Redox-controlled dissolution of monazite in fluids and implications for phase stability in the lithosphere

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Abstract

Monazite is an important host of rare earth elements in the lithosphere, including redox-sensitive Ce, which may occur as trivalent and tetravalent in terrestrial environments. Here, monazite solubility is explored as a function of oxygen fugacity through a series of dissolution experiments in alkali-rich and H₂O fluids at 925 °C and 1.5 GPa. The oxygen fugacity was controlled with 7 different solid-state buffers, and ranged from about the iron-wüstite to above the magnetite-hematite equilibrium reactions. The solubility of natural monazite increases monotonically at oxygen fugacities equal to or higher than the fayalite-magnetite-quartz equilibrium. Electron microscopy reveals incongruent dissolution at Ni-NiO and above, where Ce-oxide is observed with monazite as a stable phase. Solubility experiments were also conducted with synthetic crystals (CePO₄, LaPO₄, Th+Si-doped monazite). End-member CePO₄ exhibits profound changes to the surface of the crystal under oxidized conditions, with erosion of the crystal surface to depths of ~100 μm or greater, coupled with precipitation of Ce-oxide. In contrast, the solubility of LaPO₄ shows no sensitivity to the redox state of the experiment. The addition of Th (~3 wt%) and Si (~0.3 wt%) to monazite promotes crystal stability under oxidizing conditions, though small ThO₂-CeO₂ (5-10 μm) crystals are present on the surfaces of these crystals, whose abundance increases at higher oxygen fugacities. In aggregate, these experiments show that the stability and solubility of monazite is affected by oxygen fugacity, and that the redox state of a fluid may be partially responsible for redistribution of rare earth elements and phosphorus in the crust. Lithospheric fluids with oxygen fugacities at or above the fayalite-magnetite-quartz equilibrium may contribute to some of the complex textures, variable chemistry, and age relationships observed in natural monazite. (279 words)
Monazite is a major host of actinide and light rare earth elements (LREEs) in the crust, and is of considerable interest in geochronology because it grows over a broad P/T range in metamorphic terrains (Spear and Pyle 2002; Harrison et al., 2002; Kohn et al., 2004; Catlos, 2013). Thorium oxide (1-10%) and ~1 wt% UO$_2$ are common components due to high partition coefficients for actinide elements (Stepanov et al. 2012; Xing et al. 2013), though crystal chemistry can be highly variable even within a single grain (Catlos et al., 2002; Pyle and Spear, 2003; Kohn et al., 2004). While monazite is amorphized due to displacive radiation effects, it recovers an ordered structure at relatively low temperatures, and is therefore generally considered to be resistant to radiation damage (Meldrum et al., 1997, 2000). It is also extremely resistant to diffusive loss of U, Th, and Pb from the lattice, with closure temperatures for these elements approaching 900 °C or higher for 10 μm grains and a cooling rate of 10°C/Ma (Cherniak et al. 2004; Cherniak and Pyle, 2008). These properties make monazite a potential host for nuclear waste disposal (e.g., Ewing and Wang, 2002).

Monazite is also utilized as a geothermometer through application of mineral-mineral or mineral-fluid equilibrium reactions. For instance, Pyle et al. (2001) presented trace element partitioning data for monazite, xenotime, and garnet in prograde pelitic rocks, and showed that Y partitioning between garnet and monazite is related to temperature. Plank et al. (2009) suggested that monazite (and allanite) solubility in hydrous silicic fluids can be used to estimate subduction slab temperatures. Principally, this involves a comparison of the temperature-dependent H$_2$O/Ce ratio in fluids and melts in the presence of a LREE-buffering phases derived from 2.5–4.5 GPa experiments (Hermann and Rubatto, 2009), with the H$_2$O/Ce of mineral melt inclusions from arc magmas (Plank et al., 2009; Ruscitto et al., 2012; Cooper et al., 2012).
Key to the above applications is the P-T-X dependent stability and solubility of monazite. There are numerous studies which have investigated the alteration, stability, and solubility of monazite as a function of P,T, fluid and/or silicate melt composition (e.g., Ayers and Watson, 1991; Poitrasson et al. 1996; Spear and Pyle, 2002; Ayers et al., 2002; Hermann, 2002; Hermann and Rubatto, 2009; Klimm et al., 2008; Hetherington et al., 2010; Harlov et al., 2011; Budzyn et al., 2011; Skora and Blundy, 2012). Yet, there is no experimental work that has explored the stability and solubility of monazite as a function of oxygen fugacity ($f_{O_2}$). The goal of this contribution is to help facilitate the interpretation of monazite geochronology and geothermometry, through simple limited-component experiments that assess monazite stability dominantly as a function of oxygen fugacity and monazite chemistry. Experiments reveal a relationship between both these variables.

**Experimental strategy and design**

Cerium is present as a trivalent and tetravalent cation in natural samples, where the valence is often inferred based on anomalous partitioning of this element compared to La and Pr. For example, zircon LREE patterns often show positive Ce anomalies, reflecting the higher compatibility of Ce$^{4+}$ over Ce$^{3+}$ in the zircon lattice (e.g., Hinton and Upton, 1991; Trail et al., 2012). More direct valence inferences are possible through measurements of Ce valence in experimental or natural samples by X-ray Absorption Near Edge Structure (XANES) spectroscopy (Burnham et al., 2014; Trail et al., 2015). In rare cases, Ce$^{4+}$ exists as a primary component of the mineral formula. Schlüter et al. (2009) identified the mineral stetindite, with an ideal formula of Ce$^{4+}$SiO$_4$, in the Stetind pegmatite, northern Norway, whereas monazite is expected to contain mostly or only Ce$^{3+}$. Since Ce is redox sensitive and the most abundant REE in monazite, it is...
reasonable to expect that monazite stability and solubility will be influenced by the oxidation state of the system. Experiments were designed to test this hypothesis.

**Starting materials**

Monazite solubilities vs. $f_{O_2}$ were explored with combination of natural and synthetic crystals. Natural monazite samples consisted of single crystals from the Llallagua tin-porphyry deposit (Bolivia). Llallagua monazite has a mineralization age of ~20 Ma (Kempe et al., 2008; Kohn and Vervoort, 2008), and low actinide concentrations (average U+Th contents ~300 ppm; Catlos and Miller, 2017). Synthetic mm-size monazite crystals were grown by the flux method (e.g., Cherniak and Pyle, 2008) to explore some of the possible changes in mineral solubility as a function of crystal chemistry, and to isolate trivalent from trivalent/tetravalent LREEs. The starting flux mix composition consisted of a ~60 gram mixture of Li$_2$CO$_3$-MoO$_3$. Lithium carbonate and MoO$_3$ were added in a 1:3 ratio by mole. This was divided into three equal fractions, and to this different monazite starting compositions were mixed. The first and second batches contained respective additions of ~1.5 grams of LaPO$_4$$\times$H$_2$O or CePO$_4$. The final batch contained 1.5 grams total of LaPO$_4$$\times$H$_2$O and CePO$_4$ with trace additions of ThO$_2$ and SiO$_2$. The latter two components imply the coupled substitution Th$^{4+}$ + Si$^{4+}$ ↔ (REE)$^{3+}$ + P$^{5+}$, placing the final crystal composition along the monazite-huttonite join. Starting mixes were packed into Pt crucibles, covered with a Pt lid, and suspended in a 1 atm pre-heated vertical tube furnace at ~1350 °C. The starting material was soaked for ~3 hours, and then cooled to ~900 °C at a rate of 3°/h. Following synthesis, monazite crystals were freed of residual flux material by ultrasonic cleaning. About half of the experiments were conducted with synthetic phosphates.
Initial characterization of the monazite crystals was carried out with a Photon Machines 193 nm G2 laser ablation (LA) system equipped with a HelEx 2-volume sample chamber connected to an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) quadrupole at the University of Rochester. A laser fluence of 5 J/cm$^2$ with pulse rate of 10 Hz was used for 15 seconds of total ablation time using a 35 or 50 μm spot. The HelEx 2-volume sample chamber He flow rates were 0.6 liters per minute within the sample chamber (MFC1) whereas the He flow in the HelEx arm was set to 0.2 liters per minute (MFC2). The data were reduced using the Iolite 3.1 software package (Paton, et al., 2011), P was used as an internal standard, and concentrations were calculated by standardizing against NIST610 glass. Table 1 presents a summary of LA-ICP-MS results, with the averages of measured elements reported. Llallagua monazites typically contain sub-ppm Th and a few hundred ppm of U (single spot data can be found in the supplementary information). These observations are in broad agreement with a recent study that reported chemical information for Llallagua monazites by LA-ICP-MS (Catlos and Miller, 2017).

Experiments

Monazite solubility vs. oxygen fugacity was explored in a 2 N NaOH fluid and in H$_2$O deionized to a resistivity of 18.2 MΩ·cm with a milli-Q water filtration system. The alkali-rich fluid composition was chosen after the study of Hetherington and Harlov (2008), and after experiments conducted in the same fluid composition reported by Harlov et al. (2011). These workers proposed that altered, metasomatized regions of natural monazite were caused by interactions with alkali-dominated fluids. Single crystals or crystal fragments were dried, carefully weighed, and then placed in Ag or Pt capsules with a known amount of fluid.
**Figure 1** presents schematics of the different capsule configurations and the pressure cell. Most of the experiments were conducted in the capsule configuration presented in Figure 1a. The capsule well hosting the monazite has a low profile (~5 mm) and thick wall (~2 mm), which mitigates against thermal gradients and vapor transport/recrystallization of dissolved solutes. In these experiments, the oxygen fugacity was controlled with solid state metal-metal oxide or mineral oxide buffers placed in a separate container (Trail et al., 2012; Figure 1a). The buffer was separated from the monazite-hosted capsule by an H₂ permeable membrane of Pd metal because most buffers are soluble in aqueous solutions at high temperature. In one case, the Ru-RuO₂ buffer – see Figure 1b – was directly added to the capsule because this metal-metal oxide buffer is expected to be insoluble in aqueous solutions at the experiment conditions. Figure 1c presents the configuration for a Ni-NiO buffered experiment. In this case, the Ni metal bucket was oxidized in a muffle furnace at ~1000°C for 24 h, followed by insertion of Ni+NiO powder and a Pt capsule.

All capsules were pressure sealed with a metal gasket or lid with one of seven solid state \( f_{O_2} \) buffers. The \( f_{O_2} \) buffers cover a range of 12 log units (Table 2). The most reduced experiment was conducted at 4 log units below the fayalite-magnetite-quartz buffer (FMQ-4) while the most oxidized reached ~8 log units above the FMQ equilibrium (Ru-RuO₂). Samples were heated to 925°C, at a pressure of 1.5 GPa, and the temperature was controlled using calibrated 25%WRe–3%WRe thermocouple wire, with an accuracy of ±3 °C. Pressure was monitored using a 20 cm Heise pressure gauge. The duration for most experiments was ~48 h, though it ranged from 24 to 188 h. These time series experiments were used to evaluate apparent changes in solubility as a function of experiment duration. Experiments were quenched by cutting power to the transformer. The presence of all phases participating in the buffering reaction were verified at the completion of each experiment. Fluid in the buffer chamber (i.e., for designs presented in Figure 1a,c) was
also verified. Monazite crystals were removed from the capsules, washed, dried, and re-weighed. Crystals were mounted in epoxy, polished, and imaged using a Zeiss Auriga Scanning Electron Microscope (SEM) to explore the near surface morphologies of heat-treated crystals. Some crystals were placed on carbon tape and imaged with secondary electrons using the same instrument.

Results

The experimental information, which consists of T,P,t,fo2, crystal type, fluid composition, and calculated solubilities, is reported in Table 3. The percent mass loss to solution is calculated by taking the difference in crystal mass before and after the experiment, and expressing this as a percentage of the total fluid added at the start of the experiment.

Natural monazite

Plotting the percent of crystal dissolved in the alkali fluid vs. fo2 shows that Llallagua monazite exhibits higher solubilities for experiments that exceed the FMQ buffer (Figure 2). For the 7 experiments conducted at or below the FMQ buffer, the average solubility in the fluid is 0.17 ±0.03 wt %. While the lowest recorded solubility among the alkali-rich fluid suite is observed under the most reduced conductions (FMQ-4), a second experiment conducted with the same set of intensive variables yielded values closer to the average solubility calculated for experiments conducted at or below the FMQ buffer. Thus, at oxygen fugacities from FMQ-4 to FMQ, there is no detectable change in the solubility for natural monazites. At FMQ+0.8 (NNO), the first clear evidence for a change in solubility is detected. Experiments more oxidizing than FMQ reveal a monotonic increase in solubility as a function of oxygen fugacity, with a maximum value of ~0.5%
at RRO, which is about 2 log units above the magnetite-hematite buffer. In the most extreme comparison, the solubility of monazite in fluid with $f_{O_2}$ buffered at the RRO equilibrium is almost 300% higher than experiments buffered at FMQ.

The results of two RRO-buffered experiments presented in Figure 2 were conducted using different capsule configurations. First, the inverted buffer capsule configuration was used, which involved separating the sample chamber from the buffer with Pd foil (e.g. Fig 1a). Because Ru and RuO$_2$ are both expected to be insoluble in aqueous fluids, these two phases were added directly to the capsule in a second experiment (e.g. Fig 1b). The statistically identical solubilities provide additional confidence that the buffer readily exchanges H$_2$ through the Pd membrane to the sample chamber thereby fixing the oxygen fugacity in both chambers. Besides results presented for alkali-rich fluids, a single experiment buffered at RRO in pure H$_2$O (MD22; 925°C, 1.5 GPa) yields only a modest solubility (0.03% ±0.02%).

Calculated solubilities do not exhibit a strong dependence on experiment duration (Figure 3). For example, FMQ-buffered experiments from 24 to ~200 hours, yield statistically identical solubilities. Thus, solubilities reach a maximum in 24 h or less, consistent with monazite solubility experiments determined by in situ techniques (Schmidt et al., 2007). No strong time dependent trends for RRO-buffered experiments are evident, though subtle changes in solubility for the shortest MMO experiment exist (MD14). No evidence for mobility and recrystallization of secondary phases in the bottom of the capsule or along the capsule walls was observed.

Scanning Electron Microscope (SEM) images of natural monazites from alkali-rich fluids, post-experiment, reveal secondary phases indicating incongruent crystal dissolution in some experiments (Figure 4). At $f_{O_2}$s of FMQ+0.8, the monazite is accompanied by small, 2-5 μm britholite-(Ce) crystals, identified by EDS, attached to the surface. At and above the Re-ReO$_2$
buffer – that is, ≥ FMQ+2.8 – analysis of the images reveals Ce-oxide near the surface, or encased to depths of 5 μm or greater within the monazite. Under the most oxidized conditions (RRO), pervasive alteration of the crystal surface is evident, and the abundance of the Ce-oxide phase is higher. A monazite experiment buffered at RRO in H₂O did not show the same evidence of incongruent dissolution despite the high fₒ₂ imposed.

**Synthetic monazite**

The relationship between solubility and crystal chemistry vary quite dramatically as a function of fₒ₂ (**Figure 5**). The most soluble synthetic monazite at elevated fₒ₂S is CePO₄, which has implied solubilites – based on weight loss of the crystal – of ~2.5 wt%. Like the trend observed for natural crystals, there is a monotonic increase in solubility from FMQ to RRO. In contrast, synthetic LaPO₄ exhibits no change in solubility vs. fₒ₂. For experiments buffered at FMQ to RRO, the solubilities in the alkali-rich fluid is statistically identical to those reported for natural monazites (~0.17%). Even though the Th+Si-doped crystals contains ~30% Ce, which is comparable to natural Llallagua monazites (Table 2), they show no evidence for elevated solubilities at high fₒ₂S. For instance, experiments buffered at FMQ and RRO reveal calculated solubilites that are also statistically identical to those obtained for natural samples at oxygen fugacities ≤FMQ. Also, the solubilites are identical to experiments conducted using synthetic LaPO₄.

The SEM images of post-experiment synthetic monazites reveal intriguing characteristics (**Figure 6**). As with natural samples, evidence for incongruent dissolution is present in synthetic CePO₄ crystals, though the first appearance of Ce-oxide occurs at the FMQ buffer (compared to FMQ+0.8 for Llallagua monazites). In oxidized fluids (RRO) the dissolution features penetrate to
depths of ~100 μm into the interior of the crystals. Secondary Electron (SE) images of CePO₄ reveal convoluted “pillars” of monazite/Ce-oxide attached to the host crystal, that are almost always terminated by Ce-oxide. In contrast, synthetic LaPO₄ show no occurrences of La-oxides from FMQ- or RRO-buffered experiments. The Si+Th doped monazite contain distinct crystals of ThO₂-CeO₂ on the surface. The ThO₂-CeO₂ phase forms a solid solution (Whitfield et al., 1966; Aidhy, 2016). When the Si+Th doped crystals are viewed in polished cross section, small sub-μm ThO₂±CeO₂ phases are present in the outer 5 μm of both FMQ- and RRO-buffered experiment products. All features are only found at the termination of the experiment; that is, untreated Si+Th-doped monazite inspected by SEM do not contain ThO₂±CeO₂ phases.

**Discussion**

The results strongly imply that the mechanism of monazite dissolution varies as a function of crystal chemistry and oxygen fugacity. A few possible reactions are presented as generalizations, but are probably only broadly analogous to those occurring at experimental conditions. One possible dissolution reaction is:

\[(\text{LREEPO}_4)_{\text{solid}} \leftrightarrow (\text{LREEPO}_4)_{\text{aqueous}}, \quad (1)\]

which represents congruent dissolution without dissociation, where the constant of this dissolution reaction does not depend on \( f_O^2 \). This dissolution mechanism was proposed by Rapp and Watson (1986) for silicate melts. This was based on calculated P diffusivities that were nearly identical to the LREEs, suggesting association of these two cations in the melt. Also, consider the reaction:
(LREEPO₄)solid ↔ (LREE³⁺)aqueous + (PO₄³⁻)aqueous  (2)

which represents dissolution of dissociated species (e.g., Cetiner et al., 2005). The REE and phosphate ions may also complex with OH and H/Na, respectively (e.g., Devidal et al., 1998; Poitrasson et al., 2004; Cetiner et al., 2005; Pourtier et al., 2010; Tropper et al., 2011), where complexing with OH (e.g., REE(OH)₃) may increase the solubility of monazite (Ayers et al., 2004). Given the high activity of OH⁻ in the starting solution, phosphate ions are probably more likely to complex with Na⁺ than H⁺. The above possibilities are reasonable approximations for the dominant mechanisms of dissolution for natural monazite crystals from FMQ-4 to ~FMQ. These possibilities also apply, independent of oxygen fugacity, to synthetic crystals comprised of end-member LaPO₄.

However, the SEM images presented in Figures 4 and 6 show that dissolution can also occur incongruently with changes in oxygen fugacity, monazite chemistry, and fluid composition. A reaction that may occur at fO₂s equal to or above FMQ is:

(Ce(OH)₃)aqueous + 0.25O₂ ↔ (CeO₂)solid + 1.5H₂O  (3)

where tetravalent Ce in solid Ce-oxide is inferred based on the lack of evidence for solid REE-oxides at high fO₂s that exclusively occur as trivalent. In other words, the additional solute at high fO₂s is likely to be dominated by PO₄³⁻(aqueous) – with or without Na⁺ complexing – given the presence of Ce-oxide in the experimental products. No evidence for reaction (3) is observed for solubility experiments conducted in H₂O (MD22) at elevated fO₂s, highlighting the importance of
the NaOH solution. While reaction (3) may explain the presence of CeO$_2$ and CeO$_2$-ThO$_2$ phases, it is not meant to imply that Ce$^{4+}$ complexes are completely insoluble in solution.

It is also important to mention that Ce±Th-oxide crystals found on the surface – for example, Fig. 6f,g – do not have morphologies similar to quenched products. In particular, they have well-defined crystal habits and low aspect ratios. Moreover, several examples of CeO$_2$ and CeO$_2$-ThO$_2$ are found encased within the monazite host crystals, which is also evidence that these phases formed during the experiment (Fig. 4c, 6e). The experiments conducted at FMQ with synthetic CePO$_4$ results in a small increase in solubility when compared to the three FMQ experiments conducted on natural crystals. The former experiment also contains CeO$_2$, demonstrating that Ce$^{4+}$ is present at FMQ.

The solubility results obtained for synthetic Th+Si doped monazites (that is, LaPO$_4$ + CePO$_4$ crystals doped with ThO$_2$ and SiO$_2$, see Table 2) cannot be completely explained by reactions (1-3). Surface phases of CeO$_2$-ThO$_2$ are broadly consistent with reaction (3), but the solubility of monazite in the fluid does not change with $f_{O_2}$ as it does for Llallagua monazites, which have nearly identical Ce concentrations. One crystal chemical difference is that these synthetic monazites do not contain LREEs Pr, Nd, Sm, etc. found in natural monazite. However, this should not result in differences in solubilities as other LREEs are expected to have broadly identical behavior to La. The ~3 wt% Th added to these synthetic crystals is significantly higher than the <100 ppm Th present in the Llallagua crystals; Th may thus impede redox-induced dissolution of monazite. These results are consistent with the observations of Schmidt et al. (2007) whose experiments indicate lower mobility of Th compared LREE. Other studies have also identified Th as a stabilizing component in monazite (Oelkers and Poitrasson 2002; Breiter et al.
Additional experiments in the solid solution ternary ThSiO$_4$-Ca$_{0.5}$Th$_{0.5}$PO$_4$-LREEPO$_4$ may help explain this further.

**Implications**

**Hydrothermal alteration of monazite**

Solubility studies of accessory minerals have been used to elucidate fluid transport and redistribution of trace elements in the crust (Ayers and Watson, 1991; Ayers and Watson, 1993; Tropper et al., 2011, 2013; Hermann et al., 2013; Budzyń et al., 2013). However, most experimentally determined solubilities of monazite in aqueous fluids are typically very low over a wide range of hydrothermal, metamorphic, and igneous conditions (e.g., Rapp and Watson, 1986; Devidal et al., 1998; Poitrasson et al., 2004; Cetiner et al., 2005; Schmidt et al., 2007; Tropper et al., 2011, 2013; Pourtier et al., 2010).

This contrasts with field observations, where monazite often contains complex zoning that develops in response to fluid alteration. Cherniak and Pyle (2008) documented “perforated” rims in hydrothermally altered monazite, from the amphibolite facies quartzofeldspathic gneiss from the SE Pennsylvania, and Hetherington and Harlov, (2008) observed partially metasomatized monazite megacrysts from granite that contained thorite and uraninite inclusions. Many other examples of destabilized crystal surfaces, patchy zoning, and subsurface inclusions have been documented in natural monazites (e.g., Poitrasson et al., 1996, 2000; Rolland et al., 2003; Ayers et al., 2006; Hetherington and Harlov, 2008; Crowley et al. 2008; Bosse et al., 2009; Harlov and Hetherington, 2010; Kelly et al. 2012; Janots et al. 2012; Seydoux-Guillaume et al., 2012).

A major, first order implication of this work is that monazite stability and solubility are sensitive to the $f_{O_2}$ of the fluid, and consequently the mobility of P and LREEs in the crust may be
profoundly affected by these fluids under certain conditions. The formation of residual Ce-oxide under oxidizing conditions results in excess PO$_4^{3-}$ in solution. In simple systems, analogous to the experiments presented here, the phosphate concentration will thus be higher, and P more mobile in oxidized environments. In more complex systems, additional phosphate ions in solution due to dissolution of monazite in oxidized fluids may result in the formation or growth of other phosphate phases, such as apatite. The connection between fluid oxidation state and the stability of monazite has also been made in natural samples by Ayers et al. (2013), who argued that the stability of monazite in the country rock of the Searchlight Pluton, Southern Nevada was adversely affected by interaction with oxidized fluids.

Experiments were conducted in H$_2$O and 2N NaOH fluids, where only the latter resulted in incongruent dissolution under oxidized conditions, so the fluid composition must also be important. The alkali fluid used here may be common in some scenarios (Hetherington and Harlov 2008; Harlov et al. 2011), though alkali-halide brines and temperature may also play a prominent role in oxide and phosphate dissolution reactions (e.g., Ayers and Watson, 1991; Rapp et al., 2010; Tropper et al., 2011; 2013), and are thus worth evaluating in $f$O$_2$-buffered experiments as well.

**Geochronology**

Hydrothermal alteration of monazite has received continued attention because of concerns over how it will affect U–Th–Pb ages (e.g., Poitrasson et al., 1996; Harlov et al., 2011; Williams et al., 2011; Grand’Homme et al., 2016). Experiments conducted with synthetic Th+Si doped monazite contain ThO$_2$-CeO$_2$ inclusions on the surface. While the weight loss differences of Th+Si doped monazite experiments could not discern the difference in solubility for FMQ and RRO-buffered experiments, the occurrence of ThO$_2$-CeO$_2$ inclusions on the surfaces of the crystal is
more common at elevated oxygen fugacities (e.g., RRO). In some experimental products, ThO$_2$
and Ce-oxide appears encapsulated as inclusions within the original monazite in 2D sections (e.g.,
Fig.4c, Fig. 6e). These phases are absent in pre-treated crystals and therefore develop during the
experiments. This transport is not possible by lattice diffusion because the diffusivites of
tetravalent cations in monazite are too low (e.g., Cherniak and Pyle, 2008) and therefore must be
related to a dissolution–reprecipitation migration front through the crystal. Such observations may
partially explain why monazites have complicated ages patterns, where interior domains may yield
younger ages than the rims of crystals (e.g., Catlos, 2013). In settings with high silica activity, the
Th-rich oxides documented here would likely react to form thorite (Hetherington and Harlov 2008;
Harlov et al., 2011) or huttonite. Monazite compositions closer the huttonite end-member of the
join may form in more oxidizing environments. Furthermore, huttonite may contain Ce$^{4+}$, the
concentration of which is likely to be a function of the oxygen fugacity at the time of

crystallization.

Repository for radioactive waste

The ability of monazite to incorporate a range of other actinide elements such as Pu, Am,
Cm, Bk, Cf, and Es, while not accumulating lattice damage due to radioactive decay, has led to
the suggestion that monoclinic phosphates may be ideal for nuclear waste storage (e.g., Ewing and
Wang 2002; Montel et al., 2006; Dacheux et al., 2013). The results of this study show that
oxidizing fluids can induce significant dissolution-reprecipitation and the occurrence of secondary
phases, the magnitude of which broadly depends on the abundance of multivalent Ce in the
monazite structure. Importantly, LaPO$_4$ is not more susceptible to oxidizing fluids. In a study by
Veilly et al. (2008) rates of monazite dissolution increased by about two orders of magnitude when
multivalent U⁴⁺ was added to the monazite in place of Th⁴⁺. The decrease of chemical durability could be due to the oxidation of U⁴⁺ to some U⁶⁺ aqueous species at the solid-solution interface, resulting in weakening of the lattice (Veilly et al., 2008). The effects observed for Th-doped crystals broadly agree with the observations made here.

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**Figure Captions**

**Figure 1.** Capsule configurations and experimental cell.  (a) The most common capsule configuration separates the oxygen fugacity buffer from experimental sample by 0.15 mm thick H₂ permeable Pd foil. Capsules are thick walled, to minimize the thermal gradient and to prevent re-precipitation of the dissolved crystal though monazite is not prone to vapor-phase transport like rutile (Tropper and Mannin, 2005).  (b) A fluid insoluble oxygen fugacity buffer (Ru-RuO₂) was added directly to the capsule in a single experiment.  (c) The capsule configuration used to buffer the oxygen fugacity at the Ni-NiO equilibrium. This buffer was implemented in a similar fashion to that described in Ayers et al. (1992).  The Ni metal bucket was oxidized in a muffle furnace at ~1000 °C for 24 hours, and additional Ni-NiO powder and H₂O was added to the bottom of the Ni bucket before inserting the 5 mm Pt capsule.  (d) The experimental cell consists of a 19 mm NaCl+borosilicate glass, with crushable MgO on either side of the capsule+buffer. No pressure correction was made for this cell design (Holland, 1980). The borosilicate glass acts as a thermal insulator; additional details about the thermal structure of the NaCl-borosilicate cell are explored in Watson et al. (2002).

**Figure 2.** Solubility of Llallagua monazite in 2N NaOH solution represented as wt% monazite dissolved in the fluid (wt. loss of crystal/ wt. of fluid×100). Solubilites increase at oxygen fugacities above the FMQ buffer. The x-axis represents the difference in log units from the FMQ equilibrium buffer. The iron-wüstite (IW) and magnetite-hematite (MH) buffers are included for reference.
**Figure 3.** Solubility of monazite in 2N NaOH fluid compared to experiment duration for three different oxygen fugacities, which reveals no systematic change with time, suggesting the absence of vapor transport/recrystallization of dissolved solutes.

**Figure 4.** SEM images (SE = secondary electron; BSE backscattered electron) of Llallagua monazite showing various types of dissolution features; see Table 1 for oxygen fugacity buffer abbreviations. (a) Monazite experimental product buffered at MMO in 2N NaOH fluid showing the presence of xenotime. Also present, but not shown in the image, are ~1 μm REE-silicates near the surface of the crystal, likely allanite. Xenotime was not observed in any other experiment, including other MMO runs and is suspected to have been present at the start of the experiment. (b) MD16, also buffered at MMO. (c) Monazite experimental product after buffering at FMQ (2N NaOH). (d) An experiment buffered at FMQ+2.8 with NaOH fluid shows evidence of incongruent dissolution resulting in Ce-oxide precipitates close to the surface of the crystal. (e) Buffering the experiment at RRO in a solution of 2N NaOH results in pervasive Ce-oxide associated with the monazite at depths greater than 50 μm from the original surface of the crystal. (f) In contrast to (e), no incongruent dissolution of monazite is evident at RRO in a fluid of H2O.

**Figure 5.** Solubility of synthetic monazite crystals in 2N NaOH change as a function of chemical composition. For reference, the grey line defines the solubility for natural monazite presented in Figure 2. Synthetic CePO₄ exhibits enhanced solubilities at elevated oxygen fugacities. Synthetic LaPO₄ and Th+Si doped monazite (see Table 2 for compositions) exhibit no change in solubility as a function of oxygen fugacity. Error bars are smaller than the symbols.
Figure 6. SEM images of synthetic monazite crystals labeled with sample ID, $f_0^2$ buffer, and image type (SE = secondary electron; BSE = backscattered electron). The first row are images of synthetic CePO$_4$, the second row is Si-Th doped monazites. (a) Flux-grown monazite, untreated. (b) Ce-oxide inclusions present on the surface of the crystal after an experiment buffered at FMQ. (c-d) Deep penetration of Ce-oxide after a RRO-buffered experiment; the surface was imaged first (c), followed by mounting and polishing of the crystal (d). (e-g) Precipitates of CeO$_2$-ThO$_2$ extending to depths of ~5 μm within the crystal, and on the surface. The CeO$_2$-ThO$_2$ phase is more prevalent for the more oxidized experiment (g), and has higher abundances of CeO$_2$ as determined by EDS.
Table 1
Compositions of phosphates used in solubility experiments.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>n (Analyses)</th>
<th>Ca (wt%)</th>
<th>s.d.</th>
<th>Si (wt%)</th>
<th>s.d.</th>
<th>La (wt%)</th>
<th>s.d.</th>
<th>Ce (wt%)</th>
<th>s.d.</th>
<th>Pr (wt%)</th>
<th>s.d.</th>
<th>Nd (wt%)</th>
<th>s.d.</th>
<th>Sm (wt%)</th>
<th>s.d.</th>
<th>Th (wt%)</th>
<th>s.d.</th>
<th>U (wt%)</th>
<th>s.d.</th>
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</thead>
<tbody>
<tr>
<td>Llallagua grain 1</td>
<td>9</td>
<td>0.4</td>
<td>0.2</td>
<td>n.m.</td>
<td></td>
<td>19.0</td>
<td>0.9</td>
<td>33.4</td>
<td>1.1</td>
<td>3.4</td>
<td>0.2</td>
<td>12.3</td>
<td>1.1</td>
<td>1.8</td>
<td>0.2</td>
<td>101 ppm</td>
<td></td>
<td>303 ppm</td>
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<tr>
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<td>1.5</td>
<td>31.9</td>
<td>0.9</td>
<td>3.5</td>
<td>0.1</td>
<td>11.8</td>
<td>0.9</td>
<td>1.8</td>
<td>0.1</td>
<td>0.05 ppm</td>
<td></td>
<td>0.04 ppm</td>
<td>63</td>
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<tr>
<td>Llallagua grain 3</td>
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<td>0.1</td>
<td>n.m.</td>
<td></td>
<td>18.2</td>
<td>0.8</td>
<td>31.9</td>
<td>0.7</td>
<td>3.3</td>
<td>0.0</td>
<td>12.9</td>
<td>0.3</td>
<td>1.7</td>
<td>0.1</td>
<td>0.04 ppm</td>
<td></td>
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<td></td>
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<td>0.03</td>
<td>42.6</td>
<td>0.8</td>
<td>30.1</td>
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<td>n.m.</td>
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<td>2.94 wt%</td>
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<td></td>
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<td></td>
<td>n.m.</td>
<td></td>
<td>0.00 ppm</td>
<td></td>
<td>0.00 b.d.l.</td>
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<td>CePO₄ (synth)</td>
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<td></td>
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<td>0.0</td>
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<td>0.0</td>
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<td>n.m.</td>
<td></td>
<td>n.m.</td>
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n = number of analyses; additional spot data included in the supplementary information.
b.d.l = below detection limit
n.m. = not measured
**Table 2**

<table>
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<tr>
<th>$f_O^2$ buffer equil. reaction</th>
<th>abbreviation, ref.</th>
<th>$\Delta$FMQ</th>
<th>Capsule configuration</th>
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<td>Mo + O$_2$ = MoO$_2$</td>
<td>Mo-MoO$_2$ (MMO), 1</td>
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<tr>
<td>W + O$_2$ = WO$_2$</td>
<td>W-WO$_2$ (WWO), 2</td>
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<td>$[6/(4x-3)]$Fe$_x$O + O$_2$ = $[2x/(4x-3)]$Fe$_3$O$_4$</td>
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<td>-2.12</td>
<td>Fig 1(a)</td>
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<td>3Fe$_2$SiO$_4$ + O$_2$ = 2Fe$_3$O$_4$ + 3SiO$_2$</td>
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<td>2Ni + O$_2$ = 2NiO</td>
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<tr>
<td>Re + O$_2$ = ReO$_2$</td>
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<tr>
<td>Ru + O$_2$ = RuO$_2$</td>
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<td>7.97</td>
<td>Fig 1(a,b)</td>
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</table>

1O'Neill (1986); 2O'Neill and Pownceby (1993); 3Myers and Eugster (1983); 4O'Neill (1987); 5Pownceby and O'Neill (1994); 6O'Neill and Nell (1997)
Table 3  
Table 3  experiment conditions and results.

<table>
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<tr>
<th>Exp ID</th>
<th>T (°C)</th>
<th>P (GPa)</th>
<th>capsule config.</th>
<th>t(h)</th>
<th>fo₂</th>
<th>ΔFMQ</th>
<th>crystal type</th>
<th>fluid comp.</th>
<th>initial crystal wt. (mg)</th>
<th>fluid added (µL)</th>
<th>final crystal wt. (mg)</th>
<th>solubility (%) a</th>
<th>1 s.d. b</th>
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<td>3.58</td>
<td>0.28</td>
<td>0.02</td>
</tr>
</tbody>
</table>

a solubility represented as wt% monazite dissolved in the fluid (wt. loss of crystal/ wt. of fluid×100), using a density of 1.08 g/ml for 2N NaOH
propagated uncertainty based on 3-7 repeated measurements of initial and final crystal weight
Figure 1

[Diagram showing experimental setup with labels for Ag, fo, buffer + H₂O, Pd foil, Ni-NiO, Pt, borosilicate glass, graphite furnace, Thermocouple, pyrophyllite, Ni-NiO + H₂O, and dimensions of 20 mm and 5 mm.]
Figure 2

Llallagua monazite; 925 °C, 1.5 GPa

solubility (% in fluid) 2N NaOH

ΔFMQ

n = 3
Figure 3

Llallagua monazite, 925 °C, 1.5 GPa

Solubility (% in fluid) \(2N\) NaOH

- **RRO**
- **FMQ**
- **MMO**

experiment duration (h)
Figure 4

A) MD14, MMO; BSE

B) MD16, MMO; BSE

C) MD03, FMQ; SE

D) MD10, ReRO; SE

E) MD22, RRO; BSE

F) MD06, RRO; SE
Figure 5

Monazite; 925 °C, 1.5 GPa

- ▲ CePO₄ (synthetic)
- □ LaPO₄ (synthetic)
- ★ Th+Si doped (synthetic)

Llallagua monazite (See Fig. 2)
Figure 6