Monazite and xenotime are important accessory minerals in metasediments because they host REE and are useful for geochronology and geothermometry. It is therefore essential to understand their behavior during metasomatic processes that attend metamorphism and subduction. In order to constrain the solubility of monazite and YPO$_4$ xenotime at high pressure and temperature, we carried out weight-loss experiments on synthetic single crystals of CePO$_4$ (monazite) and YPO$_4$ (xenotime) using hydrothermal piston-cylinder methods at 800 °C and 1 GPa, in H$_2$O and H$_2$O–NaCl fluids. Results indicate that CePO$_4$ and YPO$_4$ dissolved congruently, and that their solubilities in pure H$_2$O are very low: 0.04 ± 0.04 and 0.25 millimolar, respectively. The solubility of CePO$_4$ rises to an increasing extent with added NaCl, to 7.94±0.07 millimolar at 50 mol% NaCl. In contrast, the solubility of YPO$_4$ rises to a decreasing degree with increasing NaCl, to 4.36±0.08 millimolar at 50 mol% NaCl. Best fit equations for the solubilities of the two phases are

$$m_{\text{CePO}_4} = 3.56 \cdot 10^{-7} + 5.82 \cdot 10^{-3} X_{\text{NaCl}} + 1.97 \cdot 10^{-2} X_{\text{NaCl}^2}$$

and

$$m_{\text{YPO}_4} = 2.48 \cdot 10^{-4} + 1.26 \cdot 10^{-2} X_{\text{NaCl}} - 8.89 \cdot 10^{-3} X_{\text{NaCl}^2}$$

The solubility of YPO$_4$ is greater than that of CePO$_4$ at NaCl mole fractions ($X_{\text{NaCl}}$) of 0.00–0.27. The solubility enhancement behavior implies that Ce dissolves as anhydrous chloride complexes, whereas Y forms mixed Cl–OH solutes. The results provide a simple mechanism for redistributing REE and Y in deep-crustal and upper mantle environments. The H$_2$O/REE ratio inferred for subduction-zone melts and silicate-rich fluids can also be produced by a CePO$_4$-saturated fluid with $X_{\text{NaCl}} = 0.1$. In addition, neutral-pH H$_2$O–NaCl fluids can transport substantial REE and Y, obviating the need to invoke highly acid solutions in environments where they are unlikely.

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1. Introduction

Monazite and xenotime are important accessory phases in metamorphic and igneous rocks (e.g., Spear and Pyle, 2002). Occurring in a range of metamorphic lithologies and settings, these phosphates have great utility as prograde index minerals that can be used for geochronology (e.g. Harrison et al., 2002; Wing et al., 2003; Kohn and Malloy, 2004; Corrie and Kohn, 2008; Janots et al., 2008, 2009). They represent important reservoirs for rare-earth elements (REE), and the exchange of REE between orthophosphates and silicates such as garnet provides information about metamorphic history (Gratz and Heinrich, 1997; Andrews and Heinrich, 1998; Pyle and Spear, 1999, 2000; Pyle et al., 2001). REE orthophosphates also play an important role in controlling REE, U and Th distribution during granitic crystallization (Overstreet, 1967; Miller and Mittlefehldt, 1982; Montel, 1986, 1993; Rapp and Watson, 1986; Cuney and Friedrich, 1987). Their high durability and resistance to metamictization make the REE phosphates potential hosts for nuclear waste disposal (e.g., Boatner and Sales, 1988; Ewing, 2001; Read and Williams, 2001; Boatner, 2002; Ewing and Wang, 2002).

Experimental studies of monazite and xenotime solubility in H$_2$O show that solubilities rise with pressure and temperature, but are generally very low over a wide range of igneous and metamorphic
conditions unless pH is acidic or temperatures are extremely high (e.g., Wood, 1990a;b; Wood and Williams-Jones, 1994; Haas et al., 1995; Devidal et al., 1998; Poitrasson et al., 2004; Cetiner et al., 2005; Schmidt et al., 2007; Pourtier et al., 2010).

The low monazite and xenotime solubilities returned by experimental studies make it difficult to explain their natural associations with metasomatic features in igneous and metamorphic rocks, such as hydrothermal alteration assemblages, veins and skarns (Cesbron, 1989; Philippot and Selverstone, 1991; Bingen et al., 1996; Gieré, 1996; Poitrasson et al., 1996, 2000; Townsend et al., 2000; Seydoux-Guillaume et al., 2002; Roland et al., 2003; Hetherington and Harlov, 2008; Bosse et al., 2009). Either fluid flux must be generally high enough to mobilize relatively insoluble essential constituents, or the pH must in every case be acidic. An alternative mechanism for the dissolution and transportation of orthophosphate components is a high alkali halide concentration in the fluid phase. It has been proposed that REE (and by extension, Y) mobility may be enhanced by dissolved halogens (Pan and Fleet, 2002; Schmidt et al., 2007; Antignano and Manning, 2008a; Pourtier et al., 2010). In a wide range of crustal and mantle fluids, the halogens are present in solution as dissolved alkali-halides — in some cases as highly concentrated brines (e.g., Touret, 1985, 2001; Markl and Bucher, 1998; Markl et al., 1998). For example, alkali-halide brines play an important role in mass transport and mineral-fluid-melt phase equilibria in the lower crust (e.g., Newton et al., 1998; Yardley and Graham, 2002; Newton and Manning, 2010; Rapp et al., 2010). In addition, subduction-zone fluids from some environments may also contain significant concentrations of dissolved salts (e.g., Philippot and Selverstone, 1991; Selverstone et al., 1992; Nadeau et al., 1993; Scambelluri et al., 1998; Scambelluri and Philippot, 2001). High NaCl concentrations have also been proposed as a mechanism for explaining trace element abundances in arc magmas (Keppler, 1996).

In this study, we investigated the hypothesis that dissolved NaCl influences monazite and xenotime solubilities. We report new measurements of CePO₄ monazite and YPO₄ xenotime solubility in H₂O and H₂O–NaCl at 800 °C and 1.0 GPa, in order to put experimental constraints on the dependence of REE and Y solubility on XNaCl at fixed P–T conditions. The data indicate that CePO₄ and YPO₄ have a very low solubility in H₂O, that NaCl enhances solubilities, and that different dependences of monazite and xenotime solubility on the NaCl content implies contrasting complexing behavior for Ce and Y in fluids. In the presence of NaCl, geologic fluids will have a high capacity to dissolve and transport HREE and to a certain extent LREE at high P and T.

2. Experimental methods

Most experiments used synthetic crystals of CePO₄ monazite and YPO₄ xenotime. Crystals of CePO₄ (monazite) and YPO₄ (xenotime) were grown from a very fine CePO₄ or YPO₄ precipitate thoroughly mixed dry with a Pb-free flux (Na₂CO₃;MnO₂ ≈ 1:3). The CePO₄ or YPO₄ were synthesized by mixing stoichiometric amounts of REE (NO₃)₃ · 6H₂O and (NH₄)₂HPO₄ in solution. The resulting precipitate was allowed to settle and the excess fluid poured off. The precipitate was then dried and ground up. Twenty grams of mixed flux with 0.8 g precipitate was packed in a loosely covered Pt crucible and taken up to 1200 °C at 1 atm. The molten flux was “soaked” at 1200 °C for 15 h, which was then cooled down to 870 °C with a cooling rate of 3 °C per hour (Cherniak et al., 2004). This resulted in the nucleation and growth of 0.1 to 5 mm size euhedral CePO₄ or YPO₄ crystals at the bottom of the Pt crucible.

Small crystals (0.35–3.7 mg) optically free of flux–melt inclusions were selected for the experiments. One run used natural monazite from a beach sand in Cleveland Co, North Carolina (Ward’s collection #192). Its chemical composition is given in Table 1. In each experiment a single crystal was placed in an inner Pt envelope or a 1.6 mm OD Pt capsule. To facilitate H₂O penetration while ensuring crystal containment during experiments, the encapsulating material was lightly cramped and perforated two to four times with a needle. The inner capsule precisely weighed quantities of NaCl and H₂O were then placed in an outer 3.5 mm OD Pt capsule with a 0.20 mm wall thickness (Table 1). The capsule was then sealed by arc welding. The double capsule assembly was held at 115 °C for ≥3 h to check for leakage.

All experiments were conducted in an end-loaded, piston-cylinder apparatus using 25.4 mm diameter graphite–NaCl furnace assemblies (Bohlen, 1984; Manning and Boettcher, 1994). Each capsule was placed horizontally in the furnace, packed in NaCl, and covered with a piece of Pt foil to prevent puncture by the thermocouple. Temperature was monitored and controlled using Pt/Pt₀.₃Rh₁₀ thermocouples (± 3 °C estimated precision). Pressure was monitored using a Heise gauge (± 0.01 GPa estimated precision).

At the end of each experiment, power to the apparatus was cut, causing quench to <100 °C in ≤30 s. After quenching, the outer capsule was pierced with a needle, dried for 15 min at 115 °C, and then 15 min at 400 °C. The capsule assembly was then opened and inspected, and the crystals extracted, cleaned and weighed. Comparison of H₂O weight before and after experiments showed that there was no significant change during runs (+0.5 to −0.3%; Table 2). Solubilities were calculated using H₂O added to an experiment (“H₂O in”, Table 2). The intrinsic oxygen fugacity of the experimental apparatus at these conditions is near the Ni–NiO buffer (Newton and Manning, 2005), so Ce can be assumed to be trivalent. All run products were examined optically with a binocular microscope; selected run products were examined with a scanning electron microscope.

Reported weights represent the average of three replicate weighings, with uncertainties determined by repeated weighings of a standard. We used a Mettler UMX2 ultra-microbalance (1σ = 0.2 µg) to determine crystal weight; all other weighings were done on a Mettler M3 microbalance (1σ = 2 µg). Uncertainties in CePO₄ and YPO₄ concentrations are reported as 1σ and reflect propagated weighing errors only.

3. Results

Results are given in Table 1. Run products included partly dissolved starting crystals (Figs. 1 and 2) and fine-grained, white or colorless quench

<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>Average composition of natural monazite (wt.%).</td>
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<tr>
<td>------------------------------------------</td>
</tr>
<tr>
<td>P₂O₅</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>ThO₂</td>
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<tr>
<td>UO₂</td>
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<td>Y₂O₃</td>
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<td>Ce₂O₃</td>
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<td>CaO</td>
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<td>PbO</td>
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<tr>
<td>F</td>
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<tr>
<td>Total (−O=O)</td>
</tr>
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Explanation: Mean of 5 monazite analyses determined by wavelength-dispersive electron microprobe analysis using a Cameca SX50 at the University of Massachusetts, Amherst. Operating conditions included a focused 1 µm beam diameter, 15 kV accelerating voltage, and 15 nA beam-current. Standards were cheralite (Th), UO₂ (U), synthetic phosphates (Y + REE), plagioclase (Si), fayalite (Fe), pyrite (S), fluorapatite (Ca and P), synthetic fluorides (Sr and F), chlorides (Cl), and GaAs (As). Data reduction employed the Cameca PAP correction procedure. Al₂O₃, La₂O₃ and Fe₂O₃, S, As and Cl were below detection limit.
solids. Only minor quench was observed in the H$_2$O–NaCl experiments (Figs. 1D, 2C). The original grains displayed rounded edges and, in some cases, significant new subhedral octahedral overgrowths (Fig. 1B). The absence of any residual crystals on grain surfaces indicates that CePO$_4$ and YPO$_4$ dissolve congruently in H$_2$O–NaCl.

Run duration necessary to attain equilibrium was determined in two experiments at 800 °C, 1 GPa and X$_{NaCl}$ = 0.1 (Table 1). Experiments of 12 h (Mnz-2) and 90 h (Mnz-20) gave the same solubility of respectively 0.00086 and 0.00093 m, within 1σ propagated weighing uncertainty of 4 × 10$^{-5}$ m. Attainment of constant solubility within 12 h is consistent with equilibration rates in other solubility measurements at high T and P (e.g., Caciagli and Manning, 2003; Tropper and Manning, 2005). In addition, Schmidt et al. (2007) carried out in-situ dissolution experiments in a diamond anvil cell in the system monazite–H$_2$O–HCl ± NaCl and found that equilibrium between fluid and crystal was attained in 50 min at temperatures of ≥ 300 °C.

Starting synthetic xenotime and monazite crystals were carefully screened to avoid grains with visible flux–melt inclusions. However, in several cases, examination of partially dissolved monazite crystals after runs revealed pits on the surface (Fig. 1C). These pits are interpreted to be sites of undetected flux–melt inclusions, from which the inclusion material was dissolved into the fluid. Preferential dissolution of flux–melt inclusions where they intersect the dissolving crystal surface yields a higher apparent solubility. The effect is expected to be greatest at low X$_{NaCl}$ where monazite solubility is lowest. One experiment in pure H$_2$O revealed possible etch pits during post-mortem examination, and was discarded. However, at high X$_{NaCl}$ (Fig. 1C), the much greater solubility means that any dissolution of a minute mass of inclusion material does not contribute significantly to the measured solubility. This interpretation is supported by the fact that experiment Mnz-19, with trace inclusions (Fig. 1C), returned a solubility consistent with the trend defined by experiments at higher and lower NaCl content (Fig. 3), in which no evidence for flux–melt inclusions was noted.
The experimental results at 800 °C and 1 GPa indicate very low CePO$_4$ and YPO$_4$ solubilities in H$_2$O of 0.04±0.03 millimolal/kg H$_2$O and 0.25±0.04 millimolal/kg H$_2$O (Table 1). The solubility of CePO$_4$ in H$_2$O is $<3\sigma$ of the weighing error and thus below the nominal detection limit of 0.09 millimolal.

The solubility of CePO$_4$ in H$_2$O–NaCl fluids at 800 °C, 1 GPa, increases with increasing NaCl, to 7.94±0.07 millimolal/kg H$_2$O at $X_{NaCl}=0.498$ (Fig. 3). This corresponds to an increase of ~200 times over the investigated range. Weighted least-squares regression of the data to a second-order polynomial gives:

$$m_{CePO_4} = 3.56 \cdot 10^{-5} + 5.82 \cdot 10^{-3}X_{NaCl} + 1.97 \cdot 10^{-2}X_{NaCl}^2$$  \hspace{1cm} (1)$$

where $m_{CePO_4}$ is CePO$_4$ molality ($R^2=0.998$). The fit was forced through the measured pure-H$_2$O value to facilitate assessment of the solubility enhancement (see below). Given that this point is below the nominal detection limit of 0.09 millimolal, an alternative approach is to set this datum at the midpoint between 0.00 and 0.09 millimolal, with equal probability of any solubility between these limits. The best fit under this scenario returns a constant of $9.85 \times 10^{-5}$ millimolal with $R^2$ remaining at 0.998.

In contrast to CePO$_4$, the solubility of YPO$_4$ in H$_2$O–NaCl at 800 °C, 1 GPa, initially increases steeply with increasing NaCl, indicating that YPO$_4$ solubility is greater than that of CePO$_4$ in H$_2$O-rich fluids. However, the rise in YPO$_4$ solubility with salinity decreases with increasing $X_{NaCl}$. The different dependence on NaCl concentration causes CePO$_4$ and YPO$_4$ to be roughly two times more soluble at $X_{NaCl}=0.5$, the highest salinity investigated (Table 2; Fig. 3). Weighted least-squares regression of the data to a second-order polynomial gives:

$$m_{YPO_4} = 2.48 \cdot 10^{-4} + 1.26 \cdot 10^{-2}X_{NaCl} - 8.89 \cdot 10^{-1}X_{NaCl}^2$$  \hspace{1cm} (2)$$

where the fit is again forced through the pure H$_2$O datum ($R^2=0.992$).

The solubility of a natural monazite at $X_{NaCl}=0.3$ was found to be 4.8±0.5 millimolal. This is higher than the solubility of CePO$_4$ (3.33±0.05 millimolal) at the same $X_{NaCl}$. The difference is most likely due to the presence of additional, soluble components (e.g., Nd, La, Th, U, Si, and Ca) in the natural monazite.

Fig. 2. Backscatter electron (BSE) images of the YPO$_4$ reaction products after the solubility experiments. (A) YPO$_4$ crystal after dissolution in $X_{NaCl}=0.2$ fluid [Xnt-7], showing subtle dissolution grooves. (B, C) YPO$_4$ crystal from experiment Xnt-5, at $X_{NaCl}=0.3$, displaying strong dissolution-patternning on crystal faces (B) and fine quench crystals (C). (D) YPO$_4$ crystal after dissolution in $X_{NaCl}=0.5$ fluid, showing dissolution grooves [Xnt-13].

Fig. 3. Orthophosphate molality versus $X_{NaCl}$ at 800 °C and 1 GPa. Molal solubility of natural monazite was calculated assuming congruent dissolution. The error bars are 2\sigma and are calculated based on the weighing uncertainties. The solid lines are the fitted solubilites from Eqs. (1) and (2).
4. Discussion

4.1. Solubility in H₂O

We find that YPO₄ is at least 1.5 times more soluble than CePO₄ in pure H₂O at 800 °C and 1 GPa. This result is in nominal conflict with the general observation that monazite is more common than xenotime in hydrothermal veins and other metasomatic features, which implies greater solubility of LREE relative to HREE and Y (e.g., Schmidt et al., 2007). However, REE and Y dissolution in natural fluids are controlled by ligands other than H₂O or phosphate, such as chloride, fluoride, sulfate, and aluminosilicates, all of which can be expected to occur in varying proportions. Consequently, experimental results obtained using pure H₂O do not necessarily give useful insights into the behavior of these minerals in metasomatic contexts.

Comparison of previous high P–T experimental monazite solubility data with the results from this investigation reveals substantial differences (Fig. 4). Results from solutions with near-neutral pH and up to 4 molal NaCl (XNaCl=0.07) are included in the comparison. Despite substantial scatter, the combined 0.2 GPa data set of Gibert and Montel (1996) and Pourtier et al. (2010) on NdPO₄ give the highest solubility in H₂O. Solubilities were measured either by crystal weight-loss or by analysis of quench fluid by an isotopic-dilution method. An experiment at 600 °C, 0.5 GPa in dilute 0.2 m NaCl yielded a solubility similar to that at 0.2 GPa at the same T. Ayers and Watson (1991) determined the solubility of natural monazite by weight loss at 1.0–2.8 GPa and 800–1100 °C, and also found no pressure dependence of solubility. However, Fig. 4 indicates that their solubility values are lower than would be predicted by extrapolation of a linear fit to the 0.2 GPa data of Gibert and Montel (1996) and Pourtier et al. (2010). Schmidt et al. (2007) measured solubility of monazite and xenotime at 800 °C and 2.0 GPa in a hydrothermal diamond-anvil cell by synchrotron-radiation X-ray fluorescence. Most experiments were done using acid solutions. However, one experiment on LaPO₄ in 4 m NaCl (XNaCl = 0.07) at 800 °C and 1.1 GPa gave La concentrations at or below the detection limit of 0.6 millimolal. Assuming that LaPO₄ has a similar solubility in NaCl-bearing solutions as a function XNaCl as CePO₄ (Eq. (1)), their measurement corresponds to a pure H₂O solubility of 0.15 millimolal (Fig. 4). This is similar to the CePO₄ solubility measured at the same P and T in the present study (0.045 ±0.045 millimolal), but lower than our YPO₄ solubility (0.25 ±0.04 millimolal). The very low solubilities obtained in this study in pure H₂O is supported by the trends with XNaCl. Even if we had not measured CePO₄ or YPO₄ solubility in pure H₂O, extrapolation to pure H₂O from the NaCl-bearing experiments would give a solubility similar to what we measured.

Taken together our results and those of Schmidt et al. (2007) imply substantially lower REE- or Y-phosphate solubility in pure H₂O than do the results of Ayers and Watson (1991), Gibert and Montel (1996) and Pourtier et al. (2010).

Possible reasons for the disparities in Fig. 4 include solubility contrasts between natural and synthetic minerals, intrinsic differences in the solubilities of the LREE and Y, differences in pressure, and discrepancies arising from varying experimental methods or starting materials. It is extremely unlikely that different solubilities of La, Ce, Nd and Y can account for the range of results given in Fig. 4. The very similar geochemical behavior of the REE and Y translate to only subtle solubility differences in a given fluid (e.g., Wood and Williams-Jones, 1994; Haas et al., 1995). This is supported by results of Schmidt et al. (2007) on a natural monazite, in which La and Nd were fractionated from Ce by 12% and 5%, respectively, in a 200 °C, 0.1 GPa, experimental fluid. In contrast, LaPO₄, CePO₄ and NdPO₄ solubilities in the high PT experimental studies differ by up to several orders of magnitude at any temperature. Similarly, a strong P dependence is not a plausible explanation as the required pressure dependence is negative, the opposite of that found for other oxide minerals (Dolejš and Manning, 2010). Moreover, where individual studies report solubilities at the same T and fluid composition but varying P (Ayers and Watson, 1991; Pourtier et al., 2010), any permissible P dependence is less than the uncertainties of the results.

Solubility results from synthetic orthophosphates involving a single cation should probably not be compared to those on natural monazite because of the presence of additional, soluble cations in the latter. At the same P, T, and fluid composition, we found that natural monazite was substantially more soluble than CePO₄. In addition, the large capsule geometry used by Ayers and Watson (1991) has been shown to promote growth of new crystals, which can be misinterpreted as quench. This problem evidently plagued their experiments on rutile and apatite (Tropper and Manning, 2005; Antignano and Manning, 2008a;b; Manning et al., 2008), though it is not clear that the same was true for monazite. Nevertheless, the combination of natural monazite and large-capsule geometry should conspire to produce apparent solubilities that are higher than those of synthetic monazites such LaPO₄₆, or CePO₄₆.

Because the capsule geometry and use of natural monazite in the Ayers and Watson (1991) study likely yielded apparent solubilities that were too high, their data should be treated as an upper bound. The maximum solubilities obtained in their study along with the results from Schmidt et al. (2007) and this work, are all lower than the measurements and/or extrapolated fit at 0.2 GPa from Gibert and Montel (1996) and Pourtier et al. (2010). This suggests an important difference between techniques or materials. Both of the latter studies used flux-grown NdPO₄ but Pourtier et al. (2010), using an isotopic-dilution technique, showed that weight-loss and quench-fluid analysis gave similar results. Barring a combination of flux–melt inclusions and a systematic error in the isotopic-dilution method, it is not clear why the results of these studies are so discrepant.

In summary, we find that CePO₄ and YPO₄ are only sparingly soluble in pure H₂O at high P and T. This is consistent with the results...
of Schmidt et al. (2007) on LaPO4. The use of natural monazite and possible material redistribution during experiments probably accounts for the greater solubilities of Ayers and Watson (1991) compared to this work and Schmidt et al. (2007). The solubilities returned by these studies as a group are lower at a given T than the solubility of NdPO4 reported by Gilbert and Montel (1996) and Pourtier et al. (2010); however, the reason for the discrepancy is not clear and additional experiments are required to resolve this issue.

4.2. Solubility in H2O–NaCl

The solubilities of CePO4 and YPO4 at 800 °C and 1 GPa increase with rising \( X_{\text{NaCl}} \), but the dependence of relative solubility on salinity differs (Fig. 3). The increase in CePO4 solubility with NaCl concentration is such that \( d^2 m_{\text{CePO}_4} / dX_{\text{NaCl}}^2 \) is positive, similar in form to apatite, fluorate, calcite and anhydrite, as reported by Antignano and Manning (2008a), Tropper and Manning (2007), Newton and Manning (2002) and Newton and Manning (2005), respectively. In contrast, YPO4 solubility increases such that \( d^2 m_{\text{YPO}_4} / dX_{\text{NaCl}}^2 \) is negative, similar to the behavior of corundum, wollastonite and grossular (Newton and Manning, 2006, 2007). In pure H2O and in solutions with low NaCl concentrations, YPO4 is more soluble than CePO4 in the range \( 0.00-0.27 \) whereas above this value, CePO4 is the more soluble phase.

To obtain information on the interaction of CePO4 or YPO4 with pure H2O and NaCl + H2O solutions, the following generalized dissolution reactions may be written (Newton and Manning, 2006, 2010):

\[
\text{CePO}_4 + a \text{NaCl} + b \text{H}_2\text{O} = k \text{ solute species} \]  
\[
\text{YPO}_4 + a \text{NaCl} + b \text{H}_2\text{O} = k \text{ solute species} \]  

where \( a \) and \( b \) are the number of moles of NaCl and H2O consumed to produce \( k \) moles of solutes per mole of orthophosphate dissolved. These reactions ignore molecular H2O, which implicitly complete the inner-sphere solvation shells.

The relative molar proportions of H2O and NaCl in Eqs. (3) and (4) were evaluated using the technique outlined in Newton and Manning (2006, 2010). Orthophosphate mole fractions were calculated assuming complete dissociation to Na+ and Cl− (Bradley, 1962; Aranovich and Newton, 1996; Newton and Manning, 2006). Fig. 5 shows the variation in the relative solubility enhancements, expressed as solute mole fraction at a given \( X_{\text{NaCl}} \) relative to that in pure H2O (\( X^* \)). The ratio \( X/X^* \) thus represents the magnitude of solubility enhancement by a given NaCl mole fraction.

Values of \( \log X/X^* \) for CePO4 rise with \( X_{\text{NaCl}} \) over the investigated range and are convex to salinity (Fig. 5). This implies that the activity of H2O does not significantly influence CePO4 solubility; i.e., \( b = 0 \) in Eq. (3). This and the positive dependence of solubility on the square of \( X_{\text{NaCl}} \) (Eq. (1)) in turn suggest that 2 moles of NaCl per mole of CePO4 yield anhydrous solute species upon dissolution \((a = 2)\). A simple (non-unique) equilibrium that could account for this relationship is

\[
\text{CePO}_4 + 2\text{NaCl} = \text{Ce}^{2+} + 2\text{Na}_2\text{PO}_4^- \]  

In contrast to CePO4, the negative second derivative of YPO4 molality with respect to \( X_{\text{NaCl}} \) points to a hydrous solute species. Fig. 5 shows that \( X/X^* \) for YPO4 increases to a maximum at \( X_{\text{NaCl}} = 0.33 \). Following Newton and Manning (2006), the NaCl mole fraction at which the maximum occurs, \( X_{\text{NaCl}}^* \), defines the ratio of \( a \) to \( b \) in Eq. (4) via

\[
X_{\text{NaCl}}^* = \frac{a}{a + b} \]  

The maximum at \( X_{\text{NaCl}} = 0.33 \) suggests that \( a = 1 \) and \( b = 2 \). A simple (non-unique) equilibrium that could account for this relationship is

\[
\text{YPO}_4 + \text{NaCl} + 2\text{H}_2\text{O} = \text{YCl}_2^7^- + 2\text{Na}_2\text{PO}_4^- \]  

The dissolution products proposed in Eqs. (5) and (7) suggest that, in NaCl-bearing fluids with neutral pH, the degree of Cl coordination for Y is lower than for Ce. Assuming similar geochemical behavior of Y and REE, this is consistent with the steric hindrance of chloride complexation with HREE relative to LREE proposed by Mayanovic et al. (2009).

Fig. 6 compares the \( X_{\text{NaCl}} \)-dependence of the solubility of CePO4 and YPO4 at 800 °C and 1 GPa with that of the Durango fluorapatite (Antignano and Manning, 2008a). The much greater increase in fluorapatite solubility with increasing NaCl concentration is consistent with its observed incongruent dissolution to REE phosphate + solutes (Antignano and Manning, 2008a). In addition, the different trends indicate that the solubility of the phosphate phases is controlled by Cl−-cation complexation rather than Na-phosphate complexation. More generally, Fig. 6 highlights that ligand availability for REE/Y complexation will govern the dissolution and transport of these elements where apatite and/or orthophosphates are the main mineral hosts.

4.3. H2O/Ce and subduction-zone fluids and melts

The H2O/Ce ratio of subduction-zone magmas prior to crustal degassing has been proposed as a geothermometer for slab-fluid production (Plank et al., 2009). The similar partition coefficients of H2O and Ce during mantle melting (Hauri et al., 2006) and their low background ratio in the mantle of ~200 (Dixon et al., 2002) make H2O/Ce an optimal tracer for the addition of slab components to mantle-derived arc magmas. By considering Ce solubilities in fluids saturated in allanite or monazite, Plank et al. (2009) concluded that slab components are transported to the mantle source...
Plank et al. (2009) inferred that at 800 °C, slab fluids have H2O/Ce of ~7000 to 15,000 (Fig. 7). Using Eq. (1), we find that in a H2O–NaCl fluid at XNaCl = 0.10 ± 0.03 this range of ratios would result in a salinity that is not uncommon for a wide range of metamorphic settings (e.g., Yardley and Graham, 2002). Thus, NaCl-bearing fluids of moderate salinity offer another mechanism by which to produce the H2O/Ce ratio characteristic of arc-magma source regions. However, a caveat is that this mechanism requires little shift in the NaCl concentration from liberation at the slab to the site of melting.

4.4. Cl-bearing fluids and the implications for REE transport in the deep crust

Field studies in high-grade rocks show that mobility of REE and Y is greatly enhanced in the presence of brines (e.g. Newton et al., 1998; Harlov et al., 2006; Hetherington and Harlov, 2008; Hansen and Harlov, 2009; Glassley et al., 2010). Most experimental attempts to explain REE or Y mobility in this or other settings have focused on chloride complexing at acidic pH, where solubilities of these elements are indeed elevated relative to values at acid–base neutrality. However, in metamorphic environments of low to modest water–rock ratios, the high solubilities of the major rock-forming elements provides the capacity to buffer pH at the near-neutral to alkaline pH values of feldspar–mica–quartz or amphibole–pyroxene–plagioclase–quartz assemblages, suggesting that the acidic pH that is implicitly or explicitly invoked to explain REE and Y mobility is unlikely. Our results offer a simple alternative to REE and Y transport by acid–chloride solutions. The strong enhancement of CePO4 and YPO4 solubilities by NaCl points to major REE and Y mobility at neutral pH, even at only modest salinity. Where concentrated NaCl brines occur, REE and Y mobility may be profound.

5. Conclusions

1. Ce-monazite and Y-xenotime are sparingly soluble in pure H2O at 800 °C and 1 GPa. Our measured values of 0.045 ± 0.045 and 0.25 ± 0.04 millimolal for CePO4 and YPO4, respectively, are similar to the value reported by Schmidt et al. (2007) for LaPO4. Natural monazite gives higher solubility. This and possible material redistribution during experiments may explain the high solubilities obtained by Ayers and Watson (1991). However, together this group of measurements is in conflict with the data set of Gibert and Montel (1996) and Pourtier et al. (2010) at 0.2 GPa over a range of temperatures. The reason for the disagreement is not known, and additional experiments are needed to resolve the discrepancy.

2. The solubilities of CePO4 and YPO4 are progressively enhanced by the addition of NaCl to H2O; however, the form of the dependence on XNaCl differs between the two phases. With addition of NaCl, CePO4 solubility rises to an increasing degree, whereas YPO4 rises to a decreasing degree. Solubilities of CePO4 and YPO4 at XNaCl = 0.5 are greater than in pure H2O by factors of 223 and 18, respectively.

3. YPO4 is at least 1.5 times more soluble than CePO4 in pure H2O at 800 °C and 1 GPa, and its solubility remains greater than that of CePO4 at XNaCl = 0.27. Although this appears to contradict the more common occurrence of monazite than xenotime metasomatic settings, it probably simply highlights the fact that REE and Y solubilities are a complex function of the concentrations of a range of ligands in natural fluids.

4. Stoichiometric analysis of the solubility enhancements reveals that the dominant solute species of Ce are anhydrous Ce-chlorides, whereas Y dissolves as mixed Cl–OH species. The decrease in the degree of chloride complexation is consistent with independent studies of REE complexation in acidic chloride solutions (Mayanovic et al., 2009). Phosphate complexes with Na±H.

5. The results have important implications for REE and Y transport by geologic fluids. For example, the H2O/Ce ratio is an important tracer of slab fluids in subductions zones. The data show that CePO4...
dissolution into an H₂O–NaCl fluid with XNaCl = 0.1 can produce H₂O/CO₂ identical to that inferred for slab fluids at 800 °C. This provides an alternative to transport of slab components by melts or silicate-rich fluids. More generally, the enhancement in solubility by neutral NaCl-bearing H₂O provides an alternative to acidic chloride solutions for promoting REE mobility in the middle to deep crust where extremes of pH are unlikely.

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