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Monazite solubility in hydrous silicic melts at high pressure conditions relevant to subduction zone metamorphism

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A B S T R A C T

Critical to any application of accessory phase stability to subduction zone thermal structure and processes is knowledge of the thermodynamic stability of these minerals in different types of subducted rock, their solubility in the presence of fluids, and the extent to which they fractionate trace element ratios of interest. This study focuses on monazite, which is the principal carrier of light rare earth elements (LREE) and thorium (Th) in CaO-poor subducted sediments. Relatively little is known about the mechanism of monazite dissolution in high-pressure hydrous melts (or supercritical fluids), yet monazite and allanite (the principal carrier of LREE and Th in oceanic basalts and some CaO-rich sediments) solubility has been used recently to quantify subducted slab-top temperatures (Plank, T., Cooper, L.B., Manning, C.E., 2009. Emerging geothermometers for estimating slab surface temperatures. Nature Geosci. 2, 611–615).

We have studied monazite solubility at subduction zone conditions (3 GPa, $T \geq 800$ °C) in hydrous sediment-melting experiments. Experimental results highlight the important role that phosphorous exerts on monazite solubility in hydrous silicic melts at high pressure. Thermodynamically this corresponds to a case where monazite dissolves predominantly as its dissociated constituent ions ($LREE^{3+}$ and PO_4^{3-}). This is in contrast to monazite solubility in granitic melts at low pressures (0.2 GPa) where it appears to dissolve predominantly as associate $LREEPO_4$ species, such that its solubility is essentially independent of dissolved phosphorous. Our results have implications for monazite-based thermometry, as the error introduced by not taking phosphorous into account in high-pressure fluids can amount to >100 °C.

1. Introduction

1.1. General

The distinctive trace element geochemistry of subduction zone magmas is primarily a consequence of the interaction between a fluid phase, loaded with fluid-mobile elements derived from subducted oceanic lithosphere, and the overlying mantle wedge. Just what elements are fluid-mobile in subduction zones depends to a large extent on the nature and chemistry of the fluid phase, and the temperature of the subducting slab (e.g. Ayers and Watson, 1991; Hermann and Rubatto, 2009; Kessel et al., 2005; Manning, 2004; Manning et al., 2010; Spandler et al., 2007; Stalder et al., 2000; Wohlers et al., 2011).

Recently, attention has focussed on the stability of accessory residual minerals (allanite in basalts, monazite in sediments, e.g. Ayers et al., 2002; Hermann, 2002; Hermann and Rubatto, 2009; Klimm et al., 2008; Skora and Blundy, 2010; Sorensen, 1991; Terry et al., 2000; Tribuzio et al., 1996) that can retain the light rare earth elements (LREE), uranium (U) and thorium (Th) in subducted lithologies. Plank et al. (2009) have suggested that allanite and/or monazite solubility in hydrous silicic fluids derived from the subducted slab can be used to estimate slab-top temperatures. Here we focus on monazite. Relatively little is known about the mechanism of monazite dissolution in hydrous melts (or supercritical fluids) at high-pressure conditions, and related consequences for monazite-based thermometry. We first review some aspects of monazite solubility that have been discussed in the literature. We then present a suite of experimental results that highlights the important role that phosphorous exerts on monazite solubility in high-pressure hydrous melts.

1.2. Monazite solubility—background

Monazites are REE-phosphates with the general formula $\Sigma LREEPO_4$, where $\Sigma LREE$ (called LREE hereafter) denotes any lanthanide from La to Sm, which occur commonly in evolved (granitic) igneous rocks, and high pressure/temperature metasediments. Monazite shows solid solution with huttonite ($ThSiO_4$) and brabantite ($Ca_{0.5}Th_{0.5}PO_4$) (e.g. Bowie and Horne, 1953; Spear and Pyle, 2002). The solubility of monazite in hydrous fluids (e.g. Ayers and Watson, 1991; Poitrasson et al., 2004; Pourtier et al., 2010; Schmidt et al., 2007; Tropper et al., 2011) and silicate melts (e.g. Duc Tin, 2007; Hermann and Rubatto, 2009; Keppler, 1993;

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Montel, 1986; Montel, 1993; Rapp and Watson, 1986; Rapp et al., 1987; Skora and Blundy, 2010) has been studied experimentally at a range of crustal pressure and temperatures.

Monazite solubility experiments typically assume that monazite will dissolve congruently into a fluid or melt phase until it has reached saturation level, and vice versa (e.g. Rapp and Watson, 1986). It has further been assumed that solubilities of accessory phases are governed by their "essential structural constituents (ESCs)", as defined in terms of the activity of a single, low-abundance component that is essential to the structure of the mineral of interest (Hanson and Langmuir, 1978; Rapp and Watson, 1986; Sun and Hanson, 1975). In case of monazite, ESCs are, collectively, the LREE (expressed in weight or molar fraction), rather than PO_4^{3-} (Rapp and Watson, 1986). Implicit in this assumption is that other components are either present in high enough concentrations to stabilise monazite (e.g. PO_4^{3-}), or are not essential for monazite (e.g. CaO, SiO_2, ThO_2, etc.; Rapp and Watson, 1986). It has hence been concluded that the amount of dissolved LREE in fluids or melts equates to the solubility of monazite.

Having established a means of quantifying monazite solubility, attention has focussed on identifying a set of independent parameters that influence it. Dissolved H_2O (Rapp and Watson, 1986) and melt composition (Duc Tin, 2007; Montel, 1986; 1993; Rapp et al., 1987) appear to have major effects on monazite solubility, in addition to temperature (Rapp and Watson, 1986). These parameters were combined by Montel (1993) to derive a monazite geothermometer best suited to evaluating monazite saturation in granitic magmas crystallised at crustal pressures. We are not aware of any comprehensive study on the effect of pressure on monazite solubility, but other accessory phase solubility studies suggest that it is likely to be modest compared to other parameters (e.g. Xiong et al., 2009). Lastly, it has been found that fluorine has no significant effect on monazite solubility in water-saturated, haplogranitic melts at 2 kbar (Keppler, 1993).

1.3. Monazite solubility-dissolution reactions

Dissolution of any chemical compound into a solvent can be roughly subdivided into 2 end-member scenarios: (a) simple dissolution (e.g.

$$\mathrm{LREEPO_4}_{\ \mathrm{solid}} \xleftrightarrow{K_{(1)}} \mathrm{LREEPO_4}_{\ \mathrm{aqueous}} \tag{1}$$

$$K_{(1)} = \frac{a(\mathrm{LREEPO_4})_{\mathrm{aqueous}}}{a(\mathrm{LREEPO_4})_{\mathrm{solid}}}, \tag{2}$$

where a denotes activity and K denotes the equilibrium constant; $K_{(1)}$ relates to what we will refer to as "dissolution as associated species"), and (b) dissolution with dissociation (e.g.

$$\mathrm{LREEPO_4}_{\ \mathrm{solid}} \xleftrightarrow{K_{(2)}} \mathrm{LREE^{3+}}_{\mathrm{aqueous}} + \mathrm{PO_4^{3-}}_{\ \mathrm{aqueous}} \tag{3}$$

$$K_{(2)} = \frac{a\left(\mathrm{LREE^{3+}}\right)_{\mathrm{aqueous}} * a\left(\mathrm{PO_4^{3-}}\right)_{\mathrm{aqueous}}}{a(\mathrm{LREEPO_4})_{\mathrm{solid}}}, \tag{4}$$

$K_{(2)}$ denotes to what we will refer to as "dissolution as dissociated species"). Many compounds dissolve stepwise into fluids (e.g.

$$\mathrm{LREEPO_4}_{\ \mathrm{solid}} \xleftrightarrow{K_{(1)}} \mathrm{LREEPO_4}_{\ \mathrm{aqueous}} \xleftrightarrow{K_{(3)}} \mathrm{LREE^{3+}}_{\mathrm{aqueous}} + \mathrm{PO_4^{3-}}_{\ \mathrm{aqueous}}, \tag{5}$$

with $K_{(1)}$ as defined above (Eq. (2)) and

$$K_{(3)} = \frac{a\left(\mathrm{LREE^{3+}}\right)_{\mathrm{aqueous}} * a\left(\mathrm{PO_4^{3-}}\right)_{\mathrm{aqueous}}}{a(\mathrm{LREEPO_4})_{\mathrm{aqueous}}}), \tag{6}$$

and both associated and dissociated species can coexist in the fluid.

One important difference between case (a) and (b) is that in case (b), the common ion effect must play a role in that independent change of the activity of one of the ions requires opposite change of the other to keep the product constant. Hence, if this dissolution reaction pertains to monazite, $LREE^{3+}$ and PO_4^{3-} must vary inversely, and measuring only the ESCs (LREE in case of monazite) will not suffice to characterise its solubility.

It is immediately evident from Eqs. (1)–(6) that a thermodynamically correct treatment of monazite dissolution needs knowledge on the activities of a) LREE and phosphorous species in melt and b) LREE in monazite. There are currently no activity expressions for the melt. As all of our experiments are at or close to saturation, we will assume a Raoult's Law standard state whereby the activity of component i (a_i) is equal to the molar fraction concentration of i. In the simple case where the gram formula weight (GFW) of the melt and crystal remain approximately constant then weight fractions can be used instead of molar fractions, with the ratio of GFWs subsumed into the equilibrium constant. This device enables us to work with the more tractable weight fraction concentrations, although the GFW ratio should be explicitly included in any attempt to match equilibrium constants to thermodynamic data. We acknowledge that actual activities may be different due to variation in the GFW of the melt (negligible in our experiments) and complexation of LREE and P with other melt components (e.g. Flynn and Burnham, 1978; Wolf and London, 1995). Furthermore, we note that the exact dissolution reactions may look different in reality, and that different dissolution reactions typically occur simultaneously (e.g. Poitrasson et al., 2004). In addition, we shall ignore any other elements that may be required for the actual complexation of monazite in the liquid phase (e.g. OH^-, alkalis, etc., e.g. Poitrasson et al., 2004). While this precludes a fully quantitative treatment (e.g. determination of true equilibrium constants), this does not impair evaluation of the two different dissolution mechanisms (case (a) versus (b)), provided that the experiments used have broadly similar P–T–X conditions. In the absence of available monazite activity models, we assume ideal behaviour such that

$$a\left(\mathrm{LREEPO_4^{mon}}\right) = X_{\mathrm{LREE}}^{\mathrm{mon}}, \tag{7}$$

which is calculated as

$$X_{\mathrm{LREE}}^{\mathrm{mon}} = \frac{\mathrm{apfu(LREE)^{mon}}}{\mathrm{apfu(LREE+Th)^{mon}}}\ (\mathrm{apfu = atoms\ per\ formula\ unit}). \tag{8}$$

Hence, taking into account the assumptions discussed above, we can write a reaction (9) that reflects the concentration of LREE measured in the melt to be the sum of dissolved dissociated and associated species:

$$x\left(\mathrm{LREE_{melt}^{tot}}\right) = x\left(\mathrm{LREEPO_4^{melt}}\right) + x\left(\mathrm{LREE^{3+\,melt}}\right), \tag{9}$$

where x denotes weight fraction concentration, and $LREE_{melt}^{tot}$ total denotes the total concentration of LREE that is eventually measured, in ppm. Note that it is a simple matter to prove that $K_{(2)} = K_{(1)} {}^* K_{(3)}$ and we can therefore treat reactions (1) and (3) as occurring in parallel for the following calculations. Substituting Eqs. (2) and (4) into Eq. (9) and rearranging yields equation

$$\frac{x\left(\mathrm{LREE_{melt}^{tot}}\right)}{X_{\mathrm{LREE}}^{\mathrm{mon}}} = K_{(1)} + \frac{K_{(2)}}{x\left(\mathrm{PO_4^{3-\,melt}}\right)}, \tag{10}$$