

Experimental investigation of magmatic and hydrothermal REE, Nb, Ta enrichment processes

Marion Louvel MARION LOUVEL¹, Barbara Etschmann BARBARA ETSCHMANN², Joel Brugger JOEL BRUGGER², Stephan Klemme STEPHAN KLEMME¹

¹ Institute for Mineralogy, WWU Münster, Correnstrasse 24, D-48149, Germany.

² Department of Earth, Atmosphere and Environment, Monash University, VIC 3800, Australia.

louvel@uni-muenster.de

Abstract

Rare earths (REE) and high-field strength elements (Nb, Ta, Zr) are critical metals for the development of modern green technologies. The genesis of primary economic concentration of REE, Nb and Ta in the Earth's crust depends on a combination of magmatic and hydrothermal concentration processes. In general, magmatic enrichment, through fractional crystallization and/or density contrast in alkaline magmas, is a pre-requisite. In carbonatite and phoscorite mineralization, a main source of REE, Nb and Ta is for instance found in pyrochlores, which are believed to form as liquidus phases from Nb-rich melts [1]. Yet most primary occurrences also display evidences for significant hydrothermal remobilization of the REE and HFSE, a process that may as well favor beneficial LREE/HREE fractionation [2].

The development of geochemical models that simulate the enrichment processes, from the magmatic source to the site of deposition, may facilitate more sustainable and efficient mining operations. Yet, such models require a better understanding of the behavior of rare metals in high pressure-high temperature fluids and melts. Currently, experiments describing the effect of pressure, temperature and melt composition on the solubility of rare metals and the stability of their ore minerals (e.g., pyrochlore, zircon, apatite, basnaesite) may be available for alkaline and silicic compositions [3,4] but mostly do not take into account the combined effects of H₂O, F, P and Cl on the crystallization and mineral melt partitioning of the rare metals. Experimental constraints on the hydrothermal behavior of REE, Nb and Ta are even scarcer, mostly limited to low-temperature and acidic conditions ($T \leq 250$ °C)[5].

In this contribution, we thus wish to present the results of in-situ and piston-cylinder experiments that were conducted to determine the effects of composition (i.e., presence of Cl, F, SO₄²⁻, CO₃²⁻) and temperature on 1) the formation of magmatic ore minerals in alkaline magmas and 2) REE hydrothermal remobilization.

Over the last 5 years, in-situ X-ray absorption measurements (XAS) have been used to study the solubility and speciation of REE (La, Nd, Sm, Gd, Er, Yb, +Y) in high-temperature fluids containing various amounts of HCl/NaCl, NaF, H₂SO₄/Na₂SO₄ or Na₂CO₃ ($0.2 < \text{pH} < 13$)[6,7]. Overall, in-situ experiments conducted in Cl- and S-rich

acidic fluids provide support for the available thermodynamic database for REE-Cl and REE-SO₄²⁻ hydrothermal complexation and transport up to 400-500 °C [8]. Additionally, our experiments define new trends for the potential mobilization of REE by CO₃²⁻ and F-rich alkaline fluids. Especially, we report a significant increase of LREE solubility with temperature that suggest that REE-CO₃²⁻ complexation could play an unexpected role in the early hydrothermal extraction and fractionation of the REE from their magmatic source [Figure 1].

Building on this improved understanding of REE hydrothermal mobilization, our most recent piston-cylinder experiments investigate the effect of P and F on the stability of pyrochlore and other potential HFSE- and REE-bearing phases at 900-1200 °C and 1 GPa and further enable us to determine the mineral/melt partitioning coefficients for HFSE and REE. Altogether, these new experimental results pave the way for an improved modeling of REE, Nb and Ta concentration in alkaline igneous systems.

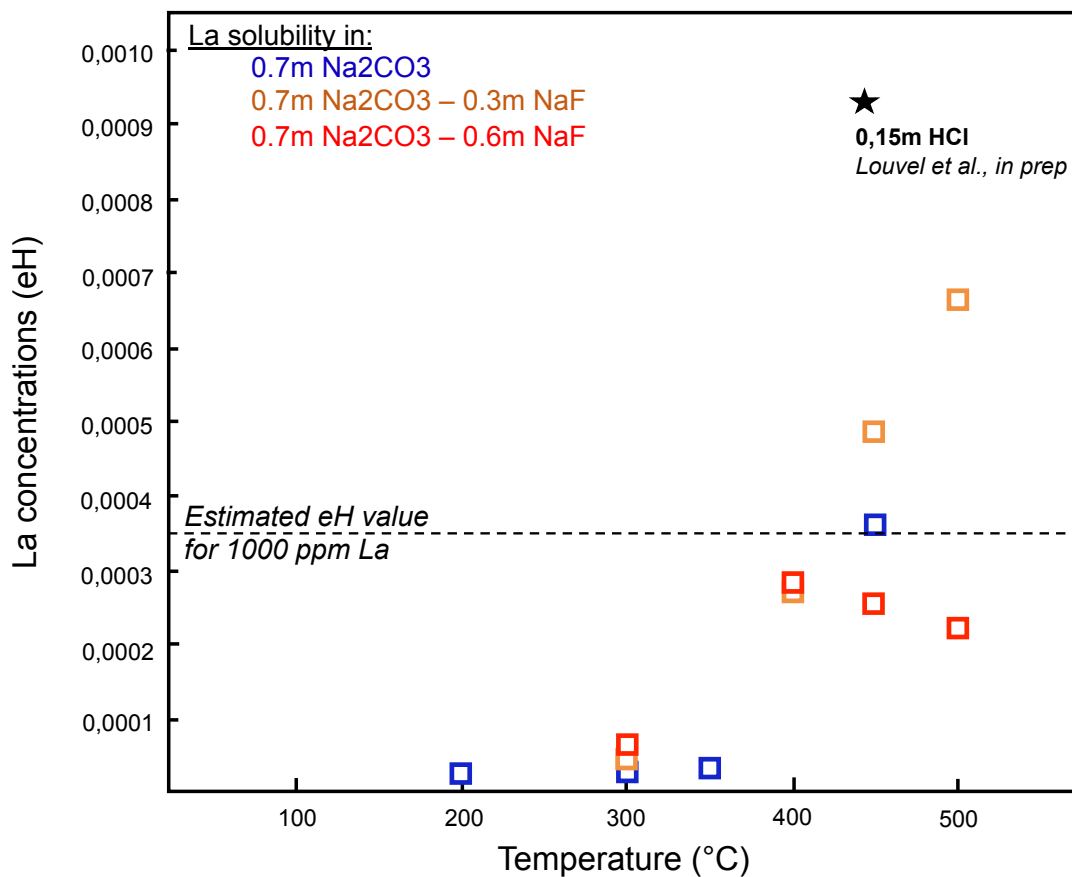


Figure 1: Apparent solubility of La with increasing temperature for 0.7m Na₂CO₃, 0.7mNa₂CO₃-0.3m NaF and 0.7mNa₂CO₃-0.6m NaF aqueous solutions. Note that the apparent solubility is here reported as the eH value that corresponds to the amplitude of the absorption edge jump of the XAS spectra. This value is proportional to the concentration of the element in solution [6].

References

1. R.H. Mitchell, "Primary and secondary niobium mineral deposits associated with carbonatites", *Ore Geol. Rev.*, **64**, 626-641 (2015).
2. A.P. Gysi, A.E. Williams-Jones, "Hydrothermal mobilization of pegmatite-hosted REE and Zr at Strange Lake, Canada: A reaction path model", *Geochim. Cosmochim. Acta*, **122**, 324-352 (2013).
3. R.H. Mitchell, B.A. Kjarsgaard, "Solubility of niobium in the system $\text{CaCO}_3\text{-CaF}_2\text{-NaNbO}_3$ at 0.1 GPa pressure: implications for the crystallization of pyrochlore from carbonatite magma", *Contrib. Mineral. Petrol.*, **148**, 281-287 (2004).
4. F. Gervasoni, S. Klemme, A. Rohrbach, T. Grutzner, J. Berndt, "Experimental constraints on the stability of baddeleyite and zircon in carbonate and silicate-carbonate melts", *Am. Min.*, **102**, 860-866 (2017).
5. A.A. Migdisov, A.E. Williams-Jones, T. Wagner, "An experimental study of the solubility and speciation of the rare earth elements in fluoride and chloride bearing aqueous solutions at temperatures up to 300 °C", *Geochim. Cosmochim. Acta*, **73**, 7087-7109 (2009).
6. M. Louvel, A. Bordage, D. Testemale, L. Zhou, J. Mavrogenes, "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)", *Chem. Geol.*, **417**, 228-237 (2015).
7. Q. Guan, Y. Mei, B. Etschmann, D. Testemale, M. Louvel, J. Brugger, "Yttrium complexation and hydration in chloride-rich hydrothermal fluids: a combined ab initio molecular dynamics and in situ X-ray absorption spectroscopy study", *submitted to Geochim. Cosmochim. Acta*.
8. A.A. Migdisov, A.E. Williams-Jones, J. Brugger, F.A. Caporuscio, "Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations", *Chem. Geol.*, **439**, 13-42 (2016).