

How fluids mobilize rare earth elements: An in-situ XAS study of REE hydrothermal speciation

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The role of hydrothermal fluids in the formation of REE (+Sc,Y) ore deposits has proven particularly difficult to assess from field observations. Fluid inclusions studies and petrological reconstructions indeed suggest that, depending on primary source and evolution of the magmatic-hydrothermal system, the poorly soluble REEs may be mobilized by highly acidic to alkaline fluids containing high amounts of F, Cl, sulfates, carbonates and/or phosphates [1,2].

The role of these different ligands is itself a matter of debate, as early studies invoked the formation of REE-fluoride complexes [3], while more recent thermodynamic model suggests that chloride and sulphate complexes may play an important role at $T > 200$ °C [4]. However, the extrapolation of these models towards magmatic-hydrothermal temperatures at which the first mineralizing fluids may be released from carbonatic or alkaline intrusions (450 - 600 °C) suffers from large uncertainties as the experimental database on which they are built is limited to $T < 300$ °C.

In order to provide a stronger basis for the development of reactive transport models applicable to REE ore genesis, we have conducted a series of *in-situ* X-ray absorption measurements (XAS) at the ESRF synchrotron (Grenoble, France) to investigate the aqueous solubility and speciation of La, Sm, Nd, Eu, Gd, Er, Yb and Y up to ~ 500 °C and 50 - 80 MPa [5,6]. These experiments provide us with an updated molecular-level understanding of rare earth complexing in Cl⁻, F⁻, PO₄³⁻, CO₃²⁻ and SO₄²⁻-bearing fluids with $1 < \text{pH} < 14$ and enable us to discuss how pressure, temperature and different ligands may control REE hydrothermal mobilization and fractionation in different environments.

References [1] Vasyukova and Williams-Jones, 2018. Chem. Geol. 483, 385-396. [2] Broom-Fendley et al., 2017. Contrib. Mineral. Petrol. 172 :96. [3] Haas et al., 1995. GCA Acta 59, 4329-4350. [4] Migdisov et al., 2016. Chem. Geol. 439, 1342. [5] Louvel et al., 2015. Chem. Geol. 417, 228-237. [6] Liu et al., 2017. Chem. Geol. 459, 61-74.