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Development of an internally consistent thermodynamic database for REE minerals and crystalline solids

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Rare Earth Elements (REE) are critical minerals (metals) for the transition from fossil fuels to renewable and clean energy. Accurate thermodynamic properties of REE minerals and other crystalline solids are crucial for geochemical modeling of the solubility, speciation, and transport of REE in ore formation, extraction, chemical processing, and recycling processes. However, the Gibbs free energies of formation ($\Delta G^{o}_{f,REEX}$) for these solids from different sources vary by 10s kJ/mol. We applied the Sverjensky linear free energy relationship (LFER) [1] to evaluate and predict the ΔG^{o}_{f} of REE solids.

By considering both the effects of ionic radii size and corresponding aqueous ion properties, the Sverjensky LFER,

$$\Delta G^{o}_{f,REEX} - \beta_{REEX} \cdot r_{REE^{Z+}} = a_{REEX} \cdot \Delta G^{o}_{n,REE^{Z+}} + b_{REEX}$$

allows estimates with much accuracy and precision. Here, $r_{REE^{Z+}}$ represents the Shannon-Prewitt ionic radii (Å) of REE^{Z+}, and $\Delta G^{o}_{n,REE^{Z+}}$ denotes the non-solvation contribution to the ΔG^{o}_{f} of the aqueous REE^{Z+} ion. X represents remainder of the compounds. In this study, the parameters a_{REEX}, b_{REEX}, and β_{REEX} were regressed from ΔG^{o}_{f} compilations in the literature for 16 isostructural families.

Based on the linear relationships, we recommend a set of internally consistent $\Delta G^{o}_{f,REEX}$ for 155 end-members of REE phosphates, oxides, hydroxides, chlorides, fluorides, carbonates, hydrous carbonates, and ferrites. These $\Delta G^{o}_{f,REEX}$ are combined with experimental or predicted values of S^{o}, V^{o}, and Cp^{o} from the literature and incorporated into a new SUPCRT database SUPCRTBL_REE, which allows the calculations of thermodynamic properties to high *P-T* conditions (e.g., 1000 °C and 5 kb) at https://models.earth.indiana.edu. The log *K*s of REE mineral reactions were incorporated into a modified USGS PHREEQC program for calculation of speciation, solubility, and reactive transport up to 1000 °C and 5 kb. These thermodynamic databases will also be incorporated into the MINES database to be used together with the GEMS code package in the future. This work is part of a collaboration with NMT and LANL on experimental and theoretical geochemistry to develop a comprehensive, internally consistent, and open-source thermodynamic database for REE minerals and aqueous species.

[1] Sverjensky and Molling (1992), *Nature* 356, 231-234.