Mineral-scale trace element and U-Th-Pb age constraints on metamorphism and melting during the Petermann Orogeny (central 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 ($T \leq 700$°C). In contrast, allanite formed at different stages of the CSZ P-T path: (1) prograde sub-solidus growth ($T < 650$°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

INTRODUCTION

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

Characteristic trace element compositions of minerals from amphibolite and granulite facies terranes have been used to constrain the processes of their formation. Few of these studies, however, have examined the trace element distribution between multiple REE-rich major and accessory phases during amphibolite-grade metamorphism at sub-solidus conditions (e.g. Sorensen & Grossman, 1989; Mulrooney & Rivers, 2005). The use of trace elements to determine the process of formation is particularly relevant for accessory minerals that can be dated via the U-Th-Pb system. Such accessory minerals are major hosts of trace elements (e.g. Hermann, 2002) and in metamorphic rocks often the correct interpretation of their U-Th-Pb age depends on how well their formation can be related to P-T conditions. In this paper we contribute to the expanding field of mineral trace element geochemistry and geochronology with a study of high-pressure (HP) migmatitic orthogneiss of the CSZ within the Mann Terrane, central Australia. Understanding the growth histories of metamorphic accessory phases is facilitated when samples of the same bulk composition but with different extents of metamorphic overprint (e.g. melted and unmelted counterparts of a rock type) can be compared (e.g. Sorensen, 1991; Rubatto *et al.*, 2001; Storkey *et al.*, 2005; Buick *et al.*, 2007; Clarke *et al.*, 2007). The investigated rocks are particularly suited for such a study because they include a suite of granodioritic orthogneisses that are cut by shear zones, in which the same bulk compositions have undergone partial melting at ~700°C (Scrimgeour & Close, 1999).

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

GEOLOGICAL SETTING

The largest HP metamorphic terrane documented in Australia is exposed in the Mann Terrane, central Australia. The Mann Terrane represents part of the basement of the Musgrave Block located south of the Amadeus Basin and is delineated by two crustal-scale, south-dipping structures, the Woodroffe Thrust and the Mann Fault (Fig. 1a). Both structures formed during the Neoproterozoic to early Palaeozoic intracratonic Petermann Orogeny, which resulted in the reworking of anhydrous Mesoproterozoic granulite-facies orthogneisses and igneous rocks of the Musgrave Block, and the northward exhumation of deep crustal mylonites along the Woodroffe Thrust (Camacho and Fanning, 1995; Camacho *et al.*, 1997; Scrimgeour and Close, 1999). North of the Mann Fault, basement outcrop is dominated by the ~1190-1120 Ma Umutju Granite Suite (Fig. 1b; Camacho and Fanning, 1995), which is intruded by ~1080-1050 Ma and ~800 Ma mafic dykes (e.g. Zhao et al. 1994; Sun *et al.*, 1996). During the Petermann Orogeny, basement rocks were metamorphosed to transitional garnet-granulite- to eclogite-facies conditions at ~11-13 kbar and ~700-750°C (Scrimgeour and Close, 1999). Metamorphic grade varies across the orogen with the highest P (and T) attained in the south, immediately north of the Mann Fault (Fig. 1b). Metamorphic grade decreases upsection, with P-T conditions of ~6-7 kbar and ~600-650°C recorded in shear zones crosscutting the Pottoyu and Mantarurr Granite Suites north of the Woodroffe Thrust (Fig. 1b; Scrimgeour and Close, 1999).

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

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

The timing of high-grade metamorphism associated with the Petermann Orogeny is poorly constrained (~560 and 520 Ma; Maboko *et al.,* 1992; Camacho and Fanning, 1995; Clarke *et al.,* 1995). This is the result of an absence of extensive high-temperature accessory mineral U-Th-Pb geochronology partly due to a lack of new zircon formation in rocks metamorphosed during the Petermann Orogeny, poor outcrop exposure and restricted land access (Scrimgeour et al., 1999). Available mineral Sm-Nd and Ar-Ar ages for basement rocks in the eastern and western Musgrave Block indicate cooling of these rocks below 550°C by *c*. 550-530 Ma (Maboko *et al*., 1992; Camacho *et al.*, 1997). There remains, however, a lack of geochronological constraints on the high-temperature history of the Petermann Orogeny in the central to northern Musgrave Block.

SAMPLE DESCRIPTION

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

Pe1

Sample Pe1 was collected from a location 20 m outside the CSZ and is representative of the unmelted and largely anhydrous, although strongly deformed, orthogneiss. This sample was investigated in order to characterise the trace element distribution during prograde to peak metamorphism of unmelted equivalents to migmatitic orthogneiss of the CSZ. It contains variably recrystallised igneous quartz + K-feldspar + plagioclase + clinopyroxene + ilmenite + apatite (e.g. relict igneous clinopyroxene, fig. 4c in Scrimgeour and Close, 1999). No REE-rich magmatic accessory phase (e.g. monazite or allanite) was detected, and on a regional scale, monazite has not been reported in Mann Terrane granites (Scrimgeour *et al.*, 1999). The relict primary assemblage is overprinted by a fine-grained (<300 μm) secondary metamorphic assemblage of garnet + hornblende + biotite + titanite + epidote/allanite (Fig. 4a-b). The two feldspars are present as mm-size relict grains (K-feldspar is cloudy, Fig. 4c), and as small, recrystallised grains. Pe1 exhibits a domainal distribution of metamorphic minerals (Fig. 4c). Hornblende forms coronal replacement textures around igneous clinopyroxene and is also found near garnet and plagioclase. Subhedral garnet forms as aggregates of small euhedral grains surrounding either hornblende or ilmenite, and adjacent to feldspar (Fig. 4b-c), and contains inclusions of ilmenite. Hornblende and garnet do not form mutual inclusion relationships. Titanite grains form as clusters around relict ilmenite (Fig. 4b), or as lone grains near garnet. Ilmenite contains magnetite exsolution features. Small epidote-allanite grains (<25 μm) are included in, or adjacent to, garnet, plagioclase, titanite and apatite. Apatite and zircon are present, although it is difficult to distinguish whether they are magmatic or metamorphic phases, based on petrography alone.

Pe6

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

Pe11, 13

Sample Pe13 is a deformed leucosome containing garnet and hornblende from inside the CSZ. Sample Pe11 contains both leucosome and mesosome, however the following description and compositional analyses are taken only from the leucosome segment. Unlike Pe1, migmatitic orthogneisses recrystallised within the shear zone are generally devoid of clinopyroxene and do not preserve the earlier igneous assemblage, with the exception of relict K-feldspar and minor plagioclase (Fig. 4h). Both samples contain a relatively hydrous major mineral assemblage of quartz + K-feldspar + plagioclase + garnet + hornblende + biotite + epidote (Fig. 3, 4f-j); Pe11 additionally contains minor scapolite. Both feldspars are present as >500 μm-sized porphyroclasts and as <250 μm-sized recrystallised grains. Garnets are mm- to cm-sized and commonly poikioblastic and anhedral. Garnet cores contain variably sized inclusions of quartz and accessory epidote, zircon, titanite and apatite. Garnet rims are typically inclusion-free; they locally contain larger (100 μm) grains of epidote, titanite and apatite, but lack the abundant small inclusions found in garnet cores (Fig. 4h). Two hornblende generations were distinguished by texture: mm- to cm-sized sub-euhedral hornblende (in Pe11 only), and a subsequent generation of foliated "matrix" hornblende (Fig. 4f, i). Biotite is fine-grained, and both biotite and matrix hornblende appear to be (sub-solidus) retrograde phases and have a fabric preferred orientation.

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

ANALYTICAL PROCEDURES

Imaging and Electron microprobe analysis

Compositional zoning was identified by high-contrast backscatter electron (BSE) imaging using a Cambridge S360 SEM at the ANU Electron Microscopy Unit (~2 nA, 15 kV and 15 mm working distance). WDS analysis of major elements was carried out on a Cameca SX100 electron microprobe at RSES, ANU and on a Cameca SX50 at the University of Melbourne. Analytical conditions were 15 kV and 20-25 nA, with the beam current defocused to 5 µm to avoid beam damage. An analytical method specific to allanite (REE) analysis was used at RSES (sample Pe13; Gregory *et al.*, 2007). In-house silicate mineral and allanite standards were analysed to monitor internal consistency. Fe^{3+} contents were recalculated based on charge balance assuming 8 cations and 12.5 oxygens for epidote-allanite. Zircon mounts were imaged using a cathodoluminescence (CL) detector at the ANU EMU on a HITACHI S2250-N SEM with operating conditions of 15kV, ~60 μm and ~20 mm working distance.

Bulk-rock analysis

Procedures followed are those described by Buick *et al.* (2006). Samples Pe1 and Pe11 were ground in a tungsten carbide mill to a grain size of 25µm, and fused into (La_2O_3-doped) lithium borate glass discs (0.84 g of sample to 4.5 g of flux) for major-element determinations, and REE-free lithium borate glass discs (Sigma® 12:22 X-Ray flux;

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

Mineral LA-ICP-MS trace element analysis

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

Zircon and allanite ion microprobe dating

CL and BSE images served as a basis for selection of zircon and allanite grains for isotopic analysis, respectively. U-Th-Pb analyses were conducted on a Sensitive High Resolution Ion Microprobe (SHRIMP II and RG) at RSES. Epoxy-mounted grains of allanite and zircon from Pe13 were analysed during different analytical sessions under similar operating conditions of a 3-4 nA, 10 kV primary O_2^- beam focussed to a ~ 20 µm diameter spot. Instrumental conditions and data acquisition and treatment were generally as described by Compston *et al.* (1992) and Williams (1998), with isotope data collected from sets of six scans through the masses. The measured $^{206}Pb/^{238}U$ ratio was corrected using the ANU reference zircon FC1 (1099 Ma). Due to ^{204}Pb overcounts and Th-deficient zircon analyses were corrected for common Pb based on measured $^{208}Pb/^{206}Pb$ calculated from Th/U, assuming equilibrium between Th and U systems. This was satisfied by all analyses by plotting ThO/UO versus $^{208}Pb/^{206}Pb$. Due to their low content in radiogenic lead, zircon rims had high proportions of common Pb (2-8 % $^{206}Pb_c$) relative to the ^{204}Pb-free standard. Therefore a model common Pb composition (Stacey and Kramers, 1975) was assumed for a population age of 550 Ma. A detailed description for allanite Th-Pb analysis is given in Gregory *et al.* (2007). The measured $^{208}Pb/^{232}Th$ ratio was corrected using the allanite standard CAP (276 Ma; Barth *et al.*, 1994). All analyses were corrected for common Pb based on measured $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ assuming a model Pb composition at 550 Ma (Stacey & Kramers, 1975). Equilibrium between Th and U systems was satisfied by plotting ThO/UO versus $^{208}Pb/^{206}Pb$. Th-Pb isochrons regressed from uncorrected data gave initial $^{208}Pb/^{206}Pb$ intercept values of 2.14 ± 0.24 for cores and 2.12 ± 0.12 for rims, which are within error of the model $^{208}Pb/^{206}Pb$ composition. Electron microprobe chemical compositions were acquired for each domain analysed by SHRIMP. Age calculation was done using RSES internal software for allanite and using the software Isoplot/Ex (Ludwig, 2000) for zircon and allanite.

Allanite laser ablation ICP-MS dating

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

RESULTS

Bulk-rock composition

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

Mineral composition

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

Pe1

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

Metamorphic minerals; Garnet aggregates adjacent to both hornblende and ilmenite are predominantly an almandine-grossular solid solution ($Alm_{54.5}Gro_{31.5}Py_{12.5}Sp_{0.02}$). Amphibole that occurs as rare grains in the feldspar-rich matrix is pargasite hornblende in composition (6.07 to 6.10 Si cpfu; Leake, 1987) and has a lower X_{Mg} of 0.45 compared to hornblende on clinopyroxene. Recrystallised plagioclase is oligoclase (An_{23-28}) and less calcic than relict plagioclase. Recrystallised K-feldspar is orthoclase (Or_{76-90}) in composition. Titanite in the feldspar-rich matrix has a variable Al content of 0.08 to 0.13 cpfu.

Pe11, 13

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

REE and trace element chemistry

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

Pe1 (orthogneiss)

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

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

Pe11, 13 (migmatitic orthogneiss)

Garnet; Garnet from both samples is heterogeneous with respect to trace element content (Fig. 6) and displays a general decrease of Y and HREEs from core to rim (Fig. 8b and f). In general, garnet also lacks an appreciable negative Eu anomaly (Eu/Eu* ~ 1.3; Fig. 6).

Amphibole; Hornblende grains occur in two textural settings, as coarse (mm-cm sized) grains (Pe11), and as smaller (<1 mm) grains, located in garnet strain shadows or aligned within the $S2_b$ fabric (Pe11, 13). Both hornblende types show LREE-depleted REE patterns and lack a negative Eu anomaly (Fig. 8b and g). Hornblende in Pe11 has slightly lower HREE abundances, compared to matrix hornblende, although overall mineral-scale trace element zoning is variable between grains (e.g. Y-HREE, Ti, Zr).

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

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

Epidote-allanite; BSE imaging of epidote-allanite grains (Fig. 9a) reveals LREE-controlled internal zoning that is correlated to major and minor elemental substitution. In the matrix, allanite grains (intermediate BSE intensity) were commonly overgrown or truncated by allanite rims (high relative BSE intensity) of higher REE and Th content, which appear to be discontinuous overgrowths (Fig. 9a). Epidote cores (low relative BSE intensity) are also observed. Epidote in garnet is relatively LREE-enriched compared to the M-HREE (although overall LREE contents are lower than allanite in the matrix) and has a positive Eu anomaly (Eu/Eu* ~ 1.5) (Fig. 8b and e). Rims of intermediate epidote-allanite composition are locally observed on epidote grains in garnet (Fig. 8a). Allanite is LREE-enriched by up to two orders of magnitude, more than any other mineral in the migmatitic orthogneisses, and shows REE patterns of decreasing chondrite-normalised abundance with increasing atomic number. Like epidote, allanite lacks a negative Eu anomaly **(**Eu/Eu* ~ 1.1**)**. Interestingly, allanite rims are less depleted in HREEs with respect to the MREE (Gd_N/Lu_N < 150) than allanite cores (Gd_N/Lu_N ~240). Of the four accessory phases, allanite incorporated the most radiogenic elements (Th > 600 ppm to > 900 ppm Th from core to rim). The textural context of epidote-allanite and garnet can provide information on the relative timing of mineral growth and therefore estimates for the P-T conditions at the time of allanite crystallisation, as discussed below.

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

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

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

Accessory phase thermometry

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

Geochronology

U-Pb in zircon

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

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

Th-Pb in allanite

BSE images and REE chemistry indicate more than one allanite generation (Fig. 9a). High- to intermediate-intensity BSE zones (All_{20-30}), which represent allanite rims and cores, respectively, were analysed by SHRIMP. The spots analysed contain between 1600-600 ppm

ThO_2 and have a Th/U of 9-15. SHRIMP Pb/Th analyses were pooled based on core-rim textural relationships observed in BSE imaging and trace element composition (Table 4). Two weighted mean ^{207}Pb-corrected ^{208}Pb/^{232}Th ages of 551 ± 6 Ma (MSWD = 0.4, N = 12) and 559 ± 6 Ma (MSWD = 0.8, N = 13) were obtained for rims and cores, respectively (Fig. 10c and d). The allanite rims have a common Pb contribution of 40-55 % of the total ^{208}Pb content and the allanite cores have a 58-70 % common Pb contribution to the total ^{208}Pb content. Figure 10b is a Th-Pb isochron plot showing uncorrected SHRIMP analyses of allanite rims (black unfilled ellipses), which provide an independent constraint on the initial Pb composition. The age of the allanite rim and cores were not statistically resolvable by SHRIMP dating due to the error introduced from the common Pb correction, however the calculation of two ages is justified by the observed core-rim textural and compositional relationships.

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

DISCUSSION

Metamorphic evolution of the Cockburn SZ

Magmatic stage

The magmatic minerals preserved in Pe1 are relicts of the anhydrous rock protolith (Walytjatjata Granodiorite). Relict igneous phases clinopyroxene, apatite and zircon cores have moderate negative Eu anomalies. This is attributed to the strong Eu fractionation of plagioclase and K-feldspar (Fig. 7b and c). Notably, bulk-rock REE patterns of granodiorite outside and inside the shear zone have virtually no Eu anomaly. The titanite that replaces ilmenite has a negative Eu anomaly and therefore, we infer that it also co-existed with feldspar as a late-stage magmatic mineral. Similarly, hornblende on clinopyroxene has a negative Eu anomaly and is likely a late-stage magmatic phase. The almost identical REE patterns of hornblende and clinopyroxene support the textural observation that clinopyroxene was being replaced by hornblende. The similar REE concentrations of the two phases also imply that they are not in trace element equilibrium, based on predicted equilibrium partitioning values $D^{REE}_{Hbl/Cpx}$ of ~2-5 (Storkey *et al.*, 2005; Buick *et al.*, 2007) at similar P-T conditions to those in this study. Hornblende formation in a late magmatic stage may have resulted from fluid release during magma cooling and crystallisation. The ages of the few zircon cores measured (1085-1108 Ma) indicate that the protolith of the orthogneisses crystallised in the Late Mesoproterozoic.

Sub-solidus metamorphic stage

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

Partial melting

Migmatitic orthogneisses in the CSZ contain abundant garnet. Garnet in felsic, metapelitic and metabasic migmatites is commonly interpreted to be a peritectic phase formed through incongruent melting reactions that consume other Fe-Mg-bearing minerals, e.g. biotite and hornblende (Vielzeuf & Schmidt, 2001; Patiño Douce, 2005). However, there is evidence that this is not the case for the rocks of the Mann Terrane, as explained below.

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

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

Metamorphic zircon overgrowths were found only in the melted rocks of the CSZ. The identical bulk-rock composition inside and outside the shear zone suggests that the presence of fluid/melt was the driving force behind new zircon precipitation. This is in agreement with previous observations regarding the influence of melt on zircon behaviour (Rubatto *et al.,* 2001, 2006),. These studies document that in amphibolite- to granulite-facies metapelites, new zircon formed only at the onset of melting (≥ 700°C) and, unlike monazite, occurred exclusively in the melt field. To help determine whether metamorphic zircon and garnet were in trace element equilibrium we calculated empirical REE zircon-garnet distribution coefficients (D_{REE}) from migmatitic orthogneiss Pe13 (Fig. 12). The absolute values of distribution coefficients, and trends in their values as a function of atomic number, are in disagreement with inferred equilibrium distributions obtained empirically from HP (e.g. Hermann and Rubatto, 2003) or UHT metamorphic granulites (e.g. Hokada and Harley, 2004), or determined experimentally (800°C partitioning experiments of Rubatto & Hermann, 2007). This suggests that zircon and garnet in the CSZ migmatitic orthogneiss are not in trace element equilibrium. Moreover, accepting that zircon is a melt product, the metamorphic zircon-garnet REE partitioning evidence supports the interpretation that within the CSZ garnet formed under sub-solidus conditions (< 650°C).

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

Allanite formation in response to metamorphic P-T conditions

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

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

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

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

The observed correlation between initial Pb content in allanite and the geological environment in which it forms may be relevant for understanding allanite growth history in the CSZ migmatitic orthogneiss. In this study, allanite cores show elevated initial Pb contents relative to rims and a small positive Eu anomaly (Fig. 13b). Both features are interpreted to reflect allanite core formation during prograde sub-solidus reactions that led to the breakdown of plagioclase and growth of garnet. Allanite formation may also be related to garnet with respect to Lu content. Allanite cores contain < 1 ppm Lu, whereas allanite rims are relatively enriched in the HREEs (Fig. 13a). A comparison of the allanite domains indicates that the rim compositions may not have been in equilibrium with an HREE-rich phase, i.e. garnet. On this basis we suggest that the allanite rims formed during incipient garnet breakdown related to melt crystallisation, which would have involved the liberation of Lu. This hypothesis is further supported by the absence of allanite rim compositions in unmelted orthogneiss outside the shear zone.

Considerations on the dating of complex allanite

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

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

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

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

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

Timing of metamorphism and partial melting

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

New zircon growth associated with the Petermann Orogeny is rare and limited to discrete partial melt shear zones (Scrimgeour *et al.*, 1999), which indicates that zircon formation within the CSZ was promoted by partial melting. We further demonstrated above that zircon was not in REE equilibrium with sub-solidus garnet and based on the Ti-in-zircon saturation thermometry, likely formed at T ≤ 700˚C, implying that zircon crystallised during cooling, close to the wet solidus. We thus interpret the zircon rim U-Pb age of 555 ± 7 Ma to constrain the timing of partial melting and crystallisation on cooling within the CSZ. This is in agreement with a metamorphic zircon SHRIMP U-Pb age of 561 ± 11 Ma obtained from a migmatite north of the CSZ (Scrimgeour *et al.*, 1999). The metamorphic zircon age provides a useful constraint with which to examine allanite isotopic behaviour.

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

CONCLUSIONS

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

Detailed trace element investigation allowed the dated U-Th-Pb accessories to be related to garnet. Outside the CSZ in the orthogneiss metamorphic zircon was absent and metamorphic allanite growth was limited. Inside the CSZ, metamorphic zircon crystallised from a cooling melt close to the wet solidus at T ≤ 700˚C based on Ti-in-zircon thermometry. In comparison, metamorphic allanite formed over an extended P-T range: allanite cores formed on the prograde sub-solidus path in equilibrium with garnet rims and zircon and allanite overgrowths formed after garnet on initial melt crystallisation. The two periods of allanite growth are not resolvable by the allanite dating as they occurred within a period of ~10 m.y.

ACKNOWLEDGEMENTS

CG thanks the EMU (ANU) for access to SEM facilities and C. Allen and C. Magee for technical assistance. Dorothy Close, Christine Edgoose and Ian Scrimgeour of the Northern Territory Geological Survey are thanked for logistic support. The reviews of P. Barbey, F. Bea and three anonymous reviewers helped to improve the manuscript. The editorial handling of R. Gieré is acknowledged. Research was financially supported by the Research School of Earth Sciences and an Australian Research Council Grant DP0556700 (DR and JH). ISB acknowledges an Australian Professorial Fellowship, Large Grant A39700909 and Discovery Grant DP0342473 from the Australian Research Council.

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Figures

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

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

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

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

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

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

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

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

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

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

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

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

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

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