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In situ determination of rare earth elements speciation in hydrothermal fluids using Raman spectroscopy

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Rare earth elements (REE) are classified as critical elements for society due to their importance in high technologies and potential supply disruptions. The speciation of REE aqueous complexes controlling the mobility of REE in magmatic-hydrothermal ore deposits, which are important critical mineral resources, are not well understood. Here we use Raman spectroscopy to measure *in situ* REE aqueous speciation at elevated temperature and pressure and derive species formation constants. Raman spectroscopy is a versatile tool that provides high-precision chemical and structural information that can identify specific bond types such as REE-O, REE-Cl, REE-SO_4 and REE-HSO_4. We measured the speciation of Dy, Nd and Y chloride and aqua ion complexes between 25–300 °C and P_{sat} using a fused quartz capillary heating cell in acidic solutions. A multivariate curve resolution method is used to resolve the mole fraction of aqua ion to chloride species at 25 °C, where the REE-Cl band overlaps with the harmonic vibrations of water. Sulfate and bisulfate complexes of Yb and Nd are investigated using a hydrothermal diamond anvil cell from 25 to 500 °C at P_{sat}–500 MPa. Systematic peak position shifts are observed in isostructural REE solids indicating that Raman spectroscopy is a sensitive tool to characterize specific REE complexes showing a shift to higher wavenumbers with decreasing ionic radii and to lower wavenumbers with decreasing coordination numbers. Chloride complexes of Nd, Dy and Y become predominant over the aqua ion with increasing temperature, showing a prevalence of light REE to complex with chloride over heavy REE. Importantly, we find that *in situ* measurements of REE chloride complexes are ~10-20% lower compared to predicted REE chloride stability based on existing thermodynamic data for REE chloride and aqua ion complexes. The solubility of REE sulfate solids is strongly retrograde at acidic pH showing significant precipitation >250 °C for $Yb_2(SO_4)_3$ and >180 °C for $Nd_2(SO_4)_3$. Furthermore, heavy REE bisulfate complexes are more prevalent at similar pH compared to the light REE bisulfate complexes indicating a potential pathway for heavy over light REE fractionation. This research is supported by DOE-BES grant DE-SC0026161.