An internally consistent thermodynamic dataset for REE aqueous species and phosphate minerals (monazite, xenotime, and rhabdophane) from 25 to 300 °C

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Rare earth elements (REE) commonly occur in hydrothermal monazite, xenotime, and rhabdophane in critical mineral deposits. Previous monazite/xenotime solubility experiments indicate the presence of large discrepancies (up to 4 orders of magnitude) between experimentally derived solubility constants versus calculated solubilities [1,2]. The latter were calculated from the calorimetric data of REE phosphates and existing thermodynamic data for aqueous REE hydroxyl species from the Supcrt92 database [3]. In this study, these discrepancies have been resolved through optimization of the standard partial molal Gibbs energy of formation ($\Delta_f G^{\circ}_{298}$) of aqueous REE species at 298.15 K and 1 bar using the GEMS and GEMSFITS code packages [4,5], while fixing the thermodynamic properties of the REE phosphates and the modified Helgeson-Kirkham-Flowers (HKF) equation of state parameters for aqueous REE species [3]. Optimization of $\Delta_f G^{\circ}_{298}$ was targeted towards REE^{3+} and/or $REE(OH)^{2+}$ aqueous species, both controlling the solubility of REE phosphates at the conditions of these experiments (i.e., 25–300 °C and pH of ~1–2) in the REE-P-O-H-Na-Cl system. Optimization of the solubility data for monazite and rhabdophane requires adjusting the $\Delta_f G^{\circ}_{298}$ values of both REE^{3+} by ~2–8 kJ/mol and $REE(OH)^{2+}$ by ~2–27 kJ/mol. Optimization of the solubility data for xenotime requires adjusting only the $\Delta_f G^{\circ}_{298}$ values of REE^{3+} by ~17–26 kJ/mol. These optimizations are drastic and indicate issues with the predicted thermodynamic properties of REE^{3+} and REE hydroxyl complexes derived by Haas et al. [3]. The optimized $\Delta_f G^{\circ}_{298}$ values don't necessarily provide accurate values for these aqueous REE species at reference conditions and experimental data are needed in a wider pH and temperature range to allow revising the HKF parameters. This work is part of a long-term project to develop the MINES thermodynamic database (https://geoinfo.nmt.edu/mines-tdb), which can be used to model fluid-rock interaction and ore-forming processes in critical mineral deposits.

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