XAFS Investigations of Lanthanide Hydration in Aqueous Solutions at Elevated Temperatures and Pressures Using a Modified Hydrothermal Diamond Anvil Cell

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INTRODUCTION

The mobility of rare earth elements (REEs) in the hydrosphere has recently been the subject of intense study because of their importance as tracers in a variety of geochemical processes, the need to understand the genesis of REE hydrothermal ore deposition, and the utility of the REE group as an analogue for studying the behavior of the actinide group. Although solubility and theoretical studies have made significant progress in predicting REE speciation in hydrothermal solutions, very little is known about the structure, stoichiometry and stability of REE complexes in hydrothermal systems.

In this study the hydration structure of La^{3+} in aqueous nitrate solutions from 25 to 300 °C is investigated in a hydrothermal diamond anvil cell (Figure 1) designed specifically for fluorescence mode XAFS analysis. Knowledge of the solvation of the light rare earth elements at elevated temperatures and pressures is needed to constrain theoretical models used for calculating speciation. Direct analysis of aqueous La^{3+} ions also serves as a starting point for XAFS studies of the complexation of REEs with ligands such as Cl^-, F^-, OH^-, CO_3^{-2}, and SO_4^{-2}. The new hydrothermal diamond anvil cell has a shallow sample chamber and grooves cut into the face of one of the diamond anvils (Figure 2 and 3) in order to minimize attenuation of X-rays. This modification extends the analytical capabilities to micromolar concentrations of elements having X-ray absorption edge energies as low as 2900 eV. Temperatures of 700°C and several kilobars of pressure can be reach making it possible to study K-edge absorption spectra of relatively low Z elements in fluids at extreme conditions (Figure 4).

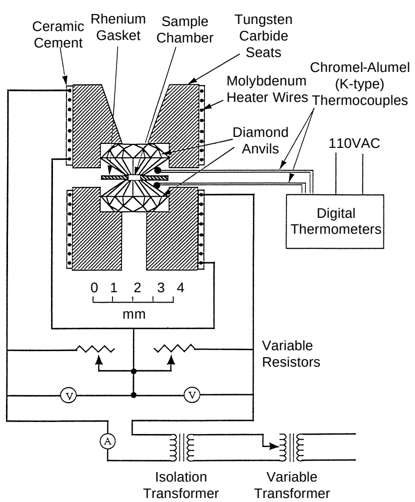

Figure 1 Schematic diagram of the Hydrothermal Diamond Anvil Cell (HDAC).

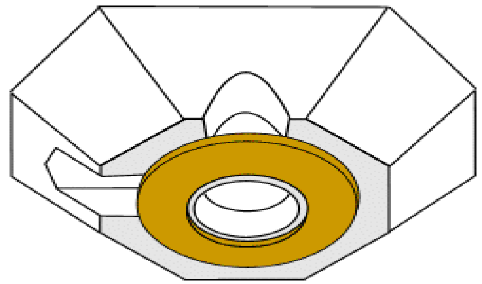

Figure 2 Schematic diagram showing the grooves and sample chamber in the culet face (shaded) of the upper diamond. The rhenium gasket (brown) is centered directly below the sample chamber which is 0.3 mm in diameter.

METHODS

The measurements were carried out using the PNC-CAT ID-20 X-ray microprobe at the Advanced Photon Source (APS), Argonne National Laboratory. La L_{III}-edge (5483 eV) XAFS spectra were collected in the fluorescence mode from solutions in the modified hydrothermal diamond anvil cell in the standard horizontal 90 ° orientation to the incident X-ray beam using a thirteen-element Ge detector. The synchrotron was operated at 7.0 GeV and 100 mA maximum fill current. Energy calibration was accomplished using vanadium foil. The crystals of the monochromator were detuned by 30-40% in order to reduce the harmonic content in the incident x-ray beam.

A 1000 ppm La solution was sealed between the upper and lower diamond anvils in a sample chamber consisting of a 300 µm diameter cup-shaped cavity in the center of the upper diamond anvil face and a 300 µm diameter hole in a 50 µm thick Re gasket (Figure 2). The solution was irradiated by an X-ray beam that traveled through the upper diamond in a direction parallel to the anvil face. A laser-milled groove in the face of the upper diamond anvil reduced the path length of the incident beam through the diamond (Figure 3). A second groove, oriented at 90 degrees to the direction of the incident x-ray beam, was milled to within 80 µm of the solution chamber in order to minimize the attenuation of fluorescence x-rays impinging upon the detector. Figure 4 illustrates the enhanced transmission of x-rays in the modified hydrothermal diamond cell relative to other cell windows used in previous XAFS studies of hydrothermal solutions.

The XAFS spectra were obtained by averaging repeated scans (up to 3 scans) at each temperature. The data analysis was done using FEFFIT2.54 program (Newville et al. 1995, Stern et al. 1995) that employs a nonlinear, least square fit to the theoretical standards calculated using FEFF8 theoretical code (Zabinsky et al. 1995).

RESULTS

The L-edge (5483 eV) XAFS spectra obtained from a nitrate solution containing 1000 ppm La from ambient conditions to 300°C and 1600 bars are shown in Figures 5. Analysis of the spectra (Anderson et al. submitted) indicate that each La ion is surrounded by 9 oxygens in a tricapped trigonal prismatic arrangement. With increasing temperature the La-OH_2 bond lengths increase at the equatorial plane of the trigonal prism. Knowledge of the solvation of aqueous lanthanide ions at elevated temperatures and pressures are needed to constrain theoretical models currently used for thermodynamic predictions of REE speciation in hydrothermal fluids. The results also provide a basis for future studies of rare earth element complexing with ligands such as Cl^-, F^-, OH^-, CO_3^{-2}, SO_4^{-2} and PO_4^{-3} that may be abundant in different hydrothermal environments.

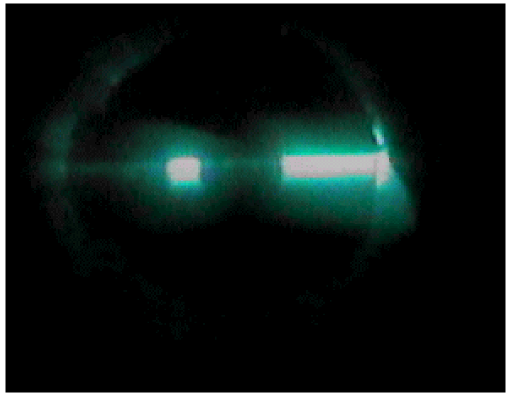

Figure 3 A photograph showing the fluorescence of the upper diamond by the incident X-ray beam. The beam travels from left to right along the groove, then through 0.08 mm of diamond, through the sample chamber and finally through 0.35 mm of diamond.

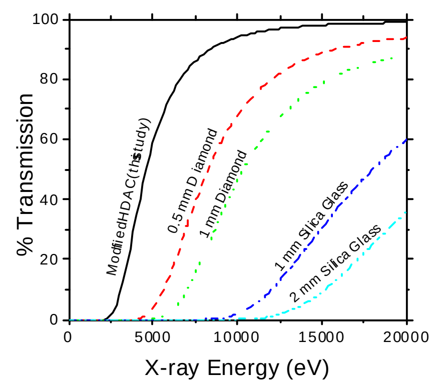

Figure 4 Percent transmission of x-rays as a function of energy through windows of different thickness and composition that have been used in X-ray spectroscopic studies of hydrothermal solutions.

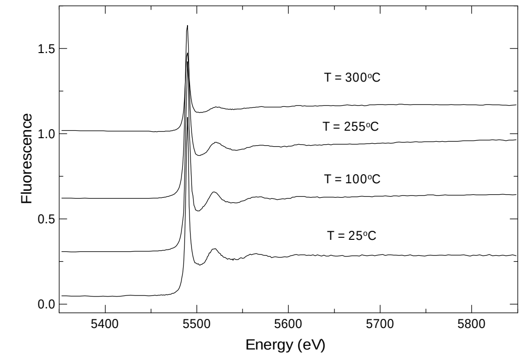

Figure 5. La *L*(III)-edge XAFS spectra from a La (1000 ppm) aqueous solution at 25, 100, 255 and 300°C.

CONCLUSIONS

The modified hydrothermal diamond anvil cell opens new opportunities for XAFS investigations of hydrothermal fluids. Our initial application of the modified cell to the problem of lanthanum hydration in hydrothermal solutions demonstrates the following attributes which make the HDAC a powerful tool for studies of crustal fluids at high T and P.

- Fluids can be studied *in situ* at higher temperatures (up to 700 °C) and pressures (up to 4000 bars) than previously possible.
- Low concentrations of dissolved metals (micromolar range) can be measured in the fluorescence mode.
- Low energy X-rays (as low as 2900 eV) can be detected which significantly extends the range of solutes that can be measured in hydrothermal solutions.
- Problematic diffraction lines from the diamond windows have been reduced or, in some cases, eliminated.

ACKNOWLEDGEMENTS

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