Hydrothermal solubility experiments and determination of the stability of La^{3+} aqua ion and La hydroxyl complexes in acidic to mildly acidic aqueous solutions from 150 to 250 °C

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Knowledge of the thermodynamic properties of rare earth elements (REE) is important for modeling their speciation and solubility in hydrothermal aqueous fluids [1]. However, the thermodynamic stability of REE hydroxyl complexes is largely unknown and still based on extrapolations and the Helgeson-Kirkham-Flowers equation of state from [2]. In this study, we present batch-type hydrothermal solubility experiments to evaluate the controls of pH and temperature on La hydroxyl speciation. Synthetic La hydroxide powders were equilibrated with perchloric acid-based aqueous solutions at 150 to 250 °C and starting pH of 2 to 5. Total La concentrations are measured in the quenched experimental solutions. The equilibrium pH is calculated at temperature using GEMS and the MINES thermodynamic database [3]. The thermodynamic properties for La aqueous species are optimized using GEMSFITS [4]. The experimental results indicate that La hydroxide solubility is retrograde with temperature and displays a strong pH dependence. With increased pH from acidic to mildly acidic, the measured $\log(m\text{La})$ values decrease from -2.5 to -5.4 at 150 °C, -2.5 to -5.8 at 200 °C, and -2.5 to -7.2 at 250 °C. Equilibrium pH initially calculated using data from [2] result in problematic slopes in a $\log(m\text{La})$ versus pH diagram, showing inconsistencies with the stoichiometry for the reaction $\text{La}^{3+} + n\text{OH}^- = \text{La(OH)}_n^{3-n}$. Conversely, thermodynamic parameter optimization of La^{3+}, LaOH^{2+}, and La(OH)_2^+ species results in $m\text{La}$ vs. pH solubility trends consistent with the expected La hydrolysis. The experimentally derived values for these species display differences of ~1 to 20 kJ/mol for the standard partial molal Gibbs energies of the optimized La species in comparison to predictions based on [2]. These results have important implications for modeling the mobility of REE in natural systems and demonstrate an increased relative importance of the LaOH^{2+} complex in controlling mineral solubility in mildly acidic fluids above 200 °C. This work is supported by the U.S. Department of Energy under Award DE-SC0021106.

[1] Perry and Gysi (2018), *Geofluids, Article ID 5382480*; [2] Haas et al. (1995), *Geochim. Cosmochim. Acta, 59(21), 4329–4350*; [3] Gysi et al. (2023), https://doi.org/10.58799/mines-tdb; [4] Miron et al. (2015), *App. Geochem., 55, 28–45*