Research paper

Monazite–allanite phase relations in metapelites

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Calculations of the transition from allanite to monazite-bearing assemblages in typical pelitic bulk compositions have been made using thermodynamic data estimated from oxide sums and inferred from natural parageneses. Calculations in the CFASHPCe and MnNCKFMASHPCe systems place the allanite to monazite transition in the middle amphibolite facies (525–600 °C) for a bulk composition similar to Shaw’s average pelite. The temperature of the transition is pressure dependent, and strongly dependent on the bulk rock CaO content, consistent with inferences from natural parageneses. The transition is also a function of the bulk Al2O3 content, although the calculated result is opposite to that inferred from natural samples. Comparison with published results in the La–Mg system suggest that the nature of the REE phosphate does not greatly influence the conditions of the transition.

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1. Introduction

The quantitative relationship among pressure, temperature and the relative stabilities of allanite and monazite is crucial for the interpretation of the ages of these minerals. A number of studies have examined progressive metamorphic sequences, with different conclusions depending on the suites examined. In general, it has been concluded that in rocks of little or no calcium (and sufficient LREE and P), monazite is formed by at least the low greenschist facies and persists throughout metamorphism (e.g., Overstreet, 1967). In rocks of sufficient CaO and LREE, allanite forms at low grades and reacts out at conditions of around garnet to lower temperatures and has the effect of shifting the P–T conditions of the transition.

This paper explores the relationship between allanite (CaCeFeAl2(SiO4)3OH) and monazite (CePO4) during progressive metamorphism by examining both the chemographic relations and through thermodynamic calculations. A similar set of calculations was undertaken by Janots et al. (2007) based on new thermodynamic data in the system SiO2–Al2O3–FeO–Fe2O3–MgO–CaO–Na2O–K2O–P2O5–L2O–CO2–H2O and equilibrium assemblage diagrams were presented for a system containing LaPO4 (monazite) and CaLaMgAl2(SiO4)3OH (dissakisite). The results from this and the present study substantiate the inferences of earlier workers and make it possible, within the errors of the thermodynamic data, to calculate the monazite isograd in rocks of any pelitic bulk composition.

2. Chemographic relations

The simplest chemical system in which to represent the chemographic relations between monazite and allanite is SiO2–Al2O3–FeO–CaO–H2O in excess. Additionally, phases such as chlorite, garnet, staurolite, chloritoid, cordierite, andalusite are typical. To simplify representation, this paper will first consider rocks in which an Al2SiO5 polymorph is in excess. Calcitic rocks will contain quartz and fluid (H2O) in excess. Additionally, phases such as chlorite, garnet, staurolite, chloritoid, pyrophylite, kyanite, sillimanite, andalusite are typical. To simplify representation, this paper will first consider rocks in which an Al2SiO5 polymorph is in excess. Projection from quartz, H2O and Al2SiO5 leaves four species to represent chemographically. Phase relations involving garnet will be examined initially because, as will be shown below, phase relations between monazite and allanite depend to a first order on the bulk CaO content of the rock and the composition of the garnet that is stable at the P–T conditions of interest.

In addition, metapelites also contain appreciable amounts of K, Mg, Na, and Mn. Muscovite may be a common phase. Projection removes K from consideration. Plagioclase projection removes Na. Projection from an additional AFM phase (e.g., chlorite, biotite, staurolite, chloritoid, cordierite) removes the need to represent an MgO component. MnO stabilizes garnet to lower temperatures and has the effect of shifting the P–T
conditions of garnet-bearing assemblages. The effects of MnO will be explored below. However, for the initial assessment of the chemistry these components will be neglected.

Projection from quartz, $\text{H}_2\text{O}$, and $\text{Al}_2\text{SiO}_5$ in the system $\text{CFASHPCe}$ leaves the components $\text{FeO-CaO-P}_2\text{O}_5-\text{Ce}_2\text{O}_3$ to be represented chemographically. Phases to be considered in this system include allanite, monazite, apatite, and garnet (Fig. 1). In this subsystem, garnet is very nearly a fixed composition, garnet is a solid solution between almandine and grossular, and allanite is a complete solid solution between end member allanite ($\text{CaCeFeAl}_2(\text{SiO}_4)_3\text{OH}$) and clinzoizite ($\text{Ca}_4\text{Al}_5(\text{SiO}_4)_3\text{OH}$) (Gérèr and Sorensen, 2004). Apatite ($\text{Ca}_3(\text{PO}_4)_2\text{OH}$) displays minor solid solution towards a LREE end member ($\text{Ca}_4\text{Ce}((\text{SiO}_4)(\text{PO}_4)_2\text{OH}$) (e.g., Bingen et al., 1996). Other phases that are possible include rhabdophane ($\text{CePO}_4\cdot\text{H}_2\text{O}$), which has been shown to have a highly restricted stability relative to monazite (Akers et al., 1993; see also Krenn and Finger, 2007, as a retrograde phase), and a $\text{Ce}_2\text{O}_3$ oxide phase, which has not been reported from natural occurrences.

Given these considerations, there is a single four-phase volume in the tetrahedral phase diagram of Fig. 1 comprised of apatite + garnet + alllanite + monazite, which is flanked by the three-phase planes apatite + monazite + garnet, apatite + allanite + garnet, apatite + monazite + allanite, and monazite + allanite + garnet. Of these, only apatite + monazite + garnet and apatite + allanite + garnet are considered to be relevant for the metamorphism of pelitic schists because the LREE elements are always far less abundant than Ce + Fe, eliminating garnet-absent assemblages, and $P_{\text{O}}$ is typically in higher concentration than LREE, which means most assemblages are apatite-bearing. Inasmuch as apatite is nearly ubiquitous, further projection from apatite onto the plane $\text{FeO-PO}_5/2-\text{CeO}_3$ results in the chemography shown in Fig. 2. Note that pure allanite ($\text{CaCeFeAl}_2(\text{SiO}_4)_3\text{OH}$) projects directly onto the plane $\text{PO}_5/2-\text{CeO}_3$ in this projection but the composition $\text{Ca}_2\text{Ce}_{0.13}\text{Fe}_{0.13}\text{Al}_{3.33}\text{Si}$ plots at infinity and pure clinzoizite ($\text{Ca}_4\text{Al}_5(\text{SiO}_4)_3\text{OH}$) plots on the P apex, but projected through infinity.

Several inferences can be drawn about the relative observance of allanite versus monazite in metapelites from Figs. 1 and 2. Firstly, at a specified $P$ and $T$, garnet + monazite will be observed in rocks low in Ca, whereas garnet + allanite will be observed in rocks of higher Ca (all assemblages with apatite). There should also be rocks with appropriate bulk composition to contain garnet + allanite + monazite. However, the LREE content of typical pelites is only a few tens to a few hundreds of ppm, so the assemblage garnet + allanite + monazite will only occur in rocks of a very restricted range of bulk compositions.

What is most important to recognize in Figs. 1 and 2 is that the phase volume garnet + monazite + allanite (apatite) will shift position depending on the grossular content of garnet. As will be shown below, with increasing temperature, garnet in the assemblage garnet + allanite + monazite + apatite becomes more grossular-rich. Therefore, a rock that contains garnet + allanite at low grade will lose allanite and grow monazite at higher grade, as is observed in natural parageneses. Quantification of this continuous reaction is discussed below.

Not so readily apparent in Fig. 1 is a field of two-phase assemblages garnet + apatite, which arises because of the incorporation (albeit limited) of Ce into apatite (Fig. 3). The field is irregularly shaped with the high-Ce surface being curved. Thus, it is possible at any $P$ and $T$ to have only garnet + apatite assemblages present.

3. Thermodynamic model

Quantification of the allanite–monazite phase relations requires thermodynamic data, which are not available for all phases of interest. In this study, data for the silicates are taken from the compilations of Berman (1988), with modifications described by Pattison et al. (1999), Spear and Kohn (1996), Spear and Wark (2009), and Spear and Pyle (2010). Values of entropy, volume and heat capacity for monazite and apatite have been taken from the compilations of Robie et al. (1978) and Robie and Hemingway (1995) or from oxide sums from data therein. Enthalpy of OH apatite is from Robie and Hemingway (1995) and enthalphy of monazite is from Ushakov et al. (2001). Values of $S$, $V$ and $C_P$ for allanite were computed from tabulated values in Berman (1988) and Robie et al. (1978) from the relation allanite = clinzoizite +...
1/3 almandine – 1/3 grossular + CeO$_{3/2}$ – AlO$_{3/2}$. Enthalpy values for allanite and Ce-apatite were computed from an assumed reference assemblage at 530 °C, 6 kbar (Table 1) and mixing was assumed to be ideal between allanite and apatite end members. This approach yields enthalpies that carry uncertainties directly related to the accuracy of the reference assemblage, but has the advantage of incorporating uncertainties in the activity models into the values (avoiding extrapolation from end-member tabulations). It is functionally equivalent to the applications of differential thermodynamics (the Gibbs method) described by Spear (1993) and is exact at the conditions of the reference assemblage. Data derived in this way are listed in Table 2.

In the system CFASHPCe the assemblage garnet + allanite + monazite + apatite (+ quartz + Al$_2$SiO$_5$ + H$_2$O) is divariant and P–T space can be contoured for the mole fraction of grossular (X$_{grs}$) for this assemblage (Fig. 4a). The grossular content of garnet in this assemblage increases with increasing temperature, as mentioned above, resulting in the shift in the phase compatibility diagram with temperature as shown in Fig. 4b.

Fig. 4 is sufficient to provide a qualitative understanding of the relative occurrences of monazite-bearing versus allanite-bearing assemblages. Typical bulk compositions are low in Ce$_2$O$_3$ (and other LREE) and will plot near garnet, so at low temperature the possible assemblages are Grt + Mnz + Apt, Grt + Mnz + Aln + Apt, or Grt + Aln + Apt. Apatite + Grt 2-phase assemblages are also possible (cf. Fig. 3). With increasing T, garnet in the assemblage Grt + Mnz + Aln + Apt becomes increasingly Ca-rich, the result being that monazite may appear in Grt + Aln + Apt assemblages or allanite may react out of Grt + Mnz + Aln + Apt assemblages. Because of the very low LREE

![Fig. 3. Schematic chemographic relations in the system CFASHPCe projected from quartz, H$_2$O, and Al$_2$SiO$_5$ into the volume FeO–CaO–CeO$_{3/2}$–PO$_{3/2}$ showing the stability field for the 2-phase assemblage garnet + apatite.](image-url)

**Table 1**


<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>1.0</td>
</tr>
<tr>
<td>Fluid</td>
<td>H$_2$O</td>
<td>1.0</td>
</tr>
<tr>
<td>Kyanite</td>
<td>Al$_2$SiO$_3$</td>
<td>1.0</td>
</tr>
<tr>
<td>Garnet</td>
<td>Fe$_3$Al$_2$Si$_3$O$_12$</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Ca$_3$Al$_2$Si$_3$O$_12$</td>
<td>0.2</td>
</tr>
<tr>
<td>Monazite</td>
<td>CePO$_4$</td>
<td>1.0</td>
</tr>
<tr>
<td>Allanite</td>
<td>CaCeFeAl$_2$(Si$_2$O$_3$)$_2$OH</td>
<td>0.76</td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca$_5$(PO$_4$)$_3$(OH)</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>Ca$_5$(PO$_4$)$_3$(F)</td>
<td>0.011</td>
</tr>
</tbody>
</table>

T = 530 C, P = 6000 bars.

System: SiO$_2$–Al$_2$O$_3$–FeO–CaO–H$_2$O–PO$_4$–CeO$_3$.

**Table 2**

Thermodynamic data used in this study.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Component Formula</th>
<th>H</th>
<th>S</th>
<th>V</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>f</th>
<th>g</th>
<th>v1</th>
<th>v2</th>
<th>v3</th>
<th>v4</th>
</tr>
</thead>
<tbody>
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<td>Apatite</td>
<td>OH-Apt</td>
<td>-6738500</td>
<td>390.40</td>
<td>15.96</td>
<td>387.8</td>
<td>18.11</td>
<td>12700000</td>
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<td>0.118600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CeOH-Apt</td>
<td>Ce$_4$(SiO$_4$)(PO$_4$)$_2$OH</td>
<td>-6612111</td>
<td>411.32</td>
<td>15.97</td>
<td>387.8</td>
<td>18.11</td>
<td>12700000</td>
<td>0</td>
<td>0.1186</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Allanite</td>
<td>Aln</td>
<td>-6303179</td>
<td>358.135</td>
<td>14.25</td>
<td>403.277</td>
<td>18.52</td>
<td>745.808</td>
<td>0</td>
<td>0.14494</td>
<td>-2.41×10$^{-6}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ca$_2$Al$_3$(SiO$_4$)$_3$OH</td>
<td>-6996970</td>
<td>287.1</td>
<td>13.67</td>
<td>749.17</td>
<td>6509.28</td>
<td>2380530</td>
<td>12485800</td>
<td>0</td>
<td>0.123</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Monazite</td>
<td>Mnz</td>
<td>-1967800</td>
<td>133.06</td>
<td>4.52</td>
<td>82.85</td>
<td>0</td>
<td>852650</td>
<td>0</td>
<td>0.123</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$H = a + b/(T^{0.5}) + c/T^2 + d/T^3 + f*T + g*T^2$.

Volume expression follows Berman (1988).
contents of typical pelites, the stable co-existence of allanite and monazite will occur over only a very small temperature interval. With increasing temperature, allanite-bearing assemblages should become increasingly restricted and most rocks should contain monazite, as is observed in natural parageneses (e.g., Smith and Barreiro, 1990; Wing et al., 2003; Kohn and Malloy, 2004; Corrie and Kohn, 2008).

4. Equilibrium assemblage diagrams

An equilibrium assemblage diagram (EAD, also referred to as a “pseudosection”) for the system CFASHPCe is presented in Fig. 5 that delineates the P–T fields for assemblages that contain allanite, monazite, or both. The bulk composition has elemental proportions that are similar to that of Shaw’s average pelite (Shaw, 1956; also used by Symmes and Ferry, 1992) and is listed in Table 3. The assemblage garnet + allanite + apatite is stable up to around 700 °C at a pressure around 5 kbar. Monazite then joins the assemblage and allanite reacts out within a few degrees leaving the assemblage garnet + monazite + apatite. The temperature width of the allanite–to-monazite transition depends on the bulk rock Ce content. Dotted lines in Fig. 5 show the increase in width of the allanite–monazite field with twice the amount of Ce₂O₃. Most importantly, the temperature of the transition is a first-order function of the bulk rock CaO content. The dashed lines show the location of the transition with half the CaO content of the original bulk composition.

A more realistic bulk composition must include K₂O, Na₂O, MgO, and MnO, with consideration of the additional phases muscovite, biotite, and plagioclase. Fig. 6a shows an EAD for a bulk composition similar to Shaw’s average pelite (Shaw, 1956). Only the phases quartz, fluid, muscovite, biotite, chlorite, garnet, Al₂SiO₅, apatite, allanite and monazite were considered, so equilibria involving staurolite (which would occupy a large central part of the diagram), cordierite (which would appear at low pressures, and melt (which would appear at high temperature) are not considered. This was done to simplify the calculations so as not to obscure the important accessory phase relations and does not strongly affect the conclusions. The allanite-to-monazite transition has a positive P–T slope and, depending on the pressure, occurs at approximately 400–550 °C in a rock with 2.17 wt.% CaO. A second EAD, constructed with twice the CaO content (CaO = 4.34 wt.%; Fig. 6b), depicts the allanite-to-monazite transition at around 480 °C at 2 kbar and 750 °C at 10 kbar.

It has been suggested by Wing et al. (2003) that the bulk rock Al₂O₃ content also affects the temperature of the allanite-to-monazite transition so a series of EADs with Al₂O₃ contents of 0.75, 1.25 and 1.5 times that of Shaw’s average pelite were constructed (Fig. 7). The transition from allanite to monazite is clearly a function of Al₂O₃.

Fig. 4. (a) P-T diagram contoured for XGrs for the assemblage garnet + allanite + monazite + apatite + quartz + Al₂SiO₅ + H₂O in the CFASHPCe system. (b) Pseudoternary FeO–PO₅/2–CeO₃/2 plot (projected from quartz, H₂O, Al₂SiO₅, and apatite) showing the shift in garnet composition with temperature (P = 6 kbar) in the assemblage garnet + allanite + monazite.

Fig. 5. P–T equilibrium assemblage diagram (EAD) for the system CFASHPCe with the bulk composition similar to Shaw’s average pelite (Shaw, 1956; CaO = 2.17 wt.%; Ce₂O₃ = 0.05 wt. %; see Table 3 for complete bulk compositions). Dotted lines show allanite-to-monazite transition with Ce₂O₃ = 0.1 wt.% (twice the value of the solid lines). Dashed lines show location of allanite-to-monazite transition with Ca = half the value of the solid lines (1.08 wt.% CaO).
content with the temperature of the transition decreasing (at 5 kbar) from 550 °C to 475 °C to 460 °C to 355 °C with Al₂O₃ contents of 12.43, 16.57, 20.71, and 24.85 wt.%, respectively (see Table 3 for bulk compositions).

5. Discussion

The calculations presented in this study are consistent with most inferences about the allanite-to-monazite transition in metapelitic bulk compositions. Smith and Barreiro (1990) and later Wing et al. (2003), Kohn and Malloy (2004), and Corrie and Kohn (2008), all report the major appearance of monazite at P–T conditions near the staurolite and/or Al₂SiO₅ isograd. Kohn and Malloy (2004) did not believe that allanite was the precursor but further study on the same rocks reported by Corrie and Kohn (2008) infer that either allanite must have been the precursor to the monazite, or there is some as yet unidentified source of Ce in the rocks (for example grain boundaries). The staurolite and/or Al₂SiO₅ isograd in most metapelites occurs at 525–575 °C, which is the same range as is observed for the calculated transition for a bulk composition of Shaw’s average pelite. The first order dependence of the transition on the bulk CaO content, noted by Kingsbury et al. (1993), Wing et al. (2003), and reviewed by Spear and Pyle (2002) is clear by comparing diagrams such as Fig. 6a and b.

Dependence of the transition of allanite-to-monazite on the bulk rock Al₂O₃ content is apparent in Fig. 7 as was suggested by Wing et al. (2003). However, the dependence revealed by the calculations in this paper are the opposite as was predicted by Wing et al. (2003), in which the transition was shown to have a negative slope on a plot of CaO vs. Al₂O₃ in rocks of similar grade (Wing et al., 2003, Figs. 7 and 8). This result can be inferred by considering the relationship shown in Fig. 7 in which increasing the Al₂O₃ content lowers the temperature of the allanite-to-monazite transition. All three diagrams in Fig. 7 are calculated with bulk compositions with the same CaO contents. If one were to "adjust" the transition to the same P–T conditions (e.g., the staurolite isograd at around 550 °C), this thought exercise would require adding the most CaO to the rock with the highest Al₂O₃.

**Table 3**

Bulk compositions used in calculation of equilibrium assemblage diagrams.

<table>
<thead>
<tr>
<th>CFASHPCe</th>
<th>MnNCKFMAHPCe</th>
<th>MnNCKFMAHPCe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 5 solid</td>
<td>Fig. 5 dashed</td>
<td>Fig. 5 dotted</td>
</tr>
<tr>
<td>SiO₂</td>
<td>59.77</td>
<td>59.77</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.57</td>
<td>16.57</td>
</tr>
<tr>
<td>MgO</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeO</td>
<td>5.88</td>
<td>5.88</td>
</tr>
<tr>
<td>MnO</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CaO</td>
<td>2.17</td>
<td>1.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>H₂O</td>
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<td>a</td>
</tr>
<tr>
<td>Ce₂O₃</td>
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<td>0.05</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

* Sufficient H₂O is added to ensure the assemblage is H₂O-saturated at all times.

Fig. 6. (a) P–T equilibrium assemblage diagram for the system MnNCKFMAHPCe showing the P–T conditions for assemblages stable in a bulk composition representative of Shaw's average pelite (Shaw, 1956; see Table 3 for composition). Only the phases indicated on the diagram were considered in the calculations. (b) EAD for a bulk composition similar to Shaw's average pelite with twice the CaO content. The maximum thermal stability of allanite is strongly dependent on the bulk rock CaO content.
Fig. 7. P–T EADs at three different bulk Al2O3 contents (see Table 3): (a) 0.75 times Shaw's average pelite (Al2O3 = 12.43 wt.%); (b) 1.25 times Shaw's average pelite (Al2O3 = 20.71 wt.%); (c) 1.5 times Shaw's average pelite (Al2O3 = 24.86 wt.%).

The allanite-to-monazite transition has a generally positive P–T slope and the temperature decreases with increasing Al2O3 content.
content. Therefore, these calculations reveal that a plot of the CaO vs. Al₂O₃ of rocks undergoing the transition at the same metamorphic grade should have a positive slope, rather than a negative one as suggested in the previous work.

A very similar set of calculations was performed on allanite and monazite phase relations by Janots et al. (2007), although their study was done using a La–monazite (LaPO₄) and Mg–allanite (dissaksite: CaLaMgAl₂(SiO₄)₃OH). Although the chemical system studied by Janots et al. (2007) and the present work differ considerably, the upper thermal stability of allanite from the two studies are reassuringly similar in that both show a positive P–T dependence and a maximum thermal stability at around the staurolite isograd. Janots et al. (2007) also show a diagram that quantifies the allanite-to-monazite transition over a range of CaO contents with results similar to those found here. To better compare the results of these two studies, the temperature of the allanite-to-monazite transition was calculated as a function of bulk rock CaO content for bulk compositions with different Al₂O₃ contents, as well as at two pressures (5 and 10 kbar), and the results of Janots et al. (2007) were redrawn on the same scale. In truth, the scales may be slightly different because their original plot of Ca in mole % did not specify (a) whether the composition axis was mole % Ca or CaO, and (b) whether the normalization was on a hydrous or anhydrous basis. Nevertheless, the results are quite similar, especially considering that they are representative of different chemical systems. In detail, the results of the two studies show different inflections, but overall the similarity suggests that the difference of REE in the theoretical system (Ce vs. La) or in the natural systems (La, Ce, Sm, Nd, etc) will not affect the calculated stability of these phases.

A significant difference between the results of the present study and that of Janots et al. (2007) is the presence of a low-grade stability field for metamorphic monazite. Such behavior was not encountered in the present study (there was no low temperature stability field encountered for monazite in any of the bulk compositions examined) and the reason for the discrepancy is not clear. Whether this is due to the different chemical systems studied or fundamental differences in the thermodynamic data employed is unclear, but multiple stability fields for a phase in a fixed bulk composition are not common in metamorphic systems, which typically do not show the most hydrated assemblages at intermediate P–T conditions. Nevertheless, low-grade growths of presumably metamorphic monazite, which at higher grades gives way to allanite, have been reported from natural parageneses (e.g., Smith and Barreiro, 1990; Wing et al., 2003; Janots et al., 2006, 2008). The significance of these observations is not clear, however. It is possible that the low-grade overgrowths represent a coarsening of detrital monazite, although in some examples the compositions of the overgrowths are distinctly different from the detrital cores (e.g., Janots et al., 2008). It is also possible that the monazite overgrowths form metastably relative to florencite, the latter having been reported as a precursor to allanite in high-pressure metapelites from Morocco (Janots et al., 2006). It should further be noted that not all studies of low-grade metapelites have reported low-grade metamorphic monazite as a precursor to allanite (e.g., Kingsbury et al., 1993; Kohn and Malloy, 2004; Tomkins and Pattison, 2007; Corrie and Kohn, 2008) so the significance of the reported occurrences must remain uncertain.

6. Conclusions

The results presented here should not be applied uncritically. Rather, they should serve as a template for further calculations on specific bulk compositions of interest. Further refinement of the thermodynamic data of accessory phases, especially allanite, monazite, and apatite are critical requirements for future improvements. In addition, it is essential that a more thorough assessment of the relative concentrations of the various trace elements in all silicates be made. Even though the concentrations may be low, it is possible that some phases under some conditions contain enough of a particular trace element to affect the stability of an accessory phase in a major way. A prime example is Y in garnet, which affects xenotime and monazite stability (e.g., Spear and Pyle, 2010), or Zr in a melt phase (e.g., Kelsey et al., 2008), which affects zircon stability. It is also possible that other, as yet unappreciated phases such as REE oxides, hydroxides, or phosphates are important reactants. The significance of rhabdophane has been downgraded (e.g., Akers et al., 1993), and searches for REE oxide phases using X-ray mapping have yielded negative results (e.g., Kohn and Malloy, 2004). Calculations with a phase of the composition CeO₂ were made during the course of the present study, but the stability field was at temperatures too high to be of importance during metamorphism. However, it is not clear that the thermodynamic data for this compound are of sufficient quality to permit ruling out CeO₂ or similar oxides as a potential source for LREE. Furthermore, it is possible that a significant part of the mass balance of accessory phases occurs between the phases and grain boundary reservoirs, as has been suggested by Corrie and Kohn (2008). Such a possibility is currently beyond our ability to model theoretically, but new instrumentation such as analytical high resolution TEMs or atom probes may permit grain boundary compositions to be assessed in natural samples in the near future.

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