dyl

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 2%

Signature: [Signature] Date: 2/22/17

Name of Co-Author: Lucy V. Forman

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 2%

Signature: [Signature] Date: 22/2/17

Name of Co-Author: Chris G. Ryan

Contribution to the Abstract: Assisted with Synchrotron analysis, editing and revision of the manuscript.

Overall Percentage: 2%

Signature: [Signature] Date: 20/02/17
### Introduction

Refractory metal alloys are predicted to be the first solids to condense from the cooling Solar Nebula [1, 2]. Assemblages of refractory metals within carbonaceous chondrites were first described by [3, 4]. These are composed of the transition elements W, Re, Os, Ir, Mo, Pt, Rh, Ru, Zr and Hf [3]. These assemblages of (OAs) or fremdlinge have been affected by oxidation, sulfidation and re-mobilization into non metallic phases [5, 6]. Sub-μm refractory metal alloys known as refractory metal nuggets (RMNs) with compositions and crystal structures consistent with a condensation origin have also been described [2, 7]. These are similar in morphology and composition to the solids predicted by [1, 2] that condense primarily from a cooling gas of solar composition. RMNs therefore can potentially provide insights into processes acting at the advent of Solar System formation. The assumption has been that RMNs occur exclusively within Ca-Al rich inclusions (CAIs) [8]: those insights have tended to be associated with CAI formation. Here we present results from in situ analyses of carbonaceous chondrites that contradict this assumption. RMNs are found within all chondritic components.

### Method

A suite of carbonaceous chondrites (Renazzo, Allende, Adelaide, Kaidun, ALH77307 and Acfer 094) were analysed on the X-Ray Fluorescence Microscopy (XFM) beamline at the Australian Synchrotron, using the Maia detector, which allows for rapid data collection and analysis at high resolution across a broad energy range (4-18 keV) [9], utilizing its custom-made 384 Si-diode detectors. This analytical protocol generated element maps covering whole thin sections (or large selected areas) at 2μm resolution and a sensitivity of 50-100 ppm for elements such as Os, Ir, and Pt [10], allowing detection of a suite of trace and minor elements. The element maps were created with the GeoPIXE software, which utilizes a dynamic analysis matrix method to deconvolve the elements spectral peaks [11]. The high energy of the XFM beamline is such that diagnostic elemental X-rays are collected from ≥100μm into the sample.

The samples were subsequently analysed on the Zeiss 1555 VP-FESEM at the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia. Energy-dispersive X-ray spectroscopy (EDS) at 25KeV confirmed the presence of some RMNs that were on the surface of the sample, validating the detection of these elements via two methods.

### Results

The Synchrotron data was analysed targeting refractory element hotspots such as Os, Ir, and Pt. This method yielded an average of 20 potential RMNs per sample with a maximum of 70 in Vigarano and a minimum of two in Adelaide (Table 1). Due to the proximity of the Kα and Lα peaks for Os, Ir and Pt with both one another and more abundant elements (i.e., Zn), as well as the thickness of the sample, it is difficult to differentiate individual peaks from the peak of the most abundant element which overprints and defines the shape of the spectra in that energy range. A detailed analysis of potential peak overlaps was undertaken for every grain in order to avoid misidentification of PGEs, and any false positives removed. For confirmed RMNs, Synchrotron and EDS analyses show that these RMNs occur as alloys of several PGEs. The size of RMNs observed in the Synchrotron data for >95% of cases are pixel size, consistent with grains ≥2μm.

The depth variations between the two techniques (100μm for Synchrotron and 1μm for EDS) generates an issue when locating RMNs in EDS maps. Given their size (>100μm-1.2μm) [8], sub-μm to μm-scale (this work), the likelihood (99%) is that the grain will be buried beneath the sample surface. However, a follow-up study of each identified hotspot with detailed Backscattered electron (BSE) and EDS mapping revealed a number of cases where grains could be identified and analysed at the surface.

### Discussion

The techniques applied here allow for rapid identification of RMNs in situ within carbonaceous chondrites at high spatial resolution. It is evident that the majority of RMNs are hosted in CAIs. But the combined data from the Synchrotron, SEM and EDS...
analyses clearly show that RMNs can also be found within other components of carbonaceous chondrites such as chondrules, and matrix (Figure 1).

This observation may have some far reaching implications. The assumption that RMNs are unique to CAIs has limited interpretations about their origin to high temperature regions close to the proto-Sun. The fact that we observe RMNs in other components in carbonaceous chondrites raises questions about how they formed.

Following a similar approach to [8], we can use the specific mix of elemental abundances within each grain to define where that grain falls on an ideal condensation curve. With data gained from in situ analysis providing a spatial context, we can obtain cooling rates for grains in different chondritic components – allowing us to choose between formation mechanisms for non-CAI RMNs. By analyzing different components, in different meteorites, this approach offers the interesting possibility of tracking cooling rates at various points in space and time within the early Solar Nebula, generating a detailed thermal history to compare to disk models.

Conclusion: The combination of Synchrotron data with SEM and EDS analysis allows us to rapidly identify PGE hotspots within carbonaceous chondrites, generating a large dataset which retains its spatial context. This opens the way to a wider spectrum of possibilities when interpreting the origin of RMNs. RMNs are not unique to CAIs but can be observed in other components in carbonaceous chondrites that have not seen such extremes of temperature such as matrix and chondrules. This could provide insights into the thermal structure of the early Solar Nebula. Further analysis of these grains in situ utilizing LA-ICP-MS, FIB, transmission electron microscopy (TEM) and atom probe analysis will help establish their value as tracers of the thermal history of the inner Solar Nebula.

Acknowledgements: The authors acknowledge the facilities and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterisation & Analysis, The University of Western Australia, a facility funded by the University, State and Commonwealth Governments. This work was funded by the Australian Research Council via their Australian Laureate Fellowship program. This research was undertaken on the XFM beamline at the Australian Synchrotron, Victoria, Australia. We also acknowledge assistance provided by Mr Timmons Erikson.

References:
B.10. **Conference Abstract H — Early Solar System Events Revealed by Analysis of Tiny Nuggets.**


*Presented at The 15th Australian Space Research Conference, 2015, Canberra, Australia.*

Abstract published in proceedings of The 15th Australian Space Research Conference

**Reason for inclusion** – This work was presented as an oral presentation at an domestic conference and outlines the work detailed in Chapter 3.
STATEMENT OF AUTHORSHIP

Title of Abstract: Early solar system events revealed by analysis of tiny nuggets.

Publication Status: Published

Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript and delivered the oral presentation for this work at The 15th Australian Space Research Conference.

Overall Percentage: 79%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Lucy V. Forman

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature]
Date: 22/2/17

Name of Co-Author: Patrick, W. Trimby

Contribution to the Abstract: Assisted with TKD analysis editing and revision of the manuscript.

Overall Percentage: 5%

Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Steve Moody


Overall Percentage: 1%

Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Limei Yang (signed on behalf by Julie Cairney)


Overall Percentage: 1%

Signature: [Signature]
Date: 20/02/17

Name of Co-Author: Hongwei W. Liu

Contribution to the Abstract: Assisted with TEM analysis and assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature]
Date: 20/02/17
Name of Co-Author: Simon P. Ringer

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Martin Saunders

Contribution to the Abstract: Assisted with TEM data collection and analysis and editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17
Early solar system events revealed by analysis of tiny nuggets.

L. Daly\textsuperscript{1}, P. A. Bland\textsuperscript{1}, L. V. Forman\textsuperscript{1}, P. W. Trimby\textsuperscript{2}, S. Moody\textsuperscript{2}, L. Yang\textsuperscript{2}, H.W. Liu\textsuperscript{2}, S. P. Ringer\textsuperscript{2}, and M. Saunders\textsuperscript{3}

\textsuperscript{1} Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845.
\textsuperscript{2} Australian Key Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, University of Sydney, NSW 2006, Australia.
\textsuperscript{3} Centre for Microscopy, Characterisation and Analysis, University of Western Australia, WA 6009, Australia.

Abstract

Carbonaceous chondrite meteorites contain micrometre sized alloys of platinum group elements known as refractory metal nuggets (RMNs). RMNs are thought to be the first solids to condense from the solar nebula. We are using high resolution techniques such as transmission Kikuchi diffraction (TKD), transmission electron microscopy (TEM), and atom probe, that can provide chemical and crystallographic data at an atomic-nanometre scale. These techniques are revealing nanometre scale textures never previously observed that provide clues to the conditions at the time of RMN formation when the sun first started to shine.

The first observed texture is annealing twins, which indicate that this particular RMN must have been reheated post-formation to temperatures >500 °C. Evidence for reheating events has previously been identified in some meteorites, but it is the first time such evidence of reheating has been found in inclusions this small.

Several isolated RMNs are also found to have identical crystal orientations to each other. These grains were unrelated to their host sulphide but once had a crystallographic relationship to other minerals in the sample. Sulphides are a secondary alteration feature; this observation indicates that crystallographic relationships can be preserved during secondary alteration.

Thirdly an entirely new mineral phase was discovered forming as a pseudomorph of the original RMN. In addition, this RMN also has a shared crystal axis with the host phase which is a potential indicator that the host phase nucleated around the RMN. The new mineral also exhibits apparent super cooling textures, which indicate that the time frame for these secondary heating events must involve very rapid cooling.

These high resolution techniques provides in situ data and analysis revealing nanometre scale structures that indicate how these grains formed and have been subsequently altered providing a window into the dynamic environment at the very dawn of the solar system.
Contact Details:

Family Name: Daly
First Name(s): Luke
Institution: Curtin University of Technology
Email: luke.daly@postgrad.curtin.edu.au
Contact Telephone: 0497840194

Paper category:

- Astrobiology and life sciences
- Education and outreach
- Planetary sciences
- Remote sensing
- Space and atmospheric physics
- Space industry
- Space technology and engineering
- Space situational awareness
- Other (indicate category here)

Type of presentation:

- Oral
- Poster
- Workshop

Membership:

- Professional Space Science Community
- National Space Society of Australia
- AIAA
- Space Industry Association of Australia
- Engineers Australia
- ASRI
- Mars Society

What area(s) are you in:

- Academic
- Advocacy
- Government
- Industry
- Postgraduate
- Undergraduate

Presenting Author short biography (200 words or less)

Luke is a PhD student at Curtin University and is part of the Desert Fireball Network research team. He moved to Australia from the UK after graduating from Imperial College London with a First Class honours degree in MSci Geology. His research focusses on identifying and analysing potential nebula condensates within primitive meteorites; using their chemistry and crystallography to determine the environmental conditions present at the dawn of the Solar System.

Completed forms should be emailed to: asrc-abstracts@nssa.com.au by 15 July 2015

Program Committee only

- Recommend
- Further information required

Additional Comments:
B.11. **Conference Abstract I – High resolution of tiny nuggets of platinum group elements in carbonaceous chondrites.**


*Presented at the The 14th Australian Space Research Conference, 2014, Adelaide, Australia*

Abstract published in proceedings of the 14th Australian Space Research Conference

**Reason for inclusion** – This work was presented as an oral presentation at an international conference and outlines the work detailed in Chapter 4.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: High resolution of tiny nuggets of platinum group elements in carbonaceous chondrites.

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Luke Daly

Contribution to the Paper: Led all aspects of this research, drafted and revised the manuscript and delivered the presentation of the work at The 14th Australian Space Research Conference.

Overall Percentage: 77%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Philip A. Bland

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20/02/17
Name of Co-Author: Kathryn A. Dyl

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature]

Date: 2/2/17

Name of Co-Author: Lucy V. Forman

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 5%

Signature: [Signature]

Date: 2/2/17

Name of Co-Author: Patrick W. Trimby

Contribution to the Abstract: Assisted with TKD analysis editing and revision of the manuscript.

Overall Percentage: 5%

Signature: [Signature]

Date: 2/2/17

Name of Co-Author: Steve Moody


Overall Percentage: 1%

Signature: [Signature]

Date: 2/2/17

Name of Co-Author: Simon P. Ringer

Contribution to the Abstract: Assisted with editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature]

Date: 2/2/17
High resolution analysis of tiny nuggets of platinum group elements in carbonaceous chondrites.

L. Daly¹, P. A. Bland¹, K. A. Dyl¹, L. V. Forman¹, P. W. Trimby², S. Moody², and S. P. Ringer².

¹Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845. ²Australian Centre for Microscopy and Microanalysis and ARC Centre of Excellence for Design in Light Metals, The University of Sydney, NSW 2006, Australia.

Abstract

Carbonaceous chondrite meteorites contain sub-micrometre metal alloy grains, composed of platinum group elements (PGEs) such as osmium, iridium and platinum, known as refractory metal nuggets (RMNs). RMNs are predicted to be the first solids to condense from the cooling nebula gas and could even be of pre-solar origin. Previous research has assumed RMNs are found exclusively within Ca-Al-rich inclusions (CAIs). However, new data obtained using the Australian Synchrotron and verified with scanning electron microscopy techniques suggest that RMNs are much more widespread. We have directly observed RMNs within the matrix and chondrule inclusions of primitive meteorites, in addition to those found already in CAIs. This has significant implications for interpreting how RMNs form, and has the potential to provide insights into the dawn of the solar system and beyond.

Diffraction patterns generated by passing an electron beam through 100 nanometre thick samples of meteorites containing RMNs, has allowed us to observe nanometre scale variations in their chemistry and crystal structure. The abundance of individual PGEs can reach up to 30 wt%. This composition is indicative of the temperature and pressure conditions within the solar nebula at the time the RMN formed. The crystal properties of RMNs found in CAIs from the Vigarano meteorite, show multiple twinning, clear crystal faces and random crystal orientations. This implies that these RMNs grew in an unconstrained environment i.e. a gas. However, PGE alloys found within sulphides in the Allende meteorite are single crystals with a near-uniform orientation. In contrast to Vigarano, this implies that their formation and orientation was influenced by geological processes. This disparity highlights the importance of analysing these grains in situ.

These observations allow us to interpret how tiny grains of PGEs form in meteorites; either RMNs from nebula condensation or PGE alloys from secondary processes on the meteorite parent body.
**Contact Details:**

<table>
<thead>
<tr>
<th>Family Name:</th>
<th>Daly</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Name(s):</td>
<td>Luke</td>
</tr>
<tr>
<td>Institution:</td>
<td>Curtin University of Technology</td>
</tr>
<tr>
<td>Email:</td>
<td><a href="mailto:luke.daly@postgrad.curtin.edu.au">luke.daly@postgrad.curtin.edu.au</a></td>
</tr>
<tr>
<td>Contact Telephone:</td>
<td>+61497840194</td>
</tr>
</tbody>
</table>

**Paper categories:**

- [ ] Astrobiology and life sciences
- [ ] Education and outreach
- [x] Planetary sciences / Exoplanets
- [ ] Remote sensing
- [ ] Space and atmospheric physics
- [ ] Space industry
- [ ] Space technology and engineering
- [ ] Materials in Space Environment
- [ ] Space Archaeology
- [ ] Other (indicate category here)

**What area(s) are you in:**

- [ ] Academic
- [ ] Advocacy
- [ ] Government
- [ ] Industry
- [x] Postgraduate
- [ ] Undergraduate

**Type of presentation:**

- [x] Oral
- [ ] Poster
- [ ] Workshop

**Membership:**

- [ ] Professional Space Science Community
- [ ] National Space Society of Australia
- [ ] AIAA
- [ ] Space Industry Association of Australia
- [ ] Engineers Australia
- [ ] ASRI
- [ ] MARS Society
- [ ] Planetary Society

**Presenting author short biography (200 words or less):**

Luke is a PhD student at Curtin University and is part of the Desert Fireball Network research team. He moved to Australia from the UK after graduating from Imperial College London with a First Class honours degree in MSci Geology. His research focusses on identifying and analysing potential nebula condensates within primitive meteorites; using their chemistry and crystallography to determine the environmental conditions present at the dawn of the Solar System.


Presented at The 79th Annual Meeting of the Meteoritical Society, July 2016, Berlin, Germany


Reason for inclusion – I was a co-author for this work which was presented as an oral presentation at an international conference.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Defining the crystallographic fingerprint of extraterrestrial treasures

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, the principle author certifies the contribution made to the manuscript by Luke Daly is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Lucy V. Forman

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and presented the results at The 79th Annual Meeting of the Meteoritical Society (2016) Berlin, Germany.

Overall Percentage: 70%

Signature: [Signature] Date: 22.2.17

Name of Co-Author: Luke Daly

Contribution to the Abstract: Assisted with data collection and editing and revision of the manuscript.

Overall Percentage: 10%

Signature: [Signature] Date: 20.2.17
DEFINING THE CRYSTALLOGRAPHIC FINGERPRINT OF EXTRATERRESTRIAL TREASURES.
L. V. Forman¹, P. A. Bland¹, N. E. Timms¹, L. Daly¹, G. K. Benedix¹ & P. W. Trimby².¹Dept. Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. ²Australian Centre for Microscopy and Microanalysis, The University of Sydney, NSW 2006, Australia.

Introduction: In describing fine grained extraterrestrial materials it is common practice to employ a geochemical shorthand, e.g. quoting the average composition of a particular mineral (frequently olivine in matrices), to constrain chemical variance and reveal some aspect of the petrogenesis of the sample. Typically, this geochemical fingerprint in olivines is expressed as a percentage of one of the olivine end members, fayalite (Fa) and forsterite (Fo), which indicate the proportions of Fe and Mg within each grain (e.g. [1]).

Determining the crystallographic characteristics of the same matrix grains would enable any relationship between grain shape, size and crystal axis coordinate to be identified. Whilst grain morphologies of matrix grains in chondrites are often quoted (e.g. [2, 3]), an accumulation of crystallographic data over a large area would allow for a standardised crystallographic fingerprint to be developed for the entire matrix of the meteorite. An understanding of the connection between crystallographic preferred orientation (CPO) and shape preferred orientation (SPO), specific to a sample of interest, allows for quick fabric interpretation and an indication of the growth and formational history of the sample. Furthermore, as the information required can be obtained using a relatively inexpensive but sensitive imaging technique, such quantification could be easily reproduced for a range of samples at a variety of scales.

Methods: In this study, we used electron backscatter diffraction (EBSD) mapping to identify phases and quantify their grain shapes, sizes, and crystallographic orientations in the CV3 meteorite Allende over a large area (4 mm², ~55800 data points). The analysed data are presented as maps, which can display various crystallographic parameters: grain size, grain shape, and primary crystal axis orientations for example. For each grain, the orientations of the major crystallographic axes are quantified, and then displayed collectively on lower-hemisphere equal-area plots to characterise the ‘shape’ and strength of CPOs. Each grain was assigned an ellipse oriented to reflect the physical longest axis of that grain and colour coded to reflect the ellipse orientation (Fig. 1A &B): Contouring of the crystallographic data (Fig. 1C) allowed for a comparison between SPO and CPO.

Figure 1 EBSD data of case-study application: a) large area map of ellipse orientation, b) expanded map of ellipse orientation, c) contoured CPO data.

Preliminary results: The (001) poles of many of the olivine matrix grains clustered to produce a weak fabric (Fig. 1C). When compared with the SPO maps (Fig. 1A & B), we found grain shape to be closely related to the (001) pole fabric therefore implying the two parameters may be co-dependent during grain formation. Further investigation in this study will fully determine the signature Allende matrix grain crystallography, complementary to the geochemical signature (Fa₄₅±[1]). This approach will enable us to examine shape and shape orientation changes around large and prominent meteoritic features, such as chondrules, and compare such results to CPO data for the same grains. We could also investigate how grain shape might impact fabric formation. By determining the average crystal shape, size and crystallographic axis coordination, we can define the crystallographic fingerprint of a chondritic sample mapped with EBSD. We suggest that identification of key crystallographic features; SPO, CPO, and their relationship should routinely form part of a comprehensive description of meteorite samples. We believe this to be important and complimentary to the geochemical data that is commonly determined for meteoritic matrix grains.

B.13. **Co-Author Conference Abstract B** — Recovering the Primordial Impact History of Chondrites in Unprecedented Detail Using Massive EBSD Datasets


*Presented at The 78th Annual Meeting of the Meteoritical Society, July 2015, Berkeley California*


**Reason for inclusion** — I was a co-author for this work which was presented as an oral presentation at an international conference.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Recovering the primordial impact history of chondrites in unprecedented detail using massive EBSD datasets

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, the principle author certifies the contribution made to the manuscript by Luke Daly is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Lucy V. Forman

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and presented the results at The 78th Annual Meeting of the Meteoritical Society (2015) Berkeley, California, USA.

Overall Percentage: 70%

Signature: [signature]

Date: 22.2.17

Name of Co-Author: Luke Daly

Contribution to the Abstract: Assisted with data collection and editing and revision of the manuscript.

Overall Percentage: 7%

Signature: [signature]

Date: 20.02.17
RECOVERING THE PRIMORDIAL IMPACT HISTORY OF CHONDRITES IN UNPRECEDENTED DETAIL USING MASSIVE EBSD DATASETS

L. V. Forman1, P. A. Bland1, N. E. Timms1, L. Daly1, G. S. Collins2, T. M. Davison2, P. W. Trimby3 & S. P. Ringer1. 1Dept of Applied Geology, Curtin University, GPO Box U1957, Perth, WA 6845, AU. E-mail: lucy.forman@curtin.edu.au 2Earth Science & Engineering Department, Imperial College London, Exhibition Road, London SW7 2BP, UK 3Australian Centre for Microscopy and Microanalysis & ARC Centre of Excellence for Design in Light Metals, University of Sydney, NSW 2006, AU.

Introduction: Chondrites are routinely classified in terms of shock level based on principles outlined by and modified from shock calibration studies of Stöffler et al. (1991). These studies characterise shock assuming parent bodies had material properties similar to extant meteorites [1], but primordial parent bodies accreted with significantly more porosity. Recent modelling has sought to understand the effects of shock and compaction of porous targets during early planetary evolution [2, 3]. Unique textures at the meso- and micro-scale are predicted, which predate the traditionally-characterised ‘shock level’ features described in meteorites. In this study we investigate compaction in the Allende CV3 chondrite using Electron Backscatter Diffraction (EBSD) mapping at unparalleled scale and resolution.

Methods & Materials: An 11.51 mm² area of Allende was mapped using EBSD with a step-size of 0.5 µm resulting in 46 million data points. The scale of this map enables the use of a novel approach—subdividing the map into 150 x 150 µm grid squares, we analysed fabrics in each area individually, allowing visualization of shock wave interaction with the primordial aggregate. Here we consider a 0.972 mm² region of interest (5,426,808 data points) where fine-grained matrix encompasses a chondrule. The crystallographic preferred orientation of poles to <100>, <110> and <001> in matrix olivines were visualised for each grid square using equal-area, lower-hemisphere plots.

Results: A strong point maxima alignment of <001> (the shortest axis) normal to the chondrule margin is seen to the right of the chondrule. This is due to a grain ‘flattening’ with elongate grains aligning in the shortest dimension against the chondrule, and no preferential alignment of <001> and <100>- <1010> in matrix olivines were visualised for each grid square using equal-area, lower-hemisphere plots.

Discussion & Conclusions: Allende is assigned shock level S1 due to the absence of ‘traditional’ shock features [4]. However, the asymmetric pattern of flattened matrix grains is consistent with model predictions of mechanical strain during earlier impact events, which cause compaction of the parent body from a bimodal mixture of initially highly-porous matrix and zero porosity chondrules. Furthermore, modelling shows that the asymmetric development of the fabric can be used as a ‘way up’ indicator with respect to the impact: the impact direction was oblique to the sample plane, and the shock wave propagated from the lower-right of the chondrule [2, 3]. The absence of a fabric to the left is due to chondrule ‘shielding’. This approach should allow us to recover the early impact histories of chondrites in great detail, by using extant fabrics to model the response of primordial aggregates to the earliest compressive impacts.

B.14. **Co-Author Conference Abstract C – Constraining the Compositional Variety of Impactors at 1 AU Over the Last 3.5 Ga: In Situ Identification and Analysis of 200 Meteoritic Grains in Lunar Soil**


*Presented at The 45th Lunar and Planetary Science Conference, March 2014, The Woodlands, Texas, USA*

Abstract published in proceedings of The 45th Lunar and Planetary Science Conference p. 2680

**Reason for inclusion** – I was a co-author for this work which was presented as an poster presentation at an international conference.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Constraining the Compositional Variety of Impactors at 1 AU Over the last ~ 3.5 Ga: In Situ Identification and Analysis of >200 Meteoritic Grains in Lunar Soil

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, the principle author certifies the contribution made to the manuscript by Luke Daly is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Lucy V. Forman

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and presented the results at The 45th Lunar and Planetary Science Conference, 2014.

Overall Percentage: 80%

Signature: [signature image] Date: 22.2.17

Name of Co-Author: Luke Daly

Contribution to the Abstract: Assisted with data collection and editing and revision of the manuscript.

Overall Percentage: 4%

Signature: [signature image] Date: 20.02.17
CONSTRAINING THE COMPOSITIONAL VARIETY OF IMPACTORS AT 1AU OVER THE LAST ~3.5 GA: IN SITU IDENTIFICATION AND ANALYSIS OF >200 METEORITIC GRAINS IN A LUNAR SOIL

Introduction: On their return from the moon, bulk chemistry of Apollo soil samples revealed an extralunar component, evidenced by an excess of siderophile and volatile elements consistent with primitive meteoritic material [1, 2]. Meteoritic material has been found in situ in regolith breccias [3, 4]. The most recent study involved a detailed analysis of 8 lunar regolith breccias and a lunar meteorite. 30 anomalous particles (identified by authors as ultramafic chondrules) were identified by optical microscopy and SEM in older regolith samples; 5 more diverse projectile relics were found in younger breccias. But given its abundance in soils (in the case of Apollo 14 soil 14163, bulk chemistry indicated 2.5wt% of extralunar material is present) it is surprising that no detailed in situ characterisation of the meteoritic component in soils has been attempted. Aside from the Bench Crater [5] and Hadley Rille [6] meteorites, the collection of studied exogenous materials found within lunar settings, consists of a mesosiderite fragment [7] and iron meteorite fragments [8, 9]. The range of meteoritic hosts for the anomalous signature elements observed in bulk chemical analyses has not been determined.

In this study we apply a range of microanalytical techniques to the detection and characterisation of extralunar material in Apollo 14 soil 14163. It has been recording impacts for an extended period based on regolith grain size distribution [10], much longer than the expected half-life of asteroid families. As such, within the 2.5wt% extralunar component that is known to be present, we might expect to find fragments of meteorites derived from asteroids that are not currently delivering material to the Earth-Moon system.

Materials and Methods: Fine and coarse portions of 14163 were mounted onto cylindrical epoxy resin stubs of 25mm diameter. Fines were set in wells of approximately 50µm depth and both 3mm and 12mm diameters, whilst coarse separates were mounted into wells 1.5mm in diameter and one grain deep.

For the purposes of initial analysis, a range of scanning electron microscopy (SEM) instrumentation was employed (Zeiss 1555 VP-FESEM, TESCAN VEGA3 & Phillips XL30 ESEM) at the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia (UWA), and secondary electron, backscatter electron and energy disperse X-ray spectroscopy (EDS) images were generated to examine the elemental make-up of the grains. In addition, the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) facility at Curtin University, Western Australia, was evaluated as a trace element mapping tool.

For whole-sample mapping of trace and minor elements at high spatial resolution we employed the X-ray Fluorescence Microscopy (XFM) facility at the Australian Synchrotron, Victoria, Australia. This technique allowed us to create quantitative, micron-
scale resolution elemental maps from a variety of lunar fine and coarse samples of soil 14163. The Maia detector allows comprehensive and rapid data collection within a large energy range of 4-18 keV [11], detecting elements with Kα peaks within this range (including elements with an atomic number up to that of Zr-40). The 384-array Si-diode detector system is energy dispersive, meaning it allows this large range of minor and trace elements to be detected at high sensitivity, down to the 10s-100s ppm scale depending upon peak energy [12], which is highly significant with respect to the initial goal of this research: identification and characterisation of extralunar material. Post data collection spectral analysis was performed using the GeoPIXE software. GeoPIXE uses a dynamic analysis method allowing for spectral deconvolution and analysis of spatial distribution of trace and major elements [13].

Results: Using the Synchrotron facility and GeoPIXE software, areas and grains were highlighted that were highly enriched in siderophile, chalcophile or volatile elements. From the Synchrotron data alone, fine grained samples show approximately 50-100 anomalous grains per mount. Coarse grains often appear in the samples as microbreccias, and also provide some anomalous grains, with up to 30 grains/mount.

<table>
<thead>
<tr>
<th>Broad Classification</th>
<th>Approximate Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>60%</td>
</tr>
<tr>
<td>Sulphides</td>
<td>20%</td>
</tr>
<tr>
<td>Matrix</td>
<td>10%</td>
</tr>
<tr>
<td>Other</td>
<td>10%</td>
</tr>
</tbody>
</table>

Table 1- Approximate summary table of types of extralunar grains present within coarse samples of 14163. ‘Hotspots’ can be identified within the Synchrotron data, containing anomalously high siderophile, chalcophile and volatile elements. Characteristic elements were identified from previous research techniques, such as those outlined in [14-19], and based upon conclusions drawn from [20] a suite of suitable elements for identification of extralunar fragments was generated. These include Fe, Mn, Zn, Cu, Ni, Ge, As, Ir, As and Pt; images of which can be seen in Figure 1. Of the grains of the coarse samples examined thus far, Table 1 indicates the proportions of each broad compositional classification, of which the dominant classification is metallic. Fine grained soils contain a greater variety of grains; a study of which is ongoing.

Discussion: Our analytical protocol has detected large numbers of non-lunar fragments. Our preliminary analysis focused on the diagnostic elements listed above, restricting us to metal, sulphide, and volatile materials. Metallic grains are the most common of the extralunar grain types present in the coarse soils, simply due to the ease with which they are identified in the Synchrotron data and under SEM. However, these meteoritic materials will be associated with a larger fraction of silicates. Refining our data reduction protocol will allow us to characterise meteoritic silicates, extending the suite of identified extralunar particles beyond the ∼200 grains already seen. This will be aided by the application of a new machine learning approach, which will enable multi-dimensional (25 element) automated identification and classification of grains.

Conclusions: This work has identified and analysed a large number of primarily metallic, sulphide and matrix grains within lunar soil 14163. Our technique, combining whole-sample mapping at high spatial resolution, with high sensitivity for a range of minor and trace elements, facilitates both the identification of anomalous grains and the generation of a detailed classification system. Future work will aim to further classify and characterise grains in terms of their origin, in a range of soils, based on geochemical signature and texture, supplementing Synchrotron analyses with additional techniques such as oxygen isotope analysis; TEM on FIB sections; and LA-ICP-MS mapping. The promising results from this initial study will contribute towards mapping the distribution of impact debris on the lunar surface, and constraining the compositional variety of impactors arriving at 1AU over the last ∼3.5 Ga.

Acknowledgments: This work was funded by the Australian Research Council via their Australian Laureate Fellowship programme. The authors acknowledge the facilities, and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterisation & Analysis, The University of Western Australia, a facility funded by the University, State and Commonwealth Governments. This research was also undertaken on the XFM beamline at the Australian Synchrotron, Victoria, Australia. We also acknowledge assistance provided by the LA-ICP-MS lab (Curtin University).

B.15. Co-Authored Conference Abstract D – Mineralogy and Petrology of the Murrili Meteorite


Presented at The 79th Annual Meeting of the Meteoritical Society, July 2016, Berlin, Germany.


Reason for inclusion – I was a co-author for this work which was presented as an oral presentation at an international conference.
STATEMENT OF AUTHORSHIP

TITLE OF ABSTRACT: Mineralogy and Petrology of the Murrili Meteorite

PUBLICATION STATUS: Published

AUTHOR CONTRIBUTIONS

By signing the Statement of Authorship, the principle author certifies the contribution made to the manuscript by Luke Daly is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

Name of Principal Author: Gretchen K. Benedix

Contribution to the Abstract: Led all aspects of this research, drafted and revised the manuscript and presented the results at The 79th Annual Meeting of the Meteoritical Society (2016) Berlin, Germany.

Overall Percentage: 80%

Signature: [Signature] Date: 20/02/17

Name of Co-Author: Luke Daly

Contribution to the Abstract: Assisted with data collection and editing and revision of the manuscript.

Overall Percentage: 1%

Signature: [Signature] Date: 20/02/17
Introduction: Murrili (pronounced moo-RRil-y) is the 3rd meteorite recovered by the Desert Fireball Network (for details of the fall and orbit see [1]). It fell as a single, heart-shaped, 1.68 kg stone, measuring ~13 × 7 × 6 cm, and was entirely fusion crusted. Two small wedges and a thin slab were cut from the main mass for examination and analyses. Cut surfaces reveal pervasive alteration with rusty staining heterogeneously distributed in a wormy pattern. Chips and powders of both altered and unaltered sample were sent for oxygen isotope, bulk composition, cosmogenic nuclide, porosity/density, and Mössbauer analyses. Mineral compositions were determined on a thick section with a JEOL 8530F electron microprobe (20kV, 20nA). Modal mineralogy was determined using a Tescan Integrated Mineral Analyzer. Oxygen isotopes were measured using the method described in [2]. Bulk trace and major element compositions were determined using the method described in [3,4]. Cosmogenic nuclides were measured as described in [5,6].

Physical characteristics: Distinct chondrule (barred olivine, the remnants of porphyritic olivine, and possible radiating pyroxene) outlines, as well as large single mineral crystal clasts, are set in a relatively coarse-grained matrix. The section is dominated (all in vol%) by olivine (32%) and orthopyroxene (32%), with smaller amounts of plagioclase (7%), metal and Fe-oxides (10%) and sulfides (6.5%). Phosphate and chromite make up < 1% of the section. Examination of the minerals in thin section shows no evidence of shock – olivine has normal extinction across the section indicating a shock stage of 1 [9].

Geochemistry: Olivine has an average composition of Fa18.8±0.5 (n=15). The orthopyroxene average is Fs16.4±0.3Wo1.1±0.3 (n=8). Chromite (n=7) Cr/Cr+Al ranges from 0.85 to 0.87 and Fe/Fe+Mg varies from 0.84 to 0.86. The oxygen isotopic composition of the unaltered material is δ17O=2.76±0.02‰, δ18O=4.18±0.04‰. Bulk elemental and cosmogenic nuclide results will be reported at the meeting.

Discussion: The overall texture of the sample indicates that the meteorite is a type 5 ordinary chondrite, which is consistent with the chromite [10] and OPX Wo values [11]. The average olivine, orthopyroxene and oxygen isotope compositions indicate the meteorite is chemically classified as an H chondrite [12,13]. The cosmic ray exposure (CRE) age of ~7 Ma coincides with the main CRE age cluster for H-chondrites. Cosmogenic nuclide ratios are compatible with a small pre-atmospheric size (few 10 cm).

Conclusions: The Murrili meteorite is classified as an H5 chondrite, based on olivine, orthopyroxene and oxygen isotope compositions, as well as textural features. It has a shock stage of S1. It is weathered due to exposure to the lake bed mud, but the alteration has not completely pervaded the rock.


Ma, C., Beckett, J. R., and Rossman, G. R. (2014). Allendeite (Sc\(_4\)Zr\(_3\)O\(_{12}\)) and


Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.