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Hydrothermal controls on the genesis of REE deposits: Insights from an *in situ* XAS study of Yb solubility and speciation in high temperature fluids (T < 400 °C)

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ABSTRACT

High pressure-high temperature experiments are used to investigate the effect of temperature, pH and fluid composition on the transport and deposition of REE and provide constraints on the role of hydrothermal fluids in the formation of rare metal deposits. *In situ* X-ray absorption (XAS) measurements were conducted at 50 MPa to determine simultaneously the solubility of Yb compounds (Yb_2O_3, $Yb_2Si_2O_7$ and $YbPO_4$) and Yb speciation from 200 to 350–400 °C in fluids involving Cl, F and P ligands. Yb concentrations were monitored down to tens of ppm from the height of the absorption edge while XANES and EXAFS analyses were used to refine the aqueous speciation of Yb in the high temperature fluids. The XAS analysis suggests that Yb solubility is retrograde from 200 °C and that 10 to 100 ppm Yb can be dissolved in acidic fluids (pH < 2) at T < 400 °C, most probably as $Yb[(H_2O)_{7,8}]^{3+}$ species. Increasing pH and adding phosphorus trigger the precipitation of Yb compounds from 200 to 400 °C. Hence buffering of acid orthomagmatic fluids and leaching of P from host rocks could be major mechanisms in the development of (H)REE enrichments in magmatic-hydrothermal systems.

1. Introduction

The growing industrial demand for rare earth elements (REE: La to Lu, +Y and Sc), especially for developing green energy and high technology sectors relies on the mining industry's capacity to identify rare metal ore deposits (that also concentrates high field strength elements HFSE as Zr, Nb, Ta) and process the ores, while limiting the cost and environmental impact of these operations. Contrary to most economic metals, REE do not occur as native metals in nature, but only in phases such as bastnaesite (*REE*CO_3F), monazite (*LREE*PO_4) or as trace elements in HFSE-rich phases (zircon, pyrochlore or more complex minerals such as euxenite ($(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$) or catapleiite ($Na_2Zr(Si_3O_9) \cdot 2H_2O$)).

Rare metal enrichments have been identified in various geological settings (Chakhmouradian and Zaitsev, 2012; Kynicky et al., 2012; Linnen et al., 2014), as the result of primary magmatic processes associated with the intrusion of carbonatite or peralkaline bodies (*e.g.*, Mountain Pass, USA; Nechalano-Thor Lake, Canada; Lovozero, Russia; Bayan Obo, China) or deeply weathered equivalents (*e.g.*, Mount Weld, Australia). Deposits found in igneous environments commonly bear evidence of significant hydrothermal remobilization involving both high temperature magmatic and meteoritic fluids (*e.g.* Bayan Obo, Nechalano-Thor Lake — Sheard et al., 2012; Smith et al., 2015). Rare metal deposits also display different geometries and light to heavy rare earth fractionation patterns (LREE/HREE) that reflect the mixed influence of the composition of the magmatic source and host rocks, of the emplacement, crystallization and hydrothermal alteration history, and subtle differences in the physico-chemical behavior of the REE. Yet, the distinct effect of magmatic and hydrothermal processes on REE concentrations and distribution in rare metal deposits are not well understood. An important step to improve the current understanding of rare metal deposits is to identify the effects of cooling, decompression and interaction with host rocks on the composition of the hydrothermal fluids and its potential control on the mobilization, transport and precipitation of REE. This requires an improved knowledge of the aqueous chemistry of REE at the pressure and temperature conditions characteristic of fluid circulation and ore deposition in the different geological settings (200 < T < 600–800 °C; P < 300 MPa).

For many years, information about the stability of REE complexes in hydrothermal fluids was limited to theoretical extrapolations of room temperature data (Haas et al., 1995; Wood, 1990). Those models suggested that REE^{3+} should form stronger complexes with hard bases as

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F^-, SO_4^{2-}, CO_3^{2-} or OH^- than with Cl^- in high temperature fluids. These extrapolations, combined with the cogenetic link frequently reported between fluorine and REE mineralization, led to the assumption that REE hydrothermal transport was favored as fluoride complexes and that REE precipitation was triggered by the destabilization of those complexes caused for instance by mixing with Ca-rich meteoritic fluids (Salvi and Williams-Jones, 1996). The development of experimental studies and thermodynamic models investigating the solubility of REE-phases and speciation of REE in high temperature fluids (T < 300 °C - Anderson et al., 2002; Cetiner et al., 2005; Mayanovic et al., 2002, 2009; Migdisov et al., 2009; Migdisov and Williams-Jones, 2014; Poitrasson et al., 2004; Pourtier et al., 2010; Williams-Jones et al., 2012) now provide evidence that the stability of REE-fluoride complexes has been significantly overestimated and that aqueous transport of high amounts of REE could be favored as REE-chloride complexes ($REECl^{2+}$ or $REECl_2^+$) as a result of the high Cl contents of hydrothermal fluids. In particular, the model of Migdisov and Williams-Jones (2014) identified buffering of the acidic mineralizing fluid by meteoritic fluids or surrounding rocks and leaching of P from the surrounding rocks as two of the main mechanisms that could account for the destabilization of REE-chloride complexes and the formation of important ores such as bastnaesite and monazite. However, the thermodynamic model of Migdisov and Williams-Jones (2014) includes only a few high temperature experimental data on $REEF_3$ and Nd-monazite solubility (*e.g.*, Cetiner et al., 2005; Migdisov and Williams-Jones, 2007; Migdisov et al., 2009; Poitrasson et al., 2004) and its validity at T > 300 °C is yet to be demonstrated. Recent experiments by Gysi et al. (2015) extend the compositional range to Y and HREE-phosphates but remain limited in temperature. This lack of data is principally due to the difficulty to conduct high temperature experiments involving aqueous fluids, and in particular to assess the speciation of the investigated species at the relevant high pressure and high temperature conditions. Recently, high P-T experiments investigated the solubility of monazite and xenotime up to 800 °C (Schmidt et al., 2007; Tropper et al., 2013; Tsay et al., 2014). Yet those data were obtained at 'extreme' pressure (P > > 500 MPa) and are hence more relevant to metamorphic alteration or metasomatism in subduction zones.

In this contribution, we present *in situ* X-ray absorption (XAS) analyses conducted in a high temperature autoclave to determine simultaneously the solubility of REE-bearing phases and REE speciation up to 400 °C at 50 MPa. The experimental data are compared to previous experimental work and field observations to define additional constraints on the factors controlling the solubility and precipitation of REE compounds in hydrothermal systems. XAS spectroscopy is element-selective so experiments were conducted at the Yb L_{III}-edge to illustrate the opportunities offered by our experimental approach. The relatively high excitation energy of Yb (L_3-edge = 8944 eV) ensured lower detection limits than for LREE or MREE and was hence optimal to validate our method. Overall, accurate knowledge of the aqueous chemistry of HREE is critical to the industry as they are scarcer and hence more valuable than most LREE and MREE.

2. Experimental section

2.1. Experimental samples

Sintered Yb_2O_3 powder, synthetic Yb-keiviite ($Yb_2Si_2O_7$) and Yb-xenotime ($YbPO_4$) were used as starting materials. While Yb_2O_3 and $Yb_2Si_2O_7$ do not occur naturally, $YbPO_4$ is a likely analog for xenotime ((Y,*HREE*)PO_4), which is one common REE-bearing phase found in rare metals deposits (mainly in deposits associated with carbonatites, but also in felsic dykes/breccia associated with peralkaline complexes – Cook et al., 2013; Linnen et al., 2014; Dostal et al., 2014; Williams-Jones et al., 2000). The keiviite was synthesized in a 1 atm furnace at 1500 °C at the ANU. Powders of Yb_2O_3 and SiO_2 were mixed in stoichiometric proportions, ground and heated overnight. The operation was repeated to ensure the complete homogeneity of the synthesized phase. $YbPO_4$ was synthesized hydrothermally in a Teflon-stainless steel autoclave at the Institute of Geochemistry of the Chinese Academy of Science, using Yb nitrate hexahydrate ($Yb(NO_3)_3.6H_2O$) and di-ammonium hydrogen phosphate as precursors (Garrido-Hernandez et al., 2014). The autoclave was heated for 4 days at 180 °C. Resulting precipitates were washed, centrifuged and finally dried at 80 °C. Both samples were characterized by X-ray diffraction prior to the experiments. Yb standard solutions with different amounts of Yb were also prepared from $YbCl_3.6H_2O$ powder and pure H_2O to be used for Yb concentrations calibration.

Finally, commercial powders of Yb_2O_3 and YbF_3 as well as the synthetic $Yb_2Si_2O_7$ and $YbPO_4$ compounds were ground to fine powders, diluted with boron nitride (BN) and pressed into pellets to be used as XAS references to standardize the atomic structural features of Yb species involving different ligands. All XAS spectra collected on samples involving the $YbCl_3.6H_2O$ and $YbPO_4$ powders (*i.e.* on solid standard but also on high temperature fluids when investigating Yb standard solutions and the dissolution of $YbPO_4$) exhibit a small feature around 9395 eV that is attributed to minor Holmium pollution of the starting materials (L_1-edge Ho = 9394 eV).

2.2. In situ XAS spectra acquisition

Yb solubility and speciation were investigated simultaneously using X-ray absorption spectroscopy (XAS). All experiments were conducted in a high temperature autoclave developed at the Institut Néel (Grenoble, France) for *in situ* spectroscopic characterization (XAS and Raman) of fluids up to 600 °C and 150 MPa (Louvel et al., 2015; Testemale et al., 2005). The autoclave consists of an externally cooled high-pressure vessel equipped with three 1.5 mm thick Be windows that allow for collection of both transmitted and fluorescence signals (axial and 90° from incoming X-ray beam, respectively). The sample (solid Yb compound + aqueous solution) is contained in a vitreous carbon internal cell that is sealed by two vitreous C pistons equipped with Viton O-rings. Those pistons can move freely inside the carbon cell to accommodate the volume change induced by increasing P-T conditions. The length of the pistons and the loaded sample volume are chosen prior to the experiments to prevent opening of the cell upon thermal expansion. The volume of the sample space at room conditions is generally ~0.1 cm^3. The internal cell is placed inside a Mo resistive heater drilled with three 5 mm holes that are aligned with the Be windows of the high-pressure vessel when the autoclave is sealed. A schematic representation of the autoclave and the sample cell are presented in Fig. 1. Pressure is applied to the sample by pressurizing He in the autoclave. All experiments are conducted isobarically. During experiments, the pressure is measured and regulated with an accuracy of about 0.1 MPa and temperature is controlled with a precision of ± 1 °C by K-type thermocouples placed within the Mo heater. The offset between the sample and thermocouples temperatures was calibrated prior to experiments calculating the density of pure H_2O with increasing temperature from the Beer-Lambert law (i.e., links the transmission of the X-ray signal through a media to its density and thickness) and the equation of state of water from the NIST database (Wagner and Pruss, 2002).

Yb solubility and speciation were investigated from 25 to 400 °C at 50 MPa. Pieces of Yb_2O_3, $Yb_2Si_2O_7$ or $YbPO_4$ were loaded in the internal vitreous C cell together with pure H_2O, 0.35–0.75 m HCl, 0.5 m NaF or 0.18 m H_3PO_4 solutions. The effect of dissolved Si and Na was also investigated by loading a piece of $Na_2Si_2O_5$ synthetic glass (NS2) with $YbPO_4$ and 0.75 m HCl solution. Both the solid samples and the aqueous solutions were weighted upon loading.

The XAS measurements were conducted at the BM30-B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Details on the beamline layout can be found in Proux et al. (2005).