Behaviour of apatite during partial melting of metapelites and consequences for prograde suprasolidus monazite growth

Chris Yakymchuk

Department of Earth and Environmental Sciences
University of Waterloo
Waterloo, Ontario, Canada, N2L 3G1
email: cyakymchuk@uwaterloo.ca

Abstract

The suprasolidus behaviour of apatite and monazite are examined for an average metapelite composition using phase equilibria modelling coupled with solubility equations of these minerals. Both closed- and open-system scenarios are considered. Partial melting above the solidus requires apatite and monazite breakdown in order to saturate the anatectic melt in phosphorus and the light rare earth elements. In general, melt loss is predicted to increase the stability of apatite and monazite at high temperature. Most apatite is predicted to survive up to ultrahigh temperature conditions except for rocks with low bulk phosphorus concentrations. By contrast, most monazite is expected to be consumed by UHT conditions. Thorium substitution in monazite is expected to increase the stability of monazite to higher temperatures. The presence of LREE-rich apatite decreases the stability of monazite above the solidus, but the breakdown of this apatite during anatexis may generate prograde monazite at the apatite–melt interface in local pockets of melt oversaturation. However, prograde suprasolidus monazite along grain boundaries is expected to be consumed during further partial melting or during melt homogenization when an interconnected melt network develops. Anatectic melts are predicted to be saturated with respect to apatite except at UHT conditions and for rocks with low initial P_2O_5 bulk concentrations.

Keywords: Accessory Minerals, Migmatite, Granulite, Partial Melting, Apatite, Monazite

1. Introduction
Apatite and monazite are ubiquitous minerals in aluminous metamorphic rocks and are the dominant repository for phosphorus and the light rare earth elements (LREE) in migmatites and granulites (e.g. Bea et al., 1994; Bea, 1996a, 1996b; Spear and Pyle, 2002; Prowatke and Klemme, 2006). While apatite is commonly used for geochronology of low-temperature processes (e.g. Farley and Stockli, 2002), monazite is frequently used to date portions of suprasolidus $P$–$T$ paths in high-temperature metamorphic rocks (e.g. Parrish, 1990; Lederer et al., 2013; Taylor et al., 2016). Both minerals are expected to break down in suprasolidus metamorphic rocks during heating and anatexis in order to saturate the anatectic melt in phosphorus and the LREE (e.g. Watson, 1979; Watson and Harrison, 1983; Rapp and Watson, 1986; Montel, 1986, 1993; Rapp et al., 1987; Pichavant et al., 1992; Wolf and London, 1994; London et al., 1999; Stepanov et al., 2012; Duc-Tin and Keppler, 2015).

Theoretical modelling of monazite behaviour in suprasolidus metamorphic rocks suggests that prograde monazite growth above the solidus is unlikely and that monazite ages record cooling and crystallization from anatectic melt (e.g. Kelsey et al., 2008; Spear and Pyle, 2010; Yakymchuk and Brown, 2014b). This contrasts with several studies that convincingly show that monazite can record prograde ages associated with heating and partial melting (e.g. Hermann and Rubatto, 2003; Dumond et al., 2015; Hacker et al., 2015; Johnson et al., 2015; Blereau et al., 2016). Therefore, the mechanisms that generate prograde monazite in suprasolidus metamorphic rocks are unclear. Furthermore, the behaviour of LREE-rich apatite during suprasolidus metamorphism has not yet been quantified using phase equilibria modelling, but the breakdown of this apatite and growth of monazite has been documented in experimental studies (e.g. Wolf and London, 1994) and has been proposed as a possible mechanism to produce prograde suprasolidus monazite (e.g. Johnson et al., 2015). However, the coupling of LREE-rich apatite to monazite behaviour during anatexis has yet to be evaluated using quantitative phase equilibria modelling because previous studies did not include phosphorus in their models (e.g. Kelsey et al., 2008; Yakymchuk and Brown, 2014b).
In this contribution, I first review the controlling factors for apatite and monazite dissolution in anatetic melt. Then I combine phase equilibria modelling of an anatetic metapelite with the experimental results of apatite and monazite dissolution to quantify the coupled behaviour of apatite and monazite during anatexis as well as evaluate if the breakdown of LREE-rich apatite can trigger prograde monazite growth above the solidus. Both closed-system and open-system (e.g. melt loss) scenarios are considered. The consequences for phosphorus saturation of anatetic melts and granites with respect to apatite are also discussed.

2. Suprasolidus behaviour of apatite and monazite

Apatite and monazite are the main carriers of phosphorus in suprasolidus metamorphic rocks and their breakdown is required to maintain phosphorus saturation of melt during anatexis. In addition, monazite is the primary repository of LREE in most metasedimentary rocks (Bea, 1996b) and it is the main contributor of the LREE to anatetic melt. Monazite breakdown will also liberate phosphorus—an essential structural constituent of monazite (~29 wt.% P$_2$O$_5$)—into the anatetic melt, although the contribution is expected to be negligible compared with any phosphorus released from apatite breakdown (e.g. London et al., 1999; García-Arias et al., 2012). Apatite can also contain significant concentrations of the LREE (e.g. Bea et al., 1994) and its breakdown may release LREE into the melt. Therefore, the breakdown and growth of apatite and monazite in suprasolidus systems depend on each other; the breakdown of one may lead to oversaturation of the melt with respect to the other.

The breakdown of apatite and monazite into melt is controlled by chemical and physical factors, including: temperature, pressure, melt chemistry and kinetics (Watson, 1979; Watson and Green, 1981; Watson and Harrison, 1983; Rapp and Watson, 1986; Piccoli and Candela, 2002; Stepanov et al., 2012). Several experimental studies have examined these factors for peraluminous melt compositions, which are applicable to metapelites and metagreywackes (e.g. Harrison and Watson, 1984; Bea et al., 1992; Pichavant et al., 1992; Wolf and London, 1994; Toplis and Dingwell, 1996; London et al., 1999).
Harrison and Watson (1984) used partial melting experiments to show that apatite solubility is related to temperature and the SiO$_2$ concentration of melt by the following relationship:

$$\ln D_{F^{\text{apatite/melt}}} = \left[ \frac{(8400+((\text{SiO}_2-0.5)2.64\times10^4)}{T} \right] - \left[ 3.1 + 12.4(\text{SiO}_2 - 0.5) \right]$$

(1)

where SiO$_2$ is the weight fraction in the melt and $T$ is in Kelvin. This relationship is predicted to be valid for melt with SiO$_2$ concentrations between 45% and 75%, for 0% to 10% wt.% H$_2$O and for the range of pressures expected in the crust (Harrison and Watson, 1984). Pichavant et al. (1992) conducted reconnaissance experiments and they demonstrated that apatite solubility increases for peraluminous melt compositions compared with the metaluminous and peralkaline melts used by Harrison and Watson (1984). Building on the work of these previous studies, Wolf and London (1994) derived a simple equation that relates the aluminum saturation index (ASI: molar Al$_2$O$_3$ / [Na$_2$O + K$_2$O + CaO]) of the melt to the concentration of P$_2$O$_5$ in melt that is in chemical equilibrium with apatite:

$$P_2O_5(\text{wt.\%}) = -3.4 + 3.1 \times ASI$$

(2)

However, their experiments were restricted to low pressure (2 kbar) and peraluminous melt compositions (ASI > 1.1), which may be applicable for partial melting of aluminous metasedimentary rocks but not for intermediate to basic rocks.

The solubility of monazite in granitic melts has been investigated in several experimental studies (Montel, 1986; Rapp and Watson, 1986; Rapp et al., 1987; Montel, 1993; Stepanov et al., 2012; Duc-Tin and Keppler, 2015). Stepanov et al. (2012) combined their experimental results with previous work and derived the following equation for monazite solubility:

$$\ln \Sigma \text{LREE} = 16.16(\pm0.3) + 0.23(\pm0.07)\sqrt{H_2O} - \frac{11494(\pm410)}{T} - 19.4(\pm4)P/T + \ln X_{\text{mnz}}^{\text{LREE}}$$

(3)

where the amount of H$_2$O in melt is in wt.\%, $T$ is in Kelvin, $P$ is in kbar, $\Sigma \text{LREE}$ is the sum of La–Sm (in ppm) in the melt and $X_{\text{mnz}}^{\text{LREE}}$ is the molar ratio of the LREE to the sum of all cations in monazite. In general, monazite solubility is higher for increasing $T$ and the H$_2$O concentration of the melt and monazite solubility decreases with increasing pressure.
3. Methodology

3.1. Phase equilibria modelling

An average amphibolite-facies metapelite (Ague, 1991; Table 1) is used to model the suprasolidus phase relations, melt compositions and behaviour of apatite and monazite during partial melting. This composition is chosen because it is generally the most fertile rock type in metasedimentary sequences and metapelites usually contain low-variance assemblages that are particularly useful for metamorphic studies. Calculations were performed using THERMOCALC v.3.40 (Powell and Holland, 1988) and the internally consistent dataset of Holland and Powell (2011). Modelling was undertaken in the MnO–Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–Fe₂O₃ (MnNCKFMASHTO) chemical system (e.g. White et al., 2014a, b). The activity–composition models are from White et al. (2014a).

Phases modelled as pure end-members include quartz, rutile, aqueous fluid (H₂O), kyanite and sillimanite. Mineral abbreviations are from Holland and Powell (2011).

Suprasolidus rocks are generally not expected to have excess free H₂O due to the low permeability of the deep crust and any free H₂O is likely partitioned into anatectic melt (White and Powell, 2002; White et al., 2005). The solubility of H₂O in anatectic melt increases with pressure along the wet solidus. For the phase equilibria modelling presented here, the amount of H₂O in the bulk composition is adjusted so that the melt is just saturated with H₂O at solidus where the modelled prograde path crosses the solidus. If the prograde path crossed the wet solidus at lower or higher pressures, the quantity of melt produced will be slightly overestimated and underestimated, respectively. Also, the melt at the wet solidus above this pressure will be slightly oversaturated in H₂O.

The average metapelite composition saturated with H₂O at the solidus at 9 kbar was used to model closed-system behaviour. This does not account for melt loss, which is a path-dependent process (e.g. Mayne et al., 2016; Guevara and Caddick, 2016) and this is discussed next. However, the closed-
system model is used as a baseline to assess the sensitivity of the modelling to different variables related to the behaviour of apatite and monazite.

3.2 Open-system behaviour

The preservation of high-grade metamorphic assemblages in migmatites and granulites requires the loss of anatectic melt (e.g. Spear et al., 1999; White and Powell, 2002). Melt loss during anatexis has important implications for the behaviour of major and accessory minerals during metamorphism (e.g. Yakymchuk and Brown, 2014b) as well as the concentration of the LREE and phosphorus in the residuum (e.g. Rapp et al., 1987). The effects of melt loss on the behaviour of apatite and monazite are modelled for two schematic $P$–$T$ paths that involve isobaric heating from the solidus up to 950°C at 9 kbar and 6 kbar. The higher pressure isobaric path was chosen to approximate a typical prograde path for collisional orogenesis (e.g. Clark et al., 2011) and the lower pressure path to model the reaction sequence experienced by high-pressure–low-temperature terranes (e.g. Kelsey and Hand, 2015). For the isobaric heating path at 6 kbar, the starting bulk composition is adjusted so that the melt is just saturated with H$_2$O at solidus at this pressure.

Melt loss is modelled following the methodology of Yakymchuk and Brown (2014a, b) whereby 6 mol.% of melt is extracted out of the system when the total amount reaches 7 mol.% (approximately equivalent to 7 vol.% on a one-oxide basis). The modelled 7 vol.% threshold approximates the melt connectivity threshold of Rosenberg and Handy (2005). The extraction of 6 mol.% melt leaves 1 mol.% melt in the system. The extracted melt has a major element composition determined from the phase equilibria modelling and phosphorus and LREE concentrations determined from the saturation models above (equations 1–3) as long as apatite and monazite are present in the system to buffer the concentrations. After each melt loss event, the melt-depleted composition is used to model the next segment of the isobaric heating path up to the next melt loss event. This process is repeated until the end of each isobaric heating path is reached at 950°C.
3.3. Monazite and apatite behaviour

The amounts of apatite and monazite dissolution and growth are modelled by similar methods to those reported in Kelsey et al. (2008). The limitations and assumptions of this approach are discussed later. First, the saturation concentrations of the melt in ppm are calculated as follows. The major element concentration of the anatectic melt at $P$–$T$ is calculated using THERMOCALC every 1°C and 0.1 kbar across the suprasolidus portion of the pseudosection shown in Figure 1. This information is combined with experimentally determined solubility equations for apatite of Harrison and Watson (1984; HW84) as well as Wolf and London (1994; WL94). Both equations are used because they are both applicable to peraluminous melts, but they yield different results. The solubility equation for monazite is from Stepanov et al. (2012). The solubility equations are combined with assumed stoichiometric concentrations of phosphorus in apatite (41 wt.% $P_2O_5$; the average of apatite compositions reported in Webster and Piccoli, 2015), LREE in monazite (566,794 ppm; Kelsey et al., 2008) and phosphorus in monazite (29 wt.% $P_2O_5$). The result is the saturation concentration of phosphorus ($P_{Sat}$) and the LREE ($LREE_{Sat}$) in the anatectic melt at each $P$–$T$ point. These ‘initial saturation concentrations’ are independent of the proportion of anatectic melt and the bulk concentrations of phosphorus and LREE.

Three bulk rock values of $P_2O_5$ (0.1, 0.3 and 0.5 wt.%) are used that represent the typical range of measured compositions in pelites (e.g. Ague, 1991; London et al., 1999). A bulk LREE concentration of 150 ppm is used that is representative of pelites and metasedimentary migmatites (e.g. Taylor and McLennan, 1985; Yakymchuk and Brown, 2014b).

At this point the methodology departs from that of Kelsey et al. (2008) in order to couple the behaviour of monazite to that of apatite. All of the phosphorus and LREE in the bulk rock are assumed to reside only in apatite, monazite and melt. No phosphorus substitution into major minerals is considered; the possible effects of this are discussed later. The amounts of these elements are then allocated from the bulk concentrations of phosphorus and LREE to form apatite and monazite based on
three values: (1) the bulk concentration of LREE in ppm \((LREE_{\text{Bulk}})\), (2) the bulk concentration of phosphorus in ppm \((P_{\text{Bulk}})\), and (3) the concentration of LREE in apatite in ppm \((A_{\text{pLREE}})\). The concentration of LREE in apatite will vary with melt composition (Prowatke and Klemme, 2006) due to partitioning of LREE between apatite and melt and the concentration of LREE in apatite can be determined by:

\[
A_{\text{pLREE}} = \frac{D_{\text{Ap/melt}}^{\text{LREE}}}{LREE_{\text{Sat}}} \times LREE_{\text{melt}} \quad (4)
\]

where \(D_{\text{Ap/melt}}^{\text{LREE}}\) is the partition coefficient of LREE between apatite and melt and \(LREE_{\text{melt}}\) is equal to \(LREE_{\text{Sat}}\) when monazite is present in the system. Here, I use a \(D_{\text{Ap/melt}}^{\text{LREE}}\) value of 10, which is an average of the experimental results reported in Prowatke and Klemme (2006) for La partitioning between apatite and melt for melts with concentrations of >45 wt.% SiO\(_2\). The amounts of phosphorus in apatite \((A_{\text{pP}})\) and monazite \((M_{\text{pP}})\) and LREE in monazite \((M_{\text{pLREE}})\) are fixed to the stoichiometric values stated above.

The bulk concentration of phosphorus and LREE is the sum of these elements allocated to each mineral:

\[
P_{\text{Bulk}} = P_{\text{Ap}} + P_{\text{Mnz}} \quad (5)
\]

\[
LREE_{\text{Bulk}} = LREE_{\text{Ap}} + LREE_{\text{Mnz}} \quad (6)
\]

where \(P_{\text{Ap}}\) and \(P_{\text{Mnz}}\) are the amounts of phosphorus allocated to form apatite and monazite, respectively and \(LREE_{\text{Ap}}\) and \(LREE_{\text{Mnz}}\) are the amount of LREE allocated to form apatite and monazite, respectively.

Starting with the assumption that all LREE in the rock resides in monazite \((LREE_{\text{Bulk}} = LREE_{\text{Mnz}})\), and that the ratio of \(\frac{M_{\text{pP}}}{M_{\text{pLREE}}}\) is fixed, the amount of phosphorus needed to form stoichiometric monazite is calculated as follows:

\[
P_{\text{Mnz}} = \frac{M_{\text{pP}}}{M_{\text{pLREE}}} \times LREE_{\text{Mnz}} \quad (7)
\]

The remaining amount of phosphorus that is allocated to form apatite is then calculated by rearranging equation (5):
\[ P_{Ap} = P_{bulk} - P_{mnz} \]  

(8)

Using this amount of phosphorus available to form apatite, the amount of LREE allocated to make apatite with the concentration of LREE (\( Ap_{LREE} \)) determined by partitioning between apatite and melt (equation 4) is then calculated:

\[ LREE_{Ap} = \frac{P_{Ap}}{A_{PLREE}} \]  

(9)

The amount of LREE remaining to form monazite is then calculated by rearranging equation (6):

\[ LREE_{Mnz} = LREE_{Bulk} - LREE_{Ap} \]  

(10)

Here, the revised amount of LREE allocated to monazite (\( LREE_{Mnz} \)) is inserted back into equation (7) and this series of equations (7–10) is solved iteratively to determine the amounts of phosphorus and LREE allocated to apatite and monazite, respectively. These values are equivalent to the ‘effective’ concentrations of Kelsey et al. (2008) and Yakymchuk and Brown (2014b) and are independent of the amount of melt in the system.

The saturation concentrations of phosphorus (\( P_{Sat} \)) and the LREE (\( LREE_{Sat} \)) calculated from the solubility equations of apatite and monazite (Harrison and Watson, 1984; Wolf and London, 1994; Stepanov, al. 2012) are now divided by the allocated values of phosphorus to apatite (\( P_{Ap} \)) and the LREE to monazite (\( LREE_{Mnz} \)) and multiplied by the fraction of anatectic melt at \( P-T \) retrieved from THERMOCALC to arrive at the fraction of apatite and monazite dissolution (\( Ap_{diss} \) and \( Mnz_{diss} \)) required to saturate the anatectic melt in these elements (e.g. Kelsey et al., 2008):

\[ Ap_{diss} = \frac{P_{Sat}}{P_{Ap}} \times \text{melt fraction} \]  

(11)

\[ Mnz_{diss} = \frac{LREE_{Sat}}{LREE_{Mnz}} \times \text{melt fraction} \]  

(12)

Finally, this last calculation is repeated considering the amount of LREE contributed by the breakdown of apatite and the amount of phosphorus contributed by the breakdown of monazite:

\[ Ap_{diss}^{\%} = \left[ \frac{P_{Sat}}{P_{Ap} + (Mnz_{diss} \times P_{Mnz})} \right] \times \text{melt fraction} \times 100 \]  

(13)
\[ Mnz_{diss\%}^* = \left( \frac{\text{LREE}_{\text{Sat}}}{\text{LREE}_{\text{Mnz}} \times (\text{Ap}_{\text{diss\%}} \times \text{LREE}_{\text{Ap}})} \right) \times \text{melt fraction} \times 100 \]  

(14)

The result is the percentage of apatite \( (\text{Ap}_{\text{diss\%}}^*) \) and monazite \( (Mnz_{\text{diss\%}}^*) \) dissolution required to saturate the volume of anatectic melt in phosphorus and the LREE with respect to apatite and monazite. These values are plotted on a \( P-T \) grid and are contoured for closed-system scenarios.

For the open-system scenarios, the same equations are employed except that the effective bulk composition of phosphorus \( (P_{\text{bulk}}) \) and the LREE \( (\text{LREE}_{\text{BULK}}) \) change along the \( P-T \) path after melt loss events. Similar to the closed system scenario, three initial bulk compositions of \( \text{P}_2\text{O}_5 \) are investigated (0.1, 0.3 and 0.5 wt.\%) for open-system behaviour and the initial bulk composition of LREE is set at 150 ppm.

The equations above are used when the system contains apatite and monazite to buffer the concentration of phosphorus and the LREE in melt \( (P_{\text{Sat}} \text{ and } \text{LREE}_{\text{Sat}}, \text{respectively}) \). In scenarios where monazite is completely consumed, the LREE concentrations of melt and apatite are determined by the partitioning expression in equation (4). In scenarios where monazite and apatite are both completely consumed, the concentrations of phosphorus and the LREE in melt are calculated from the proportion of melt in the system and the effective bulk compositions of phosphorus \( (P_{\text{bulk}}) \) and LREE \( (\text{LREE}_{\text{BULK}}) \).

4. Results for a closed system

4.1 Phase relations

The \( P-T \) pseudosection for the amphibolite-facies metapelite is shown in Figure 1. The mineral assemblages are typical of those found in metasedimentary migmatites at the amphibolite and granulite facies. Ilmenite and plagioclase are stable in each suprasolidus field across the modelled \( P-T \) range. Rutile is restricted to high pressures \( (P > 10–11.5 \text{ kbar}) \). The important peritectic minerals in the modelled composition are K-feldspar, garnet, and cordierite. K-feldspar is stable at \( T > 660–770^\circ \text{C} \) with increasing pressure. Garnet is stable across the diagram except at \( T < 700^\circ \text{C} \) at \( P < 5.5 \text{ kbar} \). Cordierite
is stable at $P < 4–7$ kbar with increasing temperature. Orthopyroxene is not stable in the modelled $P$–$T$ range.

The four important partial melting reactions for the metapelite include, from low $T$ to high $T$: (1) the consumption of a minimal amount of free H$_2$O to produce melt at the wet solidus, (2) the breakdown of muscovite to produce peritectic K-feldspar, which is represented by a narrow low-variance field that extends from the wet solidus at $\sim$4 kbar up to 780$^\circ$C at 12 kbar, (3) the progressive consumption of biotite to produce peritectic garnet at higher pressure or peritectic cordierite at lower pressure, and (4) the consumption of quartz and feldspar to produce progressively drier melt at temperatures above biotite exhaustion ($>900^\circ$C). Quartz is predicted to be completely consumed at 820–950$^\circ$C with increasing pressure. These melting reactions are similar to those documented in experimental melting studies (Clemens, 2006) and in migmatites terranes (e.g. Brown, 2013) for metasedimentary rocks.

4.2 Melt proportions and composition

The proportion of melt predicted at $P$–$T$ in the metapelite is shown in Figure 2a for a closed system. Melt isopleths are positively sloping to nearly vertical. Therefore, melting can proceed through heating or decompression in a closed-system scenario. However, this may not be the case for open-system scenarios (e.g. Yakymchuk and Brown, 2014a). Note that the melt contours are not evenly spaced, which indicates that melt production is non-linear with heating.

The composition of the melt varies across the pseudosection and the important compositional parameters for apatite and monazite dissolution are shown in Figure 2b–d. Melt ASI increases as temperature increases (Fig. 2b), which reflects the progressive breakdown of muscovite and biotite. Contours for ASI are positively sloping on the pseudosection in the stability field of an aluminosilicate mineral (sillimanite and kyanite) and are negatively sloping below the sillimanite-out line in the low $P$ and high $T$ portion of the pseudosection. This indicates that the solubility of apatite is expected to increase during prograde metamorphism and anatexis for the WL94 model of apatite solubility.
The weight fraction of SiO$_2$ in the anatexitic melt generally increases up temperature, with the exception of low $P$ and high $T$ where it decreases up temperature due to the exhaustion of quartz (Fig. 2c). Contours for the weight fraction of SiO$_2$ have moderate positive slopes at low $T$ and shallower slopes at low $P$ and high $T$ (Fig. 2c). An increase in SiO$_2$ is expected to decrease the solubility of apatite in melt and an increase in temperature increases the solubility of apatite (e.g. Harrison and Watson, 1984).

Contours of the weight fraction of H$_2$O in melt have positive slopes across the diagram and the values decrease up temperature (Fig. 2d). The decrease of the H$_2$O content of melt during heating reflects the increasing contribution of anhydrous reactants in melt-producing reactions during heating. For example, after biotite is exhausted, melting proceeds mostly through the breakdown of quartz and feldspar. Based on the solubility equation of Stepanov et al. (2012), monazite solubility is expected to decrease in drier melt. However, this decrease in solubility may be counteracted during prograde metamorphism by the increase in temperature (e.g. Yakymchuk and Brown, 2014b).

### 4.3 Phosphorus and LREE saturation of the melt

The saturation values of phosphorus ($P_{Sat}$) and the LREE ($LREE_{Sat}$) for the metapelite over the modelled $P$–$T$ range are shown in Figure 3. For apatite, the HW84 solubility equation predicts P$_2$O$_5$ concentrations of up to 0.18 wt.% at 950°C and the saturation concentrations are mostly temperature dependent (Fig. 3a). By contrast, the WL94 model predicts substantially higher concentrations of up to ~0.60 wt.% P$_2$O$_5$ at 950°C and they are strongly correlated with melt ASI (Figs 2b, 3b). Note that the WL94 model does not work for ASI values <1.1 (Fig. 2b). Therefore, this model is not applicable for the high $P$ and low $T$ portion of the diagram (Fig. 3b). LREE saturation contours are nearly vertical, which indicates that they are mostly sensitive to temperature (Fig. 3c). Monazite solubility is also sensitive to the concentration of H$_2$O in melt, which decreases during heating for the modelled composition (Fig. 2d).
4.4 Apatite behaviour

The two different apatite solubility equations (HW84 vs. WL94; equations 1 and 2) yield different results for the behaviour of apatite. For the HW84 solubility equation, apatite dissolution contours are positively sloping and nearly vertical (Fig. 4b, d, f); this is similar to the slope of melt contours in Fig. 2a. The amount of apatite dissolution is non-linear and the spacing of contours decreases at progressively higher temperatures. At 9 kbar and 900°C, the predicted amounts of apatite dissolution for the three modelled bulk compositions vary from to 45% for low P_2O_5 concentrations (0.10 wt.%), 18% for intermediate concentrations (0.30 wt.% P_2O_5), and 10% at higher concentrations (0.50 wt.% P_2O_5). Complete apatite dissolution is predicted only for the low P_2O_5 concentration at T>930°C at P<9 kbar (Fig. 4f).

For the WL94 model, the dissolution contours are strongly correlated with melt ASI (Fig. 2b) and are positively sloping at low T as well as at high P and negatively sloping at P<5 kbar at high T (Fig. 4a, c, e). The transition from positive to negative slope generally coincides with the sillimanite-out field boundary (Fig. 1). When compared with the results with the HW84 solubility equation, the WL94 model predicts more apatite dissolution across the investigated P–T range (Fig. 4). For both apatite dissolution models, apatite is predicted to grow during cooling and melt crystallization. The breakdown of monazite contributes minimal phosphorus to the melt (e.g. London et al., 1999; Garcia-Arias et al., 2012) and the dissolution of apatite is essentially independent of any phosphorus released from monazite breakdown.

4.5 Monazite behaviour

The predicted stability of monazite at suprasolidus conditions is shown in Fig. 5 for three closed-system scenarios. For the first scenario, LREE liberated from apatite breakdown is not considered (e.g. Kelsey et al., 2008; Yakymchuk and Brown, 2014b). For the second scenario, apatite breakdown is
modelled using the HW84 solubility equation and LREE is partitioned between apatite and melt using equation 4. The third scenario is similar to the second except that the WL94 solubility equation for apatite is used.

All three scenarios yield positively sloping contours for monazite dissolution that are kinked in the narrow low-variance muscovite–K-feldspar and sillimanite–cordierite fields (Figs 1, 5); this reflects the large quantity of melt produced in these relatively narrow fields, which requires a large proportion of monazite dissolution to maintain melt saturation in the LREE. The main difference between the monazite-only model (scenario 1) and the models that include LREE partitioning between apatite and melt (scenarios 2 and 3) is that the dissolution contours for monazite are shifted down temperature by \( \sim 10–20^\circ C \) (Fig. 5b, c). This reflects the reduced effective bulk composition of LREE in the system available to monazite due to the sequestration of some LREE into apatite.

5. Results for an open system

The reaction sequence for the modelled isobaric heating paths at 9 kbar and 6 kbar are compared for closed and open-system scenarios in Figure 6a–d. For the 9 kbar heating path, five melt loss events occur during heating resulting in the extraction of 30 mol.% melt from the system. The quantity of melt produced in the open-system scenario (32 mol.%) is roughly half of the amount generated in a closed system (60 mol.%). For the 6 kbar heating path, six melt loss events are predicted to occur during heating and the quantity of melt produced in the open-system scenario (39 mol.%) is also roughly half of the amount generated in a closed system (66 mol.%). While there are subtle differences in the reaction sequence and stability of minerals between closed- and open-system scenarios (e.g. the stability of quartz to higher \( T \) in open-system scenarios), the principle effect of progressive melt loss is the reduced fertility of the residuum. The differences of important melt composition variables for apatite and monazite solubility in melt (ASI, SiO\(_2\), H\(_2\)O) are negligible (<2% difference) between the closed- and
open-system models at the same $P$–$T$ condition. Therefore, Figures 2b–d and 3 are broadly applicable for evaluating both closed- and open-system behaviour during isobaric heating.

For the open-system scenarios, bulk rock values of $P_2O_5$ and LREE change along the $P$–$T$ path at each melt loss event for both modelled $P$–$T$ paths (Fig. 6e–l). Changes in the concentrations of $P_2O_5$ and LREE in the melt phase are shown in Figure 7 for calculations using the WL94 apatite solubility equation. If concentrations of $P_2O_5$ and LREE in melt (Fig. 7)—which are equivalent to the saturation concentrations of phosphorus ($P_{Sat}$) and the LREE ($LREE_{Sat}$) if apatite and monazite are present—are higher than the effective compositions ($P_{bulk}$ and $LREE_{Bulk}$), then the residue will become depleted in these elements after melt extraction (Fig. 6e–l). Extraction of melt with lower concentrations of phosphorus and the LREE will result in elevated residuum concentrations of these elements. For example, the $P_2O_5$ value of the residue increases after melt loss events for the isobaric heating path at 9 kbar and the starting compositions of 0.3 and 0.5 wt.% $P_2O_5$ (Fig. 6e, f) because the melt contains lower concentrations of these elements (Fig. 7a). By contrast, there is a step-wise decrease in the $P_2O_5$ value of the residuum for the isobaric heating path at 6 kbar and starting $P_2O_5$ concentration of 0.1 wt.% using the WL94 solubility equation (Fig. 6g) because the $P_2O_5$ concentration of the extracted melt is >0.1 wt.% (Fig. 7c). The concentration of LREE in melt (Fig. 7b, d) is higher than the bulk composition at each melt loss event and the residue becomes more depleted in LREE after each melt loss event (Fig. 6i–l).

The amounts of apatite and monazite dissolution along the isobaric heating paths are compared for closed- and open-system scenarios in Figure 8. The modes of apatite and monazite decrease during heating for both scenarios. Melt loss increases the stability of apatite and monazite to higher temperatures in open systems relative to the closed-system scenarios.

The stability of apatite to higher temperatures for the open-system scenarios reflects both the progressive enrichment of the residue in $P_2O_5$ in most cases (Fig. 6e–g) and the reduced fertility of the metapelite during progressive melt extraction along the isobaric heating path (Fig. 6a–d). An extreme
case is for a starting P₂O₅ value of 0.1 wt.% using the WL94 solubility equation for the isobaric heating path at 9 kbar. For the closed system, apatite is expected to be completely consumed at ~880°C (Fig. 8a). For the open system, less than 30% of the amount of apatite present at the solidus is predicted to be consumed by 950°C (Fig. 8a).

The increased stability of monazite to higher temperatures mainly reflects the reduced fertility of the metapelite. The decrease in the LREE value of the residue during melt loss only has a subordinate effect. The difference between closed- and open-system scenarios for monazite stability are apparent at higher temperatures where there is significant divergence between the dissolution curves for the different scenarios (Fig. 8e–h). Again, this reflects the reduced fertility of the metapelite after several melt-loss events (Fig. 6a–d).

6. Discussion

6.1. Limitations of modelling

The limitations of the modelling approach applied here for monazite behaviour are detailed in Kelsey et al. (2008), Yakymchuk and Brown (2014), and are also discussed by Taylor et al. (2016). There are some additional limitations that apply to modelling apatite behaviour in this study. No adjustment was made to the average metapelite composition to account for Ca in apatite in the phase equilibria modelling. The modelling does not consider fluorine and chlorine, which can be important for apatite stability in some magmatic, hydrothermal and metamorphic systems (e.g. Bingen et al. 1996; Piccoli and Candela, 2002; Webster and Piccoli, 2015). Model apatite is assumed to have homogeneous zoning in trace elements, although natural apatite can be zoned (e.g. Rakovan and Reeder, 1996; Smith and Yardley, 1999; Yang and Rivers, 2002).

Apatite and monazite are modelled here as stoichiometric minerals (Apatite: Ca₅(PO₄)₃(OH), and monazite [LREE]PO₄). Consequently, the value of X_{mnz}^{LREE} in the Stepanov et al. (2012) monazite solubility equation (equation 3 above) is 1. This approach ignores potentially important components
such as Th, U and Pb. Thorium concentrations in monazite usually range between 1–10 wt.% (e.g. Stepanov et al., 2012), but can be up to 30 wt.% of some monazite (e.g. Catlos, 2013). A consequence of considering Th substitution in monazite for the modelling presented here is that LREE saturation value of equation (3) will decrease. Consequently, less LREE will be allocated to apatite in the bulk composition ($LREE_{Ap}$), which is controlled by the LREE concentration of the melt (equation 4). The net effect is that high-Th monazite is expected to persist to higher temperatures than Th-poor monazite.

Various values of $X_{mnz}^{LREE}$ assuming Th substitution in monazite are investigated along the open-system isobaric heating paths using the WL94 apatite solubility equation in Fig. 9. Note that the calculations for monazite dissolution require an adjustment of the LREE composition of monazite ($Mnz_{LREE}$) to account for Th substitution. For the 6 kbar isobaric heating path, the stability of monazite is increased by ~50°C at high temperature for an $X_{mnz}^{LREE}$ value of 0.7 (Fig. 9b). The high-temperature limit of monazite stability is more significant for the 9 kbar heating path where ~30% of the monazite originally present at the solidus is preserved at 950°C for an $X_{mnz}^{LREE}$ value of 0.7 (Fig. 9a).

Although apatite and monazite are the main mineral repositories of phosphorus in most suprasolidus metamorphic rocks, garnet and plagioclase can accommodate significant quantities of phosphorus (e.g. Pyle and Spear, 2002; Villaseca et al., 2003; Kohn and Malloy, 2004; Dumond et al., 2015). For example, ultrahigh-temperature granulites from Connecticut contain garnet with $P_2O_5$ concentrations up to 0.4 wt.% (Ague and Eckert, 2012; Axler and Ague, 2015a, b). In the modelling here, the result of garnet accommodating phosphorus is a reduction of phosphorus in the system allocated to apatite and an increase in the amount of apatite dissolution required to maintain phosphorus saturation of melt. For the modelled prograde heating paths and for both closed- and open-system scenarios (Fig. 6a–d), the increasing mode of garnet would result in the partitioning of a greater proportion of the bulk phosphorus into garnet as temperature increased. This would decrease the amount of phosphorus allocated to apatite and may accelerate the consumption of apatite. However, the same heating paths would also consume
plagioclase, which may release some phosphorus into the system and contribute to phosphorus saturation of the melt.

The consequences of garnet and plagioclase behaviour on the modes of apatite (and monazite) may need to be considered in some cases where these major minerals are important hosts for phosphorus. However, these minerals are generally expected to only contain a few percent of the total phosphorus budget for metamorphic rocks. For example, a simple mass balance calculation by Spear and Pyle (2002) estimate that a rock with 10 modal % garnet with 200 ppm phosphorus accounts for ~6% of the phosphorus budget of the entire rock. Furthermore, the covariation between LREE and phosphorus concentrations in some migmatites and anatectic granites suggests that the accessory minerals are the main control on these elements during anatexis (e.g. Watt and Harley, 1993; Zeng et al., 2005a; Brown et al., 2016).

6.2 Kinetic controls on apatite and monazite dissolution

The modelling presented here assumes equilibration of the anatectic melt in major and trace elements. However, kinetics may inhibit apatite and monazite dissolution during partial melting, which may lead to undersaturation of the melt in phosphorus and the LREE (e.g. Bea et al., 1994; Ayers and Harris, 1997; Zeng et al., 2005a). The kinetics of apatite and monazite dissolution into anatectic melt are sensitive to grain size, temperature and the H$_2$O content of the melt (e.g. Rapp and Watson, 1986; Harrison and Watson, 1984). For a melt with 6 wt.% H$_2$O, it is predicted to take a maximum of ~1 ky at 750°C and <100 years at 950°C to dissolve a 500μm diameter apatite crystal (Fig. 10a; Harrison and Watson, 1984). For a dry melt, a 500μm diameter apatite crystal is expected to take >10 My to completely dissolve at 950°C (Fig. 10a). However, a completely dry melt composition is unrealistic for the modelled metapelite composition for both closed- and open-system scenarios; the lowest modelled H$_2$O content of melt in both scenarios is ~2 wt.% H$_2$O.
For monazite, Rapp and Watson (1986) evaluated the maximum time it takes to completely consume monazite grains of various sizes. It is expected to take \(\sim 1\) My at 750°C and \(<100\) years at 950°C to completely dissolve a 50μm grain of monazite in a melt with 6 wt.% H\(_2\)O (Fig. 10b). For a drier melt with 1 wt.% H\(_2\)O, the same monazite grain is predicted to take \(>1\) Gy at 750°C and \(\sim 1\) My at 950°C to completely dissolve (Fig. 10b).

For the modelled metapelite composition, the H\(_2\)O content of the melt decreases up temperature for closed-system and open-system scenarios. The difference in the predicted H\(_2\)O content of melt between these different scenarios is negligible (<0.2 wt.%) at the same \(P–T\) condition. Although drier melt compositions are expected to hinder monazite dissolution, this is counteracted by the increase in temperature. For example, the H\(_2\)O content of melt at 9 kbar and 750°C is 9.5 wt.% (Fig. 2d). At these \(P–T\) conditions a 50μm grain of monazite is predicted to take \(<1\) My to completely dissolve (Fig. 10b).

A similar duration is expected for a melt with \(\sim 3\) wt.% H\(_2\)O at 9 kbar and 950°C (Fig. 10b).

The timescales of most regional high-temperature metamorphic processes range from millions to tens of millions of years (e.g. Hermann and Rubatto, 2003; Clark et al., 2011; Harley, 2016). In general, the timescales for apatite and monazite dissolution for the modelled average metapelite are expected to be \(<1\) My for anatectic melt with realistic H\(_2\)O concentrations (>1 wt.%). Therefore, kinetics are not expected to hinder apatite and monazite dissolution in long-lived migmatite terranes except possibly for large grains of apatite (> 500 μm) and monazite (> 50 μm) or if non-equilibrated melt is periodically extracted at \(<1\) My intervals (e.g. Sawyer, 1991; Ayers and Harris, 1997).

### 6.3 Prograde monazite growth in migmatites

Theoretical modelling of monazite behaviour in suprasolidus metamorphic rocks predicts that prograde monazite growth above the solidus is unlikely because monazite breakdown is required for LREE-saturation of the increasing amount of anatectic melt generated during heating (e.g. Kelsey et al., 2008; Spear and Pyle, 2010; Yakymchuk and Brown, 2014b). Similarly, the modelling here suggests...
that apatite will be consumed during heating and partial melting and grow as melt crystallizes during cooling to the solidus for both closed- and open-system scenarios. Because apatite is generally stable to higher temperatures than monazite (Fig. 8) and partitions some of the LREE in the system, the result is a reduced stability of monazite when compared with an apatite-free model of monazite dissolution. Therefore, no new monazite is predicted to grow during heating and partial melting including from the breakdown of LREE-rich apatite in an equilibrated system.

If monazite is exhausted during prograde metamorphism, the concentration of LREE in the melt will be governed by the partitioning of LREE between it and apatite and the LREE concentration of the melt will decrease with further partial melting due to dilution (e.g. Klimm et al., 2008). The melt will remain undersaturated with respect to monazite for the remainder of the prograde path and no new monazite growth is expected.

Johnson et al. (2015) suggested that the breakdown of LREE-rich apatite during prograde metamorphism may have liberated enough LREE to oversaturate the melt and grow monazite due to an increase in melt ASI during progressive partial melting. However, the results of the modelling here suggest that the increase in ASI appears to be counteracted by the non-linear increase in the generation of melt during heating in a closed system (Fig. 6a, c), which requires progressively more apatite (and monazite) dissolution to achieve phosphorus saturation of the melt. For an open system, the fertility of the system decreases after melt loss (Fig. 6b, d), but monazite is still expected to be consumed during heating to saturate the melt in LREE and no new growth is expected (Fig. 8e–h). Both of the modelled scenarios assume that the melt is homogeneous and saturated in phosphorus (with respect to apatite) during the entire metamorphic evolution except at \( P–T \) conditions above apatite exhaustion.

One of the key assumptions of a homogeneous melt composition in this study may not be valid if there is sluggish diffusion of phosphorus and/or LREE away from apatite during dissolution. Wolf and London (1995) suggested that monazite can grow along the apatite–melt interface due to local oversaturation of LREE during apatite breakdown. This is because the diffusivities of REE and
phosphorus are generally similar (e.g. Rapp and Watson, 1986) whereas the diffusivity of calcium is approximately two orders of magnitude higher (Harrison and Watson, 1984). Consequently, a narrow region of melt adjacent to apatite may become enriched in LREE and phosphorus relative to the surrounding melt and may be locally saturated with respect to monazite. This has been called ‘pileup’ where diffusion away from the crystal interface is too slow to keep up with melt equilibration (e.g. Green and Watson, 1982; Harrison and Watson, 1984). Therefore, although monazite crystallization from apatite breakdown is not predicted by the phase equilibria modelling in this study for both closed- and open-system scenarios, new monazite growth may occur in systems where the melt composition is not homogeneous.

The extent of melting may have important implications for melt homogenization. Partial melting begins at reactant grain junctions (e.g. Sawyer, 1999; Acosta-Vigil et al., 2006) in migmatites and melt initially accumulates in isolated pockets. Further heating will increase the proportion of melt in the system and the migmatite will eventually develop an interconnected melt network that physically links individual melt pockets (e.g. Holness et al., 2011; Sawyer, 2014). This may lead to melt extraction from the system as modelled above for the open-system scenarios. Isolated melt pockets have the potential to become oversaturated with respect to monazite if LREE-rich apatite is in contact with the melt and diffusion is sluggish. However, once an interconnected melt network develops, this will drive the system towards homogenization and the preservation of oversaturated melt with respect to monazite (and apatite) becomes less likely. Rosenberg and Handy (2005) estimated that melt interconnectivity may occur when the melt proportion reaches ~7 vol.% in a static system. This value may be much less in a dynamic system undergoing syn-anatectic deformation (Vigneresse and Burg, 2000; Brown, 2013), which is more applicable to regional migmatite terranes that are generally very weak during anatexis (e.g. Diener et al., 2014). For a closed system, the preservation of prograde monazite from the breakdown of apatite is more likely in migmatites that have not undergone extensive partial melting or where melt does not form an interconnected network. For open-system scenarios, isolated melt pockets
may become temporarily connected, but in general they evolve independent from each other and have a
greater likelihood of reaching local LREE oversaturation with respect to monazite.

Monazite growth at the margin of consumed apatite has been documented in experiments (Wolf
and London, 1995; García-Arias et al., 2012) and in studies of metamorphic rocks (e.g. Harlov et al.,
monazite grains at the apatite–melt interface in their experiments. Similarly, Harlov et al. (2007)
documented small (<20 μm) monazite crystals at the margin of apatite in granulites from the Variscan
Schwarzwald of southern Germany. García-Arias et al. (2012) found <10 μm monazite grains around
apatite generated during experimental melting of an Iberian orthogneiss. Considering the kinetic
modelling of previous studies (Fig. 10; Harrison and Watson, 1984; Wolf and London, 1995), the
predicted dissolution times for these grain sizes are <1 My except for unrealistically dry melt
compositions. Therefore, prograde monazite produced through apatite breakdown is expected to be
consumed during melt equilibration and/or further partial melting. However, if these crystals are
included into a growing peritectic mineral (e.g. garnet), then they have a higher preservation potential.
As suggested by Wolf and London (1995), small monazite inclusions encased in minerals may reflect
earlier (e.g. prograde) growth whereas larger monazite grains in the matrix may grow from crystallizing
residual anatetic melt during cooling.

The reaction sequence experienced by migmatites may be an important factor in the preservation
of prograde suprasolidus monazite in peritectic minerals. For the modelled isobaric heating paths in
Figure 6, muscovite breakdown produces peritectic K-feldspar at ~700–750°C and the mode of K-
feldspar is expected to increase during biotite breakdown until ~810–850°C when biotite becomes
exhausted. For the 6 kbar isobaric heating path, cordierite grows at the expense of biotite. At
temperatures above biotite exhaustion, K-feldspar and cordierite are consumed. Therefore, any monazite
that may be generated at the margins of dissolving apatite over the interval 750–850°C has the potential
to be preserved in growing K-feldspar and/or cordierite, but at higher temperatures the rims of these
minerals may be resorbed, which may release some of the included monazite back into the melt. The amount of apatite dissolution over this temperature range for a closed system is small and is predicted to vary between 10% and 50% using the WL94 solubility equation for the modelled bulk P$_2$O$_5$ concentrations (Fig. 8). The amount is expected to be even less for the HW84 solubility equation and much less for the modelled open-system scenarios (Fig. 8).

Garnet is an important peritectic mineral that is commonly targeted for in situ monazite U–Pb geochronology (e.g. Korhonen et al., 2012; Yakymchuk et al., 2015). Similar to K-feldspar and cordierite, garnet growth is predicted to occur at the expense of biotite and is consumed during heating after biotite exhaustion in both closed- and open-system scenarios (Fig. 6). Therefore, garnet also has the potential to capture monazite derived from apatite breakdown at $T<810–850^\circ$C in the modelled metapelite along the 6 kbar and 9 kbar isobaric heating paths (Fig. 6). Dumond et al. (2015) suggested that some of their monazite inclusions in garnet are related to the breakdown of apatite (that now form rounded inclusions in garnet) during heating and partial melting.

One mechanism that has been proposed to produce prograde suprasolidus monazite is Ostwald ripening (e.g. Nemchin and Bodorkos, 2000). Ostwald ripening reduces the total surface free energy of a system by preferentially dissolving smaller solids and precipitating this material on existing larger solids (e.g. Tikare and Cawley, 1998). This is a possible mechanism for prograde monazite growth in suprasolidus metamorphic rocks if there is no net decrease in the mode of monazite (e.g. Yakymchuk et al., in press). However, monazite modes are expected to decrease during heating in both closed and open systems to saturate the melt in the LREE. Therefore, for the scenarios modelled here, Ostwald ripening may not be an appropriate mechanism for prograde monazite growth in an equilibrated system.

6.4 Apatite dissolution and granite chemistry

Apatite behaviour during partial melting has important implications for studies of the elemental and isotopic variability of granites (e.g. Ayers and Harris, 1997; Zeng et al., 2005a, 2005b; Farina and
Because apatite has a higher Sm/Nd ratio than monazite and the bulk rock (e.g. Bea et al., 1994; Ayers and Harris, 1997), apatite will develop a relatively more radiogenic Nd isotope value than the source. Detrital apatite also maintains its Nd isotope ratio during metamorphism (e.g. Hammerli et al., 2014). Therefore, the dissolution of significant amounts of apatite (e.g. non-modal melting) may result in a melt with a higher Nd isotope composition compared with the source (e.g. Zeng et al., 2005a, 2005b).

The results of the modelling presented here indicate that the proportion of apatite dissolution is sensitive to the bulk P$_2$O$_5$ concentration. For high P$_2$O$_5$ bulk concentrations, apatite progressively breaks down towards higher $T$, but some apatite is expected to survive up to UHT conditions for both closed- and open-system scenarios. Consequently, melt may develop a progressively more radiogenic Nd isotope signature as melting proceeds. By contrast, if apatite is exhausted in a low P$_2$O$_5$ bulk composition, the melt will become progressively less radiogenic due to the breakdown of minerals with lower Sm/Nd ratios during further partial melting. However, monazite is expected to be the main repository for Nd in pelites (e.g. Hammerli et al., 2014) and its breakdown will likely exert a first-order control on the Nd isotope ratio of the melt.

The equilibrium modelling here predicts that melt remains saturated with phosphorus until apatite is exhausted at high $T$. After the complete exhaustion of apatite during partial melting, additional heating is predicted to generate melt that is undersaturated with respect to phosphorus. In addition to apatite exhaustion, there are two important mechanisms that can produce undersaturated anatectic melt, including: (1) inhibited accessory mineral dissolution due to kinetic factors (e.g. Harrison and Watson, 1984; Rapp and Watson, 1986) and (2) non-Henrian behaviour of trace elements during melt–solid partitioning (Bea, 1996). Together, these mechanisms can result in a melt that is undersaturated in phosphorus with respect to apatite, which may hinder prograde monazite growth above the solidus.

An additional factor that impacts apatite dissolution is the sequestration of grains included in other minerals away from the reaction volume (e.g. Watson et al., 1989; Watt and Harley, 1993). In this
case, the effective bulk composition will be reduced and the high-temperature stability of the accessory mineral will be lowered (e.g. Yakymchuk and Brown, 2014b). This has the potential to produce undersaturated melt at temperatures below those predicted by using a measured P$_2$O$_5$ bulk concentration and reduce the stability of apatite in the reacting volume of the rock (e.g. along grain boundaries). The exhaustion of apatite also limits the use of apatite saturation temperatures to rocks where apatite was still present at high temperature.

7. Conclusions

Apatite is predicted to progressively dissolve into anatectic melt during prograde suprasolidus metamorphism in metapelites for both closed- and open-system scenarios. The stability of apatite is primarily a function of melt composition, temperature and the bulk rock concentration of P$_2$O$_5$ and whether melt loss is considered. For low bulk rock P$_2$O$_5$ concentrations, apatite may be completely dissolved at UHT conditions whereas some apatite may survive at these conditions for high P$_2$O$_5$ bulk rock concentrations. Melt loss generally extends the stability of apatite and monazite to higher temperature. Partitioning of LREE into apatite reduces the high-temperature stability of monazite and only minor prograde monazite growth may occur at the apatite–melt interface due to local oversaturation of the melt in LREE. This monazite may be preserved as inclusions in peritectic minerals that shielded them from further dissolution, but prograde suprasolidus monazite is less likely to survive in the matrix of the rock.

Acknowledgements

This work was partially funded by a Discovery Grant from the National Sciences and Engineering Research Council of Canada. I thank DE Kelsey and an anonymous reviewer for detailed and constructive reviews and M Scambelluri for his editorial work.
References


Finger, F., Krenn, E., 2007. Three metamorphic monazite generations in a high-pressure rock from the Bohemian Massif and the potentially important role of apatite in stimulating polyphase monazite growth along a PT loop. Lithos 95, 103-115.


Taylor, R.J.M., Kirkland, C.L., Clark, C., 2016. Accessories after the facts: Constraining the timing, duration and conditions of high-temperature metamorphic processes. Lithos.


**Figure captions**
**Figure 1.** $P$–$T$ pseudosection for an average amphibolite-facies metapelite (modified from Yakymchuk et al., *in press*). The dashed line is the solidus. The two isobaric heating paths are used to evaluate closed-system versus open-system behaviour in Figures 6–9.

**Figure 2.** Contours for the proportion and composition of anatectic melt important for the modelling the behaviour of apatite and monazite. (a) The proportion of anatectic melt in mol.% (approximately equivalent to vol.%) in the metapelite in a closed system. (b) The aluminum saturation value of melt. (c) the weight percentage of SiO$_2$ in melt. (d) the weight percentage of H$_2$O in melt. The dashed line is the solidus.

**Figure 3.** Contours for saturation concentrations of melt in P$_2$O$_5$ (wt.%) using the apatite solubility equations of (a) Harrison and Watson (1984): HW84, and (b) Wolf and London (1994): WL94. (c) Contours for saturation concentrations of melt in LREE (ppm) using the solubility equation of Stepanov et al. (2012) for monazite. The dashed line is the solidus.

**Figure 4.** Contours for the amount of apatite dissolution (%) in a closed system using the apatite solubility equations of Harrison and Watson (1984): HW84, and Wolf and London (1994): WL94. The assumed bulk rock concentration of LREE is 150 ppm and various concentrations of P$_2$O$_5$ are indicated. The dashed line is the solidus.

**Figure 5.** Contours for the amount of monazite dissolution in a closed system comparing the difference between excluding apatite from the system (e.g. Kelsey et al., 2008; Yakymchuk and Brown, 2014) and including it. (a) Monazite dissolution contours (%) for the apatite-free scenario. (b) Monazite dissolution contours (%) that include apatite using the Harrison and Watson (1984) apatite solubility equation. (c)
Monazite dissolution contours (%) that include apatite using the Wolf and London (1994) apatite solubility equation. The dashed line is the solidus.

**Figure 6.** Mode–temperature diagrams illustrating the changes in modal proportions (mol.%) approximately equivalent to vol.% along two isobaric heating paths from 650 to 950°C at 9 kbar (a,b) and 6 kbar (c, d) for closed- and open-system scenarios. (e–h) The concentration of P$_2$O$_5$ (wt.%) in the system during open- and closed-system scenarios for the two modelled isobaric heating paths. (i–j) The concentration of LREE (ppm) in the system during open and closed-system scenarios for the two modelled isobaric heating paths. WL94: apatite solubility equation of Wolf and London (1994). HW84: apatite solubility equation of Harrison and Watson (1994). Melt loss (ML) events are indicated by the vertical lines for the open-system scenarios.

**Figure 7.** Concentration of LREE and P$_2$O$_5$ in melt for the two isobaric heating paths in Fig. 1 using the Wolf and London (1994) apatite solubility equation. Results for initial bulk P$_2$O$_5$ contents of 0.1, 0.3 and 0.5 wt.% for the open-system scenarios are shown. The concentrations of LREE and P$_2$O$_5$ in melt are buffered to the saturation values when monazite and apatite are present. After apatite or monazite exhaustion, the concentrations of LREE and P$_2$O$_5$ in melt are diluted during further partial melting.

**Figure 8.** (a–d) Amounts of apatite dissolution required to maintain phosphorus saturation of the melt for closed- and open-system scenarios along two isobaric heating paths. In all cases, open-system behaviour extends the stability of apatite to higher temperatures compared to the closed system. (e–h) Amounts of monazite dissolution required to maintain LREE saturation of the melt for closed and open system scenarios along two isobaric heating paths. In all cases, open-system behaviour extends the stability of monazite to higher temperatures compared to the closed system. WL94: apatite solubility
Figure 9. Amount of monazite remaining relative to the amount present at the solidus for various molar ratios of the LREE to the sum of all cations in monazite ($X_{\text{REE}}^{\text{LREE}}$) for the open-system isobaric heating paths at 9 kbar (a) and 6 kbar (b). The apatite solubility equation is from Wolf and London (1994). The starting bulk concentration of P$_2$O$_5$ is 0.3 wt.%. 

Figure 10. The relationship between temperature, time, grain size and the H$_2$O content of the melt for apatite and monazite dissolution. (a) Apatite dissolution (modified from Rapp and Watson, 1986). (b) Monazite dissolution (modified from Harrison and Watson, 1984).
Table 1. Bulk composition used in phase equilibria modelling (mol.%).

<table>
<thead>
<tr>
<th>Figures</th>
<th>ML</th>
<th>H₂O</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>FeO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>MnO</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–6, 8</td>
<td>6.24</td>
<td>60.55</td>
<td>12.80</td>
<td>1.49</td>
<td>5.18</td>
<td>7.52</td>
<td>2.76</td>
<td>1.88</td>
<td>0.85</td>
<td>0.16</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Closed system – solidus saturated with H₂O at 9 kbar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6–9</td>
<td>6.24</td>
<td>60.55</td>
<td>12.80</td>
<td>1.49</td>
<td>5.18</td>
<td>7.52</td>
<td>2.76</td>
<td>1.88</td>
<td>0.85</td>
<td>0.16</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>Open system – Isobaric Heating at 9 kbar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6–9</td>
<td>4.93</td>
<td>60.67</td>
<td>13.13</td>
<td>1.55</td>
<td>5.50</td>
<td>7.98</td>
<td>2.76</td>
<td>1.77</td>
<td>0.90</td>
<td>0.17</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>ML1</td>
<td>3.56</td>
<td>60.80</td>
<td>13.48</td>
<td>1.61</td>
<td>5.84</td>
<td>8.47</td>
<td>2.75</td>
<td>1.67</td>
<td>0.96</td>
<td>0.19</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>ML2</td>
<td>2.32</td>
<td>60.78</td>
<td>13.83</td>
<td>1.67</td>
<td>6.20</td>
<td>8.98</td>
<td>2.73</td>
<td>1.56</td>
<td>1.02</td>
<td>0.20</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>ML3</td>
<td>1.17</td>
<td>60.64</td>
<td>14.17</td>
<td>1.72</td>
<td>6.57</td>
<td>9.52</td>
<td>2.70</td>
<td>1.46</td>
<td>1.08</td>
<td>0.21</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>ML4</td>
<td>0.18</td>
<td>60.33</td>
<td>14.50</td>
<td>1.76</td>
<td>6.96</td>
<td>10.08</td>
<td>2.64</td>
<td>1.37</td>
<td>1.15</td>
<td>0.22</td>
<td>0.82</td>
<td></td>
</tr>
</tbody>
</table>

Open system – Isobaric Heating at 6 kbar |
| 6–9     | 5.15| 61.23| 12.94| 1.50  | 5.24| 7.61| 2.79| 1.90| 0.86 | 0.17 | 0.61|
| ML1     | 4.10| 61.10| 13.27| 1.57  | 5.56| 8.07| 2.77| 1.82| 0.91 | 0.18 | 0.65|
| ML2     | 3.16| 60.84| 13.60| 1.64  | 5.90| 8.55| 2.74| 1.73| 0.97 | 0.19 | 0.69|
| ML3     | 2.27| 60.48| 13.93| 1.71  | 6.25| 9.05| 2.69| 1.65| 1.03 | 0.20 | 0.73|
| ML4     | 1.40| 60.05| 14.27| 1.78  | 6.63| 9.59| 2.62| 1.59| 1.10 | 0.21 | 0.78|
| ML5     | 0.81| 59.36| 14.58| 1.84  | 7.01| 10.13| 2.53| 1.53| 1.16 | 0.23 | 0.83|
| ML6     | 0.38| 58.51| 14.88| 1.89  | 7.41| 10.69| 2.41| 1.49| 1.24 | 0.24 | 0.88|

ML: melt loss event
Figure 1

Temperature (°C)

Pressure (kbar)

1: g bi mu pl ru q
2: g ky bi mu ksp pl ru q
3: g sil ksp ru q
4: g sil ksp q
5: sil bi mu pl q
6: sil ksp bi mu pl q
7: g sil cd bi ksp pl mt q
8: g cd bi ksp pl q
9: g cd ksp pl q
10: g cd ksp pl
11: g cd ksp sp pl mt
12: g cd sp pl mt
13: g sil cd ksp sp pl
14: g sil cd ksp pl
15: g sil ksp pl
16: g sil pl
17: g sil cd pl
18: g sil sp pl
19: g sil cd sp pl

Isobaric heating @ 9 kbar

Isobaric heating @ 6 kbar

+ liq + ilm
Figure 2

(a) melt (mol.%)  
(b) melt ASI  
(c) melt SiO$_2$ (wt.%)  
(d) melt H$_2$O (wt.%)
Figure 3: Closed system

(a) $P_2O_5$ (wt.%) HW84

(b) $P_2O_5$ (wt.%) WL94

(c) LREE (ppm)
Figure 4

(a) 0.5 wt.% P2O5
(b) 0.5 wt.% P2O5
(c) 0.3 wt.% P2O5
(d) 0.3 wt.% P2O5
(e) 0.1 wt.% P2O5
(f) 0.1 wt.% P2O5

Closed system

Pressure (kbar) vs. Temperature (°C)
Figure 5: Closed system. $P_2O_5 = 0.30$ wt.%

(a) no apatite

(b) HW84

(c) WL94
Figure 6

Isobaric heating at 9 kbar

Oxide molar proportion

Isobaric heating at 6 kbar

Oxide molar proportion

Initial bulk compositions:
- 0.10 wt.% P$_2$O$_5$
- 0.30 wt.% P$_2$O$_5$
- 0.50 wt.% P$_2$O$_5$
Figure 7

Isobaric heating at 9 kbar

- Initial bulk compositions
  - 0.10 wt.% P₂O₅
  - 0.30 wt.% P₂O₅
  - 0.50 wt.% P₂O₅

Isobaric heating at 6 kbar

- LREE (ppm) of melt
- P₂O₅ (wt.%) of melt

Initial bulk compositions
- 0.10 wt.% P₂O₅
- 0.30 wt.% P₂O₅
- 0.50 wt.% P₂O₅

mnz out
ap out
Isobaric heating at 9 kbar

Isobaric heating at 6 kbar

Closed system

Open system

Solidus

Figure 8
Figure 9

(a) WL94 – 9 kbar – 0.3 wt.% P$_2$O$_5$

(b) WL94 – 6 kbar – 0.3 wt.% P$_2$O$_5$
Figure 10

(a) Apatite

(b) Monazite