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Misidentification of oxide phases and of twinned kyanite: implications for inferred P-T histories of the Musgrave Block, central Australia

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Abstract: In the Musgrave Block, central Australia, Mesoproterozic granulites have been locally transformed in the Neoproterozoic to eclogite (T \approx 660°C and P \approx 12 kbar) with a clear spatial association between shear zones and eclogite formation. In these high-strain zones, peraluminous rocks contain intergrowths of kyanite and magnetite that pseudomorph granulite-facies sillimanite. A previous study misidentified the minerals that make up these intergrowths as fibrolite and ilmenite which suggested the breakdown - during decompression - of garnet in a reaction of the type: garnet + rutile = aluminosilcate + hematite + quartz. We, however, consider that the intergrowth represents transformation of sillimanite by kyanite accompanied by growth of titaniferous magnetite since Fe (sillimanite typically contains ~1% Fe) is not incorporated into the more densely packed structure of kyanite. These and additional textural relationships suggest that kyanite and magnetite are coeval with eclogite-facies deformation and did not form during decompression. Our results describe a P-T history quite different to that inferred in the previous study. This contribution shows the importance of correct mineral identification and textural interpretation and illustrates why it is essential to carefully select the best available methods and instruments when characterising phases and mineral relationships for use in P-T reconstructions.

Introduction

The pressure, temperature and time (P-T-t) path experienced by a metamorphic terrane provides significant information about metamorphic processes and the dynamics of orogenic systems. Building these P-T-t paths however, is not a trivial task and requires a full understanding of the mineralogical and textural relationships preserved within the rocks. In this study we show an example where likely mineral misidentification led to errors in inferences about both P-T-t trajectory and tectonic scenario.

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In the central Musgrave Block, central Australia, Maboko *et al.* (1991) and Ellis and Maboko (1992) reconstructed a P-T-t path that invoked changing physicochemical conditions during one metamorphic episode at ~1200 Ma to account for the textures preserved in granulites, and involved the following sequence of events.

Figure 1. Geological map of the Mt Woodroffe region

- (M1) Granulite-facies metamorphism at ~40 km depth and 850-900°C,
- (M2) isobaric cooling and deformation of the granulites to form eclogite,
- (M3-M4) rapid tectonically driven exhumation, with little cooling of the lower part of the thickened crust to a depth of 15-20 km at ~1190 Ma, and
- (M5) deformation and metamorphism at greenschistto lower amphibolite-facies during the Petermann Orogeny (~550 Ma) after a residence period of ~640 Ma in the mid-crust with a total exhumation of only 2-7 km in the interval between M4 and M5.

The tectonic mechanism envisaged to produce rapid exhumation in the time interval between M1 to M4 (<20 Ma), involved extensional unroofing, along normal faults that lie outside the immediate area.



Geological map of the Mt Woodroffe region showing the distribution of the major faults, shear zones, granulite-facies gneiss and the areas affected by the high-pressure overprint. Modified after Major (1973) and Camacho et al. (1997).

A problem with this P-T-t trajectory is that mafic dykes as young as ~840 Ma (Zhao and McCulloch, 1993) are deformed by the eclogite-facies overprint (Camacho *et al.*, 1997) indicating that the metamorphic and

deformational textures developed between M2 to M4 needed re-evaluation.





Geologic Setting

The east-west trending Musgrave Block is a Meso-Neoproterozoic mobile zone consisting of high-grade metamorphic and intrusive rocks covering an area of about 120,000 km² in the centre of the Australian continent. Felsic to mafic volcanic rocks in the central Musgraves were metamorphosed at granulite-facies during the ~1200-1150 Ma Musgravian Orogeny (Camacho and Fanning, 1995). Felsic magmatism, partly coeval and partly after this high-temperature event was followed by two episodes of extension and emplacement of dolerite dyke swarms at ~1070 Ma and ~830 Ma (Zhao and McCulloch, 1993). These rocks were heterogeneously overprinted by high-strain zones at ~550 Ma (Petermann Orogeny) under eclogite to greenschist-facies conditions (Maboko et al., 1992; Camacho et al., 1997). These zones trend east-west with a combined strike-slip and reverse movement, and occurred in an intraplate setting (Camacho and McDougall, 2000).

High-strain deformation and metamorphism at eclogite-facies conditions (T \approx 660°C and P \approx 12 kbar) in the Musgrave Block appears to be confined to the granulitefacies gneisses (Fig. 1). In shear zones, this deformation event obliterates all pre-existing fabrics by development of a strong, subhorizontal, rodding lineation on highstrain planes, and quartz and feldspar ribbons in the quartzo-feldspathic layers (Camacho *et al.*, 1997). Mylonitized gneiss preserves some of the granulite-facies minerals such as garnet and plagioclase (Fig. 2). Detailed descriptions of the eclogite-facies rocks are published elsewhere (Camacho *et al.*, 1997; Ellis & Maboko, 1992; Camacho *et al.*, 2009) but are overviewed below.

The zone affected by eclogite-facies deformation lies between the eclogite-facies north Davenport shear zone and the Mann Fault (Fig. 1).

Figure 2. Mesoproterozoic granulite felsic gneiss overprinted at ~550 Ma by high-strain deformation at ~12 kbar.



(a) Plane-polarized light. Mylonitic foliation deflected around relict granulite-facies garnets (Grt1) with fringes of new garnet growth. (b) Plane-polarized light, (c) Reflected light, same field, both rotated 45° relative to (a). New garnet (Grt2), rutile (Rt), magnetite (Mag) formed in pressure shadows and in the foliation. Magnetite (with ilmenite exsolution lamellae) and rutile, in textural equilibrium (at the margin of Grt1). Note how magnetite infills the fracture in Grt1. Section parallel to the stretching lineation and normal to the foliation. Abbreviations after Kretz (1983). Rectangles outlined in 2(a) correspond to areas shown later in Figs 3 and 4(a).

Analytical Techniques

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Raman Spectroscopy

Raman spectra were recorded using a HORIBA Jobin-Yvon confocal LabRAM ARAMIS micro-Raman system equipped with a multichannel charge-coupled device (CCD) detector, operated by Labspec5 software. The light source was the internal laser Diode pumped solidstate laser of 532 nm with a nominal output power of 50 mW. The sample was focused to a diameter of approximately 2 µm using an Olympus 100x lens. Raman spectra were obtained at room conditions. The following analytical conditions were used: 100 µm hole, 100 µm slit, grating of 1800 grooves per millimeter during 20 sec, and data accumulated over one cycle. The Raman spectrometer was calibrated by adjusting the peak (frequency of 520.7 cm⁻¹) position for silicon metal. A Gaussian curvefitting technique was applied for the precise frequency determination of the Raman bands.

Transmitted Electron Microscopy (TEM)

Selected areas were removed from thin sections to be Ar-ion-beam thinned. These thinned specimens were examined by imaging and diffraction in a Philips EM430 TEM operated at 300 kV, with minerals identified using diffraction supplemented by X-ray spectra from an EDAX thin-window energy-dispersive spectrometer mounted on the TEM.

Textures and assemblages developed in the quartzo-feldspathic granulites

Granulite-facies gneisses not overprinted by highstrain deformation during the Petermann Orogeny are generally coarse to medium grained, have a granoblastic texture and a dominantly anhydrous mineralogy. Peraluminous quartzo-feldspathic gneiss commonly contains the assemblage quartz + K-feldspar + garnet (Grt1; of composition Alm₅₀₋₆₀, Prp₃₃₋₄₅, Grs₃₋₆, Sps₂₋₃; abbreviations after Kretz, 1983) + plagioclase (An₃₀) + magnetite \pm biotite \pm spinel \pm sillimanite. Pressure estimates using the garnet-aluminosilicate-quartz-plagioclase geobarometer (GASP; Ghent, 1976) for garnet bearing quartzo-feldspathic gneiss with sillimanite inclusions range from ~7 to 8.5 kbar at 800°C (Camacho, 1997).

Textures and assemblages developed in the rocks affected by eclogite-facies deformation

During the high-pressure event, Grt1 in the felsic gneiss, developed rims of new garnet (Fig. 2; Grt2; Alm₄₇₋₅₃, Prp₂₁₋₃₀, Grs₁₇₋₂₉, Sps₁₋₂) as well as compositional changes near grain boundaries and fractures (Fig. 3). These peraluminous rocks also contain mats of intergrown, fine-grained aluminosilicate, opaque oxide, and rutile (Fig. 4). Within the mylonitic foliation, fractured grains and pressure shadows, Grt2, ilmenite, titaniferous magnetite, rutile, and small amounts of biotite and clino-zoisite formed (Fig. 2; Camacho *et al.*, 2009).

Mafic granulites preserve thin, randomly oriented needles of aluminosilicate, clinozoisite, and garnet (note: the mafic granulites contain no garnet that crystallized during the Musgravian Orogeny) that have grown inside plagioclase (Fig. 5), and may have formed by either of the following two reactions:

anorthite + H_2O = clinozoisite + aluminosilicate + quartz

$$4CaAl_2Si_2O_8 + H_2O =$$

$$2Ca_2Al_3Si_3O_{12} (OH) + Al_2SiO_5 + SiO_2$$

and

anorthite = *grossular* + *aluminosilicate* + *quartz*

$$3CaAl_2Si_2O_8 = Ca_3Al_2Si_3O_{12} + 2Al_2SiO_5 + SiO_2$$



Figure 3. Compositional maps showing the distribution of Fe, AI, Ti and Ca along grain boundaries and fractures.



Compositional maps from X-rays collected in electron mircroprobe of the same area in Fig. 2a showing raw X-ray counts for Al, Ca, Fe and Ti. Relict granulite-facies garnet (Grt1) shows enrichment of Ca along rim and across fractures. Scale bar = 1000 µm. Rainbow colour scheme, with red and yellow representing higher concentrations than green, blue and black. Detailed colour scaling given in top left of each map.



Figure 4. Kyanite + opaque oxide + rutile mats



(a) Backscattered electron (BSE) images of the aluminosilicate-mat showing the general distribution of opaque oxides and rutile within kyanite. (b) Detail of Fig. 4a showing magnetite and rutile coexisting as fine blebs within kyanite. (c) BSE image showing magnetite (Mag) with ilmenite (IIm) exsolution lamellae intergrown with rutile (Rt) and kyanite (Ky). Hercynite (Hc) partially enclosed by magnetite has a rim of ilmenite. Bright field TEM images of (d) Multiple twinning in kyanite. This twinning causes kyanite to have straight extinction under cross-polarized light. Base of photograph 2.32 μm. (e) Wormy intergrowths of dominantly magnetite (dark coloured) in twinned kyanite. Base of photograph 4.65 μm. (f) Close up of an intergrowth showing magnetite, with hercynite and ilmenite interpreted to be formed by exsolution, all enclosed in twinned kyanite. Base of photograph 1.00 μm.



Figure 5. New mineral growth resulting from plagioclase breakdown at high-pressure.



Eclogite-facies reactions of plagioclase in gneiss of mafic composition. (a) Coronas of garnet enclose plagioclase in contact with pyroxene. Clinozoisite and kyanite needles forming from the breakdown of anorthite component at high-pressure. See text for possible reactions producing these textures. Plane polarized light. (b) Bright field TEM image of clinozoisite (Czo). The trace of the needle is approximately parallel to (100). Base of photograph 2.32 μm. (c) Bright field TEM image of kyanite (Ky). The trace of the crystal is approximately parallel to (100). Note that is has a more uniform width than clinozoisite. Base of photograph 2.32 μm.

The fine-grain size of the aluminosilicates makes identification difficult using the optical microscope. Raman Spectroscopy and TEM were used to identify the aluminosilicates. In the felsic gneisses, sillimanite is preserved only as inclusions in Grt1 (Figs 2 and 6), and the mats are made up of kyanite and titaniferous magnetite (Figs 4 and 6), instead of sillimanite and ilmenite (Maboko *et al.*, 1991), and appear to pseudomorph an earlier phase. Large area electron microprobe analyses of individual mats give compositions that represent an aluminosilicate with \sim 2 weight percent FeO and indicate that the phase being replaced was most probably sillimanite. Sillimanite typically contains ~1% Fe and, as the replacement appears to be isochemical, the growth of titaniferous magnetite may result from Fe not being incorporated into the more densely packed structure of kyanite. Tiny aluminosilicates in the plagioclase of the overprinted mafic granulites have also been identified as kyanite (Fig. 5).

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Figure 6. Raman spectra, showing lattice vibration modes



(a) the sillimanite inclusion in granulite-facies garnet (Grt1) shown in Fig. 2b, and (b) kyanite in the alumino-silicate + opaque oxide mats.

Discussion

Maboko *et al.* (1989; 1991) envisaged a metamorphic history characterized by rapid decompression with little cooling from about 12 kbar and 760°C to about 5 kbar and 630°C (Fig. 7). Ilmenite-fibrolite intergrowths in quartzo-feldspathic lithologies, were considered to have resulted from the breakdown of garnet suggesting a reaction of the type:

almandine + *rutile* = *sillimanite* + *ilmenite* + *quartz*

$$Fe_3Al_2Si_3O_{12} + 3TiO_2 = Al_2SiO_5 + 3FeTiO_3 + 2SiO_2$$

This reaction texture was inferred to have formed during isothermal decompression between M2 and M4. As a consequence, in the mafic lithologies, garnet-clinopyroxene growth was also regarded to have formed during decompression, although this assemblage does not normally form during a decrease in pressure. In addition, Maboko's *et al.* (1989; 1991) P and T estimate of ~6 kbar and 715°C, respectively indicates that the geothermal gradient was ~36°C km⁻¹, which is considerably higher than current stable cratonic geotherms of about 25°C km⁻¹ and required the Petermann Orogeny to have been accompanied by an episode of increased heat flux.

Figure 7. Summary of P-T-t trajectories



Proposed by (a) Maboko et al. (1989; 1991). Red curve: Granulite-facies metamorphism at ~1200 Ma (M1) followed by isobaric cooling and rapid decompression in < 20 Ma (M2-M4). Yellow curve: Cooling history from the Mesoproterozoic to ~550 Ma (M5). (b) This study. Black path: Granulite-facies metamorphism at ~1150 Ma followed by exhumation to midcrustal level and cooling by about 1100 Ma. The granulites resided at these mid-crustal levels for ~600 Ma before rapid reburial followed by exhumation during the Petermann Orogeny at ~550 Ma (blue path). Numbers in brackets are dates in Ma.

Throughout the Musgrave Block, field and petrographic observations suggest that multiple metamorphic and deformation reaction textures are not present in the eclogite-facies mylonites, which is evidence against multiple overprinting events (Camacho *et al.*, 1997; Scrimgeour *et al.*, 1999; Raimondo *et al.*, 2010). Assemblages containing rutile and kyanite are found only in rocks that have experienced deformation at high-pressure. These minerals have not been found in any of the granulite-facies assemblages (Camacho *et al.*, 1997). In addition to these observations, the fact that the kyanite-titaniferous magnetite mats give compositions that represent an aluminosilicate rather than garnet indicate that reaction 3 did not take place. Thus, we consider that kyanite-bearing assemblages formed at ~12 kbar during peak metamorphic conditions rather than during isothermal decompression. Accordingly, our proposed geodynamic scenario is quite different from that proposed by Maboko *et al.* (1989; 1991) (Fig. 7) and is summarized as follows.

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Magmatic heat input to produce the granulites at ~1200-1150 Ma (Stage 1) was followed by a residence period of > 300 Ma in the mid-crust (Stage 2) before crustal thickening and reburial during the Petermann Orogeny (Stage 3) to depths of ~40 km followed by exhumation to the mid-crust during the same orogeny (Camacho and McDougall, 2000). The estimate for residence in

the mid-crust is based on ages of ~1100 Ma for minerals with a closure temperature of ~350°C for the argon system and mineral assemblages in mafic dykes (Camacho *et al.*, 2009). Based on the T and P estimates of Camacho *et al.*, (1997), the calculated geothermal gradient is ~16.5°C km⁻¹ and implies that the deep crust was not significantly perturbed thermally during the Petermann Orogeny, a finding that is consistent with other studies in the Musgrave Block (Scrimgeour and Close, 1999; Raimondo *et al.*, 2010).

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