



Efficient mobilization and fractionation of rare-earth elements by aqueous fluids upon slab dehydration



A. Tsay^{a,*}, Z. Zajacz^{a,b}, C. Sanchez-Valle^a

^a Institute for Geochemistry and Petrology, ETH Zurich, 8092 Zurich, Switzerland

^b Department of Earth Sciences, University of Toronto, 22 Russell St., M5S 3B1, Toronto, Canada

ARTICLE INFO

Article history:

Received 9 December 2013

Received in revised form 23 April 2014

Accepted 28 April 2014

Available online 20 May 2014

Editor: T.M. Harrison

Keywords:

subduction zone
aqueous fluids
rare earth element
solubility
mantle metasomatism
magma genesis

ABSTRACT

The characteristic REE fractionation pattern in arc magmas compared to MOR-basalts results from the selective mobilization of light rare-earth elements (LREE) by slab-derived mobile components. However, the nature and composition of the slab flux, and the actual mechanisms responsible for the transfer of rare-earth elements (REE) from the slab to the mantle wedge remain unclear. We present experimental data on the solubility of selected REE in ligand-bearing aqueous fluids and a hydrous haplogranitic melt at 2.6 GPa and 600–800 °C, spanning the conditions relevant to slab dehydration and melting. The solubilities of REE in aqueous fluids increase more than an order of magnitude with temperature increasing from 600 to 800 °C. Addition of ligands such as Cl^- , F^- , CO_3^{2-} , SO_4^{2-} in relatively small concentrations (0.3–1.5 m [mol/kg H_2O]) has a pronounced effect further enhancing REE solubilities. Each ligand yields a characteristic REE pattern by preferential dissolution of either the light or the heavy REE. For example, the addition of NaCl to the aqueous fluids yields highly elevated LREE/HREE ratios ($\text{La}/\text{Yb} = 17.4 \pm 4.3$), whereas the addition of fluoride and sulfate ligands significantly increases the solubility of all REE with moderate LREE/HREE fractionation ($\text{La}/\text{Yb} \sim 4$). The addition of Na_2CO_3 results in preferential increase of HREE solubilities, and yields La/Yb ratio of 1.6 ± 0.5 by flattening the moderately fractionated REE pattern seen in pure aqueous fluids. The solubilities in hydrous haplogranite melt are moderate in comparison to those observed in aqueous fluids and do not lead to pronounced REE fractionation. Therefore, REE can be effectively mobilized and fractionated by aqueous fluids, compared to felsic hydrous melts. Furthermore, the aqueous fluid chemistry has a major role in determining REE mobilities and fractionation upon slab dehydration in addition to the significant control exerted by temperature. Our results show that chloride-bearing slab-derived aqueous fluids have a significant contribution to the formation of REE-signatures in arc-magmas, especially at lower slab surface temperatures.

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1. Introduction

Understanding the geochemistry of REE has broad applications in various geological settings. The unique chemical behavior of REE gave rise to a wide range of geochemical applications based on their abundances, ratios (e.g. LREE/HREE, Nb/La, Ba/La, Lu/Hf, $\text{H}_2\text{O}/\text{Ce}$) and isotope composition (e.g. Sm–Nd system) (Boyett and Carlson, 2005; Hanson, 1989; McKay, 1989). In subduction-zone settings, magmas display a typical trace element abundance spectrum characterized by the enrichment in light rare earth elements (LREE: La, Ce, Nd) and depletion in the heaviest rare earth elements (HREE: Yb, Lu) relative to MOR-basalt (Elliott et al., 1997; McCulloch and Gamble, 1991). It is generally accepted that a mobile phase (e.g. an aqueous fluid, hydrous melt or supercritical

liquid) released from the subducting slab is responsible for the slab to wedge element transfer and the metasomatism of the mantle wedge, resulting in the characteristic geochemical signatures of arc lavas (Manning, 2004; Poli and Schmidt, 2002; Scambelluri and Philippot, 2001; Tatsumi et al., 1986; Ulmer, 2001).

Evidences of REE mobilization by aqueous fluids have been documented by numerous field observations such as the hydrothermal alteration in the crust (Gysi and Williams-Jones, 2013; Maclean and Hoy, 1991; Palacios et al., 1986; Poitrasson, 2002; Wood and Ricketts, 2000), related REE ore deposit formation (Ludden et al., 1984; McLennan and Taylor, 1979) and metasomatic features in high-grade metamorphic rocks (Hetherington and Harlov, 2008; John et al., 2008; Newton et al., 1998). Based on theoretical considerations and experimental data obtained at ambient conditions, REE^{3+} are classified as hard acids and form strong complexes preferentially with hard bases such as F^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} and OH^- , whereas complexes with the intermediate base Cl^- are considered to be relatively weak in aqueous solutions (Pearson, 1963;

* Corresponding author. Tel.: +41 44 632 3802.

E-mail address: alexandra.tsay@erdw.ethz.ch (A. Tsay).

Wood, 1990a). The experimental studies on REE speciation in aqueous solutions performed at temperatures up to $\sim 500^\circ\text{C}$ and upper crustal pressures showed that the stabilities of all REE complexes increase with increasing temperature (Anderson et al., 2002; Gammons et al., 1996; Mayanovic et al., 2009a; Migdisov and Williams-Jones, 2008; Ragnarsdottir et al., 1998). Additionally, in agreement with early thermodynamic predictions (Haas et al., 1995; Wood, 1990b) it has been identified that LREE (La–Sm) and HREE (Gd–Lu) may have different preferences for complex forming ligands: for example, higher stabilities of LREE- Cl^- and HREE- F^- complexes. The results on REE partitioning between aqueous fluids and silicate minerals/melts under magmatic conditions also emphasized the effect of ligands, suggesting the formation of Cl^- complexes at 800°C and 0.1–0.4 GPa (Flynn and Burnham, 1978; Mysen, 1979).

Although REE systematics has been well investigated at P – T conditions relevant for the Earth's upper crust, the behavior of REE in higher P – T fluids related to subduction-zone processes is less understood. All the experimental studies on REE partitioning, performed in MORB/sediment– H_2O system at high P – T conditions, highlight the role of REE-rich mineral phases such as allanite, monazite, zoisite, lawsonite and garnet in controlling the solubility and bulk partition coefficients of REE between the mineral assemblages and coexisting aqueous fluids or silicate melts. The partitioning of REE into aqueous fluids has been studied in MORB– H_2O system at $T = 650$ – 700°C , $P = 3$ GPa (Green and Adam, 2003), and at $T = 700$ – 900°C , $P = 4$ GPa (Kessel et al., 2005) showing that temperature has a significant effect on REE distribution between coexisting phases. For example, LREE partition coefficients increase by more than an order of magnitude in favor of the fluid phase from 700 to 900°C . Moreover, the nature of the fluid phase plays a major role in REE transfer and hydrous melting of the subducting lithosphere is seen as the most efficient mechanism for the extraction of trace elements from the slab. A number of studies have therefore investigated the partitioning of REE during hydrous melting of the oceanic crust and sediments. It has been shown that accessory allanite and/or monazite control LREE mobilization during melting, with partition coefficients between the solid and the melt phase $D_{\text{REE}}^{\text{all(mon)}/\text{melt}}$ in the order of ~ 700 – 2800 at relatively high slab temperatures of 800 – 900°C (Hermann and Rubatto, 2009; Klimm et al., 2008; Skora and Blundy, 2010). In the case of the MORB– H_2O system, the partition coefficients $D_{\text{REE}}^{\text{all}/\text{melt}}$ decrease by a factor of ~ 3.6 with increasing temperature from 800 to 900°C (Klimm et al., 2008). Similarly, in sediment– H_2O system, the partition coefficients $D_{\text{REE}}^{\text{mon}/\text{melt}}$ decrease by a factor of ~ 3 between 800 and 1000°C and H_2O contents ranging from 2.8 to 15 wt.% (Hermann and Rubatto, 2009; Skora and Blundy, 2010; Stepanov et al., 2012). Compared to aqueous fluids and hydrous melts, a significantly higher mobility of many trace elements, including REE, has been observed in supercritical liquids formed in the MORB– H_2O system at 800 – 1200°C and 6 GPa. Yet the role of accessory phases in equilibrium with supercritical liquids remains unclear (Kessel et al., 2005). However, in all the above partitioning studies, pure H_2O was considered as the sole volatile component, ignoring the more complex chemistry of geologic fluids and the role of ligand species.

A few solubility studies have been performed on REE phosphates, such as fluorapatite, monazite and xenotime, in aqueous fluids in the presence of chlorine and fluorine at 700 – 900°C and 1–2 GPa (Antignano and Manning, 2008; Schmidt et al., 2007; Tropper et al., 2011, 2013). They found that the addition of NaCl ($\pm\text{HCl}$) significantly enhances the solubility of LREE, most likely as chloride complexes, and to a lower extent the solubility of HREE. Furthermore, compared to NaCl, the addition of NaF showed an even greater effect on REE phosphates solubility at equivalent salt concentration, with the effect being larger for YPO_4 than for

CePO_4 (Tropper et al., 2013). However, there have not been systematic studies performed on the role of ligands in the mobilization and fractionation of REE, preventing the assessment of the capacity of aqueous phase to transport and recycle REE in subduction zones.

In this study, we experimentally investigated the solubility of selected REE in high P – T fluids in order to constrain the effect of fluid chemistry and temperature on the mechanism and efficiency of REE mobilization during slab dehydration and melting. Aqueous fluids containing various ligand species (F^- , CO_3^{2-} , SO_4^{2-} and Cl^-) and a hydrous haplogranite melt were equilibrated with a $\text{REE}_2\text{Si}_2\text{O}_7$ -phase, where REE are La, Nd, Gd, Dy, Er and Yb. The experiments were conducted at T of 600 – 800°C and P of 2.6 GPa in a piston cylinder apparatus. The fluid phase was sampled at run conditions by trapping synthetic fluid inclusions in quartz, which have subsequently been analyzed by LA-ICPMS.

2. Experimental methods

2.1. Experimental strategy

The investigation of REE solubilities in high P – T fluids is particularly challenging because REE generally form multi-component minerals such as allanite [(REE, Ca) $_2\text{Al}_2(\text{Fe}^{2+}, \text{Fe}^{3+})(\text{SiO}_4)_3(\text{OH})$] or rare-earth element phosphates. If such phases are equilibrated with high P – T fluids, the measured REE concentrations in the fluid phase will not only be influenced by the solubility of REE themselves, but also the other major components in the apparent mineral phase (namely Ca, Fe and Al silicates in allanite). Therefore, the simplest possible, a REE-disilicate phase ($\text{REE}_2\text{Si}_2\text{O}_7$) was employed in these experiments to isolate the effect of fluid composition on the solubility of REE. This approach also allows us to sample the fluid phase at high P – T in the form of synthetic fluid inclusions in quartz, which in turn provides geologically relevant SiO_2 activities in the fluids at quartz saturation. Though this phase does not occur in nature, it must be noted that the obtained systematics in solubilities can be directly applied to geologic systems. Thermodynamic equilibrium requires that the chemical potential of all components in each phases of the system are equal. The chemical potential of component i in a phase is defined as:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (1)$$

where μ_i is the chemical potential of component i , μ_i^0 is the standard state chemical potential of component i and a_i is the activity of component in the solution (solid or liquid). In turn, $a_i = \gamma_i * x_i$, where γ_i and x_i are the activity coefficient and mole fraction of component i , respectively. The quantity measured in our solubility experiments is the concentration in the fluid phase, which can be considered linearly proportional to the mole fraction and molality for trace elements. A μ_i in the system is imposed by the mixed $\text{REE}_2\text{Si}_2\text{O}_7$ phase for each REE-disilicate component, the measured concentration values directly reflect the variation of the activity coefficients of the dissolved REE-component in the fluid as a function of ligand species and temperature. The relationship $\mu_{\text{REE-ds}}^{\text{minerals}} = \mu_{\text{REE-ds}}^{\text{fluid}}$, where REE-ds stands for REE-disilicate, holds when considering equilibrium partitioning of REE between minerals of the subducted slab and percolating fluids. Therefore the concentration of the REE in the fluid will be controlled by both the activity of REE-disilicate components in the minerals present and the activity coefficients of dissolved REE components in the fluid phase. The systematics in the variation of this latter quantity as a function of fluid composition and temperature is obtained in this study by directly monitoring the REE concentrations in equilibrium with a $\text{REE}_2\text{Si}_2\text{O}_7$ phase imposing a known activity for 6 different REE-disilicate components.

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