

Rare earth element partitioning in calcite as a vector of hydrothermal processes in mineral deposits

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As technologies advance, the rare earth elements (REE) are becoming more important global commodities because of their use in a variety of high-tech industries [1]. The study of REE speciation and partitioning between fluids and minerals allows us to determine physico-chemical conditions responsible for the hydrothermal mineralization in economic REE mineral deposits [2]. Quantification of these processes is paramount in order to understand how REE deposits form in natural systems and how exploration efforts for them can be directed efficiently. Hydrothermal calcite and fluid inclusions in these deposits yield important signatures regarding the pressure, temperature and salinity, and other physico-chemical conditions under which the REE can be concentrated in crustal fluids. However, to date few partitioning experiments have been carried out using calcite at ambient condition [3], and only recently has the equilibrium partitioning of REE between fluid-calcite been modeled to interpret ore-forming processes [4].

Numerical simulations are presented in this study for the speciation of REE in NaCl-H₂O-CO₂-bearing hydrothermal fluids in equilibrium with calcite [4]. We also explore the mechanisms of REE partitioning between calcite-fluid at 200 °C in hydrothermal batch-type experiments and aim to establish a new thermodynamic model for predicting the behavior of REE in crustal fluids. Numerical simulations indicate that bicarbonate/carbonate are the main transporting ligands in systems with high CO₂ concentrations, low salinity, and low temperature (≤ 150 °C), whereas in systems with both high CO₂ concentrations and high salinity, chloride-bearing complexes become dominant. In alkaline high temperature (300-350 °C) fluids, hydroxyl-bearing complexes may become important for controlling the solubility of the REE. The simulations and experiments show that significant amounts of REE partition into calcite, and that the heavy (H) and light (L)REE are predicted to fractionate considerably with decreasing temperature. These new numerical modeling tools can now be used to make quantitative interpretations of hydrothermal processes associated with REE mineral deposits. Comparison of trace element concentrations of natural calcite with the model allows the linking of quantitative mineral data to the chemistry of the fluids through thermodynamic modeling for vectoring hydrothermal processes in ore deposits.

[1] Hatch (2012), *Elements* 18, 341-346; [2] Gysi and Williams-Jones (2013), *Geochim. Cosmochim. Acta* 122, 324-352; [3] Curti et al.,(2005), *Geochim. Cosmochim. Acta* 69, 1721-1737; [4] Perry and Gysi (in press), *Geofluids*.