

Speciation of yttrium in chloride-rich hydrothermal fluids: insights from *ab initio* molecular dynamics simulations and *in situ* XAS

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Accurate knowledge of rare earth elements (REE) speciation in high pressure-temperature fluids is of critical importance to model REE transport and precipitation in subduction and magmatic-hydrothermal environments, and the formation of rare metal deposits. Several experiments have been conducted on the solubility and speciation of REE in chloride-rich solutions (lanthanum, ytterbium, erbium), demonstrating that REE chloride complexes are the main REE form in many hydrothermal fluids (Migdisov, et al., 2016). However, the speciation of yttrium (Y(III)), a cation with an ionic radius similar to that of Ho(III), in chloride-rich remains poorly constrained.

In this study, we employ *ab initio* molecular dynamics (MD) simulations to calculate the nature of Y(III)-Cl complexes and the thermodynamic properties of these species at temperature up to 500 °C and a pressure of 800 bar. The MD results were complemented by *in-situ* X-ray absorption spectroscopy (XAS) measurements. Our results indicate that at temperature below 200 °C, chloro-complexes do not form readily, even in highly concentrated solutions. At ambient condition, the Y(III) aqua ion binds to eight water molecules in a square antiprism geometry, which consists with previous *ab initio* studies (Ikeda, et al., 2005). The derived formation constants show that the stability of Y(III)-Cl complexes increases with increasing temperature, Y(III) forming high order Cl complexes (up to YCl_4^-) in high salinity solutions at high temperature. The new data provide a better understanding of the mobility of REE in hydrothermal systems.

Ikeda, T., Hirata, M., & Kimura, T. (2005). *The Journal of Chemical Physics*, 122(2), 024510.

Migdisov, A., Williams-Jones, A. E., Brugger, J., & Caporuscio, F. A. (2016). *Chemical Geology*, 439, 13–42.