Hydrothermal solubility and partitioning of REE between fluids and minerals: REE phosphates, apatite, fluorite, and calcite

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The rare earth elements (REE) are critical elements with important applications in the high-tech and green energy industries. Hydrothermal aqueous fluids can mobilize, fractionate, and even enrich the REE during fluid-rock interaction processes [1]. The fractionation of light and heavy REE is well documented in natural systems and is controlled by the formation of aqueous complexes and REE partitioning between fluids and minerals. The minerals that commonly sequester the REE include the REE phosphates (e.g. monazite and xenotime), apatite, fluorite, and calcite. Geochemical modeling is a powerful tool to interpret the REE compositions of natural minerals or potentially develop new separation and extraction strategies. However, the accuracy of the models strongly depends on the underlying thermodynamic data for aqueous species and minerals. In this study, hydrothermal solubility and partitioning experiments were conducted from 100 to 250 °C. Thermodynamic equilibrium calculations and optimizations are conducted using the GEMS code packages (https://gems.web.psi.ch/) and the MINES thermodynamic database [2]. Monazite and xenotime endmember solubility data, collected now for over a decade, indicate that the thermodynamic properties for the minerals and aqueous species are not always compatible and can result in several orders of magnitude differences. Thermodynamic optimizations permit addressing this issue [3], and allow generating new internally consistent dataset which are implemented in the MINES thermodynamic database for simulating the mobility of critical elements in geologic systems. Fluid-mineral REE partitioning experiments were conducted from super- and undersaturation to study the trace incorporation of REE into apatite, fluorite and calcite in acidic to alkaline hydrothermal aqueous fluids [4,5,6]. The experimental results indicate a complex interplay between the stability of aqueous REE species (i.e., REE chloride vs. hydroxyl complexes), the lattice strain induced by coupled substitutions of Ca^{2+} for REE^{3+}, and the stability of REE-endmembers determined via the Gibbs energy minimization approach.

[1] Gysi et al. (2016), Econ. Geol. 111, 1241-1276 [2] Gysi et al. (2023), https://doi.org/10.58799/mines-tdb [3] Pan et al. (2024), Chemical Geology 643, 121817 [4] Chappell et al. (2023) *Amer. Min. 108*, 1409-1420 [5] Payne et al. (2023) *Chem. Geol. 617*, 121256 [6] Perry E. and Gysi A. P. (2020) *Geochim. Cosmochim. Acta 286*, 177-197.