

## Determination of Dy complexation in chloride-bearing hydrothermal solutions using Raman spectroscopy

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Complexation of rare earth elements (REE) by ligands like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{OH}^-$  is of particular interest for understanding the transport and fractionation mechanisms of REE in geologic fluids. Raman spectroscopy provides a method for *in situ* characterization of aqueous ion species at the molecular level. However, Raman spectroscopic studies of REE in chloride-bearing solutions above ambient temperature are limited. In this study, we conducted *in situ* confocal Raman spectroscopic experiments to determine Dy speciation in chloride-bearing aqueous solutions from 25 to 300°C. Experimental solutions containing 0.14 to 1.8 mol/kg dissolved  $\text{DyCl}_3$  and HCl with pH of 2-5 were sealed in fused quartz capillary cells for analysis in a newly designed heating stage. Raman spectra were collected at ambient temperature and every 50°C from 100 to 300°C using a 532 nm Nd-YAG excitation laser. Additional spectra were collected for ultra-pure water and NaCl background solutions. Comparison of the spectra for  $\text{DyCl}_3$  solutions with those for background solutions allowed us to isolate Raman bands specific to the Dy-bearing solutions. A Raman band near 370  $\text{cm}^{-1}$  is attributed to the Dy-O stretching mode of the hydrated  $\text{Dy}^{3+}(\text{aq})$  ion ( $[\text{Dy}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$ ) and a Raman band near 240  $\text{cm}^{-1}$  is attributed to the Dy-Cl stretching mode of Dy-chloro complexes ( $[\text{Dy}(\text{H}_2\text{O})_{8-n}\text{Cl}_n]_{3-n}(\text{aq})$ ). The Dy-O band decreases systematically with increasing temperature, becoming indistinguishable from the background at 100°C for 0.14 *mDyCl*<sub>3</sub> to 300°C for 1.8 *mDyCl*<sub>3</sub>. A simultaneous increase of the Dy-Cl band from 150 to 300°C indicates a systematic increase in Dy-chloro complex stability. These results are consistent with geochemical modeling of Dy speciation using GEMS-Selektor (<https://gems.web.psi.ch/>) [1] and the MINES thermodynamic database [2]. At 25°C and pH of 2-5,  $\text{Dy}^{3+}$  is predicted to be the dominant species, whereas at temperatures above 100°C (0.6 *mDyCl*<sub>3</sub>) to 200°C (0.14 *mDyCl*<sub>3</sub>) and pH of 1.9-3.6, Dy chloride complexes predominate. These findings form the basic framework to support the extension of Raman spectroscopic research on REE complexation to supercritical fluids.

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[1] Kulik et al. (2013), *Comp. Geosci.* 17, 1-24.

[2] Gysi et al. (2023), <https://doi.org/10.58799/mines-tdb>.