

**Western Australian School of Mines
Department of Applied Geology**

**Determination of the selenium contents of waste rocks of iron ore mining in the
Pilbara, Western Australia using ICP-MS**

Donya Rajabian Tabesh

**This thesis is presented for the Degree of
Master of Philosophy (Geology)
of
Curtin University**

September 2014

Declaration

To the best of my knowledge and belief this thesis contains no materials 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.

Signature:

Date:

ABSTRACT

The metalloid element selenium (Se) has very low concentration (estimated mean 0.05 ppm) in rocks of the Earth's crust but is of increasing environmental interest on account of its critical role in animal and human health. Recently there has been concern regarding the possible environmental risk associated with mining of sedimentary iron ores as practised in the Pilbara region of Western Australia, since the ironstones and associated shales are potential sources of Se. The very low concentrations found in most rocks and the environment, together with selenium's complex chemical behaviour, make it a difficult subject for geochemical analysis. While a variety of analytical techniques have been used to determine the concentration of Se in geological materials, the most widely applied is inductively-coupled mass spectrometry (ICP-MS) and a large majority of Se data obtained by the mining industry in Western Australia has been through routine procedures of sample dissolution and ICP-MS trace element analysis.

This study investigates the efficacy of such a routine approach to ICP-MS determination of Se, particularly when applied to rocks with high iron content. The effectiveness of acid digestion of rocks and routine ICP-MS techniques was tested through the preparation and analysis of standard reference materials (geostandards) with known Se content. The concentrations and distribution of Se occurring in waste rocks from three of BHP Billiton's iron ore mines in the Pilbara was subsequently determined.

Experimental work in this study suggests that hot multi-acid ($\text{HNO}_3 + \text{HClO}_4 + \text{HF}$) digestion can be effective for the quantitative dissolution of a wide variety of rock types prior to ICP-MS analysis, with a high level of reproducibility obtained. Variations from the published values were frequently significantly greater than for a suite of other trace elements (As, Cr, V, Mn, Cu) and there is evidence for a more complex behaviour of Se during acid dissolution than for these other trace elements.

There is a strong indication that Se values produced by ICP-MS analysis are prone to inaccuracy where routine procedures are used, and that careful correction of results against multiple calibration curves obtained from the analysis of certified materials is required to guarantee accuracy.

Analysis of a range of waste rock samples Pilbara iron ore mines, including high grade iron ore, low-grade ore, dolerite, black shale, mudstone and lignite, revealed an overall significant enrichment of Se in these wastes when compared to mean crustal values. Particularly elevated concentrations in samples of lignite (max. 17.16 ppm) and carbonaceous “black” shales (max. 4.07 ppm) indicate the prime geochemical association of Se is with organic matter and/or sulphide minerals, rather than iron. Oxidation and leaching of waste rocks during long-term storage at iron ore mines of the Pilbara region has the potential to release Se to the surrounding environment, at each of the three mines (Mt Goldsworthy mine, Yandicoogina mine and South Jumblebar mine) sampled in this study. Reliable and accurate Se determination is required to ascertain the extent of such Se releases and this will require more sophisticated calibration of the ICP-MS technique than is normally applied in routine trace element analysis if this technique is to be used in future environmental studies of Se in the Pilbara and from iron ore mining in general.

Although, the concentration of Se in individual waste rock types at BHP Iron Ore mines in the Pilbara, WA was not more than the Health Investigation Levels for Soil Contaminants (2013) guideline values, there is potential for a degree of contamination of the environment neighbouring iron ore mines in the Pilbara if leachate from stored waste rocks should be released. Assessing the environmental risk will require understanding of the geochemical and biochemical behaviour of mobilised Se and identification of the sensitive receptors in the environment of the Pilbara.

ACKNOWLEDGMENTS

I would never have been able to finish my Master's thesis without the guidance of my supervisor, help from my co-supervisor, and support from my lovely parents and sister. Thus, in this section, I would like to express my deepest appreciation to all those who provided me the possibility to complete this project.

Firstly, I would like to express my special appreciation and thanks to my supervisor Associate Professor Ron Watkins, you have been a tremendous mentor for me and my deepest gratitude to you, for your patience, support, knowledge, and providing me with an excellent atmosphere for doing research. I would also like to thank you for encouraging my research and for allowing me to grow as a research scientist.

Special thanks to my Co-supervisor Dr David Oldmeadow, for helping and guiding my research for the past two years. My sincere thanks also go to Professor R. John Watling for his advice during this project.

I would like to thank BHP Billiton Iron Ore Mining, who financed my research project and kindly provided waste rock samples from their mines. I would also like to acknowledge with much appreciation the support of staff of EIGG (A/Prof Ron Watkins, Dr David Oldmeadow and Deborah Watkins) and Applied Geology (Andy) in Curtin University, TSW Analytical and Forensic & Analytical Chemistry (Professor R. John Watling, Dr Christopher May and Dr Cameron Scadding) at UWA.

Moreover, I thank my friends in Curtin University for all the fun we have had in the last two years. I wish to express my love and gratitude to my beloved families, for their understanding and endless love through the duration my study.

TABLE OF CONTENTS

| | |
|--|-----------|
| ABSTRACT | i |
| ACKNOWLEDGMENTS | iii |
| TABLE OF CONTENTS | iv |
| LIST OF FIGURES | vii |
| LIST OF TABLES | ix |
| | |
| Chapter 1: Introduction | 1 |
| 1.1. Background to Study | 2 |
| 1.2. Aims of Study | 5 |
| 1.3. Previous Work | 6 |
| 1.4. The Study Area | 7 |
| 1.4.1. Location | 7 |
| 1.4.2. Geological Background | 8 |
| 1.4.3. Geological Context of Sampled Iron Ore Mines | 12 |
| 1.5. Selenium and Health | 15 |
| 1.5.1. Physical Characteristics of Selenium | 15 |
| 1.6. Geochemical Character of Selenium | 17 |
| 1.7. Selenium in Human and Animal Health | 18 |
| 1.7.1. Deficiency | 19 |
| 1.7.2. Toxicity | 20 |
| 1.8. Difficulties of Routine Selenium Determination in Rocks from the Pilbara Iron Ore Mines | 21 |
| 1.9. Outcomes of Present Study | 23 |
| | |
| Chapter 2: Methodology | 24 |
| 2. Methodology | 25 |
| 2.1. Sourcing of Samples | 25 |
| 2.1.1. International Standard Reference Materials Used in Evaluation of Accuracy of Results | 26 |
| 2.1.1.1. U.S. Geological Survey, NIST, and CCRMP | 26 |
| 2.1.1.2. JGS Reference Materials | 29 |
| 2.1.2. Waste Rocks from Iron Ore Mining | 30 |
| 2.3. Sample Preparation | 32 |
| 2.3.1. Rock Crushing | 32 |

| | |
|--|-----------|
| 2.4. Analytical Techniques | 34 |
| 2.4.1. Total Carbon and Total Sulphur | 34 |
| 2.4.2. Preparation of Samples by Acid Digestion | 35 |
| 2.4.3. Determination of Selenium and Other Trace Elements | 38 |
| 2.4.3.1. Inductively-Coupled Plasma Mass-Spectrometry (ICP-MS) | 38 |
| 2.4.3.2. Problems of Selenium Determination Using ICP-MS | 39 |
| 2.5. Data Quality Assurance and Quality Control | 40 |
| 2.6. Procedural Quality Control (QC) | 41 |
| 2.6.1. Quality Control in the Field | 41 |
| 2.6.2. Quality Control in the Laboratory | 41 |
| Chapter 3: Results from International Reference Materials | 42 |
| 3.1. Results from International Standard Reference Materials | 43 |
| 3.1.1. Results for Reagent Blanks | 43 |
| 3.1.2. Results for CH ₄ and NIST coal fly-ash | 44 |
| 3.1.3. Other International Standards Reference Materials Used for Evaluation of Results | 46 |
| 3.1.4. Results for JGS Reference Materials | 50 |
| Chapter 4: Results from Waste Rocks of Iron Ore Mining | 55 |
| 4.1. Results from Waste Rocks of Pilbara Mines | 56 |
| 4.1.1. Results for Reagent Blanks | 56 |
| 4.1.2. Distribution of Selenium in Waste Rock Types | 56 |
| 4.2. Selected Trace Element Values | 63 |
| 4.3. Carbon/Sulphur Determination | 65 |
| 4.3.1. The Relationship between C and S and Fe with Se | 65 |
| 4.4. Effects of Different Acid Matrix in Dissolved Iron Rich Rock Samples | 68 |
| Chapter 5: Discussion and Conclusion | 69 |
| 5.1. Discussion | 70 |
| 5.1.1. Addressing Objectives | 70 |
| 5.1.2. Efficiency of Acid Digestion - Evidence from Analysis of Standard Reference Materials and Waste Rocks of Iron Ore Mining | 72 |
| 5.1.3. Efficacy of ICP-MS Instrumental Analysis | 74 |

| | |
|--|-----------|
| 5.1.4. The Variation of Selenium in the Waste Rocks of Three BHP Iron Ore Mines | 75 |
| 5.2. Conclusion | 80 |
| 5.2.1. Standard Reference Material | 80 |
| 5.2.2. Waste Rock Types from Iron Ore Mining | 81 |
| 5.3. Recommendations for Future Work | 82 |
| 5.4. Addendum to Study | 83 |
| REFERENCES | 85 |

Appendices

| |
|--|
| Appendix # 1: Geological Reference Materials Used in this Study and Their Results |
| Appendix #2: Various Waste Rocks from Iron Ore Mining and Results Obtained from Waste Rocks Supplied by BHP Billiton Iron Ore Mining |

LIST OF FIGURES

| Figure | | Page |
|---------------|--|-------------|
| Figure 1.1 | Location of BHP Billiton’s iron ore mine sites and geological map of the Hamersley Province, within the Pilbara region, showing key localities relevant to the study | 8 |
| Figure 1.2 | Geological units of the Yandicoogina Junction Deposit | 12 |
| Figure 1.3 | A geological map of the Jimblebar area | 13 |
| Figure 1.4 | Geological map of the Pilbara Block (above) and below a geological map of Mt. Goldsworthy | 14 |
| Figure 1.5 | Native, trigonal elemental selenium species, found at Ronneburg Uranium deposit, Thuringia, Germany (A) and AnnaMine, Alsdorf-Aachen, North Rhine Westphalia, Germany (B) | 16 |
| Figure 1.6 | Effects of selenium deficiency in lambs seen as chalky-white necrosis and mineralization of the heart muscles, so called “white muscle disease” | 19 |
| Figure 1.7 | Selenium toxicity in human in a patient from the Enshi district, China (lose hair) | 21 |
| Figure 2.1 | Hydraulic press (A) and mechanical jaw crusher (B) used to reduce the size of rock material prior to pulverising in the swing mill. Tema® swing mill (C-left) used to reduce the rock fragments to powder of < 75 µm; (C-right) tungsten carbide ring mill showing iron powder staining characteristic of Pilbara ironstones and quartz fragments used to clean the apparatus before use | 33 |
| Figure 2.2 | Eltra® 4000 Carbon/Sulphur analyser at EIGG (Department of Applied Geology, Curtin University) | 34 |
| Figure 2.3 | Acid digestion of rock samples: (right) open Teflon® beakers on a hot-plate; and (left) samples evaporated to insipient dryness during the preparation of solutions for analysis by ICP-MS | 35 |
| Figure 2.4 | Digested samples made up to volume in 50 ml volumetric flasks. Dark residue in some of the flasks is highly insoluble oxides | 36 |
| Figure 2.5 | Acid Distillation in quartz glass sub-boiling acid | 37 |
| Figure 2.6 | An Agilent Technologies 7500cs ICP-MS at the | |

| | | |
|------------|--|----|
| | TSW Analytical Laboratory for analysis of trace elements | 39 |
| Figure 4.1 | (A) total carbon vs selenium were compared and (B) total sulphur vs selenium | 67 |
| Figure 5.1 | Se concentrations in 20 prospective waste rock samples from South Jimblebar prospect displayed according to rock types (values in ppm) | 75 |
| Figure 5.2 | The mean Se concentration in 11 waste rock samples from Goldsworthy mine according to rock type (values in ppm) | 76 |
| Figure 5.3 | The mean Se concentration in 14 waste rock samples from Yandicoogina mine according to rock type (values in ppm) | 76 |

LIST OF TABLES

| Table | | page |
|--------------|--|-------------|
| Table1.1 | Regional stratigraphic divisions of the late-Archaeon to early-Proterozoic succession in the Pilbara region | 10 |
| Table1.2 | Stratigraphic summary of the Pilbara region | 11 |
| Table1.3 | Main physical properties of selenium | 15 |
| Table1.4 | Abundances and stability of selenium isotopes | 16 |
| Table2.1 | Geological reference materials used in this study in assessing accuracy of analytical results | 28 |
| Table2.2 | (A) 11 waste rock samples provided from Mt. Goldsworthy mine, (B) 20 waste rock samples collected from South Jumblebar, and (C) waste rock samples collected from Yandicoogina mine (20 samples) | 31 |
| Table3.1 | Concentration of trace elements in the reagent blanks | 44 |
| Table3.2 | Concentrations of Se and selected trace elements in International Standard Reference Material CH ₄ compared to certified values; and NIST coal fly-ash compared to recommended values. The coal ash was employed by the ICP-MS analytical laboratory (TSW Analytical) as a reference material | 45 |
| Table3.3 | Concentrations of Se and selected trace elements in various ISRMs for which there are published (but not certified) Se values, as indicated | 49 |
| Table3.4 | Concentrations of Se and selected trace elements in various JGS standards | 52 |
| Table4.1 | Concentration of trace elements in the reagent blanks | 56 |
| Table4.2 | Concentrations of Se and selected trace elements in different types rock and soil samples provided from South Jumblebar, and Goldsworthy compared with West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010). Values exceeding (EIL) are shown with yellow and results higher than both guidelines are highlighted with pink. | 59 |
| Table4.3 | Comparison of Se concentration in different waste rock types from the Yandicoogina mine compared with | |

West Australia Department of Environment and Conservation
Guideline values for health investigation levels (HIL) and
Ecological investigation levels (EIL). Values exceeding (EIL)
are shown with yellow and results higher than both
guidelines are highlighted with pink 62

Table4.4 The comparison of the average duplicate values for
Selenium with sulphur and carbon 66

Table4.5 Investigated concentration of trace elements by acid
digestion method and made up using HCl/HNO₃ in batch 8.
The highest values of selenium among duplicates are marked
with green colour. All results are in ppm 68

Table5.1 Selenium concentrations determined in solutions of
standard reference materials from in this study, using
CF-AFS, with comparison to results obtained by
ICP-MS and the published values. All values in ppm 84

Chapter 1

Introduction

1.1. Background to Study

Selenium¹ was discovered as a chemical element in 1818 by the Swedish chemist Jons Jakob Berzelius in a deposit from a lead chamber during the manufacture of sulphuric acid (Lenz and Lens 2009). The element with atomic number 34 and atomic weight of 78.93 lies in Group 16 of the periodic table, immediately below sulphur, for which it behaves as an analog, and above tellurium, with which it shares chemical attributes in the environment (Nazarenko and Ermakov 1972). It is commonly considered to be a metalloid (Nazarenko and Ermakov 1972), a variously defined category of elements with intermediate or hybrid properties between those of metals and non-metals (Plant et al., 2005).

The geochemical behaviour of selenium (Se) in the environment is complex (Exponent, 2010). Its average concentration as a solid in the Earth's crust is a mere 0.05 mg/kg or 50 parts per billion (ppb) (Wen and Carignan, 2011), the lowest of all elements known to be necessary for animal and human health (Plant et al., 2005). While it is a micronutrient for animals and humans, it poses a degree of ecological risk (Hartikainen, 2005) when present at elevated concentrations. Despite the nutritional benefits of Se, high concentrations are toxic (Milne, 1998). The range of intake between Se deficiency (<40 µg/day) and toxicity or selenosis (>400 µg/day) is quite narrow in humans (Plant et al., 2005).

In terms of geological setting, Se does not typically form independent deposits but most frequently occurs in association with ores of other elements. Ore bodies of volcanic genesis, such as massive sulphide deposits associated with base metals and gold, are the chief sources of Se for industry (Wen and Carignan, 2011). The element has usually been seen in rocks and soil as an impurity, which associates with more common elements such as Ni, Pb, Cu, S and Ag (Irwin, 1997). However, it may be found in larger proportions in rare, complex combinations with metals and metalloids that are the 'sulphosalts', examples of which are juninite and related seleniferous

¹ Se

bismuth sulphosalts from the Juno Mine, Northern Territory, Australia (Mumme, 1976).

The highest Se concentrations are found in Cu-Pb-Zn sulphide deposits, while significant concentrations may be present also in sedimentary U and phosphatic V deposits. Shales and siltstones can be considered as host rocks for Se (Lemly, 2007), with hydrothermal activity and supergene alteration significant factors in the Se enrichment in black shale (Wen and Carignan, 2011).

One of the most significant sources, and sinks, of Se in the environment is the iron sulphide mineral, pyrite. Selenium isomorphically replaces reduced S in the structure of pyrite during its formation in chemically reducing sediments (Presser and Swain, 1990). Selenium can readily form organic compounds by bonding with H-, O-, N- and S-bearing organic matter (Wen and Carignan, 2011). High levels of Se found in plants are generally due to the high Se concentrations in soils formed from black shale and sandstones (Moxon, 1937).

Volcanic activity has been the primary source of Se in the surface environment (Wen and Carignan, 2011). It is widely believed that volcanic emissions during early Earth history led to enrichment of Se in solution in the oceans, alongside soluble ferrous iron. With the arrival of free oxygen in the atmosphere, and the oxidation of oceanic iron, it is reasoned that Se was precipitated together with ferric iron as Banded Ironstone Formations (BIF), since Se is partly siderophile, as well as being chalcophile and biophile in character (Luttrell, 1959).

The present study relates to the occurrence of Se in rocks of the Pilbara region of Western Australia, as encountered during exploitation of abundant sedimentary iron ore deposits. It was conceived in response to the perception that Se might be mobilised and released into the environment as a result of widespread and lucrative iron ore mining operations in the region. It comprises two main components that address firstly, the difficulties faced in obtaining reliable and accurate determination of Se contents of

iron-rich rocks through routine commercial geochemical analysis and, secondly, the general distribution of Se within the ores and various waste rock types produced by iron ore mining in the Pilbara region.

It is only in the past five, or so, years that attention has been drawn to the possibility of Se release to the environment during large-scale iron ore mining in the Pilbara region. Increased environmental awareness, in general, and the drive by iron ore companies, such as BHP Billiton, for best practice in mine closure has led to increased interest in waste rock characterisation. The known affinity of Se for sulphide minerals, carbonaceous materials, and sedimentary ironstones, gives credence to the contention that Se may be mobilised by the excavation and long-term surface storage of waste rocks that include pyritic black shales and BIF (Strawn et al., 2002).

Despite recent questioning of the possible risk of Se contamination from Pilbara iron ore mining, there are few reliable data for Se concentration in the rocks of the province with which to address the question. Most information that exists is to be found in company and consultants' reports. Where Se concentrations are reported, the data have normally been produced on behalf of the mining companies by commercial analytical laboratories. Given the very low overall content of Se in crustal rocks, it is inevitable that most, or all, recent Se data for rocks of the Pilbara have been produced using inductively-coupled plasma mass spectrometry (ICP-MS), which has a lower limit of determination in the ppb or ppt (parts per trillion) range for many elements.

The Se data would have been generated by ICP-MS as part of broad element assays, with neither sample preparation (rock digestion) nor instrumental conditions having been optimised for the determination of Se. It is thus conceivable that past results for Se have not been an accurate reflection of the true concentrations in the waste rocks, particularly given the huge prevalence of iron that may influence both the character of acid dissolution and the performance of the ICP-MS instrumentation (Stephan et al., 2014).

This project seeks to determine the efficacy of the use of available Se data in future detailed evaluation of the environmental risk posed by iron ore mining, and to provide

better understanding of the potential sources of Se contamination to the environment among various rock types encountered in iron ore mining in the Pilbara region of Western Australia.

1.2. Aims of Study

The present research project was conceived as an initial part of a larger research program designed to broaden our understanding of the extent and potential sources of Se contamination arising from the mining of iron ore in the Pilbara region, WA. As a precursor to detailed appraisal of the distribution of Se in the Pilbara iron ore mines operated by BHP Billiton, and its release and subsequent behaviour in the environment, it was necessary to evaluate the accuracy of the procedures most frequently employed in determining the Se concentration in rocks, particularly those having very substantial iron content. To this end, the project aimed to:

- evaluate the effectiveness of commonly applied, routine procedures for acid digestion of rocks prior to analysis of Se by ICP-MS;
- in conjunction with personnel of a commercial analytical company (TSW Analytical Pty Ltd), to test for the optimal set up of the inductively-coupled plasma mass-spectrometer for determination of low concentrations of Se in digest solutions of rocks containing significant quantities of iron; and to
- determine the broad content of Se in a variety of waste rock types generated by a major iron ore mining company in the Pilbara region (BHP Billiton), and so elucidate the nature of lithological associations of Se and thus the potential sources of Se contamination to the environment arising from iron ore mining and waste rock storage.

The above aims were progressed by the preparation and ICP-MS analysis of a number of pertinent geological International Standard References Materials and a suite of waste rocks, and potential waste materials, from various BHP Billiton iron ore operations throughout the Pilbara region of Western Australia.

1.3. Previous Work

There are no published studies known to the author which focus upon the partitioning of Se amongst the diverse rocks encountered in iron ore mining in the Pilbara. World-wide there are very few references linking iron ore mining to Se contamination of groundwater or the surface environment. However, as a result of selenium's significance to human health, this trace element has become increasingly studied.

A recent study had shown that the amount of Se in pit lakes (flooded open-cut mine voids) can rise in response to mine dewatering and evaporative concentration at mine sites in the Pilbara and can have impact on bird populations (API Management Pty Ltd, 2011). Drainage from waste rock piles at iron ore mines may contain metals and metalloids such as Se and As (Fortescue, 2011). According to a report by Strategen (2011), pyritic black shales of the Mount McRae Formation in the Pilbara are enriched in As, S, and Se. Therefore, there is potential for elevated concentrations of elements including S (as SO₄), As, Fe, Al, Cu, and Se in the area, although the concentration of Se reported in the Brockman Pit of the Tom Price Mine was below that of the ANZECC/ARMCANZ (2000) drinking water guideline (Strategen, 2011).

Roga (2009) reported that shale samples from Mt. Goldsworthy mine site contained appreciable arsenic, whilst the Se content of 12 of the 13 shale samples analysed contained < 50 ppm Se. A single shale sample, however, contained 75.1 ppm Se, which was more than values obtained for As in this rock type. The order of abundance of the trace elements in shales of the Rosemary waste rock pile at the Mt. Goldsworthy mine site according to Roga (2009) was: Cr > Ni > Co > Se > Pb > Cu > As > Bi > U > Th > Sb.

1.4. The Study Area

1.4.1. Location

The Pilbara region covers an area of 507,896 km² (Barber and Jackson, 2011) in the northern part of Western Australia. Once remote and with few people, the region has grown in population to about 45,000 over the past decade as a result of a mineral resources boom (Barber and Jackson, 2011). Iron ore mining and associated transport and export of the raw products are predominant for the economy of the region, which is otherwise based around cattle and sheep ranching (Kneeshaw et al., 2003). BHP Billiton is the largest iron ore mining company in the region, with production in 2014 of 212 million tonnes (Ker, 2014).

Samples for Se analysis in this study were provided from three iron ore mines: Mt Goldsworthy, the first working iron ore mine in W.A. and the only one that has been subject to closure; Yandicoogina (“Yandi”) mine, which has been operating since 1986 (Kneeshaw et al., 2003); and South Jimblebar, a major new operation that came on-line in 2013. Figure 1.1 shows the geological map and locations of the three mine sites.

It should be noted that the ore types and local geology vary between the three sampled mines. Mt Goldsworthy is located in the northern Pilbara and is related to ore deposits in the Chichester Ranges (Morris and Kneeshaw, 2011). Yandicoogina situated in the eastern Pilbara (Abzalov et al., 2007) and South Jimblebar in the south-east of the province mine deposits of the Archaean – Early Proterozoic Hamersley Group (Stone et al., 2003; Kerr et al., 1994).

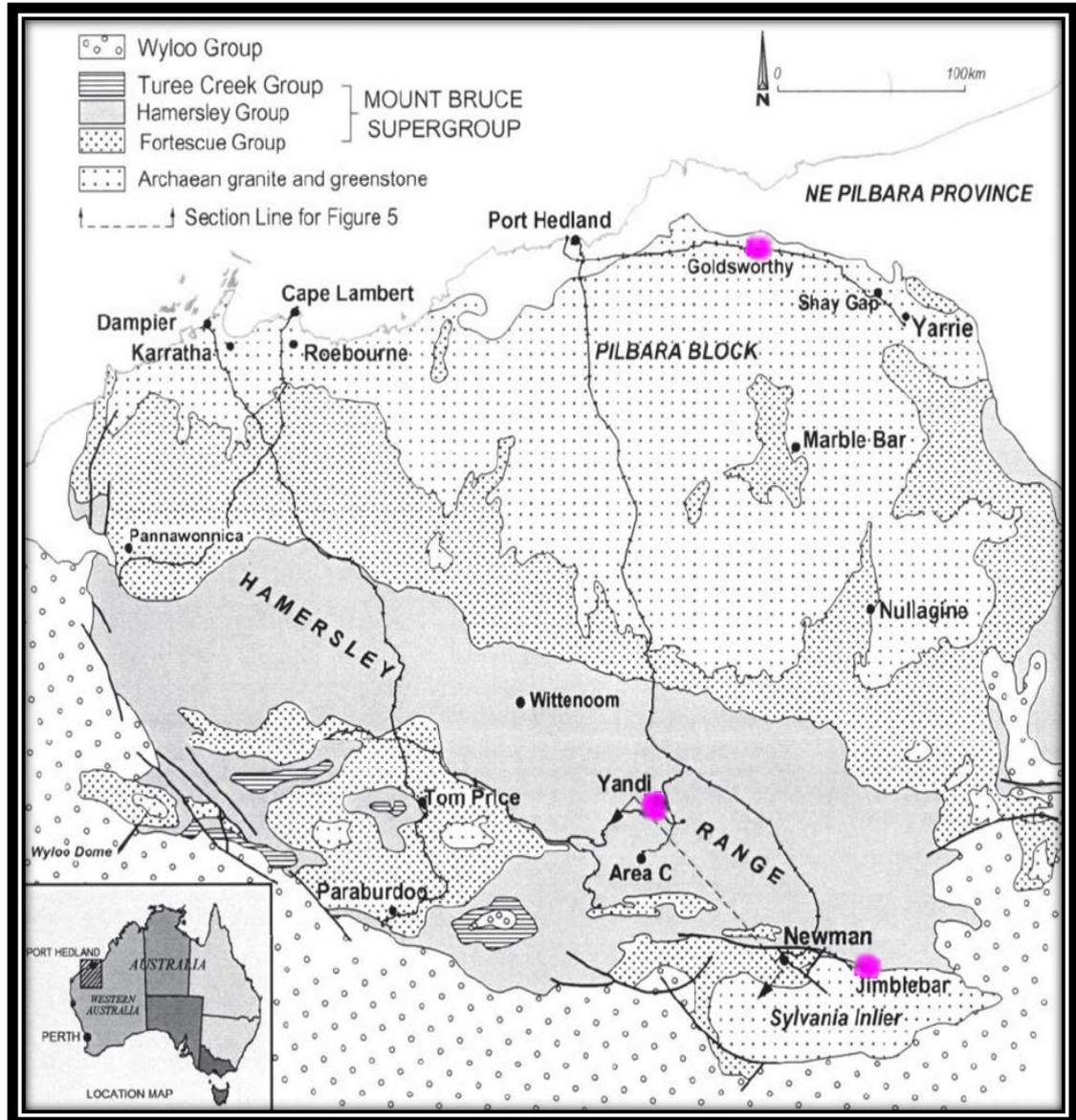


Figure 1.1: Location of BHP Billiton’s iron ore mine sites and geological map of the Hamersley Province, within the Pilbara region, showing key localities relevant to the study (Kneeshaw et al., 2003).

1.4.2. Geological Background

Detailed description of the stratigraphy and geological structure of the Pilbara region is beyond the scope of the present project. The following brief information is presented to provide context to the waste rock sample suite, the analysis of which was a major component of the research.

Most of Australia's identified iron ore resources are situated in the Pilbara region. The iron ore reserves are sedimentary in nature being dominated by bedded, channel and detrital deposits (Storkey et al., 2007). They comprise:

- Bedded iron deposits (BID), otherwise known as banded iron formation (BIF) containing martite-goethite/martite-ochreous goethite ores. These types of ore deposits are some of the largest and thickest ironstone layers in the Precambrian stratigraphy (Trendall, 2002);
- Channel iron deposits (CID) or iron-rich fluvial rocks comprising goethite-haematite pisolitic ores. These lie in meandering river channels draining the Hamersley Ranges, including the Yandicoogina (Marillana Formation) and Robe River (Robe Formation) regions;
- Detrital iron deposits (DID) – relatively minor alluvial and colluvial deposits of haematite-goethite that are the product of eroded BID (Storkey et al., 2007).

The stratigraphy of the Hamersley Group within the Hamersley region comprises the Marra Mamba Iron Formation, Wittenoorn Formation, Mount McRae Shale, Dales Gorge Member, Joffre Member (Blake, 2007) and Brockman Formation hosting wide-ranging bedded iron ore deposits (Bodycoat, 2010). The regional stratigraphic and lithological classifications are shown in Table 1.1.

Exploration in the Chichester Ranges has revealed the presence of basalt, mafic, and porphyritic felsic lavas, felsic tuffs and terrigenous clastic sedimentary rocks (Blake, 2001). Significant pods of microplaty hematite mineralisation are sited along cross-cutting fault sectors in the Nammuldi Member of the Marra Mamba Iron Formation (Clout, 2006). Table 1.2 shows a summary of the stratigraphic succession in the Pilbara region.

| UNCONFORMITY BASED FRAMEWORK | | | | | | LITHOSTRATIGRAPHIC FRAMEWORK | | | Tectono-Stratigraphic Sequences (Throne and Trendall, 2001) | | |
|-------------------------------|-----------------------------------|---------------------------------------|--|---|--|---|---------------------------------------|-------------------------------|--|------------------|------------|
| Mount Bruce Megasequence Set | | | | | | Mount Bruce Supergroup | | | | | |
| Mega-sequences (Krapez, 1997) | Super-sequences (Krapez, 1997) | Mega-sequences (Blake & Barley, 1992) | Super-sequences (Blake & Barley, 1992) | Sequences (Goddard, 1992; Blake, 1993; Krapez, 1996) | Super-sequences & Packages in Nullagine Synclinorium (Blake, 2001) | Members | Formations | Groups | | | |
| 1st Order | 2nd Order | 1st Order | 2nd Order | 3rd Order | 2 nd Order | 2 nd , 3 rd or Higher Order | | | | | |
| Hamersley Range Megasequence | Turee Creek Supersequence | Hamersley Range Megasequence | Turee Creek Supersequence | Defined | | | | Kazput Fm Koolbye Fm | Turee Creek Group | | |
| | Brockman Supersequence | | Woongarra Supersequence | None yet defined | | | Meteorite Bore Mb (part of formation) | Kungarra Formation | | | |
| | | | Carawine Supersequence | Brockman Supersequence Package | | | None yet defined | | Boolgeeda Iron Fm Woongarra Volcanics Weeli Wolli Fm | | |
| | | | | Chichester Range Megasequence | | | Position | Uncertain | Yandicoogina Shale Mb Joffre Mb Whaleback Shale Mb Dales Gorge Mb | Brockman Iron Fm | |
| Marra Mamba Supersequence | Marra Mamba Supersequence Package | None yet defined | | | | | Mt McRae Shale Mt Sylvia Fm | | | | |
| | | | | | | | | Bee Gorge Mb Paraburdoo Mb | Wittenoorn Fm | | |
| | | | | Mount Newman Mb Mount MacLcod Mb Nammuldi Mb Roy Hill Shale Mb | | | Marra Mamba Iron Fm | | | | |
| | | | | | | | ? | 12 | Warrie Mb Woodiana Sandstone Mb | Jeerinah Fm | Sequence 4 |
| | | | | | | | MJ (2)S | 8-11 | | Fortescue Group | Sequence 3 |
| | | | | | | | MJ (1)S | 7 | Maddina Fm Tumbiana Fm Kylena Fm | | |
| | | | | | | | NS | 1-6 | Hardey Fm | | |
| | | | | | | | | | Mount Roe Basalt | | |
| | Mount Jope Supersequence | | Mount Jope Supersequence | Maddina Seq Package Tumbiana Seq Kylena Seq | | | | | Sequence 2 | | |
| | Nullagine Supersequence | | Nullagine Supersequence | Hardey Seq Package Mount Roe Seq | | | | | Sequence 1 | | |

Table 1.1: Regional stratigraphic divisions of the late-Archaean to early-Proterozoic succession in the Pilbara region (Blake et al., 2004).

| <i>Age</i> | <i>Group</i> | <i>Formation</i> | <i>Member</i> | <i>Dominant lithology</i> |
|-----------------------------------|----------------------|-------------------------------|--|--|
| Quaternary | | | | Alluvium, colluvium |
| Tertiary | | Oakover Fm Robe Pisolite * | | Calcrete Pisolitic limonite |
| Early Proterozoic- Archaean | Turee Creek Group | Kungarra Fm | | Shale, dolerite, quartzite |
| Early Proterozoic- Archaean | Hamersley Group | Boolgeeda Iron Fm | | BIF, shale |
| | | Woongarra Volcanics | | Felsic volcanics, tuff, minor BIF |
| | | Weeli Wollie Fm | | BIF, dolerite, shale |
| | | Brockman Iron Fm * | Yandicoogina Shale Joffre Member Whaleback Shale Dales Gorge Member | Shale, chert BIF, minor shale Shale, chert BIF, minor shale |
| | | Mount McRae Shale | Colonial Chert | BIF, shale, pyritic shale, dolomite |
| | | Mount Sylvia Fm | | Shale, chert, dolomite, BIF |
| | | Wittenoom Fm * | Bee Gorge Member Paraburdoo Member West Angela Member | Shale, tuff Dolomite, chert, shale Dolomite, shale |
| | | Marra Mamba Iron Fm * | Mt Newman Member MacLeod Member Nammuldi Member | BIF, minor shale BIF, shale BIF, chert, shale |
| Archaean | Fortescue Group | Jeerinah Fm | Roy Hill Shale | Shale, chert, sandstone, basalt |
| | | Bunjinah Fm | | Basalt, sandstone, minor chert |
| | | Pyradie Fm | | Basalt |
| | | Boongal Fm | | Basalt, pelite, minor chert |
| | | Hardey Fm | Hardey Sandstone | Sandstone, conglomerate |

* Units that are of greatest interest to this study

Table 1.2: Stratigraphic summary of the Pilbara region (Johnson and Wright, 2001).

1.4.3. Geological Context of Sampled Iron Ore Mines

The Yandicoogina (Yandi) open-cut mine is situated in the Hamersley Province, part of Pilbara Craton, in Western Australia. The Yandicoogina Junction Deposit comprises pisolitic iron-oxide mineralisation dispersed within a meandering palaeo-river channel (Hall and Kneeshaw, 1990). The deposit is characterised by goethite and haematite in the form of pisolites. The majority of iron ore resources of the Yandicoogina iron ore deposit are identified as channel iron deposits (CID). The lithologies encountered in the vicinity of the mine include alluvium (ALL), banded iron formation (BIF), laterite, weathered channel deposits (WCH), “vitreous goethite lower/upper”, limonite goethite channel material (LGC), basal clay conglomerate (BCC) and Weeli Wolli Formation (WW) (Boyle, 2007). Figure 1.2 illustrates the geological section of Yandicoogina Junction ore.

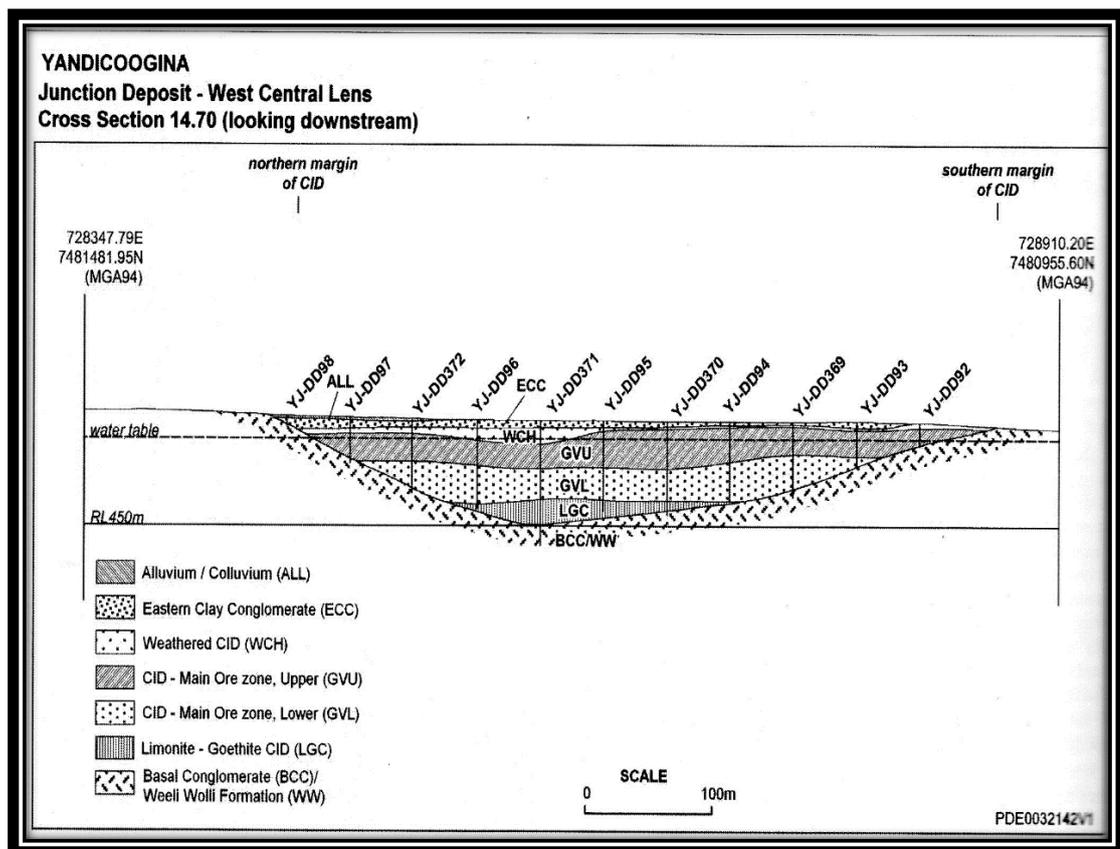


Figure 1. 2: Geological units of the Yandicoogina Junction Deposit (Boyle, 2007).

The Jimblebar iron ore deposits display the signatures of deposits of the Archaean-Early Proterozoic Hamersley Group. The general stratigraphic column of this area consists of interbedded oxide BIF and silicate iron formation (shale) macrobands (Kerr et al., 1994). Jimblebar ore deposit also contains clastic metasediments, cherts, low- to medium- grade mafic and ultramafic volcanics and banded iron-formation (BIF) and it has been intruded by mafic to ultramafic sills such as the Coobina intrusion (Barnes and Jones 2013). Figure 1.3 shows the geological map of Jimblebar in the Pilbara.

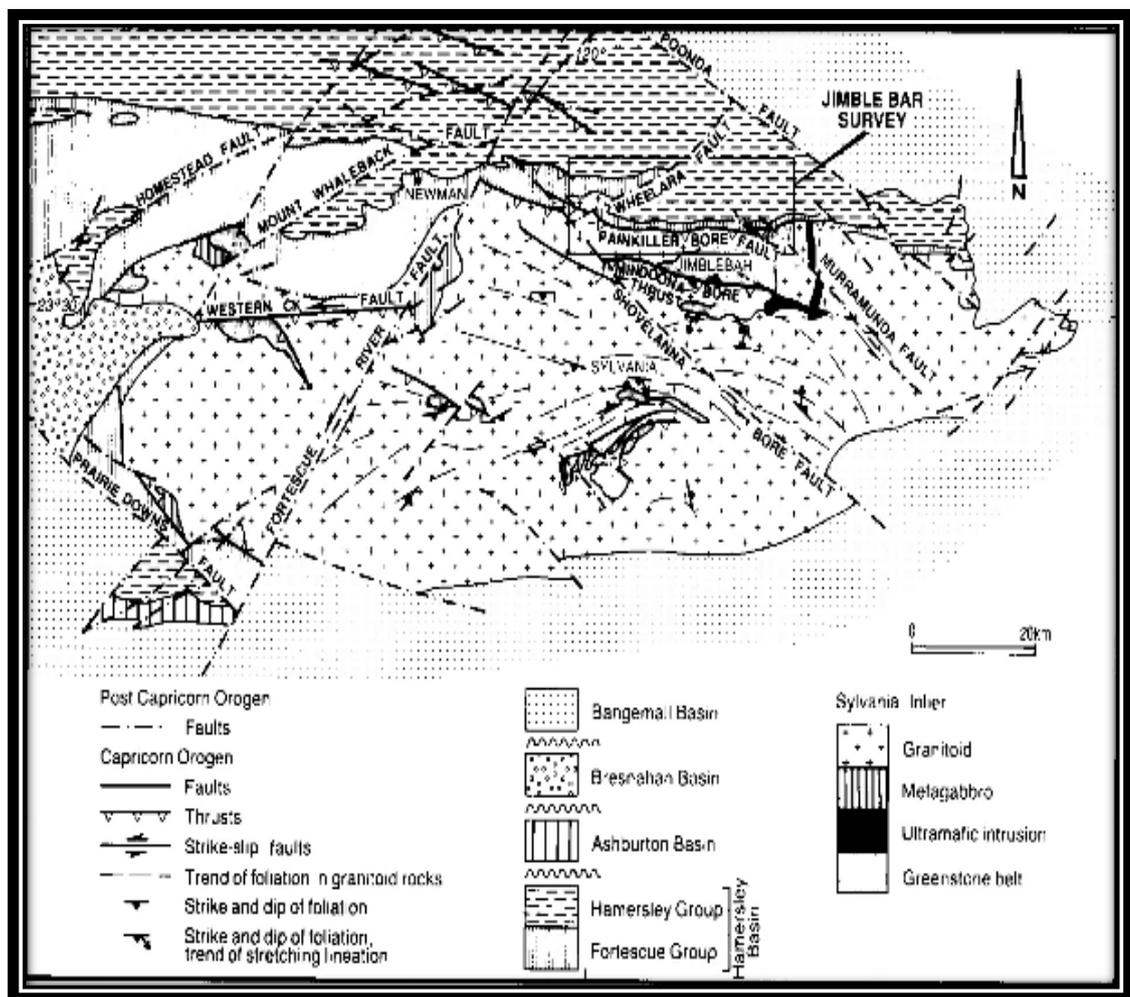


Figure 1.3: A geological map of the Jimblebar area (Kerr et al., 1994).

The third BHP Billiton mine site in the Pilbara from which waste rock samples were sourced for this study is Mt Goldsworthy mine, located 100 km east of Port Hedland in the north-western part of the Pilbara Block (Figure 1. 4) (Sugitani et al., 2002). The

sedimentary succession of Mt. Goldsworthy comprises Early- to Middle-Archean volcanic rocks, banded cherts, siliciclastic rocks and ferruginous cherts. The iron ores at Mt. Goldsworthy are hosted by the Gorge Creek Group, such as the Cleaverville and the Corboy Formations and the Lalla Rookh Sandstone (Sugitani et al., 2002). Figure 1. 4 is a geological map of Pilbara Block and Mt. Goldsworthy that displays the stratigraphy of sedimentary rocks in the area.

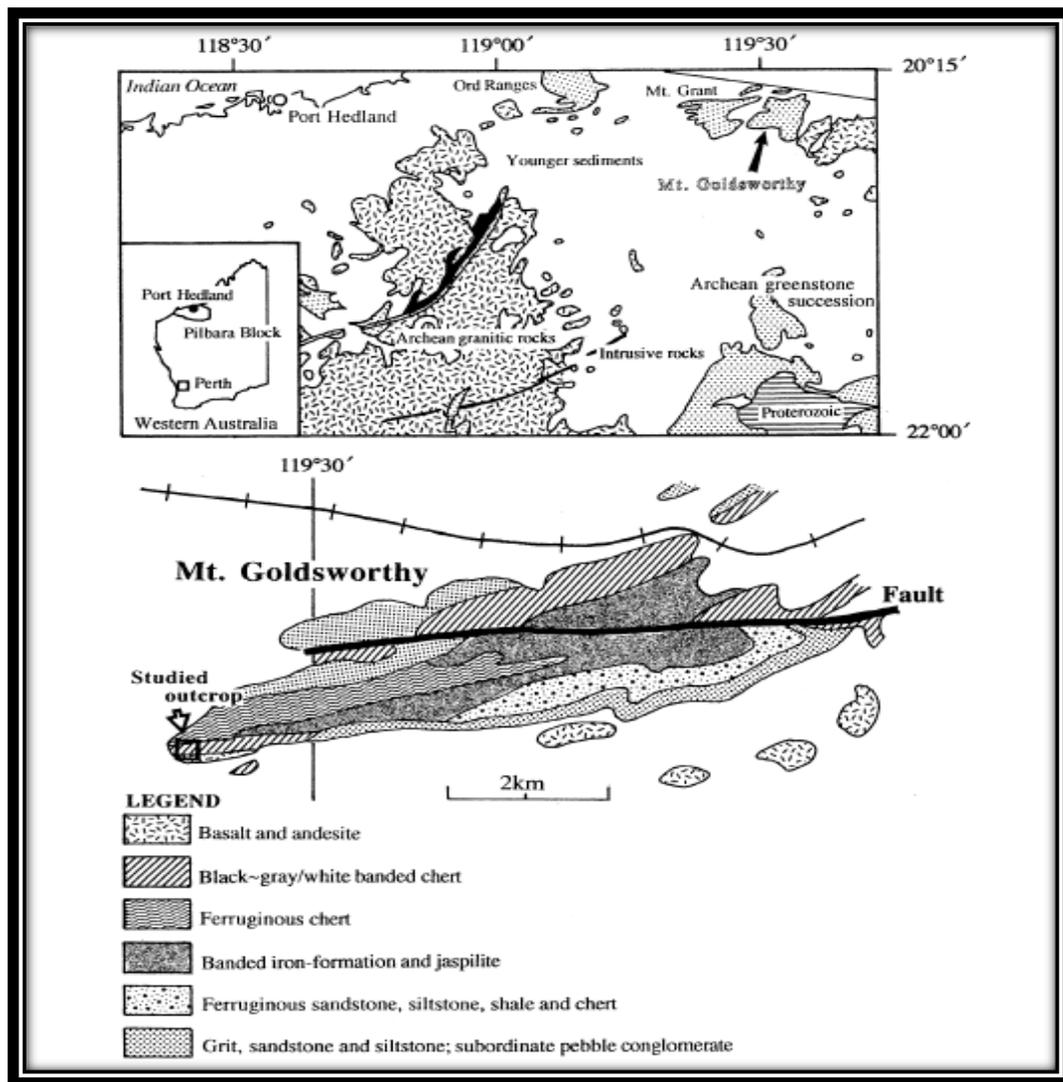


Figure 1.4: Geological map of the Pilbara Block (above) and below a geological map of Mt. Goldsworthy (Sugitani et al., 2002).

1.5. Selenium and Health

1.5.1. Physical Characteristics of Selenium

Selenium is a metalloid which exhibits a maximum negative valence of two (Nazarenko and Ermakov, 1972). Its main physical properties are shown in Table 1.3.

| Property | Selenium |
|----------------------------|----------|
| Atomic number | 34 |
| Atomic mass | 78.96 |
| Density, g/cm ³ | 4.79 |
| Melting point, °C | 217 |
| Mboiling point, °C | 685.4 |
| Atomic radius, mμ | 0.117 |
| Hardness, relative unites | 2 |
| E ⁻² | 0.198 |
| E ⁺⁴ | 0.069 |
| E ⁺⁶ | 0.035 |

Table 1.3: Main physical properties of selenium (Nazarenko and Ermakov, 1972).

Selenium exists as six stable isotopes of which the heavier are more abundant in the environment. Abundances and stabilities of these isotopes are displayed in Table 1.4 (Nazarenko and Ermakov, 1972).

| Isotope | Abundance in nature, % | Half-life | Isotope | Abundance in nature, % | Half-life |
|---------|------------------------|------------------------|---------|------------------------|-----------|
| Se73 | - | 7.1hr | Se79m | - | 3.91min |
| Se74 | 0.83 | - | Se80 | 49.82 | - |
| Se75 | - | 120.4days | Se81 | - | 18.6 |
| Se76 | 9.02 | - | Se81m | - | 62min |
| Se77 | 7.58 | 17.5sec | Se82 | 9.19 | - |
| Se7m | - | - | Se83m | - | 69sec |
| Se78 | 23.52 | | Se83 | - | 25min |
| Se79 | - | $6.5 \cdot 10^4$ years | | | |

Table 1.4: Abundances and stability of selenium isotopes (Nazarenko and Ermakov, 1972).

There are seven different crystalline forms of Se in nature, including trigonal (grey) (Figure 1.5 A, B), different monoclinic (red), different cubic, rhombohedral and orthorhombic forms. Also, black, red and vitreous amorphous forms can exist (Minaev, Timoshenkov and Kalugin, 2005). In addition, in any condition, Se can be combined with S (Lenz and Lens, 2009). The chemically reduced forms of Se, which are produced under strongly reducing conditions, include inorganic metal selenides, organic Se compounds and highly toxic, volatile H_2Se (Lenz and Lens, 2009).

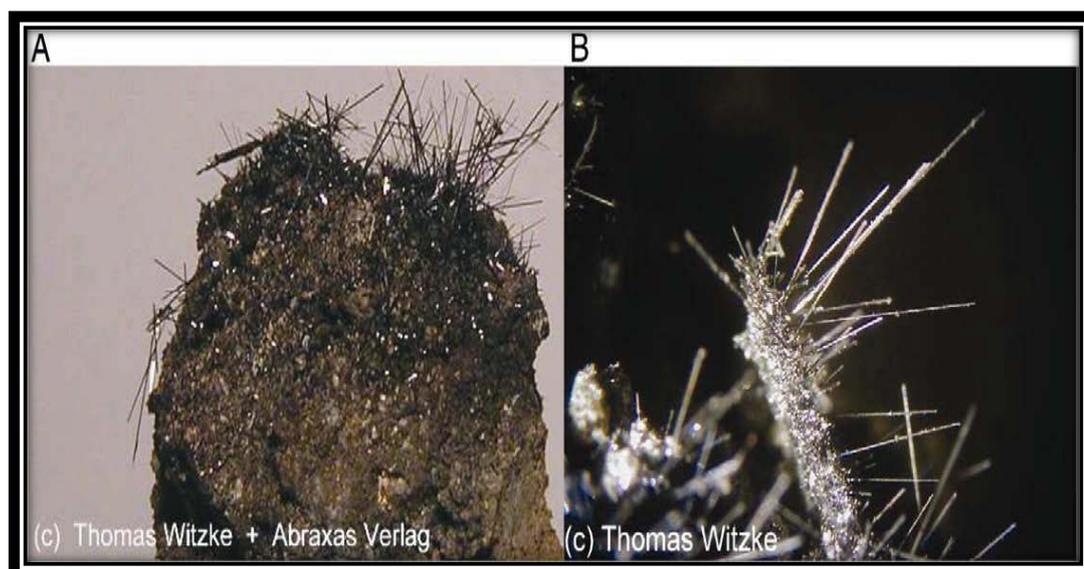


Figure 1.5: Native, trigonal elemental selenium species, found at Ronneburg Uranium deposit, Thuringia, Germany (A) and AnnaMine, Alsdorf-Aachen, North Rhine Westphalia, Germany (B) (Lenz and Lens, 2009).

1.6. Geochemical Character of Selenium

Geochemical behaviour of Se is complex (Exponent, 2010). Selenium is a solid substance, which is naturally occurring, but distributed unevenly in the Earth's crust, with an average concentration of only 0.05 mg/kg. This element has been usually seen in rocks and soil but as an impurity substance, which associates with other minerals such as Ni, Pb, Cu, sulfide and Ag. Although, this metalloid is a naturally happening in soil and Earth's crust, it is a rare element in the soil (Irwin, 1997). The transport, distribution and cycling mechanisms of the metalloid in the environment are related to biological, geophysical and industrial processes (World Health Organization, 1987). The Se concentration in soil is variable and dependent upon various factors such as pH, presence or absence of oxygen and the concentration of other elements, particularly Fe, Mn, and Al oxides (Exponent, 2010), redox condition of soil, the general climatic features, and Se levels in the soil- forming foundation rocks (Nazarenko and Ermakov, 1972).

In terms of a geological setting, the highest Se concentration is in Cu-Pb-Zn sulfide deposits, but some deposits like sedimentary U and phosphatic V also contain appreciable concentrations (Lemly, 2007). Hydrothermal systems and supergene alteration are significant factors in Se enrichment in black shale (Wen and Carignan, 2011). Furthermore, Se can form Se organic compounds by bonding with H-, O-, N- and S-bearing organic molecules. Although, there is little information on the complexed forms of Se in living organisms and its role in metabolic enzyme activity, studies show that this element is highly stable in organic matter (Wen and Carignan, 2011).

Another source of Se in the ecosystem is reduced iron sulphur minerals, such as pyrite. While sedimentary pyrite is being formed in reducing ecosystems, Se isomorphically replaces reduced sulphur in the atomic structure (Strawn, et al 2002). Consequently, as pyrite and other sulphide minerals are exposed to atmospheric oxygen by human activities, such as mining, groundwater drawdown, and wetland drainage, and undergo oxidation, Se is released. Selenium primarily occurs in the environment in 4^+ and 6^+

oxidation states, while reduced Se compounds can form in anoxic soils. Selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), which are oxidized forms of Se, predominate in soils. Changes in Se speciation can have impacts on the availability of this trace element, its transport in surface and groundwater, and its ultimate fate and bioavailability (Strawn, et al 2002).

It may be difficult to determine the geochemical behaviour (mobility, solubility, diagenesis and transport) and biological accessibility and toxicity of Se in an area which has been impacted by Se contamination (Belzile et al., 2000). Studies show that when selenate (SeO_4^{2-}) is in its highly soluble form in oxic water, it is thermodynamically stable. On the contrary, selenite (SeO_3^{2-}) formed in less oxygen-rich conditions may be adsorbed onto Fe and Mn oxyhydroxides (Belzile et al., 2000).

1.7. Selenium in Human and Animal Health

The biological importance of Se was reported for the first time in the 1930s when the economic impacts of Se poisoning on farm animals were realised. Selenium is a constituent of proteins in animals and humans, with these seleno-proteins being involved in regulation of redox intracellular signalling, redox homeostasis and thyroid hormone metabolism (Lenz and Lens, 2009).

Selenium is a critical trace nutrient in animals and humans, and can pose some ecological risk (Hartikainen, 2005). The recommended adult daily intake of Se is 55 - 60 μg daily: more or less than this dose may be harmful. As a result, whereas this metalloid is essential for human and animals, both deficiencies and excesses can have adverse effects and there is a low boundary concentration between essentiality and toxicity (Exponent, 2010).

1.7.1. Deficiency

A low intake of Se can cause “white muscle disease” in livestock (Figure 1.6), hepatitis dietetica in pigs and exudative diathesis in chickens. These kinds of diseases

are significant problems in regions worldwide where the concentration of the trace element in the soil available for uptake by plants is very low (World Health Organization, 1987). However, this problem may be addressed through fertilization of selenium depleted soils (Santana et al., 2006).

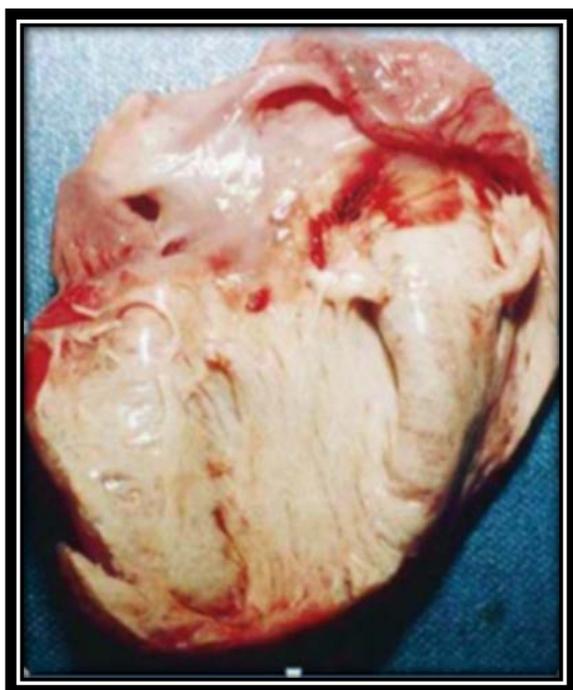


Figure 1.6: Effects of selenium deficiency in lambs seen as chalky-white necrosis and mineralization of the heart muscles, so called “white muscle disease” (Beytut et al. 2002).

The effects of diseases that are created by Se deficiency may be fatal for humans. It has been determined that men require about 30 to 85 μg of Se per day while for women between 30 to 70 μg of Se per day are required (Lenz and Lens, 2009).

Worldwide, approximately 0.5 to 1 billion people are exposed to health problems related to Se deficiency (Haug et al., 2007) and thus this matter is most important. For example, low levels of Se in China and Eastern Siberia have led to two endemic diseases. One of these is Keshan disease, a multifocal myocarditis that occurs primarily in children (2–10 years old) and among women of child-bearing age. The second endemic disease is Kashin-Beck disease. This is a “big-joint disease” producing a human rheumatoid condition (Hartikainen. 2005). Moreover, deficiency of Se in the human body has been associated with increased risk of some cancers, such as breast

and prostate cancer (Ansong et al., 2014). However, human deficiency diseases through low levels of available Se can be prevented by the use of inorganic Se supplements (World Health Organization, 1987).

1.7.2. Toxicity

Food grown and consumed from Se-rich soils can lead to several diseases, such as “alkali disease”, that may be fatal to animals and humans (Schilling, Johnson, and Wilcke, 2011). Before the 1930s, Se was not known to be the toxic agent, yet scientists from the U.S. Department of Agriculture recognized that certain plants can be poisonous and cause “alkali disease” in cattle and horses with symptoms of loss of nail, hair and hoofs (World Health Organization, 1987). The impacts of alkali disease were even reported during Marco Polo’s expedition across Asia as horses lost their hoofs due to grazing Se hyperaccumulating plants (Exponent, 2010).

Research on humans has shown that Se concentration in human tissue typically is more than 0.1 µg/g (Thornton 1983). Thornton (1983) reported a significant relationship between people who live in areas that have high Se levels in soils (seleniferous areas) and their reported health conditions. These health conditions include oral complaints, fatigue, dizziness, and changes to the skin and nails, such as skin hyper-pigmentation. Moreover, there has been a reported link between individuals that have high Se concentration in their blood and the birth rate of deformed infants (Thornton, 1983). Although human selenosis is uncommon, bioaccumulation of this element can have serious impacts on human health and fauna such as cancers of the skin and pancreas, and hair loss (Plant, et al 2005) (Figure 1.7).



Figure1.7: Selenium toxicity in human in a patient from the Enshi district, China (lose hair) (Fordyce, 2007).

1.8. Difficulties of Routine Selenium Determination in Rocks from the Pilbara Iron Ore Mines

A number of problems arise in the routine analysis of Se in geological samples, in particular those encountered in iron ore mining in the Pilbara. Selenium is estimated to have an average crustal abundance of only 50 ppb ($\mu\text{g}/\text{kg}$) (Exponent, 2010) and thus is therefore out of the normal detection range of many analytical techniques. Since the 1980s, inductively-coupled plasma mass spectrometry (ICP-MS) has been employed to determine the distribution and behaviour of Se found in environmental and biological media. The low detection limits, multi-element capabilities and relatively simple sample preparation add to the attractiveness of the ICP-MS method for documenting the distribution of a wide variety of trace elements, including Se (Plant et al., 2005). The other advantages of ICP-MS for Se analysis include speed (Ralston, Unrine and Wallschalger, 2003) and the ability to determine Se routinely as part of a broad scan of numerous trace elements.

Despite the benefits of conducting ICP-MS analyses, there are some concerns regarding the interpretation of trace elemental variation through analysis by ICP-MS. Difficulties in Se detection by ICP-MS arise from its high first ionization potential compared to argon plasma (Ar) (Bueno et al., 2007). Furthermore, ^{40}Ar , $^{40}\text{Ar}^+$ and $^{40}\text{Ar}^{38}\text{Ar}^+$ prevent determination of Se from its most abundant isotopes ^{80}Se and ^{78}Se (Table 1.4).

The acid digestion procedure is an effective way of preparing samples in order to analyse them by the ICP-MS technique. In this study, dissolution of powdered rock samples was by means of a hot mixture of HNO_3 , HClO_4 , and HF acids. According to Nazarenko and Ermakov (1972), the main advantage of the use of $\text{HNO}_3 + \text{HClO}_4$ is that these acids readily decompose organic compounds present in rocks and soils to release Se. The mixture of nitric and perchloric acid also breaks down the less resistant silicate minerals and ores more rapidly than other acids. Addition of a few millilitres of HF can readily decompose all but the most resilient, silicate and oxide minerals into solution. In spite of these advantages, the mixture of these acids can create some problems:

- When $\text{HNO}_3 + \text{HClO}_4$ are used, the resulting solutions must not be evaporated to complete dryness, otherwise Se can volatilize;
- To avoid Se losses through volatilization from solution, during decomposition and evaporation of samples, HCl should not be added. (Nazarenko and Ermakov, 1972).

In this study, a further practical problem was encountered, where during the digestion of certain organic-rich materials, such as carbonaceous shale, the sample could spit out of the open digestion vessel while solutions were evaporating. Accordingly, the hot-plate temperature was reduced from 210°C to 195°C , with resulting increase in the time required for sample preparation.

Despite the potential difficulties of Se analysis in geological materials using ICP-MS, such analysis is widely applied in industrial practice for determination of total Se

concentration (Bueno et al., 2007), since it is currently the most widely available technique with the capability of analysing Se at the concentrations found in crustal rocks.

1.9. Outcomes of Present Study

This study lays an essential foundation for evaluation of Se concentration in the various rock types occurring as waste products of iron ore mining. It allows for the better understanding of the environmental risk of contamination with this element arising from mining and waste rock storage in the Pilbara region of Western Australia. The study provides insight into the efficacy of methods of sample preparation and ICP-MS analysis routinely employed by commercial laboratories for the determination of Se concentration in rocks, including rocks with high Fe content. It thus provides most valuable information for the accurate monitoring and validation of Se releases to the environment from Pilbara iron ore mines against current regulatory guidelines.

Chapter 2

Methodology

This chapter presents the scientific methods used in this study to assess the concentration and geochemical behaviour of selenium

2. Methodology

This chapter focuses on the methods employed in this study for the determination of Se in geological materials, in particular assessment of the Se content of a variety of rock types encountered in iron ore mining in the Pilbara region. It provides information on the laboratory procedures and analytical techniques undertaken in the EIGG² laboratories at Curtin University and TSW Analytical at the University of Western Australia (UWA), in Perth, Western Australia.

2.1. Sourcing of Samples

A number of current international standard reference materials (ISRM) having certified values for Se were acquired for this study. Additional ISRMs were sourced from the collection held by EIGG that were either of considerable age or had only information values for Se.

A comprehensive range of waste rock types was provided by the Mine Closure Group of BHP Billiton Iron Ore from a number of their Pilbara mines. Eleven samples were sourced from the Mt Goldsworthy Mine; 20 samples were collected from exploration core from the South Jimblebar prospect; and a further 20 samples were supplied from Yandicoogina Mine. Golder Associates was responsible for drilling and collection of rock samples from Yandicoogina mine. These samples have been taken from different depths in stockpiles and waste rocks heaps of iron ore mining operations. The rock samples were delivered in muslin bags that were themselves contained in large plastic bags. Individual sample sizes were between approximately 1 and 5 kg.

2.1.1. International Standard Reference Materials Used in Evaluation of Accuracy of Results

Various geological reference materials (geostandards) were analysed in this study to investigate the accuracy of routine ICP-MS analysis of Se and other selected trace

² Environmental Inorganic Geochemistry Group

elements. Individual reference materials were selected from U.S. Geological Survey Standard References, National Institute of Standards and Technology (NIST), the Canadian Certified Reference Materials project (CCRMP), and the Geological Survey of Japan (GSJ). A total of 25 international standard reference materials, with published values for Se and other selected trace elements were analysed in this study, for the evaluation of the accuracy of the method of acid digestion and analysis of resultant solutions using ICP-MS are listed in Table 2.1.

Limitations of the use of international standard reference materials became apparent early in the study on account of the paucity of certified values for Se amongst rock standards in general, and particularly those having considerable iron content. There was also uncertainty regarding the correctness of former published values for Se in some older series of standard rock materials. Focus of this study used standards CH₄ (gold ore) for which there was a certified value for Se of 2.10 ppm, and NIST fly-ash 1633c with a reference value for Se of 13.9 ± 0.5 ppm. The Se, As, Cr, Mn, V and Cu values obtained in this study for CH₄ and NIST fly-ash 1633c are presented in Table 3.2, and those for other selected geostandards in Tables 3.3 and 3.4.

2.1.1.1. U.S. Geological Survey, NIST, and CCRMP

Published concentration values for Se are available for a relatively limited number of geological reference materials. Where they exist, they are variously described as certified values, recommended values, reference values, information values, or provisional values (Table 2.1). It is particularly difficult to find values for Se that have the highest confidence levels, namely certified values. A single appropriate reference material with certified value for Se was obtained for this study, CH₄, from the CCRMP series. This is a gold ore containing 5.42 wt % Fe and 7.73 wt % Al. The certified Se value is 2.1 ± 0.2 µg/g (ppm) (Canadian Certified Reference Materials project, 2010). A certified value is one that has been characterised with the highest confidence in its accuracy with a low standard deviation (Potts and Kane, 1992). It is assumed that this value provides the best estimate of true value based on the results obtained from

analysis of the reference material in collaborating laboratories using classical test methods (Wise and Watters, 2011).

Reference values for Se were available for the NIST coal fly ash (Wise and Watters, 2011), the latter employed by TSW Analytical as a check material in ICP-MS analysis in the current project. All data quoted by NIST for the Coal Fly Ash sample were obtained using INAA only and no attempt has been made to indicate potential bias between techniques (INAA and ICP-MS). RTS-1, RTS-2 and RTS-3 sulphide ore mill tailings had only information values (Canadian Certified Reference Materials project, 2009) (Table 2.1).

A recommended value refers to a value that is published with a lower degree of confidence. Despite the lower level of confidence, values from reference materials in this category are of sufficient confidence to be useable as calibration standards for instrumental methods used in a geoanalytical laboratory and to assess accuracy of results obtained (Potts and Kane, 1992). Six reference materials with recommended values of Se were available for this study. Of these, two were marine sediments from an old USGS series (BCSS-1 and MESS-1, containing 0.43 ppm, and 0.34 ppm Se, respectively).

| Geostandards | Rock types | Centre/ Institute | Selenium | Arsenic | Vanadium | Chromium | Manganese | Copper |
|-----------------------------|----------------------------|--|-----------------|---------------|---------------|--------------|------------------|---------------|
| MAG-1 | Marine Mud | U.S. Geological Survey | | 9.2® | 140® | 97® | | 30® |
| BIR-1 | Icelandic Basalt | U.S. Geological Survey | | 0.44(I) | 310+/-11(I) | 382® | 104.55+/-20(I) | 125+/-4 (I) |
| JSO-1 | Soil | Geological Survey of Japan | | 8.10+/-0.1(m) | 300+/-3(m) | 71.0+/-2(m) | 0.152+/-0.002(m) | 169+/-2(m) |
| JMS-1 | Marine Sediment | Geological Survey of Japan | | 18 (m) | 127(m) | 133(m) | | 88(m) |
| JMS-2 | Marine Sediment | Geological Survey of Japan | | 35(m) | 183(m) | 78(m) | | 447(m) |
| BCSS-1(June-30-1988) | Marine Sediment | National Research Council Canada | 0.43® | 11.1® | 93.4® | 123® | 300® | 18.5® |
| BCSS-1 (Feb-6-1986) | Marine Sediment | National Research Council Canada | 0.43® | 11.1® | 93.4® | 123® | 300® | 18.5® |
| MESS-1 (July-9-1986) | Marine Sediment | National Research Council Canada | 0.34® | 10.6® | 72.4® | 71® | 660® | 25.1® |
| CH4 | Gold Ore | Natural Resources Canada | 2.1 © | 8.8(P) | | 114(P) | 430(P) | 2000© |
| RTS-1 | Sulphide Ore Mill Tailings | Canadian Certified Referece Materials Project | 40(I) | 8.2+/-1.6(P) | | 50(I) | 1900(I) | 595© |
| RTS-2 | Sulphide Ore Mill Tailings | Canadian Certified Referece Materials Project | 57(I) | 6.3+/-1.8(P) | | 125(I) | 400(I) | 670© |
| RTS-3 | Sulphide Ore Mill Tailings | Canadian Certified Referece Materials Project | 61(I) | 9.1+/-2.6© | | 75(I) | 2000(I) | 2820© |
| NIST | Coal Fly Ash | National Institute of Standards and Technology | 13.9 ± 0.5 (Re) | 186.2 ± 3.0 © | 286.2 ± 7.9 © | 258 ± 6 (Re) | 240.2 ± 3.4 © | 173.7 ± 6.4 © |
| JCU-1 | Copper Ore | Geological Survey of Japan | | | | | | |
| JDo-1 | Dolomite | Geological Survey of Japan | 0.05® | 0.114® | 3.14® | 7.93® | | 1.41® |
| JR-3 | Rhyelite | Geological Survey of Japan | | | | | | |
| JS1-1 | Slate | Geological Survey of Japan | | 14.9® | | 60.9® | | 40.8® |
| JCh-1 | Chert | Geological Survey of Japan | | 0.567® | 10.4® | 7.04® | | 15.3® |
| JH-1 | Hornblendte | Geological Survey of Japan | | | | | | |
| JLK-1 | Lake sediment | Geological Survey of Japan | 0.641® | 26.8® | 117® | 69® | | 62.9® |
| JSd-3 | Stream Sediment | Geological Survey of Japan | 1.29® | 252® | | 35.3® | | 426® |
| JSd-2 | Stream Sediment | Geological Survey of Japan | 18.8(P) | 38.6® | | 108® | | 1117® |
| JSd-1 | Stream Sediment | Geological Survey of Japan | 0.25(P) | 2.42® | | 21.5® | | 22® |
| JGb-2 | Gabbro | Geological Survey of Japan | | | | | | |
| JSo-2 | Soil | Geological Survey of Japan | | 1076(m) | | 1118(m) | | 1276(m) |

® is referred to recommended values

(m) is the mean value from the study of (Imai et al., 1996)

(Re) is referred to reference value

(I) is referred to information values

(P) is referred to provisional values

© is referred to certified values

Table 2.1: Geological reference materials used in this study in assessing accuracy of analytical results.

A further six reference materials analysed in this study had published values for Se of lower confidence, i.e. “reference”, “informational” or “provisional values” (Table 2.1). The information value is a value that may be used, but the information from analytical laboratories participating in the initial certification of the CRM is not sufficient to judge the uncertainty associated with the value (Wise and Watters, 2011). In comparison with a “recommended” value for an analyte, the “information value” obtained for elements cannot be viewed with the same level of confidence (Jochum and Seufert, 1990). A reference value that is not identified as a certified value can be the present best estimate of the real value. Although the value is provided with associated uncertainties, all sources of the value can be uncertain (Wise and Watters, 2011). A provisional value is referred to values that cannot be used to monitor accuracy (Geo, 2011).

2.1.1.2. JGS Reference Materials

Reference materials of the Geological Survey of Japan are one of the most comprehensive and readily available series of international geological standard materials. A total of 15 of these standards were prepared and analysed in the present study as an exercise to elucidate the reproducibility of the sample digestion in a wide range of rock compositions. None of the JGS series of standards currently has a certified value for Se. Recommended values are available for three of the standards: JDo-1, a dolomite rock; JLK-1, lake sediment; and JSd-3, stream sediment, while a provisional Se value is available for JSd-2 and JSd-1, stream sediment (Table 2.1). Recommended values have been published for the additional five trace elements recorded in this study in numerous of the JGS standards, in particular for As, Cr and Cu (Table 2.1).

Published values are not available for reference materials JSO-1 (soil), JMS-1 (marine sediment), JMS-2 (marine sediment), JCU-1 (copper ore), JR-3 (rhyolite), JS1-1 (slate), JCh-1 (chert), JH-1 (hornblendte), JSd-1 (stream sediment), JGb-2 (gabbro), and JSO-2 (soil). Additional analyses of these reference materials would be useful in order to

develop and increase our geochemical knowledge of Se in a currently available reference suite.

2.1.2. Waste Rocks from Iron Ore Mining

This section presents the results of analysis of a suite of 51 samples of various waste rocks occurring at three mine sites in the Pilbara region operated by BHP Billiton Iron Ore. This component of the study was not designed to provide a comprehensive account of the Se chemistry in such waste rocks. Instead it represents a preliminary investigation of the relative abundances of Se amongst the predominant rock types encountered during iron ore mining. The waste rocks were selected to include samples of the three lithologies suspected as hosting Se, and thus potential sources of Se release to the environment during the storage of wastes. These are (1) iron-rich rocks (BIF, haematite); (2) organic-rich rocks (e.g. black shales and lignite), and (3) sulphide-bearing rock types (pyritic shales) (Table 2.2).

The rock samples were analysed in four batches. With the exception of a single sample (SJ0847D-041) of which the duplicate preparation was spilled, each of the rock samples was analysed at least in duplicate. Numerous of the samples were prepared and analysed multiple times in order to elucidate the degree of variation of result within, and between, batches.

| Sample ID | Description |
|-----------|--|
| RWG10-R1* | Shale |
| RWG18-R1• | BIF |
| RWG3-R1* | Dolerite |
| RWG14-R1* | Dolerite |
| RWG21-R5• | Banded chert (Iron stained) |
| RWG24-R1• | Hematite |
| RWG1-R1• | Phyllite |
| RWG2-R2• | Volcanic ash(quartz vein) |
| RWG4-R1• | Shale -Interbanded with chert+ BIF (quartz vein) |
| RWG21-R4* | Banded phyllite |
| RWG12-R1• | Sheared dolerite |

| Sample ID | Description |
|--------------|-------------|
| SJ0847D-035 | Black Shale |
| SJ0848D-021 | Black Shale |
| SJ0845RD-015 | Black Shale |
| SJ0848D-025 | Black Shale |
| SJ0848D-029 | Black Shale |
| SJ0847D-041 | Black Shale |
| SJ1102-002 | Lignite |
| SJ1102-006 | Lignite |
| SJ0772D-016 | Lignite |
| SJ0772D-019 | Lignite |
| SJ0785-005 | Lignite |
| SJ0785-003 | Lignite |
| SJ0849D-002 | Mudstone |
| SJ0848D-041 | Mudstone |
| SJ0848D-017 | Mudstone |
| SJ0848D-043 | Mudstone |
| SJ0847D-010 | BIF |
| SJ0847-020 | BIF |
| SJ0847-009 | BIF |
| SJ0847-008 | BIF |

| Sample ID | Code | Description | Depth from (m) | Depth to (m) |
|-----------|------|---|----------------|--------------|
| C370723 | TD1 | Tertiary detritals | 141 | 144 |
| E115011 | D1 | Colonial Chert Member | 45 | 48 |
| E118098 | RN | Mt. McRae Shale- Nodule Zone | 60 | 63 |
| E118008 | R | Mt. McRae Shale- Undifferentiated | 21 | 24 |
| HYM0029 | HE | Weeli Wolli Dolerite | 7 | 8.5 |
| HYM0002 | HJ | Weeli Wolli Iron Formation | 29 | 29.5 |
| HYM0005 | WW | Weeli Wolli Iron Formation Undifferentiated | 29 | 29.5 |
| N505637 | J1 | Joffre Member-J1 | 99 | 102 |
| N505657 | D4 | Dales Gorge Member-D4 | 141 | 144 |
| N505563 | W | Whaleback Shale | 30 | 33 |
| N416410 | J6 | Joffre Member- J6 | 21 | 24 |
| N416291 | Y | Yandicoogina Shale Member | 36 | 39 |
| N505546 | R | Mt. McRae Shale- Undifferentiated | 105 | 108 |
| N505758 | TD3 | Tertiary detritals | 3 | 6 |
| N505639 | J1 | Joffre Member-J1 | 102 | 105 |
| N505643 | WC | Whaleback Shale- Central Chert | 108 | 111 |
| N505655 | D4 | Dales Gorge Member- D4 | 138 | 141 |
| N416412 | J6 | Joffre Member- J6 | 24 | 27 |
| N416220 | HJ | Weeli Wolli Iron Formation | 12 | 15 |
| N416182 | Y | Yandicoogina Shale Member | 72 | 75 |

*Soil samples •Rock samples

Table 2.2: (A) 11 waste rock and soil samples provided from Mt. Goldsworthy mine, (B) 20 waste rock samples collected from South Jimblebar prospect, and (C) waste rocks samples collected from Yandicoogina mine (20 samples).

2.3. Sample Preparation

2.3.1. Rock Crushing

Rock samples received at the EIGG laboratories were dried at 50°C in a ventilated oven. This low temperature was selected to minimise the risk of oxidation of sulphide-bearing and carbonaceous samples. Once dried, the samples were crushed and pulverised in the Department of Applied Geology, Curtin University.

Large pieces of rock in each sample were first reduced in size using a hydraulic rock splitter. The rock fragments were then passed through a jaw crusher to produce gravel-sized material. These fragments were then added back to the original finer particles of the sample and passed through a riffle splitter to produce a representative sample of approximately 200 g. This was then ground to <75 µm using a Tema® tungsten carbide ring mill. The apparatuses are shown in Figure 2.1.

The powdered samples were stored in a screw-capped 250 ml plastic container and then transferred to the EIGG Laboratory for acid digestion and analysis of total carbon and sulphur.

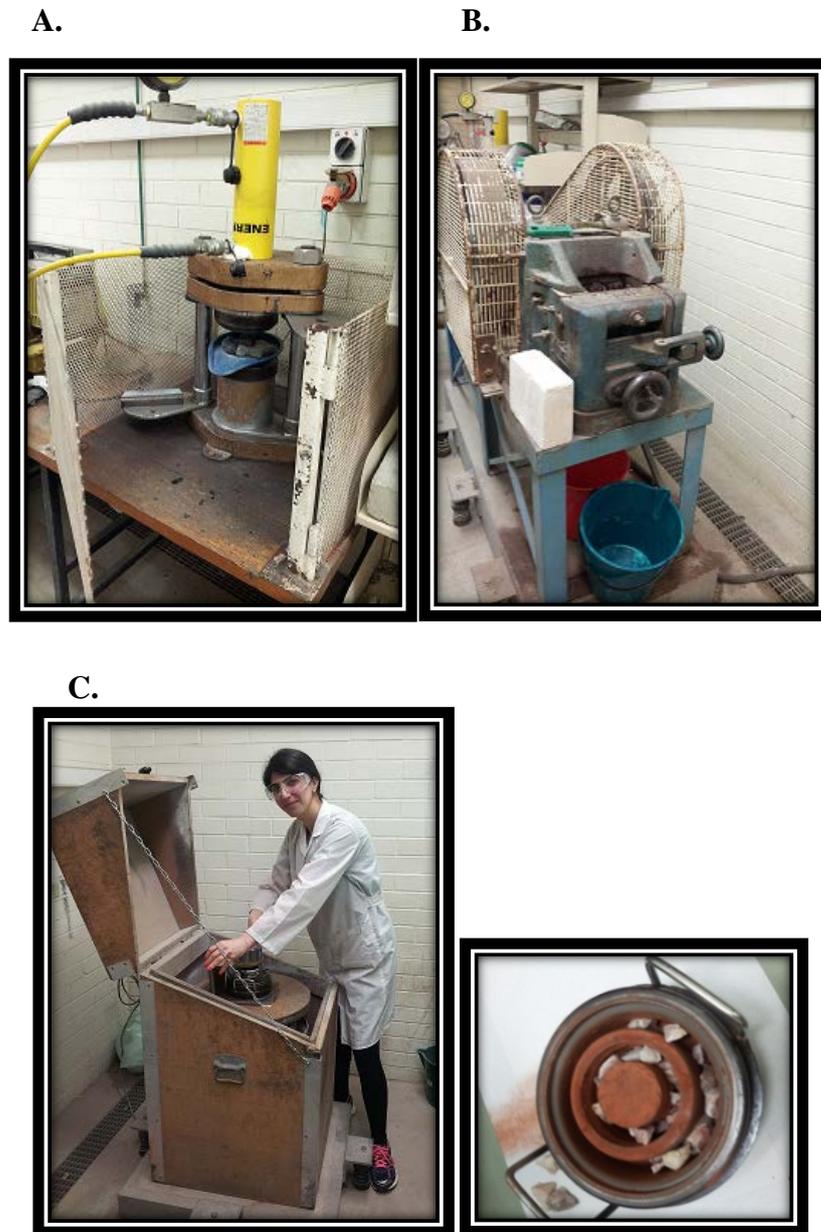


Figure 2.1: Hydraulic press (A) and mechanical jaw crusher (B) used to reduce the size of rock material prior to pulverising in the swing mill. Tema® swing mill (C-left) used to reduce the rock fragments to powder of $< 75 \mu\text{m}$; (C-right) tungsten carbide ring mill showing iron powder staining characteristic of Pilbara ironstones and quartz fragments used to clean the apparatus before use.

2.4. Analytical Techniques

2.4.1. Total Carbon and Total Sulphur

An ELTRA[®] 4000 carbon/sulphur analyser (Figure 2.2) was utilised to determine the total carbon (wt % C_{total}) and total sulphur (wt % S_{total}) of waste rocks collected from the South Jimblebar prospect. A high temperature induction furnace was used in the analysis.

150 mg of powdered sample was accurately weighed into a tared ceramic crucible. Approximately 0.7 g of pure Fe metal and 1.3 g of pure W metal were added to the crucible and mixed with the sample to act as accelerants. The contents of the crucible were combusted in oxygen in an induction furnace at around 2200°C. The evolved carbon and sulphur gases passed through filter materials in the instrument removing moisture and halogens, and reducing any SO₃ to SO₂. The concentrations of CO₂ and SO₂ were measured using infrared spectrometers. Appropriate international standard reference materials with certified values for C (STSD-2 1.6 wt % C) and S (RTS-1 1.66 wt % S; RTS-2 9.98 wt % S) were employed in calibration of the instrument.



Figure 2.2: Eltra[®] 4000 Carbon/ Sulphur analyser at EIGG (Department of Applied Geology, Curtin University).

2.4.2. Preparation of Samples by Acid Digestion

Sample digestion involves the chemical breakdown of powdered rock to produce solutions for analysis by ICP-MS. Sample solutions were produced in open 75 ml Teflon® beakers by hot acid digestion using nitric (HNO_3), perchloric (HClO_4), and hydrofluoric (HF) acids (Figure 2.3).



Figure 2.3: Acid digestion of rock samples: (right) open Teflon® beakers on a hot-plate; and (left) samples evaporated to insipient dryness during the preparation of solutions for analysis by ICP-MS.

The generalised procedure for the $\text{HNO}_3/\text{HClO}_4/\text{HF}$ digestion is described below:

A half gram of powdered sample was accurately weighed on a five figure electronic balance and placed into a Teflon® beaker using an electronic 5-figure balance. Sixteen millilitres of ultra-pure (redistilled analytical grade) concentrated nitric acid (HNO_3) was added to the beaker that was placed on a hotplate at 140°C . The sample was allowed to react for a minimum of 2 hours to remove the most reactive organic material. Four millilitres of HClO_4 acid was then added and the beaker covered with a Teflon® lid, and the sample allowed to reflux overnight. The next morning, 10 ml of HF was added in the beaker and the sample again allowed to reflux for 4 hours. The hot-plate temperature was then increased to 210°C , the Teflon® lid was carefully removed, and samples allowed to evaporate to near dryness. Care was taken to prevent

spitting of the sample as it approached dryness: the beaker was immediately removed from the hot-plate and temperature reduced if sample loss by spitting appeared likely to occur.

It was necessary to repeat the initial HNO_3 step where samples contained significant quantities of organic matter (e.g. lignite and carbonaceous shales), since residual organic material can create a potential explosive hazard through the formation of perchloric esters during the final evaporation. Further additions of $\text{HNO}_3/\text{HClO}_4/\text{HF}$ were made where initial mineral dissolution was incomplete, followed by evaporation to insipient dryness.

Concentrated HNO_3 2.5 ml was added to the precipitate in the bottom of the beaker and the sample was warmed on the hotplate for 2 or 3 minutes. A small quantity of Milli-Q® >18 Ohm deionised water was added and the sample was fully dissolved. When cool, the solution was transferred quantitatively into a 50 ml volumetric flask and made up to the mark (Figure 2.4). Prepared solutions were transferred, when cool, to clean, 50 ml plastic centrifuge tubes.

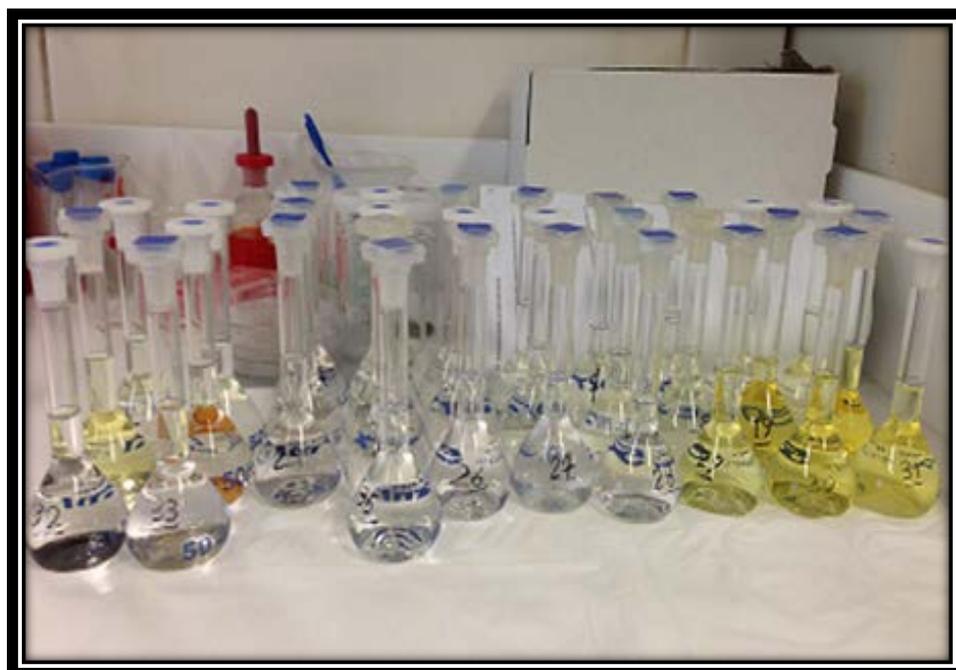


Figure 2.4: Digested samples made up to volume in 50 ml volumetric flasks. Dark residue in some of the flasks is highly insoluble oxides.

A total of 221 sample digestions were performed in this study in eight separate batches. Sample weight was in all cases 0.5 g; except in batch 3 where 0.25 g, 0.5 g and 1 g aliquots of individual samples and ISRM were prepared to ascertain any influence of sample quantity on Se recovery.

In regards to rock and international standard reference types, analytical (reagent) blanks and sample duplicates were also prepared within each batch to provide Quality Assurance (QA) and Quality Control (QC). All acids used were analytical grade: HNO_3 and HClO_4 were further distilled in a sub-boiling quartz-glass acid still (Figure 2.5). All H_2O used in sample digestion was >18 Ohm Milli-Q[®] grade.

Teflon beakers were employed because HF is able to dissolve glass. These beakers were cleaned with 5% Decon[®] detergent, rinsed with water, and then soaked for 24 hrs in 5% HNO_3 solution. Beakers were rinsed three times with Milli-Q[®] water immediately prior to use. Volumetric glassware used was A-grade.

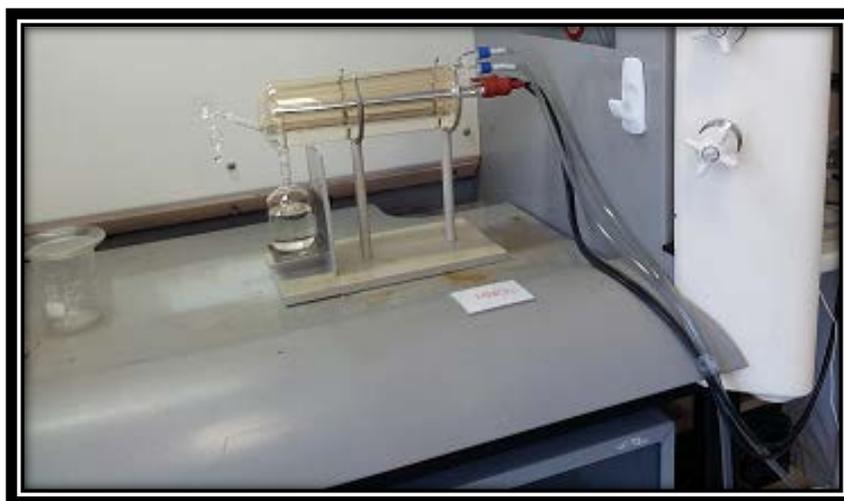


Figure 2.5: Acid Distillation in quartz glass sub-boiling acid.

2.4.3. Determination of Selenium and Other Trace Elements

Numerous methods of analysis have been employed for measurement of trace element concentrations in rock samples. On account of the frequently very low natural abundance of Se, few methods are suitable for the study of Se in rocks and the environment. Amongst these, Instrumental Neutron Activation Analysis (INAA) and Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) have been applied in mining studies, notably because Se can be a pathfinder element in mineral exploration. Neither of these methods, however, lends itself to routine geochemical analysis as performed by the numerous commercial laboratories that service the mining industry in Western Australia and world-wide.

2.4.3.1. Inductively- Coupled Plasma Mass-Spectrometry (ICP-MS)

Although there are alternative methods for determination of trace element concentrations in rocks, the ICP-MS technique was chosen for the analysis of selenium (Se), arsenic (As), vanadium (V), chromium (Cr), manganese (Mn) and copper (Cu) in rock samples in this study, because it is highly sensitive and has detection limits of parts per trillion in solution, which is important because Se is generally present in only trace amounts in the environment (Plant et al., 2005). The prepared samples were analysed using the Agilent Technologies 7500cs ICP-MS in the laboratories of TSW Analytical (Figure 2.6). Sample solutions were diluted using a Hamilton auto-diluter before analysis to minimise matrix effects. The instrument was calibrated using multi-element standards made by diluting commercially available ICP-MS grade standards (Claritas 10 ppm ICP-MS standards).



Figure 2.6: An Agilent Technologies 7500cs ICP-MS at the TSW Analytical Laboratory for analysis of trace elements.

2.4.3.2. Problems of Selenium Determination Using ICP-MS

The current study employed ICP-MS for the analysis of rock samples and reference materials, since this technique is the favoured and ubiquitous method employed by commercial laboratories servicing the mining industry in W.A. The technique experiences relatively few spectral interferences when compared to other methods of trace element analysis.

Atomic (isobaric) interferences arising from elements in the sample matrix are corrected for by the instrumental software. However, poly-atomic interferences arising from ions and molecules from the plasma, cannot be similarly corrected for. These interferences arise when combinations of the plasma ions have the same mass as the isotope of interest. In the case of Se, $^{40}\text{Ar}^{2+}$ and $^{40}\text{Ar}^{+} \ ^{38}\text{Ar}^{+}$ dimers produced in the plasma interfere with the two most abundant isotopes ^{80}Se and ^{78}Se , accounting for 49.82% and 23.52% of the Se, respectively. As a result, the Se concentration is normally measured using the ^{82}Se isotope comprising only 9.2 % of the natural abundance (Table 1.4). This limits the detection capability for Se using conventional ICP-MS to 0.5 - 10 $\mu\text{g/L}$ range in the solution. With the requirement of dilution of

solutions prepared from rock digestion to remove matrix effects on the plasma, this limits ICP-MS for Se determination in geological studies (Bueno et al., 2007).

2.5. Data Quality Assurance and Quality Control

The raw data obtained from the ICP-MS analysis was recalculated to account for sample preparation and analytical dilutions using Microsoft office Excel. The formula below was used to calculate ICP-MS results:

$$\text{Concentration in ppm} = (\text{dilution factor} \times \text{measured concentration in ppb} \times (0.5/\text{wt sample}))/1000$$

Wt = the weight of sample in grams used in sample preparation

International Standard Reference Materials employed in this study were mostly prepared and analysed multiple times, and at least twice. All waste rock samples were analysed at least in duplicate. The difference in individual results obtained for each ISRM or rock sample was calculated as the percentage coefficient of variation as follows:

$$\text{CoV \%} = (\text{standard deviation} / \text{mean}) \times 100$$

CoV % is a convenient means by which to express the variance of concentration from the mean obtained by multiple analysis of a sample. It should be noted that, as a percentage, CoV %, has the effect of emphasising the difference for those samples containing low concentrations of an element.

To compare the trace element concentrations of different samples in this study, the measurement error has been considered. Measurement error is divided in two components: systematic and random error. Random error is generally created by unpredictable or unknown variations in the experiments. It is inherent error in a

measurement that is repeated several times with the same instrument and conditions. In contrast, systematic error is predictable and arises from variations occurring during the experiment. It is usually calculated by dividing mean measurements obtained for a sample into the lowest measurement.

$$\text{Systematic Error} = (\text{Mean measurement for a sample}) / (\text{the lowest value for that sample})$$

2.6. Procedural Quality Control (QC)

2.6.1. Quality Control in the Field

Owing to restrictions of access to waste rock storage facilities at BHP Billiton's iron ore mines, the rock samples used in this study were collected by BHP staff, or were available from other recently completed or on-going research projects of EIGG at Curtin University. In all cases, care was taken to prevent contamination of individual samples that were contained in sealable plastic or muslin bags, correctly labelled on site, and delivered to EIGG laboratories at Curtin University.

2.6.2. Quality Control in the Laboratory

All rock samples were dried prior to sample preparation. All equipment used in crushing/pulverising was first cleaned by processing an amount of unmineralised quartz. During crushing, equipment was cleaned with water and acetone between samples to prevent sample cross-contamination. All Teflon® beakers and volumetric glassware were thoroughly washed between batches of sample preparation.

Chapter 3

Results from International Reference Materials

This chapter is based on the results obtained from the analysis of reference standards

3.1. Results from International Standard Reference Materials

This section focused on the results obtained from various geological reference materials analysed in this study to investigate the accuracy of routine ICP-MS analysis of Se. The number of certified reference materials with accredited Se values is not large and many of the ones used in this study, while having values that range from certified to information, are also relatively old. Analysis of the old geostandards give the possibility of comparing the accuracy of results obtained using the acid digestion and ICP-MS method with original geostandards results. Furthermore, there is no possibility of selective contamination by Se and As that could explain the higher than expected results obtained in the present study. It was considered useful to compare the literature published values with those obtained using ICP-MS to give an indication of reproducibility and bias exhibited by the dissolution and analytical techniques used.

Two reagent blanks were also prepared and analysed for Se (Table 3.1). Selenium values obtained using ICP-MS analysis of digested reference materials in this study are shown in Tables 3.2 - 3.4. These data have been corrected for any dilution used during the digestion process.

3.1.1. Results for Reagent Blanks

Generally, blanks are used to identify the amount of contamination of the sample occurring during sample preparation. These data have been corrected for dilution during the digestion process. The reagent blank values were very low for Se (mean 0.02 ppb), and also As and V (Table 3.1). They were significantly greater for the remaining three elements investigated, especially Cr (mean 1.14 ppb). The type and quality of reagents used in sample preparation were equivalent for all batches of prepared samples.

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|----------------|--------|------------|------------|------------|------------|------------|------------|
| Blank | | ppb | ppb | ppb | ppb | ppb | ppb |
| <i>Batch 1</i> | 28 | 0.03 | 0.08 | 0.01 | 1.58 | 0.43 | 0.22 |
| | 9 | 0.01 | 0.08 | 0.01 | 0.70 | 0.35 | 0.13 |

Table 3.1: Concentration of trace elements in the reagent blanks.

3.1.2. Results for CH₄ and NIST Coal Fly-Ash

A total of 12 analyses were performed on international standard reference materials CH₄ and NIST. The gold ore CH₄ was prepared and analysed seven times (Table 3. 2). The seven results obtained for Se varied between 1.54 and 1.78 ppm (CoV 5.4%), compared to the certified value of 2.10 ppm. The mean of the seven results for Se was 1.65 ppm, which is equivalent to 79% of the certified value. Lower than expected values were also recorded for As, Cr, Mn, and Cu when compared to the provisional and certified values. The reproducibility of results for Cr, Mn and Cu was good with coefficients of variation less than +/- 2.5% relative in in all cases. The mean values were 0.86, 0.86 and 0.67 of the certified values for Cr, Mn and Cu, respectively. In contrast, results of the 7 determinations of As varied significantly (CoV 23%) with a minimum of 4.37 ppm and maximum of 7.86 ppm compared to the certified value 8.8 ppm. Vanadium results show a CoV of +/- 15% but their accuracy could not be evaluated in the absence of a certified value. The low degree of variance in results for Cr, Mn and Cu suggest that random errors of weighing or sample loss during digestion may not be the cause of the lower than expected results. It is difficult to be definitive in these cases as the chemistry of the analytes differs significantly and losses due to precipitation, adsorption and volatilisation during the dissolution process may possibly account for some or all of the loss. In addition, there are also several mechanisms by which the calibration curves used by analytical organisations can be compromised and final data normalised following comparison to “certified values”. While this is acceptable analytical practice, the increased rigour with which these data have been scrutinised in the present study highlights potential for analytical error, with data not normalised with respect to the CRM values but received “as is”.

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|---------------------------|--------|-------------------|--------------------------|--------------------------|-------------|----------------------------|--------------------------|
| | | ppm | ppm | ppm | ppm | ppm | ppm |
| CH₄ | | 2.10 [©] | 8.80 (P) | | 114 (P) | 430 (P) | 2000 [©] |
| <i>Batch 5</i> | 19 | 1.61 | 4.37 | 78.2 | 98.8 | 360 | 1331 |
| | 21 | 1.61 | 4.65 | 79.7 | 99.2 | 370 | 1351 |
| | 22 | 1.63 | 5.41 | 50.4 | 101 | 376 | 1376 |
| | 30 | 1.54 | 6.86 | 76.9 | 95.8 | 357 | 1285 |
| | 31 | 1.63 | 6.93 | 82.6 | 101 | 377 | 1370 |
| | 32 | 1.77 | 7.86 | 80.4 | 100 | 370 | 1350 |
| | 33 | 1.78 | 7.68 | 79.9 | 100 | 369 | 1357 |
| CoV% | | 5.43 | 22.8 | 14.8 | 2.13 | 2.07 | 2.25 |
| NIST(Coal Fly Ash) | | 13.90+/- 0.5 (Re) | 186.2+/-3.0 [©] | 286.2+/-7.9 [©] | 258+/-6(Re) | 240.2 +/- 3.4 [©] | 173.7+/-6.4 [©] |
| <i>Batch 3</i> | 10 | 13.8 | 171 | 235 | 194 | 199 | 132 |
| | 11 | 13.8 | 174 | 244 | 202 | 203 | 135 |
| | 12 | 14.2 | 179 | 248 | 207 | 209 | 138 |
| CoV% | | 1.68 | 2.38 | 2.80 | 3.25 | 2.50 | 2.33 |
| Systematic Error | | 1.02 | 1.03 | 1.05 | 1.05 | 1.04 | 1.04 |
| <i>Batch 4</i> | 26 | 12.4 | 162 | 240 | 190 | 197 | 130 |
| | 25 | 12.1 | 157 | 227 | 176 | 186 | 116 |
| CoV% | | 1.53 | 2.29 | 3.93 | 5.32 | 3.78 | 8.19 |

Table 3.2: Concentrations of Se and selected trace elements in International Standard Reference Material CH₄ compared to certified and provisional values; and NIST coal fly-ash compared to reference and certified values. The coal ash was employed by the ICP-MS analytical laboratory (TSW Analytical) as a reference material. All values are expressed in ppm.

The five values of Se for NIST coal fly-ash obtained from two batches of analysis are close to the recommended value of 13.90 ppm (Table 3.2). The mean of three determinations from sample batch 3 was 13.94 ppm equal to the reference value, while the mean of the duplicates in batch 4 was 12.32 ppm, 88% of the higher value obtained for batch 3. Mean values of the results from both sample batches for the five other trace elements were lower than the recommended values in all cases. The variance within results of samples of batch 3 was low at < 3.25% CoV for all five elements. In the case of the duplicate preparation in batch 4, the results of all five elements were consistently lower than the other by a factor of 0.90. The lower values for one

preparation are consistent with quantitative loss of the analyte during digestion such as may result from spitting during the drying down stage. It is however noted that samples were dried at 210 °C in batch 3, but a lower temperature of 195°C in batch 4, specifically to reduce the likelihood of such spitting. Slightly different procedures were used for the two sample batches. In the case of batch 3, 15ml HNO₃ and 4 ml HClO₄ were added at the same time into the samples and after 4 hours HF was added. For batch 4, HNO₃ was added alone and after 4 hours HClO₄ was added, and the sample refluxed overnight before addition of HF. The loss of Se could be attributed to these changes in dissolution procedure and this possibility would need to be investigated in more detail in any future studies.

3.1.3. Other International Standards Reference Materials Used for Evaluation of Results

A total of 37 analyses were performed on 7 further international standard reference materials (ISRM) for which there were published values for Se. Two of the materials had recommended values of Se, namely BCSS-1 marine sediment, MESS-1 marine sediment (Govindaraju, 1989). Information values for Se were available for three of the remainder, RTS-1, RTS-2 and RTS-3 sulphide ore mill tailings had only (Canadian Certified Reference Materials project, 2009) (Table 2.1).

The marine mud MAG-1 was digested and analysed seven times (Table 3.3). The values obtained for Se from the seven preparations varied between 1.34 ppm and 2.23 ppm (CoV 10.9%). The results for Se and the other 5 trace elements were consistently low for beaker 37 compared to the other six results. This indicates quantitative loss of this analyte during this particular preparation. This sample result was omitted when calculating the mean value obtained for each element. The mean of the remaining six results for Se was 1.92 ppm, and is substantially higher than the recommended value of 1.16 ppm. The results were also significantly higher than the published values in the case of As and V. The reproducibility for five trace elements was good with CoV less than 5.8% in each case. The mean values for As, V, Cr, were 10%, 4%, <1% greater than the recommended values, respectively, while that for Cu was 11% lower than the

recommended value. The recommended value for Mn was not available. The results obtained for Mn show good reproducibility with a low CoV of approximately 4%.

The MAG-1 standard was old (1970s) but had been opened for sampling on only a small number of occasions. There is no possibility of selective contamination by Se and As that could explain the higher than expected results obtained in the present study. Mean values obtained for V, Cr and Cu are considered to be in reasonable agreement with the recommended values.

Marine sediment BCSS-1 was prepared and analysed 10 times in 3 different batches (Table 3.3). The variance in results for all 6 trace elements was small within each individual batch, except for Se in batch 1. In all, Se varied between 1.05 and 1.88 ppm, substantially higher than the recommended value of 0.43 ppm. The concentrations recorded for batch 7 were lower than for the other batches where the ranges were similar. The difference between the two batches was 0.68. The mean Marine sediment BCSS-1 was prepared and analysed 10 times in 3 different batches (Table 3.3). The variance in results for all 6 trace elements was small within each individual batch, except for Se in batch 1. The uniform shortfall in the Se concentrations recorded for each of the tailings materials when compared with the published values is noteworthy.

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|-----------------------------|--------|-------------------|-------------------|-------------------|-------------------|------------------|-------------------|
| | | ppm | ppm | ppm | ppm | ppm | ppm |
| MAG-1 | | | 9.20 [®] | 140 [®] | 97.0 [®] | | 30.0 [®] |
| <i>Batch 1</i> | 19 | 2.02 | 10.8 | 153 | 101 | 666 | 28.1 |
| | 7 | 1.96 | 10.8 | 154 | 101 | 675 | 28.1 |
| | 39 | 1.91 | 10.1 | 146 | 95.8 | 632 | 26.2 |
| | 11 | 2.23 | 10.8 | 155 | 104 | 649 | 28.2 |
| | 36 | 1.63 | 9.31 | 141 | 93.4 | 606 | 26.2 |
| | 37 | 1.34 | 8.79 | 123 | 82.3 | 527 | 23.3 |
| | 22 | 1.75 | 10.3 | 148 | 97.3 | 625 | 27.3 |
| CoV % | | 10.9 | 5.80 | 3.61 | 3.99 | 4.05 | 3.32 |
| BCSS-1(June-30-1988) | | 0.43 [®] | 11.1 [®] | 93.4 [®] | 123 [®] | 300 [®] | 18.5 [®] |
| <i>Batch 1</i> | 12 | 1.88 | 12.1 | 99.9 | 105 | 198 | 17.9 |
| BCSS-1 (Feb-6-1986) | | 0.43 [®] | 11.1 [®] | 93.4 [®] | 123 [®] | 300 [®] | 18.5 [®] |
| <i>Batch 1</i> | 32 | 1.64 | 11.9 | 97.0 | 100 | 197 | 17.3 |
| | 6 | 1.56 | 11.8 | 97.4 | 100 | 205 | 17.3 |
| | 27 | 1.11 | 11.8 | 96.1 | 105 | 192 | 17.6 |
| | 26 | 1.71 | 11.6 | 96.9 | 99.6 | 207 | 17.5 |
| CoV % | | 18.2 | 1.50 | 1.46 | 2.62 | 3.16 | 1.33 |
| <i>Batch 3</i> | 7 | 1.61 | 10.9 | 82.6 | 89.6 | 198 | 15.6 |
| | 8 | 1.53 | 11.1 | 83.2 | 90.0 | 200 | 15.9 |
| | 9 | 1.52 | 10.6 | 80.3 | 89.2 | 194 | 15.8 |
| CoV% | | 3.18 | 2.20 | 1.89 | 0.43 | 1.42 | 0.86 |
| Systematic Error | | 1.03 | 1.04 | 1.03 | 1.00 | 1.02 | 1.00 |
| <i>Batch 7</i> | 2 | 1.05 | 8.85 | 80.0 | 79.3 | 161 | 23.3 |
| | 3 | 1.06 | 9.09 | 81.9 | 80.8 | 161 | 23.1 |
| cov% | | 1.04 | 1.89 | 1.60 | 1.28 | 0.22 | 0.84 |
| MESS-1(Jul-9-1986) | | 0.34 [®] | 10.6 [®] | 72.4 [®] | 71.0 [®] | 660 [®] | 25.1 [®] |
| <i>Batch 1</i> | 31 | 1.30 | 10.8 | 75.6 | 58.2 | 395 | 25.4 |
| | 8 | 2.03 | 11.6 | 77.5 | 60.2 | 426 | 24.7 |
| | 17 | 2.18 | 11.9 | 79.3 | 58.1 | 444 | 27.8 |
| | 13 | 1.99 | 12.4 | 80.7 | 57.8 | 455 | 26.1 |
| | 40 | 1.37 | 11.6 | 75.9 | 57.7 | 406 | 25.8 |
| | 20 | 1.57 | 11.0 | 78.2 | 60.6 | 409 | 24.8 |
| CoV % | | 21.5 | 5.06 | 2.53 | 2.14 | 5.57 | 4.41 |
| <i>Batch 3</i> | 4 | 1.76 | 9.66 | 60.9 | 47.2 | 407 | 21.6 |
| | 5 | 1.73 | 10.4 | 62.8 | 48.6 | 406 | 20.6 |
| | 6 | 2.02 | 11.1 | 67.1 | 52.3 | 439 | 22.5 |
| CoV% | | 8.68 | 7.30 | 4.99 | 5.31 | 4.58 | 4.35 |
| <i>Batch 7</i> | 1 | 1.23 | 8.37 | 63.0 | 44.2 | 331 | 28.1 |
| | 50 | 1.34 | 9.46 | 65.5 | 46.5 | 347 | 31.0 |
| CoV% | | 6.00 | 8.65 | 2.72 | 3.60 | 3.22 | 7.17 |
| BIR-1 | | | 0.44 (I) | 310+/-11 (I) | 382 [®] | 104.5+ /-20 | 125+/-4 (I) |
| <i>Batch 1</i> | 24 | 1.39 | 0.872 | 377 | 385 | 1410 | 115 |
| | 15 | 1.15 | 0.561 | 377 | 416 | 1401 | 115 |
| | 35 | 1.19 | 0.646 | 372 | 365 | 1401 | 113 |
| CoV% | | 10.3 | 23.3 | 0.76 | 6.63 | 0.36 | 1.00 |

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|----------------|--------|----------|---------------|------|----------|----------|--------|
| RTS-1 | | 40.0 (I) | 8.2+/-1.6 (P) | | 50.0 (I) | 1900 (I) | 595 © |
| <i>Batch 5</i> | 7 | 24.6 | 8.35 | 87.5 | 22.2 | 1435 | 373 |
| | 8 | 24.8 | 8.41 | 86.1 | 21.4 | 1409 | 362 |
| CoV% | | 0.74 | 0.51 | 1.18 | 2.65 | 1.32 | 2.03 |
| RTS-2 | | 57.0 (I) | 6.3+/-1.8(P) | | 125 (I) | 400 (I) | 670 © |
| <i>Batch 5</i> | 9 | 35.4 | 7.56 | 66.9 | 89.4 | 276 | 473 |
| | 10 | 35.5 | 7.64 | 68 | 77.5 | 282 | 481 |
| CoV% | | 0.10 | 0.74 | 1.15 | 10.03 | 1.46 | 1.15 |
| RTS-3 | | 61.0 (I) | 9+/-2.6 © | | 75.0 (I) | 2000 (I) | 2820 © |
| <i>Batch 5</i> | 17 | 38.7 | 9.85 | 84.1 | 41.6 | 1573 | 1887 |
| | 18 | 37.4 | 9.20 | 79.1 | 38.2 | 1483 | 1824 |
| CoV% | | 2.30 | 4.83 | 4.32 | 6.02 | 4.13 | 2.37 |

Table 3.3: Concentrations of Se and selected trace elements in various ISRMs for which there are published (but not certified) Se values, as indicated.

Marine sediment MESS-1 was prepared and analysed a total of 11 times within three batches of analysis (Table 3.3). The maximum result obtained for Se was 2.18 ppm in batch 1, while the minimum value was 1.23 ppm in batch 7. The results in all batches were higher than the recommended value. The mean result for Se in the three different batches was 1.68 ppm, compared with recommended value of 1.04 ppm. The mean values for As, V, Cr and Cu in all batches were in close agreement with the recommended values, but the results obtained for As and V were slightly higher in batch 1 and lower in batches 3 and 7 when compared to the recommended values.

The Icelandic basalt BIR-1 was prepared and analysed three times (Table 3.3). The three results for Se obtained for BIR-1 varied between 1.15 - 1.39 ppm (mean 1.24 ppm, CoV 5.4%). The latest, 1998 revised certificate for BIR-1 does not list Se and this may be because the former reference value is inconsistent. The mean value of results for V and As was higher than the information value. That for Cr was equal to the recommended value and variability was 6% CoV. Copper and Mn results were slightly lower than the information values in each case.

The duplicate results for the three mill tailings reference materials, RTS-1, RTS-2, and RTS-3 were in very close agreement. However, the values for each trace element were lower than the information values, except for As which was in agreement (Table 3.3). The Se results were considerably below the published values for all three tailings materials, being 61.8 %, 62.2 % and 62.4 %, of the published values for RTS-1, RTS-2 and RTS-3, respectively. The substantially lower than expected values contrast with those of the other five trace elements. This fact, along with the good duplication (CoV < 2.3%) invalidates a cause by quantitative sample loss during preparation, pointing to a chemical or analytical factor singular to Se for the analytes determined. There is an equivalent shortfall in the Se concentrations recorded for each of the tailings materials when compared with the published values

Generally, it was observed that the values obtained for Se were commonly variable between repeated analysis, however those for As and the other trace metals were significantly more consistent. It appears that Se behaves differently from other elements in the dissolution process or during analysis in the ICP-MS instrument. So, when the concentrations of the other five trace elements were consistently close to published values, often the value obtained for Se was significantly greater or smaller than the published values.

3.1.4. Results for JGS Reference Materials

A total of 24 analyses were performed on 15 reference materials of the JGS series. Multiple preparations and analyses were performed on samples JMS-1 and JMS-2, marine sediments with contrasting Se values (Table 3.5). The remaining 13 reference samples were analysed only singly, to elucidate the range of Se concentrations displayed by the reference rock suite.

Reference material JMS-1 was prepared and analysed in duplicate in two separate sample batches (Table 3.4). Duplication of Se values was excellent in batch 7 but variance between duplicates was somewhat greater in Batch 1. Significantly, the

duplication for the other 5 trace elements was the converse, being excellent in the case of batch 1 samples and less for those of batch 7. Furthermore, the values for each of the five trace elements were in close accord with that reported by (Imai et al., 1996) (Table 2.1). This indicates that the results for Se alone have been influenced by aspects of sample preparation and/or the instrumental determination of Se. It has been pointed out previously that the chemistry of the analytes differs appreciably and so too will the host minerals in which the analytes occur. Therefore, it is possible that these differences are in part contributory to the variation in the “recovery” of the various analytes. However, there does appear to be a significant batch to batch variation which in part must be attributed to a less than rigorous validation procedure for the methodology used by the reporting laboratory.

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|------------------|--------|----------|------------------|--------------|----------------|--------------------|-------------|
| JMS-1 | | | 18.0 (m) | 127 (m) | 133 (m) | | 88.0 (m) |
| <i>Batch 1</i> | 33 | 1.21 | 18.8 | 126 | 126 | 636 | 78.7 |
| | 2 | 1.49 | 18.6 | 125 | 125 | 658 | 79.2 |
| CoV% | | 14.6 | 0.81 | 0.62 | 0.62 | 2.34 | 0.48 |
| <i>Batch 7</i> | 46 | 1.08 | 14.2 | 106 | 104 | 539 | 72.8 |
| | 47 | 1.01 | 14.1 | 98.8 | 99.3 | 522 | 67.2 |
| CoV% | | 4.81 | 0.922 | 5 | 3.65 | 2.23 | 5.7 |
| JMS-2 | | | 35.0 (m) | 183 (m) | 78.0 (m) | | 447 (m) |
| <i>Batch 1</i> | 25 | 15.0 | 39.9 | 183 | 71.0 | 15999 | 388 |
| | 16 | 16.2 | 40.1 | 183 | 43.2 | 15814 | 401 |
| CoV% | | 5.51 | 0.42 | 0.31 | 34.45 | 0.82 | 2.21 |
| <i>Batch 3</i> | 1 | 11.2 | 33.4 | 155 | 54.4 | 14309 | 348 |
| | 2 | 10.0 | 30.8 | 140 | 50.0 | 12884 | 319 |
| | 3 | 9.81 | 30.3 | 142 | 50.6 | 12834 | 320 |
| CoV% | | 7.66 | 5.26 | 5.59 | 4.54 | 6.28 | 4.94 |
| Systematic Error | | 0.88 | 0.91 | 0.91 | 0.93 | 0.90 | 0.92 |
| <i>Batch 7</i> | 49 | 7.13 | 27.3 | 138 | 48.0 | 11928 | 290 |
| | 48 | 9.15 | 29.2 | 147 | 56.2 | 12984 | 299 |
| CoV% | | 17.5 | 4.80 | 4.49 | 11.1 | 6 | 2.20 |
| JSd-2 | | 18.8 (P) | 38.6 ® | 125 ® | 108 ® | | 1117 ® |
| <i>Batch 7</i> | 16 | 10.7 | 32.9 | 110 | 73.5 | 707 | 782 |
| JSd-1 | | 0.25 (P) | 2.42 ® | 76.0 ® | 21.5 ® | | 22.0 ® |
| <i>Batch 7</i> | 17 | 0.658 | 1.81 | 68.1 | 16.6 | 525 | 25.3 |
| JLK-1 | | 0.641 ® | 26.8 ® | 117 ® | 69.0 ® | | 62.9 ® |
| <i>Batch 7</i> | 12 | 1.61 | 20.0 | 101 | 55.0 | 1386 | 59.4 |
| JSO-2 | | | 1076 (m) | | 1118 (m) | | 1276 (m) |
| <i>Batch 7</i> | 18 | 4.79 | 715 | 110 | 854 | 767 | 867 |
| JDO-1 | | 0.05 ® | 0.11 ® | 3.14 ® | 7.93 ® | | 1.41 ® |
| <i>Batch 7</i> | 6 | 0.312 | 0.313 | 3.33 | 7.41 | 45.1 | 1.30 |
| JCh-1 | | | 0.567 ® | 10.4 ® | 7.04 ® | | 15.3 ® |
| <i>Batch 7</i> | 9 | 0.073 | 0.485 | 7.91 | 6.05 | 112 | 22.8 |
| JSO-1 | | | 8.10 +/- 0.1 (m) | 300 +/-3 (m) | 71.0 +/- 2 (m) | 0.197 +/-0.002 (m) | 169 +/-2(m) |
| <i>Batch 7</i> | 13 | 1.64 | 6.34 | 285 | 58.6 | 1110 | 127 |
| JSd-3 | | 1.29 ® | 252 ® | | 35.3 ® | | 426 ® |
| <i>Batch 7</i> | 14 | 1.61 | 221 | 64.9 | 29.5 | 899 | 313 |
| JS1-1 | | | 14.9 ® | | 60.9 ® | | 40.8 ® |
| | 8 | 1.31 | 12.3 | 114 | 45.6 | 343 | 42.8 |
| JR-3 | 7 | 1.36 | 0.70 | 0.927 | 0.979 | 485 | 12.4 |
| JGb-2 | 15 | 0.16 | 1.24 | 156 | 78.6 | 756 | 18.3 |
| JH-1 | 11 | 0.615 | 1.12 | 192 | 496 | 1141 | 14.7 |
| JCU-1 | 5 | 14.4 | 163 | 6.28 | 6.42 | 3998 | 26172 |

Table 3.4: Concentrations of Se and selected trace elements in various JGS standards.

In batch 1 the two JMS-1 samples were left on hot plate with the mixtures of HNO_3 and HClO_4 to decompose completely organic matter prior to addition of HF. In contrast, in batch 7 attempts to digest samples quickly resulted in significantly less time for dissolution in the acid mixture and possibly less efficient digestion of the sample. Consistently lower values across the range of elements for analyses in batch 7 in comparison with batch 1, indicate trace elements Se and As in batch 7 are approximately 23 % lower than results obtained in batch 1, while this difference for trace elements V, Mn and Cr is around 18%. The averaged values of the 5 trace elements in JMS-1 for batch 1 were in a close agreement with the mean published values (Imai et al.1996). Thus, it can be considered that the results obtained in batch 1 are robust and most closely reflect the true concentrations present, while lower values from batch 7 may reflect a less than complete digestion of the rocks. However, this seems unlikely as it was recorded that when the solutions were transferred to volumetric flasks they were in each case clear and devoid of undigested minerals or colloidal precipitate.

JMS-2 (marine sediment) was analysed in duplicate in three separate batches (batch 1, 3 and 7) (Table 3.4). Duplication in batch 1 was good in comparison to that in the other 2 batches. The results obtained for Cr, V, Cu and As were similar to the published values, ranging from slightly above and below than the mean values (Imai et al., 1996). The values for Se in batch 3 were 33% less than batch 1 and the average result for Se in batch 7 was 47% lower than that of batch 1. These variations can be due to differential digestion of samples in each batch.

Therefore, the concentrations of elements obtained in batch 1 were greater than the other two batches (batch 3 and 7). This may be due to the changes in the temperature while the solutions were drying. In order to avoid spitting of the samples, the temperature of hotplate was turned down from 210 to 195°C in batch 3. As there is correlation between temperature and chemical reaction, it is possible that lower concentration of analytes have been released to solution in comparison to batch 1. However, the solutions appeared clear and devoid of undissolved solids when transferred into volumetric flasks.

The Se concentrations recorded for the remaining 13 reference materials ranged from a minimum of 0.07 ppm in the chert sample (JCh-1), to a maximum of 14.5 ppm in copper ore (JCu-1). Such variation is consistent with that expected from the differing petrologies represented. The results obtained for Se in this study vary higher or lower than published values. The results obtained for reference materials JSd-1, JLK-1, and JDO-1 have shown the Se values higher than published values and JCh-1 and JSd-2 indicate lower values in comparison to published values. This trend has been typically seen in other trace elements. The results for Cr and V for reference materials JCh-1, JDO-1, JLK-1 and JSd-1 are close to published values. Also, the As concentration reported for reference materials JSd-2 and JLK-1 are in good agreement with published values (Table 3.4). The result obtained for Se in JSd-3 is almost the same as the published value.

There are not published values for reference materials JSO-1 (soil), JMS-1(marine sediment), JMS-2 (marine sediment, JCU-1 (copper ore), JR-3 (rhyolite), JS1-1 (slate), JCh-1 (chert), JH-1 (hornblendte), JSd-1 (stream sediment), JGb-2 (gabbro), and JSo-2 (soil). Additional analyses of these reference materials would be useful to improve our geochemical knowledge of Se in a currently available reference suite.

Chapter 4

Results from Waste Rocks of Iron Ore Mining

This chapter focuses on the analytical results obtained from the waste rocks from
BHP Billiton iron ore mines

4.1. Results from Waste Rocks of Pilbara Mines

4.1.1. Results for Reagent Blanks

One reagent blank was prepared for each analysis batch. The blank values are presented (in ppb) in Table 4.1. The reagent blank values were very low in most cases. The concentration of Se in the blanks for all batches of analyses in this study was less than 0.2 ppb. The same maximum blank value was found for V, while that of As was only a little greater at 1.2 ppb. Slightly higher blank concentrations were recorded consistently for Cr and Mn, although the maxima were still less than 2 ppb. Whereas, blank values for Cu obtained in analytical batches 2 and 3 were very low, there was evidence of a small degree of Cu contamination of the reagents during sample preparation in batches 4 and 6 with blank values of 295 and 109 ppb, respectively.

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu |
|-------------------------------|----------------|--------|--------|------|--------|------|--------|--------|
| Blank | | | ppb | ppb | ppb | ppb | ppb | ppb |
| <i>Batch 2- Jimblebar</i> | | 23 | 0.01 | 0.10 | 0.01 | 0.68 | 0.22 | 0.15 |
| <i>Batch 3-Jimblebar</i> | | 35 | 0.17 | 0.73 | < 0.10 | 1.38 | 1.71 | < 0.10 |
| <i>Batch 4-Mt-Goldsworthy</i> | | 27 | 0.13 | 1.15 | 0.22 | 1.67 | 0.25 | 295 |
| <i>Batch 6 - Yandi</i> | | 16 | < 0.10 | 0.58 | 0.12 | 1.02 | < 0.10 | 109 |

Table 4.1: Concentration of trace elements in the reagent blanks

4.1.2. Distribution of Selenium in Waste Rock Types

The analytical results from Mt. Goldsworthy and South Jimblebar are shown in Table 4.2 according to the different rock types. Seven samples of black shales were analysed, six of which were from the South Jimblebar prospect, with one obtained from Mt. Goldsworthy mine (Table 4.2). A maximum of 4.07 ppm Se was recorded in a sample a black shale from South Jimblebar, whereas the minimum value recorded in a black shale from South Jimblebar was 1.31 ppm (SJ0847D-035) (Table 4.2). Values from the single sample from Mt. Goldsworthy mine at around 1.70 ppm were at the lower end of the composition range for the black shales from South Jimblebar.

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-------------------------------|---------------------|--------|-------|------|------|--------|------|------|--------|
| | | | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| EIL Guideline | | | | 20 | 50 | 400 | 500 | 100 | |
| HIL Guideline | | | 10000 | 100 | 550 | 120000 | 1500 | 1000 | |
| Black shale | | | | | | | | | |
| <i>Batch 2- Jimblebar</i> | SJ0847D-035 | 1 | 2.14 | 5.69 | 37.5 | 43.5 | 3374 | 53.6 | 0.5 |
| | SJ0847D-035 | 9 | 1.58 | 6.37 | 34.8 | 44.3 | 3177 | 46.1 | 0.5 |
| CoV% | | | 21.2 | 8.06 | 5.41 | 1.21 | 4.24 | 10.6 | |
| <i>Batch 3-Jimblebar</i> | SJ0847D-035 | 13 | 1.31 | 3.44 | 30.3 | 40.4 | 2963 | 45.3 | 0.5 |
| | SJ0847D-035 | 14 | 1.37 | 3.44 | 30.6 | 39.8 | 3020 | 42.7 | 1 |
| | SJ0847D-035 | 15 | 1.43 | 3.42 | 31.0 | 44.3 | 3041 | 46.1 | 0.25 |
| CoV% | | | 4.33 | 0.46 | 1.05 | 5.89 | 1.36 | 3.93 | |
| <i>Batch 2- Jimblebar</i> | SJ0848D-021 | 15 | 3.39 | 15.1 | 192 | 372 | 6.82 | 188 | 0.5 |
| | SJ0848D-021 | 37 | 2.85 | 22.0 | 184 | 372 | 5.37 | 184 | 0.5 |
| CoV% | | | 12.1 | 26.1 | 3.00 | 0.00 | 16.8 | 1.52 | |
| <i>Batch 2- Jimblebar</i> | SJ0845RD-015 | 17 | 4.01 | 17.0 | 455 | 440 | 21.6 | 139 | 0.5 |
| | SJ0845RD-015 | 49 | 2.64 | 17.1 | 425 | 408 | 21.2 | 137 | 0.5 |
| CoV% | | | 29.3 | 0.58 | 4.92 | 5.43 | 1.24 | 0.76 | |
| <i>Batch 3-Jimblebar</i> | SJ0845RD-015 | 16 | 3.91 | 10.5 | 404 | 418 | 22.4 | 132 | 0.5 |
| | SJ0845RD-015 | 17 | 3.28 | 4.69 | 249 | 401 | 20.6 | 124 | 1 |
| | SJ0845RD-015 | 18 | 4.07 | 11.5 | 413 | 427 | 23.0 | 141 | 0.25 |
| CoV% | | | 11.1 | 41.3 | 25.9 | 3.13 | 5.59 | 6.36 | |
| <i>Batch 2- Jimblebar</i> | SJ0848D-025 | 26 | 1.62 | 29.4 | 46.1 | 101 | 2.97 | 184 | 0.5 |
| | SJ0848D-025 | 32 | 1.51 | 22.9 | 51.9 | 118 | 3.22 | 248 | 0.5 |
| CoV% | | | 5.21 | 17.4 | 8.34 | 10.6 | 5.74 | 20.8 | |
| <i>Batch 2- Jimblebar</i> | SJ0848D-029 | 28 | 1.56 | 14.5 | 106 | 201 | 4.02 | 158 | 0.5 |
| | SJ0848D-029 | 35 | 1.51 | 15.5 | 107 | 193 | 5.28 | 163 | 0.5 |
| CoV% | | | 2.38 | 4.64 | 0.59 | 2.59 | 19.1 | 2.13 | |
| <i>Batch 2- Jimblebar</i> | SJ0847D-041 | 31 | 3.34 | 19.5 | 113 | 143 | 401 | 203 | 0.5 |
| | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG10-R1 | 2 | 1.66 | 10.4 | 17.7 | 77.1 | 16.1 | 29.8 | 0.5 |
| | RWG10-R1 | 1 | 1.74 | 10.6 | 18.2 | 86.5 | 17.0 | 30.7 | 0.5 |
| CoV% | | | 3.24 | 1.03 | 1.83 | 8.10 | 3.77 | 2.11 | |
| Lignite | | | | | | | | | |
| <i>Batch 2- Jimblebar</i> | SJ1102-002 | 2 | 9.19 | 7.75 | 110 | 119 | 595 | 56.8 | 0.5 |
| | SJ1102-002 | 13 | 9.08 | 7.77 | 114 | 125 | 600 | 57.2 | 0.5 |
| CoV% | | | 0.83 | 0.15 | 2.31 | 3.26 | 0.62 | 0.53 | |
| <i>Batch 2- Jimblebar</i> | SJ1102-006 | 4 | 17.2 | 8.32 | 193 | 149 | 114 | 101 | 0.5 |
| | SJ1102-006 | 6 | 17.0 | 8.51 | 187 | 145 | 117 | 99.9 | 0.5 |
| CoV% | | | 0.52 | 1.58 | 1.97 | 1.55 | 1.73 | 1.02 | |
| <i>Batch 2- Jimblebar</i> | SJ0772D-016 | 11 | 3.96 | 14.8 | 75.4 | 127 | 36.9 | 59.5 | 0.5 |
| | SJ0772D-016 | 16 | 4.51 | 14.9 | 74.7 | 127 | 36.2 | 60.6 | 0.5 |
| CoV% | | | 9.11 | 0.06 | 0.69 | 0.06 | 1.29 | 1.36 | |
| <i>Batch 3-Jimblebar</i> | SJ0772D-016 | 29 | 3.86 | 10.7 | 74.9 | 129 | 35.4 | 63.4 | 0.25 |
| | SJ0772D-016 | 30 | 3.69 | 9.88 | 70.0 | 120 | 32.8 | 57.3 | 0.5 |
| | SJ0772D-016 | 31 | 3.75 | 10.6 | 73.6 | 124 | 33.9 | 56.8 | 1 |

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|--------------------|----------------|--------|------|------|------|-------|-------|-------|--------|
| CoV% | | | 2.29 | 4.38 | 3.46 | 3.69 | 3.86 | 6.24 | |
| Batch 2- Jimblebar | SJ0772D-019 | 19 | 2.48 | 13.4 | 68.1 | 73.3 | 12.9 | 29.6 | 0.5 |
| | SJ0772D-019 | 25 | 2.23 | 18.1 | 58.7 | 56.6 | 11.2 | 26.2 | 0.5 |
| CoV% | | | 7.50 | 21.3 | 10.5 | 18.2 | 9.71 | 8.42 | |
| Batch 3-Jimblebar | SJ0772D-019 | 19 | 1.97 | 8.72 | 61.6 | 69.5 | 12.0 | 27.6 | 0.5 |
| | SJ0772D-019 | 20 | 2.12 | 9.41 | 68.1 | 75.5 | 12.7 | 28.3 | 1 |
| | SJ0772D-019 | 22 | 2.25 | 8.71 | 62.6 | 70.4 | 12.5 | 28.9 | 0.25 |
| CoV% | | | 6.47 | 4.52 | 5.48 | 4.49 | 2.91 | 2.31 | |
| Batch 2- Jimblebar | SJ0785-005 | 24 | 1.07 | 1126 | 1.48 | 2.52 | 52.0 | 3.36 | 0.5 |
| | SJ0785-005 | 44 | 0.96 | 950 | 1.34 | 2.32 | 43.8 | 3.14 | 0.5 |
| CoV% | | | 7.35 | 12.0 | 6.89 | 5.91 | 12.0 | 4.71 | |
| Batch 2- Jimblebar | SJ0785-003 | 33 | 2.31 | 618 | 1.84 | 5.23 | 94.1 | 5.41 | 0.5 |
| | SJ0785-003 | 36 | 2.39 | 599 | 1.87 | 3.15 | 90.5 | 5.20 | 0.5 |
| CoV% | | | 2.26 | 2.30 | 1.29 | 35.2 | 2.77 | 2.79 | |
| Mudstone | | | | | | | | | |
| Batch 2- Jimblebar | SJ0849D-002 | 5 | 1.14 | 27.4 | 84.8 | 98.5 | 2136 | 93.9 | 0.5 |
| | SJ0849D-002 | 45 | 0.67 | 33.2 | 75.6 | 72.5 | 1867 | 85.4 | 0.5 |
| CoV% | | | 36.7 | 13.5 | 8.08 | 21.5 | 9.51 | 6.65 | |
| Batch 2- Jimblebar | SJ0848D-041 | 8 | 2.03 | 70.7 | 300 | 367 | 79.4 | 29.5 | 0.5 |
| | SJ0848D-041 | 27 | 1.45 | 65.4 | 272 | 331 | 73.1 | 27.5 | 0.5 |
| CoV% | | | 23.5 | 5.54 | 7.10 | 7.24 | 5.87 | 5.14 | |
| Batch 2- Jimblebar | SJ0848D-017 | 29 | 2.76 | 26.9 | 149 | 92.4 | 19.5 | 63.2 | 0.5 |
| | SJ0848D-017 | 50 | 3.10 | 26.3 | 142 | 84.9 | 29.1 | 62.4 | 0.5 |
| CoV% | | | 8.15 | 1.72 | 3.54 | 5.98 | 28.06 | 0.91 | |
| Batch 3-Jimblebar | SJ0848D-017 | 23 | 2.93 | 17.9 | 141 | 104 | 24.0 | 64.0 | 0.5 |
| | SJ0848D-017 | 24 | 2.76 | 20.7 | 147 | 93.0 | 23.8 | 61.5 | 1 |
| | SJ0848D-017 | 25 | 2.83 | 18.8 | 129 | 97.6 | 19.5 | 65.9 | 0.25 |
| CoV% | | | 2.96 | 7.65 | 6.57 | 5.39 | 11.21 | 3.46 | |
| Batch 2- Jimblebar | SJ0848D-043 | 34 | 1.96 | 38.6 | 61.2 | 48.7 | 2603 | 68.3 | 0.5 |
| | SJ0848D-043 | 46 | 1.63 | 31.1 | 56.8 | 46.4 | 2415 | 63.3 | 0.5 |
| CoV% | | | 12.6 | 15.2 | 5.24 | 3.38 | 5.32 | 5.34 | |
| BIF | | | | | | | | | |
| Batch 2- Jimblebar | SJ0847D-010 | 7 | 0.37 | 8.69 | 3.10 | 3.45 | 134 | 19.6 | 0.5 |
| | SJ0847D-010 | 40 | 0.23 | 7.32 | 2.75 | 2.75 | 121 | 16.9 | 0.5 |
| CoV% | | | 34 | 12.0 | 8.56 | 16.09 | 7.28 | 10.2 | |
| Batch 2- Jimblebar | SJ0847D-020 | 12 | 0.81 | 6.69 | 20.4 | 6.83 | 52.6 | 27.5 | 0.5 |
| | SJ0847D-020 | 22 | 0.90 | 6.64 | 21.3 | 6.93 | 56.4 | 27.9 | 0.5 |
| CoV% | | | 7.75 | 0.57 | 2.99 | 1 | 4.96 | 0.79 | |
| Batch 3-Jimblebar | SJ0847D-020 | 26 | 0.84 | 5.47 | 18.8 | 6.67 | 48.3 | 28.1 | 0.5 |
| | SJ0847D-020 | 27 | 0.85 | 5.56 | 18.5 | 5.93 | 47.7 | 24.2 | 1 |
| | SJ0847D-020 | 28 | 0.65 | 4.78 | 18.5 | 6.39 | 46.9 | 28.1 | 0.25 |
| | SJ0847D-020 | 32 | 0.86 | 4.78 | 17.8 | 6.15 | 45.9 | 32.5 | 0.5 |
| | SJ0847D-020 | 33 | 0.79 | 5.12 | 18.4 | 5.88 | 46.6 | 32.1 | 1 |
| CoV% | | | 11.1 | 7.17 | 2.07 | 5.31 | 1.98 | 11.75 | |

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|--------------------------|----------------|--------|------|------|------|-------|------|------|--------|
| Batch 2- Jimblebar | SJ0847D-009 | 18 | 0.11 | 11.7 | 4.91 | 6.19 | 101 | 15.2 | 0.5 |
| | SJ0847D-009 | 39 | 0.01 | 12.3 | 4.51 | 5.35 | 103 | 15.0 | 0.5 |
| CoV% | | | 119 | 3.82 | 6.06 | 10.30 | 1.77 | 1.26 | |
| Batch 2- Jimblebar | SJ0847D-008 | 20 | 0.66 | 12.4 | 21.3 | 21.3 | 2487 | 23.6 | 0.5 |
| | SJ0847D-008 | 38 | 0.49 | 9.32 | 19.7 | 20.1 | 2313 | 22.4 | 0.5 |
| CoV% | | | 21.2 | 20.2 | 5.29 | 3.87 | 5.12 | 3.49 | |
| Batch 4-Mt-Goldsworthy | RWG18-R1 | 4 | 0.21 | 21.0 | 32.4 | 37.7 | 306 | 7.11 | 0.5 |
| | RWG18-R1 | 3 | 0.24 | 21.5 | 32.6 | 41.7 | 309 | 7.72 | 0.5 |
| CoV% | | | 10.2 | 1.62 | 0.41 | 7.03 | 0.77 | 5.79 | |
| Sheared dolerite | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG12-R1 | 24 | 0.21 | 0.53 | 177 | 173 | 76.5 | 6.72 | 0.5 |
| | RWG12-R1 | 23 | 0.25 | 0.52 | 186 | 208 | 63.6 | 5.92 | 0.5 |
| CoV% | | | 12.9 | 0.58 | 3.22 | 12.9 | 13.1 | 8.98 | |
| Banded phyllite | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG21-R4 | 22 | 1.10 | 3.63 | 12.4 | 144 | 991 | 11.8 | 0.5 |
| | RWG21-R4 | 21 | 1.10 | 3.87 | 11.3 | 162 | 984 | 10.9 | 0.5 |
| CoV% | | | 0.18 | 4.65 | 6.70 | 8.24 | 0.52 | 5.62 | |
| shale, chert, BIF | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG4-R1 | 20 | 1.22 | 8.62 | 4.47 | 4.77 | 21.8 | 11.6 | 0.5 |
| | RWG4-R1 | 19 | 1.14 | 8.42 | 4.40 | 4.76 | 20.9 | 12.2 | 0.5 |
| | RWG4-R1 | 18 | 1.32 | 8.54 | 4.33 | 4.84 | 22.0 | 11.7 | 0.5 |
| CoV% | | | 7.42 | 1.16 | 1.66 | 0.88 | 2.59 | 2.53 | |
| Volcanic ash | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG2-R2 | 17 | 0.90 | 2.14 | 120 | 1438 | 138 | 19.0 | 0.5 |
| | RWG2-R2 | 16 | 0.67 | 1.99 | 111 | 1496 | 131 | 18.7 | 0.5 |
| CoV% | | | 20.5 | 5.03 | 5.11 | 2.82 | 3.58 | 1.27 | |
| Phyllite | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG1-R1 | 15 | 0.20 | 44.3 | 31.6 | 37.8 | 166 | 4.95 | 0.5 |
| | RWG1-R1 | 14 | 0.45 | 43.6 | 31.7 | 42.6 | 161 | 3.92 | 0.5 |
| CoV% | | | 53.3 | 1.18 | 0.24 | 8.43 | 2.19 | 16.5 | |
| Hematite | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG24-R1 | 13 | 0.04 | 11.3 | 1.77 | 7.42 | 4910 | 5.27 | 0.5 |
| | RWG24-R1 | 12 | <0.1 | 14.0 | 2.04 | 6.61 | 5616 | 3.27 | 0.5 |
| CoV% | | | | 15.1 | 10.0 | 8.19 | 9.49 | 33 | |
| Banded chert | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG21-R5 | 11 | 0.67 | 3.60 | 14.0 | 6.16 | 20.3 | 6.44 | 0.5 |
| | RWG21-R5 | 10 | 0.68 | 3.55 | 14.4 | 6.41 | 23.7 | 7.85 | 0.5 |
| CoV% | | | 0.66 | 0.85 | 2.00 | 2.74 | 11.1 | 14.0 | |
| Dolerite | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG14-R1 | 9 | 0.25 | 0.49 | 193 | 261 | 156 | 6.65 | 0.5 |
| | RWG14-R1 | 8 | 0.24 | 0.50 | 193 | 288 | 158 | 6.59 | 0.5 |
| CoV% | | | 0.69 | 0.91 | 0.19 | 7.14 | 0.89 | 0.65 | |
| Dolerite | | | | | | | | | |
| Batch 4-Mt-Goldsworthy | RWG3-R1 | 6 | 0.32 | 2.55 | 64.8 | 3273 | 713 | 14.7 | 0.5 |
| | | 5 | 0.36 | 2.61 | 71.8 | 3070 | 706 | 17.2 | 0.5 |
| CoV% | | | 7.38 | 1.75 | 7.26 | 4.52 | 0.73 | 10.8 | |

Table 4.2. Concentrations of Se and selected trace elements in different types rock and soil samples provided from South Jimblebar, and Goldsworthy compared with West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010). Values exceeding (EIL) are shown with yellow and results higher than both guidelines are highlighted with pink.

Lignite was present only in the overburden at the South Jimblebar site. Six samples of lignite gave a range of Se concentration from 1 to 17 ppm. In general, the values of Se in lignite are higher than black shale samples, and represent a major enrichment when compared to the average crustal value of Se (0.05 ppm).

Iron-rich rocks (BIF and haematite ore) from Mt. Goldsworthy mine and South Jimblebar yielded Se concentrations in the range of 0.1 - 0.9 ppm, very much lower than in the carbonaceous lithologies, but still appreciably above the mean estimated crustal value. Four samples of mudstone, each from South Jimblebar gave a range of Se content from 0.9 - 2.9 ppm.

When comparing the variance of the duplicates for black shale SJ0847D-035 analysed in batch 2 with results for other trace elements, it is evident that the difference is not mirrored in the results of the other elements. Differences that were recorded in the Se results appear not to be a result of spillage or contamination of samples during preparation. A similar observation is made by the variance in duplication of SJ0772D-016 lignite in batch 2 of South Jimblebar, where a difference of almost 10% CoV between 4.50 and 3.96 ppm is not reflected in the excellent agreement obtained for the other elements. Mineral inhomogeneity of samples seems an unlikely cause for the variance in Se values, as it should result in variance also in As and the other trace metals that would be concentrated within pyrite grains.

Twenty samples of rocks of diverse compositions from Yandicoogina Iron Ore mine were analysed. The concentration of Se throughout these different rock types was lower than 1.50 ppm in Yandicoogina mines. The analytical results from Yandicoogina mine are shown in Table 4.3. A total of seven samples of black shales were analysed. Also, the analytical results of three samples of iron formation are reported. Typically, the concentration of Se in shale samples of Yandicoogina was higher than iron formation samples from this area. The high value found in shale and in lignite suggests there is a strong association of Se with C and S. Much lower values were reported in iron-rich rocks indicating less association of Se with Fe.

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-------------------------------------|----------------|--------|-------|------|------|--------|------|------|--------|
| | | | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| EIL Guideline | | | | 20 | 50 | 400 | 500 | 100 | |
| HIL Guideline | | | 10000 | 100 | 550 | 120000 | 1500 | 1000 | |
| Whaleback Shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505643 | 12 | 0.49 | 14.8 | 17.7 | 22.4 | 400 | 29.3 | 0.5 |
| | N505643 | 13 | 0.45 | 14.9 | 17.7 | 23.3 | 399 | 21.1 | 0.5 |
| CoV% | | | 6.55 | 0.23 | 0.09 | 2.56 | 0.20 | 22.9 | |
| Yandicoogina shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416182 | 14 | 1.11 | 36.2 | 84.1 | 101 | 156 | 50.8 | 0.5 |
| | N416182 | 15 | 1.13 | 37.5 | 87.5 | 101 | 160 | 57.2 | 0.5 |
| CoV% | | | 0.77 | 2.47 | 2.78 | 0.21 | 2.19 | 8.32 | |
| Joffre | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505639 | 36 | 0.23 | 19.0 | 11.0 | 11.8 | 766 | 11.8 | 0.5 |
| | N505639 | 35 | 0.35 | 20.0 | 11.6 | 11.3 | 788 | 12.1 | 0.5 |
| CoV% | | | 29.4 | 3.41 | 3.39 | 3.09 | 2.02 | 1.62 | |
| Weeli Wollli formartion | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | HyM0005 | 25 | 0.37 | 2.47 | 10.8 | 6.14 | 39.4 | 11.9 | 0.5 |
| | HyM0005 | 26 | 0.30 | 2.34 | 11.1 | 5.81 | 29.2 | 11.8 | 0.5 |
| CoV% | | | 13.7 | 3.68 | 1.62 | 3.89 | 21.1 | 0.38 | |
| Joffre member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505637 | 28 | 0.18 | 9.93 | 8.31 | 6.95 | 819 | 16.2 | 0.5 |
| | N505637 | 27 | 0.14 | 9.53 | 8.36 | 7.43 | 818 | 15.5 | 0.5 |
| CoV% | | | 21.2 | 2.91 | 0.45 | 4.79 | 0.05 | 3.23 | |
| Weeli Wollli iron formartion | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | HyM0002 | 24 | 0.66 | 29.8 | 22.7 | 32.1 | 1044 | 54.2 | 0.5 |
| | HyM0002 | 23 | 0.82 | 30.8 | 22.8 | 30.9 | 1042 | 54.8 | 0.5 |
| CoV% | | | 15.9 | 2.34 | 0.52 | 2.64 | 0.11 | 0.75 | |
| Whaleback Shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505563 | 5 | 1.46 | 19.8 | 63.1 | 64.1 | 363 | 22.2 | 0.5 |
| | N505563 | 6 | 1.29 | 19.6 | 62.1 | 63.5 | 356 | 23.8 | 0.5 |
| CoV% | | | 8.69 | 0.65 | 1.13 | 0.74 | 1.27 | 4.98 | |
| Mt.McRae shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | E118008 | 3 | 1.17 | 147 | 77.9 | 82.7 | 227 | 26.3 | 0.5 |
| | E118008 | 4 | 1.00 | 146 | 78.4 | 82.8 | 223 | 26.5 | 0.5 |
| CoV% | | | 11.0 | 0.58 | 0.46 | 0.10 | 1.01 | 0.41 | |
| Mt.McRae shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | E118098 | 2 | 1.39 | 181 | 81.6 | 86.4 | 783 | 36.7 | 0.5 |
| | E118098 | 1 | 1.29 | 183 | 81.4 | 84.7 | 770 | 38.0 | 0.5 |
| CoV% | | | 5.47 | 1.05 | 0.14 | 1.38 | 1.17 | 2.54 | |
| Yandicoogina shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416291 | 7 | 0.53 | 20.3 | 217 | 110 | 74.8 | 48.2 | 0.5 |
| | N416291 | 8 | 0.59 | 20.9 | 224 | 113 | 78.9 | 42.7 | 0.5 |
| CoV% | | | 8.44 | 2.01 | 2.16 | 1.55 | 3.77 | 8.54 | |
| Weeli Wollli dolerite | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | HyM0029 | 21 | 1.19 | 2.14 | 243 | 98.1 | 991 | 99.3 | 0.5 |
| | HyM0029 | 22 | 1.34 | 1.84 | 253 | 100 | 1026 | 101 | 0.5 |
| CoV% | | | 8.06 | 10.6 | 2.73 | 1.54 | 2.43 | 1.08 | |
| Teriary detrital | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505758 | 34 | 1.26 | 13.6 | 113 | 114 | 371 | 36.5 | 0.5 |
| | N505758 | 33 | 0.99 | 13.8 | 115 | 115 | 381 | 35.1 | 0.5 |
| CoV% | | | 16.9 | 1.20 | 1.20 | 1.19 | 1.95 | 2.79 | |
| Joffre member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416412 | 40 | 0.52 | 2.07 | 11.2 | 7.39 | 2766 | 22.6 | 0.5 |
| | N416412 | 38 | 0.67 | 3.20 | 13.1 | 9.03 | 2847 | 23.1 | 0.5 |
| CoV% | | | 16.9 | 30.4 | 11.2 | 14.1 | 2.03 | 1.55 | |
| Mt.McRae shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505546 | 11 | 0.56 | 202 | 73.6 | 41.4 | 1426 | 18.3 | 0.5 |
| | N505546 | 10 | 0.72 | 206 | 76.1 | 43.5 | 1472 | 17.2 | 0.5 |
| | N505546 | 9 | 0.56 | 205 | 75.1 | 42.5 | 1441 | 21.7 | 0.5 |
| CoV% | | | 14.6 | 1.11 | 1.70 | 2.49 | 1.63 | 12.3 | |

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-----------------------------------|----------------|--------|------|------|------|------|------|------|--------|
| Weeli Wolli iron formation | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416220 | 43 | 1.10 | 31.9 | 114 | 160 | 459 | 38.8 | 0.5 |
| | N416220 | 42 | 1.19 | 31.6 | 119 | 153 | 459 | 37.7 | 0.5 |
| CoV% | | | 5.79 | 0.67 | 2.53 | 3.23 | 0.14 | 2.07 | |
| colonial chert member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | E115011 | 20 | 0.66 | 46.4 | 44.8 | 75.4 | 443 | 32.2 | 0.5 |
| | E115011 | 19 | 0.75 | 44.7 | 43.8 | 73.1 | 446 | 31.1 | 0.5 |
| CoV% | | | 9.70 | 2.75 | 1.51 | 2.20 | 0.53 | 2.55 | |
| Joffre member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416410 | 32 | 0.98 | 2.44 | 11.5 | 10.9 | 899 | 26.0 | 0.5 |
| | N416410 | 31 | 0.94 | 2.83 | 12.7 | 10.7 | 895 | 24.3 | 0.5 |
| CoV% | | | 2.70 | 10.3 | 7.03 | 1.18 | 0.29 | 4.77 | |
| Weeli Wolli | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505657 | 29 | 0.19 | 13.5 | 3.40 | 3.09 | 101 | 14.0 | 0.5 |
| | N505657 | 30 | 0.15 | 13.2 | 3.18 | 3.20 | 99.0 | 9.81 | 0.5 |
| CoV% | | | 13.7 | 1.56 | 4.70 | 2.57 | 1.73 | 24.7 | |
| Dales gorge member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505655 | 39 | 0.18 | 11.7 | 4.64 | 3.61 | 117 | 14.8 | 0.5 |
| | N505655 | 37 | 0.14 | 10.5 | 4.52 | 3.32 | 117 | 13.9 | 0.5 |
| CoV% | | | 15.9 | 7.4 | 1.85 | 5.93 | 0.38 | 4.44 | |
| Tertiary detrital | C370723 | 18 | 1.83 | 18.5 | 89.5 | 127 | 124 | 50.6 | 0.5 |
| | C370723 | 17 | 1.58 | 18.6 | 90.4 | 128 | 126 | 46.5 | 0.5 |
| CoV% | | | 10.7 | 0.37 | 0.69 | 0.34 | 1.10 | 6.01 | |

Table 4.3: Concentrations of Se and selected trace elements in different types rock and soil samples provided from Yandicoogina mine compared with West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010). Values exceeding (EIL) are shown with yellow and results higher than both guidelines are highlighted with pink.

The overall range Se concentration in rocks suite from Yandicoogina mine is between 0.1 and 1.29 ppm (Table 4.3). The Se concentrations of South Jimblebar were between 0.67 and 17.03 ppm and Mt. Goldsworthy mine were from 0.01 to 1.6 ppm (Table 4.3).

The shale and lignite samples generally show the highest Se concentrations in the waste rocks in the three mines. The highest values of Se were found in lignite samples from the South Jimblebar site. At South Jimblebar and Mt Goldsworthy, the Se content of shale is generally high. Overall, the range of Se in BIF is lower than shale at South

Jimblebar prospect and Mt Goldsworthy mine. The value of Se in BIF samples was up to 0.6 ppm at South Jimblebar.

Analysis of the seven different shales from Yandicoogina mine shows a considerable range in Se content from 0.4 to 1.3 ppm. The maximum concentration of Se in shale is approximately the same as maximum values of Se found in other type rocks. Overall the value of Se in waste rocks from the Yandicoogina mine is less than that in waste rocks from the other two mines. Thus, Yandicoogina may not pose as much a problem from Se as the other mines. For example, the highest Se content in Tertiary detrital deposits is 1 ppm and in iron 1.2 ppm and in shale also 1.2 ppm. Samples of N416410, N416412, N505637, N505639 (Joffre Member) and N505655 (Dale Gorge) and N505657 (Weeli Wollie) are highly oxidized and weathered rock samples and therefore identification of precise rock type proved difficult, but these are assumed to be ironstone samples due to their stratigraphic designation and red-brown colour.

4.2. Selected Trace Element Values

The analysis of As is also of interest, as Se and As are metalloids that behave similarly in the environment. This study also aims to focus on assessing the relationship between Fe content in rocks and Se distribution. As a result, V, Cr and Mn were also selected for analysis because these elements are often associated with iron ore, being siderophile elements. Copper was measured as an element of environmental interest.

Significant As in black shale from South Jimblebar was up to 30 ppm. The overall concentration of As in lignite was commonly between 7 and 1130 ppm. However, extremely high values were found in two samples such as SJ0785-005 and SJ0785-003. Similar extremely high values of Se were not found in these two samples of lignite. It is suggested that As is present as arsenious pyrite.

The level of As varied from 5.14 to 21.20 ppm in BIF waste rocks. Arsenic concentration in BIF sample from Mt. Goldsworthy was higher than Ecological

Investigation Level guideline in DEC, 2010. Also, the contents reported at Mt. Goldsworthy were higher than As concentrations in South Jimblebar. The highest As value was found in the Mt. McRae shale samples from waste rocks of Yandicoogina Iron Ore mining. The concentration was higher than West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological (EIL) (DEC, 2010). Arsenic concentrations in South Jimblebar prospect were more than As concentrations in Yandicoogina mine.

Vanadium values was variable but more for V was more in Black shale compared with BIF rocks. Generally, the level of V in three BHP Billiton Iron Ore mines was higher than West Australia Department of Environment and Conservation guideline values for ecological (EIL) (DEC, 2010). Furthermore, the maximum concentration of V was found in black shales of South Jimblebar. There is no any direct association between Se and V found in this study.

Results generated from Cr were variable in deferent types of samples. In general, the highest level of Cr was analysed in dolerite (3171 ppm) and volcanic ash (1467 ppm) at Mt. Goldsworthy. These values exceed West Australia Department of Environment and Conservation guideline values for ecological (EIL) (DEC, 2010). The concentration of Cr in black shale in South Jimblebar was more than BIF. No relationship was recognised between Se and Cr.

Generally, the concentration of Mn was high in all rock types of three mine sites of the Pilbara. The highest level of Mn was in hematite in Mt. Goldsworthy (5616 ppm). The lowest value of Mn was found in lignite in Jimblebar (11.2 ppm). Manganese was generally associated with iron.

The Cu contents were variable in waste rock types analysed. The highest concentration of Cu was in black shale of South Jimblebar (203 ppm) and lowest level of this element was found in hematite (3.3 ppm) and phyllite from Mt. Goldsworthy (4 ppm). In

general the value of Cu in black shale of South Jimblebar was higher than Ecological guideline value in (DEC, 2010).

4.3. Carbon/Sulphur Determination

4.3.1. The Relationship Between C/S and Fe with Se

Eleven samples of waste rock obtained from exploration cores from the South Jimblebar prospect were analysed for total C and S. The average Se concentration from duplicates analysed by ICP-MS in batch 2 are also shown with Cu and C/S in Table 4.4 to elucidate the relationship between Se and C and S.

Results obtained from each rock type at South Jimblebar varied for carbon, with a maximum of 36.0 wt % in lignite and minimum of 0 wt % in BIF. Similarly, the highest level of S was found in the lignite with a value of 35.1 wt %, while the lowest value of S was 0.01 wt % in a sample of BIF. A positive relationship between the concentrations of C and S and Se exists (Table 4.4).

| Rock Number | Total Carbon wt % | Total Sulphur | Selenium Mean sample and duplicate (ppm) | Copper Average duplicate values (ppm) |
|-------------|----------------------|---------------|---|--|
| Lignite | 36.04 | 0.72 | 4.23 | 60.00 |
| Lignite | 35.79 | 1.41 | 2.36 | 40.00 |
| Lignite | 27.72 | 21.36 | 2.35 | 5.31 |
| Lignite | 13.85 | 35.10 | 1.01 | 3.25 |
| Black Shale | 3.75 | 0.34 | 3.32 | 135 |
| BIF | 0.07 | 0.02 | 0.57 | 23.00 |
| BIF | 0.02 | 0.01 | 0.06 | 45.09 |
| BIF | 0.00 | 0.02 | 0.30 | 18.25 |
| BIF | 0.24 | 0.05 | 0.86 | 28.62 |
| Black Shale | 9.47 | 3.10 | 1.86 | 47.00 |
| Black Shale | 4.46 | 2.17 | 3.34 | 203 |
| Mudstone | 0.04 | 0.03 | 2.93 | 63.00 |
| Black Shale | 3.37 | 0.10 | 3.12 | 186 |
| Black Shale | 1.73 | 0.06 | 1.57 | 216 |
| Mudstone | 0.07 | 0.05 | 1.54 | 29.00 |
| Black Shale | 5.41 | 0.06 | 1.74 | 170 |
| Mudstone | 0.12 | 0.05 | 1.80 | 66.00 |
| Mudstone | 0.03 | 0.04 | 0.91 | 90.00 |
| Lignite | 22.03 | 0.22 | 9.14 | 57.00 |

Table 4.4: Comparison of the average duplicate values for selenium and copper with sulphur and carbon

Selenium has a strong affinity for S and can be concentrated in sulphurous materials (Nazarenko and Ermakov 1972). Selenium has been found to be elevated in stratigraphic units which contain black shales (Wen and Carignan, 2011), pyrite (Strawn et al., 2002) and sedimentary rock such as sandstone and limestone (World Health Organization, 1987). These types of rocks typically contain organic matter with which Se is relatively stably combined (Wen and Carignan, 2011). Carbon and S are a major constituent of organic matter in shale (Figure 4.1). When natural oxidation of sulphide minerals (enriched in Se) occurs, Se may be released into the environment along with S. Consequently, Se has the potential to be associated with sulphate minerals (Luttrell, 1959) (Figure 4.1). In regard to the Pilbara region, it is likely that

Se is released to the environment following natural weathering predominantly of pyritic shale.

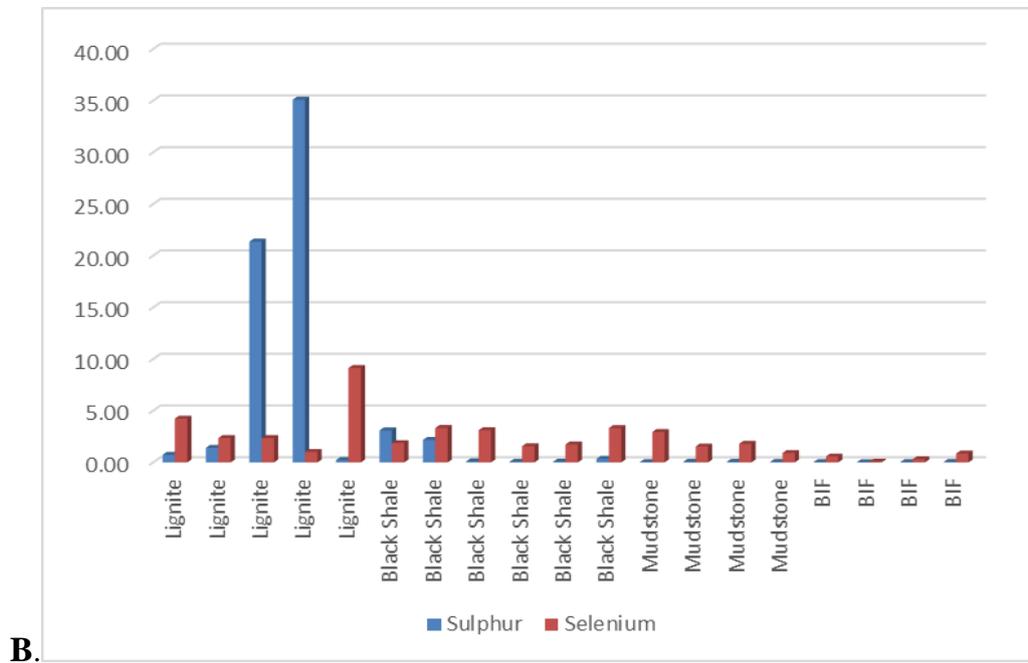
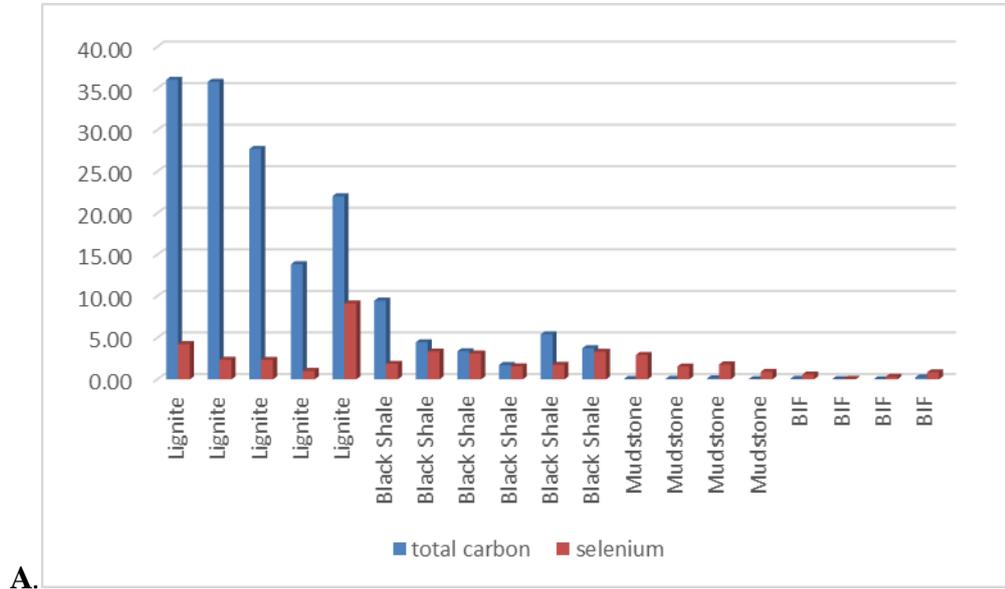


Figure 4.1: (A) total carbon vs selenium were compared and (B) total sulphur vs selenium.

4.4. Effects of Different Acid matrices on Se values determined in dissolved iron-rich rock samples

All samples which were analysed in batch 8 had been analysed in previous sample batches (Table 4.5), where the digests were not entirely clear and free from solid material. The aim of the further analysis of this batch of samples was to compare results obtained after making up of the digested sample using HNO₃, in the normal way, with those obtained when HCl or a mix of HCl and HNO₃ was used. As can be seen in Table 4.5, the selenium concentration is generally higher in replicate samples which were made up to volume in the mixture of HCl + HNO₃. All data in the table have been presented in ppm. The highest value found for Se in each case is highlighted with green.

| Samples Number | Se | As | V | Cr | Mn | Cu | Comment |
|----------------|--------|------|--------|------|------|------|-----------------------|
| | ppb | ppb | ppb | ppb | ppb | ppb | |
| Blank | < 0.10 | 2.00 | < 0.10 | 2.02 | 2.35 | 0.16 | HNO ₃ |
| | ppm | ppm | ppm | ppm | ppm | ppm | |
| RWG1-1 | 0.25 | 32.5 | 20.3 | 41.0 | 152 | 4.15 | HNO ₃ +HCl |
| RWG1-1 | 0.15 | 43.9 | 20.7 | 34.3 | 134 | 3.13 | HNO ₃ |
| RWG1-1 | 0.17 | 37.6 | 20.4 | 36.3 | 143 | 2.96 | HCl |
| SJ0847D-035 | 1.74 | 3.30 | 21.9 | 33.6 | 257 | 32.8 | HNO ₃ +HCl |
| SJ0847D-035 | 1.55 | 3.32 | 21.4 | 33.0 | 2481 | 32.5 | HNO ₃ |
| SJ0847D-035 | 1.59 | 3.76 | 22.2 | 34.3 | 2596 | 35.0 | HCl |
| SJ0848D-017 | 2.82 | 17.8 | 98.4 | 85.8 | 16.9 | 44.5 | HNO ₃ +HCl |
| SJ0848D-017 | 2.63 | 17.3 | 92.4 | 80.8 | 15.8 | 41.6 | HNO ₃ |
| SJ0848D-017 | 2.57 | 17.9 | 98.6 | 77.6 | 15.7 | 43.6 | HCl |
| N416220 | 1.41 | 40.3 | 114 | 153 | 445 | 24.3 | HNO ₃ +HCl |
| N416220 | 1.76 | 39.8 | 110 | 152 | 436 | 23.9 | HNO ₃ |
| N416220 | 0.64 | 28.7 | 91 | 114 | 334 | 20.2 | HCl |
| N505655 | 0.44 | 14.2 | 5.42 | 4.60 | 114 | 2.94 | HNO ₃ +HCl |
| N505655 | 0.16 | 12.2 | 4.94 | 4.74 | 98.3 | 2.52 | HNO ₃ |
| N505655 | 0.33 | 14.1 | 5.32 | 4.72 | 111 | 2.74 | HCl |
| N505546 | 0.94 | 178 | 62.6 | 38.0 | 1308 | 10.7 | HNO ₃ +HCl |
| N505546 | 0.66 | 181 | 62.6 | 38.3 | 1305 | 10.6 | HNO ₃ |
| N505546 | 0.77 | 202 | 70.7 | 41.6 | 1476 | 11.4 | HCl |

Table 4.5: Investigated concentration of trace elements by acid digestion method and made up using HNO₃, HCl and a 1:1 HNO₃/HCl mixture in batch 8. The highest values of selenium recorded for each sample are marked with green colour.

Chapter 5

Discussion and Conclusions

This chapter provides overall interpretation of the results of this study, indicates its limitations and suggests what further research would be useful

5.1. Discussion

5.1.1. Addressing Objectives

This project has focused on two main aims. The first was to assess the effectiveness of routine procedures of acid sample digestion and ICP-MS analysis to determine accurately the Se concentration in a variety of geological standard reference materials. The close agreement of results obtained by ICP-MS analysis in this study with the published value shows that the acid digestion technique was effective to detect the low concentration of Se in soils and rocks. The second aim was to provide a preliminary picture of the relative distribution of Se amongst common rock types stored as waste products at three of BHP Billiton Iron Ore's mine sites in the Pilbara region of Western Australia. Generally, the concentration of Se found in rock types of South Jimblebar was higher rock types of Goldworthy and Yandicoogina. Furthermore, results obtained for Se in this study indicates that Se concentrated chiefly in lithologies of shale and lignite, because shale and lignite contain high level of organic matters (Wen and Carignan, 2011). Sulphur and C are a major components of organic matter. Thus, when withering and natural oxidation of sulphide materials occurs, Se that has a strong affinity for S can be released to the environment (Luttrell, 1959).

Selenium plays an important role in human and animal health, particularly that of grazing animals and other livestock. It has a very low natural concentration in rocks of the Earth's crust, and is able to be deficient, or locally in excess, in soils. A geochemical association of Se with sedimentary ironstones (BIF) has long been known (Savard, Bedard and Barnes, 2009), and it is surmised that Se emitted by volcanoes went into solution in ancient seawater and was subsequently co-precipitated with iron when the oceans became chemically oxidising (Luttrell, 1959). Since Se has an affinity for sulphides and organic matter it is possible that carbonaceous and/or pyritic shales encountered during iron ore mining would be a potential source of Se in waste rock (Strawn et al., 2002).

Recently, the possible risk of environmental contamination through release of Se from stored waste rocks has been raised by regulatory authorities, such as those controlling iron ore mining in the Pilbara (BHP Iron Ore, 2011). There is, consequently, interest from mining companies in the content and behaviour of the metalloid element in iron ores and associated rock types that are stored as waste rocks at mine sites. A considerable cohort of Se data is commonly in the possession of mining companies as a result of the ubiquitous use of ICP-MS in the trace element analysis of rocks, either in-house or by commercial analytical laboratories. Most frequently Se concentrations have been measured within routine programs of sample digestion and ICP-MS analysis designed to provide results for a wide spectrum of 30, or more, trace elements. As the chemical characteristics of individual trace elements varies considerably, so too will the behaviour of individual analytes during the digestion process and instrumental analysis. Until now, there has been no major driver for precise and reliable Se data for rocks by ICP-MS and, as a consequence, the procedures employed by analytical laboratories have not been optimised for Se determination. Where routine procedures are employed in the analysis of mine waste rocks by commercial laboratories, Se is frequently reported as below the lower limit of detection (e.g. 10 - 50 ppm) across a broad suite of samples (Bueno et al., 2007).

In the current study, a commercial analytical laboratory, TSW Analytical (Perth, WA), was commissioned to optimise the conditions for instrumental analysis of Se by ICP-MS whilst still operating in a manner that would efficiently generate results for Se and a further five trace elements (As, Cr, V, Mn, and Cu). Each of these trace elements is commonly associated with ore and waste rocks from iron ore mines, although they exhibit differing geochemical behaviour. This resulted in employment of a collision cell due to its high sensitivity and the retained ability of multi-elemental analysis. This technique brought the lower limit of detection down to 0.05 – 0.09 ppb depending upon the Se isotope measured (Stroud, McGrath and Zhao 2012), enabling the reporting of values for Se, and the other trace elements, in all standard reference materials and waste rock samples analysed in this study.

TSW Analytical performed tests to compare the efficiency of the hot HNO₃, HClO₄, and HF digestion with the alternative of fusing the solid 1:10 with lithium tetraborate with subsequent dissolution of the fused bead in 15% hydrochloric acid. Hydride generation was also found to be a useful procedure in combination with ICP-MS analysis of Se, and allowed for high levels of dilution as required when there is a high concentration of matrix elements (Stroud, McGrath and Zhao 2012).

As a result of the TSW test, an overall methodology for sample preparation and analysis using ICP-MS was determined and considered to have equivalent, or superior, ability to that typically employed by commercial laboratories for the accurate determination of the Se content of rock samples.

5.1.2. Efficiency of Acid Digestion - Evidence from Analysis of Standard Reference Materials and Waste Rocks of Iron Ore Mining

Analytical precision was assessed on basis of at least duplicate and commonly multiple preparations of each reference standard. Percent CoV of results from the preparations for individual rock standards was generally less than 5.5%. In some instances where the % CoV was greater than 5.5%, a uniform variation affecting all six analytes suggested that some loss of sample through “spitting” during the drying stage of sample digestion may have occurred. Since the temperatures of individual beakers could not be controlled precisely during batch-wise sample preparation and depended upon the position of the beaker on the hot-plate, the generally low % CoV between repeated sample preparations suggested that loss of Se through volatilisation was not a significant problem. Such was further implied where closely equivalent values for Se were obtained for individual rock standards prepared as part of more than one sample batch, where the conditions during acid digestion were inevitably different (e.g. total time taken for acid reflux and evaporation).

An experiment was undertaken using different amounts of sample (1.0g, 0.5g, 0.25g) in the acid digestion of six waste rock samples from South Jimblebar prospect (Table

4.2), in order to discount the effects of sample size on the results obtained for selenium. Overall differences in the results for the five trace elements (As, Cr, V, Mn and Cu) were similar, and variations showed no bias to a particular sample size. It was noted that results for Se were significantly more variable, although the relative variation was emphasised by the smaller concentration of Se. It is clear from the results (Table 4.2) that the behaviour of individual analytes either during sample digestion or instrumental analysis resulted in complex variations in the values obtained from individual prepared samples. Crucially, significant variation occurred in the Se values of duplicates. This is illustrated, for example, in 0.5g samples of black shale SJ0845D-015 and SJ0848D-021 prepared in batch 2 (Table 4.2). In the former, the values obtained for As, Mn and Cu were precisely the same, while those V (93.2%) and Cr (92.5%) were slightly lower in the duplicate. The duplicate value for Se was a mere 58.5% of the first. In the case of sample SJ0848D-021, the duplicate values for Cr, V and Cu are the same, while those for Mn and Se are lower in the duplicate and that for As is significantly higher in the duplicate.

In addition to volatile loss during hot acid digestion of powdered rock samples, low values of Se might also occur as a result of incomplete sample digestion. Repeated additions of acid and subsequent evaporation to near dryness were employed for samples where initial dissolution was incomplete, as indicated by the presence of undigested mineral grains. After repeated acid treatments, a majority of samples retained no, or very few, coloured and/or opaque mineral particles. An exception occurred for a small number of samples in which numerous opaque grains remained undissolved (Figure 2.4). An example was black shale SJ0848D-025 which in Figure 2.4 has shown high precipitate. The results for this sample indicates that values obtained for As and Se were lower than duplicate, while the V, Cr, Mn and Cu values of this sample were greater than the duplicate.

Whereas residual particles of highly resistant minerals, such as zircon and magnetite, were generally not a significant problem, it was observed that a small amount of very fine colloidal material, either white or reddish-orange in colour, occurred as a precipitate in some digests of iron ore waste rocks when made up (to 50 ml) in volumetric flasks in dilute HNO₃. This fine solid material, considered to be remnant

silica or iron, would sometimes dissolve in the sample solution prior to the decanting of solution into plastic centrifuge tubes. In order to effect dissolution of the fine precipitates, a number of samples in which it was most developed were subject to a further test, in which dilute HCl or an equal mix of dilute HNO₃ and HCl was substituted for dilute HNO₃ as the final solution matrix. The results (Table 4.6) show that whereas there were some differences between results obtained for As, Cr, V, Mn and Cu in the different acid matrixes, these were normally minor and did not show a common bias across the five trace elements. However, differences in the results for Se were mostly significantly greater and in each case the highest value was measured from the solution containing a mix of dilute HNO₃ and HCl. The Se value in this matrix was as much as 92% higher than that recorded for HNO₃ and 91% higher than that measured in the HCl matrix. The very different variations in values of Se between the different solution matrices, and those for the other trace elements are difficult to explain. If they arise from different development of the fine precipitate, then it would imply that Se alone, was associated with the precipitate. Alternatively, the different matrix may have caused difference in the behaviour of the analytes in the ICP-MS analysis, either as a result of further dilution of the sample or as an artefact of the instrumental technique.

5.1.3. Efficacy of ICP-MS Instrumental Analysis

The accuracy of this technique was estimated by comparison of the analysed data for the selected geostandards (international reference materials) with their published values. In this study, the published values are presented in recommended values, mean values, reference value, information values, provisional values and certified values. The geostandards values of Se determined by ICP-MS were typically close to published values reported. Most of the geostandards values for Se were within 60% to 80% of published values. The majority of reference materials values for other trace elements determined fall within 80% to 90% of published values. Overall, multi-acid digestion and ICP-MS can be an effective dissolution/ analytical procedure for the analysis of As, V, Cr, Mn, Cu and Se at trace levels of detection. However, it should be considered that it possible to lose volatile elements such as Se during digestion and evaporation of solutions (Nazarenko and Ermakov 1972).

5.1.4. The Variation of Selenium in the Waste Rocks of Three BHP Iron Ore Mines

Representative samples of waste rocks occurring at three of BHP's iron ore mines in the Pilbara were analysed to ascertain the Se contents. The rock samples, which included carbonaceous shale, lignite, BIF, phyllite, mudstone and dolerite, were collected by BHP staff from waste rock piles at Yandicoogina and Mt. Goldsworthy mines. Samples analysed from South Jimblebar were sourced from a suite of prospective waste rock types collected from drill cores provided by BHP as part of a previous research study (Fajrin, 2012).

The highest concentrations of Se were recorded in the lignite, shale, phyllite and mudstone samples (Figures 5.1 - 5.3) which contained the greatest concentrations of organic matter, carbon and sulphides. The concentration of Se reached a maximum of 17.2 ppm in a sample of lignite from South Jimblebar.

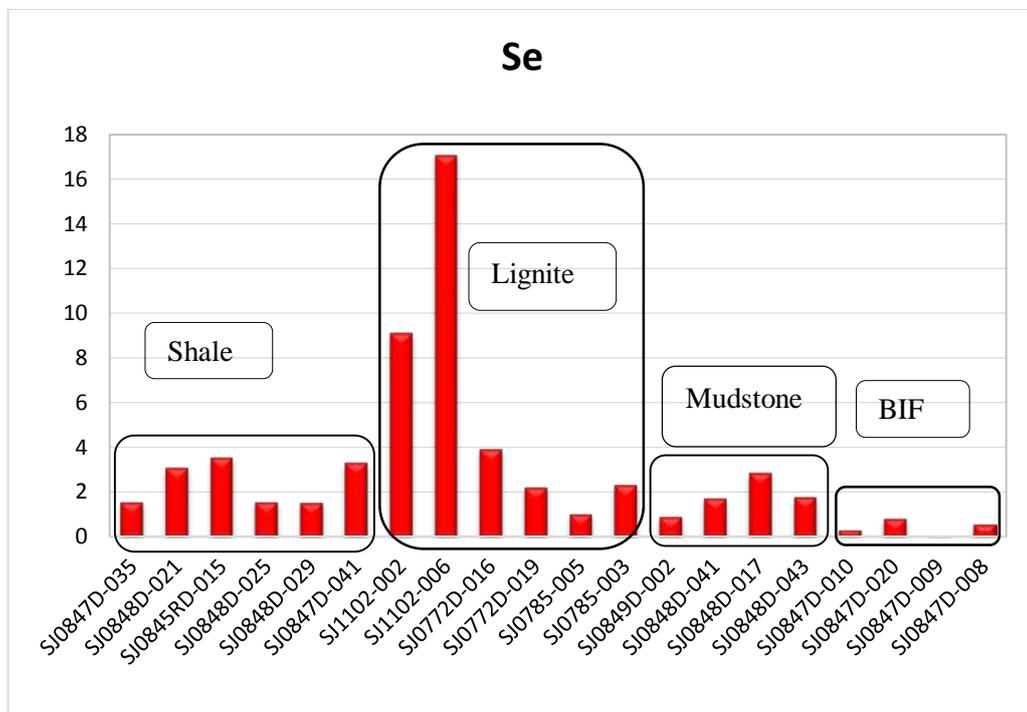


Figure 5.1: Se concentrations in 20 prospective waste rock samples from South Jimblebar prospect displayed according to rock types (values in ppm).

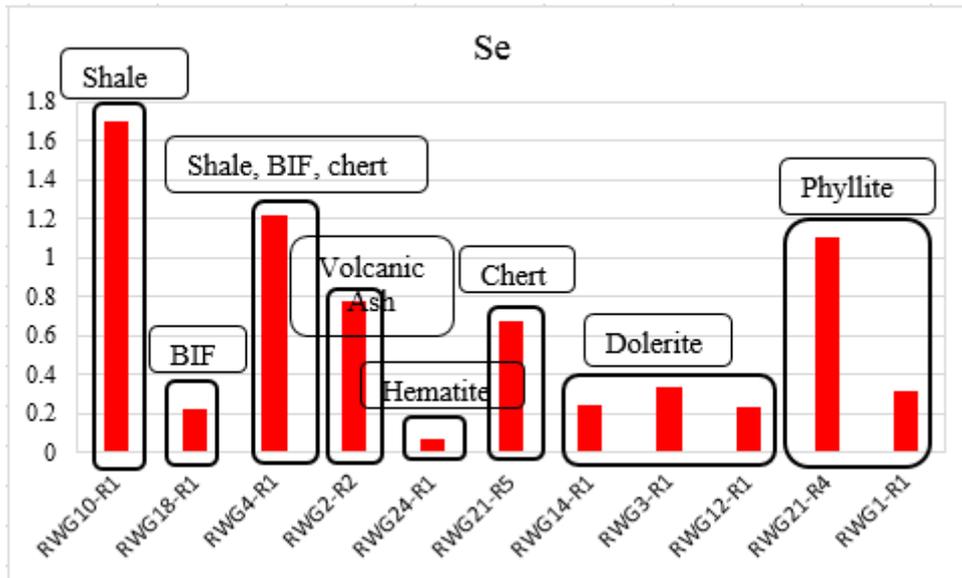


Figure 5.2: The mean Se concentration in 11 waste rock samples from Goldsworthy mine according to rock type (values in ppm).

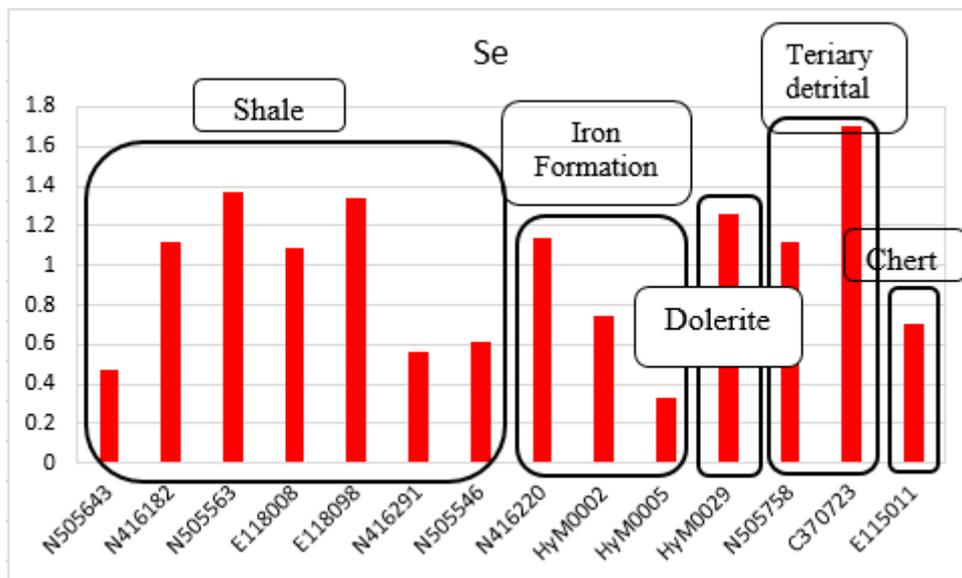


Figure 5.3: The mean Se concentration in 14 waste rock samples from Yandicoogina mine according to rock type (values in ppm).

Shale and lignite deposits commonly contain sulphide minerals and this is a likely source of the Se (Wen and Carignan, 2011). Generally, pyrite minerals contain shale and lignite in the Pilbara. When pyrite is exposed in the Earth's surface to oxygen and

water it reacts to form sulfuric acid, which in turn dissolves salts and heavy metals forming a toxic seepage known generally as acid and metalliferous drainage or acid mine drainage. As such, AMD risks are a comparatively recent but significant environmental development in the Pilbara as mining proceeds (Roche and Mudd 2014). Mining operations thus excavate shale and lignite and bring them to the surface environment where they are exposed to oxidising conditions. The weathering of lignite and shale oxidizes the sulphide minerals and produces local acidity which can then facilitate environmental release of elements such as Se. Although, the concentration of Se in the rocks was not more than the West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010), there is the possibility of an increase in the levels of Se in the environment as a result of the weathering process.

Selenium contents were also high in the mudstone samples in comparison with other types of waste rock in this study. The mudstone and phyllite also have a significant content of S and organic materials. Consequently, the results obtained from waste rocks from the three mine sites in the Pilbara region confirm that high Se contents can be contained in S rich sedimentary deposits (Strawn et al., 2002).

In batch 6 samples from Mt. Goldsworthy mine were analysed that contains phyllite, dolerite, shale, chert, hematite and BIF. BIF and hematite samples were selected for analysis as rocks that contain high level of iron. Phyllite, dolerite and shale were selected as rocks containing relatively high level of C and S and organic matters. Chert was considered as a rock type with a very low level of iron. From the comparison of the analytical results for these rock types, it can be seen that the concentration of Se in the shale, phyllite, and dolerite was greater than in the BIF and hematite. Chert with a low level of iron contained higher Se than BIF and hematite. So, in this study no correlation between Se and Fe was observed while there is a positive correlation between C/S and Se (Figure 5.2).

Selenium is commonly substituted in S and when natural oxidation and weathering of sulphide minerals containing Se occurs, the Se may naturally be released into environment (Moreno-Jiménez et al., 2013). In this study, the maximum concentration of Se in the three regions of Pilbara was assessed in the lignite and shale samples. Generally, shale and lignite present in the rock and soils of Pilbara area contain pyrite. According to Strawn et al., (2002), pyrite can be a significant source of Se. Human activities including mining processes and groundwater drawdown have exposed pyritic minerals to weathering and subsequent oxidization of iron sulphur materials. This can cause Acid Mine Drainage (AMD), resulting in the accelerated release of elements in acidic drainage and the precipitation of secondary minerals. When sulphide minerals and pyrite are weathering, Se present in them will undergo oxidation. The speciation of this trace element to selenite and selenate will allow transport to groundwater and surface water and subsequent absorption by plants and animals (Strawn et al., 2002). Hence, in regard to the results obtained in this study for shale and lignite, there is likely some potential for Se to be released from stratigraphic units containing sulphide materials such as shale and lignite (when the weathering occurs).

The speciation of Se depending on redox conditions and geological setting of the area may release Se to the environment. Adsorbed SeO_3^{2-} selenium-bearing pyrite and ferroselite (that are comprised iron sulphide) are important geochemical forms of selenium. Ferroselite is typically formed from the interface between altered sandstone containing limonite, goethite, and hematite and pyritic minerals which contain low selenium level. With oxidation and destruction pyrite and ferroselite, selenium and ferrous iron are released to environment. Ferroselite, then, is stable in an environment more oxidizing than is pyrite (Howard, 1977). In the Pilbara, most mining processes are performed below ground level and almost near groundwater, requiring dewatering. Consequently, pyrite, shale and lignite may be exposed to oxidation. Also, these minerals are brought to surface by mining activities and oxidation often occurs in conditions found in waste rock piles (Roga 2009). In this study was found that there is a positive relationship between accumulation of Se and C/S, but no found any association with Fe.

Generally, in the South Jimblebar prospect area, the abundance of trace elements in shale, lignite and mudstone was more than BIF. The average concentration of trace elements present in the waste rocks of iron ore mining in South Jimblebar prospect in decreasing concentration was: Mn > Cr > V > As > Cu > Se. The concentration of these elements in stockpiles of Goldsworthy mine was in decreasing: Mn > Cr > V > Cu > As > Se. the level of trace elements in the waste rocks of Yandicoogina mine was in declining: Mn > V > Cr > As > Cu > Se. As it is observed the concentration of Mn, Cr, As and V were high in three locations of the Pilbara and their concentration have even exceeded guideline values in some case. Increasing in As and Mn concentrations can have a positive influence on Se contents as there is relationship between accumulation of Se and Mn/As (Nazarenko and Ermakov 1972). However, in this research no correlation between Se and Mn/As was observed. Overall, the level of Se in the samples prepared from stockpiles of iron ore mining in the South Jimblebar area was more than other selected regions in the Pilbara. For examples, the concentration of Mn, Cr, V, Cu and As in stockpiles of iron ore mine waste from the South Jimblebar prospect exceed the West Australia Department of Environment and Conservation guideline values for ecological (EIL) and health investigation levels (HIL) (DEC, 2010). Mine wastes (i.e., waste rock, tailings) are commonly the largest volume of materials handled in the environment. The generation of AMD releases high concentrations of dissolved heavy metals from such sulfidic wastes, an environmental problem of international scale (Blowes et al., 2003).

Acid mine drainage management is a significant global challenge. Unmanaged, it causes ecological destruction in watersheds and the contamination of drinking water by sulphuric acid and heavy metals, including arsenic, lead and copper (Lottermoser, 2010). Remediation of heavy metal contaminated soils is essential to reduce the associated risks. However, the costs of remediating historic mine sites releasing AMD in Australia was estimated at \$100,000 per hectare in 1997, since which time it is likely to have significantly increased (Lottermoser, 2010). Impacts of AMD in the environment can be controlled on three basic levels: i) through prevention of the acid-generating process; ii) deployment of acid drainage migration prevention measures; and iii) the collection and treatment of effluent (Akcil and Koldas, 2006). Furthermore,

the use of saponin was effective for removal of heavy metals from polluted rocks. The removal of heavy metals from rocks increased with decreasing pH of saponin solution. Saponin treatment was effective in removing the exchangeable and carbonate fractions of heavy metals. By precipitation method, heavy metals could be successfully recovered from the soil leachates after saponin treatment (Hong, Tokunaga and Kajiuchi, 2002).

5.2. Conclusion

The study on Se in environmental materials is essential because whilst this element is a necessary micronutrient in the food chain, in excess it can lead to toxicity. Human activities such as mining process can increase potential release of Se to the environment. As a result, in this research, the concentration and distribution of Se in the various rock types encountered in BHP Billiton iron ore mining in the Pilbara region of Western Australia were determined, using ICP-MS method, to provide a better understanding of possible sources of Se contamination to the environment. ICP-MS employing collision cell technology has also proven to be a viable means of determining total Se at the low concentrations commonly present in rocks and soils. However, this study shows that instrumental conditions are critically important during ICP-MS analysis to obtain good quality when dealing with dissolved rocks with various matrices.

5.2.1. Standard Reference Materials

Accurate characterisation of Se in geostandards or reference materials is critical in order to develop the analytical methods for Se measurement. The acid digestion preparation and ICP-MS technique explained in this study, and used for assessment of this element in several geostandards, yielded reasonable accuracy and reproducibility. This was also found for geostandards which contain shale, lignite and coal such as NIST reference materials. Results obtained on reference materials are in agreement with data reported in published values.

Overall, although Se can be simply lost by volatilisation in various protocols which involved acid digestion, ICP-MS method and acid dissolution is an effective technique for Se determination. The estimated average COV% for Se analysis was 10.8%. Additional analyses were applied on the some geostandards without available published values to increase and improve our geochemical knowledge of Se.

5.2.2. Waste Rock Types from Iron Ore Mining in the Pilbara

In this study it was found that, Se concentration is associated with inorganic and organic materials present in the lithologies of shale and lignite stratigraphic section. Hence, it is more likely that Se may be released from weathering and oxidizing of sulphide minerals contained in lignite, shale, mudstone, phyllite and dolerite. In contrast, results obtained in the laboratory do not show any direct relationship between Se contents and iron in the rock suite of the Pilbara. It is just several years that attention has been drawn to the probability of Se release to the environment during iron ore mining in the Pilbara area. Increased environmental awareness, in general, and the drive by iron ore companies, such as BHP Billiton, for best practice in mine closure has caused increased interest in waste rock characterisation. The known affinity of Se for sulphide minerals, and sedimentary ironstones, carbonaceous materials, gives believability that Se may be mobilised by the excavation of waste rocks that include pyritic black shales (Strawn et al., 2002).

Despite current questioning of the potential risk of Se contamination from Pilbara iron ore mining, there are very few reliable data for the concentration of Se in the rocks of the province with which to address the question. Most of this information can be found in company and consultants' reports. The data that have been generally obtained by commercial analytical laboratories for the mining companies have given the very low overall content of selenium in crustal rocks. The most Se data for rocks of the Pilbara have been produced using ICP-MS, which has a lower limit of determination in the ppb or ppt (parts per trillion) range for many elements (Plant et al., 2005).

Generally, determination of the waste rocks of iron ore mining of South Jimblebar prospect contained the highest Se concentration, in comparison to Mt. Goldsworthy and Yandicoogina mine sites. However, the level of Se in these regions was not more than the West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010). Nevertheless, there is potential for release of Se during weathering of certain waste rocks, and thus possible effects on sensitive components of the environment.

5.3. Recommendations for Future Work

The known importance of Se to human and animal health, and the increasing interest in the behaviour of trace elements in the environment requires both reliable means of analysis of the element and its chemical species in geological materials and also materials of known Se content by which to evaluate the results. Studies are also required to increase the availability of geological standards with reliably known Se content. Further detailed study is required to investigate the effects of different matrixes on the analysis by ICP-MS, such as high Fe and Al. While not a part of the present study, continuous-flow atomic fluorescence spectrometry (CF-AFS) using hydride generation shows considerable promise in the analysis of Se in digested rock samples free from chemical matrix interferences and with little matrix effects for most rock solutions (Bakirdere, 1980). A study that employs both ICP-MS and CF-AFS could be most illuminating as to the cause of variance in results.

Although the Se concentration in the BHP Billiton iron ore mining was lower than West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010), the continuous weathering of sulphide materials can have negative impact on the environment. Consequently, it is suggested that the results obtained from waste rocks of iron ore mining in previous research are compared with recent results to assess potential future Se release and impacts. Moreover, to investigate the mobilization and exposure of Se to air, water and soil, the accumulation of Se should be determined in

the different layers of sediments, water and plants. The analysing of plant material can be important because it provides a transfer pathway for this element to enter the food chain.

5.4. Addendum to Study

After completion of data collection for this study, during the writing of this thesis, a PSA Millennium Excalibur® Continuous Flow Atomic Fluorescence Spectrometer (CF-AFS) was acquired by EIGG. Employing hydride generation, the instrument has the capability of determining Se at concentrations of 1 ppt (part per trillion) in solution with no chemical interference from matrix elements. One session was made available for this study during the trialling of the technique for Se analysis of geological materials. Analysis of Se using CF-AFS was beyond the original scope of the present study.

Using CF.AFS, it was possible to analyse the same digested rock samples that were prepared for this study, after dilution with 40% hydrochloric acid, thus providing a useful comparison with the results obtained by ICP-MS. The instrument was calibrated using a suite of six standard solutions prepared from a commercially available certified 1000 mg/l Se standard solution (SpectrosoL®). Digest solutions of five standard reference materials were selected for CF-AFS analysis. The Se concentrations were CH₄ and NIST fly-ash (1633c) for which there were the most secure published values, and three mine tailings reference standards (RTS-1, RTS-2, RTS-3) for which the results produced by ICP-MS were significantly, and uniformly, lower than the published values (Table 3.4). Results of CF-AFS analysis for Se are shown in Table 5.1. Each is the mean of a duplicate analysis using the digest solution originally prepared for ICP-MS analysis. It must be stressed that the results were produced very shortly after installation of the Millennium Excalibur instrument and some instrumental errors and imprecision may have occurred.

Values for Se produced using CF-AFS were equivalent to the published recommended value of 13.9 ppm, and also that produced using ICP-MS where the fly-ash was

employed as a check standard for Se by TSW Analytical (Table 5.1). The close agreement of both results with the published value indicates that the acid digestion procedure was effective in placing the analyte quantitatively into solution. The mean of the results of analysis of two preparations of the gold ore CH₄ using CF-AFS was a little below (94% of) the certified value. This is in contrast with the mean of values for the same two prepared solutions obtained using ICP-MS that was just 76% of the certified value. This is indicative that the shortfall in the ICP-MS result for Se, which was consistently obtained from 7 separate sample preparations, is a product of the instrumental analysis, rather than incomplete dissolution, or volatile loss of the analyte during sample preparation.

The Se results obtained for the three mine tailings standards (RTS1-3) were indicative of the complexity arising when attempting to determine one analyte in a matrix comprising many more concentrated elements having very different chemical behaviour (Table 5.1). It also highlights the limitations, experienced in the present study, of the uncertain nature of published values for Se in many standard reference materials for which values of other trace elements are securely known. In the case of RTS-1, RTS-2 and RTS-3, the values for Se obtained using CF-AFS were less than those generated by ICP-MS, although they were more similar than the considerably greater published values. In this case, results of between 8 - 15% reflects differences in the analytical techniques.

| ISRM | Beaker | CF-AFS | ICP-MS | Published value |
|-----------------------|--------|--------|--------|-----------------|
| CH₄ | 19 | 2.01 | 1.61 | 2.1 |
| | 21 | 1.94 | 1.61 | |
| NIST | 10 | 14.0 | 13.8 | 13.9 |
| | 11 | 13.9 | 13.8 | |
| RTS-1 | 7 | 21.5 | 24.6 | 40 |
| RTS-2 | 9 | 30.4 | 35.9 | 57 |
| RTS-3 | 18 | 34.5 | 37.5 | 61 |

Table 5.1: Selenium concentrations determined in solutions of standard reference materials from in this study, using CF-AFS, with comparison to results obtained by ICP-MS and the published values. All values in ppm.

REFERENCES

- Abzalov, M. Z. Menzel, B. Wlasenko, M. and Phillips, J. 2007. "Grade Control at the Yandi Iron Ore Mine, Pilbara Regin, Western Australia- Comparative Study of the Blastholes and Reverse Circulation Holes Sampling." Iron Ore Conference 2007, 37-43. Carlton, Victoria: Australasian Institute of Mining and Metallurgy.
- Akcil, A., Koldas, S. 2006. Acid Mine Drainage (AMD): Causes, Treatment and Case Studies. Journal of Cleaner Production 14: 1139-1145.
- Ansong, E. Yang, W and Diamond, A.N. 2014. "Molecular cross-talk between members of distinct families of selenium containing proteins." Molecular Nutrition & Food Research no. 58 (1):117-123.
- API Management Pty Ltd. 2011. West Pilbara Iron Ore Project Stage 1 Mine and Rail Proposal.
<http://www.epa.wa.gov.au/EIA/EPAREports/Documents/1409/Rep1409%20-%20WPIOP%20-%20App5%20-%20Main%20report.pdf>.
- Bakirdere, S., ed. 1980. Speciation studies in soil, sediment, and environmental samples. Turkey: Boca Raton : Taylor & Francis

<http://www.crcnetbase.com.dbgw.lis.curtin.edu.au/isbn/9781466594852>
- Barber, M. and Jackson, S. (2011). Indigenous water values and resource development pressures in the Pilbara region of north-west Australia. Australian Aboriginal Studies 2011(2): 32-49

<http://search.informit.com.au/documentSummary;dn=822790039777820;res=IELIND>
- Barnes, S. and Jones, S. 2013. "Deformed Chromitite Layers in the Coobina Intrusion, Pilbara Craton, Western Australia." Economic Geology no. 108 (2):337-354.
- Belzile, N., Y. w. Chen, et al. (2000)."Early diagenetic behaviour of Selenium in freshwater sediments." Applied Geochemistry 15: 1439-1454.

- Beytut, E. Karatas, F. Beytut, E. 2002. "Lambs with white muscle disease and selenium content of soil and meadow hay in the region of Kars." Turkey. Vet. 163:214–7.
- BHP Billiton outer harbour development. 2011. Proposed dewatering and discharge to salmon Creek: impact assessment. Adelaide Terrace
- Blake, J R. 2007. "Application of Borehole Imagery in Iron Ore- Examples from the Hamersley Group, Western Australia." Iron Ore Conference 2007, 45-50. Carlton, Victoria: The Australasian Institute of Mining and Metallurgy.
- Blake, T. S. 2001. "Cyclic continental mafic tuff and flood basalt volcanism in the Late Archaean Nullagine and Mount Jope Supersequences in the eastern Pilbara, Western Australia." Precambrian Research no. 107 (3-4):139-177.
- Blake, T. S., R. Buick, S. J. A. Brown, and M. E. Barley. 2004. "Geochronology of a Late Archaean flood basalt province in the Pilbara Craton, Australia: constraints on basin evolution, volcanic and sedimentary accumulation, and continental drift rates." Precambrian Research no. 133:143-173.
- Bodycoat, F. M. 2010. "Stratigraphic and structural setting of iron mineralisation at E Deposit (East), Area C, Hamersley Province, Western Australia. "Applied Earth Science 119 (1).
- Boyle, C. 2007. "Comparison of Multivariate Conditional Simulation Methods at the Yandicoogina Iron Ore Deposit." Iron Ore Conference 2007 57-77. Carlton, Victoria: Australasian Institute of Mining and Metallurgy.
- Blowes, D.W., Ptacek, C. J., Jambor, J. L., Weisener. C. G. 2003. The Geochemistry of Acid Mine Drainage. Treatise on Geochemistry 9: 149-204.
- Bueno, M. Pannier, F. and Potin-Gautier, M. 2007. Determination of organic and inorganic selenium species using HPLC-ICP-MS. Agilent Technologies.
- Canadian Certified Reference Materials Project, 2010. "Certificate of Analysis, CH4." edited by CanmetMINES, Canada.
- Canadian Certified Reference Materials Project, 2009. "Certificate of Analysis RTS-1, RTS-2 and RTS-3". Edited by CanmetMINES, Canada.

- Clout, J. M. F. 2006. "Iron formation-hosted iron ores in the Hamersley Province of Western Australia." *Applied Earth Science (Trans. Inst.Min. Metall.B)*. 115 (4):115-125.
- Department of Environment and Conservation, 2010. Assessment levels for Soil, Sediment and Water.
- Exponent .2010. Selenium technical memorandum.
<http://www.tva.com/kingston/exponent/Selenium%20technical%20paper.pdf>.
- Fajrin, A. M. 2013. "Environmental Impact of the Storage of Black Shale and Lignite Waste Rocks at the South Jimblebar Iron Ore Mine, Western Australia." Master of Philosophy, Department of Applied Geology, Curtin University of Technology.
- Fordyce, F.F. 2007. "Selenium geochemistry and health." *Ambio*. 36:94–7.
- Fortescue.2011. Cloud break Life of Mine Public Environmental Review.
http://reports.fmgf.com.au/Cloudbreak_Expansion_Project_PER/Report/Fortescue%20Cloudbreak%20Life%20of%20Mine%20%20Public%20Environmental%20Review%20-%20April%202011.pdf
- Geo, T. M. P. 2011. Ni 43-101 Technical Report and Resource Estimation of the Cerro Aeropuerto and La Luna Deposits, Borosi Concessions, Región Autónoma Del Atlántico Norte, Nicaragua. British Columbia.
<http://www.calibremining.com/i/pdf/techreports/43-101-report-April-2011.pdf>
- Govindaraju, K. 1989. "1989 Compilation of Working Values and Samples Description for 272 Geostandards." *Geostandards Newsletter* 13: 1-113.
<http://onlinelibrary.wiley.com/doi/10.1111/j.1751-908X.1989.tb00476.x/epdf>
- Hall, G. C. Kneeshaw, M. 1990. "Yandicoogina- Marillana pisoltic iron deposits." *Geology of the Mineral Deposits of Australia and Papua New Guinea*:1581-1586.
- Hartikainen, H. 2005. "Biogeochemistry of selenium and its impact on food chain quality and human health." *Journal of Trace Elements in Medicine and Biology* 18: 309-318.

- Haug, A. Graham, R. D. Christophersen, O. A., and Lynos. G. H. 2007. "How to Use the World's Scarce Selenium Resources Efficiently to Increase the Selenium Concentration in Food." *Microbial Ecology in Health and Disease* 19: 209_228.
- Hong, K. J., S. Tokunaga, and T. Kajiuchi. 2002. "Evaluation of Remediation Process with Plant-Derived Biosurfactant for Recovery of Heavy Metals from Contaminated Soils." *Chemosphere* 49 (4): 379-387.
- Howard, J. and Hatten, III. 1977. "Geochemistry of Selenium: Formation of Ferroselite and Selenium Behavior in the Vicinity of Oxidizing Sulfide and Uranium Deposits." *Geochimica et Cosmochimica Acta*, 41 (11): 1665-1678.
- Imai, N. Terashima, S. Itoh, S. and Ando, A. 1996. 1996 compilation of analytical data on nine GSJ geochemical reference samples, "Sedimentary rock series", *Geostandards Newsletter*, 20,165-216.
- Irwin, R. J. 1997. Environmental contamination encyclopaedia selenium entry.
<http://www.nature.nps.gov/hazardssafety/toxic/vanadium.pdf>.
- Jochum, K. P. and Seufert H. M. 1990. "Multi- Element Analysis of 15 International Standard Rocks by Isotope- Dilution Spark Source Mass Spectrometry." *Geostandards and Geoanalytical Research* no. 14 (3):469-473.
- Johnson, S. L., and Wright, A. H. 2001. Central Pilbara Groundwater Study. In *Hydrogeological Records Series: Water and Rivers Commission Resource Science Division*.
- Ker, P. 2014. "BHP Bullish on Iron Ore Production." *Business Day-Sydney Morning Herald*
<http://www.smh.com.au/business/mining-and-resources/bhp-bullish-on-iron-ore-production-20140416-36qlh.html>
- Kerr, T. L. OSullivan, A. P. Podmore, D.C. Turner, R. and Waters, P. 1994. "Geophysics and iron ore exploration: examples from the Jimblebar and Shay Gap-Yarrie regions, Western Australia." *Exploration Geophysics* no. 25 (3):169-170.

- Kneeshaw, M. Kepert, D. A. Tenas, I. J. and Pudovskis, M. A.2003. "From Mount Goldsworthy to Area C – reflections on forty years of iron ore exploration in the Pilbara." *Applied Earth Science*. 112.
- Lemly, D. 2007. "A procedure for NEPA assessment of Selenium hazards associated with mining." *Spring Science* 125: 361-375.
- Lenz, M., and Lens, P. N. L. 2009. "The essential toxin: The changing perception of selenium in environmental sciences." *Science of the total environment* 407: 3620-3633.
- Li, F. Goessler, W and Irgolic, K. J. 1999. "Determination of Selenium Compounds by HPLC with ICP-MS or Faas as Selenium-Specific Detector." *Europe PubMedCentral* 17 (3): 240-244.
- <http://europepmc.org/abstract/med/12549116>
- Lottermoser, B. G. 2010. *Mine Wastes: Characterization, treatment and environmental impacts*.
- Luttrell, G. W. 1959. *Annotated Bibliography on the Geology of Selenium-Geological Survey Bulletin*. Washington, U. S.
- Milne, J. B. 1998. "The uptake and metabolism of inorganic Se species." In *Environmental Chemistry of Selenium*, edited by Eds W. T. Frankenberger Jr and R. A. Engberg. Marcel Dekker: New York.
- Minaev, V. S. Timoshenkov, S. P. Kalugin, V.V. 2005. "Structural and phase transformations in condensed selenium." *J Optoelectron Adv M*.7:1717.
- Moreno-Jiménez, E. Clemente, R. Mestrot, A. Mehrag, A.A.2013. "Arsenic and selenium mobilisation from organic matters treated mine spoil with and without inorganic fertilisation". *Environmental pollution*. 173:238-244.
- Morris, RC. and Kneeshaw, M. 2011. "Genesis modelling for the Hamersley BIF-hosted iron ores of Western Australia: a critical review." *Australian Journal Of Earth Sciences* no. 58 (5):417-451.

- Moxon A. L. 1937. Alkali disease or selenium poisoning. South Dakota State College Bulletin. 311:99
- Mumme, W. G. 1976. "Prouditite from Tennant Creek, Northern Territory, Australia: its crystal structure and relationship with weibullite and wittite." American Mineralogist. 61:839-852.
- Nazarenko, I. I., and Ermakov, A. N. 1972. "Analytical chemistry of selenium and tellurium." Jerusalem: Israel Program for Scientific Translations; New York: Halsted Press.
- Presser, T.S., Swain, W.C., 1990. "Geochemical evidence for Se mobilization by the weathering of pyritic shale". Applied Geochemistry 5: 703–717.
- Plant, J.A. Kinniburgh, D.G. Smedley, P.L. Fordyce, F. M. and Klinck. B.A. 2005. "Arsenic and Selenium." In Treatise on Geochemistry ed. Barbara Sherwood Lollar. Amsterdam; Elsevier
- Potts, P. J., and Kane, J. S. 1992. "Terminology for geological reference material values: A proposal to the international organisation for standardisation (ISO), producer and users." Geostandards and Geoanalytical Research no. 16 (2):333-341.
- Ralston, N.V.C., Unrine, J. & Wallschläger, D. (2008): Biogeochemistry and analysis of selenium and its species, North American Metals Council, Washington, DC.
- <http://www.namc.org/docs/00043673.PDF>
- Roche, C., and Mudd, G. 2014. "An Overview of Mining and the Environment in Western Australia." In Resource Curse or Cure? On the Sustainability of Development in Western Australia, edited by Martin Brueckner, Angela Durey, Robyn Mayes and Christof Pforr. Springer-Verlag Berlin Heidelberg.
- http://link.springer.com/chapter/10.1007/978-3-642-53873-5_12#page-2
- Roga, C. J. 2009. "Acid Generating Characterisation of Stored Waste Rocks and Current Impact Upon the Surface Environment, Mt Goldsworthy Iron Ore

- Mining, Western Australia." Master of Philosophy, Department of Applied Geology, Curtin University of Technology, Perth, WA.
- Santana, R.R. McDowell, L. R. Macchiavelli, R. Vázquez, A. Wilkinson, N.S.2006. "Selenium fertilization of star grass pastures in central Puerto Rico. "Commun Soil Sci Plant Anal.37:673-8.
- Savard, D. Bedard, L. P, and Barnes. S. J. 2009. "Selenium Concentrations in Twenty-Six Geological Reference Materials: New Determinations and Proposed Values." Geostandards and Geoanalytical Research 33: 249-259.
- Schilling, K. Johnson, T. and Wilcke, W. 2011. "Selenium partitioning and stable isotope-ratios in urban Topsoils." Soil Science Society of America 75 (4):1328-1338.
- Stephan, C. Hineman, A. 2014. Iron Nanoparticles by Sp-ICP-MS: Overcoming Spectral Interferences Using Universal Cell Technology. PerkinElmer Inc, CA
- Stone, M. S. George, A. D. Kneeshaw, M. and Barley. M. E. 2003. "Stratigraphy and sedimentary features of the Tertiary Yandi channel iron deposits, Hamersley Province, Western Australia." Applied Earth Science 112.
- Strawn, D. Doner H. Zavarin, M. McHgo, S. (2002). "Microscale Investigation into the Geochemistry of Arsenic, Selenium, and Iron in Soil Developed in Pyritic Shale Materials." Geoderma 108: 237-57.
- Strategen. 2011. Brockman 2 Detrital Iron Ore Mine Extension Phase 2B. Subiaco WA: Strategen Environmental Consultants Pty Ltd.
- Stroud, J. L. McGrath, S. P. and Zhao, F. J. 2012. "Selenium speciation in soil extracts using LC-ICP-MS." International Journal of Environmental Analytical Chemistry 92 (2):222-236.
- <http://www.tandfonline.com/doi/abs/10.1080/03067310903111661>
- Storkey, A. Doecke, A. and Whaanga, A. 2007. "Stratigraphy of the Western Channel Iron Deposits of the BHP Billiton Iron Ore Marillana Creek Operations, Western

Australia. "Iron Ore Conference 2007. Carlton, Victoria: Australasian Institute of Mining and Metallurgy.

Sugitani, K. Mimura, K. Suzuki, K. Nagamine, K. and Sugisaki, R. 2003. "Stratigraphy and sedimentary petrology of an Archean volcanic-sedimentary succession at Mt. Goldsworthy in the Pilbara Block, Western Australia: implications of evaporite (nahcolite) and barite deposition." *Precambrian Research* no. 120 (1-2):55-79.

Thornton, I. 1983. "Applied environmental Geochemistry." London: Academic Press.

Trendall, A. F. 2002. "The significance of Iron-Formation in the Precambrian Stratigraphic Record." *International Association of Sedimentology*: 33-66.

Wen, H., and Carignan, J. 2011. "Selenium isotopes trace the source and redox processes in the black shale-hosted Se-rich deposits in China." *Geochimica et Cosmochimica Acta* (75): 1411–1427.

Wise, S. A., and Watters, R. L. 2011. "Certificate of Analysis, Standard Reference Material, Trace Elements in Coal Fly Ash."

World Health organization. 1987. Selenium. Geneva: World Health Organization.

Appendix # 1

Geological Reference Materials Used in this Study and Their Results

| Geostandards | Rock types | Centre/ Institute | Selenium | Arsenic | Vanadium | Chromium | Manganese | Copper |
|-----------------------------|----------------------------|--|-----------------|---------------|---------------|--------------|------------------|---------------|
| MAG-1 | Marine Mud | U.S. Geological Survey | 1.16 | 9.2® | 140® | 97® | | 30® |
| BIR-1 | Icelandic Basalt | U.S. Geological Survey | 0.02 (Re) | 0.44(I) | 310+/-11(I) | 382® | 135+/-20(I) | 125+/-4 (I) |
| JSO-1 | Soil | Geological Survey of Japan | | 8.10+/-0.1(m) | 300+/-3(m) | 71.0+/-2(m) | 0.197+/-0.002(m) | 169+/-2(m) |
| JMS-1 | Marine Sediment | Geological Survey of Japan | | 18 (m) | 127(m) | 133(m) | | 88(m) |
| JMS-2 | Marine Sediment | Geological Survey of Japan | | 35(m) | 183(m) | 78(m) | | 447(m) |
| BCSS-1(June-30-1988) | Marine Sediment | National Research Council Canada | 0.43® | 11.1® | 93.4® | 123® | 300® | 18.5® |
| BCSS-1 (Feb-6-1986) | Marine Sediment | National Research Council Canada | 0.43® | 11.1® | 93.4® | 123® | 300® | 18.5® |
| MESS-1 (July-9-1986) | Marine Sediment | National Research Council Canada | 0.34® | 10.6® | 72.4® | 71® | 660® | 25.1® |
| CH4 | Gold Ore | Natural Resources Canada | 2.1 © | 8.8(P) | | 114(P) | 430(P) | 2000© |
| RTS-1 | Sulphide Ore Mill Tailings | Canadian Certified Referece Materials Project | 40(I) | 8.2+/-1.6(P) | | 50(I) | 1900(I) | 595© |
| RTS-2 | Sulphide Ore Mill Tailings | Canadian Certified Referece Materials Project | 57(I) | 6.3+/-1.8(P) | | 125(I) | 400(I) | 670© |
| RTS-3 | Sulphide Ore Mill Tailings | Canadian Certified Referece Materials Project | 61(I) | 9.1+/-2.6© | | 75(I) | 2000(I) | 2820© |
| NIST | Coal Fly Ash | National Institute of Standards and Technology | 13.9 ± 0.5 (Re) | 186.2 ± 3.0 © | 286.2 ± 7.9 © | 258 ± 6 (Re) | 240.2 ± 3.4 © | 173.7 ± 6.4 © |
| JCU-1 | Copper Ore | Geological Survey of Japan | | | | | | |
| JDo-1 | Dolomite | Geological Survey of Japan | 0.05® | 0.114® | 3.14® | 7.93® | | 1.41® |
| JR-3 | Rhyelite | Geological Survey of Japan | | | | | | |
| JS1-1 | Slate | Geological Survey of Japan | | 14.9® | | 60.9® | | 40.8® |
| JCh-1 | Chert | Geological Survey of Japan | | 0.567® | 10.4® | 7.04® | | 15.3® |
| JH-1 | Hornblendte | Geological Survey of Japan | | | | | | |
| JLK-1 | Lake sediment | Geological Survey of Japan | 0.641® | 26.8® | 117® | 69® | | 62.9® |
| JSd-3 | Stream Sediment | Geological Survey of Japan | 1.29® | 252® | | 35.3® | | 426® |
| JSd-2 | Stream Sediment | Geological Survey of Japan | 18.8(P) | 38.6® | | 108® | | 1117® |
| JSd-1 | Stream Sediment | Geological Survey of Japan | 0.25(P) | 2.42® | | 21.5® | | 22® |
| JGb-2 | Gabbro | Geological Survey of Japan | | | | | | |
| JSo-2 | Soil | Geological Survey of Japan | | 1076(m) | | 1118(m) | | 1276(m) |

® is referred to recommended values

(m) is the mean value from the study of (Imai et al., 1996)

(Re) is referred to reference value

(I) is referred to information values

(P) is referred to provisional values

© is referred to certified values

Table 1A: Geological reference materials used in this study in assessing accuracy of analytical results

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|---------------------------|--------|-------------------|--------------------------|--------------------------|-------------|----------------------------|--------------------------|
| | | ppm | ppm | ppm | ppm | ppm | ppm |
| CH₄ | | 2.10 [©] | 8.80 (P) | | 114 (P) | 430 (P) | 2000 [©] |
| <i>Batch 5</i> | 19 | 1.61 | 4.37 | 78.2 | 98.8 | 360 | 1331 |
| | 21 | 1.61 | 4.65 | 79.7 | 99.2 | 370 | 1351 |
| | 22 | 1.63 | 5.41 | 50.4 | 101 | 376 | 1376 |
| | 30 | 1.54 | 6.86 | 76.9 | 95.8 | 357 | 1285 |
| | 31 | 1.63 | 6.93 | 82.6 | 101 | 377 | 1370 |
| | 32 | 1.77 | 7.86 | 80.4 | 100 | 370 | 1350 |
| | 33 | 1.78 | 7.68 | 79.9 | 100 | 369 | 1357 |
| CoV% | | 5.43 | 22.8 | 14.8 | 2.13 | 2.07 | 2.25 |
| NIST(Coal Fly Ash) | | 13.90+/- 0.5 (Re) | 186.2+/-3.0 [©] | 286.2+/-7.9 [©] | 258+/-6(Re) | 240.2 +/- 3.4 [©] | 173.7+/-6.4 [©] |
| <i>Batch 3</i> | 10 | 13.8 | 171 | 235 | 194 | 199 | 132 |
| | 11 | 13.8 | 174 | 244 | 202 | 203 | 135 |
| | 12 | 14.2 | 179 | 248 | 207 | 209 | 138 |
| CoV% | | 1.68 | 2.38 | 2.80 | 3.25 | 2.50 | 2.33 |
| Systematic Error | | 1.02 | 1.03 | 1.05 | 1.05 | 1.04 | 1.04 |
| <i>Batch 4</i> | 26 | 12.4 | 162 | 240 | 190 | 197 | 130 |
| | 25 | 12.1 | 157 | 227 | 176 | 186 | 116 |
| CoV% | | 1.53 | 2.29 | 3.93 | 5.32 | 3.78 | 8.19 |

Table 1B: Concentrations of Se and selected trace elements in International Standard reference material CH₄ compared to certified and provisional values; and NIST coal fly-ash compared to reference and certified values. The coal ash was employed by the ICP-MS analytical laboratory (TSW Analytical) as a reference material

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|-----------------------------|--------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------|-------------------------|
| | | ppm | ppm | ppm | ppm | ppm | ppm |
| MAG-1 | | 1.16 | 9.20[®] | 140[®] | 97.0[®] | | 30.0[®] |
| <i>Batch 1</i> | 19 | 2.02 | 10.8 | 153 | 101 | 666 | 28.1 |
| | 7 | 1.96 | 10.8 | 154 | 101 | 675 | 28.1 |
| | 39 | 1.91 | 10.1 | 146 | 95.8 | 632 | 26.2 |
| | 11 | 2.23 | 10.8 | 155 | 104 | 649 | 28.2 |
| | 36 | 1.63 | 9.31 | 141 | 93.4 | 606 | 26.2 |
| | 37 | 1.34 | 8.79 | 123 | 82.3 | 527 | 23.3 |
| | 22 | 1.75 | 10.3 | 148 | 97.3 | 625 | 27.3 |
| CoV % | | 10.9 | 5.80 | 3.61 | 3.99 | 4.05 | 3.32 |
| BCSS-1(June-30-1988) | | 0.43[®] | 11.1[®] | 93.4[®] | 123[®] | 300[®] | 18.5[®] |
| <i>Batch 1</i> | 12 | 1.88 | 12.1 | 99.9 | 105 | 198 | 17.9 |
| BCSS-1 (Feb-6-1986) | | 0.43[®] | 11.1[®] | 93.4[®] | 123[®] | 300[®] | 18.5[®] |
| <i>Batch 1</i> | 32 | 1.64 | 11.9 | 97.0 | 100 | 197 | 17.3 |
| | 6 | 1.56 | 11.8 | 97.4 | 100 | 205 | 17.3 |
| | 27 | 1.11 | 11.8 | 96.1 | 105 | 192 | 17.6 |
| | 26 | 1.71 | 11.6 | 96.9 | 99.6 | 207 | 17.5 |
| CoV % | | 18.2 | 1.50 | 1.46 | 2.62 | 3.16 | 1.33 |
| <i>Batch 3</i> | 7 | 1.61 | 10.9 | 82.6 | 89.6 | 198 | 15.6 |
| | 8 | 1.53 | 11.1 | 83.2 | 90.0 | 200 | 15.9 |
| | 9 | 1.52 | 10.6 | 80.3 | 89.2 | 194 | 15.8 |
| CoV% | | 3.18 | 2.20 | 1.89 | 0.43 | 1.42 | 0.86 |
| Systematic Error | | 1.03 | 1.04 | 1.03 | 1.00 | 1.02 | 1.00 |
| <i>Batch 7</i> | 2 | 1.05 | 8.85 | 80.0 | 79.3 | 161 | 23.3 |
| | 3 | 1.06 | 9.09 | 81.9 | 80.8 | 161 | 23.1 |
| cov% | | 1.04 | 1.89 | 1.60 | 1.28 | 0.22 | 0.84 |
| MESS-1(Jul-9-1986) | | 0.34[®] | 10.6[®] | 72.4[®] | 71.0[®] | 660[®] | 25.1[®] |
| <i>Batch 1</i> | 31 | 1.30 | 10.8 | 75.6 | 58.2 | 395 | 25.4 |
| | 8 | 2.03 | 11.6 | 77.5 | 60.2 | 426 | 24.7 |
| | 17 | 2.18 | 11.9 | 79.3 | 58.1 | 444 | 27.8 |
| | 13 | 1.99 | 12.4 | 80.7 | 57.8 | 455 | 26.1 |
| | 40 | 1.37 | 11.6 | 75.9 | 57.7 | 406 | 25.8 |
| | 20 | 1.57 | 11.0 | 78.2 | 60.6 | 409 | 24.8 |
| CoV % | | 21.5 | 5.06 | 2.53 | 2.14 | 5.57 | 4.41 |
| <i>Batch 3</i> | 4 | 1.76 | 9.66 | 60.9 | 47.2 | 407 | 21.6 |
| | 5 | 1.73 | 10.4 | 62.8 | 48.6 | 406 | 20.6 |
| | 6 | 2.02 | 11.1 | 67.1 | 52.3 | 439 | 22.5 |
| CoV% | | 8.68 | 7.30 | 4.99 | 5.31 | 4.58 | 4.35 |
| <i>Batch 7</i> | 1 | 1.23 | 8.37 | 63.0 | 44.2 | 331 | 28.1 |
| | 50 | 1.34 | 9.46 | 65.5 | 46.5 | 347 | 31.0 |
| CoV% | | 6.00 | 8.65 | 2.72 | 3.60 | 3.22 | 7.17 |
| BIR-1 | | 0.02 | 0.44 (I) | 310+/-11 (I) | 382[®] | 135+/-20 | 125+/-4 (I) |
| <i>Batch 1</i> | 24 | 1.39 | 0.872 | 377 | 385 | 1410 | 115 |
| | 15 | 1.15 | 0.561 | 377 | 416 | 1401 | 115 |
| | 35 | 1.19 | 0.646 | 372 | 365 | 1401 | 113 |
| CoV% | | 10.3 | 23.3 | 0.76 | 6.63 | 0.36 | 1.00 |

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|----------------|---------------|-----------------|----------------------|----------|-----------------|-----------------|---------------|
| RTS-1 | | 40.0 (I) | 8.2+/-1.6 (P) | | 50.0 (I) | 1900 (I) | 595 © |
| <i>Batch 5</i> | 7 | 24.6 | 8.35 | 87.5 | 22.2 | 1435 | 373 |
| | 8 | 24.8 | 8.41 | 86.1 | 21.4 | 1409 | 362 |
| CoV% | | 0.74 | 0.51 | 1.18 | 2.65 | 1.32 | 2.03 |
| RTS-2 | | 57.0 (I) | 6.3+/-1.8(P) | | 125 (I) | 400 (I) | 670 © |
| <i>Batch 5</i> | 9 | 35.4 | 7.56 | 66.9 | 89.4 | 276 | 473 |
| | 10 | 35.5 | 7.64 | 68 | 77.5 | 282 | 481 |
| CoV% | | 0.10 | 0.74 | 1.15 | 10.03 | 1.46 | 1.15 |
| RTS-3 | | 61.0 (I) | 9+/-2.6 © | | 75.0 (I) | 2000 (I) | 2820 © |
| <i>Batch 5</i> | 17 | 38.7 | 9.85 | 84.1 | 41.6 | 1573 | 1887 |
| | 18 | 37.4 | 9.20 | 79.1 | 38.2 | 1483 | 1824 |
| CoV% | | 2.30 | 4.83 | 4.32 | 6.02 | 4.13 | 2.37 |

Table 1C: Concentrations of Se and selected trace elements in various ISRMs for which there are published (but not certified) Se values, as indicated

| Rock No | Beaker | Se | As | V | Cr | Mn | Cu |
|------------------|--------|----------|------------------|--------------|----------------|-------------------|-------------|
| JMS-1 | | | 18.0 (m) | 127 (m) | 133 (m) | | 88.0 (m) |
| <i>Batch 1</i> | 33 | 1.21 | 18.8 | 126 | 126 | 636 | 78.7 |
| | 2 | 1.49 | 18.6 | 125 | 125 | 658 | 79.2 |
| CoV% | | 14.6 | 0.81 | 0.62 | 0.62 | 2.34 | 0.48 |
| <i>Batch 7</i> | 46 | 1.08 | 14.2 | 106 | 104 | 539 | 72.8 |
| | 47 | 1.01 | 14.1 | 98.8 | 99.3 | 522 | 67.2 |
| CoV% | | 4.81 | 0.922 | 5 | 3.65 | 2.23 | 5.7 |
| JMS-2 | | | 35.0 (m) | 183 (m) | 78.0 (m) | | 447 (m) |
| <i>Batch 1</i> | 25 | 15.0 | 39.9 | 183 | 71.0 | 15999 | 388 |
| | 16 | 16.2 | 40.1 | 183 | 43.2 | 15814 | 401 |
| CoV% | | 5.51 | 0.42 | 0.31 | 34.45 | 0.82 | 2.21 |
| <i>Batch 3</i> | 1 | 11.2 | 33.4 | 155 | 54.4 | 14309 | 348 |
| | 2 | 10.0 | 30.8 | 140 | 50.0 | 12884 | 319 |
| | 3 | 9.81 | 30.3 | 142 | 50.6 | 12834 | 320 |
| CoV% | | 7.66 | 5.26 | 5.59 | 4.54 | 6.28 | 4.94 |
| Systematic Error | | 0.88 | 0.91 | 0.91 | 0.93 | 0.90 | 0.92 |
| <i>Batch 7</i> | 49 | 7.13 | 27.3 | 138 | 48.0 | 11928 | 290 |
| | 48 | 9.15 | 29.2 | 147 | 56.2 | 12984 | 299 |
| CoV% | | 17.5 | 4.80 | 4.49 | 11.1 | 6 | 2.20 |
| JSd-2 | | 18.8 (P) | 38.6 ® | 125 ® | 108 ® | | 1117 ® |
| <i>Batch 7</i> | 16 | 10.7 | 32.9 | 110 | 73.5 | 707 | 782 |
| JSd-1 | | 0.25 (P) | 2.42 ® | 76.0 ® | 21.5 ® | | 22.0 ® |
| <i>Batch 7</i> | 17 | 0.658 | 1.81 | 68.1 | 16.6 | 525 | 25.3 |
| JLK-1 | | 0.641 ® | 26.8 ® | 117 ® | 69.0 ® | | 62.9 ® |
| <i>Batch 7</i> | 12 | 1.61 | 20.0 | 101 | 55.0 | 1386 | 59.4 |
| JSO-2 | | | 1076 (m) | | 1118 (m) | | 1276 (m) |
| <i>Batch 7</i> | 18 | 4.79 | 715 | 110 | 854 | 767 | 867 |
| JDO-1 | | 0.05 ® | 0.11 ® | 3.14 ® | 7.93 ® | | 1.41 ® |
| <i>Batch 7</i> | 6 | 0.312 | 0.313 | 3.33 | 7.41 | 45.1 | 1.30 |
| JCh-1 | | | 0.567 ® | 10.4 ® | 7.04 ® | | 15.3 ® |
| <i>Batch 7</i> | 9 | 0.073 | 0.485 | 7.91 | 6.05 | 112 | 22.8 |
| JSO-1 | | | 8.10 +/- 0.1 (m) | 300 +/-3 (m) | 71.0 +/- 2 (m) | 0.197+/-0.002 (m) | 169 +/-2(m) |
| <i>Batch 7</i> | 13 | 1.64 | 6.34 | 285 | 58.6 | 1110 | 127 |
| JSd-3 | | 1.29 ® | 252 ® | | 35.3 ® | | 426 ® |
| <i>Batch 7</i> | 14 | 1.61 | 221 | 64.9 | 29.5 | 899 | 313 |
| JS1-1 | | | 14.9 ® | | 60.9 ® | | 40.8 ® |
| | 8 | 1.31 | 12.3 | 114 | 45.6 | 343 | 42.8 |
| JR-3 | 7 | 1.36 | 0.70 | 0.927 | 0.979 | 485 | 12.4 |
| JGb-2 | 15 | 0.16 | 1.24 | 156 | 78.6 | 756 | 18.3 |
| JH-1 | 11 | 0.615 | 1.12 | 192 | 496 | 1141 | 14.7 |
| JCU-1 | 5 | 14.4 | 163 | 6.28 | 6.42 | 3998 | 26172 |

Table 1D: Concentrations of Se and selected trace elements in various JGS standards.

Appendix # 2

**Various waste rocks from iron ore mining and results obtained from waste
rocks BHP Billiton iron ore mining**

| Sample ID | Description |
|-----------|--|
| RWG10-R1* | Shale |
| RWG18-R1• | BIF |
| RWG3-R1* | Dolerite |
| RWG14-R1* | Dolerite |
| RWG21-R5• | Banded chert (Iron stained) |
| RWG24-R1• | Hematite |
| RWG1-R1• | Phyllite |
| RWG2-R2• | Volcanic ash(quartz vein) |
| RWG4-R1• | Shale -Interbanded with chert+ BIF (quartz vein) |
| RWG21-R4* | Banded phyllite |
| RWG12-R1• | Sheared dolerite |

A.

| Sample ID | Description |
|--------------|-------------|
| SJ0847D-035 | Black Shale |
| SJ0848D-021 | Black Shale |
| SJ0845RD-015 | Black Shale |
| SJ0848D-025 | Black Shale |
| SJ0848D-029 | Black Shale |
| SJ0847D-041 | Black Shale |
| SJ1102-002 | Lignite |
| SJ1102-006 | Lignite |
| SJ0772D-016 | Lignite |
| SJ0772D-019 | Lignite |
| SJ0785-005 | Lignite |
| SJ0785-003 | Lignite |
| SJ0849D-002 | Mudstone |
| SJ0848D-041 | Mudstone |
| SJ0848D-017 | Mudstone |
| SJ0848D-043 | Mudstone |
| SJ0847D-010 | BIF |
| SJ0847-020 | BIF |
| SJ0847-009 | BIF |
| SJ0847-008 | BIF |

B.

| Sample ID | Code | Description | Depth from (m) | Depth to (m) |
|-----------|------|---|----------------|--------------|
| C370723 | TD1 | Tertiary detritals | 141 | 144 |
| E115011 | D1 | Colonial Chert Member | 45 | 48 |
| E118098 | RN | Mt. McRae Shale- Nodule Zone | 60 | 63 |
| E118008 | R | Mt. McRae Shale- Undifferentiated | 21 | 24 |
| HYM0029 | HE | Weeli Wolli Dolerite | 7 | 8.5 |
| HYM0002 | HJ | Weeli Wolli Iron Formation | 29 | 29.5 |
| HYM0005 | WW | Weeli Wolli Iron Formation Undifferentiated | 29 | 29.5 |
| N505637 | J1 | Joffre Member-J1 | 99 | 102 |
| N505657 | D4 | Dales Gorge Member-D4 | 141 | 144 |
| N505563 | W | Whaleback Shale | 30 | 33 |
| N416410 | J6 | Joffre Member- J6 | 21 | 24 |
| N416291 | Y | Yandicoogina Shale Member | 36 | 39 |
| N505546 | R | Mt. McRae Shale- Undifferentiated | 105 | 108 |
| N505758 | TD3 | Tertiary detritals | 3 | 6 |
| N505639 | J1 | Joffre Member-J1 | 102 | 105 |
| N505643 | WC | Whaleback Shale- Central Chert | 108 | 111 |
| N505655 | D4 | Dales Gorge Member- D4 | 138 | 141 |
| N416412 | J6 | Joffre Member- J6 | 24 | 27 |
| N416220 | HJ | Weeli Wolli Iron Formation | 12 | 15 |
| N416182 | Y | Yandicoogina Shale Member | 72 | 75 |

C.

*Soil samples

•Rock samples

Table 2A: (A) 11 waste rock and soil samples provided from Mt. Goldsworthy mine, (B) 20 waste rock samples collected from Jimblebar, and (C) waste rocks samples collected from Yandi (20 samples).

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-------------------------------|----------------|--------|-------|------|------|--------|------|------|--------|
| | | | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| EIL Guideline | | | | 20 | 50 | 400 | 500 | 100 | |
| HIL Guideline | | | 10000 | 100 | 550 | 120000 | 1500 | 1000 | |
| Black shale | | | | | | | | | |
| <i>Batch 2- Jimblebar</i> | SJ0847D-035 | 1 | 2.14 | 5.69 | 37.5 | 43.5 | 3374 | 53.6 | 0.5 |
| | SJ0847D-035 | 9 | 1.58 | 6.37 | 34.8 | 44.3 | 3177 | 46.1 | 0.5 |
| CoV% | | | 21.2 | 8.06 | 5.41 | 1.21 | 4.24 | 10.6 | |
| <i>Batch 3- Jimblebar</i> | SJ0847D-035 | 13 | 1.31 | 3.44 | 30.3 | 40.4 | 2963 | 45.3 | 0.5 |
| | SJ0847D-035 | 14 | 1.37 | 3.44 | 30.6 | 39.8 | 3020 | 42.7 | 1 |
| | SJ0847D-035 | 15 | 1.43 | 3.42 | 31.0 | 44.3 | 3041 | 46.1 | 0.25 |
| CoV% | | | 4.33 | 0.46 | 1.05 | 5.89 | 1.36 | 3.93 | |
| <i>Batch 2- Jimblebar</i> | SJ0848D-021 | 15 | 3.39 | 15.1 | 192 | 372 | 6.82 | 188 | 0.5 |
| | SJ0848D-021 | 37 | 2.85 | 22.0 | 184 | 372 | 5.37 | 184 | 0.5 |
| CoV% | | | 12.1 | 26.1 | 3.00 | 0.00 | 16.8 | 1.52 | |
| <i>Batch 2- Jimblebar</i> | SJ0845RD-015 | 17 | 4.01 | 17.0 | 455 | 440 | 21.6 | 139 | 0.5 |
| | SJ0845RD-015 | 49 | 2.64 | 17.1 | 425 | 408 | 21.2 | 137 | 0.5 |
| CoV% | | | 29.3 | 0.58 | 4.92 | 5.43 | 1.24 | 0.76 | |
| <i>Batch 3- Jimblebar</i> | SJ0845RD-015 | 16 | 3.91 | 10.5 | 404 | 418 | 22.4 | 132 | 0.5 |
| | SJ0845RD-015 | 17 | 3.28 | 4.69 | 249 | 401 | 20.6 | 124 | 1 |
| | SJ0845RD-015 | 18 | 4.07 | 11.5 | 413 | 427 | 23.0 | 141 | 0.25 |
| CoV% | | | 11.1 | 41.3 | 25.9 | 3.13 | 5.59 | 6.36 | |
| <i>Batch 2- Jimblebar</i> | SJ0848D-025 | 26 | 1.62 | 29.4 | 46.1 | 101 | 2.97 | 184 | 0.5 |
| | SJ0848D-025 | 32 | 1.51 | 22.9 | 51.9 | 118 | 3.22 | 248 | 0.5 |
| CoV% | | | 5.21 | 17.4 | 8.34 | 10.6 | 5.74 | 20.8 | |
| <i>Batch 2- Jimblebar</i> | SJ0848D-029 | 28 | 1.56 | 14.5 | 106 | 201 | 4.02 | 158 | 0.5 |
| | SJ0848D-029 | 35 | 1.51 | 15.5 | 107 | 193 | 5.28 | 163 | 0.5 |
| CoV% | | | 2.38 | 4.64 | 0.59 | 2.59 | 19.1 | 2.13 | |
| <i>Batch 2- Jimblebar</i> | SJ0847D-041 | 31 | 3.34 | 19.5 | 113 | 143 | 401 | 203 | 0.5 |
| | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG10-R1 | 2 | 1.66 | 10.4 | 17.7 | 77.1 | 16.1 | 29.8 | 0.5 |
| | RWG10-R1 | 1 | 1.74 | 10.6 | 18.2 | 86.5 | 17.0 | 30.7 | 0.5 |
| CoV% | | | 3.24 | 1.03 | 1.83 | 8.10 | 3.77 | 2.11 | |
| Lignite | | | | | | | | | |
| <i>Batch 2- Jimblebar</i> | SJ1102-002 | 2 | 9.19 | 7.75 | 110 | 119 | 595 | 56.8 | 0.5 |
| | SJ1102-002 | 13 | 9.08 | 7.77 | 114 | 125 | 600 | 57.2 | 0.5 |
| CoV% | | | 0.83 | 0.15 | 2.31 | 3.26 | 0.62 | 0.53 | |
| <i>Batch 2- Jimblebar</i> | SJ1102-006 | 4 | 17.2 | 8.32 | 193 | 149 | 114 | 101 | 0.5 |
| | SJ1102-006 | 6 | 17.0 | 8.51 | 187 | 145 | 117 | 99.9 | 0.5 |
| CoV% | | | 0.52 | 1.58 | 1.97 | 1.55 | 1.73 | 1.02 | |
| <i>Batch 2- Jimblebar</i> | SJ0772D-016 | 11 | 3.96 | 14.8 | 75.4 | 127 | 36.9 | 59.5 | 0.5 |
| | SJ0772D-016 | 16 | 4.51 | 14.9 | 74.7 | 127 | 36.2 | 60.6 | 0.5 |
| CoV% | | | 9.11 | 0.06 | 0.69 | 0.06 | 1.29 | 1.36 | |
| <i>Batch 3- Jimblebar</i> | SJ0772D-016 | 29 | 3.86 | 10.7 | 74.9 | 129 | 35.4 | 63.4 | 0.25 |
| | SJ0772D-016 | 30 | 3.69 | 9.88 | 70.0 | 120 | 32.8 | 57.3 | 0.5 |
| | SJ0772D-016 | 31 | 3.75 | 10.6 | 73.6 | 124 | 33.9 | 56.8 | 1 |

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|--------------------|----------------|--------|------|------|------|-------|-------|-------|--------|
| CoV% | | | 2.29 | 4.38 | 3.46 | 3.69 | 3.86 | 6.24 | |
| Batch 2- Jimblebar | SJ0772D-019 | 19 | 2.48 | 13.4 | 68.1 | 73.3 | 12.9 | 29.6 | 0.5 |
| | SJ0772D-019 | 25 | 2.23 | 18.1 | 58.7 | 56.6 | 11.2 | 26.2 | 0.5 |
| CoV% | | | 7.50 | 21.3 | 10.5 | 18.2 | 9.71 | 8.42 | |
| Batch 3- Jimblebar | SJ0772D-019 | 19 | 1.97 | 8.72 | 61.6 | 69.5 | 12.0 | 27.6 | 0.5 |
| | SJ0772D-019 | 20 | 2.12 | 9.41 | 68.1 | 75.5 | 12.7 | 28.3 | 1 |
| | SJ0772D-019 | 22 | 2.25 | 8.71 | 62.6 | 70.4 | 12.5 | 28.9 | 0.25 |
| CoV% | | | 6.47 | 4.52 | 5.48 | 4.49 | 2.91 | 2.31 | |
| Batch 2- Jimblebar | SJ0785-005 | 24 | 1.07 | 1126 | 1.48 | 2.52 | 52.0 | 3.36 | 0.5 |
| | SJ0785-005 | 44 | 0.96 | 950 | 1.34 | 2.32 | 43.8 | 3.14 | 0.5 |
| CoV% | | | 7.35 | 12.0 | 6.89 | 5.91 | 12.0 | 4.71 | |
| Batch 2- Jimblebar | SJ0785-003 | 33 | 2.31 | 618 | 1.84 | 5.23 | 94.1 | 5.41 | 0.5 |
| | SJ0785-003 | 36 | 2.39 | 599 | 1.87 | 3.15 | 90.5 | 5.20 | 0.5 |
| CoV% | | | 2.26 | 2.30 | 1.29 | 35.2 | 2.77 | 2.79 | |
| Mudstone | | | | | | | | | |
| Batch 2- Jimblebar | SJ0849D-002 | 5 | 1.14 | 27.4 | 84.8 | 98.5 | 2136 | 93.9 | 0.5 |
| | SJ0849D-002 | 45 | 0.67 | 33.2 | 75.6 | 72.5 | 1867 | 85.4 | 0.5 |
| CoV% | | | 36.7 | 13.5 | 8.08 | 21.5 | 9.51 | 6.65 | |
| Batch 2- Jimblebar | SJ0848D-041 | 8 | 2.03 | 70.7 | 300 | 367 | 79.4 | 29.5 | 0.5 |
| | SJ0848D-041 | 27 | 1.45 | 65.4 | 272 | 331 | 73.1 | 27.5 | 0.5 |
| CoV% | | | 23.5 | 5.54 | 7.10 | 7.24 | 5.87 | 5.14 | |
| Batch 2- Jimblebar | SJ0848D-017 | 29 | 2.76 | 26.9 | 149 | 92.4 | 19.5 | 63.2 | 0.5 |
| | SJ0848D-017 | 50 | 3.10 | 26.3 | 142 | 84.9 | 29.1 | 62.4 | 0.5 |
| CoV% | | | 8.15 | 1.72 | 3.54 | 5.98 | 28.06 | 0.91 | |
| Batch 3- Jimblebar | SJ0848D-017 | 23 | 2.93 | 17.9 | 141 | 104 | 24.0 | 64.0 | 0.5 |
| | SJ0848D-017 | 24 | 2.76 | 20.7 | 147 | 93.0 | 23.8 | 61.5 | 1 |
| | SJ0848D-017 | 25 | 2.83 | 18.8 | 129 | 97.6 | 19.5 | 65.9 | 0.25 |
| CoV% | | | 2.96 | 7.65 | 6.57 | 5.39 | 11.21 | 3.46 | |
| Batch 2- Jimblebar | SJ0848D-043 | 34 | 1.96 | 38.6 | 61.2 | 48.7 | 2603 | 68.3 | 0.5 |
| | SJ0848D-043 | 46 | 1.63 | 31.1 | 56.8 | 46.4 | 2415 | 63.3 | 0.5 |
| CoV% | | | 12.6 | 15.2 | 5.24 | 3.38 | 5.32 | 5.34 | |
| BIF | | | | | | | | | |
| Batch 2- Jimblebar | SJ0847D-010 | 7 | 0.37 | 8.69 | 3.10 | 3.45 | 134 | 19.6 | 0.5 |
| | SJ0847D-010 | 40 | 0.23 | 7.32 | 2.75 | 2.75 | 121 | 16.9 | 0.5 |
| CoV% | | | 34 | 12.0 | 8.56 | 16.09 | 7.28 | 10.2 | |
| Batch 2- Jimblebar | SJ0847D-020 | 12 | 0.81 | 6.69 | 20.4 | 6.83 | 52.6 | 27.5 | 0.5 |
| | SJ0847D-020 | 22 | 0.90 | 6.64 | 21.3 | 6.93 | 56.4 | 27.9 | 0.5 |
| CoV% | | | 7.75 | 0.57 | 2.99 | 1 | 4.96 | 0.79 | |
| Batch 3- Jimblebar | SJ0847D-020 | 26 | 0.84 | 5.47 | 18.8 | 6.67 | 48.3 | 28.1 | 0.5 |
| | SJ0847D-020 | 27 | 0.85 | 5.56 | 18.5 | 5.93 | 47.7 | 24.2 | 1 |
| | SJ0847D-020 | 28 | 0.65 | 4.78 | 18.5 | 6.39 | 46.9 | 28.1 | 0.25 |
| | SJ0847D-020 | 32 | 0.86 | 4.78 | 17.8 | 6.15 | 45.9 | 32.5 | 0.5 |
| | SJ0847D-020 | 33 | 0.79 | 5.12 | 18.4 | 5.88 | 46.6 | 32.1 | 1 |
| CoV% | | | 11.1 | 7.17 | 2.07 | 5.31 | 1.98 | 11.75 | |

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-------------------------------|----------------|--------|------|------|------|-------|------|------|--------|
| <i>Batch 2- Jimblebar</i> | SJ0847D-009 | 18 | 0.11 | 11.7 | 4.91 | 6.19 | 101 | 15.2 | 0.5 |
| | SJ0847D-009 | 39 | 0.01 | 12.3 | 4.51 | 5.35 | 103 | 15.0 | 0.5 |
| CoV% | | | 119 | 3.82 | 6.06 | 10.30 | 1.77 | 1.26 | |
| <i>Batch 2- Jimblebar</i> | SJ0847D-008 | 20 | 0.66 | 12.4 | 21.3 | 21.3 | 2487 | 23.6 | 0.5 |
| | SJ0847D-008 | 38 | 0.49 | 9.32 | 19.7 | 20.1 | 2313 | 22.4 | 0.5 |
| CoV% | | | 21.2 | 20.2 | 5.29 | 3.87 | 5.12 | 3.49 | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG18-R1 | 4 | 0.21 | 21.0 | 32.4 | 37.7 | 306 | 7.11 | 0.5 |
| | RWG18-R1 | 3 | 0.24 | 21.5 | 32.6 | 41.7 | 309 | 7.72 | 0.5 |
| CoV% | | | 10.2 | 1.62 | 0.41 | 7.03 | 0.77 | 5.79 | |
| Sheared dolerite | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG12-R1 | 24 | 0.21 | 0.53 | 177 | 173 | 76.5 | 6.72 | 0.5 |
| | RWG12-R1 | 23 | 0.25 | 0.52 | 186 | 208 | 63.6 | 5.92 | 0.5 |
| CoV% | | | 12.9 | 0.58 | 3.22 | 12.9 | 13.1 | 8.98 | |
| Banded phyllite | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG21-R4 | 22 | 1.10 | 3.63 | 12.4 | 144 | 991 | 11.8 | 0.5 |
| | RWG21-R4 | 21 | 1.10 | 3.87 | 11.3 | 162 | 984 | 10.9 | 0.5 |
| CoV% | | | 0.18 | 4.65 | 6.70 | 8.24 | 0.52 | 5.62 | |
| shale,chert,BIF | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG4-R1 | 20 | 1.22 | 8.62 | 4.47 | 4.77 | 21.8 | 11.6 | 0.5 |
| | RWG4-R1 | 19 | 1.14 | 8.42 | 4.40 | 4.76 | 20.9 | 12.2 | 0.5 |
| | RWG4-R1 | 18 | 1.32 | 8.54 | 4.33 | 4.84 | 22.0 | 11.7 | 0.5 |
| CoV% | | | 7.42 | 1.16 | 1.66 | 0.88 | 2.59 | 2.53 | |
| Volcanic ash | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG2-R2 | 17 | 0.90 | 2.14 | 120 | 1438 | 138 | 19.0 | 0.5 |
| | RWG2-R2 | 16 | 0.67 | 1.99 | 111 | 1496 | 131 | 18.7 | 0.5 |
| CoV% | | | 20.5 | 5.03 | 5.11 | 2.82 | 3.58 | 1.27 | |
| Phyllite | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG1-R1 | 15 | 0.20 | 44.3 | 31.6 | 37.8 | 166 | 4.95 | 0.5 |
| | RWG1-R1 | 14 | 0.45 | 43.6 | 31.7 | 42.6 | 161 | 3.92 | 0.5 |
| CoV% | | | 53.3 | 1.18 | 0.24 | 8.43 | 2.19 | 16.5 | |
| Hematite | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG24-R1 | 13 | 0.04 | 11.3 | 1.77 | 7.42 | 4910 | 5.27 | 0.5 |
| | RWG24-R1 | 12 | <0.1 | 14.0 | 2.04 | 6.61 | 5616 | 3.27 | 0.5 |
| CoV% | | | | 15.1 | 10.0 | 8.19 | 9.49 | 33 | |
| Banded chert | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG21-R5 | 11 | 0.67 | 3.60 | 14.0 | 6.16 | 20.3 | 6.44 | 0.5 |
| | RWG21-R5 | 10 | 0.68 | 3.55 | 14.4 | 6.41 | 23.7 | 7.85 | 0.5 |
| CoV% | | | 0.66 | 0.85 | 2.00 | 2.74 | 11.1 | 14.0 | |
| Dolerite | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG14-R1 | 9 | 0.25 | 0.49 | 193 | 261 | 156 | 6.65 | 0.5 |
| | RWG14-R1 | 8 | 0.24 | 0.50 | 193 | 288 | 158 | 6.59 | 0.5 |
| CoV% | | | 0.69 | 0.91 | 0.19 | 7.14 | 0.89 | 0.65 | |
| Dolerite | | | | | | | | | |
| <i>Batch 4-Mt-Goldsworthy</i> | RWG3-R1 | 6 | 0.32 | 2.55 | 64.8 | 3273 | 713 | 14.7 | 0.5 |
| | | 5 | 0.36 | 2.61 | 71.8 | 3070 | 706 | 17.2 | 0.5 |
| CoV% | | | 7.38 | 1.75 | 7.26 | 4.52 | 0.73 | 10.8 | |

Table 2B: Concentrations of Se and selected trace elements in different types rock and soil samples provided from South Jimblebar, and Goldsworthy compared with West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels. Values exceeding (EIL) are shown with yellow and results higher than both guidelines are highlighted with pink.

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-------------------------------------|----------------|--------|-------|------|------|--------|------|------|--------|
| | | | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| EIL Guideline | | | | 20 | 50 | 400 | 500 | 100 | |
| HIL Guideline | | | 10000 | 100 | 550 | 120000 | 1500 | 1000 | |
| Whaleback Shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505643 | 12 | 0.49 | 14.8 | 17.7 | 22.4 | 400 | 29.3 | 0.5 |
| | N505643 | 13 | 0.45 | 14.9 | 17.7 | 23.3 | 399 | 21.1 | 0.5 |
| CoV% | | | 6.55 | 0.23 | 0.09 | 2.56 | 0.20 | 22.9 | |
| Yandicoogina shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416182 | 14 | 1.11 | 36.2 | 84.1 | 101 | 156 | 50.8 | 0.5 |
| | N416182 | 15 | 1.13 | 37.5 | 87.5 | 101 | 160 | 57.2 | 0.5 |
| CoV% | | | 0.77 | 2.47 | 2.78 | 0.21 | 2.19 | 8.32 | |
| Joffre | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505639 | 36 | 0.23 | 19.0 | 11.0 | 11.8 | 766 | 11.8 | 0.5 |
| | N505639 | 35 | 0.35 | 20.0 | 11.6 | 11.3 | 788 | 12.1 | 0.5 |
| CoV% | | | 29.4 | 3.41 | 3.39 | 3.09 | 2.02 | 1.62 | |
| Weeli Wollli formartion | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | HyM0005 | 25 | 0.37 | 2.47 | 10.8 | 6.14 | 39.4 | 11.9 | 0.5 |
| | HyM0005 | 26 | 0.30 | 2.34 | 11.1 | 5.81 | 29.2 | 11.8 | 0.5 |
| CoV% | | | 13.7 | 3.68 | 1.62 | 3.89 | 21.1 | 0.38 | |
| Joffre member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505637 | 28 | 0.18 | 9.93 | 8.31 | 6.95 | 819 | 16.2 | 0.5 |
| | N505637 | 27 | 0.14 | 9.53 | 8.36 | 7.43 | 818 | 15.5 | 0.5 |
| CoV% | | | 21.2 | 2.91 | 0.45 | 4.79 | 0.05 | 3.23 | |
| Weeli Wollli iron formartion | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | HyM0002 | 24 | 0.66 | 29.8 | 22.7 | 32.1 | 1044 | 54.2 | 0.5 |
| | HyM0002 | 23 | 0.82 | 30.8 | 22.8 | 30.9 | 1042 | 54.8 | 0.5 |
| CoV% | | | 15.9 | 2.34 | 0.52 | 2.64 | 0.11 | 0.75 | |
| Whaleback Shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505563 | 5 | 1.46 | 19.8 | 63.1 | 64.1 | 363 | 22.2 | 0.5 |
| | N505563 | 6 | 1.29 | 19.6 | 62.1 | 63.5 | 356 | 23.8 | 0.5 |
| CoV% | | | 8.69 | 0.65 | 1.13 | 0.74 | 1.27 | 4.98 | |
| Mt.McRae shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | E118008 | 3 | 1.17 | 147 | 77.9 | 82.7 | 227 | 26.3 | 0.5 |
| | E118008 | 4 | 1.00 | 146 | 78.4 | 82.8 | 223 | 26.5 | 0.5 |
| CoV% | | | 11.0 | 0.58 | 0.46 | 0.10 | 1.01 | 0.41 | |
| Mt.McRae shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | E118098 | 2 | 1.39 | 181 | 81.6 | 86.4 | 783 | 36.7 | 0.5 |
| | E118098 | 1 | 1.29 | 183 | 81.4 | 84.7 | 770 | 38.0 | 0.5 |
| CoV% | | | 5.47 | 1.05 | 0.14 | 1.38 | 1.17 | 2.54 | |
| Yandicoogina shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416291 | 7 | 0.53 | 20.3 | 217 | 110 | 74.8 | 48.2 | 0.5 |
| | N416291 | 8 | 0.59 | 20.9 | 224 | 113 | 78.9 | 42.7 | 0.5 |
| CoV% | | | 8.44 | 2.01 | 2.16 | 1.55 | 3.77 | 8.54 | |
| Weeli Wollli dolerite | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | HyM0029 | 21 | 1.19 | 2.14 | 243 | 98.1 | 991 | 99.3 | 0.5 |
| | HyM0029 | 22 | 1.34 | 1.84 | 253 | 100 | 1026 | 101 | 0.5 |
| CoV% | | | 8.06 | 10.6 | 2.73 | 1.54 | 2.43 | 1.08 | |
| Tertiary detrital | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505758 | 34 | 1.26 | 13.6 | 113 | 114 | 371 | 36.5 | 0.5 |
| | N505758 | 33 | 0.99 | 13.8 | 115 | 115 | 381 | 35.1 | 0.5 |
| CoV% | | | 16.9 | 1.20 | 1.20 | 1.19 | 1.95 | 2.79 | |
| Joffre member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416412 | 40 | 0.52 | 2.07 | 11.2 | 7.39 | 2766 | 22.6 | 0.5 |
| | N416412 | 38 | 0.67 | 3.20 | 13.1 | 9.03 | 2847 | 23.1 | 0.5 |
| CoV% | | | 16.9 | 30.4 | 11.2 | 14.1 | 2.03 | 1.55 | |
| Mt.McRae shale | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505546 | 11 | 0.56 | 202 | 73.6 | 41.4 | 1426 | 18.3 | 0.5 |
| | N505546 | 10 | 0.72 | 206 | 76.1 | 43.5 | 1472 | 17.2 | 0.5 |
| | N505546 | 9 | 0.56 | 205 | 75.1 | 42.5 | 1441 | 21.7 | 0.5 |
| CoV% | | | 14.6 | 1.11 | 1.70 | 2.49 | 1.63 | 12.3 | |

| Rock No | Samples number | Beaker | Se | As | V | Cr | Mn | Cu | Weight |
|-----------------------------------|----------------|--------|------|------|------|------|------|------|--------|
| Weeli Wolli iron formation | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416220 | 43 | 1.10 | 31.9 | 114 | 160 | 459 | 38.8 | 0.5 |
| | N416220 | 42 | 1.19 | 31.6 | 119 | 153 | 459 | 37.7 | 0.5 |
| CoV% | | | 5.79 | 0.67 | 2.53 | 3.23 | 0.14 | 2.07 | |
| colonial chert member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | E115011 | 20 | 0.66 | 46.4 | 44.8 | 75.4 | 443 | 32.2 | 0.5 |
| | E115011 | 19 | 0.75 | 44.7 | 43.8 | 73.1 | 446 | 31.1 | 0.5 |
| CoV% | | | 9.70 | 2.75 | 1.51 | 2.20 | 0.53 | 2.55 | |
| Joffre member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N416410 | 32 | 0.98 | 2.44 | 11.5 | 10.9 | 899 | 26.0 | 0.5 |
| | N416410 | 31 | 0.94 | 2.83 | 12.7 | 10.7 | 895 | 24.3 | 0.5 |
| CoV% | | | 2.70 | 10.3 | 7.03 | 1.18 | 0.29 | 4.77 | |
| Weeli Wolli | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505657 | 29 | 0.19 | 13.5 | 3.40 | 3.09 | 101 | 14.0 | 0.5 |
| | N505657 | 30 | 0.15 | 13.2 | 3.18 | 3.20 | 99.0 | 9.81 | 0.5 |
| CoV% | | | 13.7 | 1.56 | 4.70 | 2.57 | 1.73 | 24.7 | |
| Dales gorge member | | | | | | | | | |
| <i>Batch 6 - Yandi</i> | N505655 | 39 | 0.18 | 11.7 | 4.64 | 3.61 | 117 | 14.8 | 0.5 |
| | N505655 | 37 | 0.14 | 10.5 | 4.52 | 3.32 | 117 | 13.9 | 0.5 |
| CoV% | | | 15.9 | 7.4 | 1.85 | 5.93 | 0.38 | 4.44 | |
| Tertiary detrital | C370723 | 18 | 1.83 | 18.5 | 89.5 | 127 | 124 | 50.6 | 0.5 |
| | C370723 | 17 | 1.58 | 18.6 | 90.4 | 128 | 126 | 46.5 | 0.5 |
| CoV% | | | 10.7 | 0.37 | 0.69 | 0.34 | 1.10 | 6.01 | |

Table 2C: Concentrations of Se and selected trace elements in different types rock and soil samples provided from Yandi compared with West Australia Department of Environment and Conservation guideline values for health investigation levels (HIL) and ecological investigation levels (EIL) (DEC, 2010). Values exceeding (EIL) are shown with yellow and results higher than both guidelines are highlighted with pink.