

A new perspective for improving the thermodynamic properties of rare earth elements (REE) aqueous complexes in sub to supercritical hydrothermal fluids

ALEXANDER P GYSI¹, NICOLE C HURTIG¹, HANNAH JUAN HAN¹, LAURA WATERS¹, DANIEL E. HARLOV², GEORGE DAN MIRON³, DMITRII A. KULIK³, ARTACHES MIGDISSOV, PHD⁴ AND PROF. CHEN ZHU, M SC PHD⁵

¹New Mexico Institute of Mining and Technology

²GFZ German Research Centre for Geosciences

³Paul Scherrer Institute

⁴Los Alamos National Laboratory

⁵Indiana University - Bloomington

Presenting Author: alexander.gysi@nmt.edu

The rare earth elements (REE) are critical elements with important applications in the high-tech and green energy industries. In geologic systems, REE mineral deposits form through a complex interplay of magmatic and hydrothermal processes, which can fractionate the light from the heavy REE [1]. Hydrothermal aqueous fluids can mobilize and even enrich the REE during fluid-rock interaction processes [2,3]. Despite their similar chemical properties, the fractionation of light and heavy REE is well documented in natural studies and is thought to be controlled by the formation of aqueous complexes and REE partitioning between fluids and minerals. These processes may be simulated using geochemical modeling. However, these models strongly depend on the underlying thermodynamic data for aqueous species and minerals, some of which, are barely known at subcritical and entirely unknown at supercritical conditions. The MINES thermodynamic database [4] has been under development for over a decade and we have generated and reviewed experimental data for the solubility of monazite and xenotime between 25 and 300 °C [5]. Efforts are underway, through a collaborative Critical Minerals Thermodynamics Research Hub to integrate a wide array of experimental methods and expand our current knowledge of REE speciation into the region of supercritical fluids. In this study, we combine new experimental solubility, potentiometric, calorimetric, and spectroscopic (Raman, UV-Vis, and EXAFS) data with thermodynamic optimization methods, and explore ways to identify and determine the stability of REE

aqueous species. The focus of this work is on the REE³⁺ aqua ion, the REE hydroxyl, sulfate/bisulfate and chloride complexes. We present a new experimental compilation for REE data and its integration into thermodynamic databases for geochemical modeling of hydrothermal fluid-rock interaction and ore-forming processes in critical mineral deposits. This work is supported by DOE, Office of Science, Basic Energy Sciences, Geosciences, under Awards DE-SC0021106 and DE-SC0022269.

[1] Gysi et al. (2016), *Econ. Geol.* 111, 1241-1276; [2] Migdisov et al. (2016), *Chem. Geol.* 439, 13-42; [3] Gysi and Perry (2018), *Geofluids* 2018, <https://doi.org/10.1155/2018/5382480>; [4] Gysi et al. (2023), <https://doi.org/10.58799/mines-tdb>; [5] Pan et al. (2024), *Chem. Geol.* 643, 121817.