

An *in situ* Raman spectroscopy study of the speciation of Yb and Nd in hydrothermal fluids: Chloride, sulfate, and bisulfate aqueous complexes

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Chloride and sulfate are important ligands for mobilizing rare earth elements (REE) in hydrothermal fluids [1]. Aqueous speciation can be predicted if accurate thermodynamic data is available as a function of temperature and pressure [2,3]. However, many experimental studies that derive thermodynamic constants are based on solubility measurements [1], not direct speciation measurements. *In situ* Raman spectroscopy provides a means to identify and potentially quantify REE speciation to improve thermodynamic datasets for modeling REE mobility in hydrothermal fluids [2,3]. Here, we present confocal Raman spectroscopic measurements of Yb and Nd in acidic sulfate- and chloride-bearing aqueous solutions. Observation of the Raman REE-Cl vibrational band is only visible in solutions with >10 wt% REE. We present a new method for determining REE chloride speciation based on the perturbation of the O-H stretching bands represented by three Gaussian subpeaks at $\sim 3200\text{ cm}^{-1}$, 3450 cm^{-1} , and 3600 cm^{-1} . The addition of REE to HCl-NaCl-H₂O solutions systematically increases the relative peak intensity of the 3200 cm^{-1} over the other subpeaks. Multivariate curve resolution deconvolutes the water band into contributions from the different REE species. The quantification of REE speciation from Raman is within 10% of thermodynamic models in the YbCl₃-NaCl-HCl-H₂O system at room temperature. The Raman REE-S vibrations for sulfate ($\sim 980\text{ cm}^{-1}$) and bisulfate ($\sim 1052\text{ cm}^{-1}$) are distinguishable at concentrations down to 1 wt%. The speciation of REE mono/disulfate and bisulfate complexes were measured in a HDAC and quartz capillary cells from 50 to 500 °C. In pH 1.5 solutions at 25 °C, REE bisulfate and sulfate species were identified at $\sim 1047\text{ cm}^{-1}$ and $\sim 990\text{ cm}^{-1}$, respectively. At 300 °C the REE bisulfate species dominates. The REE disulfate species is also present in pH 2.5 solutions at 300 °C. These experiments highlight the need to evaluate the stability of the REE bisulfate complexes, which display increasing stability with temperature and can account for significant REE fractionation. This work is supported by the U.S. Department of Energy under Award DE-SC0022269.

References

[1] Migdisov et al. (2016), *Chem. Geol.* 439, 13-42; [2] Gysi et al. (2023), <https://doi.org/10.58799/mines-tdb>; [3] Pan et al. (2024), *Chem. Geol.* 643, 121817.