Micro-beam XAFS measurements of zinc complexes in highly saline fluid inclusions to 400°C before and after experimental re-equilibration at high hydrogen pressure

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Our current understanding of metal speciation in natural hydrothermal systems is based largely on experimental data derived from relatively simple H_2O-salt systems. However, complexing in natural multicomponent systems may be influenced by additional fluid components that are not considered in this experimental data base. Direct spectroscopic analyses of aqueous species in fluid inclusions at elevated temperatures may provide the most accurate representation of metal complexing in palaeohydrothermal solutions. However, it has been suggested that, in some cases, aqueous species in fluid inclusions may be influenced by the loss or addition of hydrogen by re-equilibration with an ambient fluid reservior (Mavrogenes and Bodnar, 1994; Sterner *et al.*, 1995).

In this study, the possible influence of hydrogen diffusion on zinc complexing in high salinity fluid inclusions from polymetallic sulphide quartz veins was investigated by analysing X-ray absorption fine structure (XAFS) spectra obtained from individual fluid inclusions at temperatures up to 400°C before and after experimental re-equilibration at high hydrogen pressures.

Methods

Temperature-dependent Zn K-edge XAFS spectra were collected, in the fluorescence mode, from individual high salinity (*c.* 35 wt.% NaCl equiv.) fluid inclusions before and after re-equilibration at high hydrogen pressures, using the X-ray microprobe (X26A) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York. Spectra were also collected from synthetic $ZnCl_2$-NaCl-H_2O solutions within sealed SiO_2 capillary tubes. The X-rays were focussed to a spot size of about 20 μm using Kirkpatrick-Baes (KB) mirrors. Inclusions selected for analysis were situated between 10 and 20 μm below the polished surface of the quartz wafer. A programmable heating stage controlled the temperature of the fluid inclusion during spectrum acquistion.

Fluid inclusions were re-equilibrated at a high hydrogen pressures at 600°C following the method described by Mavrogenes and Bodnar (1994), except that CH_4 instead of H_2O was used as an external pressure medium, and the pressure was held at 2 kbars for 6 days.

The XAFS spectra were analysed using the University of Washington software package *UWXAFS* version 2.10. Quantitative structural information on the aqueous zinc complexes was derived from theoretical spectra generated using *FEFF 6* (Zabinsky *et al.*, 1995).

Results

Figure 1 shows the Zn K-edge X-ray absorption spectra for a standard ($ZnCl_4^{2-}$) solution at room temperature and an experimentally re-equilibrated fluid inclusion at 400°C.

Fourier transforms calculated from the isolated extended XAFS data indicate that the dominant zinc species in the fluid inclusions, before and after experimental re-equilibration and up to 400°C, is $ZnCl_4^{2-}$. Furthermore, there is a significant reduction observed in the Zn-Cl bond length with increasing temperature by nearly 0.01 Å/100°C.

Discussion

The high hydrogen pressures generated in the experimentally re-equilibrated fluid inclusions had

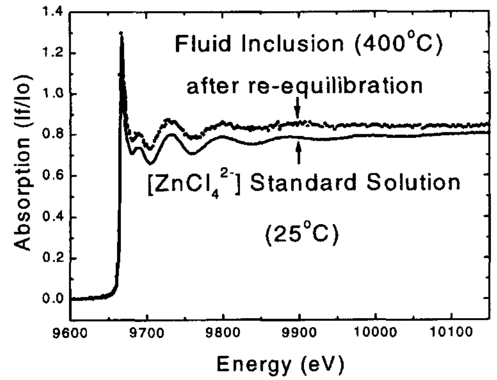

FIG. 1. XAFS spectra.

no apparent effect on the observed zinc species ($ZnCl_4^{2-}$) up to the temperature of inclusion entrapment. Although the actual f_{H_2} of the original trapped fluid is not known, it is probably small relative to that in our experimentally re-equilibrated fluid inclusions. We suggest, therefore, that natural re-equilibration of hydrogen in the studied fluid inclusions did not influence the chlorozinc species, and that the dominant zinc complex in the hydrothermal fluid at the time of fluid inclusion trapping was $ZnCl_4^{2-}$.

References

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