

REE+Y transport in hydrothermal fluids: An updated view from in situ XAS measurements

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Knowledge of the mobility of REE in crustal fluids is important for understanding both the formation of REE deposits and their use as geochemical tracers. Despite the continuously growing demand for rare metals, the mechanisms that enable the hydrothermal mobilization, (re)concentration and deposition of HFSE and REE (+Sc and Y) in different environments remain poorly understood.

For example, whereas petrological observations and early thermodynamic modeling suggested a significant role for fluoride in the development of economic REE concentrations [1], solubility experiments and thermodynamic models developed by Migdisov et al. [2, 3] have revealed that REE are most likely transported in the form of chloride and sulfate complexes. The extrapolation of these data to higher temperature, however, suffers from large uncertainties as the experimental database on which this model is built is limited to $T < 300^{\circ}\text{C}$.

We conducted *in situ* X-ray absorption measurements (XAS) to investigate the aqueous solubility and speciation of Sm, Nd, Eu, Gd, Er, Yb and Y up to $\sim 500^{\circ}\text{C}$, 50-80MPa [4]. The EXAFS analyses, complemented by MD simulations, enable us to describe the effect of increasing temperature on REE aqueous speciation in Cl, F, PO_4^{3-} and SO_4^{2-} -bearing fluids with $1 < \text{pH} < 14$. These data provide a molecular-level view of REE complexing and hydration to magmatic hydrothermal conditions. They also provide an independent verification of the validity of the available thermodynamic database at $T > 200\text{-}300^{\circ}\text{C}$, and allow to extend the modeling of the hydrothermal transport and deposition of REE up to magmatic-hydrothermal conditions. This information underpins our understanding of the physico-chemical controls on the formation of REE deposits.

Here we use Eu to illustrate the approach. Europium exists in both Eu(II) and Eu(III) states in natural fluids, making it a sensitive probe of hydrothermal redox processes. Currently, our understanding of Eu complexation in hydrothermal fluids relies mainly on extrapolations from room-temperature data, as there are no high-temperature experimental data available for Eu(II) species. We investigated the complexing of Eu(II) and Eu(III) in chloride- and bromide-rich acidic solutions and Eu(III) sulfate complexes, at $35\text{-}400^{\circ}\text{C}$, 60MPa. For Eu(III) complexes, both the total number of ligands decreased and the ratio of $\text{H}_2\text{O}:\text{Cl}$ ligands in the first coordination shell decreased with increasing temperature. For Eu(II) system, our data confirm Sverjensky's [5] theoretical predictions that Eu(II) species become increasingly stable at elevated temperatures. However the new data indicate that complexation between Eu(II) and chloride is much weaker than Haas's [1] theoretical estimates. The thermodynamic properties of Eu(II) chloride complexes have been reassessed in light of the new data. Thermodynamic calculations reveal that the identity of the Eu(III) aqueous complexes (e.g., chloride or hydroxide species) has significant impact on the oxidation state of Eu in hydrothermal fluids at elevated temperatures.

References: [1] Haas et al., 1995. *Geochim. Cosmochim. Acta* 59, 4329-4350. [2] Migdisov and Williams-Jones, 2007. *Geochim. Cosmochim. Acta* 71, 3056-3069. [3] Migdisov et al., 2016. *Chem. Geol.* 439, 13-42. [4] Louvel et al., 2015. *Chem. Geol.* 417, 228-237. [5] Sverjensky, 1984, *Earth Planet. Sci. Lett.* 67, 70-78.