

# XAFS Investigations of Lanthanum Chloride Aqueous Solutions under Hydrothermal Conditions

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## Introduction

Rare earth elements (REEs) are important as tracers of geochemical processes and for the petrogenesis determination of igneous rocks [1]. The hydrothermal transport of REE ions over substantial distances in the lithosphere is clearly evident in economic deposits at Snowbird Deposit, Montana, in the Gallinas Mountains, New Mexico, and in Bayan Obo, China. A detailed understanding of the interaction of REE ions with ligands common in fluids of the Earth's crust, such as  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{CO}_3^{2-}$ , under a range of pressures and temperatures representative of hydrothermal conditions is presently lacking. Such knowledge is critical for a better understanding of the transport, fractionation, and mineralization of REE in deposits of hydrothermal origin. There is presently insufficient experimental data on the structure and bonding properties of aqueous REE complexes in hydrothermal solutions. In the present study, we discuss our results from x-ray absorption fine structure (XAFS) experiments on lanthanum chloride aqueous solutions measured in our modified hydrothermal diamond anvil cell under hydrothermal conditions.

## Methods and Materials

La  $L_3$ -edge (5483 eV) XAFS spectra were measured from a 0.5 m  $\text{LaCl}_3$ /1.5 m  $\text{HCl}$  aqueous solution sample in fluorescence mode at temperatures up to 500°C and pressures up to 230 MPa. The measurements were made by using our modified hydrothermal diamond anvil cell on the PNC-CAT undulator beamline ID-20 at the APS. The modifications to the original cell design include grooves milled in the culet face of the upper diamond anvil, one each for the incident x-ray beam and the fluorescence x-rays. In addition, a 300- $\mu\text{m}$ -diameter cup-shaped sample cavity was milled in the center of the culet face [2]. The grooves were milled to within 80  $\mu\text{m}$  of the sample cavity in order to minimize the attenuation of x-rays. The sample was sealed between the upper and lower diamond anvils in a sample chamber consisting of the sample cavity and a 300- $\mu\text{m}$  diameter hole in a 50- $\mu\text{m}$ -thick Re gasket.

## Results and Discussion

Figure 1 shows select Fourier transformed spectra and their fits in radial distance (R) space. The Fourier transforms (FTs) were obtained from XAFS ( $k^2\chi$ ) data. The measured data are shown as solid circles, and the best fits (generated from using FEFF8) of these data are shown as solid lines. The FTs of the data were calculated in the 1.8 to 8.8-9.4  $\text{\AA}^{-1}$  k-range. Figure 2 shows the inverse FTs of the data shown in Fig. 1 and the best fits to these spectra. The inverse Fourier transformed data were calculated in the 1.3 to 2.8  $\text{\AA}$  R-range. The measured data are shown as solid circles, and the best fits of these data are shown as solid lines. Our analysis, which is in good agreement with results from our previous studies made on lanthanum nitrate aqueous solutions [3], indicates that each  $\text{La}^{3+}$  aquo ion at room temperature in the chloride solution has a hydration number of  $\sim 9$ .

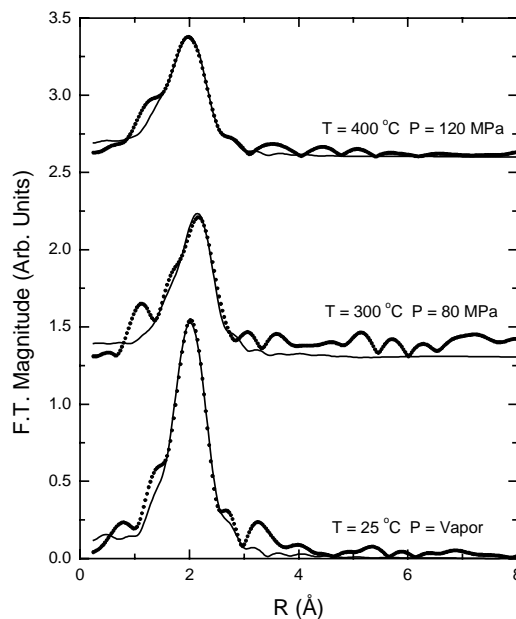


FIG. 1. Spectra for select FTs and their fits in radial distance space.

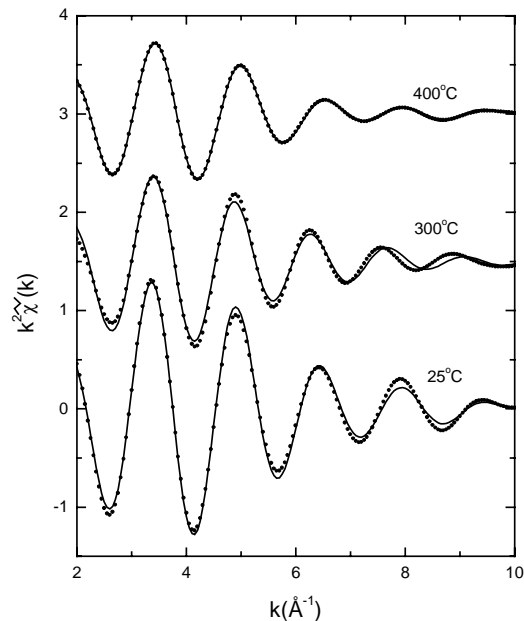


FIG. 2. Inverse FTs of the data shown in Fig. 1.

Preliminary results show that  $\text{La}^{3+}\text{-Cl}^-$  ion association occurs at  $150^\circ\text{C}$  and becomes more substantial with temperatures up to  $500^\circ\text{C}$ . The number of chloride ligands of each  $\text{La}^{3+}$  ion at  $150^\circ\text{C}$  is 0.7 and increases gradually to 1.6 at  $500^\circ\text{C}$ . These results are generally in good agreement with the thermodynamic calculations of REE speciation in hydrothermal solutions made by Hass et al. [4]. Results from our previous study of the  $\text{La}^{3+}$  aquo ion clearly showed that the inner hydration water molecules occupy two distinct shells (inferred to be in a tricapped trigonal prismatic structure) at  $100^\circ\text{C}$  and above [3]. Our present study shows clear evidence for disruption of the two-shell inner-hydration shell structure toward a single-shell distribution, because of the presence of the chloride ligand in the  $\text{La}^{3+}$  complex ion under

hydrothermal conditions. The total number of water molecules in the inner hydration shell of the  $\text{La}^{3+}$  ion decreases from 7 at  $150^\circ\text{C}$  to  $\sim 5$  at  $500^\circ\text{C}$ . These results are consistent with chloride speciation results obtained from our study of ytterbium chloride solutions under hydrothermal conditions [5]. Future directions include studies of REE complexes covering more elements of the lanthanide series, with  $\text{Cl}^-$  and other ligands such as  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{CO}_3^{2-}$ .

### Acknowledgments

This work was funded by Natural Sciences and Engineering Research Council of Canada (NSERC) research and equipment grants to A.J. Anderson and a grant from the Research Corporation to R.A. Mayanovic. NSERC is also thanked for a major facility access grant. Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38, and use of the PNC-CAT facility was supported by DOE BES under Contract No. DE-FG03-97ER45628.

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