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The solubility of $ErPO_4$ in hydrothermal fluids at varying pH and salinity between 350 and 450°C

CHARLES T KERSHAW[1], NICOLE C HURTIG[2], ALEXANDER P GYSI[1,3], ARTACHES MIGDISSOV, PHD[4], LAURA E WATERS[1] AND DANIEL E. HARLOV[5]

[1]New Mexico Institute of Mining and Technology

[2]New Mexico Institute of Mining and Technology, Department of Earth & Environmental Sciences

[3]New Mexico Institute of Mining and Technology, New Mexico Bureau of Geology and Mineral Resources

[4]Los Alamos National Laboratory

[5]GFZ German Research Centre for Geosciences

Presenting Author: charles.kershaw@student.nmt.edu

Heavy rare earth elements (HREE) are becoming increasingly important due to their use in modern technologies [1]. HREE mobility in hydrothermal fluids is controlled by mineral stability [2] and aqueous speciation at elevated temperatures [3]. Thermodynamic data for some aqueous REE species are extrapolated from low temperatures [4], producing large discrepancies between experimentally derived and predicted xenotime solubilities [2]. This greatly limits our predictive capabilities to model REE transport in high temperature magmatic-hydrothermal fluids. Here we used batch-type Inconel 625 Parr reactors to investigate synthetic $ErPO_4$ solubility between 350 and 450°C at 500 bar, varying pH (2, 3, 4, and 10), and salinities (0.01, 0.1, and 0.5 molal NaCl). At 350°C, xenotime solubility in acidic and alkaline pH solutions is higher with a depression proximal to pH 4.5 (Fig. 1). Aqueous Er concentrations are 47.1±5.9 ppt for pH 2, 17.1±2.3 ppt for pH 3, 4.3±2.9 ppt for pH 4, and 16.1±4.2 ppt for pH 10. Measured Er concentrations were compared to simulated Er speciation and total predicted Er solubility using the GEMS code package [5] and existing thermodynamic data [2,4]. Measured Er concentrations are 2-3.5 orders of magnitude lower versus simulated solubility using aqueous REE chloride and hydroxyl species from the Supcrt92 dataset [4] (Fig. 1). Er speciation is controlled by chloride complexes (i.e., $ErCl^{2+}$) at acidic pH and by hydroxyl complexes in alkaline pH (i.e., $Er(OH)_3^0$, $Er(OH)_4^-$). Simulated and experimental results contrast due to extrapolation of low temperature thermodynamic data for xenotime or aqueous Er chloride and hydroxyl species to 350°C. Previous work at lower temperatures resolved such discrepancies by adjusting the thermodynamic properties of xenotime [2]. Similar adjustments will need to be made with the data from this study. These obstacles highlight the unreliability of high temperature extrapolations and the need for high temperature experimental data.

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