

Rare earth elements: Standard and mixing thermodynamic properties for solids and co-precipitation with iron oxyhydroxides

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Rare Earth Elements (REE) are critical for the transition from fossil fuels to renewable and clean energy. Accurate thermodynamic properties of REE solid, aqueous, and surface species are crucial for geochemical modeling of the solubility, speciation, and mobilization, fractionation, and transport of REE in ore formation, extraction, and recycling processes. Recently, we applied the Sverjensky Linear Free Energy Relationship (LFER) [1] to evaluate reported Gibbs free energy of formation in the literature and predict the ΔG_f° of REE solids. Based on these linear relationships, we recommend, preliminarily, a set of internally consistent ΔG_f° for 155 end-members of REE phosphates, oxides, hydroxides, chlorides, fluorides, carbonates, hydrous carbonates, and ferrites [2, 3]. These ΔG_f° are combined with experimental or predicted values of S° , V° , and Cp° from the literature and incorporated into a new SUPCRTBL [4] database. The log K s of REE mineral reactions were incorporated into a modified database for the USGS program PHREEQC for calculation of speciation, solubility, and reactive transport up to 1000 °C and 5 kb. Additionally, we re-fitted the binary Margules parameter (W) from previous theoretical calculations into linear correlations and predicted binary W values for which no experimental or calculational data are available.

To evaluate REE mobilization in surficial environments, we also carried out experiments of coprecipitation of REE with ferric iron with pH titration experiment at ambient temperature and pressure. The coprecipitation process was simulated with a generalized diffuse layer model. However, higher surface site densities and larger complexation constants for surface species than those retrieved in adsorption experiments were required to fit the coprecipitation data, indicating a higher efficiency of REE uptake with coprecipitation process. log K values for REE sorption onto ferrihydrite increase with increasing atomic number across the REE series, indicating that the affinity for REE coprecipitation generally increase from LREEs to HREEs.

1. Sverjensky, D.A. and P.A. Molling, Nature, 1992. **356**(6366): p. 231-234.
2. Pan et al. Minerals, 2024. **14**(3).
3. Pan and Zhu, arXiv:2405.03515, 2024.
4. Zimmer et al., Computers & Geosciences, 2016. **90**, Part A: p. 97-111