

Hydrothermal solubility experiments and Raman spectroscopy for the determination of Dy hydroxyl complex stabilities as a function of pH and temperature

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Prediction of the stability of REE hydroxyl complexes and their importance in hydrothermal systems is limited at elevated temperature [1]. The problem is that thermodynamic properties of some REE species are still based on the Helgeson-Kirkham-Flowers equation of state parameters presented in Haas et al. [2], which are derived by extrapolation of low temperature data. Moreover, the formation of REE hydroxyl, chloride and/or hypothetical combinations thereof, has not yet been investigated as a function of pH at temperatures >100°C up to supercritical conditions.

In this study, hydrothermal batch-type experiments were conducted at 150-250°C to measure the solubility of Dy(OH)_{3(s)} and determine the thermodynamic properties of aqueous Dy complexes in perchloric acid solutions with initial pH of 2-5. Calculated experimental pH values (pH_{calc}) are strongly influenced by the stability of aqueous Dy hydroxyl complexes, and were determined *a priori* using the data derived by [2]. Solutions equilibrated with Dy(OH)_{3(s)} have measured Dy concentrations decreasing from 160 ppm (pH_{calc}=3.3) to 770 ppb (pH_{calc}=5.3) at 150°C, and decreasing from 370 ppm (pH_{calc}=2.3) to 21 ppb (pH_{calc}=5.0) at 250°C. The experimental solubility data presented here deviate as much as 1 order of magnitude less to 1 order of magnitude more in comparison to the predicted Dy concentrations using the thermodynamic data by Haas et al. [2]. Therefore, the solubility data were optimized using GEMSFITS [3] to derive the standard Gibbs energy of formation (ΔG^0) of Dy⁺³ and Dy hydroxyl species.

A detailed study of Raman spectra of Dy hydroxyl/chloride-bearing solutions was conducted using a newly designed capillary cell heating stage to identify the dominant Dy complexes as a function of pH, chlorinity, and temperatures up to 300°C. Combining the Raman spectra and results from the solubility experiments, will allow development of a speciation model for Dy aqueous complexes to 300°C, and provide a foundation for investigations of Dy speciation in supercritical fluids.

[1] Migdisov et al (2016), Chemical Geology, 439, 13–42.

[2] Haas et al. (1995), Geochim. Cosmochim. Acta, 59, 4329-4350.

[3] Miron et al. (2015), Appl. Geochem. 55, 28–45.