

# X-Ray Spectroscopic Investigations of Scandium Chloride Aqueous Solutions using the Hydrothermal Diamond Anvil Cell

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## Introduction

There is considerable interest in the use of scandium metal in the high tech industry, such as for spacecraft materials, because of its lightness and high melting point (1541 °C). Although scandium is nearly  $10^4$  times more abundant than gold in the Earth's crust, ore deposits of the element are scarce. An example of an abundant deposit of scandium of hydrothermal origin is found in the Heftejern pegmatite near Tørdal, Telemark, Norway.<sup>1</sup> A greater knowledge of the interaction of the  $\text{Sc}^{3+}$  ion with ligands common in the aqueous fluids of the Earth's crust (e.g.  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{CO}_3^{2-}$ ) under hydrothermal conditions is needed in order to understand fully the geochemistry of hydrothermal or metasomatic scandium mineralization. There are presently no direct experimental data on the structure and bonding properties of aqueous  $\text{Sc}^{3+}$  complexes under elevated temperature (T) and pressure (P) conditions. Here, we describe our results from XAFS experiments on scandium chloride aqueous solutions measured in our modified hydrothermal diamond anvil cell at up to 500 °C and 660 MPa.

## Methods and Materials

Fluorescence XAFS spectra were measured at the Sc *K*-edge (4492 eV) from a 1M  $\text{ScCl}_3$  aqueous solution sample at temperatures up to 500 °C and pressures up to 660 MPa. The XAFS measurements were made on samples held at uniform P-T conditions in a hydrothermal diamond anvil cell on the PNC-CAT ID20 beam line. Because attenuation of x-rays is significant near the soft x-ray region, two grooves were laser-milled in the culet face of the upper diamond anvil, one each for the incident x-ray beam and the fluorescence x-rays.<sup>2-4</sup> In addition to the grooves, a cylindrical sample cavity (300  $\mu\text{m}$  dia.) was milled in the center of the culet face. The sample was sealed 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 sandwiched between the upper and lower diamond anvils. Fig. 1 shows an optical image

of the culet face of the upper diamond anvil of the cell taken *in situ* through a long-working distance microscope. The vertical streak shown in the figure is the visible fluorescence originating from the diamond as the x-ray beam traverses through the incoming groove and across the sample chamber. The minimal thickness of diamond between the grooves and the sample cavity is 80  $\mu\text{m}$ .

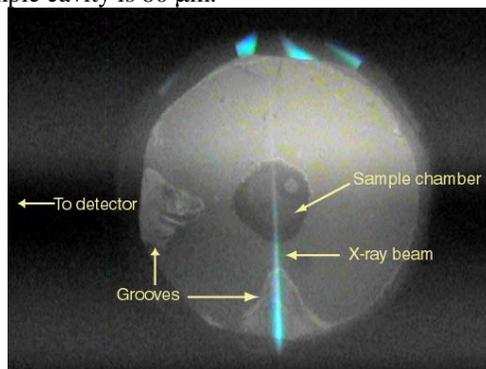


FIG. 1

## Results and Discussion

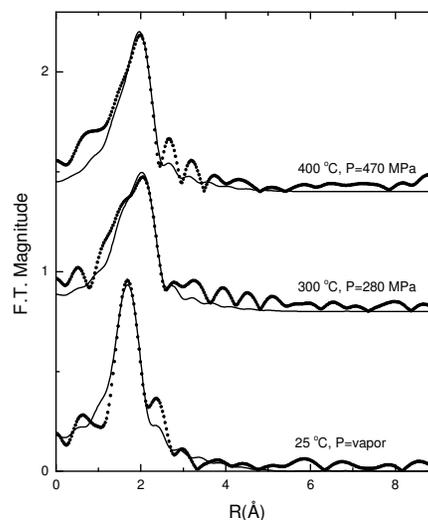


FIG. 2

Fig. 2 shows select Fourier transformed (FT) spectra

(points) in radial distance (R) space. Also shown are the fits to the individual spectra (solid lines). The Fourier transformed data were obtained from XAFS ( $k^2\chi$ ) data measured from the 1M  $\text{ScCl}_3$  aqueous solution sample. The FT's of the data were calculated in the 3.6 to 10-10.5  $\text{\AA}^{-1}$  k-range. FEFFIT was used for non-linear least squares fitting of the spectra against theoretical XAFS generated using the FEFF8 program. In Fig. 3 we show the inverse Fourier transforms, calculated in the 1.3 to 2.3-2.5  $\text{\AA}$  R-range, of data shown in Fig. 2. The measured inverse Fourier transformed data are shown as points whereas the fits of these data are shown as solid lines.

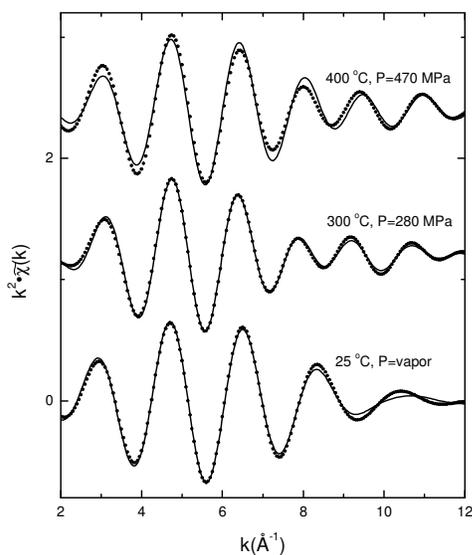


FIG. 3

Preliminary results from analysis show that  $\text{Sc}^{3+}$  is completely hydrated with  $\sim 6.5$  water molecules in the first solvation shell at room temperature. Evidence for  $\text{Cl}^-$  ligand coordination with  $\text{Sc}^{3+}$  under elevated temperature conditions is observed from analysis of spectra measured in the 150 to 500° C temperature range. The number of  $\text{Cl}^-$  ligands directly coordinated with  $\text{Sc}^{3+}$  at 150° C is  $\sim 1.0$  increasing gradually to  $\sim 2.4$  at 400° C. Conversely, the number of oxygens of water molecules in the first coordination shell of the  $\text{Sc}^{3+}$  ion decreases from  $\sim 6$  at 150° C to  $\sim 3$  at 400° C. These results suggest that  $\text{Cl}^-$  speciation may play an important role for transport of  $\text{Sc}^{3+}$  in chloride- or saline-rich hydrothermal environments in the Earth's crust. Additional XAFS studies of  $\text{Sc}^{3+}$  in the presence of other ligands, such as  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{CO}_3^{2-}$ , in aqueous solutions under hydrothermal conditions should yield more insight into the transport and deposition of scandium via crustal fluids.

### Acknowledgments

This work was funded by NSERC research and equipment grants to A.J.A. and a grant from the Research Corporation to R.A.M. NSERC is also thanked for a major facility access grant. Use of the Advanced Photon Source was supported by the U.S Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contracts W-31-109-Eng-38 (APS) and DE-FG03-97ER45628 (PNC-CAT).

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