

1 Mineral-scale trace element and U-Th-Pb age constraints on
2 metamorphism and melting during the Petermann Orogeny (central
3 Australia)

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Abstract

High-pressure amphibolite-facies migmatitic orthogneiss from the Cockburn Shear Zone (CSZ), northern Musgrave Block (central Australia), were formed during the 580-520 Ma intraplate Petermann Orogeny. The shear-zone hosted orthogneisses are of an intermediate bulk composition that promoted the growth of REE-bearing major phases (garnet, hornblende), as well as numerous accessory phases (zircon, titanite, apatite, epidote and allanite), all of which are potential U-Th-Pb geochronometers and are involved in the distribution of REEs. We have integrated petrology and detailed in-situ trace element analysis of major and accessory phases in samples collected outside and inside the CSZ to establish the relative timing of metamorphic mineral growth. This paper presents one of the first applications of the newly developed in-situ dating protocols on metamorphic allanite. Sensitive High Resolution Ion Microprobe geochronology on metamorphic zircon and allanite indicate that metamorphism and partial melting occurred between 559 ± 6 and 551 ± 6 Ma. Peak temperatures of 720-750°C determined from rutile included in garnet necessitate the presence of fluids to flux partial melting in the CSZ quartzofeldspathic rocks. Metamorphic zircon formed during cooling in the presence of melt near the granitic wet solidus ($T \leq 700^\circ\text{C}$). In contrast, allanite formed at different stages of the CSZ P-T path: (1) prograde sub-solidus growth ($T < 650^\circ\text{C}$) in the presence of fluids, and (2) as melt-precipitated Th- and REE-rich overgrowths on pre-existing allanite. The ages of the two growth episodes are not isotopically resolvable by allanite dating. Trace element compositions indicate that in both melted and unmelted rocks, garnet and hornblende growth was primarily controlled by prograde sub-solidus hydration reactions that consumed feldspar below the metamorphic peak. REE compositions of the metamorphic zircon and allanite overgrowths that formed in the presence of melt also suggest disequilibrium with garnet. Thus, the major period of garnet and hornblende growth was not coeval with partial melting.

KEY WORDS: allanite; ion microprobe dating; zircon; sub-solidus mineral growth; disequilibrium

69 **INTRODUCTION**

70

71 The integration of the rapidly developing field of in-situ trace element geochemistry with well
72 established U-Th-Pb dating techniques has proved to be a powerful tool for understanding
73 complex metamorphic pressure-temperature (P-T)-time paths (e.g. Rubatto, 2002; Hermann
74 & Rubatto, 2003; Kelly & Harley, 2005; Rubatto *et al.*, 2006; Buick *et al.*, 2007). The relative
75 resistance of trace elements, such as the rare earth elements (REEs), to diffusive re-
76 equilibration compared to (divalent) major elements in minerals (e.g. Pyle & Spear, 1999;
77 Otamendi *et al.*, 2002; Van Orman *et al.*, 2002), makes them an effective recorder of
78 metamorphic processes, including potential mineral thermometers (Pyle & Spear, 1999; 2000;
79 Degeling, 2003; Zack *et al.*, 2004; Watson & Harrison, 2005). The trace element composition
80 of different mineral phases is a function of P, T and bulk composition, but it is also sensitive
81 to the competitive co-crystallisation of trace element-rich minerals (e.g. Pyle and Spear,
82 2000). The latter can be used to infer apparent disequilibrium-equilibrium of mineral phases
83 within a metamorphic assemblage. For example, LREE-depleted patterns imply simultaneous
84 growth of a mineral of interest with a phase that strongly fractionates the LREEs (e.g.
85 Sorenson and Grossman, 1989). Similarly, HREE-depletion is generally consistent with the
86 presence of garnet (e.g. Sorensen & Grossman, 1989; Rubatto, 2002; Hoskin & Schaltegger,
87 2003).

88 Characteristic trace element compositions of minerals from amphibolite and granulite
89 facies terranes have been used to constrain the processes of their formation. Few of these
90 studies, however, have examined the trace element distribution between multiple REE-rich
91 major and accessory phases during amphibolite-grade metamorphism at sub-solidus
92 conditions (e.g. Sorensen & Grossman, 1989; Mulrooney & Rivers, 2005). The use of trace
93 elements to determine the process of formation is particularly relevant for accessory minerals
94 that can be dated via the U-Th-Pb system. Such accessory minerals are major hosts of trace
95 elements (e.g. Hermann, 2002) and in metamorphic rocks often the correct interpretation of
96 their U-Th-Pb age depends on how well their formation can be related to P-T conditions. In
97 this paper we contribute to the expanding field of mineral trace element geochemistry and
98 geochronology with a study of high-pressure (HP) migmatitic orthogneiss of the CSZ within
99 the Mann Terrane, central Australia. Understanding the growth histories of metamorphic
100 accessory phases is facilitated when samples of the same bulk composition but with different
101 extents of metamorphic overprint (e.g. melted and unmelted counterparts of a rock type) can
102 be compared (e.g. Sorensen, 1991; Rubatto *et al.*, 2001; Storkey *et al.*, 2005; Buick *et al.*,

103 2007; Clarke *et al.*, 2007). The investigated rocks are particularly suited for such a study
104 because they include a suite of granodioritic orthogneisses that are cut by shear zones, in
105 which the same bulk compositions have undergone partial melting at ~700°C (Scrimgeour &
106 Close, 1999).

107 Dating amphibolite-grade rocks is commonly attempted using zircon and monazite.
108 However, in relatively low-Al, high-Ca bulk compositions (for example, metamorphosed
109 calc-alkaline granites, tonalites and granodiorites, such as those investigated here), monazite
110 is largely absent and metamorphic zircon typically forms at higher temperatures (> 700°C,
111 e.g. Rubatto *et al.* 2001, 2006). Instead, accessory (epidote)-allanite is stable, and has great
112 potential to both date high-grade events (Oberli *et al.* 2004) and act as a tracer of mineral-
113 scale processes. As a chemically complex mineral, allanite should ideally be dated by spot
114 analysis rather than bulk dilution methods, as this may average any chemical or isotopic
115 zoning. Gregory *et al.* (2007) developed LA-ICP-MS and SHRIMP micro-analytical
116 techniques for the Th-Pb dating of igneous allanite. Here we examine the potential of dating
117 metamorphic allanite using a SHRIMP and LA-ICP-MS approach and the sensitivity of the
118 allanite REE composition to metamorphic processes. U-Pb dating of zircon provided an
119 independent age constraint for comparison with the allanite isotopic system. These U-Th-Pb
120 ages are then linked to stages of mineral growth through mineral-scale trace element
121 geochemistry.

122

123 **GEOLOGICAL SETTING**

124

125 The largest HP metamorphic terrane documented in Australia is exposed in the Mann
126 Terrane, central Australia. The Mann Terrane represents part of the basement of the Musgrave
127 Block located south of the Amadeus Basin and is delineated by two crustal-scale, south-
128 dipping structures, the Woodroffe Thrust and the Mann Fault (Fig. 1a). Both structures
129 formed during the Neoproterozoic to early Palaeozoic intracratonic Petermann Orogeny,
130 which resulted in the reworking of anhydrous Mesoproterozoic granulite-facies orthogneisses
131 and igneous rocks of the Musgrave Block, and the northward exhumation of deep crustal
132 mylonites along the Woodroffe Thrust (Camacho and Fanning, 1995; Camacho *et al.*, 1997;
133 Scrimgeour and Close, 1999). North of the Mann Fault, basement outcrop is dominated by the
134 ~1190-1120 Ma Umutju Granite Suite (Fig. 1b; Camacho and Fanning, 1995), which is
135 intruded by ~1080-1050 Ma and ~800 Ma mafic dykes (e.g. Zhao *et al.* 1994; Sun *et al.*,
136 1996). During the Petermann Orogeny, basement rocks were metamorphosed to transitional

137 garnet-granulite- to eclogite-facies conditions at ~11-13 kbar and ~700-750°C (Scrimgeour
138 and Close, 1999). Metamorphic grade varies across the orogen with the highest P (and T)
139 attained in the south, immediately north of the Mann Fault (Fig. 1b). Metamorphic grade
140 decreases upsection, with P-T conditions of ~6-7 kbar and ~600-650°C recorded in shear
141 zones crosscutting the Pottoyu and Mantarurr Granite Suites north of the Woodroffe Thrust
142 (Fig. 1b; Scrimgeour and Close, 1999).

143 Despite the widespread presence of generally anhydrous and clinopyroxene-bearing
144 granite in the Mann Terrane (Scrimgeour *et al.*, 1999), melting occurred within discrete shear
145 zones active during the Petermann Orogeny, such as the Cockburn Shear Zone (CSZ). These
146 zones, however, represent < 1 % of exposed outcrop (Scrimgeour *et al.*, 1999). The CSZ is a
147 shallow, WSW-dipping ductile thrust located immediately north of the Mann Fault (Fig. 1b),
148 which crosscuts a porphyritic K-feldspar- and clinopyroxene-bearing granodiorite. P-T
149 estimates taken from recrystallised mafic dykes immediately south of the CSZ record near
150 eclogite-facies conditions of ~13 Kbar and ~750°C (Fig. 1b; Scrimgeour and Close, 1999).

151 Localised fabric inside the CSZ truncates the regional proto-mylonitic Petermann-age
152 fabric outside the CSZ. Deformed porphyritic granodiorite outside the CSZ (referred to here
153 as orthogneiss) is unmelted and contains fine-grained garnet and hornblende. The orthogneiss
154 grades relatively sharply into the shear zone-hosted partial melt zone (Fig. 2a), where rocks of
155 the same protolith contain decimetre-scale alkali feldspar + quartz + plagioclase leucosome
156 (referred to here as migmatitic orthogneiss). Leucosomes preserve varying degrees of syn- to
157 post-metamorphic strain, from strongly mylonitised and concordant leucosome (Fig. 2a-b) to
158 relatively undeformed solidified melt pods (Fig. 2c). Migmatitic orthogneiss of the CSZ
159 contain significantly coarser (cm-sized) garnet and hornblende grains (Fig. 2c), as well as
160 abundant accessory minerals compared to the orthogneiss. Mafic dykes in orthogneiss were
161 partially recrystallised during the Petermann Orogeny, whereas dykes located within the CSZ
162 were transformed into amphibolite boudins, which preserve solidified melt pods in strain
163 shadows and stringers of melt entrained from the surrounding migmatitic orthogneiss (Fig.
164 2b). Scrimgeour and Close (1999) proposed a mechanism of focussed fluid-fluxed melting
165 within the shear zones to explain the mineralogical differences between rocks located inside
166 and outside the CSZ.

167 The timing of high-grade metamorphism associated with the Petermann Orogeny is
168 poorly constrained (~560 and 520 Ma; Maboko *et al.*, 1992; Camacho and Fanning, 1995;
169 Clarke *et al.*, 1995). This is the result of an absence of extensive high-temperature accessory

170 mineral U-Th-Pb geochronology partly due to a lack of new zircon formation in rocks
171 metamorphosed during the Petermann Orogeny, poor outcrop exposure and restricted land
172 access (Scrimgeour *et al.*, 1999). Available mineral Sm-Nd and Ar-Ar ages for basement
173 rocks in the eastern and western Musgrave Block indicate cooling of these rocks below 550°C
174 by *c.* 550-530 Ma (Maboko *et al.*, 1992; Camacho *et al.*, 1997). There remains, however, a
175 lack of geochronological constraints on the high-temperature history of the Petermann
176 Orogeny in the central to northern Musgrave Block.

177

178 **SAMPLE DESCRIPTION**

179

180 Four representative samples from rocks outside and inside the CSZ were investigated in order
181 to compare the extent of the metamorphic overprint of rocks outside and inside the shear
182 zone. These are: samples Pe1, 6 and 11 (S25° 58.35' E129° 25.85') and Pe13 (S25° 57.98'
183 E129° 25.94'). Mineral assemblage evolution determined from chemical information and
184 textural observations of Pe1, Pe11 and Pe13 is summarised in Figure 3.

185

186 **Pe1**

187

188 Sample Pe1 was collected from a location 20 m outside the CSZ and is representative of the
189 unmelted and largely anhydrous, although strongly deformed, orthogneiss. This sample was
190 investigated in order to characterise the trace element distribution during prograde to peak
191 metamorphism of unmelted equivalents to migmatitic orthogneiss of the CSZ. It contains
192 variably recrystallised igneous quartz + K-feldspar + plagioclase + clinopyroxene + ilmenite
193 + apatite (e.g. relict igneous clinopyroxene, fig. 4c in Scrimgeour and Close, 1999). No REE-
194 rich magmatic accessory phase (e.g. monazite or allanite) was detected, and on a regional
195 scale, monazite has not been reported in Mann Terrane granites (Scrimgeour *et al.*, 1999).
196 The relict primary assemblage is overprinted by a fine-grained (<300 µm) secondary
197 metamorphic assemblage of garnet + hornblende + biotite + titanite + epidote/allanite (Fig.
198 4a-b). The two feldspars are present as mm-size relict grains (K-feldspar is cloudy, Fig. 4c),
199 and as small, recrystallised grains. Pe1 exhibits a domainal distribution of metamorphic
200 minerals (Fig. 4c). Hornblende forms coronal replacement textures around igneous
201 clinopyroxene and is also found near garnet and plagioclase. Subhedral garnet forms as
202 aggregates of small euhedral grains surrounding either hornblende or ilmenite, and adjacent to

203 feldspar (Fig. 4b-c), and contains inclusions of ilmenite. Hornblende and garnet do not form
204 mutual inclusion relationships. Titanite grains form as clusters around relict ilmenite (Fig.
205 4b), or as lone grains near garnet. Ilmenite contains magnetite exsolution features. Small
206 epidote-allanite grains (<25 µm) are included in, or adjacent to, garnet, plagioclase, titanite
207 and apatite. Apatite and zircon are present, although it is difficult to distinguish whether they
208 are magmatic or metamorphic phases, based on petrography alone.

209

210 **Pe6**

211

212 Pe6 is an amphibolite boudin (Fig. 2b), a representative mafic dyke that has been reworked
213 within the CSZ. This rutile-bearing sample was analysed to provide constraints on the
214 temperature of peak metamorphism. It contains leucosomes of plagioclase and quartz, within
215 a matrix of hornblende + plagioclase + garnet + clinopyroxene + rutile + titanite + zircon +
216 traces of quartz (Fig. 4d-e). Rutile grains are 50 µm to 1 mm in diameter, inclusion-free and
217 are present both in the matrix and commonly as inclusions in mm- to cm-sized garnet, where
218 they are rimmed by titanite.

219

220 **Pe11, 13**

221

222 Sample Pe13 is a deformed leucosome containing garnet and hornblende from inside the
223 CSZ. Sample Pe11 contains both leucosome and mesosome, however the following
224 description and compositional analyses are taken only from the leucosome segment. Unlike
225 Pe1, migmatitic orthogneisses recrystallised within the shear zone are generally devoid of
226 clinopyroxene and do not preserve the earlier igneous assemblage, with the exception of relict
227 K-feldspar and minor plagioclase (Fig. 4h). Both samples contain a relatively hydrous major
228 mineral assemblage of quartz + K-feldspar + plagioclase + garnet + hornblende + biotite +
229 epidote (Fig. 3, 4f-j); Pe11 additionally contains minor scapolite. Both feldspars are present as
230 >500 µm-sized porphyroclasts and as <250 µm-sized recrystallised grains. Garnets are mm-
231 to cm-sized and commonly poikiloblastic and anhedral. Garnet cores contain variably sized
232 inclusions of quartz and accessory epidote, zircon, titanite and apatite. Garnet rims are
233 typically inclusion-free; they locally contain larger (100 µm) grains of epidote, titanite and
234 apatite, but lack the abundant small inclusions found in garnet cores (Fig. 4h). Two
235 hornblende generations were distinguished by texture: mm- to cm-sized sub-euhedral

236 hornblende (in Pe11 only), and a subsequent generation of foliated “matrix” hornblende (Fig.
237 4f, i). Biotite is fine-grained, and both biotite and matrix hornblende appear to be (sub-
238 solidus) retrograde phases and have a fabric preferred orientation.

239 Compared to Pe1, the migmatitic orthogneisses contain a notable amount of accessory
240 mineral growth, including <500 µm-sized, inclusion-free titanite, epidote-allanite, zircon and
241 apatite. Allanite and titanite grains are subhedral to euhedral, and are commonly associated
242 with matrix hornblende and biotite within the fabric, or alongside garnet (Fig. 4f, i). REE-rich
243 allanite is a matrix phase, whereas epidote is a common inclusion in garnet (Fig. 4g, j).
244 Compositional zoning of allanite is observed in thin section; grains show pale yellow cores
245 and yellow-brown rims (Fig. 4f).

246

247 **ANALYTICAL PROCEDURES**

248

249 **Imaging and Electron microprobe analysis**

250

251 Compositional zoning was identified by high-contrast backscatter electron (BSE) imaging
252 using a Cambridge S360 SEM at the ANU Electron Microscopy Unit (~2 nA, 15 kV and 15
253 mm working distance). WDS analysis of major elements was carried out on a Cameca SX100
254 electron microprobe at RSES, ANU and on a Cameca SX50 at the University of Melbourne.
255 Analytical conditions were 15 kV and 20-25 nA, with the beam current defocused to 5 µm to
256 avoid beam damage. An analytical method specific to allanite (REE) analysis was used at
257 RSES (sample Pe13; Gregory *et al.*, 2007). In-house silicate mineral and allanite standards
258 were analysed to monitor internal consistency. Fe³⁺ contents were recalculated based on
259 charge balance assuming 8 cations and 12.5 oxygens for epidote-allanite. Zircon mounts were
260 imaged using a cathodoluminescence (CL) detector at the ANU EMU on a HITACHI S2250-
261 N SEM with operating conditions of 15kV, ~60 µm and ~20 mm working distance.

262

263 **Bulk-rock analysis**

264

265 Procedures followed are those described by Buick *et al.* (2006). Samples Pe1 and Pe11 were
266 ground in a tungsten carbide mill to a grain size of 25µm, and fused into (La₂O₃-doped)
267 lithium borate glass discs (0.84 g of sample to 4.5 g of flux) for major-element
268 determinations, and REE-free lithium borate glass discs (Sigma® 12:22 X-Ray flux;

269 sample:flux = 1:2) for trace-element determinations. Major elements were analysed on the
270 Siemens SR303AS XRF spectrometer (XRFS) with Rh end-window X-ray tube at La Trobe
271 University (Melbourne, Australia) and trace elements were analysed using the LA-ICP-MS
272 facility at RSES, ANU, using a spot size of 142 μm and SiO_2 as the internal standard. The
273 resulting data are an average of 4-5 ablation spots and 1 standard deviation from the average
274 is <5 % relative for most elements.

275

276 **Mineral LA-ICP-MS trace element analysis**

277

278 Polished thin sections used for electron microprobe analysis were used to determine mineral
279 trace element contents. Analyses were performed using a pulsed ArF Excimer laser system
280 (193nm wavelength) coupled to a quadrupole ICP-MS (Agilent 7500S) at RSES, ANU. The
281 instrumental setup generally followed that described by Eggins *et al.* (1998). Depending on
282 the target mineral, the laser was focused to produce an ablation pit ranging in diameter from
283 24 to 84 μm , with 100 mJ energy at a repetition rate of 5 Hz. Data acquisition for each
284 element during a single analysis included a total of 70 to 80 mass spectrometer sweeps,
285 comprising a gas background of 20-25 sweeps. During the time-resolved analysis,
286 contamination or alteration was detected by monitoring several elements and only the relevant
287 part of the signal was integrated. NIST612 (Pearce *et al.*, 1997) was used as the external
288 standard except for Zr in rutile when NIST610 was used. Internal standards were major
289 elements (SiO_2 , CaO , ZrO_2 , TiO_2) measured by electron microprobe or determined
290 stoichiometrically. Reproducibility of results for BCR glasses using ANU analytical protocols
291 is generally 2-5 % 1σ for multiple analyses. REE plots are normalized to the values of
292 McDonough and Sun (1995).

293

294 **Zircon and allanite ion microprobe dating**

295

296 CL and BSE images served as a basis for selection of zircon and allanite grains for isotopic
297 analysis, respectively. U-Th-Pb analyses were conducted on a Sensitive High Resolution Ion
298 Microprobe (SHRIMP II and RG) at RSES. Epoxy-mounted grains of allanite and zircon
299 from Pe13 were analysed during different analytical sessions under similar operating
300 conditions of a 3-4 nA, 10 kV primary O_2^- beam focussed to a $\sim 20 \mu\text{m}$ diameter spot.
301 Instrumental conditions and data acquisition and treatment were generally as described by
302 Compston *et al.* (1992) and Williams (1998), with isotope data collected from sets of six

303 scans through the masses. The measured $^{206}\text{Pb}/^{238}\text{U}$ ratio was corrected using the ANU
304 reference zircon FC1 (1099 Ma). Due to ^{204}Pb overcounts and Th-deficient zircon analyses
305 were corrected for common Pb based on measured $^{208}\text{Pb}/^{206}\text{Pb}$ calculated from Th/U,
306 assuming equilibrium between Th and U systems. This was satisfied by all analyses by
307 plotting ThO/UO versus $^{208}\text{Pb}/^{206}\text{Pb}$. Due to their low content in radiogenic lead, zircon rims
308 had high proportions of common Pb (2-8 % $^{206}\text{Pb}_c$) relative to the ^{204}Pb -free standard.
309 Therefore a model common Pb composition (Stacey and Kramers, 1975) was assumed for a
310 population age of 550 Ma. A detailed description for allanite Th-Pb analysis is given in
311 Gregory *et al.* (2007). The measured $^{208}\text{Pb}/^{232}\text{Th}$ ratio was corrected using the allanite
312 standard CAP (276 Ma; Barth *et al.*, 1994). All analyses were corrected for common Pb based
313 on measured $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ assuming a model Pb composition at 550 Ma (Stacey
314 & Kramers, 1975). Equilibrium between Th and U systems was satisfied by plotting ThO/UO
315 versus $^{208}\text{Pb}/^{206}\text{Pb}$. Th-Pb isochrons regressed from uncorrected data gave initial $^{208}\text{Pb}/^{206}\text{Pb}$
316 intercept values of 2.14 ± 0.24 for cores and 2.12 ± 0.12 for rims, which are within error of
317 the model $^{208}\text{Pb}/^{206}\text{Pb}$ composition. Electron microprobe chemical compositions were
318 acquired for each domain analysed by SHRIMP. Age calculation was done using RSES
319 internal software for allanite and using the software Isoplot/Ex (Ludwig, 2000) for zircon and
320 allanite.

321

322 **Allanite laser ablation ICP-MS dating**

323

324 The analytical procedure for U-Th-Pb analyses by LA-ICP-MS was generally as described by
325 Gregory *et al.* (2007). Each isotopic analysis on a 32 μm spot took 65s in time-resolved (peak
326 hopping) analysis mode, including 25s background. Data were processed off-line using an in-
327 house macro-based EXCEL reduction spreadsheet, enabling selective integration of 'clean'
328 isotope signals. Inter-elemental fractionation of U-Th-Pb ratios was corrected for using an
329 external AVC allanite standard (~276 Ma, Barth *et al.*, 1994) and calculating a matrix
330 normalisation factor F ($F = ^{208}\text{Pb}/^{232}\text{Th}_{\text{known}} / ^{208}\text{Pb}/^{232}\text{Th}_{\text{measured}}$), from the average of
331 replicate standard measurements (~ 12), for each down-hole mass sweep, and applying this to
332 each unknown for the same depth interval. Unknowns were referenced directly to NIST610
333 for $^{232}\text{Th}/^{238}\text{U}$, Si, P, Ca and REEs. The standard allanite data were vetted for outliers (those
334 deviating by > 2 % from the mean $^{208}\text{Pb}/^{232}\text{Th}$). Isochron plots were constructed from
335 uncorrected data using Isoplot/Ex software (Ludwig, 2000).

336

337 **RESULTS**

338

339 **Bulk-rock composition**

340

341 A bulk-rock REE plot of Pe1 and Pe11 is shown in Figure 5 and bulk-rock compositional data
342 for Pe1 and Pe11 are given in Table 1. Both samples display identical bulk-rock REE patterns
343 characterised by steep LREE-enrichments ($\sim 200 \times$ chondrite) with respect to the HREEs, and
344 show negligible Eu anomalies. The major element compositions are also similar outside and
345 inside the shear zone. The similarity of bulk-rock REE contents outside and inside the shear
346 zone indicates there was a lack of (or very limited) metasomatism of rocks within within the
347 CSZ. This suggests that trace elements were redistributed within a closed system during
348 prograde metamorphism and partial melting, and that the trace element budget was not likely
349 to have been modified by an external source (e.g. fluids).

350

351 **Mineral composition**

352

353 Average major element mineral analyses are provided in Appendix 1 and 2. Electron
354 microprobe traverses of garnet in Pe11 are shown in Figure 6. In general, major element
355 zoning is limited. As the composition of minerals in Pe11 and Pe13 are very similar, we
356 discuss them together.

357

358 *Pe1*

359

360 *Magmatic relicts;* Clinopyroxene shows only minor internal zoning from core to rim,
361 with an X_{Mg} of 0.58 to 0.60 and 0.12 to 0.15 Al cations per formula unit (cpfu), respectively.
362 Plagioclase is predominantly andesine (An_{36} at core to An_{33} at rim), with minor orthoclase. K-
363 feldspar has orthoclase (Or_{88}) compositions, with a minor decrease in Na and Ca from core to
364 rim. Amphibole replacing clinopyroxene is pargasite hornblende according to the
365 classification of Leake (1987), with 6.13 to 6.16 Si cpfu and an X_{Mg} of ~ 0.50 . Titanite
366 overgrowths on ilmenite contain ~ 0.10 Al cpfu.

367

368 *Metamorphic minerals;* Garnet aggregates adjacent to both hornblende and ilmenite
369 are predominantly an almandine-grossular solid solution ($Alm_{54.5}Gro_{31.5}Py_{12.5}Sp_{0.02}$).

370 Amphibole that occurs as rare grains in the feldspar-rich matrix is pargasite hornblende in

371 composition (6.07 to 6.10 Si cpdf; Leake, 1987) and has a lower X_{Mg} of 0.45 compared to
372 hornblende on clinopyroxene. Recrystallised plagioclase is oligoclase (An_{23-28}) and less calcic
373 than relict plagioclase. Recrystallised K-feldspar is orthoclase (Or_{76-90}) in composition.
374 Titanite in the feldspar-rich matrix has a variable Al content of 0.08 to 0.13 cpdf.

375

376 *Pe11, 13*

377

378 *Garnet grains* are almandine-grossular-dominant solid solutions ($Alm_{53}Gro_{32-36}Py_{7-11}Sp_{7-1}$;
379 Table 2). Electron microprobe traverses of garnet revealed subtle zoning in the major
380 elements from core to rim, i.e. (1) a compositionally homogeneous core, and (2) a broad rim
381 that shows a small but progressive change in composition towards the edge, with increasing
382 % grossular and X_{Mg} and decreasing % spessartine (Fig. 6). Garnet rim major-element
383 compositions overlap with those of the fine-grained garnet in Pe1. *Amphibole* is pargasite
384 hornblende in composition (Leake, 1978). Both hornblende generations have $X_{Mg} \sim 0.37$ and
385 lack significant major element zoning. *Plagioclase* is oligoclase (An_{22}), similar to
386 recrystallised plagioclase in Pe1, with minor orthoclase. *Titanite* is unzoned in the major
387 elements and no clear core to rim relationship is observed for Al content (0.07-0.09 Al cpdf).
388 *Epidote-Allanite* grains show major element zoning from core (REE-poor epidote) to rim
389 (REE-rich allanite) along the coupled-substitution: $Ca^{2+} + Fe^{3+}[Al^{3+}] \leftrightarrow REE^{3+} + Fe^{2+}[Mg,$
390 $Mn^{2+}]$. Here we describe grains having REE+Th > 0.2 cpdf as allanite rather than REE-rich
391 epidote to distinguish between garnet inclusions (epidote) and matrix grains (allanite) (see
392 Gieré & Sorensen, 2004, for discussion). Epidote in garnet has a $Fe^{3+}/Fe_{total} \sim 1$, a clinzoisite
393 component of 2.3 Al cpdf and a REE+Th content < 0.15 cpdf. Matrix allanite compositions
394 vary from Fe^{3+}/Fe_{total} of 0.8-0.6 and REE+Th of 0.22-0.31 cpdf (or All_{22-30}), from cores to
395 rims, respectively. Strontium content decreases from epidote cores (~2000 ppm) to allanite
396 rims (~600 ppm).

397

398 **REE and trace element chemistry**

399

400 Thin sections and epoxy mounts of allanite and zircon were used for LA-ICP-MS trace
401 element analysis. Individual analyses of mineral domains are given in Tables 2a-c. Chondrite-
402 normalised REE plots of minerals from sample Pe1 are shown in Figure 7 and from Pe11 and
403 13 in Figure 8.

404

405 *Pe1 (orthogneiss)*

406

407 *Magmatic relicts;* Clinopyroxene REE analyses were taken from a single relict grain
408 and are characterised by a relatively enriched MREE content and moderate negative Eu
409 anomalies ($\text{Eu}/\text{Eu}^* \sim 0.6$) (Fig. 7b). Plagioclase is noted for its strong enrichment in the
410 LREEs relative to HREEs, up to 350 times chondrite, compared to K-feldspar (Fig. 7b). Both
411 plagioclase and K-feldspar strongly fractionate Eu over all other phases. In addition, the
412 feldspars are primary Sr repositories (plagioclase 599-850 ppm; K-feldspar 594-901 ppm).
413 Rubidium occurs primarily in K-feldspar (344-393 ppm) and biotite (798-834 ppm), and Ba is
414 mostly abundant in the feldspars (plagioclase 75-192 ppm; K-feldspar 6482-9054 ppm) and
415 biotite (3307-3807 ppm; Table 2a). Zircon shows a typical steep M-HREE pattern and strong
416 positive Ce anomaly. Apatite and zircon REE patterns show negative Eu anomalies ($\text{Eu}/\text{Eu}^* =$
417 $0.46-0.61$ and $\text{Eu}/\text{Eu}^* = 0.31-0.35$, respectively; Fig. 7c). Titanite grains replacing ilmenite
418 are L-MREE enriched compared to HREEs and also have negative Eu anomalies (Fig. 7c).
419 Similarly, hornblende overgrowths on clinopyroxene have clinopyroxene-like REE patterns
420 (Fig. 7c), characterised by a negative Eu anomaly ($\text{Eu}/\text{Eu}^* \sim 0.65$).

421 *Metamorphic minerals;* Fine-grained garnet is characterized by small negative, to
422 significant positive, Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.8-3.3$, mostly >0.90 ; Fig. 7a). Compared to the
423 LREE, garnet displays relatively enriched but variable M-HREE contents. In contrast to
424 hornblende near relict clinopyroxene, hornblende in leucocratic (K-feldspar + plagioclase +
425 quartz) layers is characterised by a relative enrichment in MREEs and has no negative Eu
426 anomaly (Fig. 7a). Titanite in leucocratic layers is enriched in L-MREEs relative to HREEs
427 (Fig. 7a). Unlike titanite on ilmenite, these titanite grains either have no Eu anomaly, or show
428 a small positive Eu anomaly. Similarly, some apatite grains also lack a negative Eu anomaly
429 ($\text{Eu}/\text{Eu}^* = 1.0$; Fig. 7a). BSE imaging revealed zoned epidote-allanite grains, which formed in
430 association with the new metamorphic mineral growth. The grains were too small, however,
431 to be analysed for trace elements by LA-ICP-MS.

432

433 *Pe11, 13 (migmatitic orthogneiss)*

434

435 *Garnet;* Garnet from both samples is heterogeneous with respect to trace element
436 content (Fig. 6) and displays a general decrease of Y and HREEs from core to rim (Fig. 8b
437 and f). In general, garnet also lacks an appreciable negative Eu anomaly ($\text{Eu}/\text{Eu}^* \sim 1.3$; Fig.
438 6).

439 *Amphibole*; Hornblende grains occur in two textural settings, as coarse (mm-cm sized)
440 grains (Pe11), and as smaller (<1 mm) grains, located in garnet strain shadows or aligned
441 within the S_{2b} fabric (Pe11, 13). Both hornblende types show LREE-depleted REE patterns
442 and lack a negative Eu anomaly (Fig. 8b and g). Hornblende in Pe11 has slightly lower HREE
443 abundances, compared to matrix hornblende, although overall mineral-scale trace element
444 zoning is variable between grains (e.g. Y-HREE, Ti, Zr).

445 *Plagioclase & K-feldspar*; Plagioclase and relict K-feldspar strongly fractionate Eu
446 from the other REEs and hence, have large positive Eu anomalies ($\text{Eu}/\text{Eu}^* > 15$; Fig. 8d and
447 h). Both feldspars are relatively enriched in the LREEs, and the M-HREEs were commonly
448 below detection levels. Plagioclase grains in migmatitic orthogneiss are significantly REE-
449 depleted compared to magmatic plagioclase in Pe1 (compare Fig. 7b and 8h). This can be
450 explained by differences in the relative abundance of REE-bearing accessory minerals (e.g.
451 allanite) between sample Pe1 and samples Pe11-13. Feldspar competes with allanite and
452 apatite for Sr (Table 2b, c).

453 *Scapolite*; Scapolite was found in only one sample (Pe11) and contains inclusions of
454 titanite. Scapolite has feldspar-like REE patterns, at higher concentrations, characterised by a
455 decrease in relative normalised abundance from LREEs to HREEs (Fig. 8d), and a moderate
456 positive Eu anomaly ($\text{Eu}/\text{Eu}^* > 2.0$).

457 *Epidote-allanite*; BSE imaging of epidote-allanite grains (Fig. 9a) reveals LREE-
458 controlled internal zoning that is correlated to major and minor elemental substitution. In the
459 matrix, allanite grains (intermediate BSE intensity) were commonly overgrown or truncated
460 by allanite rims (high relative BSE intensity) of higher REE and Th content, which appear to
461 be discontinuous overgrowths (Fig. 9a). Epidote cores (low relative BSE intensity) are also
462 observed. Epidote in garnet is relatively LREE-enriched compared to the M-HREE (although
463 overall LREE contents are lower than allanite in the matrix) and has a positive Eu anomaly
464 ($\text{Eu}/\text{Eu}^* \sim 1.5$) (Fig. 8b and e). Rims of intermediate epidote-allanite composition are locally
465 observed on epidote grains in garnet (Fig. 8a). Allanite is LREE-enriched by up to two orders
466 of magnitude, more than any other mineral in the migmatitic orthogneisses, and shows REE
467 patterns of decreasing chondrite-normalised abundance with increasing atomic number. Like
468 epidote, allanite lacks a negative Eu anomaly ($\text{Eu}/\text{Eu}^* \sim 1.1$). Interestingly, allanite rims are
469 less depleted in HREEs with respect to the MREE ($\text{Gd}_N/\text{Lu}_N < 150$) than allanite cores
470 ($\text{Gd}_N/\text{Lu}_N \sim 240$). Of the four accessory phases, allanite incorporated the most radiogenic
471 elements (Th > 600 ppm to > 900 ppm Th from core to rim). The textural context of epidote-
472 allanite and garnet can provide information on the relative timing of mineral growth and

473 therefore estimates for the P-T conditions at the time of allanite crystallisation, as discussed
474 below.

475 *Titanite*; Three titanite generations, identified from textural location and BSE
476 imaging, are also observed: (1) titanite included in garnet, (2) cores in matrix titanite, and (3)
477 rims on matrix titanite. Titanite is a major host of the M-HREEs and shows considerable
478 variation in these elements (Fig. 8c and g). Titanite grains in garnet are markedly depleted in
479 HREEs with respect to the L-MREEs. Like allanite, titanite does not show a negative Eu
480 anomaly ($\text{Eu}/\text{Eu}^* \sim 1.3$). Notably, LREE contents of titanite in these rocks are significantly
481 lower than those of titanite in the orthogneiss (compare Fig. 7a, c and 8c). This is due to the
482 direct influence of allanite as a strongly LREE-fractionating phase. Garnet and titanite show
483 opposing compositional growth zoning in Y. Yttrium content increases from titanite in garnet
484 (< 600 ppm) through to rims on matrix titanite (> 1370 ppm). Titanite is the major repository
485 for Nb and Ta (Table 2). Titanite is insufficiently radiogenic for dating, being hampered by a
486 greater initial Pb content than zircon (Table 2b-c).

487 *Zircon*; CL images of zircon grains from Pe13 (Fig. 9b) reveal partially resorbed,
488 oscillatory-zoned or weakly zoned cores, typical of an igneous origin, which are inclusion-
489 rich. Zircon cores are commonly overgrown by rounded, unzoned, inclusion-free rims. Grains
490 are commonly crosscut by fractures filled by new zircon (Fig. 9b). Zircon rims are chemically
491 distinct from igneous cores by their low trace element contents, including Y, REE, P, Nb, Th
492 and U (Table 2). Zircon cores in the migmatitic orthogneiss have identical REE
493 characteristics to zircon from the orthogneiss. Compared with magmatic cores, zircon rims
494 have no negative Eu anomaly ($\text{Eu}/\text{Eu}^* \sim 1.2$), a reduced Ce anomaly, and lower HREE
495 abundances. They are also depleted in U and show low Th/U (< 25 ppm and < 0.05 ,
496 respectively).

497 *Apatite*; Matrix apatite has relatively LREE-depleted, M-HREE-enriched patterns
498 (Fig. 8c and h). In contrast, apatite included garnet is relatively HREE-depleted, suggesting
499 equilibrium with its host phase. Like titanite, apatite in the migmatitic orthogneiss also
500 contains lower absolute LREE contents than grains in the orthogneiss. Whereas some apatite
501 grains display a small positive Eu anomaly ($\text{Eu}/\text{Eu}^* \sim 1.1-1.3$), others show a negative Eu
502 anomaly ($\text{Eu}/\text{Eu}^* \sim 0.4$), depending on their textural position in the rock. Apatite included in
503 garnet is richer in Sr, Ba and Pb than matrix apatite. Overall, apatite is poor in radiogenic
504 elements (Th and U content < 1 ppm).

505

506 **Accessory phase thermometry**

507

508 Trace-element thermometry of accessory minerals was applied to the Pe13 migmatitic
509 orthogneiss and Pe6 amphibolite boudin from the CSZ. Metamorphic rims of zircon grains
510 analysed by SHRIMP contained 2-5 ppm Ti (Table 2c). Using the Ti-in-zircon thermometer
511 calibrated by Watson *et al.* (2006), temperatures of $664-707 \pm 15^\circ\text{C}$ were obtained for
512 crystallisation of metamorphic zircon rims, assuming Ti buffering by titanite and αTiO_2 of \approx
513 0.7 (Lowery Claiborne *et al.*, 2006). Amphibolite boudins (recrystallised former mafic dykes)
514 provided the best estimate of peak metamorphic temperatures within the shear zone.
515 Zirconium thermometry on rutile in garnet gave temperatures of $720-747 \pm 24^\circ\text{C}$, based on
516 the calibration of Watson *et al.* (2006) for measured Zr concentrations of 722-955 ppm (Table
517 2c). Quartz and zircon are present in the Pe6 assemblage (Fig. 4e) therefore these T estimates
518 represent buffered temperatures. These constraints agree with previous temperature estimates
519 from recrystallised mafic dykes of $\sim 700-750^\circ\text{C}$ (Scrimgeour and Close, 1999).

520

521 **Geochronology**

522

523 *U-Pb in zircon*

524

525 It was not the purpose of this study to investigate zircon inheritance so only 7 analyses of
526 zircon cores were obtained from migmatitic orthogneiss Pe13. Four concordant analyses (> 96
527 %) gave ages from 1085 to 1108 Ma (Table 3). Unzoned, U-poor rims (< 27 ppm) were found
528 on the terminations of nearly all zircon grains. Poor counting statistics for U and Pb isotopes
529 resulted in large within-spot errors (Table 3). A ^{208}Pb -corrected Concordia age of 555 ± 7 Ma
530 (probability of concordance = 0.9, MSWD of single $^{206}\text{Pb}/^{238}\text{U}$ age population = 1.1), was
531 obtained from 14 of 19 analyses (Fig. 10a). Three of the remaining analyses were discarded
532 due to poor precision (> 4 % error, < 1 ppm radiogenic ^{206}Pb), and two analyses were rejected
533 as statistical outliers (588 and 525 Ma).

534

535 *Th-Pb in allanite*

536

537 BSE images and REE chemistry indicate more than one allanite generation (Fig. 9a). High- to
538 intermediate-intensity BSE zones (All₂₀₋₃₀), which represent allanite rims and cores,
539 respectively, were analysed by SHRIMP. The spots analysed contain between 1600-600 ppm

Comment [DR1]: I moved this interpretation to the discussion part

540 ThO₂ and have a Th/U of 9-15. SHRIMP Pb/Th analyses were pooled based on core-rim
541 textural relationships observed in BSE imaging and trace element composition (Table 4). Two
542 weighted mean ²⁰⁷Pb-corrected ²⁰⁸Pb/²³²Th ages of 551 ± 6 Ma (MSWD = 0.4, N = 12) and
543 559 ± 6 Ma (MSWD = 0.8, N = 13) were obtained for rims and cores, respectively (Fig. 10c
544 and d). The allanite rims have a common Pb contribution of 40-55 % of the total ²⁰⁸Pb content
545 and the allanite cores have a 58-70 % common Pb contribution to the total ²⁰⁸Pb content.
546 Figure 10b is a Th-Pb isochron plot showing uncorrected SHRIMP analyses of allanite rims
547 (black unfilled ellipses), which provide an independent constraint on the initial Pb
548 composition. The age of the allanite rim and cores were not statistically resolvable by
549 SHRIMP dating due to the error introduced from the common Pb correction, however the
550 calculation of two ages is justified by the observed core-rim textural and compositional
551 relationships.

552 Distinguishing between LA-ICP-MS analyses of allanite rims and cores proved to be
553 more difficult. Given the depth of drilling for the LA-ICP-MS method in this study is ~25
554 μm, compared to 2 μm for SHRIMP analysis, it is possible that the laser drilling may have
555 sampled more than one allanite domain. Additionally, despite the larger volume sampled, LA-
556 ICP-MS analyses resulted in an inferior analytical precision than SHRIMP analyses. Pooled
557 core and rim analyses fell, within error, along a ²³²Th-²⁰⁸Pb isochron whose slope gave an age
558 of 560 ± 36 Ma (MSWD = 0.2, N = 26) and an initial ²⁰⁸Pb/²⁰⁶Pb intercept of 2.2 ± 0.1 (Table
559 5, Fig. 10b).

560

561 **DISCUSSION**

562

563 **Metamorphic evolution of the Cockburn SZ**

564

565 *Magmatic stage*

566

567 The magmatic minerals preserved in Pe1 are relicts of the anhydrous rock protolith
568 (Walytjatjata Granodiorite). Relict igneous phases clinopyroxene, apatite and zircon cores
569 have moderate negative Eu anomalies. This is attributed to the strong Eu fractionation of
570 plagioclase and K-feldspar (Fig. 7b and c). Notably, bulk-rock REE patterns of granodiorite
571 outside and inside the shear zone have virtually no Eu anomaly. The titanite that replaces
572 ilmenite has a negative Eu anomaly and therefore, we infer that it also co-existed with

573 feldspar as a late-stage magmatic mineral. Similarly, hornblende on clinopyroxene has a
574 negative Eu anomaly and is likely a late-stage magmatic phase. The almost identical REE
575 patterns of hornblende and clinopyroxene support the textural observation that clinopyroxene
576 was being replaced by hornblende. The similar REE concentrations of the two phases also
577 imply that they are not in trace element equilibrium, based on predicted equilibrium
578 partitioning values $D_{\text{Hbl/Cpx}}^{\text{REE}}$ of ~2-5 (Storkey *et al.*, 2005; Buick *et al.*, 2007) at similar P-T
579 conditions to those in this study. Hornblende formation in a late magmatic stage may have
580 resulted from fluid release during magma cooling and crystallisation. The ages of the few
581 zircon cores measured (1085-1108 Ma) indicate that the protolith of the orthogneisses
582 crystallised in the Late Mesoproterozoic.

583

584 *Sub-solidus metamorphic stage*

585

586 Outside the shear zone, sub-solidus metamorphic reactions were not complete, as indicated by
587 the preferential domainal development of new metamorphic minerals on relict igneous
588 phases. Despite the presence of two feldspars, metamorphic minerals have small negative,
589 negligible or even positive Eu anomalies (Fig. 7a). The corona textures in Pe1 indicate that
590 chemical exchange pathways during metamorphism were short or limited, which suggests that
591 Eu signatures of the metamorphic minerals were inherited from the minerals they replaced.
592 For example, metamorphic garnet, hornblende, titanite and apatite in leucocratic layers do not
593 have negative Eu anomalies, and likely formed when Eu was liberated by the breakdown of
594 feldspar. The transition from an anhydrous igneous assemblage to a hydrous metamorphic
595 assemblage is an indication that fluid was added to the rock. In the presence of K-feldspar +
596 quartz + plagioclase, fluid addition above the wet solidus would lead to melting. The absence
597 of melt outside the CSZ, however, indicates that there was fluid addition at sub-solidus
598 conditions.

599

600 *Partial melting*

601

602 Migmatitic orthogneisses in the CSZ contain abundant garnet. Garnet in felsic, metapelitic
603 and metabasic migmatites is commonly interpreted to be a peritectic phase formed through
604 incongruent melting reactions that consume other Fe-Mg-bearing minerals, e.g. biotite and

605 hornblende (Vielzeuf & Schmidt, 2001; Patiño Douce, 2005). However, there is evidence that
606 this is not the case for the rocks of the Mann Terrane, as explained below.

607 The approximate position of rocks from the CSZ in P-T space with respect to the
608 fluid-present and fluid-absent solidus in quartzo-feldspathic rocks is shown in Figure 11 (after
609 Patiño Douce, 2005; their fig. 11). Over a P range of ~5-12 kbar, wet melting for two feldspar
610 plus quartz-bearing rock occurs at $\sim 650 \pm 25^\circ\text{C}$. In contrast, a temperature of at least 850°C is
611 needed to produce garnet from dehydration melting of biotite and hornblende in a broadly
612 granitic composition. Such temperatures are far in excess of estimates for the Petermann
613 Orogeny, obtained from accessory phase thermometry ($720\text{-}750^\circ\text{C}$; this study) and previous
614 conventional thermobarometry (Camacho *et al.*, 1997; Scrimgeour & Close, 1999). Both
615 approaches to thermometry yielded comparable results for the central Musgrave Block (Fig.
616 11). Therefore, garnet in the CSZ migmatites must have formed from a process other than
617 dehydration melting.

618 It has been documented extensively that garnet formed as a product of fluid-absent
619 melting commonly has a strong negative Eu anomaly due to the co-production of K-feldspar
620 during dehydration melting reactions (Bea *et al.*, 1994, 1997, Bea and Montero, 1999; Jung
621 and Hellebrand, 2006; Buick *et al.*, 2006; Rubatto *et al.*, 2006). It is possible that biotite
622 breakdown reactions during partial melting may occur under non-equilibrium conditions
623 leading to the dissolution of feldspar (Barbey, 2007). The T required for such non-equilibrium
624 melting would however still be too high compared to that indicated by our accessory phase
625 thermometry. Therefore, on the basis of the low metamorphic T and lack of Eu anomaly in
626 metamorphic garnet and hornblende from orthogneiss inside and adjacent to the CSZ (Fig.
627 8), we suggest that these minerals formed during sub-solidus reactions that involved feldspar
628 and liberated Eu, for example, via a general sub-solidus hydration reaction: K-feldspar +
629 plagioclase + clinopyroxene + H_2O \rightarrow garnet + biotite + epidote + quartz \pm hornblende.
630 Alternatively, garnet would also lack a significant negative Eu anomaly if it formed as a result
631 of feldspar breakdown at or above the wet solidus. Therefore, while we can demonstrate that
632 it did not form through fluid-absent melting reactions, the lack of a negative Eu anomaly
633 alone is not sufficient to establish whether it grew under sub-solidus or near supra-solidus
634 conditions. The relationships with accessory zircon place additional constraints on the
635 relative timing of garnet growth.

636 Metamorphic zircon overgrowths were found only in the melted rocks of the CSZ.
637 The identical bulk-rock composition inside and outside the shear zone suggests that the
638 presence of fluid/melt was the driving force behind new zircon precipitation. This is in

639 agreement with previous observations regarding the influence of melt on zircon behaviour
640 (Rubatto *et al.*, 2001, 2006). These studies document that in amphibolite- to granulite-facies
641 metapelites, new zircon formed only at the onset of melting ($\geq 700^{\circ}\text{C}$) and, unlike monazite,
642 occurred exclusively in the melt field. To help determine whether metamorphic zircon and
643 garnet were in trace element equilibrium we calculated empirical REE zircon-garnet
644 distribution coefficients (D_{REE}) from migmatitic orthogneiss Pe13 (Fig. 12). The absolute
645 values of distribution coefficients, and trends in their values as a function of atomic number,
646 are in disagreement with inferred equilibrium distributions obtained empirically from HP (e.g.
647 Hermann and Rubatto, 2003) or UHT metamorphic granulites (e.g. Hokada and Harley,
648 2004), or determined experimentally (800°C partitioning experiments of Rubatto & Hermann,
649 2007). This suggests that zircon and garnet in the CSZ migmatitic orthogneiss are not in trace
650 element equilibrium. Moreover, accepting that zircon is a melt product, the metamorphic
651 zircon-garnet REE partitioning evidence supports the interpretation that within the CSZ
652 garnet formed under sub-solidus conditions ($< 650^{\circ}\text{C}$).

653 It must be cautioned here that it is difficult to confidently identify an equilibrium
654 assemblage for geothermobarometry of the CSZ migmatitic orthogneisses because the trace
655 element partitioning clearly shows that (local) chemical equilibrium between co-existing
656 minerals during prograde metamorphism cannot be assumed. This is highlighted by garnet
657 and plagioclase, which are commonly used for garnet-hornblende-plagioclase-quartz
658 geobarometry (Kohn & Spear, 1989). These phases were in apparent disequilibrium for the
659 entire rock history, as inferred from petrographic observations and trace element
660 geochemistry. Plagioclase is present as a relict magmatic phase and a retrograde sub-solidus
661 phase and therefore is not in equilibrium with any stage of garnet growth (Fig. 3).

662 **Allanite formation in response to metamorphic P-T conditions**

663
664
665 The value of trace elements for reconstructing complicated metamorphic histories is well
666 demonstrated in high-grade terranes, where they are more sensitive monitors of geological
667 processes than major element compositions based on the preservation of mineral-scale zoning
668 (e.g. Hickmott & Shimuzu, 1990; Lanzirotti, 1995; Otamendi *et al.*, 2002; Van Orman *et al.*,
669 2002). In such a way trace elements have provided a tool to help link U-Th-Pb ages of trace
670 element-rich accessory minerals (principally zircon and monazite) to metamorphic P-T
671 conditions (e.g. Rubatto, 2002; Hermann & Rubatto, 2003; Hokada & Harley, 2004; Kelly &

672 Harley, 2005; Rubatto *et al.*, 2006). In this section, the trace element compositions of dated
673 allanite domains are used to relate these domains to major mineral phases in the rock.

674 Allanite preserves “reverse” core to rim REE zoning (Fig. 9a), previously interpreted
675 in the Catalina Schist to represent prograde growth zoning developed during sub-solidus
676 metasomatic reactions (Sorenson, 1991). The occurrence of metamorphic allanite in both the
677 melted and unmelted counterparts of the CSZ suggests that allanite growth initiated prior to
678 the development of metamorphic zircon. In fact, metamorphic epidote appears as an early
679 phase in the prograde metamorphic sequence as inclusions in garnet and as cores in allanite
680 grains.

681 Trace element analyses of the two dated allanite domains identified using BSE images
682 indicate compositional differences in Lu content, the size of the Eu anomaly, and initial Pb
683 content (Fig. 13a-b). In igneous rocks, primary magmatic allanite typically contains 0-15 %
684 common ^{208}Pb of the total ^{208}Pb (Gregory *et al.*, 2007; Gregory, unpublished). In contrast,
685 initial Pb concentrations in sub-solidus metamorphic (or hydrothermal) allanite are commonly
686 substantially higher (above 60 % common ^{208}Pb of total ^{208}Pb), particularly in allanite from
687 (ultra) HP metamorphic terranes (Davis *et al.*, 1994; Catlos *et al.*, 2000; Spandler *et al.*, 2003;
688 Frei *et al.*, 2004; Romer & Xiao, 2005; Rubatto *et al.*, 2008; Janots *et al.* in press). Allanite
689 crystallising from a melt is involved in competitive partitioning of Pb with feldspar. Thus,
690 melt precipitated allanite commonly displays relatively low initial Pb contents. On the other
691 hand, the high initial Pb contents in sub-solidus allanite can be explained in some cases by the
692 breakdown of another sub-solidus phase, such as feldspar that releases Pb^{2+} (effective ionic
693 radius of 1.19 Å; Shannon, 1967), which is subsequently incorporated into the Ca^{2+} (1.00 Å)
694 A2-site of crystallising allanite. Likewise, allanite strongly partitions Sr^{2+} (1.18 Å) in HP
695 rocks where plagioclase is no longer stable (Sorensen, 1991; Nagasaki & Enami, 1998;
696 Spandler *et al.*, 2003; Frei *et al.*, 2004; Rubatto *et al.*, 2008). Because migmatization involves
697 a combination of metamorphic and igneous processes we would expect the common ^{208}Pb
698 content of melt-precipitated allanite to reflect this (i.e. sub-solidus metamorphic > migmatitic
699 > igneous).

700
701 The observed correlation between initial Pb content in allanite and the geological
702 environment in which it forms may be relevant for understanding allanite growth history in
703 the CSZ migmatitic orthogneiss. In this study, allanite cores show elevated initial Pb contents
704 relative to rims and a small positive Eu anomaly (Fig. 13b). Both features are interpreted to
705 reflect allanite core formation during prograde sub-solidus reactions that led to the breakdown

706 of plagioclase and growth of garnet. Allanite formation may also be related to garnet with
707 respect to Lu content. Allanite cores contain < 1 ppm Lu, whereas allanite rims are relatively
708 enriched in the HREEs (Fig. 13a). A comparison of the allanite domains indicates that the rim
709 compositions may not have been in equilibrium with an HREE-rich phase, i.e. garnet. On this
710 basis we suggest that the allanite rims formed during incipient garnet breakdown related to
711 melt crystallisation, which would have involved the liberation of Lu. This hypothesis is
712 further supported by the absence of allanite rim compositions in unmelted orthogneiss outside
713 the shear zone.

714

715 **Considerations on the dating of complex allanite**

716

717 Performing geochronology on the CSZ migmatitic orthogneiss is dependent on zircon and
718 allanite, both of which display multiple stages of formation. Therefore, in order to extract U-
719 Th-Pb isotopic information that discriminates between distinct growth zones, a high-spatial
720 resolution dating approach is necessary. In this case, analysis by thermal ionisation mass
721 spectrometry is inappropriate and would lead to a mixing of different populations, irrespective
722 of the timescale over which the formation of the mineral zone occurred. Two micro-analytical
723 techniques have been proposed for allanite dating, i.e. SHRIMP and LA-ICP-MS (Gregory *et al.*,
724 2007). The smaller sampling volume and higher sensitivity afforded by the ion
725 microprobe made SHRIMP preferable for dating the strongly zoned CSZ allanite grains and
726 which exhibit moderate to high amounts of common Pb.

727 Two episodes of allanite growth in the CSZ have been identified on the basis of
728 textural and chemical evidence. This information requires that the isotopic analyses be
729 grouped as separate populations, from which ages can be calculated. In the specific case of
730 the CSZ, the analytical uncertainty on the ages does not allow the age difference of the two
731 episodes of allanite growth to be resolved. However, because the two allanite domains
732 distinguished chemically can be related to different assemblages and their relative P-T stages,
733 their unresolvable ages yield additional information, i.e. an estimate on the maximum
734 duration of prograde to peak metamorphism.

735 The small volume sampled for isotopic analysis, combined with low contents in
736 radiogenic elements (particularly for zircon) has the inevitable repercussion of relatively large
737 uncertainties on individual U-Th-Pb data: <6 % and <5 % at 2-sigma level, for zircon and
738 allanite respectively (Tables 3 and 4). Particularly for allanite, which is relatively non-
739 radiogenic, these uncertainties do not allow for recognition of minor anomalies in the form of

740 Pb loss or inheritance of exotic Pb (e.g. Romer, 2001; Romer and Siegesmund, 2003). A
741 robust approach for correcting samples with significant amount of initial Pb (e.g. allanite,
742 titanite, apatite) is by regressing uncorrected U-Pb data on a Tera-Wasserburg diagram
743 (Rubatto and Hermann, 2001; Aleinikoff *et al.*, 2002; Gregory *et al.*, 2007). An alternative
744 approach would be to determine the initial Pb composition from other minerals in the rock,
745 e.g. leached K-feldspar (Romer, 2001). For the present study, however, this approach would
746 be incorrect as we have shown using trace elements that the predominant K-feldspar present
747 in the rock is inherited from the ~1 Ga igneous protolith. As allanite is a high Th/U mineral,
748 we obtained an estimate of initial Pb composition from a Th-Pb isochron regression of
749 uncorrected data (Fig. 10b) and then ascertained that the Th-Pb and U-Pb systems had not
750 been significantly disturbed. The uncertainty on individual spots may limit the accuracy of the
751 regression and potential uncertainties of initial Pb and variable initial Pb through time could
752 account for a few m.y. apparent age shift (Romer, 2001). This would have limited impact on
753 the conclusions reached above on the timing of metamorphism and partial melting.

754 For the investigated samples, the general agreement of allanite and zircon ages
755 provides evidence that allanite with relatively high initial Pb contents can be successfully
756 dated by in-situ methods. The suitability of metamorphic allanite for geochronology however,
757 is likely to remain sample dependent, based on the assessment of initial Pb content and
758 composition.

759

760 **Timing of metamorphism and partial melting**

761

762 Determining the timing of shear zone development within a ductile regime (550 to 750°C) is a
763 non-trivial task due to the difficulty in finding suitable geochronometers. The Ar-Ar method
764 of dating remains one of the best ways to directly date deformation fabrics (e.g. Camacho &
765 Fanning, 1995; Camacho *et al.*, 1997). However, for HT shear zones the $^{40}\text{Ar}/^{39}\text{Ar}$ system
766 typically records the timing of closure of micas or amphiboles to volume diffusion under
767 relatively low T (< 550°C). In the relatively high-Ca, low-Al rocks of the CSZ, accessory
768 allanite and zircon were the most important U-Th-Pb chronometers. Titanite and apatite were
769 sufficiently low in radiogenic elements as to make them unsuitable for in-situ dating. In
770 particular, the Th-depleted compositions of titanite, apatite and metamorphic zircon are a sign
771 that these phases formed in the presence of Th-bearing allanite.

772 New zircon growth associated with the Petermann Orogeny is rare and limited to
773 discrete partial melt shear zones (Scrimgeour *et al.*, 1999), which indicates that zircon

774 formation within the CSZ was promoted by partial melting. We further demonstrated above
775 that zircon was not in REE equilibrium with sub-solidus garnet and based on the Ti-in-zircon
776 saturation thermometry, likely formed at $T \leq 700^\circ\text{C}$, implying that zircon crystallised during
777 cooling, close to the wet solidus. We thus interpret the zircon rim U-Pb age of 555 ± 7 Ma to
778 constrain the timing of partial melting and crystallisation on cooling within the CSZ. This is
779 in agreement with a metamorphic zircon SHRIMP U-Pb age of 561 ± 11 Ma obtained from a
780 migmatite north of the CSZ (Scrimgeour *et al.*, 1999). The metamorphic zircon age provides a
781 useful constraint with which to examine allanite isotopic behaviour.

782 From petrography and trace element analysis we have established that, in contrast to
783 zircon, two episodes of metamorphic allanite formation occurred along the CSZ P-T path:
784 allanite core compositions are present in melted and unmelted counterparts of the CSZ and
785 have high Gd/Lu suggestive of concomitant garnet growth. In comparison, allanite rim
786 compositions are limited to migmatitic orthogneisses, are relatively HREE-enriched and show
787 small Eu anomalies and initial ^{208}Pb contents, attributed to the competitive formation of
788 feldspar and allanite from a crystallising melt. Petrography and mineral chemistry allow
789 calculating an age for each allanite domain, which bracket the zircon age. Allanite cores
790 formed at 559 ± 6 Ma during sub-solidus hydration reactions occurring below the granitic wet
791 solidus, and allanite rims formed at 551 ± 6 Ma during the initial stages of cooling and melt
792 crystallisation near or at the wet solidus ($\sim 650^\circ\text{C}$). This implies that the prograde path from
793 sub-solidus hydration to melt crystallization likely lasted in the order of 10 m.y.

794

795

796 CONCLUSIONS

797

798 Amphibolite-grade metamorphism and melting in the CSZ occurred around ~ 559 and ~ 551
799 Ma as indicated by zircon and allanite U-Th-Pb dating. Notably, fluid-present melting
800 ($>650^\circ\text{C}$) in the CSZ was not synchronous with the major episode of garnet and hornblende
801 formation. Instead garnet growth occurred from prograde sub-solidus hydration reactions at
802 the expense of feldspar below the metamorphic peak. Peak T of $720\text{--}750^\circ\text{C}$ from Zr-in-rutile
803 thermometry support the requirement of fluid-induced partial melting in the quartzo-
804 feldspathic rocks.

805 Detailed trace element investigation allowed the dated U-Th-Pb accessories to be
806 related to garnet. Outside the CSZ in the orthogneiss metamorphic zircon was absent and

807 metamorphic allanite growth was limited. Inside the CSZ, metamorphic zircon crystallised
808 from a cooling melt close to the wet solidus at $T \leq 700^\circ\text{C}$ based on Ti-in-zircon thermometry.
809 In comparison, metamorphic allanite formed over an extended P-T range: allanite cores
810 formed on the prograde sub-solidus path in equilibrium with garnet rims and zircon and
811 allanite overgrowths formed after garnet on initial melt crystallisation. The two periods of
812 allanite growth are not resolvable by the allanite dating as they occurred within a period of
813 ~10 m.y.

814

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816

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825

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991 **Figures**

992

993 Figure 1: (a) Regional geological setting of the intracratonic Musgrave Block and Mann
994 Terrane, and the Amadeus and Officer sedimentary basins in central Australia (modified after
995 Scrimgeour and Close, 1999); (b) Simplified geological map of the central Mann Ranges
996 (after Scrimgeour and Close, 1999 and Scrimgeour *et al.*, 1999). Rock type between the Mann
997 Fault and Woodroffe Thrust was inferred from sparse rock outcrops of the Umutju Granite
998 Suite. P-T estimates were determined from recrystallised mafic dykes metamorphosed during

999 the Petermann Orogeny (Scrimgeour and Close, 1999). Inset: enlarged view of granite
1000 outcrop around the CSZ and locations of samples used in this study. Sample Pe1 was
1001 collected outside the CSZ and samples Pe6, 11 and 13 were collected within the CSZ.

1002

1003 Figure 2: (a) Outcrop (north of the CSZ) showing representative field relations in the central
1004 Mann Ranges. A relatively sharp strain gradient is observed from regionally foliated
1005 orthogneisses ($D2_a$), into migmatitic orthogneiss ($D2_b$), such as those of the CSZ; (b)
1006 Amphibolite boudin (derived from a mafic dyke) in $S2_b$ fabric within the CSZ. Note the cm-
1007 sized garnets within the migmatitic fabric; (c) Relatively low-strain zone in the CSZ, where
1008 melt appears as solidified “pods” within $S2_b$ and contain cm-sized hornblende grains.

1009

1010 Figure 3: Summary of mineral stability during the different stages of development within the
1011 CSZ (Pe11, Pe13). The horizontal axis indicates increasing strain accumulation within the
1012 shear zone and the overprinting of the migmatites by strong mylonitic fabrics.

1013

1014 Figure 4: (a) BSE image of accessory apatite and zoned epidote-allanite in a plagioclase-rich
1015 domain (Pe1); (b) Photomicrograph of domainal equilibrium of metamorphic minerals outside
1016 the shear zone (Pe1); (c) High-resolution thin section scan of Pe1 orthogneiss showing the
1017 domainal distribution of minerals, note the large igneous K-feldspar grains, e.g. bottom left
1018 corner, field of view = 1cm; (d) Rutile grains rimmed by titanite in garnet, (PPL, Pe6); (e)
1019 BSE image of zircon adjacent to rutile and titanite in the amphibolite boudin (Pe6); (f)
1020 Abundant accessory mineral growth of epidote-allanite, titanite and apatite, aligned with the
1021 fabric, along with matrix hornblende (PPL, Pe11); (g) Photomicrograph of almandine-
1022 grossular garnet, wrapped by $S2_b$ fabric. Garnet strain shadows contain accessory phases and
1023 hornblende. Note the inclusion of epidote (and not allanite) in garnet (Pe11); (h) High
1024 resolution thin section scan of Pe11 migmatitic orthogneiss, note relict igneous K-feldspar
1025 bottom left corner, field of view = 2cm; (i) Recrystallised feldspar and matrix hornblende
1026 fabric wrapping coarse-grained garnet and hornblende (Pe11); (j) Photomicrograph of garnet
1027 adjacent to relict K-feldspar. Garnet includes titanite, apatite, and epidote (PPL, Pe13).

1028

1029 Figure 5: Chondrite-normalised bulk-rock REE patterns from Pe1 and Pe11. Normalization
1030 values taken from McDonough and Sun (1995).

1031

1032 Figure 6: Electron microprobe major element and LA-ICP-MS trace element traverses of
1033 garnet in sample Pe11. Y in ppm, Mn in cations per formula unit. Scatter in trace element data
1034 measured from the BCR glass standard was 2-3 % (reproducibility at 1σ). Detection limit for
1035 Mn concentrations determined by EMP was ~300 ppm.

1036

1037 Figure 7: Chondrite-normalised mineral REE patterns from Pe1 determined by LA-ICP-MS.
1038 (a) metamorphic grains in Pe1; (b) and (c) magmatic relicts in Pe1.

1039

1040 Figure 8: Chondrite-normalised mineral REE patterns of Pe11 (a-d) and Pe13 (e-h)
1041 determined by LA-ICP-MS.

1042

1043 Figure 9: (a) BSE images of Pe13 allanite. LREE zoning is observed from epidote cores to
1044 allanite rims, which often truncate allanite cores. Ca and LREE are in oxide wt %; (b) CL
1045 imaging of zircon from Pe13 reveal unzoned overgrowths on oscillatory-zoned cores, with
1046 grain-scale fracturing and “infill” of new zircon.

1047

1048 Figure 10: (a) U-Pb Concordia of ^{208}Pb -corrected SHRIMP analyses of zircon rims (sample
1049 Pe13); (b) Isochron of uncorrected Th-Pb data from SHRIMP (white ellipses) and LA-ICP-
1050 MS (grey ellipses), using common ^{206}Pb as the stable reference isotope. Extrapolation of the
1051 data gives an intercept that provides an initial $^{208}\text{Pb}/^{206}\text{Pb}$ composition; (c and d) Weighted
1052 mean Th-Pb age plot of allanite rims and cores, identified from electron-backscatter. Grey
1053 shaded analyses were excluded as outliers.

1054

1055 Figure 11: Schematic P-T diagram (adapted after Patiño Douce, 2005) showing P-T estimates
1056 for upper amphibolite-grade metamorphism in the central Mann Ranges (e.g. Scrimgeour and
1057 Close, 1999), the wet solidus for tonalite bulk compositions and the fluid absent solidus for
1058 biotite and amphibole melt curves for tonalite bulk compositions.

1059

1060 Figure 12: Apparent REE distribution coefficients for zircon-garnet obtained from average
1061 compositions (sample Pe13) and previous work. H & R = Hermann and Rubatto (2003); H &
1062 H = Hodaka and Harley (2004); R & H Rubatto and Hermann (2007), exp = experimental
1063 partitioning at 800°C.

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1065 Figure 13: a) Common Pb vs. Lu content in allanite cores and rims (sample Pe13). Lu content
1066 was obtained for each allanite zone analysed by SHRIMP; b) Average common Pb content vs.
1067 Eu anomaly for each epidote-allanite population. Epidote Pb_c was determined from a single
1068 SHRIMP analysis of an epidote core.
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