

The timing of sub-solidus hydrothermal alteration in the Central Zone, Limpopo Belt (South Africa): Constraints from titanite U–Pb geochronology and REE partitioning

Ian S. Buick^{a,*}, Jörg Hermann^a, Roland Maas^b, Roger L. Gibson^c

^a *Research School of Earth Sciences, Australian National University, Canberra, A.C.T. 0200, Australia*

^b *School of Earth Sciences, University of Melbourne, Parkville, Vic. 3010, Australia*

^c *School of Geosciences, University of the Witwatersrand, Private Bag 3, WITS 2050, South Africa*

Received 9 September 2006; accepted 13 February 2007

Available online 12 March 2007

Abstract

In the Central Zone of the Limpopo Belt (South Africa), Palaeoproterozoic granulite-facies metamorphism was superimposed on an earlier Archaean orogenic history. Previously determined ages of ~2030–2020 Ma obtained from high-temperature chronometers (zircon, garnet, monazite) are generally thought to provide the best estimate of the peak of Palaeoproterozoic granulite-facies metamorphism in the Central Zone, whereas ages as young as ~2006 Ma from late melt patches suggest that temperatures remained above the wet solidus for an extended period. We present a new MC-ICP-MS ²⁰⁷Pb–²⁰⁶Pb age of 2030.9 ± 1.5 Ma for titanite found in amphibolite- to greenschist-facies alteration zones developed adjacent to quartz vein systems and related pegmatites that cut a strongly deformed Central Zone metabasite. This age could potentially date cooling of rocks at this locality to temperatures below the wet solidus. Alternatively, the titanite could be inherited from the metabasite host, and the age determined from it date the peak of metamorphism. Integration of the geochronology with LA-ICP-MS trace element data for minerals from the metabasite, the hydrothermal vein systems and comparable rocks elsewhere shows that the titanite formed during the amphibolite-facies hydrothermal alteration, not at the metamorphic peak or during the greenschist-facies phase of veining. This suggests that high-grade rocks in the Central Zone have cooled differentially through the wet solidus, and provides timing constraints on when Palaeoproterozoic reworking in the Central Zone began. This study illustrates the potential of combined geochronological and high-resolution geochemical studies to accurately match mineral ages to distinct crustal processes.

© 2007 Elsevier B.V. All rights reserved.

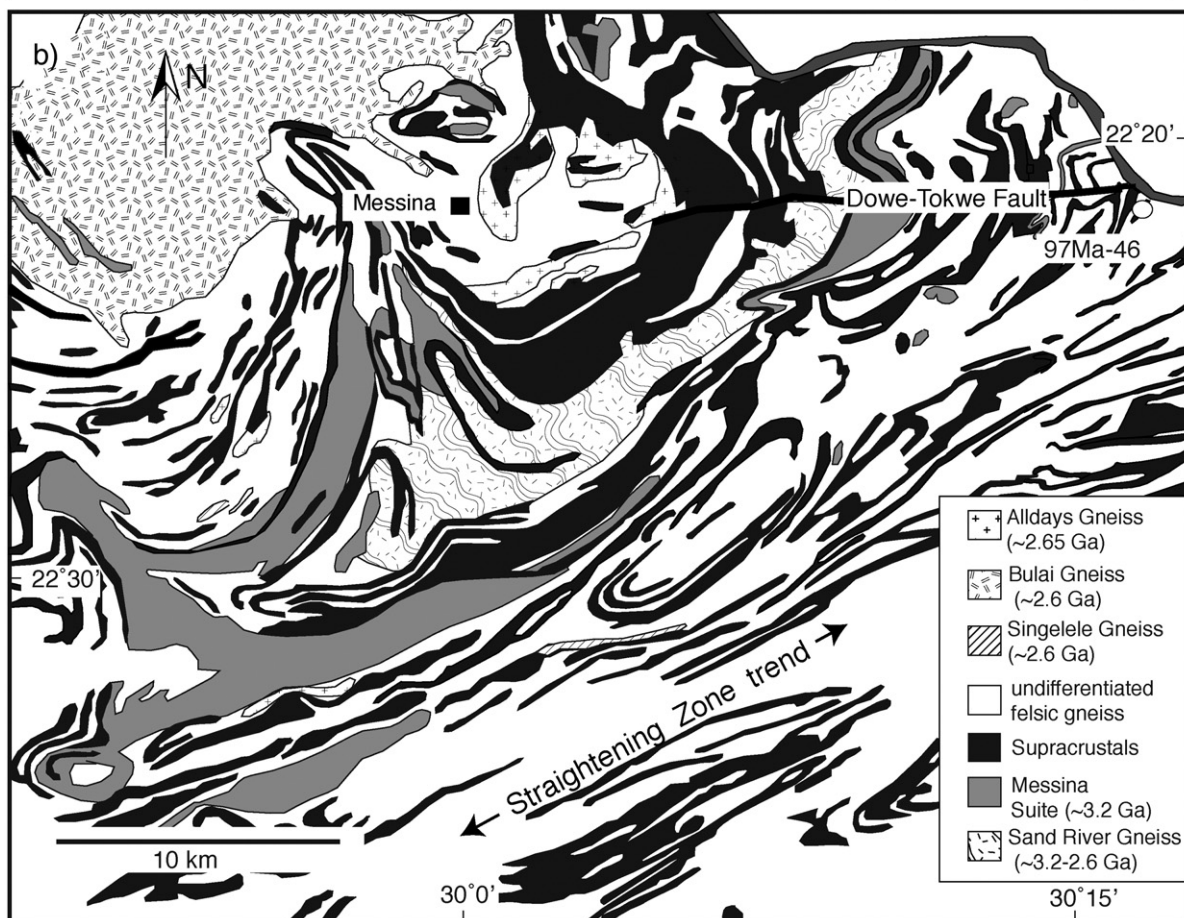
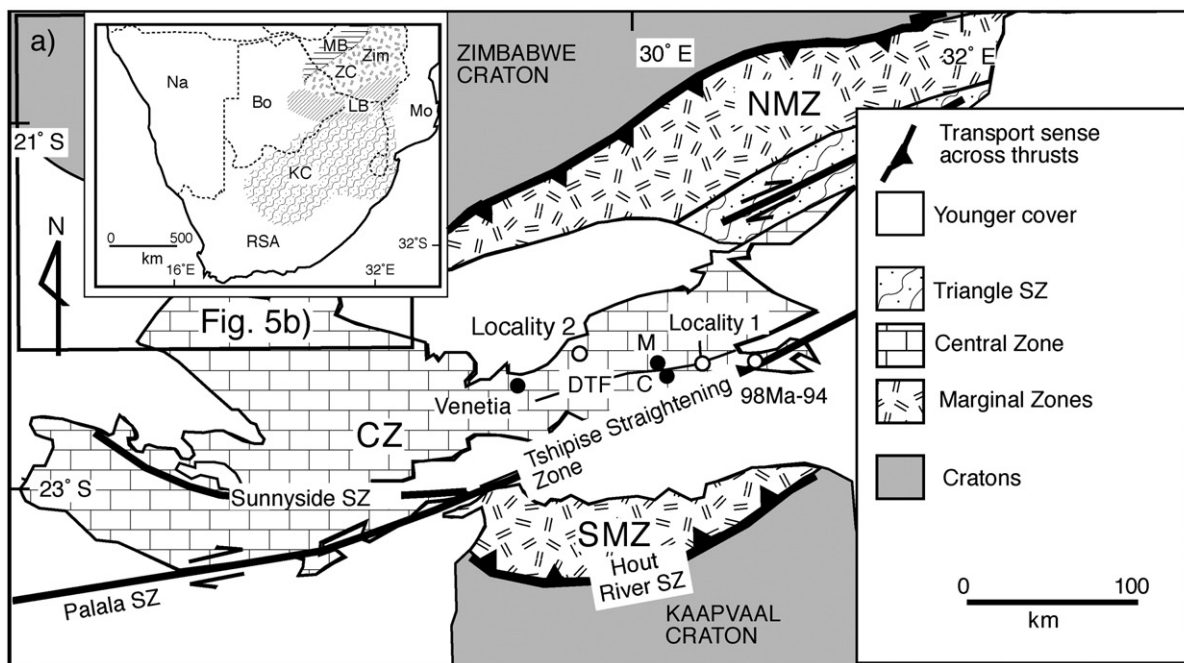
Keywords: Titanite; Geochronology; Retrogression; Central Zone; Limpopo Belt

1. Introduction

Titanite is a particularly useful mineral for understanding metamorphic histories. It is stable in a range of relatively Ca-rich and Al-poor bulk compositions

(typically marbles, calcsilicate rocks, metabasites and some felsic orthogneisses) over a large range of metamorphic grades (Frost et al., 2000, and references therein). In these bulk compositions it participates in prograde and retrograde reactions (e.g. Hunt and Kerrick, 1977; Ghent et al., 1993; Rubatto and Hermann, 2001; Storkey et al., 2005). Both its major (e.g. Troitzsch and Ellis, 1999; Rubatto and Hermann, 2001) and trace

* Corresponding author. Tel.: +61 2 61255174; fax: +61 2 61258345.
E-mail address: Ian.Buick@anu.edu.au (I.S. Buick).



element compositions (e.g. [Storkey et al., 2005](#)) are potentially sensitive monitors of metamorphic processes. Moreover, metamorphic titanite commonly, but not always, has radiogenic U/Pb high enough to allow its use in geochronology (e.g. [Cliff et al., 1993](#); [Verts et al., 1996](#); [Frost et al., 2000](#); [Rubatto and Hermann, 2001](#); [Buick et al., 2001, 2003](#)). It has a relatively high closure temperature ([Cherniak, 1993](#); [Scott and St-Onge, 1995](#)), thus allowing its use to date metamorphic growth at least into the upper amphibolite facies. In high-grade regional metamorphic environments, titanite is also a common crystallisation product of hydrothermal alteration. This commonly occurs where crystallisation of silicate melts near the wet solidus has led to exsolution of water-rich fluids and their infiltration into Ca-rich country rocks to form various skarn-like calcsilicate rocks (e.g. [Cartwright et al., 1996](#); [Buick et al., 1997](#); [Buick et al., 2001](#)).

In metabasic rocks, titanite is potentially a stable phase from greenschist- to granulite-facies conditions appropriate to medium-pressure metamorphism ([Frost et al., 2000](#); their Fig. 5). The wide P – T stability of titanite, while of considerable use in metamorphic petrology, can also be a hindrance to accurately linking titanite U–Pb ages to metamorphic events in regional metamorphic terrains with complex histories. In this study, we integrate titanite geochronology with mineral-scale trace element geochemistry in order to interpret a titanite U–Pb age obtained from a high-grade metabasite from the Central Zone of the Limpopo Belt (South Africa) that has been hydrothermally altered and retrogressed. This approach has previously been used successfully to link the growth of accessory phases (e.g. zircon, titanite and monazite) to that of petrologically important minerals such as garnet (e.g. [Hermann and Rubatto, 2003](#); [Kelly and Harley, 2005](#); [Storkey et al., 2005](#); [Buick et al., 2006](#)) and has the potential to greatly enhance our ability to interpret U–Pb ages obtained from accessory phases.

2. Geological setting

The Limpopo Belt ([Fig. 1a](#)) occurs between the Kaapvaal and Zimbabwe cratons and comprises a threefold division — the Central Zone (CZ) and the

flanking Southern and Northern Marginal Zones (SMZ and NMZ, respectively; [Fig. 1a](#)), whose mutual boundaries are typically shear zones. The granulite-grade SMZ and NMZ were metamorphosed and thrust over their granite–greenstone low-grade equivalents on the adjacent cratons at ~ 2.7 – 2.6 Ga (e.g. [Barton et al., 1994](#); [Berger et al., 1995](#); [Kamber et al., 1996](#); [Kreissig et al., 2001](#)). The Northern Marginal Zone was partially re-worked under high-grade conditions during the Palaeoproterozoic (~ 2.0 Ga; [Kamber et al., 1995](#)), predominantly in strike-slip shear zones such as the Triangle Shear Zone ([Fig. 1a](#)).

The Central Zone ([Fig. 1a, b](#)) comprises metasediments, together with a range of felsic and mafic to ultramafic meta-igneous rocks ([Brandl, 1983](#)). Protoliths to metasediments were deposited at ~ 3.3 – 3.2 Ga ([Barton, 1983](#); [Kröner et al., 1999](#)) and during the late Archaean–Palaeoproterozoic ([Buick et al., 2003](#); [Barton et al., 2003](#)). A range of felsic and mafic igneous bodies were emplaced at ~ 3.3 – 3.1 Ga, ~ 2.7 – 2.5 Ga and ~ 2.05 – 2.02 Ga ([Barton, 1983](#); [McCourt and Armstrong, 1998](#); [Kröner et al., 1998, 1999](#)).

There is debate about the importance of orogenesis in the Central Zone during the Archaean and Palaeoproterozoic, and hence to what extent the orogenic histories of the Central and Marginal Zones are related. Some models interpret the Central Zone as having formed largely by late Archaean collision ([Roering et al., 1992](#)) or terrane accretion ([Barton and Key, 1981](#)). More recently, [Barton et al. \(2006\)](#) suggested that the Limpopo Belt as a whole experienced a protracted (~ 700 Ma) interval of terrane accretion related to repeated episodes of transpression and transtension. There is abundant evidence for late Archaean felsic magmatism, some of which post-dates high-grade fabrics in granulite-grade metasediments (e.g. [Barton et al., 1994](#); [Holzer et al., 1998](#)). However, there is relatively little direct geochronological evidence for ~ 2.7 – 2.5 Ga metamorphic event(s) in the metasediments themselves (e.g. [Holzer et al., 1998](#)). Instead, recent studies using minerals and isotope systems with high closure temperatures have yielded a range of ages from ~ 2032 Ma to ~ 2006 Ma ([Jaekel et al., 1997](#); [Holzer et al., 1998](#); [Kröner et al., 1998, 1999](#); [Schaller et al., 1999](#); [Buick et al., 2003, 2006](#); [Table 1](#)). The data have generally

Fig. 1. (a) Simplified geological map of the Limpopo Belt and adjacent cratons. Abbreviations: Bo = Botswana; C = Causeway geochronological locality; CZ = Central Zone; DTF = Dowe–Tokwe Fault; KC = Kaapvaal craton; LB = Limpopo Belt; M = Messina; MB = Magondi Belt; Na = Namibia; NMZ = Northern Marginal Zone; RSA = Republic of South Africa; SMZ = Southern Marginal Zone; Zim = Zimbabwe; ZC = Zimbabwe craton. Sample localities discussed in the text are given by open circles; (b) detailed geology of the Central Zone around Messina (modified after Council for Geosciences 2230 Messina 1:250,000 Geological Map, 1981; [Brandl and Pretorius, 2000](#)). Approximate emplacement ages of intrusive rocks from [Barton \(1983\)](#), [Jaekel et al. \(1997\)](#) and [Kröner et al. \(1999\)](#). The Tshipise Straightening Zone used in this contribution is comparable to the Zoutfontein–Palala Shear Zone of [Barton et al. \(2003, 2006\)](#).

Table 1

Summary of geochronological constraints on the timing of Palaeoproterozoic metamorphism in the Central Zone, Limpopo belt (South Africa)

Age (Ma)	Method	Mineral	Rock type	Interpretation	Reference
2032±12	SHRIMP U–Pb	Zircon	Granulite-facies metapelite	Peak metamorphic	Kröner et al. (1999)
2030±6	Vap-Dig U/Pb	Zircon	Granulite-facies metapelite	Peak metamorphic	Jaekel et al. (1997)
2028±3	SHRIMP U–Pb	Monazite	Granulite-facies metapelite	Peak metamorphic	Buick et al. (2006)
2028±7	SHRIMP U–Pb	Zircon	Granulite-facies metapsammite	Peak metamorphic	Buick et al. (2003)
2026±12	Vap-Dig U/Pb	Zircon	Granulite-facies metapelite	Peak metamorphic	Jaekel et al. (1997)
2026.8±0.5	Pb evaporation	Zircon	Granulite-facies metapelite	Peak metamorphic	Jaekel et al. (1997)
2026.0±0.5	Pb evaporation	Zircon	Granulite-facies metapelite	Peak metamorphic	Jaekel et al. (1997)
2025.7±0.3	Pb evaporation	Zircon	Granulite-facies metapelite	Peak metamorphic	Jaekel et al. (1997)
2022±11	SHRIMP U–Pb	Zircon	Granulite-facies metapelite	Peak metamorphic	Buick et al. (2003)
2022.1±0.4	Pb evaporation	Zircon	Granite emplacement	Peak metamorphic	Kröner et al. (1999)
2020±8	PbSL	Titanite	Granulite-facies calcsilicate rock	Peak metamorphic	Schaller et al. (1999)
2015±7	SHRIMP U–Pb	Titanite	Granulite-grade calcsilicate rock	Peak metamorphic	Buick et al. (2003)
2011±20	ID-TIMS	Monazite	Granulite-grade calcsilicate rock	Recrystallisation in straightening zone	Holzer et al. (1998)
2010±17	PbSL	Garnet	Granulite-grade calcsilicate rock	Recrystallisation in straightening zone	Holzer et al. (1998)
2007.5±0.3	Pb evaporation	Zircon	Sand River Gneiss	Late crystallisation in melt	Jaekel et al. (1997)
2007±5	PbSL	Titanite	Granulite-grade calcsilicate rock	Recrystallisation in straightening zone	Holzer et al. (1998)
2006±8	Vap-Dig U/Pb	Zircon	Sand River Gneiss	Late crystallisation in melt	Jaekel et al. (1997)
2003±11	Vap-Dig U/Pb	Zircon	Sand River Gneiss	Late crystallisation in melt	Jaekel et al. (1997)
2005.6±0.7	Pb evaporation	Zircon	Sand River Gneiss	Late crystallisation in melt	Jaekel et al. (1997)
2005.9±0.2	Pb evaporation	Zircon	Sand River Gneiss	Late crystallisation in melt	Jaekel et al. (1997)
1983±14	ID-TIMS U–Pb	Apatite	Granulite-grade calcsilicate rock	Cooling to ~600 °C	Holzer et al. (1998)

Abbreviations: ID-TIMS = isotope dilution thermal ionisation mass spectrometry; PbSL = lead stepped leaching; SHRIMP = sensitive high resolution ion microprobe; Vap-Dig U–Pb = vapour digestion U–Pb.

been used to infer that widespread high-grade metamorphism (~8–12 kbar and ~800–850 °C; Watkeys, 1984; Holzer et al., 1998; Zeh et al., 2004), anatexis and subsequent high-temperature decompression occurred during the Palaeoproterozoic. The tectonic setting of this event is itself the subject of debate, with both transpressional (Holzer et al., 1998) or thrust-related (Zeh et al., 2005) models having been proposed.

The recent geochronological studies in the Central Zone have led to a general consensus that the older (~2030–2020 Ma) Palaeoproterozoic ages approximately date the peak of granulite-facies metamorphism (Jaekel et al., 1997; Holzer et al., 1998; Buick et al., 2003, 2006). The youngest of these ages (~2006 Ma; Table 1) were obtained by Jaekel et al. (1997) from anatectic zircon in late partial melt patches and pegmatites in the well-known Causeway locality near Messina (Fig. 1a), and were interpreted by these authors to reflect late-stage zircon crystallisation from a melt. If this is correct, then the Central Zone in the area close to Messina (Fig. 1a) cooled through the wet solidus for quartzofeldspathic rocks at some time later than ~2006 Ma. A similarly young age of 2002±10 Ma was obtained by Chavagnac et al. (2001; U–Pb monazite) from the western continuation of the Central Zone into Botswana.

The major structural trends in the Central Zone (Fig. 1b) can be divided into two main types: (a) domains

of typically N–S to NW–SE trending folds oriented at a high angle to the boundaries of the Central Zone (“cross-folds”; Söhne, 1946), and NE–SW-oriented closed folds that have a sheath-like geometry and (b) kilometre- to tens of kilometre-wide ENE–WSW trending and steeply dipping transpressional high-strain zones (“straightening zones”; Bahnmann, 1972) that typically occur adjacent to its southern and northern margins (e.g. the Triangle and Palala shear zones, and the Tshipise Straightening Zone in Fig. 1a). Limited geochronology suggests that the sheath folds and cross folds developed in the late Archaean and Palaeoproterozoic, respectively (Holzer et al., 1998; Boshoff et al., 2006); the straightening zones involve reorientation of these structures and formed during the ~2.0 Ga event (e.g. Holzer et al., 1998; Schaller et al., 1999).

In this study, we present U–Pb isotopic and *in situ* trace element data for titanite from a metasomatic alteration zone developed around a hydrothermally altered granulite-grade metabasite from the Central Zone on the edge of the Tshipise Straightening Zone (Fig. 1b). These data, in conjunction with data obtained from the metabasite host and similar rock types elsewhere, show that the titanite in the alteration halo grew during sub-solidus hydrothermal alteration at ~2030 Ma, rather than being inherited from the metabasite. The implications of these results for the tectonic history of the Central Zone are then discussed.

3. Sample description

3.1. Locality 1

The samples for this study primarily come from ~20 km east of Messina (Fig. 1a; Locality 1). At this

locality layers of steeply dipping, NE-striking (Fig. 1b), strongly lineated and layered metabasite (amphibolite *sensu lato*; Fig. 2a) are cut by locally epidote-bearing pegmatites (Fig. 2a, b). The layering and fabric in the metabasites dip steeply (83°) to the NW, and the mineral elongation lineation plunges $\sim 60^\circ$ towards $\sim 234^\circ$. The

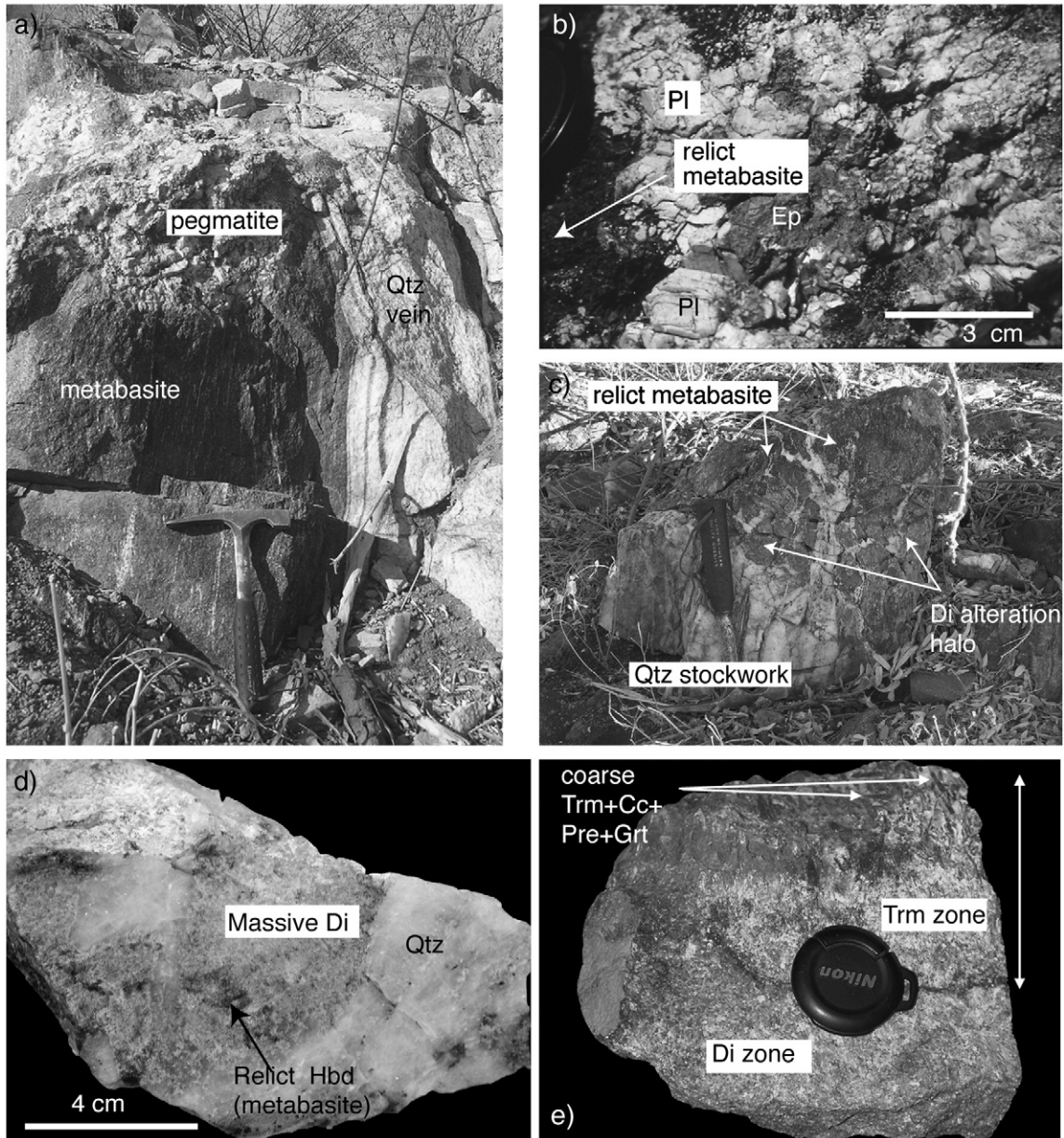


Fig. 2. (a) Steeply-dipping metabasite cross-cut by an epidote-bearing pegmatite that is associated with quartz veins (image courtesy of Reiner Klemmd); (b) coarse patches of euhedral epidote and albite in discordant pegmatite; (c) irregular veins of quartz (collectively, the quartz stockwork) surrounded by a patchy metasomatic diopside-rich halo in the surrounding metabasite (image courtesy of Reiner Klemmd); (d) lenses of monomineralic diopside within the quartz stockwork; (e) sample 97Ma-46; comprising a diopside (Di)-rich inner zone and an outer tremolite (Trm)-rich zone that is itself zoned from almost monomineralic tremolite close to the contact with the Di zone into an outermost tremolite-calcite (Cc)-prehnite (Pre)-garnet (Grt) zone. Width of lens cap = 2 cm. The composite alteration zone sample 97Ma-46 (e) was taken from the margin of the quartz stockwork in (d).

foliation has a constant orientation for ~1 km to the east (~700 m across strike), but within ~150 m further east trends are typical of those of the Tshipise Straightening Zone (Fig. 1b). The mineral elongation lineation remains approximately constant in orientation across this transition zone. Nearby metabasites and felsic gneisses show evidence of anatexis and are locally orthopyroxene-bearing, consistent with granulite-facies conditions. The sample locality is just to the south of the E–W trending Dowe–Tokwe Fault, (Fig. 1b). However, the orientation of fabrics and the lack of evidence of cataclasis suggest that alteration is unrelated to movement on this fault.

At Locality 1, the pegmatites occur as decimetre to metre-scale lenticular bodies that are oriented semi-concordant to, but locally cross cut, the foliation and layering in the host metabasites, indicating that they were emplaced late in the deformation history. The pegmatites are spatially associated with anastomosing milky quartz vein networks (stockworks; Fig. 2a, c). The quartz stockworks are separated from the metabasite country rocks by metasomatic, near-monomineralic, diopside (Fig. 2c) and/or rarer tremolite-rich alteration zones that obliterate the foliation in the metabasite, indicating that the alteration post-dates high-grade metamorphism and deformation. Less altered, relict metabasite is locally present in the alteration halos (Fig. 2c) and as clasts within the quartz stockwork. The least altered metabasite contains the assemblage hornblende–clinopyroxene–plagioclase (the latter extensively replaced by sericite+epidote). The discordant quartz stockworks (Fig. 2a) vary in width from one to several tens of centimetres, and contain local lenses of pale green, almost monomineralic diopside (Fig. 2d). In places, the alteration at the margin of the quartz stockwork is composite, comprising an inner ~5–20 cm wide zone of near monomineralic diopside and an outer, ~5–10 cm thick zone dominated by coarse-grained, randomly oriented tremolite (Fig. 2e). The contact between the two is sharp and slightly irregular (Fig. 2e). The tremolite zone is itself internally mineralogically zoned from almost monomineralic tremolite (closest to the diopside-rich layer) to tremolite+calcite+grossular garnet+prehnite assemblages further away (Fig. 2e). The pegmatites contain coarse-grained (10–40 mm diameter), euhedral plagioclase and clusters of euhedral, prismatic epidote (Fig. 2b) in a weakly recrystallised quartz matrix. Other diopside-bearing rocks that occur elsewhere in the Central Zone (marbles and calcsilicate rocks) typically contain different mineral assemblages (Brandl, 1983; Watkeys, 1984; Buick

et al., 2003) to those in the alteration zones and were not observed at Locality 1.

Mineral assemblages at Locality 1 are summarised in Fig. 3. Mineral trace element and/or geochronological data were obtained from an incipiently altered metabasite (97Ma-49), and the composite diopside–tremolite alteration zone (97Ma-46Di and 97Ma-46Trm; Fig. 2e) on the margin of a quartz stockwork. In thin section, the metabasite comprises a polygonal, granoblastic mosaic of hornblende and altered plagioclase, with subordinate clinopyroxene and minor apatite. Clinopyroxene is partially replaced by tremolite.

The diopside-rich layer (97Ma-46Di; Di>95%) additionally comprises subhedral to rounded titanite, plagioclase (adjacent to the quartz stockwork) and texturally late tremolite (close to the tremolite layer). The diopside occurs in subhedral polygonal granoblastic mosaics. Titanite occurs as ~200 µm diameter grains that contain inclusions of diopside and are very rarely intergrown with apatite (Fig. 4a). Relict diopside occurs as inclusions within coarse prismatic tremolite in the tremolite layers (Fig. 4b). The tremolite layer (97Ma-46Trm) additionally contains titanite (Fig. 4b), garnet, calcite, quartz and prehnite (Fig. 4c). Two texturally different types of garnet occur; colourless, rounded grains that are non-isotropic, and pale yellow, blocky, isotropic grains. The former show evidence for very fine scale, concentric growth zonation (Fig. 4d). The two different garnet types have different compositions (see below); however, both are locally intergrown with, and appear to partly post-date, tremolite (e.g. Fig. 4d). Titanite grains identical in size and morphology to those in the diopside layer occur in the tremolite layer (Fig. 4a, b), where they are included by tremolite and garnet. The garnet occurs in calcite-rich domains located farthest

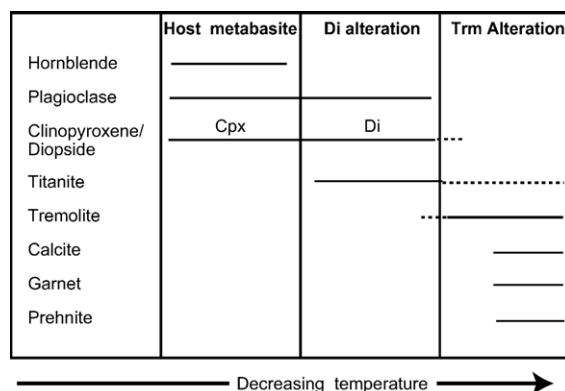


Fig. 3. Summary of mineral stability in the different rock types at Locality 1. The horizontal axis is a measure of decreasing relative metamorphic grade.

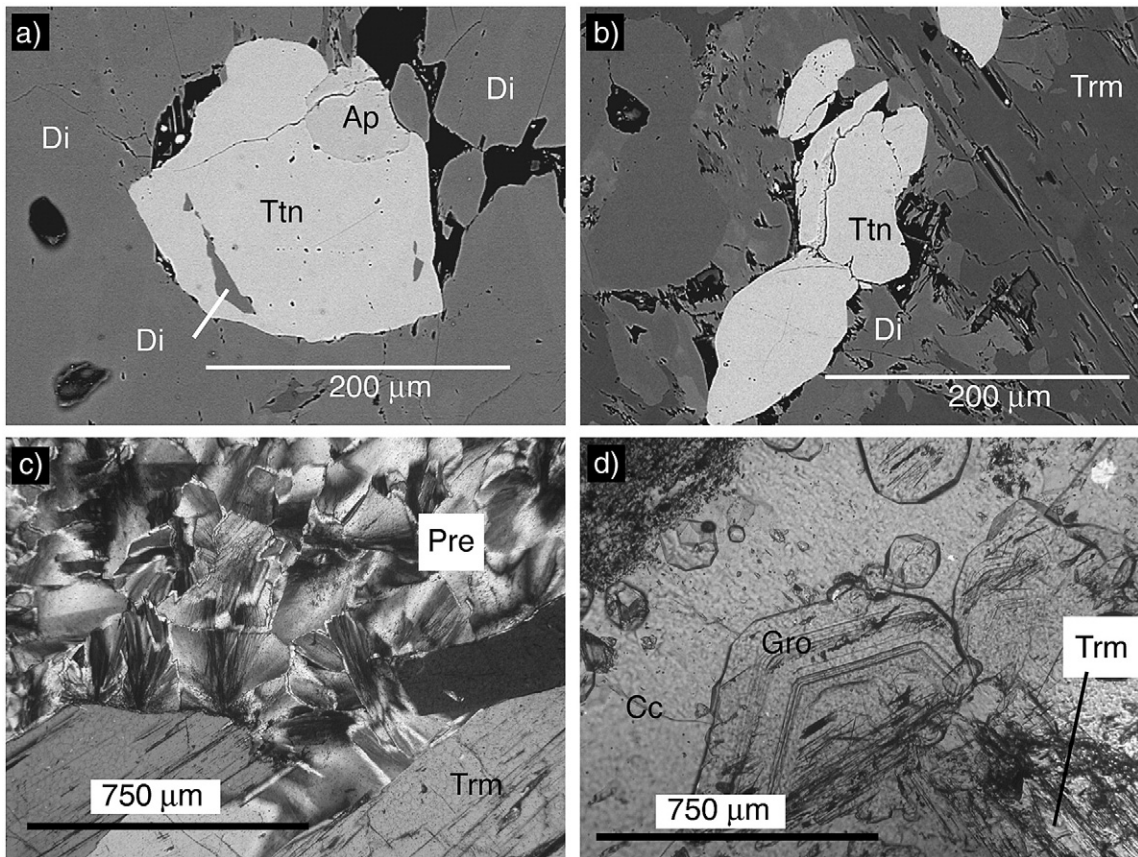


Fig. 4. (a) SEM image of titanite containing inclusions of diopside optically continuous with diopside in the vein matrix, 97Ma-46Di (Locality 1); (b) SEM image of the tremolite-rich reaction zone in sample 97Ma-46. It contains titanite similar in grain size and composition to that in the diopside-rich reaction zone, and relict diopside. This suggests that the tremolite-rich layer grew at the expense of the diopside-rich layer; (c) photomicrograph showing intergrowth of tremolite and prehnite, 97Ma-46Trm (crossed-polarised light); (d) photomicrograph of finely zoned grossular garnet intergrown with tremolite in a matrix of calcite, 97Ma-46Trm. Plane-polarised light. Mineral abbreviations as per Fig. 2.

from the Di–Trm zone contact (Fig. 2e), as do patches of prehnite intergrown with tremolite (Fig. 4c).

3.2. Localities 2 and 3

Because no titanite was found in the host metabasite 97Ma-49, for comparative purposes intra-mineral REE abundances were also determined in another sample of Central Zone metabasite from the farm Koningsmark, ~30 km to the west of Messina (97Ma-62; Locality 2, Fig. 1a). This sample contains quartz, hornblende, clinopyroxene, plagioclase, titanite (Fig. 5a) and ilmenite in a granoblastic polygonal matrix. Other metabasites at this locality show evidence of partial melting to form garnet–clinopyroxene±orthopyroxene-bearing leucosomes, suggesting that the local grade reached granulite facies.

In addition, the inter-mineral REE partitioning obtained from the alteration zones at Locality 1 was compared with similar data from a mid-to-upper amphib-

olite facies, diopside–tremolite–titanite–calcite–apatite vein (97Bo-47; Locality 3 in Fig. 5b) that cuts diopside- and titanite-free marble in the amphibolite-facies Matsiama–Motloutse Complex (McCourt et al., 2004), a terrane close to the margin of the Zimbabwe craton in northeastern Botswana (Fig. 5c). These veins are in contact with diopside-bearing quartz stockworks that themselves can be laterally traced into muscovite + garnet-bearing pegmatites. The relationships between metasomatism, quartz veining and pegmatites are similar to that at Locality 1, although the pegmatites and locally metasomatised country rocks have different compositions. Based on its mineral assemblage, 97Bo-47 is likely to have formed at a comparable metamorphic grade to 97Ma-46Di (Locality 1). Similar to 97Ma-46Di, titanite in this vein occurs as clusters grains that contain inclusions of diopside (Fig. 5d) in optical continuity with diopside grains that make up the bulk of the granoblastic vein matrix.

4. Analytical methods

A titanite mineral separate from 97Ma-46Di (Locality 1) was prepared using standard heavy mineral separation techniques at the School of Geosciences, University of the Witwatersrand, South Africa. U–Pb geochronology of the titanite was undertaken at the School of Earth Sciences, University of Melbourne. Relatively large (>1 mg) samples of un-abraded titanite were cleaned in warm 1 M HNO₃, followed by rinsing in distilled water. Sample dissolution was done with HF–HNO₃ (3:1, 12 h cold, 48 h hot) on a hotplate. After drydown, fluorides were dissolved in 6 M HCl. The clear HCl solutions were diluted to 2 M HCl, aliquotted and spiked with mixed ²³⁵U–²⁰⁸Pb spike. Pb was extracted by loading the homogenized HCl solutions directly onto 0.1 ml beds of AG1-X8 (100–200

mesh), followed by Pb purification with HBr/HCl. Uranium was purified using EICHROM TRU resin (Luo et al., 1997). Isotopic analyses were carried out on a NU Instruments MC-ICP-MS coupled to a CETAC Aridus desolvating nebulizer (uptake rate ≈ 40 μl/min, sensitivity for Pb–U near 120 V/ppm). All Pb isotopes (plus ²⁰²Hg and Tl) were measured on Faraday cups. Mass bias was corrected using the Tl doping method described in Woodhead (2002). U mass bias was corrected using standard bracketing with SRM960. Data reduction and age calculation were accomplished using the programs PBDAT and Isoplot/Ex (Ludwig, 1993, 2001).

Major element analysis of minerals (WDS) in polished thin sections was carried out at the University of Melbourne on a Cameca SX50 electron microprobe. Analytical conditions were 15 kV and 25 nA, and data were

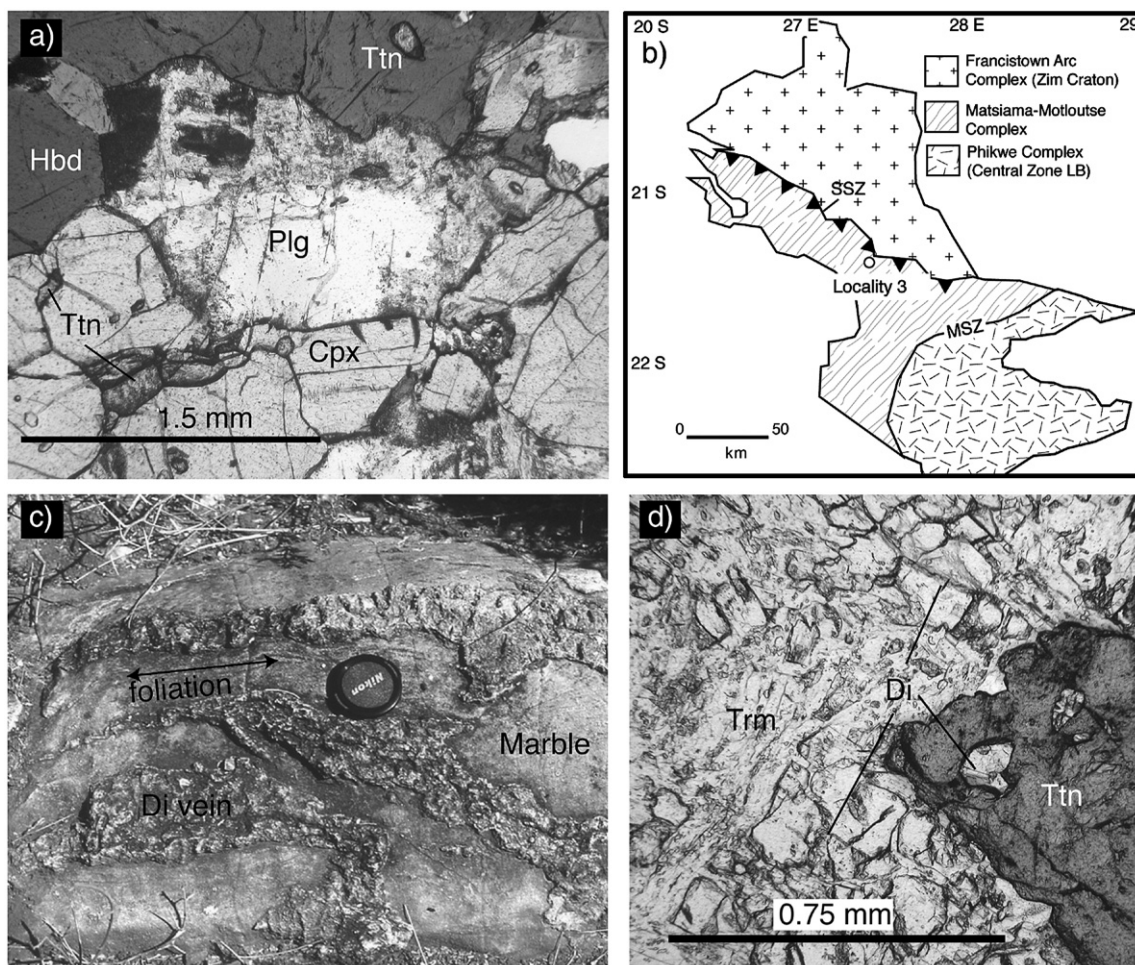


Fig. 5. (a) Photomicrograph of textural relationships in metabasite 97Ma-62, Central zone, Limpopo Belt (plane-polarised light; Locality 2); (b) lithological division of part of northeastern Botswana, modified after McCourt et al. (2004). Sample Locality 3 (97Bo-47) is given by open circle, and discussed in the text; (c) field photograph showing the cross cutting diopside–tremolite vein system from which amphibolite-faces vein 97Bo-47 was obtained (Locality 3); (d) photomicrograph showing textural relationships between diopside, tremolite and titanite in 97Bo-47 (plane-polarised light).

Table 2
Representative major element mineral compositions

Sample	97Ma-49 (Locality 1)			97Ma-46Di (Locality 1)						97Ma-46Trm (Locality 1)						97Ma-62 (Locality 2)						97Bo-47 (Locality 3)					
	Hbd	Hbd	Cpx	Cpx	Trm	Di	Di	Ttn	Ttn	Trm	Di	Ttn	Grt1	Grt2	Hbd	Hbd	Cpx	Cpx	Ttn	Ttn	Trm	Act	Di	Di	Ttn	Grt	
																											Core rim
SiO ₂	43.72	43.92	51.23	51.10	56.37	55.98	53.23	53.41	29.60	29.80	56.78	53.71	29.83	39.07	38.62	43.61	43.17	51.11	50.53	29.85	30.20	55.14	55.82	54.03	54.52	30.50	37.70
TiO ₂	1.59	1.58	0.14	0.16	0.01	—	0.02	—	38.18	38.03	0.02	0.04	37.27	—	0.07	2.09	2.48	0.25	0.15	39.00	39.37	0.08	0.07	0.05	0.07	37.61	0.25
Al ₂ O ₃	10.38	10.17	1.66	1.75	0.52	0.72	0.31	0.11	1.50	1.58	0.51	0.11	1.73	20.94	17.30	9.82	10.73	1.64	1.12	1.05	1.00	3.26	1.89	0.44	0.22	1.98	20.57
MgO	11.67	12.05	13.26	13.07	21.15	21.83	16.85	17.35	—	0.00	21.15	17.64	0.01	0.14	0.08	9.93	9.59	11.49	11.73	—	—	18.58	19.17	14.56	15.05	—	1.24
CaO	11.67	11.86	23.59	23.36	13.40	13.22	25.91	25.91	28.57	28.58	12.94	25.08	27.88	35.72	33.90	11.68	11.33	22.05	21.87	28.56	29.01	12.29	12.97	24.32	25.10	27.36	10.89
MnO	0.20	0.26	0.36	0.44	0.93	0.71	0.66	0.77	0.06	—	0.71	0.57	0.07	0.93	1.67	0.16	0.24	0.38	0.43	0.13	0.04	2.10	1.60	2.67	2.23	0.32	22.12
FeO	14.95	15.12	9.18	8.86	5.13	4.45	2.46	2.47	0.20	0.16	4.62	2.07	0.18	2.21	7.68	17.67	17.75	13.27	13.69	0.33	0.31	5.55	4.95	4.46	3.63	0.13	6.09
Na ₂ O	1.48	1.53	0.48	0.45	0.12	0.10	0.08	0.07	0.03	0.03	0.04	0.03	0.02	0.01	0.01	1.42	1.52	0.26	0.23	0.02	0.02	0.29	0.40	0.11	0.17	0.05	0.04
K ₂ O	1.23	1.16	—	—	0.03	0.04	—	—	—	—	0.04	—	—	—	—	0.80	1.00	—	—	—	—	0.19	0.24	—	—	—	—
F	0.02	0.03	—	—	—	0.02	—	—	0.47	0.23	—	—	0.07	—	—	0.08	—	—	—	0.02	0.28	—	—	—	—	—	—
Cl	0.08	0.08	—	—	0.04	—	—	—	—	—	0.02	—	—	—	—	0.04	0.05	—	—	—	—	—	—	—	—	—	—
Total	97.01	97.81	99.90	99.20	97.75	97.14	99.53	100.01	98.60	98.42	96.83	99.27	97.15	99.12	99.33	97.35	97.87	100.44	99.75	98.97	100.22	97.52	97.12	100.63	100.99	97.96	98.92
O=F	0.01	0.01	—	—	—	0.01	—	—	0.20	0.10	—	—	0.03	—	—	0.03	—	—	—	0.01	0.12	—	—	—	—	—	—
O=Cl	0.02	0.02	—	—	0.01	—	—	—	—	—	—	—	—	—	—	0.01	0.01	—	—	—	—	—	—	—	—	—	—
Total	96.98	97.77	99.90	99.20	97.74	97.06	99.53	100.01	98.40	98.33	96.83	99.27	97.12	99.12	99.34	97.31	97.86	100.44	99.75	98.97	100.10	97.52	97.12	100.63	100.99	97.96	98.92
No Ox	23	23	6	6	23	23	6	6	5	5	23	6	5	12	12	23	23	6	6	5	5	23	23	6	6	5	12
Si	6.52	6.49	1.91	1.92	7.83	7.77	1.95	1.94	0.98	0.99	7.90	1.97	1.00	2.98	2.99	6.56	6.45	1.93	1.92	0.99	0.99	7.69	7.87	1.99	1.99	1.01	3.03
Ti	0.18	0.18	—	—	—	—	—	—	0.95	0.95	—	—	0.94	—	—	0.24	0.28	0.01	—	0.97	0.97	0.01	0.01	—	—	0.94	0.02
Al	1.82	1.77	0.07	0.08	0.09	0.12	0.01	—	0.06	0.06	0.08	—	0.07	1.88	1.58	1.74	1.89	0.07	0.05	0.04	0.04	0.54	0.31	0.02	0.01	0.08	1.95
Fe ³⁺	0.40	0.48	0.13	0.11	0.23	0.38	0.08	0.08	0.01	—	0.23	0.06	—	0.14	0.44	0.35	0.41	0.07	0.11	0.01	0.01	0.28	—	—	0.02	—	—
Fe ²⁺	1.46	1.39	0.15	0.17	0.37	0.13	—	—	—	—	0.31	—	—	—	0.06	1.88	1.81	0.35	0.32	—	—	0.37	0.58	0.13	0.09	—	0.41
Mn	0.03	0.03	0.01	0.01	0.11	0.08	0.02	0.02	—	—	0.08	0.02	—	0.06	0.11	0.02	0.03	0.01	0.01	—	—	0.25	0.19	0.08	0.07	0.01	1.51
Mg	2.59	2.66	0.74	0.73	4.38	4.52	0.92	0.94	—	—	4.39	0.96	—	0.02	0.01	2.23	2.14	0.65	0.67	—	—	3.87	4.03	0.80	0.82	—	0.15
Ca	1.88	1.90	0.94	0.94	2.00	1.98	1.02	1.01	1.01	1.01	1.94	0.98	1.00	2.92	2.81	1.90	1.83	0.89	0.89	1.01	1.01	1.85	1.95	0.96	0.98	0.97	0.94
Na	0.43	0.44	0.03	0.03	0.03	0.03	0.01	—	—	—	0.06	—	—	—	—	0.42	0.44	0.02	0.02	—	—	0.15	0.11	0.01	0.01	—	0.01
K	0.24	0.22	—	—	0.01	0.01	—	—	—	—	0.01	—	—	—	—	0.15	0.19	—	—	—	—	0.03	0.04	—	—	—	—
Total	15.55	15.56	4.00	4.00	15.04	15.02	4.00	4.00	3.00	3.01	15.00	4.00	3.01	7.99	8.00	15.47	15.46	4.00	4.00	3.02	3.01	15.03	15.10	4.00	4.00	3.01	8.00
X _{Mg}	0.64	0.66	0.83	0.81	0.92	0.97	1.00	1.00	—	—	0.93	1.00	—	1.00	0.13	0.54	0.54	0.65	0.67	—	—	0.91	0.87	0.86	0.90	—	0.27
X _{Al}	—	—	—	—	—	—	—	—	0.06	0.06	—	—	0.07	—	—	—	—	—	—	0.04	0.04	—	—	—	—	0.08	—
X _{Grs}	—	—	—	—	—	—	—	—	—	—	—	25.08	—	0.91	0.74	—	—	—	—	—	—	—	—	—	—	—	0.31
X _{Alm}	—	—	—	—	—	—	—	—	—	—	—	—	—	0.00	0.02	—	—	—	—	—	—	—	—	—	—	—	0.14
X _{Py}	—	—	—	—	—	—	—	—	—	—	—	—	—	0.01	0.00	—	—	—	—	—	—	—	—	—	—	—	0.05
X _{Adr}	—	—	—	—	—	—	—	—	—	—	—	—	—	0.01	0.11	—	—	—	—	—	—	—	—	—	—	—	0.00
X _{Sps}	—	—	—	—	—	—	—	—	—	—	—	—	—	0.08	0.14	—	—	—	—	—	—	—	—	—	—	—	0.50

— = below detection.

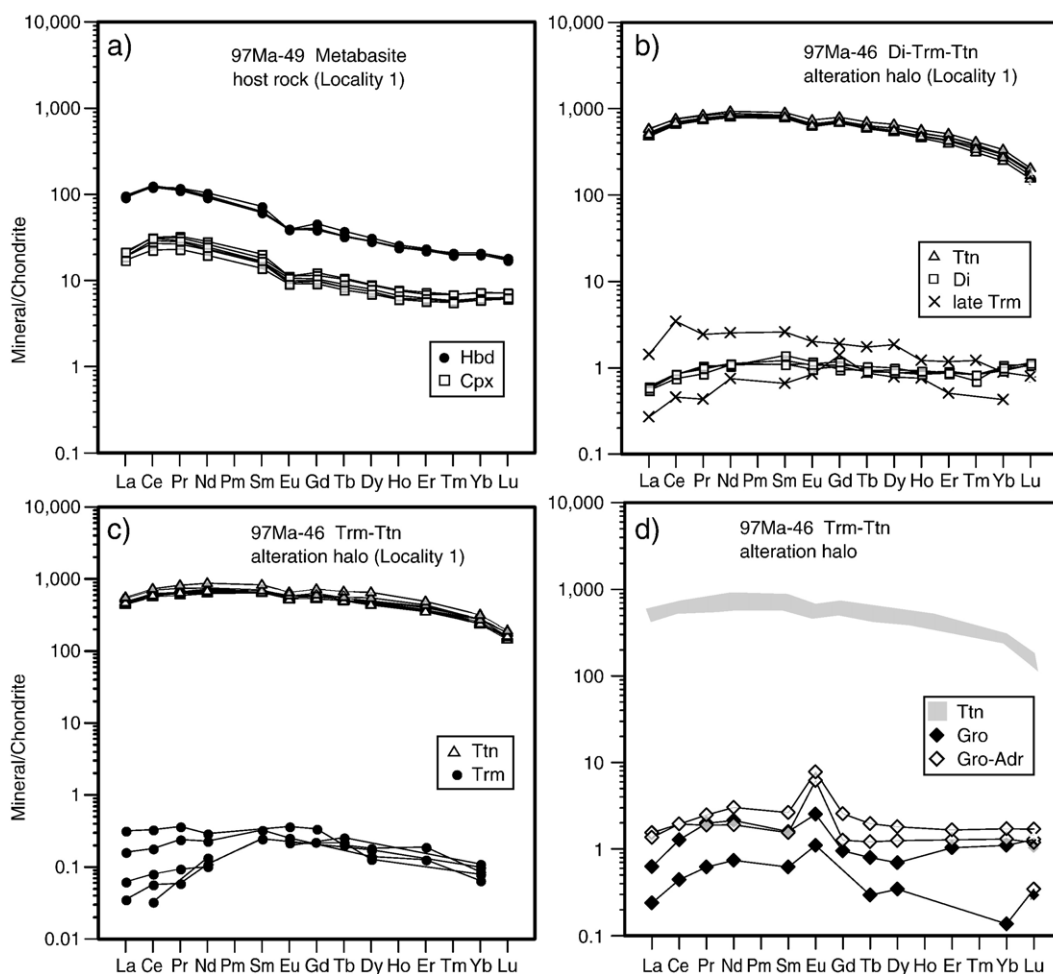


Fig. 6. Chondrite-normalised (Sun and McDonough, 1989) REE patterns for minerals from: (a) metabasite 97Ma-49; (b) the metasomatic diopside layer (97Ma-46Di); (c) titanite and tremolite from the metasomatic tremolite layer (97Ma-46Trm); and (d) garnet from the metasomatic tremolite layer. The shaded field gives the REE patterns for titanite from the same sample for ease of comparison with (c).

reduced using Cameca PAP matrix corrections. Fe^{3+} contents were recalculated subject to charge balance for clinopyroxene and garnet, and assuming 13 cations (excluding Ca, Na, K) for amphibole (Droop, 1987). BSE images of textural relationships between accessory phases and major silicate minerals were taken on a Phillips XL30 electron microscope (20 kV, 2 nA; University of Melbourne) and the phases identified using EDS. Using the same polished thin sections, *in situ* REE analyses of the same minerals were performed by laser-ablation ICP-MS at the Research School of Earth Sciences, Australian National University. A pulsed 193 nm ArF Excimer laser with 100 mJ energy at a repetition rate of 5 Hz coupled to an Agilent 7500 quadrupole ICP-MS was used for ablation. During the time-resolved analysis of minerals, possible contamination from inclusions and fractures were detected by monitoring several elements and integrating

only the ‘clean’ part of the signal. Spot sizes from 86 to 112 μm were used for most minerals, excepting titanite (32 μm). NIST-612 (Pearce et al., 1997) and BCR glasses were employed as external and secondary standards, respectively. The reproducibility of trace element results for the BCR glasses using the ANU analytical protocols is discussed in Storkey et al. (2005) and Buick et al. (2006). Si and Ca contents determined by electron microprobe were used as an internal standard for silicate minerals.

5. Results

5.1. Country rock metabasite (97Ma-49, Locality 1): mineral major and REE chemistry

Hornblende from the host metabasite is magnesio-hornblende to tschermakite in composition (Leake et al.,

Table 3

Representative REE contents for mineral from 97Ma-49, 97Ma-46Di and 97Ma-46Trm (Locality 1)

97Ma-49 metabasite (Locality 1)							97Ma-46Di (Locality 1)							97Ma-46Trm (Locality 1)										
Hornblende				Clinopyroxene			Diopside			Titanite			Late Tremolite		Tremolite			Titanite			Gro-Adr Grt		Gro Grt	
(ppm)	Hbd1	Hbd2	Hbd3	Cpx1	Cpx2	Cpx3	Di2	Di4	Di5	Ttn2	Ttn3	Ttn4	Trm2	Trm3	Trm1	Trm2	Trm3	Ttn1	Ttn2	Ttn3	Grt1	Grt2	Grt15	Grt16
Y	38	37	37	11	8.9	9.0	1.4	1.4	1.4	822	886	825	2.8	1.1	0.16	0.31	0.17	662	658	703	0.39	1.9	1.2	1.1
La	24	23	23	4.8	4.4	4.4	0.14	0.13	0.14	113	126	115	0.37	0.07	0.07	0.07	0.04	108	127	115	0.46	0.37	0.04	0.15
Ce	80	76	79	19	18	16	0.52	0.45	0.51	400	432	415	2.3	0.31	0.19	0.21	0.11	348	425	383	0.99	1.2	0.18	0.79
Pr	11	11	11	3.0	2.6	2.4	0.09	0.08	0.09	68	73	70	0.25	0.04	0.03	0.03	0.02	58	69	61	0.11	0.18	0.02	0.19
Nd	45	43	46	13	10	10	0.50	0.49	0.50	362	383	375	1.3	0.38	0.13	0.15	0.10	291	344	318	0.43	0.88	0.14	0.99
Sm	9.6	9.4	9.7	3.0	2.4	2.3	0.18	0.16	0.16	115	123	119	0.42	0.11	bdl	0.05	0.05	97	104	98	bdl	0.23	bdl	0.24
Eu	2.3	2.3	2.3	0.62	0.55	0.52	0.06	0.05	0.06	35	37	37	0.13	0.05	0.02	0.02	0.01	30	33	32	0.23	0.35	0.07	0.14
Gd	8.3	8.0	8.3	2.4	1.9	1.9	0.21	0.20	0.23	135	143	139	0.42	0.30	0.06	0.06	bdl	117	127	118	bdl	0.25	bdl	0.19
Tb	1.2	1.2	1.2	0.38	0.30	0.30	0.04	0.03	0.03	21	23	22	0.07	0.03	0.01	0.01	bdl	18	20	19	bdl	0.04	bdl	0.03
Dy	7.3	7.3	7.2	2.2	1.8	1.8	0.24	0.22	0.23	135	145	138	0.50	0.21	0.04	0.05	0.03	119	120	122	0.07	0.31	0.15	0.17
Ho	1.4	1.4	1.4	0.42	0.33	0.32	0.05	0.05	0.05	26	28	27	0.07	0.05	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Er	3.8	3.7	3.7	1.1	0.9	1.0	0.14	0.14	0.14	69	74	70	0.21	0.09	0.03	0.03	0.02	59	59	64	0.05	0.21	0.16	0.17
Tm	0.53	0.51	0.50	0.17	0.14	0.14	0.02	0.02	0.02	9.0	9.5	8.9	0.03	bdl	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Yb	3.5	3.3	3.3	1.1	0.94	1.0	0.16	0.15	0.16	48	48	47	0.16	0.08	0.01	0.04	0.01	44	39	45	0.04	0.21	0.17	0.18
Lu	0.47	0.44	0.46	0.17	0.15	0.15	0.03	0.03	0.03	4.7	4.6	4.5	0.02	bdl	bdl	bdl	bdl	4.4	3.8	4.4	bdl	0.03	0.03	0.03
Pb	2.5	2.5	2.4	0.76	0.93	0.84	2.8	3.0	2.5	23	18	23	0.64	0.47	0.45	0.41	0.28	21	23	25	bdl	0.38	0.48	0.24
Th	0.77	0.76	0.72	0.07	0.16	0.12	0.01	0.00	0.01	115	83	114	0.34	0.04	bdl	bdl	bdl	100	110	115	bdl	bdl	bdl	0.14
U	0.23	0.23	0.22	0.033	0.048	0.044	0.00	0.00	0.00	56	53	57	0.38	0.04	bdl	bdl	bdl	57	55	60	0.45	0.49	0.05	0.16
Eu/Eu*	0.80	0.80	0.79	0.71	0.77	0.75	0.94	0.91	0.98	0.87	0.86	0.87	0.91	0.88		1.40		0.87	0.87	0.91		4.44		2.06

bdl = below detection limits.

N/A = not analysed.

1997), halogen-poor and has X_{Mg} ($\text{Mg}/\text{Mg}+\text{Fe}^{2+}$) in the range 0.65–0.70 (Table 2). The clinopyroxene has low Al contents (0.074–0.078 Al a.p.f.u.) and higher X_{Mg} ($X_{\text{Mg}}=0.81$ –0.83) than the coexisting hornblende. No analyses were obtained from plagioclase because it was extensively replaced by sericite. Clinopyroxene and hornblende show chondrite-normalised (Sun and McDonough, 1989) REE patterns with generally similar shapes but different abundances (Fig. 6a; Table 3). These are characterised by an increase in normalised abundance from La to Ce, followed by a decrease with increasing atomic number, and moderate to small negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.65$ –0.77 and 0.72–0.83 for hornblende and clinopyroxene, respectively). Chondrite-normalised clinopyroxene REE abundances show little change from Er to Lu. Hornblende is consistently more REE-rich than coexisting clinopyroxene. Apparent distribution coefficients ($D^{\text{Hbd/Cpx}} = \text{concentration element}_{(\text{Hbd})} / \text{concentration element}_{(\text{Cpx})}$) vary between ~ 4.8 (La) and ~ 2.7 (Lu), with most REE having distribution coefficients between 3.5 and 4.0.

5.2. Di–Trm alteration zone (97Ma46, Locality 1): mineral major and REE chemistry

The diopside-rich part of the alteration zone predominantly contains Al-poor diopside ($\text{Al}=0.00$ –0.01 a.p.f.u.; $X_{\text{Mg}}=0.98$ –1.00; Table 2) that is different in composition to that in the host metabasite. Tremolite that partially replaces diopside has high X_{Mg} (0.92–0.97). Titanite is also Al-poor (0.06 Al a.p.f.u.; Table 2) and is the only phase containing appreciable levels of REE (Fig. 6b; Table 3). Titanite REE patterns are characterised by increasing normalised REE abundance from La to Nd, decreasing chondrite-normalised abundance from Sm to Lu, and small negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.84$ –0.87). REE abundances in the other minerals are much lower, and measured REE patterns are clearly affected by degraded analytical accuracy at $\approx 1 \times$ chondrite level. The metasomatic diopside has REE abundances at least an order of magnitude lower than that of clinopyroxene in the host metabasite (Fig. 6a; Table 3). REE patterns are characterised by a increase in abundance from La_N (~ 0.58) to Nd_N (~ 1.09), chondrite-normalised abundances of ~ 1 for the M-HREE, and no appreciable Eu anomaly ($\text{Eu}/\text{Eu}^*=0.91$ –1.02; Fig. 6b). Tremolite shows similar REE patterns to the diopside that it replaces (Fig. 6b; Table 3).

The tremolite-rich part of the alteration zone contains titanite and relict Al-poor diopside that are identical in major element composition to that in the Di-rich portion (Table 2). The tremolite has X_{Mg} in the range 0.93–0.95.

The colourless non-isotropic, oscillatory and sector zoned garnet is close in composition to pure grossular ($\text{Alm}_{0-1}\text{Py}_{0-1}\text{Sps}_2\text{Gro}_{92-95}\text{Adr}_{5-7}$). The isotropic garnet is more andradite-rich and significantly more variable in composition ($\text{Alm}_{0-2}\text{Py}_0\text{Sps}_{1-6}\text{Gro}_{71-86}\text{Adr}_{11-24}$; Table 2). Titanite from the tremolite alteration zone has identical major element compositions and REE patterns to that from the adjacent diopside-rich alteration zone (Tables 2 and 3; Fig. 6b, c). Tremolite from the tremolite zone is extremely REE-poor (Table 3); REE patterns show maximum normalised abundances for the MREE and these do not exceed 0.4 times chondrite levels (Fig. 6c). While all tremolite REE patterns show a similar monotonic decrease in normalised abundance from Eu to Yb, LREE levels vary significantly with $(\text{La}/\text{Sm})_\text{N}$ varying 10-fold from ≈ 0.03 to 3 (Fig. 6c). Both types of garnet are characterised by very low overall REE abundances (Table 3; chondrite-normalised abundances for the M-HREE < 3), Eu enrichment and approximately constant or decreasing chondrite-normalised abundances with increasing atomic number from Gd to Lu (Fig. 6d).

5.3. Titanite U–Pb geochronology

Titanite REE patterns in high-grade metabasites can vary significantly on a thin section scale as a function of local mineral assemblage and reaction history (Storkey et al., 2005). The uniformity of titanite REE patterns therefore suggests that 97Ma-46Cpx contains a single titanite generation. This is supported by the coherent U–Pb isotope systematics of three titanite

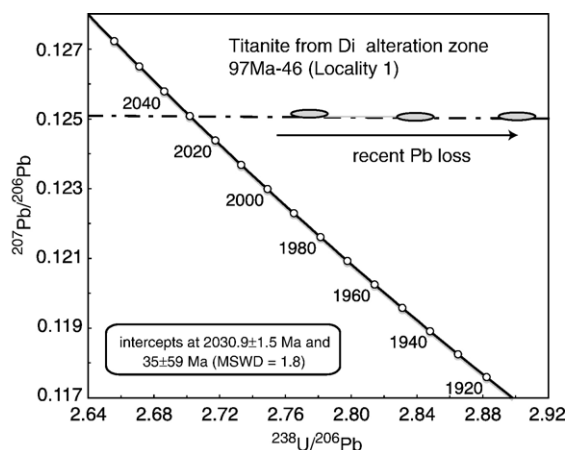


Fig. 7. Tera–Wasserburg U–Pb diagram showing data for three titanite splits from sample 97Ma-46Di. Data plotted after common Pb correction with a 2000 Ma Stacey–Kramers model Pb composition. Data are consistent with recent Pb loss from a system established at 2031.9 ± 1.5 Ma.

Table 4

U–Pb isotopic results, titanite 97Ma-46Di (Locality 1)

#	Concentrations				Atomic ratios ($\pm 2\sigma$, %)					Ages, Ma		
	Wt	U	Pb _{tot}	Pb _{com}	²⁰⁶ Pb	²⁰⁸ Pb	²⁰⁶ Pb*	²⁰⁷ Pb*	²⁰⁷ Pb*	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁶ Pb
	mg	ppm	ppm	ppm	²⁰⁴ Pb	²⁰⁴ Pb	²³⁸ U	²³⁵ U	²⁰⁶ Pb	²³⁸ U	²³⁵ U	²⁰⁶ Pb
46.1	2.74	61.28	34.99	5.04	260.2	153.7	0.3523 $\pm$ 0.31	6.074 $\pm$ 0.32	0.12505 $\pm$ 0.058	1946	1987	2029.5
46.2	1.58	67.91	37.78	5.34	265.7	155.8	0.3447 $\pm$ 0.31	5.944 $\pm$ 0.32	0.12508 $\pm$ 0.054	1909	1968	2029.9
46.3	4.95	68.24	39.86	5.84	256.2	150.3	0.3605 $\pm$ 0.32	6.221 $\pm$ 0.32	0.12513 $\pm$ 0.063	1985	2007	2030.7

²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb corrected for mass bias and blank (50 pg Pb, 20 pg U). Pb*/U and Pb*/Pb* corrected for mass bias, blank and common Pb using a Stacey–Kramers model Pb at 2000 Ma. Decay constants: $\lambda_{238}=0.155125 \cdot 10^{-9}/\text{yr}$, $\lambda_{235}=0.98485 \cdot 10^{-9}/\text{yr}$.

fractions from the Di-rich portion of the 97Ma-46 vein U (60.1–67.0 ppm), total Pb (34.5–39.3 ppm) and common Pb (5.0–5.8 ppm) contents show narrow ranges, consistent with the uniformity of the REE patterns in Fig. 6. On a Tera–Wasserburg concordia diagram (Fig. 7) the three splits are slightly (2–5%) normally discordant and define a horizontal trend indicative of recent Pb loss. The calculated upper and lower intercept ages of the discordia line are 2030.9 ± 1.5 Ma (MSWD=1.8) and 35 ± 59 Ma. The upper intercept age is taken as the best age estimate for titanite in 97Ma-46Di (Table 4).

5.4. Central Zone metabasite (97Ma-62, Locality 2): mineral major and REE chemistry

Sample 97Ma-62 contains a granoblastic mosaic (Fig. 5a) of quartz, plagioclase (An_{51–55}), low-Al clinopyroxene (Al=0.05–0.08 a.p.f.u.; $X_{\text{Mg}}=0.64–0.69$), halogen-poor hornblende (tschermakite to Mg-hornblende in composition; Leake et al., 1997; $X_{\text{Mg}}=0.50–0.54$; Table 2) and Al-poor titanite (Al=0.04 a.p.f.u.; Table 2). The REE are concentrated in the different minerals in the order titanite>hornblende>clinopyroxene (Fig. 8a; Table 5). REE patterns for clinopyroxene typically show a small increase from La_N (~3–4) to Sm_N (~6–7), moderate negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.59–0.69$) and almost flat HREE. REE patterns for hornblende parallel those of clinopyroxene, but with more variable Eu anomalies ($\text{Eu}/\text{Eu}^*=0.61–0.99$) at higher abundances of typically 20–30 times chondrite for all REE (Fig. 8a). REE patterns for titanite show abundances of ~900–1100 from La_N to Sm_N, moderate to small negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.65–0.81$) and mildly fractionated HREE (Gd_N ~1000 to Lu_N ~500; Fig. 8a). Apparent REE distribution coefficients obtained from the average of hornblende and clinopyroxene REE analyses are very similar to those obtained from 97Ma-49 i.e. $D^{\text{Hbd/Cpx}} \sim 5.4$ for La and between 4 and 5 for all other REE.

5.5. Matsiama–Motloutse Complex Di–Trm–Ttn–Grt vein (97Bo-47, Locality 3): mineral major and REE chemistry

Vein 97Bo-47 contains the mineral assemblage Mn-bearing diopside (~2.0–2.8 wt.% MnO; $X_{\text{Mg}}=0.86–$

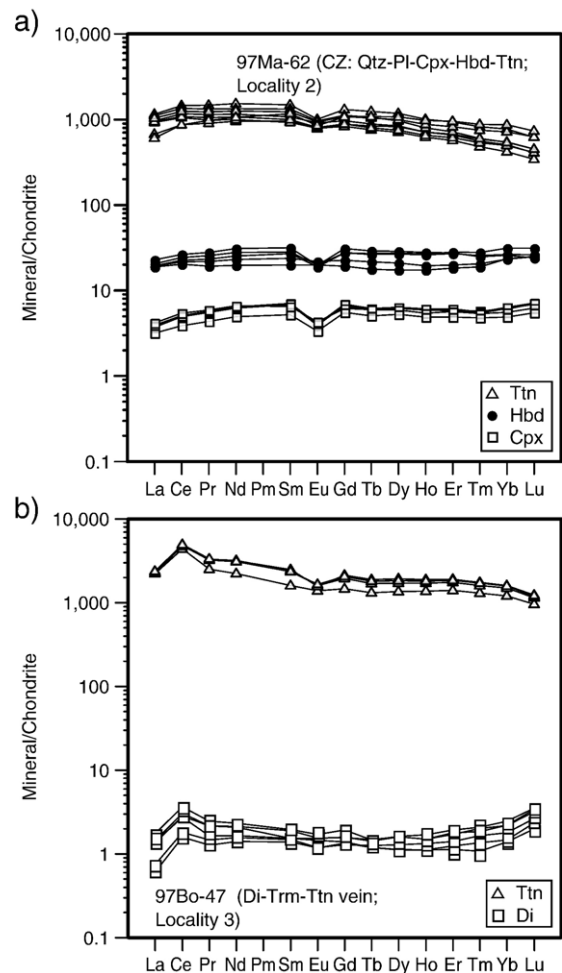


Fig. 8. Chondrite-normalised (Sun and McDonough, 1989) REE patterns for minerals in: (a) 97Ma-62 and (b) 97Bo-47.

Table 5

Representative REE contents for minerals from 97Ma-62 and 97Bo-47

(ppm)	97Ma-62 metabasite (Locality 2)									97Bo-47 Di vein (Locality 3)					
	Hornblende			Clinopyroxene			Titanite			Diopside			Titanite		
	Hbd1	Hbd2	Hbd4	Cpx2	Cpx3	Cpx4	Ttn2	Ttn3	Ttn4	Di6	Di7	Di8	Ttn1	Ttn9	Ttn10
Y	38	36	38	7.9	7.9	7.6	833	905	1110	2.9	2.9	3.4	2548	3392	3410
La	5.3	4.5	4.8	0.88	0.97	0.99	220	223	261	0.32	0.34	0.41	529	544	564
Ce	16	14	15	3.0	3.3	3.4	643	667	825	1.7	1.9	2.2	2702	2902	3050
Pr	2.5	2.1	2.3	0.52	0.56	0.55	92	98	123	0.20	0.20	0.23	232	307	308
Nd	14	11	13	2.9	3.1	3.0	456	488	614	1.0	0.95	1.1	1017	1448	1408
Sm	4.6	3.9	4.1	1.0	1.1	0.97	137	147	196	0.28	0.23	0.29	237	369	348
Eu	1.1	1.0	1.1	0.22	0.23	0.24	45	45	54	0.09	0.09	0.10	79	89	93
Gd	6.0	5.4	5.4	1.3	1.3	1.2	165	176	223	0.31	0.32	0.38	294	424	409
Tb	1.0	0.93	1.0	0.22	0.22	0.22	27	29	38	0.05	0.05	0.05	47	68	65
Dy	6.9	6.5	6.7	1.5	1.5	1.5	174	184	237	0.39	0.39	0.40	335	473	450
Ho	1.5	1.4	1.4	0.33	0.32	0.30	34	36	44	0.08	0.08	0.09	75	103	99
Er	4.3	4.2	4.4	0.95	0.93	0.91	91	98	114	0.27	0.29	0.31	225	306	297
Tm	0.60	0.62	0.68	0.14	0.14	0.13	12	13	15	0.05	0.05	0.05	32	43	42
Yb	4.1	4.2	4.9	1.0	0.94	0.90	68	80	87	0.35	0.36	0.40	195	256	254
Lu	0.58	0.63	0.76	0.17	0.17	0.15	8.4	10	11	0.08	0.08	0.09	24	29	30
Pb	1.7	2.2	1.7	0.36	0.37	0.38	10	12	16	1.8	1.9	2.1	24	23	23
Th	0.21	0.22	0.22	0.04	0.02	0.03	55	62	97	0.01	0.01	0.01	111	127	127
U	0.11	0.16	0.15	0.02	0.02	0.03	18	32	95	0.01	0.01	0.01	300	258	270
Eu/Eu*	0.63	0.69	0.71	0.58	0.57	0.68	0.90	0.86	0.79	0.90	0.99	0.88	0.91	0.68	0.75

0.90), Mn-bearing actinolite to tremolite (~2 wt.% MnO; Leake et al., 1997; $X_{\text{Mg}}=0.87\text{--}0.91$), low-Al titanite (0.08 a.p.f.u.), spessartine-grossular garnet ($\text{Alm}_{8-15}\text{Py}_{2-6}\text{Gro}_{31-40}\text{Sps}_{42-52}$), apatite and calcite (Table 2). Diopside is partially replaced by actinolite/tremolite (Fig. 5d). Titanite is included by, and includes (Fig. 5d) diopside. Trace element data (Table 5) were collected only for diopside and titanite, given that amphibole is texturally late and replaces diopside. REE patterns for titanite are characterised by an increase in normalised abundance from La to Ce, followed by a slight decrease from Ce to the MREE, small Eu anomalies (both negative and positive, $\text{Eu}/\text{Eu}^*=0.69\text{--}1.33$; Fig. 8b), little change in abundance from Gd to Er, and a small decrease in abundance from Er to Lu. Titanite contains high concentrations of U and has $\text{Th}/\text{U}<1$, probably reflecting a U-enriched protolith. Normalised REE abundances for diopside show an initial increase from La to Ce, very small positive and negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.86\text{--}1.13$), little change in normalised abundance from Nd to Er, and a slight increase from Er to Lu (Fig. 8b).

6. Discussion

The alteration zones developed around quartz vein systems at Locality 1 potentially place an important time constraint on metamorphic processes in the Central

Zone. The Trm alteration zone sample contains a mineral assemblage that is consistent with formation under greenschist-facies conditions. In contrast, the Di alteration zone sample contains almost monomineralic diopside with minor plagioclase and titanite that could potentially be stable under a wide range of pressure–temperature conditions from lower amphibolite- to granulite-facies grades. The high variance of the assemblage in this rock, and the adjacent metabasite, precludes further discrimination of P – T conditions. However, the field observations that the diopside alteration has an occurrence restricted to lenses within (Fig. 2d) and irregular zones at the margins of the structurally late quartz stockworks (Fig. 2c) places tighter constraints on the conditions of formation. In particular, the quartz veins are clearly fluid-related features that record the infiltration of Si-bearing, water-rich metasomatic fluids. Water-rich fluids cannot be transported at suprasolidus P – T conditions because such fluid would be consumed to flux further melting in the felsic orthogneisses that surround Locality 1 (Fig. 1b); thus the quartz veining and intimately related diopside alteration must have occurred at temperatures at or below the wet solidus of the host rocks, i.e. at lower to mid-amphibolite facies conditions (Fig. 9). Hydrothermal diopside-rich veins formed under lower to mid-amphibolite facies conditions have previously been recorded in altered mafic rocks from mid-ocean ridge

(e.g. Vanko and Stakes, 1991) and contact (e.g. the Bushveld Layered Igneous Complex; Schiffries and Skinner, 1987) metamorphic settings.

The close spatial link between pegmatites, the quartz stockworks and the alteration zones suggests that the exsolution of fluids from crystallising pegmatites caused the hydrothermal alteration, as has been documented elsewhere (e.g. Cartwright, 1988; Cartwright et al., 1996; Buick et al., 1997; Matthews et al., 2002; Katzir et al., 2002) and is an expected result of melt segregation and crystallisation in high-grade terrains (e.g. Clemens and Droop, 1998; Spear et al., 1999). The exact position of the wet solidus will vary as a function of bulk composition, but for a range of bulk compositions corresponds in general to upper-amphibolite facies conditions (Fig. 9) for pressures relevant to post-peak P – T – t paths in the Central Zone (e.g. Zeh et al., 2004). Given the occurrence of plagioclase and lack of alkali feldspar in the pegmatite at Locality 1, the wet solidus for tonalite is probably the most appropriate of those given in Fig. 9 for the temperature at which fluid would have been exsolved. The occurrence of epidote in this pegmatite is consistent with the limited stability of epidote in tonalitic melts to conditions at, and just above the wet solidus at intermediate pressures (e.g. ~660–680 °C at ~4–6 kbar; Schmidt and Thompson, 1996).

Based on these constraints, dating of the 97Ma-46Di alteration zone provides a time marker for when rocks at Locality 1 were at grades no higher than the upper amphibolite facies. However, it can be difficult to relate ages obtained from dating accessory phases to meta-

morphic events. This is particularly the case in the present study because titanite is potentially stable in metabasic rocks over the whole of the Pressure–Temperature–time path followed by Central Zone rocks (Frost et al., 2000), to grades as low as the greenschist facies (Fig. 9). Therefore, in order to provide such a link we use mineral REE data from the alteration zones (97Ma-46Di and 97Ma-46Trm), the host metabasite (97Ma-49) at Locality 1, and from comparable rock types (97Ma-62, Locality 2 and 97Bo-47, Locality 3) to assess the petrological significance of the ~2031 titanite age for 97Ma-46Di.

6.1. Titanite–clinopyroxene–hornblende REE systematics

Titanite in the 97Ma-46 alteration zones from Locality 1 could have grown during metasomatism that accompanied formation of the alteration zones within and on the margins of the quartz stockwork. Alternatively, it could have been inherited from the metabasite host rock, even though no titanite was observed in thin section, perhaps due to inhomogeneous distribution of accessory phases in the metabasite. High-grade metabasites elsewhere in the Central Zone locally contain titanite. The two possibilities would have different consequences for interpretation of the ~2031Ma titanite age, and one of them needs to be discounted.

Several lines of evidence suggest that the ~2031 Ma titanite grew in the alteration zones and not in the metabasite host. Firstly, the titanite locally contains inclusions of almost pure end-member diopside, which

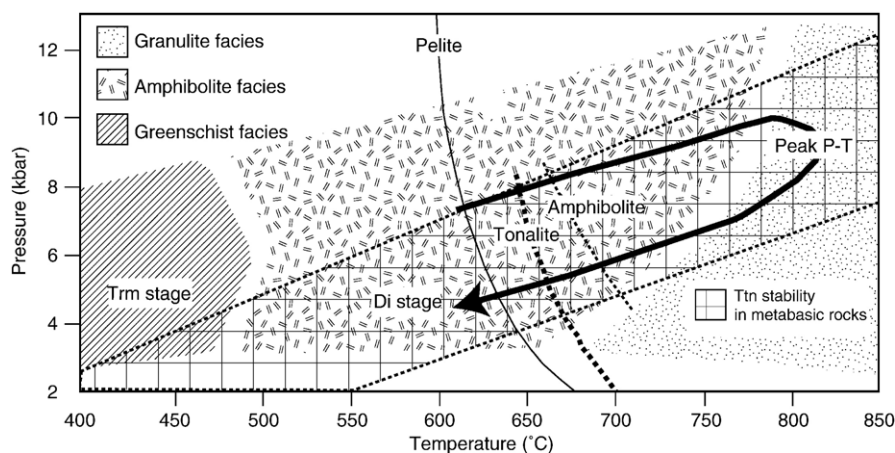


Fig. 9. P – T diagram showing a representative P – T path for granulite-grade metamorphism in the Central Zone (Zeh et al., 2004), the wet solidi for pelite, tonalite and amphibolite bulk compositions (Wyllie, 1977; Thompson, 1982; Wyllie and Wolf, 1993) and the facies boundaries of Spear (1993). Also shown is the approximate stability field for titanite in medium- to high-grade metabasites (Frost et al., 2000), extrapolated into the granulite-facies to be consistent with the occurrence of titanite in granulite-facies metabasites from the Central Zone. Such an extrapolation is also consistent with the documented stability of titanite in migmatitic metabasites that reached similar P – T conditions elsewhere (e.g. in the Harts Range, central Australia; Storkey et al., 2005).

makes up the bulk of the Di alteration zone and that is distinct in composition from the more Fe-rich clinopyroxene in the host metabasite. Secondly, the REE pattern of titanite in the diopside alteration zone is also inconsistent with it being inherited from the host metabasite. Fig. 10a shows the range of REE patterns of titanite predicted to be in approximate equilibrium with clinopyroxene and hornblende in metabasite 97Ma-49 (Locality 1) based on apparent REE distribution coefficients obtained from coexisting titanite, clinopyroxene and hornblende from Central Zone metabasite 97Ma-62 (Table 6) and from a texturally simple metabasite from the Harts Range, central Australia (sample 02-169; Storkey et al., 2005). The latter was metamorphosed to slightly lower (lower granulite-facies; ~750–800 °C and ~8–10 kbar) grade than experienced in the Central Zone but contains the same mineral assemblage as 97Ma-62 (Locality 3). In 97Ma-49, 97Ma-62 and 02-169 the uniformity of apparent hornblende–clinopyroxene distribution coefficients from the LREE to the HREE is consistent with theoretical predictions (Klein et al., 1997). While the normalised abundances for hypothetical titanite obtained from the two samples differ slightly, the shapes of the REE patterns are very similar; they show a small initial increase in abundance from La to Ce, small Eu anomalies and an otherwise relatively steep monotonic decrease in normalised abundance from Ce to Lu (Fig. 10a). By

contrast, measured REE patterns for titanite in the alteration zones (Fig. 10a) are characterised by much lower LREE abundances and lack the strong LREE to HREE fractionation predicted for titanite in equilibrium with the clinopyroxene and hornblende in the host metabasite 97Ma-49 from Locality 1 (Fig. 10a). Moreover, clinopyroxene REE patterns predicted to be in equilibrium with titanite from 97Ma-46Di, based on the measured partitioning from granulite-facies metabasite 97Ma-62 (Locality 2), are significantly different both in normalised REE abundance and shape of REE pattern (e.g. they predict a moderate negative Eu anomaly; Fig. 10b) compared to that actually analysed from this alteration zone. In contrast, partitioning obtained from a similar metasomatic Di–Trm–Ttn vein (97Bo-47, Locality 3; Table 6) results in overall very similar REE patterns, albeit with slightly lower normalised abundances, to those measured for titanite in 97Ma-46Di.

Titanite also occurs in the tremolite-rich zone in 97Ma-46 and has identical REE patterns to that in the Di-rich portion of the alteration zone (Fig. 6b, c). Incipient tremolite in the Di alteration zone has very low REE abundances and REE patterns that are similar to those of the diopside that it replaces (Fig. 6b). In contrast, hornblende in the metabasites is consistently more REE-rich than co-existing clinopyroxene, by a factor of 2–5 times (Figs 6 and 8). The tremolite REE pattern in 97Ma-46Di appears to have been inherited from the diopside

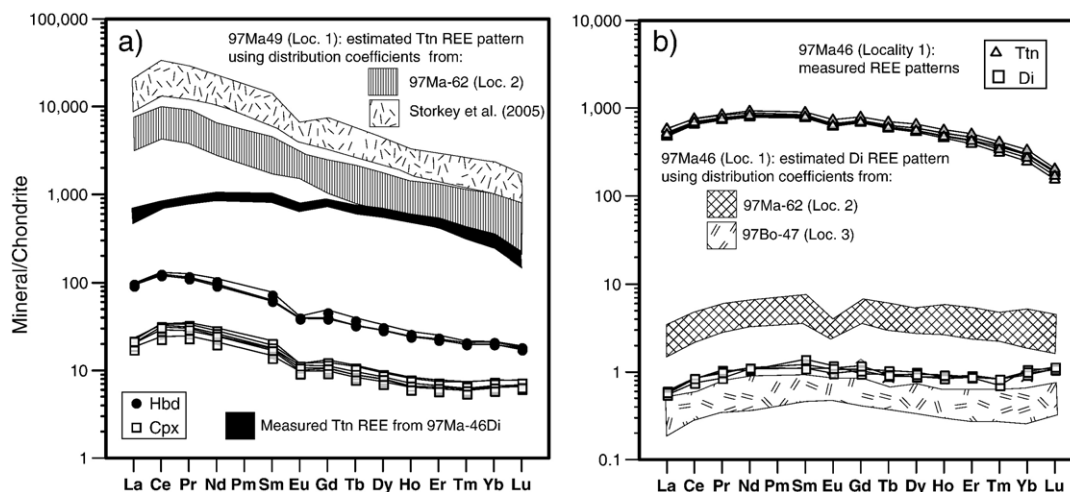


Fig. 10. (a) Chondrite-normalised (Sun and McDonough, 1989) plot showing the hornblende and clinopyroxene REE patterns from 97Ma-49 (Locality 1), together with the REE patterns (stippled fields) of a hypothetical titanite predicted to be in trace element equilibrium with these minerals based on empirical partitioning obtained from 97Ma-62 (Locality 2) and 02-169, a lower granulite-facies metabasite from central Australia (Storkey et al., 2005). Also shown are the measured REE patterns for titanite (black field) from the 97Ma-46 Di alteration zone (Locality 1); (b) Chondrite-normalised (Sun and McDonough, 1989) plot showing the measured diopside and titanite REE patterns for 97Ma-46Di, together with the titanite REE patterns predicted from empirical REE partitioning between clinopyroxene and titanite in granulite-facies 97Ma-62 and amphibolite-facies vein 97Bo-47 (Locality 3). In both figures the width of the bands reflects the compositional variability of multiple LA-ICP-MS analyses of clinopyroxene, hornblende and titanite. See text for discussion.

Table 6

Apparent REE distribution coefficients obtained from average compositions of mineral pairs in this study and from [Storkey et al. \(2005\)](#)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
<i>97Ma-49: metabasite (Locality 1)</i>														
$D^{Hbd/Cpx}$	4.8	4.3	4.0	4.0	3.9	3.8	3.9	3.7	3.7	3.7	3.6	3.3	3.1	2.7
Error	0.5	0.6	0.6	0.7	0.8	0.4	0.7	0.8	0.6	0.6	0.4	0.4	0.4	0.3
<i>97Ma-62: metabasite (Locality 2)</i>														
$D^{Tm/Cpx}$	222	209	187	172	158	201	145	148	138	126	118	109	94	69
Error	69	65	55	48	46	38	35	38	35	35	33	32	35	26
$D^{Tm/Hbd}$	41	44	43	41	39	40	36	36	34	30	28	25	21	17
Error	12	13	14	14	14	6	12	13	13	12	11	10	8	7
$D^{Hbd/Cpx}$	5.4	4.7	4.3	4.1	4.0	5.1	4.0	4.1	4.1	4.2	4.3	4.4	4.5	4.0
Error	1.0	1.1	1.1	1.2	1.2	0.7	1.1	1.1	1.1	1.2	1.2	1.0	1.0	0.9
<i>02-162 (Storkey et al., 2005)</i>														
$D^{Tm/Cpx}$	722	745	684	627	562	473	482	442	395	357	342	309	264	199
Error	255	247	212	153	144	97	122	90	97	75	75	73	62	46
$D^{Tm/Hbd}$	163	169	155	136	119	112	96	91	83	74	71	66	60	53
Error	54	48	40	27	18	12	12	10	9	8	7	7	7	7
$D^{Hbd/Cpx}$	4.4	4.4	4.4	4.6	4.7	4.2	5.0	4.8	4.8	4.8	4.8	4.7	4.4	3.8
Error	0.7	0.9	1.0	1.0	1.1	0.9	1.2	1.0	1.2	1.0	1.0	1.0	0.9	0.7
<i>97Bo-47: sub-solidus Di vein (Locality 3)</i>														
$D^{Tm/Di}$	1842	1775	1619	1544	1342	1074	1239	1243	1212	1221	1121	950	760	395
Error	739	616	609	521	414	223	365	307	378	355	370	331	260	123

Error = propagated from variability of typically 3–6 analyses of each mineral.

and cannot be in trace element equilibrium with it, or with the titanite. The REE abundances of tremolite from the Trm alteration zone are typically even lower than those in the Di zone, suggesting that this tremolite is also not in trace element equilibrium with the titanite in this alteration zone. Inheritance of REE patterns of earlier formed minerals is also evident in the positive Eu anomalies and overall very low trace element contents exhibited by garnet (Fig. 6d). These features suggest that the garnet formed by sub-solidus reactions that consumed plagioclase (e.g. [Hermann and Rubatto, 2003](#)), which occurs locally in the Di zone sample. Evidence for inheritance of REE patterns in turn suggests that the tremolite portion of the reaction zone formed, at least in part, by replacement of the earlier formed, high-temperature Di zone, rather than by direct precipitation from the fluid during cooling. This is consistent with the local preservation of relict diopside as inclusions (Fig. 4b) in tremolite of the Trm zone.

The presence of prehnite, together with grossular-rich garnet, suggests that the outermost part of the Trm Zone formed at maximum temperatures of ~400 °C ([Deer et al., 1992](#)). Therefore, although the alteration zones appear to record hydrothermal processes that occurred over a significant temperature range during cooling (from mid-amphibolite to greenschist-facies)

the titanite grew at an early stage of the alteration process, and the age obtained from it dates only the higher temperature part of the alteration. Without the REE data it would be difficult to relate the ~2031 Ma titanite age to a particular part of the metamorphic history at Locality 1.

6.2. Uncertainties in the empirical approach

Comparisons based on empirical mineral–mineral partitioning are subject to a number of assumptions, including that the assemblages being compared formed at the same metamorphic grades and that mineral major element compositions were similar. In the present study, the assumed metamorphic grade for 97Ma62 (Locality 3) and 02-169 are similar, as are mineral compositions (this study; [Storkey et al., 2005](#)). Similarly, the alteration halo 97Ma-46 and the metasomatic Di–Trm–Ttn vein 97Bo-47 appear to have formed by hydrothermal processes related to exsolution of fluids from crystallising pegmatites. This places a constraint that fluid-related processes occurred at temperatures close to, but below, the wet solidus i.e. mid- to upper amphibolite-facies conditions. Mineral assemblages and compositions in 97Ma-46Di (Locality 1) and 97Bo-47 (Locality 3) are closely comparable except that diopside from the latter contains

higher Mn contents, and that the titanite at the two localities has different Th/U (Th/U=0.37–0.49 and 1.7–2.1 for the Botswanan and Central Zone samples, respectively). The Th/U of accessory phases depends on competition with other minerals that partition Th and U, as well as P – T and bulk compositional controls. In both samples the only other phase that partitions Th and U appreciably is apatite. In the case of the diopside-rich vein from Botswana, apatite coexisting with the titanite also has low Th/U (0.15–0.35; Buick, unpublished data). We were unable to obtain LA-ICP-MS data from the apatite in the Central Zone alteration zone because it was very rare, fine grained and exploded under the laser. Given the occurrence of low Th/U apatite and titanite in the Botswanan vein and that the inferred P – T conditions for formation of titanite–diopside assemblages in the two localities are similar, it is likely that the difference in Th/U reflects a primary chemical difference in the source for the vein-forming fluid. In the case of the Botswanan vein this is a highly fractionated (and thus likely to be relatively U-rich and Th-poor) muscovite–garnet-bearing peraluminous pegmatite, whereas in the Central Zone sample the pegmatites appear to be broadly tonalitic in composition.

An additional uncertainty is the metamorphic grade experienced by the metabasite 97Ma-49 at Locality 1. It contains a mineral assemblage that is characteristic of, but not restricted to, the amphibolite facies. The same assemblage may occur under lower- to mid-granulite-facies conditions, where the lack of indicator minerals such as orthopyroxene and/or garnet probably reflects the lack of quartz to participate in solid-state dehydration or dehydration-melting reactions (cf. Hartel and Pattison, 1996). The lack of partial melting in quartz-absent leucogabbros of the Messina Layered Suite (Fig. 2), which was emplaced prior to late Archaean granulite-facies metamorphism, also reflects this compositional control. While a mid- to upper-amphibolite facies klippe occurs to the west of Messina (near Venetia, Fig. 1a; Klemd et al., 2003; Zeh et al., 2005), sample 97Ma-49 was obtained from a part of the Central Zone previously described as being uniformly of granulite-facies grade (Brandl, 1983). Metabasic rocks ~700 m across strike from Locality 1 are net-veined migmatites, consistent with this. Similarly, sample 97Ma-62, sampled to the west of Locality 1 (Fig. 1a) is interlayered (on a scale of tens of metres) with migmatised garnet-bearing granulite-facies metabasites.

It appears likely that metabasites from Locality 1, Locality 2 and the central Australian metabasite described by Storkey et al. (2005) reached similar (lower granulite) grades. Therefore, based on both textural and mineral-scale trace element evidence, we

conclude that the ~2031 Ma titanite in 97Ma-46Di from Locality 1 grew in the alteration halo associated with structurally late quartz veining, and could not have been inherited from the country rocks.

6.3. Implications and conclusions

The titanite dated in this study grew during amphibolite-facies hydrothermal alteration adjacent to quartz stockworks. The latter are spatially associated with pods of pegmatite; both cross-cut strongly deformed metabasites. Titanite of the grain size observed in the alteration assemblages would have closed to Pb diffusion at ~660–700 °C, based on the Pb-diffusion experiments of Cherniak (1993) and assuming reasonable regional metamorphic cooling rates of 2–10 °C/Ma. These estimates are comparable to estimates of the position of the wet solidi for a range of rock types in the pressure window (~4–5 kbar; e.g. Zeh et al., 2004) for which retrograde P – T – t paths calculated for high-grade Central Zone rocks would have reached near-solidus conditions (Fig. 9). Hence, the titanite in the alteration zones grew at or below its likely closure temperature, and the age obtained from it dates titanite growth. Therefore, we interpret the ~2031 Ma titanite crystallisation age obtained from 97Ma-46Di to date the earliest, high-temperature part of the sub-solidus hydrothermal alteration, thus placing a maximum age constraint on when these rocks went through the wet solidus. This constraint is comparable to, or older than, ages obtained from a number of studies that were inferred to date the peak of metamorphism (see Table 1). Moreover, it is significantly older than the youngest of the ages obtained from the late stage melt patches from the Causeway locality (Fig. 1a) close to Messina. The ~2.03 Ga age from the 97Ma-46Di alteration zone therefore has an important tectonic implication for the Central Zone, as it suggests that different parts of the orogen cooled below the solidus at different times over a period of at least tens of millions of years. It further indicates that the fabric in the host metabasite (Fig. 2a) can have developed no later than ~2.03 Ga.

The metabasite at Locality 1 was sampled just outside of the Tshipise Straightening Zone. However, its NW–SE strike and the constant orientation of the mineral elongation lineation from Locality 1 eastwards into domains that have the true ENE–WSW-trending straightening zone fabric suggests that the fabric orientation at Locality 1 is related to an early stage of the processes that formed the Tshipise Straightening Zone. If this is the case, then initiation of the straightening zones may have begun pre-2.03 Ga. Geochronological data from the Tshipise

Straightening Zone are generally lacking. Buick et al. (2003) obtained a SHRIMP ^{207}Pb – ^{206}Pb age of 2015 ± 7 Ma from titanite in a calcsilicate rock with a high-strain, ductile ENE–WSW trending fabric within the Tshipise Straightening Zone (98Ma-94; Fig. 1a). Titanite in this sample is wrapped by the fabric, suggesting that deformation in the straightening zone continued after 2015 ± 7 Ma. In addition, Holzer et al. (1998) obtained ages as young as 2007 ± 5 Ma (titanite) by Pb step-leaching dating of minerals in a calcsilicate rock recrystallised in high-strain fabrics developed outside of, but with the same orientation and kinematics, as those in the Tshipise Straightening Zone. The available geochronological constraints therefore suggest that development of fabrics associated with this straightening zone may have occurred over a period of at least 15–20 Ma.

In a recent paper, Storkey et al. (2005) showed that the trace element chemistry of titanite is a sensitive monitor of a range of partial melting processes (melting reactions, melt loss, melt crystallisation and hydration of peritectic melt products) in high-grade metabasites. The current study highlights the utility of *in situ* trace element determinations, in particular of the REE, in providing a link between the ages obtained from the U–Pb dating of titanite and the petrological evolution of its host rock. In this respect it extends the approach used in a number of recent studies to understand the petrological significance of U–Pb ages obtained from monazite and zircon (e.g. Hermann and Rubatto, 2003; Whitehouse and Platt, 2003; Kelly and Harley, 2005; Buick et al., 2006).

Acknowledgements

M.J. Aphané (mineral separation, School of Geosciences, University of the Witwatersrand), A. Priymak (Electron Microprobe facility, University of Melbourne), and C. Allen and M. Shelley (Laser-Ablation ICP-MS facility, RSES, ANU) are thanked for technical assistance. B. Paya assisted with collection of sample 97Bo-47 and Reiner Klemd kindly provided some of the field photographs. ISB acknowledges support from the Australian Research Council (ARC; Professorial Fellowship and Discovery Grant No. DP0342473). JH acknowledges financial support from the ARC and the Swiss National Science Foundation. Jay Barton, Massimo Tiepolo and Armin Zeh are thanked for constructive reviews.

References

Bahnemann, K.P., 1972. A review of the structure, stratigraphy and metamorphism of the basement rocks in the Messina District, Northern Transvaal. Unpublished Ph.D. thesis, Uni. Pretoria, 156 pp.

- Barton Jr., J.M., 1983. Pb-isotopic evidence for the age of the Messina Layered Intrusion, Central Zone, Limpopo Mobile Belt. In: Van Biljon, W.J., Legg, J.H. (Eds.), *The Limpopo Mobile Belt*. Geol. Soc. Sth. Afr. Spec. Pub., vol. 8, pp. 39–41.
- Barton Jr., J.M., Key, R.M., 1981. The tectonic development of the Limpopo mobile belt and the evolution of the Archaean cratons of southern Africa. In: Kroner, A. (Ed.), *Precambrian Plate Tectonics*. Elsevier, Amsterdam, pp. 185–212.
- Barton Jr., J.M., Holzer, L., Kamber, B.S., Doig, R., Kramers, J.D., Nyfeler, D., 1994. Discrete metamorphic events in the Limpopo Belt, southern Africa. Implications for the application of P–T paths in complex metamorphic terrains. *Geology* 22, 1035–1038.
- Barton Jr., J.M., Barnett, W.P., Barton, E.S., Barnett, M., Doorgapershad, A., Twigg, C., Klemd, R., Martin, J., Mellonig, L., Zenglein, R., 2003. The geology of the area surrounding the Venetia kimberlite pipes, Limpopo Belt, South Africa: a complex interplay of nappe tectonics and granitoid magmatism. *S. Afr. J. Geol.* 106, 109–128.
- Barton Jr., J.M., Klemd, R., Zeh, A., 2006. The Limpopo Belt: a result of Archaean to Proterozoic, Turke-type orogenesis? In: Reimoldt, U., Gibson, R. (Eds.), *Processes on the Early Earth*. Geol. Soc. Am. Spec. Pap., vol. 405, pp. 315–332.
- Berger, M., Kramers, J.D., Nägler, T.F., 1995. Geochemistry and geochronology of charno-enderbites in the Northern Marginal Zone of the Limpopo Belt, southern Africa and genetic models. *Schweiz. Mineral. Petrogr. Mitt.* 75, 17–42.
- Boshoff, R., Van Reenen, D.D., Smit, C.A., Kramers, J.D., Armstrong, R., 2006. Geologic history of the Central Zone of the Limpopo Complex: the West Alldays area. *J. Geol.* 114, 699–761.
- Brandl, G., 1983. Geology and geochemistry of various supracrustal rocks of the Beit Bridge Complex east of Messina. In: Van Biljon, W.J., Legg, J.H. (Eds.), *The Limpopo Mobile Belt*. Geol. Soc. Sth. Afr. Spec. Pub. 8, 103–112.
- Brandl, G., Pretorius, S.J., 2000. 1: 250,000 Geological Map of the 2228 Alldays Sheet. South African Council for Geosciences (Pretoria). Explanatory notes.
- Buick, I.S., Cartwright, I., Williams, I.S., 1997. High-temperature retrogression of granulite-facies marbles from the Reynolds Range. *J. Petrol.* 38, 877–910.
- Buick, I.S., Maas, R., Gibson, R.L., 2001. Precise U–Pb titanite age constraints on the emplacement of the Bushveld Complex, South Africa. *J. Geol. Soc. Lond.* 158, 3–6.
- Buick, I.S., Williams, I.S., Gibson, R.L., Cartwright, I., Miller, J.A., 2003. $\delta^{13}\text{C}$ and U–Pb evidence for a Palaeoproterozoic crustal component in the Central Zone of the Limpopo Belt, South Africa. *J. Geol. Soc. Lond.* 160, 601–612.
- Buick, I.S., Hermann, J., Williams, I.S., Gibson, R.L., Rubatto, D., 2006. Age and petrogenesis of garnet–cordierite–orthoamphibole gneisses from the Central Zone of the Limpopo Belt, South Africa. *Lithos* 88, 150–172.
- Cartwright, I., 1988. Melt crystallization, pegmatite intrusion and the Inverian retrogression of the Scourian complex of NW Scotland. *J. Metamorph. Geol.* 6, 77–93.
- Cartwright, I., Buick, I.S., Vry, J.K., 1996. Polyphase metamorphic fluid flow in the Lower Calcsilicate Unit, Reynolds Range, central Australia. *Precambrian Res.* 77, 211–229.
- Chavagnac, V., Kramers, J.D., Naegler, Th.F., Holzer, L., 2001. The behaviour of Nd and Pb isotopes during 2.0 Ga migmatization in paragneisses of the Central Zone of the Limpopo Belt (South Africa and Botswana). *Precambrian Res.* 112, 51–86.
- Cherniak, D.J., 1993. Lead diffusion in titanite and preliminary results on the effects of radiation damage on Pb transport. *Chem. Geol.* 110, 177–194.

- Clemens, J.D., Droop, G.T.R., 1998. Fluids, P–T paths and the fates of anatectic melts in the earth's crust. *Lithos* 44, 21–36.
- Cliff, R.A., Yardley, B.W.D., Bussy, F., 1993. U–Pb isotopic dating of fluid infiltration and metasomatism during Dalradian regional metamorphism in Connemara, western Ireland. *J. Metamorph. Geol.* 11, 185–191.
- Deer, W.A., Howie, R.A., Zussmann, J., 1992. An introduction to the rock-forming minerals, Longman Scientific and Technical, second edition, p. 696.
- Droop, G.T.R., 1987. A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag.* 51, 431–435.
- Frost, B.R., Chamberlain, K.R., Schumacher, J.C., 2000. Sphene (titanite): phase relations and role as geochronometer. *Chem. Geol.* 172, 131–148.
- Ghent, E.D., Stout, M.Z., Erdmer, P., 1993. Pressure–temperature evolution of lawsonite-bearing eclogites, Pinchi Lake, British Columbia. *J. Metamorph. Geol.* 11, 279–290.
- Hartel, T.H.D., Pattison, D.R.M., 1996. Genesis of the Kapuskasing (Ontario) migmatitic mafic granulites by dehydration melting of amphibolite: the importance of quartz to reaction progress. *J. Metamorph. Geol.* 14, 591–611.
- Hermann, J., Rubatto, D., 2003. Relating zircon and monazite domains to garnet growth zones: age and duration of granulite facies metamorphism in the Val Malenco lower crust. *J. Metamorph. Geol.* 21, 833–852.
- Holzer, L., Frei, R., Barton Jr., J.M., Kramers, J.D., 1998. Unravelling the record of successive high-grade events in the Central Zone of the Limpopo Belt using Pb single phase dating of metamorphic minerals. *Precambrian Res.* 87, 87–115.
- Hunt, J.A., Kerrick, D.M., 1977. The stability of sphene: experimental redetermination and geologic implications. *Geochim. Cosmochim. Acta* 41, 279–288.
- Jaekel, P., Kröner, A., Kamo, S.L., Brandl, G., Wendt, J.I., 1997. Late Archaean to early Proterozoic granitoid magmatism and high-grade metamorphism in the central Limpopo Belt, South Africa. *J. Geol. Soc. Lond.* 154, 25–44.
- Kamber, B.S., Blenkinsop, T.G., Villa, I.M., Dahl, P.S., 1995. Proterozoic transpressive deformation in the Northern Marginal Zone, Limpopo Belt, Zimbabwe. *J. Geol.* 103, 493–508.
- Kamber, B.S., Biino, G.G., Wijbrans, J.R., Davies, G.R., Villa, I.M., 1996. Archaean granulites of the Limpopo Belt, Zimbabwe: one slow exhumation or two rapid events? *Tectonics* 15, 1414–1430.
- Katzir, Y., Valley, J.W., Matthews, A., Spicuzza, M.J., 2002. Tracking fluid flow during deep crustal anatexis; metasomatism of peridotites (Naxos, Greece). *Contrib. Mineral. Petrol.* 142, 700–713.
- Kelly, N.M., Harley, S.L., 2005. An integrated microtextural and chemical approach to zircon geochronology: refining the Archaean history of the Napier complex, east Antarctica. *Contrib. Mineral. Petrol.* 149, 57–84.
- Klein, M., Stosch, H.-G., Seck, H.A., 1997. Partitioning of high field-strength and rare-earth elements between amphibole and quartz-dioritic to tonalitic melts: an experimental study. *Chem. Geol.* 138, 257–271.
- Klemd, R., Martin, J., Schmidt, A., Barton Jr., J.M., 2003. P–T path constraints from calc-silicate metapelitic rocks east of the Venetia kimberlite pipes, Central Zone, Limpopo Belt, South Africa: have these rocks seen granulite-facies conditions? *S. Afr. J. Geol.* 106, 129–148.
- Kreissig, K., Holzer, L., Frei, I.M., Kramers, J.D., Kröner, A., Smit, C.A., Van Reenen, D.D., 2001. Geochronology of the Hout River Shear Zone and the metamorphism in the Southern Marginal Zone of the Limpopo Belt, southern Africa. *Precambrian Res.* 109, 145–173.
- Kröner, A., Nemchin, A.A., Jaekel, P., Hofmann, A., Brandl, G., Pidgeon, R.T., 1998. Field relationships and age of supracrustal Beit Bridge Complex and associated granitoid gneisses of the Central Zone of the Limpopo Belt, South Africa. *S. Afr. J. Geol.* 101, 201–213.
- Kröner, A., Jaekel, P., Brandl, G., Nemchin, A.A., Pidgeon, R.T., 1999. Single zircon ages for granitoid gneisses in the Central Zone of the Limpopo Belt, Southern Africa and geodynamic implications. *Precambrian Res.* 93, 299–337.
- Leake, B.E., Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M.C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J.W., Youzhi, G., 1997. Nomenclature of amphiboles: report of the Subcommittee on Amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Mineral. Mag.* 61, 295–321.
- Ludwig, K.R., 1993. PBDAT, version 1.24. USGS Open-File Report 88-542.
- Ludwig, K.R., 2001. User's Manual for Isoplot/Ex, Rev. 2.49, A Geochronological Toolkit for Microsoft Excel. Berkeley Geochronology Center Special Publication, vol. 1a, p. 59. Berkeley California.
- Luo, X., Rehkämper, M., Lee, D.-C., Halliday, A.N., 1997. High precision ²³⁰Th/²³²Th and ²³⁴U/²³⁸U measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spectrom. Ion Process.* 171, 105–117.
- McCourt, S., Armstrong, R.A., 1998. SHRIMP U–Pb zircon geochronology of granites from the Central Zone, Limpopo Belt, southern Africa: implications for the age of the Limpopo Orogeny. *S. Afr. J. Geol.* 101, 329–338.
- McCourt, S., Kampunzu, A.B., Bagai, Z., Armstrong, R.A., 2004. Crustal architecture of Archaean terranes in Northeastern Botswana. *S. Afr. J. Geol.* 107, 146–158.
- Matthews, A., Baker, J.M., Matthey, D.P., 2002. High-temperature metamorphism in marbles as a consequence of volatile release from crystallizing anatectic melts, Naxos, Greece. *Eur. J. Mineral.* 14, 37–47.
- Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., Chenery, S.P., 1997. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostand. Newsl.* 21, 115–144.
- Roering, C., van Reenen, D.D., Smit, C.A., Barton, J.M., de Beer, J.H., de Wit, M.J., Strettlér, E.H., van Schalkwyk, J.F., Stevens, G., Pretorius, S., 1992. Tectonic model for the Limpopo Belt. *Precambrian Res.* 55, 539–552.
- Rubatto, D., Hermann, J., 2001. Exhumation as fast as subduction? *Geology* 29, 3–6.
- Schaller, M., Steiner, O., Studer, I., Holzer, L., Herwegh, M., Kramers, J.D., 1999. Exhumation of Limpopo Central Zone granulites and dextral continental-scale transcurrent movement at 2.0 Ga along the Palala Shear Zone, Northern Province, South Africa. *Precambrian Res.* 96, 263–288.
- Schiffries, C.M., Skinner, B.J., 1987. The Bushveld hydrothermal system: field and petrological evidence. *Am. J. Sci.* 287, 566–595.
- Schmidt, M.W., Thompson, A.B., 1996. Epidote in calc-alkaline magmas: an experimental study of stability, phase relationships and the role of epidote in magmatic evolution. *Am. Mineral.* 81, 462–474.
- Scott, D.J., St-Onge, M.R., 1995. Constraints on Pb closure temperature in titanite based on rocks from the Ungava Orogen,

- Canada: implications for U–Pb geochronology and P–T–t path determinations. *Geology* 23, 1123–1126.
- Söhne, P.G., 1946. The geology of the Messina copper mines and surrounding country. *Mem. Geol. Surv. S. Afr.* 40 (280 pp.).
- Spear, F.S., 1993. Metamorphic phase equilibria and Pressure–Temperature–Time paths. *Mineral. Soc. Amer. Mon.* 1, 799.
- Spear, F.S., Kohn, M.J., Cheney, J.T., 1999. P–T paths from anatectic pelites. *Contrib. Mineral. Petrol.* 134, 17–32.
- Storkey, A., Hermann, J., Hand, M., Buick, I.S., 2005. Using *in-situ* trace element determinations to monitor partial melting processes in metabasites. *J. Petrol.* 46, 1283–1308.
- Sun, S.-S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders, A.D., Norry, M.J. (Eds.), *Magmatism in the Ocean Basins*. *Geol. Soc. Lond. Spec. Pub.*, vol. 42, pp. 313–345.
- Thompson, A.B., 1982. Dehydration melting of pelitic rocks and the generation of H₂O-undersaturated granitic liquids. *Am. J. Sci.* 282, 1567–1595.
- Troitzsch, U., Ellis, D.J., 1999. The synthesis and crystal structure of CaAlFSiO₄, the Al–F analog of titanite. *Am. Mineral.* 84, 1162–1169.
- Vanko, D.A., Stakes, D.S., 1991. Fluids in Oceanic Layer 3: evidence from veined rocks, Hole 735B, Southwest Indian Ridge. *Proc. Ocean Drill. Prog. Sci. Results* 181–215.
- Verts, L.A., Chamberlain, K.R., Frost, C.D., 1996. U–Pb sphene dating of metamorphism: the importance of sphene growth in the contact aureole of the Red Mountain Pluton, Laramie Mountains, Wyoming. *Contrib. Mineral. Petrol.* 125, 186–199.
- Watkeys, M.K., 1984. The Precambrian geology of the Limpopo Belt north and west of Messina. Unpublished Ph.D. thesis, University of the Witwatersrand, Johannesburg.
- Whitehouse, M.J., Platt, J.P., 2003. Dating high-grade metamorphism—constraints from rare-earth elements in zircon and garnet. *Contrib. Mineral. Petrol.* 145, 61–74.
- Woodhead, J.D., 2002. A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS. *J. Anal. At. Spectrom.* 17, 1–6.
- Wyllie, P.J., 1977. Crustal anatexis: an experimental review. *Tectonophysics* 43, 41–71.
- Wyllie, P.J., Wolf, M.B., 1993. Amphibolite dehydration-melting: sorting out the solidus. In: Prichard, H.M., Alabaster, T., Harris, N.B.W., Neary, C.R. (Eds.), *Magmatic Processes and Plate Tectonics*. *Geol. Soc. Lond. Spec. Pub.*, vol. 76, pp. 405–416.
- Zeh, A., Klemm, R., Buhlmann, S., Barton, J.M., 2004. Pro- and retrograde P–T evolution of granulites of the Beit Bridge Complex (Limpopo Belt, South Africa): constraints from quantitative phase diagrams and geotectonic implications. *J. Metamorph. Geol.* 22, 79–95.
- Zeh, A., Klemm, R., Barton, J., 2005. Petrological evolution in the roof of the high-grade metamorphic Central Zone of the Limpopo Belt, South Africa. *Geol. Mag.* 142, 229–240.