

In Situ Determination of REE Complexes Using Raman Spectroscopy: Implications for Mobility of REE in Hydrothermal Fluids

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Rare earth elements (REE) are important critical minerals relevant to society for high technology and green energy sectors. The speciation of REE elements in hydrothermal solutions controls their mobility in magmatic-hydrothermal systems, which comprise an important deposit class hosting REE resources. Raman spectroscopy provides high-precision chemical and structural information that can identify specific bond types such as REE-O, REE-Cl, and REE-SO₄, and thus directly measures REE complexes in solution. Here, we combine a Horiba confocal Raman microscope with different experimental stages including a fused quartz capillary heating stage built at NMT (25 – 300 °C), a hydrothermal diamond anvil cell from Almax (25 to 500 °C, <500 MPa) and a flow-through Linkam CAP500 stage (25 to 500 °C, <500 bar). Systematic changes in peak positions for stretching vibrations of REE-O and REE-Cl bands in solids indicate that Raman spectroscopy provides information on the coordination chemistry of how many O and Cl surround the REE species. Furthermore, we observe systematic changes in the water band and around REE³⁺ aqua ion species, providing information about hydration shells around aqueous REE complexes. At 25 °C, in acidic Cl-bearing fluids the Nd, Dy and Y aqua ions dominate over a wide range of salinity (0.05 – 18 wt% NaCl), whereas with increasing temperature the REE chloride species become prevalent. In acidic sulfate-bearing solutions, a range of Yb and Nd species were detected including REE(SO₄)⁺, REE(SO₄)²⁻ and REE(HSO₄)²⁺. However, solubility was strongly retrograde and immiscible sulfate liquids and polynuclear species were not observed indicating that there are important knowledge gaps for understanding the H₂O-SO₄ system relevant to natural REE deposits. Raman spectroscopy is therefore a highly sensitive technique to investigate the behavior of REE species at hydrothermal conditions providing new insights into their mobility and complexation chemistry. This research is supported by DOE-BES grant DE-SC0026161.