An improved understanding of Zr-in-rutile thermometry in application to ultrahigh temperature metamorphic rocks

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ZIR thermometry

Zirconium in rutile (ZIR) concentrations were analysed in samples from two localities in ultrahigh temperature (UHT: >900 °C) metamorphic terranes: Anakapalle, Eastern Ghats Province, India (~1030 °C), and Ayatollah Island, Napier Complex, Antarctica (~1050 °C). ZIR temperatures from analyses of these rocks were categorised according to their microstructural setting—inclusion versus grain boundary—and distance from xenocrystic zircon. ZIR temperatures from three of four samples were all or mostly well below UHT conditions—up to 400 °C in some cases. However, upon reintegrating exsolved zirconium back into rutile grains the distribution of ZIR temperatures in all samples becomes bimodal, more typical of the global UHT ZIR thermometry dataset. There is no obvious trend in the ZIR concentration or temperature data relating to the proximity of rutile to xenocrystic zircon, or to the microstructural setting of rutile, suggesting that rutile and zircon (and quartz) communicate over sufficiently long length scales during the prograde and retrograde history. Stunted Si diffusion does not appear to have been a dominant factor in determining ZIR concentrations and temperatures (contrast with Taylor-Jones & Powell, 2015), as there are no known examples of rutile grains preserving peak (i.e. >1000 °C) temperatures that have not exsolved zircon. The major consequence is that ZIR thermometry may almost never preserve the peak UHT conditions in regional terranes where cooling is prolonged. The bimodal ZIR concentration and temperature distribution may relate to a subtle, undetected microstructural control on access to Si and Zr reservoirs combined with different timing of growth of different rutile grains.

Zirconium in rutile, trace element thermometry, UHT, Eastern Ghats, Napier Complex, pseudosection
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INTRODUCTION

Determining peak conditions of ultrahigh temperature (>900 °C, (Harley, 1998)), UHT, metamorphic rocks has traditionally been difficult, as common thermometers that rely on Fe–Mg exchange are diffusively active well below peak temperatures of UHT rocks (Fitzsimons & Harley, 1994; Pattison & Begin, 1994; Pattison et al., 2003). Hence, they rarely successfully record the peak conditions of these rocks (Fitzsimons & Harley, 1994; Pattison & Begin, 1994; Pattison et al., 2003). More recently, the ability to calculate phase diagrams (i.e. pseudosections) in model chemical systems closely approximating the major element chemistry of rocks has greatly assisted our understanding of peak temperatures achieved in UHT metamorphism (e.g. Kelsey et al., 2004; Kelsey et al., 2005; Korhonen et al., 2011; Taylor-Jones & Powell, 2015). However, the calculation of phase diagrams is commonly time-consuming and complex.

The rise of single mineral trace element thermometry has offset and/or value added to the calculation and use of pseudosections.

In the context of UHT rocks, ZIR thermometry (Zack et al., 2004; Ferry & Watson, 2007; Tomkins et al., 2007) has found widespread use (Zack et al., 2004; Watson et al., 2006; Ferry & Watson 2007; Tomkins et al., 2007; Racek et al., 2008; Luvizotto and Zack, 2009; Jiao et al., 2011; Meyer et al., 2011; Kooijman et al., 2012; Korhonen et al., 2014; Pape et al., 2016). Rutile is a common oxide mineral and can incorporate Zr$^{4+}$ into its lattice, replacing Ti$^{4+}$, and this substitution has a measurable temperature and pressure dependence (Zack et al., 2004; Ferry & Watson, 2007; Tomkins et al., 2007). Because of this, concentrations of Zr in rutile can be used to determine metamorphic temperatures. To be applied, the ZIR thermometer depends on the presence of rutile, a
Zr-bearing phase (i.e. zircon) and a SiO$_2$ bearing phase (i.e. quartz). Each of these minerals is stable at UHT conditions, and hence this thermometer may be a powerful tool when applied to these rocks.

ZIR thermometry from a global dataset of UHT rocks reveals a distinctly bimodal temperature distribution (Kelsey & Hand, 2015), with the lower temperature peak corresponding to a mean temperature of ~775 °C and comprising ~40% of the dataset. The higher temperature peak corresponds to a mean temperature of ~925 °C. Multiple studies have attempted to explain this bimodal temperature distribution with contrasting interpretations (Ewing et al., 2013; Taylor-Jones & Powell, 2015; Pape et al., 2016). In order for the ZIR thermometer to be successfully applied to, and interpreted from, UHT rocks, it is necessary to understand the cause of this bimodal temperature distribution. In this study I investigate a potential influence on ZIR temperature that is hitherto unstudied, namely the microstructural location of rutile with respect to quartz and xenocrystic zircon$^1$.

The ZIR data in this study is provided within a calculated pressure–temperature ($P$–$T$) pseudosection framework for three of the four samples—to constrain and demonstrate the UHT nature of the samples prior to undertaking ZIR analysis—and additionally takes into consideration two other novel approaches: The abundance of zircon and rutile in the rocks, and the distance separating rutile from xenocrystic zircon.

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$^1$ Xenocrystic in this context refers to zircon that is foreign to the rutile, i.e., not formed by exsolution from rutile during cooling.
BACKGROUND

Ultra high temperature (UHT) metamorphism is a subcategory of granulite facies metamorphism in which non-igneous crustal temperatures exceed 900 °C (e.g. Harley, 1998; Kelsey & Hand, 2015). UHT metamorphism can also be defined by apparent thermal gradients ≥75 °C.kbar⁻¹ (Brown, 2007; Brown, 2014) and therefore indicates a highly perturbed crustal thermal regime.

UHT metamorphism is commonly recognised via diagnostic silicate mineral assemblages. These assemblages are generally found in Mg- and Al-rich pelitic rocks (Harley, 1998; Harley, 2008; Kelsey 2008; Kelsey & Hand, 2015), and include sapphirine–quartz, Al-rich orthopyroxene–sillimanite–quartz, and osumilite (Kelsey et al., 2005). As these exotic assemblages are rare in nature, it is imperative that a method of identifying UHT conditions by other means exists for application to rocks containing more common silicate minerals. Thermometers based on Fe-Mg exchange between common silicate minerals are often diffusively active until well below UHT conditions and will therefore rarely, if ever, record the peak or elevated conditions of granulite and UHT rocks (Fitzsimons & Harley, 1994; Pattison & Begin, 1994; Pattison et al., 2003).

Rutile is a common accessory mineral in crustal rocks, and Zr-in-rutile thermometry is one of several single mineral trace element thermometers that have been proposed over the past decade (Zack et al., 2004; Watson & Harrison, 2005; Wark & Watson, 2006; Kawasaki & Motoyoshi, 2007). For UHT rocks, ZIR thermometry is a promising trace element thermometer (Kelsey & Hand, 2015) that created the possibility that UHT metamorphism can and will be recognised in a far greater number of terranes. Indeed, UHT conditions have been obtained from ZIR thermometry in a large number of studies (Baldwin & Brown, 2008; Racek et al., 2008; Luvizotto and Zack, 2009; Kotková and
Harley, 2010; Jiao et al., 2011; Meyer et al., 2011; Ague and Eckert, 2012; Blackburn et al., 2012; Kooijman et al., 2012; Ague et al., 2013; Ewing et al., 2013; Korhonen et al., 2014; Pape et al., 2016). However, in all cases, a bimodal temperature distribution occurs (global dataset compiled in Kelsey & Hand, 2015), where the lower-temperature peak (~40% of dataset) occurs at ~750–800 °C, well below UHT conditions. The higher-temperature peak (~60% of dataset) occurs at ~900–1000 °C with a mean of ~925 °C (Kelsey & Hand, 2015). This temperature distribution is thought to be due to exsolution of zircon or another Zr-bearing mineral, e.g. baddelyite, from rutile with cooling (e.g. Ewing et al., 2013; Taylor-Jones & Powell, 2015; Pape et al., 2016), rather than diffusive loss of Zr from rutile with cooling (e.g. Ewing et al., 2013). Importantly, the temperature distribution is not thought to be due to post-peak retrogression of UHT rocks, as demonstrated clearly by Ewing et al. (2013).

Rutile (TiO₂), when in equilibrium with quartz and zircon, incorporates Zr⁴⁺ into its structure as a substitute for Ti⁴⁺ (Zack et al., 2004; Watson et al., 2006). This substitution has a positive temperature dependence (Zack et al., 2004; Watson et al., 2006; Ferry & Watson, 2007), and a lesser negative pressure dependence (Tomkins et al., 2007). There are two ZIR thermometers in use, both of which are based on the pioneering work by Zack et al. (2004). The two thermometers are based on the equilibrium relationship Zr(in rutile) + SiO₂ \rightarrow zircon (Zack et al., 2004; Watson et al., 2006; Ferry & Watson, 2007; Tomkins et al., 2007). The first, by Ferry & Watson (2007) (herein referred to as FW07) does not have a pressure dependence, but has a dependence upon the activity of silica (aSiO₂), whereas the later Tomkins et al. (2007) formulation (herein referred to as To07) has a pressure dependence but is independent of aSiO₂.
The To07 thermometer in the β-quartz field is described mathematically as:

\[
T(°C) = \frac{85.7 + 0.473P}{0.1453 - R\ln\phi} - 273
\]

Where \( \phi \) is ppm Zr, \( P \) is in kbar and \( R \) is the gas constant, 0.0083144 kJ K\(^{-1}\).

The FW07 thermometer is described mathematically as:

\[
T(°C) = \left( \frac{4530 \pm 111}{(7.420 \pm 0.105) \times log_{ppm \ Zr-in-rutile}} - log_{\alpha SiO_2} \right) - 273
\]

If \( \alpha \text{SiO}_2 \) is less than unity the retrieved temperatures will be lower for a given ZIR concentration (Ferry & Watson, 2007), as a reduction in \( \alpha \text{SiO}_2 \) will result in reduced efficacy of exsolution of Zr from rutile, and hence rutile will be over-saturated in Zr during cooling, giving inaccurately high ZIR thermometry results (Ferry & Watson, 2007; Taylor-Jones & Powell, 2015).

Numerous studies (Zuvizotto & Zack, 2009; Jiao et al., 2011; Meyer et al., 2011; Kooijman et al., 2012; Ewing et al., 2013; Pape et al., 2016) present compositional profiles across rutile grains that commonly show unchanging (‘flat’) Zr concentrations. This is consistent with rapid diffusion of Zr in and out of rutile, despite experimental data that contrasts with this observation (Cherniak et al., 2007). However, Zr concentrations ranging more than two orders of magnitude between rutile grains from the same sample (e.g. Zack et al., 2004; Ewing et al., 2013) are common. This suggests there is a control upon retention of Zr by rutile grains that is not yet fully understood, but may relate to the proximity of rutile to xenocrystic zircon (Zack et al., 2004; Taylor-Jones & Powell, 2015) and/or whether the rutile has exsolved a Zr-bearing phase during cooling. The proposed scenarios by which the bimodal temperature distribution may
occur are internal (no net Zr loss) versus external (net Zr loss) exsolution of a Zr-bearing mineral (zircon or baddelyite) from rutile during cooling, as well as no exsolution or diffusive Zr loss during cooling (Ewing et al., 2013; Taylor-Jones & Powell, 2015; Pape et al., 2016). Of these, the third is least understood, but may relate to the ability of rutile to diffuse Si (e.g. Ferry & Watson, 2007; Taylor-Jones & Powell, 2015). With specific regard to microstructural location of rutile, Zack et al. (2004) provide data suggesting that rutile grains held as inclusions in garnet or orthopyroxene commonly record the highest temperatures, whereas grains outside of garnet or orthopyroxene commonly recorded the lowest temperatures (see also Ewing et al., 2013). Zack et al. (2004) postulated that rutile within the rock matrix, or located along fracture planes or at grain boundaries, will more readily re-equilibrate to record lower temperature conditions (Taylor-Jones & Powell, 2015). Crucially, what remains unknown is the critical distance—if it exists—that rutile must be from xenocrystic zircon to disallow chemical communication between rutile and zircon and preserve high Zr concentrations in rutile pertaining to UHT conditions. I investigate this in this study using samples from two well-known UHT terranes.

**Study Area**

Rock samples selected for analysis were chosen from localities in terranes with well-constrained UHT conditions. Samples AK-3, AK-5 and AK-6 are from Anakapalle, Eastern Ghats Province, India (Fig. 1). Sample R31180 is from Ayatollah Island, Khmara Bay, part of the Napier Complex of Enderby land, Antarctica (Fig. 2).
ANAKAPALLE

The Eastern Ghats Province (Fig. 1) is a granulite facies terrane that records $P-T$ conditions exceeding ~9–10 kbar and 1000 °C. Numerous studies have attempted to quantify the pressure and temperature conditions of the province (Sengupta et al., 1990; Dasgupta et al., 1994, 1995; Bose et al., 2000; Sarkar et al., 2003; Bose & Das, 2007; Korhonen et al., 2011, 2013, 2014), however confusion remains regarding the timing of parts of the $P-T$ history. Nevertheless, the metamorphic history is characterised by an early up-pressure, anticlockwise-shape $P-T$ path at UHT conditions (Korhonen et al., 2014) and a later down-pressure, clockwise-shape $P-T$ path (Simmat & Raith, 2008), arguably also at UHT conditions (Rickers et al., 2001). Metamorphic ages between 1500–520 Ma provide evidence for polymetamorphism. Recent U–Pb geochronology indicates that UHT metamorphism occurred between c. 1000–930 Ma, or possibly c. 1130–930 Ma (Korhonen et al., 2013). The lack of resolution largely relates to the difficulty in interpreting geochronology from UHT terranes, which is typically spread along concordia (e.g. Kelly & Harley, 2005; Halpin et al., 2012; Korhonen et al., 2013; Taylor et al., 2015; Walsh et al., 2015; Morrissey et al., 2016).
Figure 1 (A) Location of Eastern Ghats Province (green) in India; (B) Simplified map of a portion of the Eastern Ghats Province, India, showing the location of Anakapalle and sample locations with respect to other localities in the Province where metamorphic studies of UHT rocks have been conducted. Figure adapted from (Marshall, 2010).

ENDERBY LAND

The Napier Complex is an Archaean cratonic block in Enderby Land in the East Antarctic Shield (Fig. 2; Kelly & Harley, 2005). The Napier complex is characterised by regionally pervasive UHT mineral assemblages that are indicative of peak metamorphic conditions of 7–11 kbar and 1050–1120 °C (Harley, 1998; Harley & Motoyoshi, 2000; Kelly & Harley, 2005). The terrane experienced three main phases of metamorphism between c. 2990–2450 Ma (Harley 1998; Kelly & Harley, 2005), and resided in the deep crust for up to c. 1500 Myr after the UHT event which involved near-isobaric cooling (Sandiford, 1985a; Harley & Motoyoshi, 2000; Kelly & Harley, 2005). UHT metamorphism is thought to have occurred at c. 2450 Ma (Kelly & Harley, 2005).
Figure 2 Simplified map of the Napier Complex, Antarctica, with inset of Casey Bay. Sample R31180 sourced from Ayatollah Island. (Modified from Kelly & Harley 2005). Regional UHT metamorphism, with rocks containing sapphirine + quartz, orthopyroxene + sillimanite + quartz and osmulite-bearing assemblages, occurs inside of the dashed UHT zone boundary.


**Petrography**

Full petrographic descriptions for each sample are provided in Appendix A.

**AK-3**

The interpreted peak metamorphic assemblage for sample AK-3 is biotite\textsubscript{1}–garnet\textsubscript{1}–orthopyroxene\textsubscript{1}–spinel\textsubscript{1}–plagioclase–K-feldspar–rutile–melt. The interpreted post-peak, retrograde minerals are sapphirine\textsubscript{2} and orthopyroxene\textsubscript{2} (± plagioclase\textsubscript{2}) followed by sillimanite\textsubscript{3}, biotite\textsubscript{3} and plagioclase\textsubscript{3}; and then garnet\textsubscript{4} (Fig. 3).

![Optical microscope images showing reaction microstructures from sample AK-3. g = garnet, opx = orthopyroxene, sa = sapphirine, pl = plagioclase, sp = spinel, bi = biotite, sill = sillimanite. (A) Coarse-grained garnet (g\textsubscript{1}) and orthopyroxene (opx\textsubscript{1}) separated by finer-grained symplectite of sapphirine (sa\textsubscript{2}) and orthopyroxene (opx\textsubscript{2}), with later development of plagioclase (pl\textsubscript{3})](image-url)
and fine-grained garnet (g₄). (B) Coarse-grained spinel separated from sa₂ + opx₂ symplectites by a corona of sapphirine. Post-peak plagioclase (as pl₂) is reasonably extensively developed. Later biotite–sillimanite patches (sill₃, bi₃) occur in bottom right of picture. (C) Detail of late biotite (bi₃) and sillimanite (sill₃) that post-dates the sapphirine (sa₂) + orthopyroxene (opx₂) symplectites. In rare cases, the bi + sill patches can be seen to surround sa₂ + opx₂ symplectites and separate them from coarse-grained garnet and orthopyroxene. (D) Close-up photo of late garnet (g₄) containing inclusions of rib-like sapphirine (sa₂) and orthopyroxene (opx₃).

AK-5

The interpreted peak metamorphic assemblage for sample AK-5 is orthopyroxene₁–garnet–sillimanite₁–quartz–K-feldspar₁–rutile (and melt), where K-feldspar is ternary feldspar. The post-peak minerals are interpreted to be sapphirine₂, plagioclase₂, K-feldspar₂, cordierite₂, biotite₂ and orthopyroxene₂, followed by sillimanite₃, cordierite₃, biotite₃, and then garnet₄ (Fig. 4).

Figure 4 Optical microscope images of sample AK-5, showing reaction microstructures and textural relationships of peak and post-peak minerals. g = garnet, opx = orthopyroxene, pl = plagioclase, ksp = k-feldspar, sa = sapphirine, sill = sillimanite, fsp = feldspar (perthitic), q = quartz,
ru = rutile, cd = cordierite. (A) Photo collage of one of the AK-5 thin sections showing garnet at centre mantled by coronas of sapphirine, feldspar, and orthopyroxene. Quartz does not occur in the corona region between garnet and the thick ‘ring’ of orthopyroxene, but does occur outside the orthopyroxene ‘ring. (B) Close up of the quartz-bearing matrix showing perthitic and mesoperthitic feldspar along with orthopyroxene and quartz. (C) Close up of sapphirine in the symplectite structure, which is isolated from symplectic orthopyroxene by later sillimanite and abundant cordierite. Presence of cordierite can be identified by common yellow radiation damage halos.

**AK-6**

![Sample images](image.png)

*Figure 5* Optical microscope images of sample AK-6, showing reaction microstructures and relationships is peak and retrograde minerals. g = garnet, sa = sapphirine, opx = orthopyroxene, fps = feldspar, q = quartz, ru = rutile. (A) Garnet porphyroblast with inclusions of early sapphirine and rutile. Garnet is separated from orthopyroxene by feldspar. (B) Elongate porphyroblast of garnet containing inclusions of sapphirine and rutile set in a quartz- and feldspar-rich matrix. Feldspar immediately surrounds garnet.

The interpreted peak metamorphic assemblage for sample AK-6 is orthopyroxene–garnet–K-feldspar–quartz–rutile–melt. Prograde minerals are interpreted to be sillimanite, sapphirine and rutile. The post-peak minerals are interpreted to be biotite and K-feldspar. The significance of matrix sillimanite is unclear (Fig. 5).

**R31180**

The interpreted peak mineral assemblage for sample R31180 is quartz–sapphirine–mesoperthitic K-feldspar–rutile–melt. Retrograde minerals are interpreted to be sillimanite, orthopyroxene, corundum and biotite (Fig. 6).
Figure 6 Optical microscope images of sample R31180, showing reaction textures and relationships is peak and retrograde minerals. sa = sapphire, opx = orthopyroxene, q = quartz, ru = rutile. (A) Classic double-layer corona structure of sillimanite and orthopyroxene separating sapphire porphyroblast from quartz. A large rutile grain occurs in the top right of the orthopyroxene corona. (B) Close up of sapphire mantled successively by corundum (at left), sillimanite and orthopyroxene as corona layers that separate sapphire from quartz.

METHODS

Phase Equilibria Forward Modelling

Phase equilibria calculations were performed using the software program THERMOCALC (Powell & Holland, 1988; Holland & Powell, 2011) in the model chemical system Na$_2$O–CaO–K$_2$O–FeO–MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O–TiO$_2$–O–ZrO$_2$, where ‘O’ is a proxy for Fe$_2$O$_3$, using the latest internally-consistent thermodynamic dataset ‘ds6’ (filename tc-ds62.txt; Holland & Powell, 2011) and activity–composition (a–x) models (Powell et al., 2014; White et al., 2014). The Zr-bearing end-members for garnet, rutile and silicate melt in the a–x models are from Tomkins et al. (2007) and Kelsey & Powell (2011) and the Ti end-member of silicate melt is from Tomkins et al. (2007). The initial stable assemblage is determined by performing a Gibbs energy minimisation calculation at a set pressure–temperature ($P$–$T$) condition. The diagram is built up from and around that initial assemblage and involves many trial and error calculations in order to determine phase changes as a function of pressure, temperature
and/or composition. Therefore, a single diagram commonly comprises ~100-150 total line and point calculations, and the user is intellectually involved in the calculations at every step along the way, amounting to weeks of calculation per diagram. The most uncertain compositional variables are Fe$_2$O$_3$ and H$_2$O, commonly requiring that these be constrained with $T$–$M$ type diagrams (where $M$ refers to amount of an oxide component). The choice of pressure at which to calculate the $T$–$M$ diagrams is based on broadly estimating the pressure at which the petrographically-determined peak metamorphic assemblage is stable. The inclusion of Zr in the calculations means that the Zr content of rutile (including ppm ZIR) can be calculated as a direct function of $P$–$T$–$X$.

Phase diagrams were contoured for phase abundance (‘mode’) and ZIR concentration using the software program TCInvestigator (Pearce et al., 2015). As input, this program requires a completed THERMOCALC pseudosection, the $a$–$x$ and thermodynamic dataset files used to calculate the pseudosection, and a list of stable assemblages corresponding to the fields in the pseudosection.

**Rock compositions**

Rock compositions used for the calculation of phase diagrams for Anakapalle samples were based on whole-rock geochemistry obtained from Franklin and Marshall College, Pennsylvania. Major elements were analysed by fusing 0.4g of the powdered sample (sample powdered at Franklin and Marshall College) with lithium tetraborate for analysis by XRF. Trace elements—including Zr—were analysed by mixing 7g of crushed rock powder with Copolywax powder and measurement by XRF. The composition used for the calculation of phase diagrams for sample R31180 involved
combining measured mineral chemistry from the sample (Sandiford, 1984) and the abundance of minerals estimated from thin section. The ZrO$_2$ concentration of the sample R31180 was estimated using the calculated abundance of zircon and rutile in the thin section as determined by MLA mapping (see below), and the average ZIR concentration in the sample.

**LA–ICP–MS monazite U–Pb geochronology**
In-situ monazite U–Pb dating was undertaken for the purpose of demonstrating that the Anakapalle samples in this study record the effectively same age of metamorphism as other localities in the Eastern Ghats Province. The methods and results are provided in Appendix D.

**Scanning Electron Microscope (SEM) and Mineral Liberation Analysis (MLA)**
The QUANTA 600 SEM at Adelaide Microscopy was used to produce back-scattered electron (BSE) image mosaics of the entire thin sections of samples AK-3, AK-5, AK-6 and R31180 (Appendix E). These images were produced from carbon-coated thin sections using a 25 KeV accelerating voltage, under high vacuum conditions, at a working distance of 10 mm.

Mineral Liberation Analysis (MLA) mapping was also undertaken using the QUANTA 600 SEM (under the same conditions), for identification of mineralogy, mineral abundance and distribution. Full size thin section maps were obtained for presence of rutile and zircon (Appendix E).
Electron Probe Microanalysis (EPMA)

Electron probe microanalysis (EPMA) was undertaken at Adelaide Microscopy on individual grains of rutile in order to measure trace element concentrations. Beam operating conditions were 1 µm width and current and voltage of 50 nA and 20 kV, respectively. Two of the five wavelength dispersive spectrometers were used to count Zr with a long dwell time of 45 s. Dwell times for other measured elements were: 25s for Si, Mg, Al, 12s for Ti, and 45s for Cr, Fe, V, Nb. A BSE image of each rutile grain analysed was captured for the purpose of calculating distances between rutile and xenocrystic zircon.

Zr reintegration and Zr thermometry

To reintegrate exsolved zircon (or Zr) back into rutile grains, BSE images of analysed rutile grains were processed using Adobe Photoshop. Pixels with a grey scale corresponding to rutile were counted. Pixels with a grey scale corresponding to zircon were counted, with care being taken not to include xenocrystic zircon grains. The pixel ratio of rutile to zircon was then used in conjunction with the measured ZIR content (from EPMA) in ppm and the known Zr ppm in perfectly stoichiometric zircon (ZrSiO₄, 497,664ppm Zr) to calculate the total amount of Zr contained in a rutile grain before exsolution occurred.

ZIR thermometry in this study used the To07 formulation for these scenarios: (a) no reintegration of exsolved Zr back into rutile, for the purpose of quantifying the extent of ZIR temperature reduction due to exsolution loss of Zr; and (b) reintegrated of exsolved Zr (as zircon) back into rutile to quantify the ZIR temperature prior to exsolution occurring. As both the FW07 and To07 thermometers give the same temperatures
within ~5 °C I predominantly use the more recent To07 formulation. The FW07 formulation is used only for quartz-absent sample AK-3.

RESULTS

Phase Equilibria Forward Modelling

In order to calculate a $P$–$T$ pseudosection for a particular rock, an appropriate rock composition must first be constrained by calculating $P$– or $T$–$M_O$ and $P$– or $T$–$M_{H_2O}$ diagrams to constrain the amount of FeO vs Fe$_2$O$_3$ (i.e. the oxidation state) and the amount of H$_2$O, since these are the most uncertain components of rock composition. In this study, $P$–$M_O$ and $P$–$M_{H_2O}$ diagrams were calculated only for sample AK-6, and a $T$–$M_O$ diagram was calculated for sample R31180. No $P$–$T$ pseudosection was calculated for sample R31180 due to time constraints, but the $P$–$T$ path can be interpreted from the $T$–$M_O$ pseudosection. $P$–$M$ diagrams were previously calculated by D. Kelsey (unpublished data) for samples AK-3 and AK-5, such that only $P$–$T$ pseudosections were required to be calculated for those samples. The $P$–$M$ diagrams are presented in Appendix F.

AK-3

The calculated $P$–$T$ pseudosection for sample AK-3 is shown in Fig. 7. The peak assemblage biotite$_1$–garnet$_1$–orthopyroxene$_1$–spinel$_1$–plagioclase–K-feldspar–rutile–melt occurs over the $P$–$T$ range ~8.8 to >12 kbar, ~900–1100 °C (without spinel) and ~9.8–11.5 kbar, 1030–1085 °C (with spinel). Post-peak sapphirine occurs in fields to lower pressure than the peak field(s), that is to pressures lower than ~8.8–10 kbar. Other post-peak minerals, interpreted to post-date sapphirine (and orthopyroxene$_2$), such as
sillimanite, biotite and plagioclase and garnet all occur within fields to lower temperature than the first appearance of sapphirine. The $P-T$ pseudosection, contoured for the modal abundance (‘modes’) of some phases, and the ZIR concentration in ppm, is shown in Fig. 8. ZIR concentration increases with increasing temperature.

Figure 7 Calculated $P-T$ pseudosection graphically representing changes in mineralogy for the composition of sample AK-3 across $P-T$ space. Abbreviations: bi = biotite; crn = corundum; g = garnet; ilm = ilmenite; ksp = K-feldspar; liq = silicate melt; opx = orthopyroxene; pl = plagioclase; q = quartz; ru = rutile; sa = sapphirine; sill = sillimanite; sp = spinel; zc = zircon. The composition (in mole%) used to calculate the pseudosection is provided above the diagram. FeO* = FeO + 2 $'$O'. Two fields are highlighted with bold outline as the peak fields, one with spinel and one without, due to the scarcity of coarse-grained spinel in the sample. This constraint of low spinel abundance must place peak conditions near to the boundary between the two fields. The solidus is given as a dashed line and the semi-transparent ellipse and arrow show the interpreted peak $P-T$ conditions and post-peak, retrograde path, respectively. Fields are shaded according to their variance: higher variance field are darker, lower variance fields are lighter.
Figure 8 TCInvestigator outputs for the $P$–$T$ pseudosection for sample AK-3 graphically representing: A–E: changes in modal proportions of key silicate minerals as a function of pressure–temperature; F: Zirconium concentration in rutile in ppm as a function of pressure–temperature, showing ZIR to be positively proportional to temperature and negatively proportional to pressure. White space represents regions of $P$–$T$ space in which the mineral being represented is not stable. These diagrams were used to estimate the peak conditions experienced by sample AK-3 by correlating modal mineral abundances in the sample to those calculated, as well as to delineate the post-peak, retrograde $P$–$T$ path.
AK-5

The calculated $P–T$ pseudosection for sample AK-5 is shown in Fig. 9. The peak assemblage orthopyroxene$_1$–garnet–sillimanite$_1$–quartz–K-feldspar$_1$–rutile–melt occurs over the $P–T$ range of ~9.0–11.2 kbar, ~910–1140 °C. The post-peak minerals sapphire$_2$, plagioclase$_2$ and K-feldspar$_2$ occur in lower pressure fields than the peak assemblage field, and cordierite$_2$ stability occurs to lower pressure than where sapphire first stabilizes. Biotite stability occurs to lower temperature than the high-temperature fields containing sapphire and cordierite. The $P–T$ pseudosection, contoured for the modal abundance (‘modes’) of some phases, and the ZIR concentration in ppm, is shown in Fig. 10. ZIR concentration increases with increasing temperature.
Figure 9 Calculated $P$–$T$ pseudosection graphically representing changes in mineralogy for the composition of sample AK-5 across $P$–$T$ space. Abbreviations: bi = biotite; cd = cordierite; g = garnet; ksp = K-feldspar; ky = kyanite; liq = silicate melt; opx = orthopyroxene; pl = plagioclase; q = quartz; ru = rutile; sa = sapphirine; sill = sillimanite; zc = zircon. The composition (in mole%) used to calculate the pseudosection is provided above the diagram. FeO* = FeO + 2 × ‘O’. The field highlighted by bold boundaries is the peak field, and as such the $P$–$T$ path (arrow) must begin within that field from the peak conditions (ellipse). By comparison with the $P$–$T$ path of sample AK-3, which is from the same locality, and retrograde mineralogy (retrograde biotite, cordierite, K-feldspar) the $P$–$T$ path is constrained. The solidus is shown as a dashed line.
Figure 10 TCInvestigator outputs for the $P$–$T$ pseudosection for sample AK-5 graphically representing: A–E: changes in modal proportions of key minerals as a function of pressure–temperature; F: Zirconium concentration in rutile in ppm as a function of pressure–temperature, showing ZIR to be positively proportional to temperature and negatively proportional to pressure. White space represents regions of $P$–$T$ space in which the mineral being represented is not stable. These diagrams were used to constrain the retrograde $P$–$T$ path recorded by sample AK-5 by correlating modal mineral abundances in the sample to those calculated.
AK-6

The calculated $P$--$T$ pseudosection for sample AK-6 is shown in Fig. 11. The peak assemblage orthopyroxene–garnet–K-feldspar–quartz–rutile–melt occurs as a triangular-shaped field over the $P$--$T$ range of ~6.9–11.0 kbar, ~920–1140. The peak field is bound to lower temperature by the absence of orthopyroxene and to lower pressure by the appearance of sillimanite. The post-peak mineral biotite occurs to lower temperature than the peak assemblage field. The $P$--$T$ pseudosection, contoured for the modal abundance (‘modes’) of some phases, and the ZIR concentration in ppm, is shown in Fig. 12. ZIR concentration increases with increasing temperature.
Figure 11 Calculated $P$–$T$ pseudosection graphically representing changes in mineralogy for the composition of sample AK-6 across $P$–$T$ space. Abbreviations: bi = biotite; ilm = ilmenite; g = garnet; ksp = K-feldspar; ky = kyanite; liq = silicate melt; opx = orthopyroxene; q = quartz; ru = rutile; sa = sapphirine; sill = sillimanite; zc = zircon. The composition (in mole%) used to calculate the pseudosection is provided above the diagram. FeO* = FeO + 2 × 'O'. The field highlighted in bold represents the peak field, and as such the $P$–$T$ path (arrow) must begin within that field from peak $P$–$T$ conditions (ellipse). By comparison with the $P$–$T$ path of samples AK-3 and AK-5, which are from the same locality, the $P$–$T$ path can be broadly constrained. Due to few retrograde minerals and reaction microstructures in this sample, determination of a retrograde path relies more heavily on the $P$–$T$ paths for other rocks from the same locality.
Figure 12 TCIInvestigator outputs for the $P$–$T$ pseudosection for sample AK-6 graphically representing: A–E: changes in modal proportions of key minerals as a function of pressure–temperature; F: Zirconium concentration in rutile in ppm as a function of pressure–temperature, showing ZIR to be positively proportional to temperature and negatively proportional to pressure. White space represents regions of $P$–$T$ space in which the mineral being represented is not stable.
Figure 13 Calculated $T$–$M$O pseudosection at 8.5 kbar for sample R31180. Abbreviations: bi = biotite; ilm = ilmenite; g = garnet; ksp = K-feldspar; liq = silicate melt; opx = orthopyroxene; pl = plagioclase; q = quartz; ru = rutile; sa = sapphirine; sill = sillimanite; zc = zircon. The compositions (in mole%) used to calculate the pseudosection are provided above the diagram, where the top line represents that at $M$=0 (left-hand side) and the bottom line represents that at $M$=1 (right-hand side). $\text{FeO}^* = \text{FeO} + 2 \times 'O'$. This shows how phase assemblages change with varying oxidation state in the rock. From this diagram, an oxidation state can be chosen on the basis of mineralogy in the rock (bold vertical line at $M_{O} = 0.8$). Due to the isobaric nature of cooling in the Napier Complex (see discussion), the $P$–$T$ path for R31180 can be presented on this diagram.

The $T$–$M_{O}$ pseudosection calculated at 8.5 kbar for sample R31180 is shown in Fig. 13.

The peak assemblage of quartz–sapphirine–mesoperthitic K-feldspar–rutile–melt does...
not appear in the diagram. Instead, orthopyroxene- and/or sillimanite- and/or garnet-bearing assemblages occur. The reasons for these minerals occurring along with the peak minerals in the calculated diagram are provided in the Discussion. On this basis, an oxidation state and composition corresponding to that at \( M_O = 0.80 \) was chosen, and the peak field (with orthopyroxene) is outlined by bold lines. This oxidation state does not allow garnet to be stable at any temperature at 8.5 kbar but does allow sillimanite stability at lower temperature, faithful to observations from the rock.

**SEM and MLA maps**

SEM and MLA maps (Figs. 14–17) provide a framework that allowed rutile grains to be analysed as a function of microstructural location (inclusion versus grain boundary) and with different relationships to zircon (internally or externally exsolved zircon, proximal to or contacting xenocrystic zircon, or in locations sparsely populated with zircon). The vast majority of rutile grains in AK-3 are located at grain boundaries (Fig. 14). A greater proportion of rutile grains occur as inclusions in AK-5 compared to AK-3 (compare Fig. 14 to 15). Most rutile in AK-6 and R31180 occurs at grain boundaries (Figs. 16, 17). The maps also allowed the abundances of rutile and zircon and the ratio of the two values to be calculated for each sample (Table 1). Sample AK-3 had the most total zircon and the lowest rutile:zircon ratio (1.13:1.00). Samples AK-5 and AK-6 had equally low zircon concentrations (0.02% of total area of thin section); however, due to the abundance of rutile in sample AK-5, it had the highest rutile:zircon ratio (32:1) of all samples (Table 1). AK-6 has the second lowest rutile:zircon ratio (5:1). Sample R31180 had the second highest rutile:zircon ratio (12.75:1).
Table 1 Rutile:zircon ratios for all samples as calculated using MLA maps to determine the total amount of rutile and zircon in the thin section.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rutile (%)</th>
<th>Zircon (%)</th>
<th>Normalised Rutile Area</th>
<th>Normalised Zircon Area</th>
<th>Ratio Rutile:Zircon</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK3</td>
<td>0.17</td>
<td>0.15</td>
<td>53.125</td>
<td>46.875</td>
<td>1.13</td>
</tr>
<tr>
<td>AK5</td>
<td>0.64</td>
<td>0.02</td>
<td>96.970</td>
<td>3.030</td>
<td>32.00</td>
</tr>
<tr>
<td>AK6</td>
<td>0.10</td>
<td>0.02</td>
<td>83.333</td>
<td>16.667</td>
<td>5.00</td>
</tr>
<tr>
<td>R31180</td>
<td>0.51</td>
<td>0.04</td>
<td>92.727</td>
<td>7.273</td>
<td>12.75</td>
</tr>
</tbody>
</table>

Figure 14 (A) BSE image mosaic of a part of sample AK-3, with the MLA map (colours) superimposed on top, showing the spatial distribution and location of monazite (white), zircon (blue) and rutile (red). The full thin section map images are provided in Appendix E. The sample is dominated by symplectic intergrowths of sapphire + orthopyroxene ± plagioclase; (B) MLA image mosaic of sample AK-3 that allows the abundance of zircon and rutile to be seen more clearly. Rutile is depicted by red, and zircon by blue.
Figure 15 (A) BSE image mosaic of a part of sample AK-5, with the MLA map (colours) superimposed on top, showing the spatial distribution and location of monazite (white), zircon (blue) and rutile (red). The full thin section map images are provided in Appendix E. The part of the sample shown is dominated by orthopyroxene, feldspar and quartz; (B) MLA image mosaic of sample AK-5 that allows the abundance of zircon and rutile to be seen more clearly. Rutile is depicted by red, and zircon by blue.

Figure 16 (A) BSE image mosaic of a part of sample AK-6, with the MLA map (colours) superimposed on top, showing the spatial distribution and location of monazite (white), zircon (blue) and rutile (red). Black is holes in the slide. The full thin section map images are provided in Appendix E. The part of the sample shown is dominated by quartz and garnet that is surrounded by K-feldspar; (B) MLA image mosaic of sample AK-6 that allows the abundance of zircon and rutile to be seen more clearly. Rutile is depicted by red, and zircon by blue.
Figure 17 (A) BSE image mosaic of a part of sample R31180, with the MLA map (colours) superimposed on top, showing the spatial distribution and location of monazite (white), zircon (blue) and rutile (red). Black is holes in the slide. The full thin section map images are provided in Appendix E. Quartz and a rare grain of biotite dominate the part of the sample shown; (B) MLA image mosaic of sample R31180 that allows the abundance of zircon and rutile to be seen more clearly. Rutile is depicted by red, and zircon by blue.

Trace Element concentrations and thermometry and distance between rutile and xenocrystic zircon

ZIR CONCENTRATION DATA

Rutile grains from the two microstructural locations and with a variety of relationships with zircon were analysed via EPMA from the four samples. The full dataset of analyses is provided in Appendix B.

Forty-seven spot analyses were obtained on rutile grains from sample AK-3 via EPMA (Fig. 18, Table 2). Two of these analyses came from rutile classified as inclusions and forty-five were classified as grain boundary-hosted. Sixty-two analyses were obtained from rutile grains in sample AK-5 (Fig. 19, Table 2). Fifteen of these data came from rutile grains classified as inclusions, and forty-seven from grains classified as grain boundary-hosted. Eighty-one analyses were obtained from rutile grains in sample AK-6.
(Fig. 20, Table 2), with seventeen from inclusion of rutile grains, and sixty-four from grain boundary hosted grains. Seventy analyses were performed on rutile grains from sample R31180 (Fig. 21, Table 2), with seven of those coming from rutile grains held as inclusions and sixty-three from grains at grain boundaries. In AK-3, AK-5, AK6 inclusion grains had a higher mean ZIR concentration than grain-boundary located grains (Table 2), whereas in sample R31180 the opposite held. The concentration data was plotted as a function of distance from the nearest xenocrystic zircon grain (Figs. 18–21c,d,g,h,k,l).

Table 2 Mean ZIR concentrations for all samples classified by microstructural setting

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean ZIR concentration (All data) (ppm)</th>
<th>Mean ZIR concentration (inclusion) (ppm)</th>
<th>Mean ZIR concentration (grain boundary) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK-3</td>
<td>1498.66 ± 52.88 (n=47)</td>
<td>1865.86 ± 54.78 (n=2)</td>
<td>1482.34 ± 52.80 (n=45)</td>
</tr>
<tr>
<td>AK-5</td>
<td>1269.41 ± 50.58 (n=62)</td>
<td>1330.08 ± 50.56 (n=15)</td>
<td>1250.05 ± 50.59 (n=47)</td>
</tr>
<tr>
<td>AK-6</td>
<td>3547.06 ± 65.04 (n=81)</td>
<td>3942.38 ± 66.38 (n=17)</td>
<td>3442.05 ± 64.68 (n=64)</td>
</tr>
<tr>
<td>R31180</td>
<td>587.94 ± 45.82 (n=70)</td>
<td>422.97 ± 43.71 (n=7)</td>
<td>606.27 ± 46.05 (n=63)</td>
</tr>
</tbody>
</table>

ZR REINTEGRATION

BSE images of analysed rutile grains were examined for evidence of zircon exsolution, and, where possible, Zr in exsolved zircon was reintegrated back into rutile. After all possible reintegrations were performed, the ZIR concentration data was replotted (Figs. 17–20b,f j), including against the distance from the nearest xenocrystic zircon grain (Figs. 17-20d,h,l).

Of the forty-seven rutile grains analysed in AK-3, fifteen had visible zircon exsolution and reintegrations were performed for these grains (Table 3). Thirty-six of sixty-two data from sample AK-5 could be reintegrated (Table 3), namely seven of fifteen rutile inclusions, and twenty-nine of the forty-seven grain boundary-hosted grains. Eleven of eighty-one data from AK-6 could be reintegrated, namely two of seventeen rutile
inclusions, and nine of the sixty-four grain boundary-hosted grains (Table 3). Thirty-two of seventy data from sample R31180 could be reintegrated, namely one of seven inclusions and thirty-one of the sixty-three grain boundary-hosted grains (Table 3). Grain boundary-located grains had a higher mean ZIR concentration than inclusion grains after reintegration for all samples (Table 3; contrast to Table 2).

Table 3 Post-reintegration mean ZIR concentrations for all samples classified by microstructural setting

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean reintegrated ZIR concentration (All data) (ppm)</th>
<th>Mean reintegrated ZIR concentration (inclusion) (ppm)</th>
<th>Mean reintegrated ZIR concentration (grain boundary) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK-3</td>
<td>3648.86 ± 112.696 (n=47, including 15 reintegrated grains)</td>
<td>1865.86 ± 54.782 (n=2; no reintegrated grains)</td>
<td>3728.11 ± 116.173 (n=45, including 15 reintegrated grains)</td>
</tr>
<tr>
<td>AK-5</td>
<td>4968.11 ± 171.973 (n=62, including 36 reintegrated grains)</td>
<td>3946.28 ± 127.666 (n=15, including 7 reintegrated grains)</td>
<td>5294.22 ± 189.211 (n=47, including 29 reintegrated grains)</td>
</tr>
<tr>
<td>AK-6</td>
<td>5310.35 ± 91.36 (n=81, including 11 reintegrated grains)</td>
<td>4896.24 ± 82.546 (n=17, including 2 reintegrated grains)</td>
<td>5420.35 ± 93.360 (n=64, including 9 reintegrated grains)</td>
</tr>
<tr>
<td>R31180</td>
<td>3101.41 ± 205.062 (n=70, including 32 reintegrated grains)</td>
<td>846.62 ± 75.242 ppm (n=7, including 1 reintegrated grain)</td>
<td>3351.94 ± 220.366 (n=64, including 31 reintegrated grains)</td>
</tr>
</tbody>
</table>
Figure 18 Ppm Zr results for rutile grains from sample AK-3. Results have been separated into three categories: graphs including all data (n = 47) (a, b, c, d); graphs including only data from inclusions of rutile in other minerals (n = 2) (e, f, g, h); graphs including only data from grain boundary-hosted rutile (n = 45) (i, j, k, l). The first row of graphs summarises ppm Zr values without reintegrating Zr from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegartion of exsolved Zr (in zircon) into rutile done where possible (see Table 3). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon into rutile where possible (see Table 3).
Figure 19 Ppm Zr results for rutile grains from sample AK-5. Results have been separated into three categories: graphs including all data (n = 62) (a, b, c, d); graphs including only data from inclusions of rutile in other minerals (n = 15) (e, f, g, h); graphs including only data from grain boundary hosted rutile (n = 47) (i, j, k, l). The first row of graphs summarises ppm Zr values without reintegrating Zr from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegration of exsolved Zr (in zircon) into rutile done where possible (see Table 3). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon into rutile where possible (see Table 3).
Figure 20 Ppm Zr results for rutile grains from sample AK-6. Results have been separated into three categories: graphs including all data (n = 81) (a, b, c, d); graphs including only data from inclusions of rutile in other minerals (n = 17) (e, f, g, h); graphs including only data from grain boundary hosted rutile (n = 64) (i, j, k, l). The first row of graphs summarises ppm Zr values without reintegrating Zr from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegration of exsolved Zr (in zircon) into rutile done where possible (see Table 3). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon into rutile where possible (see Table 3).
ZIR THERMOMETRY

ZIR thermometry results are shown in Table 4 (To07 thermometer). Prior to reintegration of exsolved Zr (Table 3), all samples but AK-6 showed a single peak in temperature distribution and sample AK-6 showed a bimodal distribution (Figs. 22–25 a, e, i). Sample AK-3 shows temperature peaks corresponding to ~700–800 °C (Fig. 22; Table 4), sample AK-5 shows temperature peaks corresponding to ~700–800 °C (Fig. 23; Table 4), sample AK-6 shows a bimodal distribution, with a lower peak at ~750–
800°C, and an upper peak at ~900–950 °C (Fig. 24; Table 4), and sample R31180 shows a single peak at ~650–700 °C (Fig. 25; Table 4).

After Zr reintegration, temperature distributions for all samples were bimodal. All samples saw significant increases in ZIR temperatures after reintegration (compare diagrams (a) and (b) in Fig. 22–25). Sample AK-3 shows a lower peak of ~750–850 °C and upper peak of ~1000–1100 °C (Fig. 21; Table 5), sample AK-5 shows a lower peak of ~750–900 °C and upper peak of ~1125 °C (Fig. 23; Table 5), sample AK-6 shows a lower peak of ~775 °C and upper peak of ~900–950 °C (Fig. 24; Table 5) and sample R31180 shows a lower peak of ~700–750 °C and upper peak of ~975 °C (Fig. 25; Table 5).

Table 4 Summary of mean temperatures using the To07 thermometer for each sample classified by 3 categories: all data, data from rutile grains classified as inclusions, and data from rutile grains from grain boundaries. No Zr reintegration was performed for calculation of these temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean temperature (To07) (All data) (°C)</th>
<th>Mean temperature (To07) (inclusion) (°C)</th>
<th>Mean temperature (To07) (grain boundary) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK-3</td>
<td>790 ± 30 (n=47)</td>
<td>814 ± 25 (n=2)</td>
<td>789 ± 30 (n=45)</td>
</tr>
<tr>
<td>AK-5</td>
<td>773 ± 32 (n=62)</td>
<td>777 ± 31 (n=15)</td>
<td>771 ± 33 (n=47)</td>
</tr>
<tr>
<td>AK-6</td>
<td>892 ± 19 (n=81)</td>
<td>906 ± 16 (n=17)</td>
<td>888 ± 20 (n=64)</td>
</tr>
<tr>
<td>R31180</td>
<td>698 ± 60 (n=70)</td>
<td>669 ± 83 (n=7)</td>
<td>701 ± 58 (n=63)</td>
</tr>
</tbody>
</table>

As sample AK-3 is a quartz absent rock the $a$SiO$_2$ value for this rock would be less than unity. Therefore, the FW07 thermometer was used to present the thermometry data from sample AK-3 with several different $a$SiO$_2$ values (Fig. 26). As $a$SiO$_2$ decreases, a decrease in ZIR temperatures is observed (Fig. 26).
Figure 22 ZIR thermometry results for rutile grains from sample AK-3 using the To07 thermometer. Results have been separated into three categories: graphs including all data (n = 47) (a, b, c, d); graphs including only data from inclusion hosted rutile (n = 2) (e, f, g, h); graphs including only data from grain boundary hosted rutile (n = 45) (i, j, k, l). The first row of graphs summarises ZIR temperatures without reintegrating Zr from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegration of exsolved Zr (in zircon) into rutile done where possible (see Tables 6 & 7). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon back into rutile where possible (see Table 4).
Figure 23 ZIR thermometry results for rutile grains from sample AK-5 using the To07 thermometer. Results have been separated into three categories: graphs including all data (n = 62) (a, b, c, d); graphs including only data from inclusion hosted rutile (n = 15) (e, f, g, h); graphs including only data from grain boundary hosted rutile (n = 47) (i, j, k, l). The first row of graphs summarises ZIR temperatures without reintegrating zirconium from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegration of exsolved Zr (in zircon) into rutile done where possible (see Tables 6 & 7). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon back into rutile where possible (see Table 4).
Figure 24 ZIR thermometry results for rutile grains from sample AK-6 using the To07 thermometer. Results have been separated into three categories: graphs including all data (n = 81) (a, b, c, d); graphs including only data from inclusion hosted rutile (n = 17) (e, f, g, h); graphs including only data from grain boundary hosted rutile (n = 64) (i, j, k, l). The first row of graphs summarises ZIR temperatures without reintegrating zirconium from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegration of exsolved Zr (in zircon) into rutile done where possible (see Tables 6 & 7). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon back into rutile where possible (see Table 4).
Figure 25 ZIR thermometry results for rutile grains from sample R31180 using the To07 thermometer. Results have been separated into three categories: graphs including all data (n = 70) (a, b, c, d); graphs including only data from inclusion hosted rutile (n = 7) (e, f, g, h); graphs including only data from grain boundary hosted rutile (n = 63) (i, j, k, l). The first row of graphs summarises ZIR temperatures without reintegrating zirconium from exsolved zircon back into any rutile grains. The second row of graphs shows the same data, but with reintegration of exsolved Zr (in zircon) into rutile done where possible (see Tables 6 & 7). The third row of graphs shows the data as a function of rutile grain distance from xenocrystic zircon, and the fourth shows the same data but with reintegration of Zr from exsolved zircon into rutile where possible (see Table 4).
Figure 26 Sample AK-3 is quartz-absent, so thermometry for the sample requires $a$SiO$_2$ values less than unity. The FW07 thermometer allows for $a$SiO$_2$ to be varied. As $a$SiO$_2$ decreases (simulating the sample becoming progressively more silica-deficient) the ZIR temperatures decrease: compare C to B to A, and F to E to D.

**DISCUSSION**

**Phase Equilibria Forward Modelling**

Phase diagrams were calculated to quantify that the studied rocks reached UHT conditions at the peak of metamorphism, constrain their $P$–$T$ path, and calculate trends and absolute ZIR contents as a function of $P$–$T$–$X$ space (Kelsey & Powell, 2011; Skrzypek et al., 2012), for the purpose of comparing and interpreting calculated to
measured ZIR data (Skrzypek et al., 2012). $P-T$ paths for the rocks are defined by integrating the petrographic observations of interpreted prograde, peak and retrograde minerals with the trends in changing mineral abundance in $P-T$ space as calculated by TCInvestigator.

**AK-3**

Sample AK-3 has a peak mineral assemblage of biotite$_1$–garnet$_1$–orthopyroxene$_1$–spinel$_1$–plagioclase–K-feldspar–rutile–melt, where coarse-grained spinel is rare. Due to the scarcity of spinel, the peak metamorphic conditions must lie close to (or within) the spinel-bearing field, as depicted by the semi-transparent ellipse on Fig. 7, at $P-T$ conditions of $\sim10.5$ kbar and 1000–1050 °C. The size of the ellipse is reasonably large to convey uncertainty in the exact peak $P-T$ conditions. Sapphirine–orthopyroxene symplectites are interpreted to be the first developed retrograde products, followed by plagioclase, biotite, sillimanite and, lastly, garnet. From the trends in mineral abundance in the contoured pseudosections, Fig. 8, the retrograde $P-T$ path as shown on Fig. 7 is deduced, satisfying all petrographic observations. Dasgupta et al. (1994) interpreted a similarly shaped $P-T$ path in their study of rocks from Anakapalle. I have not attempted to propose a prograde $P-T$ path for any sample, as this is uncertain in granulite facies rocks (White & Powell, 2002). However, if the early metamorphic record of rocks in the Eastern Ghats Province holds for Anakapalle, the prograde $P-T$ path (in the granulite facies) likely involved an increase in pressure along an anti-clockwise path (Korhonen et al., 2014). Rare inclusions of sapphirine in relict garnet$_1$ provide circumstantial support for this interpretation. Along the deduced $P-T$ path the ZIR concentration decreases from a maximum of $\sim11,000–12,000$ ppm (Figs. 7, 8f; 1060–1070 °C, To07) at the metamorphic peak to $\sim3000–4000$ ppm (Fig. 7, 8f, To07) along the near-isobaric
cooling segment of the $P$–$T$ path at ~7.5–8 kbar. These ZIR values cover some of the measured ZIR data for AK-3 (reintegrated data, Fig. 18b), discussed later.

AK-5
Sample AK-5 records a peak mineral assemblage of garnet–orthopyroxene–rutile–plagioclase–sillimanite–quartz–melt–zircon, constraining peak $P$–$T$ conditions to that field (Fig. 9). Exact $P$–$T$ conditions within that peak field are difficult to determine, due to ambiguity in estimating peak mineral abundances. However, as AK-5 is from the same location as sample AK-3, the peak $P$–$T$ conditions are likely to be shared. Therefore, I interpret that the peak $P$–$T$ conditions and retrograde $P$–$T$ path for AK-5, are the same as for AK-3 (Fig. 9). This $P$–$T$ path satisfies the observations from petrography that orthopyroxene, sapphirine, K-feldspar, plagioclase and cordierite are all retrograde minerals that increase in abundance down-pressure and/or temperature (Fig. 10b, c, feldspar and cordierite abundance not shown in Fig. 10), and that the abundance of garnet decreases down-pressure (Fig. 10a). Sillimanite is problematic in that its preserved abundance in AK-5 is very low, and almost entirely of retrograde origin, yet the calculated pseudosection indicates sillimanite abundance should be quite high (up to ~15–19%). This discrepancy may relate to favourable reactivity of (peak) sillimanite compared to other minerals (White & Powell, 2011). The ZIR concentrations are calculated to be ~7,000–9,000 ppm (~990–1030 °C for To07) at the metamorphic peak, decreasing to ~3000–4000 ppm (~875–910 °C) along the near-isobaric cooling segment of the retrograde $P$–$T$ path. These lower temperatures are similar to or greater than the majority of ZIR data from this sample (Fig. 23b), as discussed later.
Sample AK-6 has a peak assemblage of orthopyroxene–garnet–quartz–feldspar–rutile–melt in a mostly quartz–feldspar rock. Due to the low abundance of orthopyroxene in this sample, the peak metamorphic conditions may be close to the orthopyroxene-in-out line (bold diagonal line from 7 to 11 kbar in Fig. 11). However, following the logic from sample AK-5, it is reasonable to assume that the peak metamorphic conditions—and retrograde $P$–$T$ path—for AK-6 were similar to or the same as those for sample AK-3. If true, this may mean that either: 1) the composition used for the calculation of the $P$–$T$ pseudosection was not hydrous enough. More hydrous compositions would result in orthopyroxene stability expanding up-pressure ($P$–$M_{H2O}$ diagram, Appendix F); and/or 2) that orthopyroxene is actually an early retrograde mineral. In AK-6, orthopyroxene is separated from garnet by K-feldspar (Figs. 5a, 12a). Therefore, arguably, orthopyroxene is a peak rather than retrograde mineral that reacted with garnet to produce K-feldspar (Fig. 11a). The peak metamorphic conditions, depicted by an ellipse on Fig. 11, are shown at lower pressure than for samples AK-3, AK-5. This is to convey that orthopyroxene is interpreted to be a peak mineral, rather than indicate that the peak conditions in AK-6 were different than in AK-3 and AK-5. AK-6 has very minor ($<<1\%$) sillimanite occurring in the matrix, but its paragenetic significance is unclear. However, given the presence of a sillimanite-bearing field to lower pressure than the peak assemblage field, it could be that matrix sillimanite is a minor retrograde product. From TCInvestigator outputs (Fig. 14), the abundance of sillimanite is constrained to be very low (Fig. 12d), so if a sillimanite-bearing field was accessed by the $P$–$T$ path, the abundance of sillimanite is not expected to be significant. The ZIR concentrations are calculated to be ~7000–9000 ppm (~990–1030 °C, To07) at the
metamorphic peak, decreasing to ~1000–4000 ppm (~750–910 °C) along the near-isobaric cooling segment of the retrograde $P$–$T$ path. This entire temperature range (i.e. ~750–1030 °C) is covered by the spread of ZIR data from this sample (Fig. 25b), as discussed later.

R31180

Sample R31180 has a peak assemblage of quartz–sapphire–mesoperthitic K-feldspar–rutile–melt. This assemblage does not appear in the $T$-$M_O$ pseudosection (Fig. 13). The field corresponding to the peak assemblage is chosen to be one that also includes orthopyroxene (see text for $T$–$M_O$ diagram, Fig. 13). The reason the field corresponding to what is observed in the thin section does not occur is a consequence of the composition of orthopyroxene versus sillimanite in the context of typical sapphire–quartz rock compositions (see figure in Appendix G). Therefore, in sample R31180, the peak field of quartz–sapphire–mesoperthitic K-feldspar–rutile–melt–orthopyroxene occurs at temperatures >1050°C (Fig. 13). Constraining tighter peak conditions in this field are difficult but existing estimates of peak temperatures in the Napier Complex UHT rocks are ~1050 to >1120 °C (Sandiford & Powell, 1986; Harley, 1987; Hensen and Motoyoshi, 1992; Harley and Motoyoshi, 2000; Hollis & Harley, 2002; Hokada et al., 2008; Harley, 1998; Harley, 2008; Shimuzu et al., 2013). Regardless of the specific peak temperature, the peak metamorphic conditions are well within the UHT realm. The Napier Complex is well-known as a near-isobarically cooled terrane (Sheraton et al., 1980; Harley, 1989; Sandiford, 1985a), and so I have interpreted the post-peak $P$–$T$ path to pass into the stability field of orthopyroxene–sillimanite–bearing assemblages, as per the petrographic interpretations (Fig. 13).
ZIR concentrations and thermometry

The $P-T$ and geochronology (Appendix D) framework provides a sound basis for interpreting the main focus of this study, ZIR concentration and thermometry results in the context of the microstructural setting of rutile and its proximity to zircon.

A ZIR concentration of $\sim$4000 ppm produces a ZIR temperature of $\sim$900 °C, and thus represents the minimum amount of ZIR required to show UHT conditions. Interestingly, the data in Table 3, and in Figs. 18b,f,j–21b,f,j, show that the vast majority of rutile grains in all four samples preserve ZIR concentrations $< \sim$4000–6000 ppm, after reintegration of exsolved Zr back into rutile. Sample AK-6 has the largest proportion of ZIR ppm $>4000$ ppm (Fig. 20b,f,j), whereas sample R31180 records the smallest proportion of ZIR ppm $>4000$ ppm (Fig. 21b,f,j). The majority of ZIR ppm data for R31180 are $<1000$ ppm, even after reintegration of exsolved Zr (Fig. 21b,j). Several options may explain the preponderance of low ZIR ppm in R31180. First is that the majority of the analysed rutile grew at either an earlier or later stage than the peak of metamorphism, thus never witnessing the peak UHT conditions. Second, the ratio of rutile:zircon in the sample could indicate there was a deficiency of Zr (in zircon) to allow ZIR concentrations to become high. Third, there may be out-of-plane influences on ZIR concentrations by xenocrystic zircon not seen in the 2D plane of a thin section. Fourth may be the long-lived residence time of the Napier Complex in the deep crust.

For the first option, it is highly likely that rutile grew during the prograde evolution and was stable at the metamorphic peak. Rutile forms during prograde metamorphism by the breakdown of Ti reservoirs such as biotite (White et al., 2014a,b). At the peak UHT conditions, well above biotite stability (White et al., 2014a,b), rutile is the only Ti-bearing mineral in the rock. If at least some rutile is preserving low Zr concentrations
from earlier in the prograde history, I might expect these grains to occur as inclusions in other minerals. Indeed, Figs. 21f,h show that all rutile inclusions in this rock preserve lower Zr concentrations. This could mean that at least some rutile was shielded from obtaining more Zr as temperature increased. For grain boundary-hosted rutile, the lower Zr concentrations (Fig. 21j, l) are more problematic as retrograde rutile growth is difficult to explain for this sample.

The relative abundance of rutile to zircon (12.75:1.0 in Table 1), indicates that rutile is far more abundant than zircon in this sample (see also Fig. 16). Although this is not the highest rutile:zircon ratio of all investigated samples, it does suggest that a lack of Zr reservoirs could have prevented a majority of rutile grains from preserving UHT conditions. However, the data in Figs. 21d,l contrast with this notion as low (reintegrated) ZIR concentrations occur in rutile that is very proximal (<100 μm) to zircon (Fig. 21l). Out-of-plane zircon grains not imaged by BSE and MLA mapping are unlikely to explain the low ZIR ppm concentrations, because proximity to xenocrystic zircon does not appear to have influenced ZIR ppm concentrations.

The last option, the long residence time of ca. 1000–1500 Myr of the Napier Complex granulites in the deep crust (Sandiford, 1985a, b; Carson et al., 2002a, b; Black et al., 1983) has merit as it allows for ample high-temperature diffusion to occur. Indeed, many of the ZIR temperatures for R31180 are in the range 600–800 °C after Zr reintegration (Fig. 21). Grains that preserve very low ZIR temperatures are predominantly located at grain boundaries (Fig. 25l). Resetting of ZIR to temperatures ~500–300 °C lower than the metamorphic peak strongly suggests the equilibrium relation between quartz, rutile and zircon was sustained for many of the rutile grains in
the rock. This would imply that diffusion of Si out of rutile—which is argued to be slow and a determining factor for Zr retention in rutile (e.g. Taylor-Jones and Powell, 2015)—was sustained over that full cooling range. However, to complicate things, other rutile grains in R31180 located along grain boundaries preserve ZIR concentrations indicative of UHT conditions after reintegration (Figs. 25l). The simplest interpretation is that these grains became isolated from zircon during cooling (Taylor-Jones & Powell, 2015), however calculations of distance to xenocrystic zircon (Fig. 25l) show that these grains are not more distal from zircon than those that did not preserve UHT conditions. Therefore, it remains unclear why some grains have reset their ZIR chemistry and others have not.

The distribution of reintegrated ZIR temperatures in sample AK-3, specifically that the majority of them are <900 °C with $a_{\text{SiO}_2} = 1.0$ (Figs. 21j,l), can be partly attributed to the absence of quartz, which implies $a_{\text{SiO}_2} < 1.0$ and a reduced ability of rutile to intake Zr (with Si; Taylor-Jones & Powell, 2015) during heating. AK-3 has 51.60 wt% SiO$_2$, which translates to $a_{\text{SiO}_2} \sim 0.5$ (see Ferry & Watson, 2007). Therefore, reintegrated ZIR temperatures shown in Fig. 26e, clustering around 600–700 °C, are more appropriate. However, consideration still needs to be given to when rutile may have grown. If rutile is predominantly relict (i.e. was formerly inclusions in now-resorbed peak minerals) then rutile is prograde and peak and preserves a mix of temperatures towards, and at, the peak of metamorphism. This could be argued to explain the distribution of ZIR temperatures for $a_{\text{SiO}_2} = 0.5$, which reach a maximum of ~900 °C (Fig. 26e). If rutile is predominantly retrograde it may be expected to show a range of temperatures, analogous to relict rutile, decreasing from the peak of metamorphism (but adjusted down due to lower $a_{\text{SiO}_2}$) to some temperature along the retrograde path. The
growth of rutile during retrograde metamorphism would require a Ti source, such as silicate melt and/or garnet (Ague & Eckert, 2012; Ague et al., 2013; Kawasaki & Motoyoshi, 2007) and/or orthopyroxene (Kawasaki & Motoyoshi, 2007). I tentatively interpret that the ZIR temperatures in AK-3 are a combination of the possibilities, i.e. relict (and peak) and retrograde rutile, in the absence of being able to make a definitive distinction between generations of growth.

ZIR temperatures, with Zr reintegration, in sample AK-5 span a wide range, from ~730 to ~1210 °C (Fig. 20b,d,j,l). Rutile grain size shows a strong correlation with its location in the rock. Coarser grains typically occur within or in direct contact with coarse-grained orthopyroxene (which is a combination of opx$_1$ and opx$_2$) and finer-grained rutile occurs concentrated in symplectic parts of the rock (Fig. 15). This suggests that the finer-grained rutile may be of different (retrograde) origin to the coarser-grains. Fine-grained rutile does not preserve systematically different ZIR temperatures than coarse-grained examples. Fine-grained rutile may originate from decomposition of garnet during retrograde metamorphism, analogous to that proposed for AK-3 (Ague et al., 2013; Kawasaki & Motoyoshi, 2007), while coarse-grained rutile could be peak or prograde. Despite the lack of correlation between rutile size and ZIR concentrations, this does not preclude the possibility that different generations of rutile growth may preserve differing ZIR concentrations. Sample AK-5 has the highest rutile:zircon ratio (Table 1), suggesting that of all samples, this one has potential for chemical communication via element exchange between zircon and rutile to be inhibited. However, a significant proportion of analyses record UHT conditions after Zr reintegration (compare Fig. 23c to 23d), indicating the ZIR + SiO$_2$ = zircon equilibrium was sustained up to and beyond the metamorphic peak, providing clear evidence there is
no apparent limit to the length scale over which xenocrystic zircon may chemically interact with rutile (Figs. 23c,d,g,h,k,l). Last, the ZIR concentrations and (Zr-reintegrated) temperatures recorded by rutile in this sample match very well with the ZIR concentrations and temperatures shown in the calculated $P$–$T$ pseudosection, Figs. 9, 10. Therefore, the calculated $P$–$T$ pseudosection may be used to argue that at least some rutile in this sample grew during the retrograde history of the rock.

Sample AK-6 is the only one to record a number of ZIR temperatures from rutile grains without reintegration of exsolved Zr back into rutile (Figs. 25a,e,i,c,g,k). What this implies is that Si (and Zr) communication was broken between rutile, quartz and zircon during cooling. This seems odd as AK-6 is more quartz-rich than AK-5; however, AK-6 is more felsic and drier than AK-5, which may indicate that Zr exsolution from rutile was less commonly inhibited by a lack of Si. The majority of the ZIR temperatures for AK-6 cluster in the interval ~890–960 °C (Figs. 25, 26) which could reflect either that: Si diffusion out of zircon stopped in this range (Taylor-Jones & Powell, 2015); or rutile grew along the retrograde $P$–$T$ path as a result of decomposition of other Ti-reservoirs such as garnet and/or orthopyroxene (Ague et al., 2013; Kawasaki & Motoyoshi, 2007), as argued above for other samples. This temperature interval corresponds reasonably well with the interpreted near-isobaric cooling part of the retrograde $P$–$T$ path (Fig. 11), where the $P$–$T$ path involves crossing rutile abundance contours at a high angle (Fig. 12f), i.e. more rapid, abundant rutile growth than compared to the steeply decompressional segment of the $P$–$T$ path. Therefore, I interpret that the rutile in AK-6 is probably a combination of prograde, peak and retrograde grains, reflected well in the ZIR concentration and thermometry data.
Microstructural location and proximity to xenocrystic zircon

ZIR concentration data (Figs. 18-21) show that for the total dataset for each sample there is no obvious correlation with the distance to xenocrystic zircon grains (Figs. 18–21c,d), regardless of whether exsolved Zr is reintegrated back into rutile. In addition, though ZIR ppm data are dominated by rutile grains located at grain boundaries, there is no clear correlation between the microstructural setting of rutile and its ZIR concentration in relation to the nearest xenocrystic zircon grain (compare Figs. 18–21g,h,k,l), despite mean ZIR ppm statistics typically showing higher ZIR ppm in rutile grains located along grain boundaries (Table 3). Moreover, no noticeable correlation was determined between the magnitude of the increase in Zr concentration post-reintegration and distance to xenocrystic zircon. That is, the amount of Zr exsolved was apparently not consistent among rutile grains throughout a sample (Appendix C).

A number of existing studies have documented a strong correlation between rutile Zr composition and proximity to exsolved zircon (Luvizotto & Zack, 2009; Jiao et al., 2011; Kooijman et al., 2012; Ewing et al., 2013). I have also found this in my study. However, I have progressed understanding to show that the ZIR + SiO₂ = zircon equilibrium operates effectively over length scales much greater than the typical size of individual rutile and zircon grains. This means that prograde rutile grains could very likely attain Zr concentrations corresponding to the thermal peak of UHT metamorphism. However, my data also strongly suggests that during the retrograde evolution this equilibrium remains operational causing many grains to no longer record UHT conditions, even after exsolved Zr is reintegrated. Therefore, in the three quartz-bearing samples, stunted Si diffusion does not appear to have been a dominant factor in determining ZIR concentrations and temperatures (contrast with Taylor-Jones &
Powell, 2015), as there are no known examples of rutile grains preserving peak (i.e. >1000 °C) temperatures that have not exsolved zircon. The major consequence is that ZIR thermometry may almost never preserve the peak UHT conditions in regional terranes where cooling is prolonged. In terranes where sustained cooling has occurred (Napier Complex), the ZIR + SiO$_2$ = zircon equilibrium operates to remove the record of UHT metamorphism from almost all rutile grains.

The dominant ZIR temperatures without any Zr reintegration are in the range of ~650–800 °C (Figs. 22–25 a,c) which correlates well with the lower-temperature peak of ~780 °C in the bimodal distribution of ZIR temperatures in the global dataset (Kelsey & Hand, 2015). The bimodal distribution has been explained as being due to exsolution combined with Zr diffusion closure (e.g. Taylor-Jones & Powell, 2015; Pape et al., 2016). However, bimodality occurs even after Zr reintegration (Figs. 22-25), possibly reflecting a microstructural control on access to Si and Zr reservoirs that remained buried in my dataset, perhaps combined with the timing of growth of different rutile grains.

CONCLUSIONS

The main aims of the study were to investigate whether the microstructural location (inclusion vs grain boundary) of rutile plays a role in controlling its ZIR temperature by means of facilitating or restricting its access to Zr; as well as to investigate whether the distance from xenocrystic zircon plays a role in controlling ZIR concentrations and temperatures.

Four samples were investigated, and all were shown to be UHT samples with peak $P$–$T$ conditions of >1000 °C, but mostly preserve less-than-UHT ZIR temperatures. No
correlation was found between microstructural location and ZIR temperatures, nor distance to xenocrystic zircon. However, a more comprehensive dataset may yet prove that rutile grown at different stages of the rocks history have a correlation to ZIR temperatures. This suggests that the ZIR + SiO$_2$ = zircon equilibrium operates effectively over length scales much greater than the typical size of individual rutile and zircon grains for the prograde as well as part of the retrograde history. The major consequence is that ZIR thermometry may almost never preserve the peak UHT conditions, especially for very slowly-cooled terranes such as the Napier Complex.
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REFERENCES


LUVIZOTTO, G. L., & ZACK, T. (2009). Nb and Zr behavior in rutile during high-grade metamorphism and retrogression: An example from the Ivrea–Verbano


examples of contact polymetamorphism and infiltration-driven metasomatism. *Journal of Metamorphic Geology, 19*(563-582).


Appendix A: Petrography

AK-3

In thin section the coarse-grained assemblage in the sample comprises very coarse garnet (~500 µm to >2–3 cm), brown orthopyroxene (0.5–1 cm), spinel (up to 7 mm), biotite (4–6 mm), K-feldspar and plagioclase. Garnet contains inclusions of sapphire and euhedral rutile grains. Rare biotite and rutile are dispersed throughout the sample. All coarse-grained Fe–Mg minerals are isolated by extensively-developed fine-grained symplectites and coronas. Garnet and orthopyroxene are mantled by symplectic intergrowths of sapphire and orthopyroxene (Fig. 3a). The sapphire and orthopyroxene symplectites occur in contact with local patches of biotite, sillimanite and plagioclase (Fig. 3c). Plagioclase also occurs as an ~50 µm moat between garnet and sapphire-orthopyroxene symplectites (Fig. 3a). Small garnet grains with inclusions of sapphire and orthopyroxene ribs (symplectites) are interpreted to postdate the symplectite (Fig. 3d). Spinel is rare and is mantled by a corona of sapphire and possibly plagioclase (Fig. 3b). Rare coarse-grained perthite/mesoperthite-bearing (i.e. K-feldspar and plagioclase) veins, interpreted as leucosomes, provide evidence for at least some melt being present in the sample at the time of metamorphism. The sample is devoid of quartz.

The interpreted peak metamorphic assemblage is biotite–garnet–orthopyroxene–spinel–plagioclase–K-feldspar–rutile–melt. The interpreted post-peak, retrograde minerals are sapphire and orthopyroxene (± plagioclase) followed by sillimanite, biotite and plagioclase; and then garnet.
AK-5

In thin section the mineralogy of the rock is orthopyroxene, garnet, plagioclase, K-feldspar, quartz, sillimanite, rutile, sapphire and cordierite. Post-peak reaction microstructures are well developed in this sample and occur in parts of the rock where garnet occurs (or is interpreted to have occurred) (Fig. 4a). There is no evidence that sapphire and quartz coexisted as part of a stable mineral assemblage in the sample. Ternary feldspar$_1$ (now exsolved to K-feldspar and plagioclase), orthopyroxene$_1$, quartz$_1$ and garnet$_1$ are coarse-grained and, except for garnet, are all in direct contact (Fig. 4b). Sillimanite$_1$ is extremely rare in the sample, occurring sporadically along grain boundaries of orthopyroxene$_1$ aggregates. Rutile occurs as small grains throughout the sample (Fig. 4b, 4c).

Around garnet is a rich record of mineral development (Fig. 4a, 4c). A multi-layered corona structure is comprised of symplectic intergrowth of Na-rich plagioclase$_2$ and ribs of sapphire$_2$ and sillimanite$_2$ adjacent to garnet, Na-rich feldspar$_2$ and K-feldspar$_2$ between orthopyroxene$_2$ and the sapphire-bearing symplectites, and an outer composite moat of orthopyroxene$_2$ and orthopyroxene$_1$ adjacent to the orthopyroxene$_1$—K-feldspar—quartz—plagioclase matrix (Fig. 4a). Rib-like sapphire$_2$ grains are commonly mantled by coronas of sillimanite$_3$ and cordierite$_3$ (Fig. 4c). Leucosomes are not obvious in this rock at hand-specimen or thin section scale but melt is assumed to be present in (very) small quantities on the basis that the formation of retrograde products such as hydrous cordierite typically requires the presence of melt (Sawyer, 1999; Brown, 2002; Johnson & Brown, 2005; White & Powell, 2011; Korhonen et al., 2013a; Kelsey & Hand, 2015).
Small, irregularly-shaped garnet grains occur in the sapphire-bearing symplectites and contains inclusions of rib-like sapphire and Na-rich plagioclase and partly contains rib-like grains of sillimanite and sapphire. These garnet grains are interpreted as late (garnet4). Rare biotite occurs in the symplectic corona layer and also in the outermost orthopyroxene1–orthopyroxene2 corona. Due to the hydrous nature of biotite it is interpreted as late, possibly at a similar time to cordierite3.

The interpreted peak metamorphic assemblage is orthopyroxene1–garnet–sillimanite1–quartz–K-feldspar–rutile (and melt), where K-feldspar is ternary feldspar. The post-peak minerals are interpreted to be sapphire2, plagioclase2, K-feldspar2, cordierite2, biotite2 and orthopyroxene2, followed by sillimanite3, cordierite3, biotite3, and then garnet4.

AK-6
Coarse-grained garnet (up to 8 mm), K-feldspar (3–10 mm) and orthopyroxene (6–9 mm) occur as porphyroblasts within a matrix of very abundant quartz (Fig. 5b). Garnet contains rare inclusions of sapphire, rutile and sillimanite (Fig. 5a). Garnet and orthopyroxene are separated by K-feldspar when they occur in proximity (Fig. 5a).

Small (up to 1.5 mm) grains of rutile occur throughout the matrix. Rare (<<1%), tiny sillimanite grains occur in the matrix spatially distal from garnet and orthopyroxene. Biotite occurs around and in direct contact with orthopyroxene. Biotite contains very rare inclusions of rutile and sillimanite, suggesting that orthopyroxene may have formerly contained inclusions. Leucosomes are not obvious in this rock at hand-specimen or thin section scale as there are so few ferromagnesian minerals present but melt is assumed to be present in (very) small quantities on the basis that the formation of the retrograde product (hydrous biotite) typically requires the presence of melt.
The interpreted peak metamorphic assemblage is orthopyroxene–garnet–K-feldspar–quartz–rutile–melt. Prograde minerals are interpreted to be sillimanite, sapphirine and rutile. The post-peak minerals are interpreted to be biotite and K-feldspar. The significance of matrix sillimanite is unclear.

R31180

Coarse-grained sapphirine (2–8 mm) porphyroblasts are consistently and systematically separated from matrix quartz (2–8 mm) by either a two-layer corona of sillimanite (3–4 mm, inner layer adjacent to sapphirine) and orthopyroxene (3–4 mm diameter, outer layer) (Fig. 6a, 6b) or a three-layer corona of corundum (inner layer adjacent to sapphirine), sillimanite (middle layer) and orthopyroxene (outer layer, adjacent to quartz). The matrix is predominantly quartz, but additionally contains rare, very coarse mesoperthitic K-feldspar (up to 14 mm). The mesoperthitic K-feldspar is observed with small clusters of fine-grained biotite and quartz at its edges. Rutile is typically coarse-grained (2–4 mm) and occurs within the corona structure (Fig. 6a, 6b) as well as in the matrix. Leucosomes are not obvious from the thin section. However, the presence of coarse mesoperthitic K-feldspar may attest to melting reactions having taken place in the sample, and the presence of rare biotite may attest to the former presence of melt.

The interpreted peak mineral assemblage is quartz–sapphirine–mesoperthitic K-feldspar–rutile–melt. Retrograde minerals are interpreted to be sillimanite, orthopyroxene, corundum and biotite.
### APPENDIX B: ZIR DATA

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## Appendix C: Reintegrated ZIR data

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Appendix D: LA-ICP-MS

METHODS

U–Pb geochronology was done using the Resonetics ASI M50 laser coupled with an Agilent 7700 ICP–MS at Adelaide Microscopy. Prior to dating, high resolution reflected light images were taken using an optical microscope to aid in determining the microstructural location of monazite grains. U–Pb analyses were acquired in a He ablation atmosphere with a frequency of 5 Hz and a spot size of 20 μm.

The primary monazite standard MAdel (TIMS normalisation data: $^{207}\text{Pb} / ^{206}\text{Pb} = 491.0 \pm 2.7$ Ma, $^{206}\text{Pb} / ^{238}\text{U} = 518.37 \pm 0.99$ Ma and $^{207}\text{Pb} / ^{235}\text{U} = 513.13 \pm 0.19$ Ma: updated from Payne et al. (2008) with additional TIMS analyses) was utilised to account for elemental fractionation and mass bias. Data accuracy was monitored using secondary monazite standards 222 (SHRIMP data: $^{206}\text{Pb} / ^{238}\text{U} 450.2 \pm 3.4$ Ma) and Ambat (c. 525 Ma). Bracketing monazite runs with standards accounted for instrument drift. During the course of this study the data collected on standards was: MAdel standards reported a mean $^{206}\text{Pb} / ^{238}\text{U}$ age of $518.4 \pm 10.35$ Ma (n=20), 222 gave a mean $^{206}\text{Pb} / ^{238}\text{U}$ age of $447.7 \pm 8$ Ma (n=12), and Ambat gave a mean $^{206}\text{Pb} / ^{238}\text{U}$ age of $514 \pm 11.5$ Ma (n=8). All data quoted are at the two-sigma level.

AK-3

Twenty-four (24) monazite grains from sample AK-3 were in situ analysed by laser ablation. The majority of data (n=21) is concordant (concordancy >90% and <110%) and defines a spread along concordia of $^{206}\text{Pb} / ^{238}\text{U}$ ages between $882 \pm 19$ Ma and $945 \pm 18$ Ma. Concordia, intercept and weighted mean ages were not calculated due to the
spread of data. Of the remaining data, one data point gave a $^{206}\text{Pb}/^{238}\text{U}$ age of 507 ± 9.8 Ma, and the final two data gave $^{206}\text{Pb}/^{238}\text{U}$ spot age results of 1464 ± 40 Ma and 1501 ± 43 Ma.

**AK-5**

Eight (8) monazite grains from sample AK-5 were also analysed by laser ablation. The limited data collected from this sample has two main age ‘clusters’. The first, comprising two data points, has concordant (concordancy >90% and <110% concordant) $^{206}\text{Pb}/^{238}\text{U}$ spot ages of 813 ± 14 and 837 ± 13 Ma. The second age range contains three concordant data points ranging between 887 ± 17 Ma and 923 ± 7.9 Ma. Due to the limited size of the dataset it is not possible to calculate any meaningful weighted mean ages for the sample.

In situ monazite geochronology was not collected from samples AK-6 and R31180 as there was insufficient monazite in the thin sections to be able to define an age population. As geochronology was not the primary focus of the project this was deemed reasonable. Zircon is more abundant than monazite in these samples.

Monazite is a U–Pb chronometer widely applied to constraining high-temperature crustal/tectonic processes. As UHT conditions are thought to be close to or even exceed the temperature at which Pb diffusion in monazite is open to resetting (Cherniak et al., 2004), monazite age data may be interpreted as closure ages. However, in dry rocks such as UHT granulites, it has been argued that monazite can remain closed to Pb diffusion at extreme temperatures (approximately >1000 °C; Sajeev et al., 2010; Schmitz & Bowring, 2003; Walsh et al., 2015). Further, monazite growth in granulite facies rocks is thought to be largely a consequence of crystallisation from melt during the retrograde evolution (Kelsey et al., 2008; Yakymchuk & Brown, 2014), as UHT
conditions are through to be close to or exceed the temperature at which all existing (prograde) monazite dissolves into melt (Rapp et al., 1987; Kelsey et al., 2008; Stepanov et al., 2012). In actuality, monazite age data from UHT rocks may some combination of all the above possibilities, as well as from recrystallisation due to deformation, giving rise to the common ‘smear’ of age data along concordia.

Monazite U–Pb geochronology was undertaken on two of the Anakapalle samples to broadly constrain the age of metamorphism. There is no published isotopic age data for the Anakapalle locality, only monazite chemical age data obtained by EPMA analysis (Simmat & Raith, 2008). Therefore, the data presented in this study is to confirm that metamorphism at Anakapalle is effectually the same age as UHT metamorphism elsewhere in the Eastern Ghats Province (Korhonen et al., 2013). Age data from sample AK-3 older than 1000 Ma is interpreted to be of detrital origin, located in the interiors of large monazite grains, analogous to Simmat & Raith (2008). The spread of age data from 882 ± 19 Ma to 945 ± 18 Ma along concordia are interpreted to define the age and partial duration of UHT metamorphism at Anakapalle. I attribute the spread of age data to a process of continual growth and/or recrystallisation as the retrograde evolution proceeded. The abundance of monazite amongst the symplectite, rather than in coarse-grained minerals, may suggest that the symplectite-forming reaction helped drive monazite production. The age spread is consistent at least partly with the spread of the majority of recent age data (c. 970–930 Ma) (Korhonen et al., 2013), which they attribute to crystallisation of monazite from crystallising melt during cooling. They attribute younger ages to a cryptic fluid-infiltration event. The age data for AK-3 is closely consistent with EPMA monazite age data for numerous parts of the Eastern Ghats Province (e.g. the western khondalite, charnockite–migmatite and eastern
khondalite zones shown in Fig. 1) including that from Anakapalle (see fig. 9 in Simmat & Raith, 2008). Leptynite (garnet–biotite gneiss) dated by Simmat & Raith from Anakapalle shows a major age peak at 907 ± 22 Ma, which coincides extremely well with the isotopic data from AK-3. Mg–Al-rich granulite (analogous to sample AK-3) dated by Simmat & Raith from Anakapalle shows many older (>1000 Ma) ages that are chiefly hosted within relict garnet, the most significant age peak is at 980 ± 25 Ma (interpreted a garnet growth age) and few data are < c. 950 Ma. However, spot ages of 945 ± 24 Ma from monazite located in the sapphire–orthopyroxene symplectites are interpreted to date decompression (Simmat & Raith, 2008). The similarity between this age and the dominant spread of ages in this study (882 ± 19 Ma to 945 ± 18 Ma) suggests that the amount of common Pb in monazite in this sample is low.

With the total geochronology dataset I have collected it is not possible to argue definitively for any particular interpretation made by Korhonen et al. (2013) or Simmat & Raith (2008). However, importantly, my age data is broadly comparable to the known ages of UHT metamorphism in the Eastern Ghats Province. Indeed, Korhonen argue that the total timescale of UHT metamorphism in the Province is unconstrained, but potentially as long as 200 Ma. As their geochronology samples are from rocks preserving the apparently earlier anticlockwise-style $P$–$T$ evolution, the concordant age data from Anakapalle in this study raises the possibility that a previously unrecognised younger component of UHT metamorphism in the Province is present at the Anakapalle locality as a consequence of it preserving the apparently later, clockwise-style $P$–$T$ evolution.
In situ monazite U–Pb geochronology results for sample AK-3 (n = 25). (A) All data for AK-3 regardless of concordancy. Most data define a spread of data between 882 ± 19 Ma and 945 ± 18 Ma (2⁰⁶Pb/²³⁸U ages); (B) Close up of n=22 concordant data that define a spread of 2⁰⁶Pb/²³⁸U ages between 882 ± 19 Ma and 945 ± 18 Ma; (C) Probability density plot of the concordant data in B (n=22).
In situ monazite U–Pb geochronology results for sample AK-5 (n = 8). (A) The majority of concordant data (n = 5) cluster from 906.4 ± 8.1 Ma to 923 ± 7.9 Ma (all ages quoted are $^{206}\text{Pb}/^{238}\text{U}$ ages). Two data present results of 813 ± 14 and 837 ± 13 Ma. The remaining data point has an age of 887 ± 17 Ma. (B) Probability density plot of geochronology data for sample AK-5.
Appendix E: SEM/MLA maps

Full SEM and MLA maps for sample AK-3 used to calculate total rutile and zircon abundances, as well as distance from rutile to xenocrystic zircon
Full SEM and MLA maps for sample AK-5 used to calculate total rutile and zircon abundances, as well as distance from rutile to xenocrystic zircon
Full SEM and MLA maps for sample AK-6 used to calculate total rutile and zircon abundances, as well as distance from rutile to xenocrystic zircon
Full SEM and MLA maps for sample R31180 used to calculate total rutile and zircon abundances, as well as distance from rutile to xenocrystic zircon
Appendix F: P-M(O) and P-M(H2O) Phase Diagrams for sample AK-6

Calculated $P$–$M_O$ pseudosection at 1020 °C for sample AK-6. Abbreviations: ilm = ilmenite; g = garnet; ksp = K-feldspar; liq = silicate melt; opx = orthopyroxene; q = quartz; ru = rutile; sa = sapphirine; sill = sillimanite; zc = zircon. The compositions (in mole%) used to calculate the pseudosection are provided above the diagram, where the top line represents that at $M=0$ (left-hand side) and the bottom line represents that at $M=1$ (right-hand side). FeO* = FeO + 2×'O'. This shows how phases change with varying oxidation state in the rock. From this diagram, an oxidation state can be chosen on the basis of mineralogy in the rock (bold vertical line).
The $P-M_O$ pseudosection calculated at 1020 °C for sample AK-6 is shown above. The peak assemblage of orthopyroxene–garnet–K-feldspar–quartz–rutile–melt, which is stable in compositions with low $\text{Fe}_2\text{O}_3$ contents (left-hand side of diagram). The chosen oxidation state corresponds to the composition at $M_O = 0.03$ on the basis that the rock is rutile- rather than ilmenite-bearing. Compositions more oxidised than that at $M_O = 0.03$ would result in ilmenite-bearing assemblages occurring at pressures increasingly similar to the peak pressure for this sample.

Using the composition at oxidation state $M_O = 0.03$, the $P-M_{\text{H}_2\text{O}}$ pseudosection calculated at 1020 °C for sample AK-6 is shown below. The peak assemblage field occurs as a large field (outlined by bold boundaries) greater than $M_{\text{H}_2\text{O}} = 0.1$. Due to the rarity of sillimanite and biotite in the sample, the composition chosen for the calculation of the $P-T$ pseudosection is at $M_{\text{H}_2\text{O}} = 0.35$. This composition is a trade-off between too much biotite to higher $M_{\text{H}_2\text{O}}$ (biotite not shown as temperature of diagram exceeds biotite stability but its stability is enhanced by higher H$_2$O amounts) and too much sillimanite stability at lower $M_{\text{H}_2\text{O}}$. 
Calculated $P$-$M_{H2O}$ pseudosection at 1020 °C for sample AK-6. Abbreviations: ilm = ilmenite; g = garnet; ksp = K-feldspar; liq = silicate melt; opx = orthopyroxene; q = quartz; ru = rutile; sa = sapphirine; sill = sillimanite; zc = zircon. The compositions (in mole%) used to calculate the pseudosection are provided above the diagram, where the top line represents that at $M=0$ (left-hand side) and the bottom line represents that at $M=1$ (right-hand side). FeO* = FeO + 2×$’O’$. This diagram allows the amount of fluid in the rock to be estimated (bold vertical line), by showing changes in mineralogy and mineral proportions as a function of pressure and H$_2$O content.
Appendix G: Compatibility diagram and justification for peak assemblage of R31180

In the simple MgO–Al₂O₃–SiO₂ system in which reactions between sapphirine, orthopyroxene, sillimanite, quartz and cordierite can be depicted, natural rock compositions favour sapphirine–orthopyroxene–quartz-bearing assemblages (shown below). In addition, the figure below shows that sapphirine–quartz assemblages without orthopyroxene (or sillimanite) can only occur in extremely restricted parts of composition space between the green triangles defining stable mineral assemblages (e.g. a, c, below), thus explaining the absence of that assemblage from $P$–$T$ diagrams in larger systems such as used in this study. The presence of post-peak corundum in some of the corona structures (Fig. 6) cannot be explained in $P$–$T$–$X$ space as corundum and quartz are not stable together under crustal conditions of metamorphism in reduced (rutile-bearing) rock compositions such as for R31180 (Mouri et al., 2004; Kelsey & Hand 2015).
MgO–Al₂O₃–SiO₂ phase diagrams showing the possible stable mineral assemblages on the high-temperature (a, d) or high-pressure (b, c) sides of univariant reactions that define sapphirine stability in UHT rocks. The possible assemblages are shown by green triangles, and compositions of sapphirine–quartz rocks (including FeO in sum with MgO) (e.g. Ellis et al., 1980; Grew, 1980) are depicted by grey ellipse. The compositions of minerals used for the diagrams are: enstatite = Mg₂Si₂O₆, cordierite = Mg₂Al₄Si₅O₁₈, sillimanite = Al₂SiO₅, sapphirine = Mg₄Al₈Si₂O₂₀, quartz = SiO₂, corundum = Al₂O₃. For reactions depicted in (a) and (b) that allow sapphirine–quartz stability, common rock compositions sit in the stability field of sapphirine–orthopyroxene–quartz much more so than sapphirine–sillimanite–quartz (see also (c)).