



	Experiment title: Mercury speciation in sulfidic solutions	Experiment number: ME-413
Beamline: ID26	Date of experiment: from: 24 April 2002 to: 30 April 2002	Date of report: <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Dr. Laurent Alvarez	
Names and affiliations of applicants (* indicates experimentalists): Drs. Tony Bell*, John Charnock*, Professors Richard Patrick*, David Vaughan, Department of Earth Sciences, University of Manchester Professor George Helz, Water Resources Research Center and Department of Chemistry and Biochemistry, University of Maryland Drs. Alistair Lennie*, Frederick Mosselmans*, Synchrotron Radiation Department, CCLRC Daresbury Laboratory Professor Francis Livens, Department of Chemistry, University of Manchester		

Report:

The Experiment

The speciation and transformation of mercury-sulfur systems is important in the understanding of the transport and toxicity of mercury in the environment. This is of particular relevance to the bio-availability of mercury and to land clean-up technologies in contaminated areas. We had previously investigated the speciation of concentrated Hg in sulfidic solutions at high pH at S.R.S. Station 16.5. As the pH is lowered the solubility of Hg is lowered considerably, thus the high intensity of the ESRF ID26 was required for these more dilute solutions.

The solutions were made up from synthetic metacinnabar (HgS), sodium sulfide and a pH buffer (pH 9.18) in an anaerobic environment, at CLRC Daresbury. They were kept under nitrogen and loaded into the 'Lennie'¹ cell for the XAFS experiment in a glove bag under nitrogen. All samples were filtered through a 0.02 micron filter prior to loading. Either PEEK or BN windows were used with Kalrez o-rings. Stibnite was added to one solution as G. R. Helz (Pers. Comm) has suggested the formation of Hg-S-Sb complexes in solution. Spectra were measured in *k*-space mode, counting for either 1 or 2 seconds per point. For the most concentrated samples as few as 4 spectra (270 ppm Hg) were summed to give high quality data. For the most dilute sample (4 ppm Hg) 24 spectra were summed. Spectra were added in EXODUS, background subtracted in EXBROOK and simulated using EXCURV98. Some precipitation occurred as the solutions were heated. The solid tended to accumulate on the cell window thus the EXAFS spectra. We were able to collect good data on 4ppm solution in several hours, but on dilution to 0.4 ppm EXAFS proved impossible to collect. After 12 hours collection of what appeared to be on the screen a reasonable spectrum, the 24 scans were summed but there was no real EXAFS, just the influence of oscillations coming through from I0.

The Results

The Figure shows the fit for the 4ppm data at room temperature as a gauge of data quality. All the solution data could be modelled by Hg with 2 S atoms at ca. 2.30 Å in a linear geometry, the fits were improved significantly by multiple scattering. This bond distance of 2.30Å in the Hg-S complexes is similar to that found in higher concentration samples (Lennie et. al, 2002) and is typical of two coordinate Hg, and is

¹ The cell was developed for use with SR and used the SRS prior to use at the ESRF – details are in Lennie et.al (2002) – the work was funded by a NERC ROPA award (GR3/R9926).

similar to that that found in cinnabar (HgS – the main Hg ore), which has Hg-S distances of 2.368 Å in -S-Hg-S-Hg- infinite chains running through the structure. These small coordination numbers are considered to be a consequence of relativistic effects. In contrast to previous work, there is evidence of further shells suggesting dimers or larger clusters and these clusters occur in the solutions with the lowest sulfide concentration at room temperature. On heating the second shell is lost, either due to an increase in thermal vibrations that may remove evidence for the second shell or the cluster may break up. In the 4 ppm Hg sample with 0.03M Na₂S, 4 Hg atoms are at 6.23 Å while in the 37 ppm Hg sample in 0.005M Na₂S 4 Hg atoms are at 4.5 Å.

The solid formed in high temperature solutions is similar in structure to amorphous meta-cinnabar that we have seen previously studies of HgS precipitates.

Discussion

According to Barnes (1979), HgS₂²⁻ is dominant in the region above pH = 8 and a Raman spectroscopy investigation (Cooney and Hall, 1966) suggest linear complexes form. One consistency of these previous studies is the proposed presence of an HgS₂²⁻ species at high pH. The data we in this study are consistent with the formation of [S-Hg-S]²⁻ species with Hg-S bond lengths of 2.3 Å.

The identification of polynuclear Hg-S species is the first direct evidence of their presence in sulfidic solutions. The possibility that amorphous metcinnabar is present is discounted because then Hg would be 4-coordinate with Hg-S ca 2.54 Å and 12 Hg at 4.15 Å (see Lennie et al., 2002), and polysulfides (common in Hg-S systems) would involve both 4 coordinate Hg and high S:Hg ratios. Polymeric metal species have been predicted in other metal-sulfide systems but theoretical and experimental studies studies (see Tossell, 1999; 2001, Barnes and Seward , 1997) all focus on monomeric Hg-S complexes. The data presented here require a re-examination of this assumption.

Summary

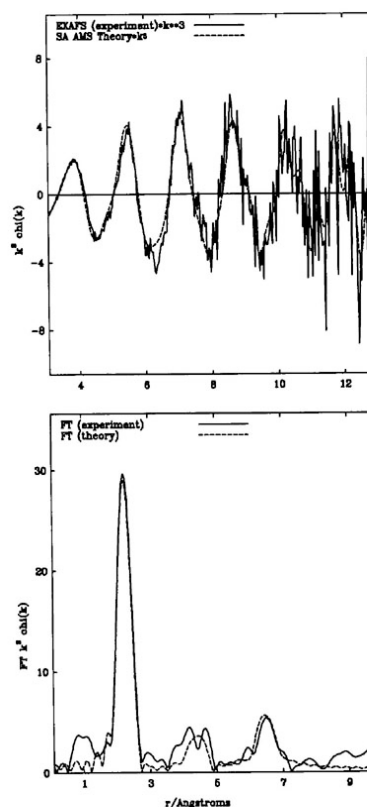
This study provides ample evidence of the value of high fluxes and high quality detectors in the study of environmentally relevant systems. These data both provide the confirmation of previous work by providing direct evidence of linear Hg-S solutions species and evidence of polynuclear Hg-S species. We believe with even better detectors we could achieve data on the 0.4ppm solution and provide confirmation of the existence of polynuclear species and produce data directly relevant to environmental systems

Acknowledgements

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References

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Tossell JA (1999) *American Mineralogist*, 84, 877-883.

k^3 -weighted EXAFS and phase-shifted Fourier transform of solution containing 0.03M Na_2S , 4 ppm Hg at pH 9.18 at room temperature. Fourier transform shows additional Hg shell at 6.23 Å.

Tossell JA (2001) *J. Physical Chemistry A*, 105, 935-941.