

Hydrothermal calcite-fluid REE partitioning experiments

DEUSAVAN C. FILHO^{1,2}, ALEXANDER P. GYSI^{1,2}, NIKOLAI KALUGIN³

¹New Mexico Bureau of Geology & Mineral Resources, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

²Department of Earth and Environment Science, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

³Department of Material Science, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

Calcite is commonly associated to critical mineral deposits and its rare earth elements (REE) signature can potentially be used for interpreting hydrothermal processes [1]. Experiments on REE³⁺ co-precipitation with calcite have been conducted at 25 °C to study the REE partitioning and incorporation mechanisms, which was complemented by spectroscopic techniques [2-4]. Curti et al 2005 [2] used a thermodynamic model and determined that REE partitioning can be explained by either the substitution (1) $\text{REE}^{3+} + \text{H}^+ = 2\text{Ca}^{2+}$ at pH of 6 or the substitution (2) $\text{REE}^{3+} + 3\text{OH}^- = \text{Ca}^{2+} + \text{CO}_3^{2-}$ at higher pH. In contrast, few experiments have been conducted in hydrothermal fluids. Perry and Gysi [5] conducted experiments at 200 °C and pH ~6 and found that the REE partitioning is controlled by reaction (2) at these conditions but more experimental data are needed to build a predictive thermodynamic model.

Here we present experiments on REE partitioning between calcite-fluid at 100 °C. The experiments were conducted in a stirred reactor and involved the injection of a 0.1 mCaCl₂ solution into the heated vessel containing a ~350 ml mixture of 0.03 mNaHCO₃ and REE (100–500 ppb) solutions. Mixing at high temperature led to instantaneous precipitation of REE-doped calcite. Fluid samples equilibrated with the calcite were collected *in situ* and later analysed for Ca and Na using ICP-OES, REE using ICP-MS, and CO₂ from titration. Equilibration with calcite and speciation of the fluids were calculated using the GEMS code package [6]. Preliminary results indicate approach to equilibrium with calcite after 3 days with measured CO₂ concentrations of 234–255 ppm. Calcite was retrieved after quenching the experiments and acid digested to analyse their REE concentrations. Raman spectra were collected on the calcite crystals and confirmed incorporation of REE³⁺ into calcite, which was detectable in experiments doped initially with 290 ppb REE or higher.

[1] Perry and Gysi (2018), *Geofluids* 2018, 21-26. [2] Curti et al 2005 *Geochim. Cosmochim. Acta* 69, 1721-1737 [3] Hellebrandt et al. (2016) *Scientific reports* 6, 1-10. [4] Voigt et al (2017) *Chem. Geol.* 462, 30-43. [5] Perry and Gysi (2020), *Geochim. Cosmochim. Acta* 289, 177-197. [6] Kulik (2013), *Comput. Geosci.* 17, 1-24.