



	Experiment title: EXAFS of Copper in Natural Waters	Experiment number: CH-532
Beamline: ID26	Date of experiment: from: 12/12/98 to: 12/12/98	Date of report: 3/3/99
Shifts: 12	Local contact(s): Dr A. Sole	<i>Received at ESRF:</i> U 8 MAR. 1999

Names and affiliations of applicants (* indicates experimentalists):

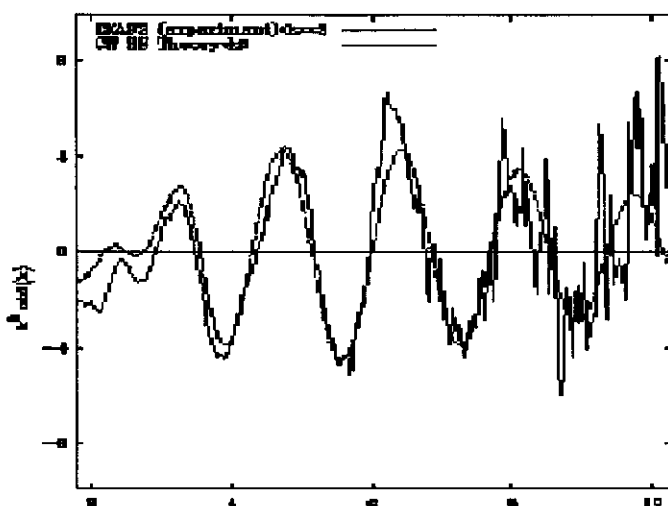
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Report:

The importance of copper in biogeochemical cycles has prompted much research into its speciation in natural waters. Most of these studies have been by indirect methods such as solubility studies. The total amount of dissolved copper rarely exceeds 100 μM except at very high sulfide concentration. This has resulted in a paucity of direct structural studies. Indeed the only previous EXAFS study of copper (Helz *et al.*, 1993) in bisulfide solution used 9M NaHS solution to dissolve enough copper to obtain Cu EXAFS spectra. This study reports on the use of X-ray absorption spectroscopy to study the speciation of copper in bisulfide solutions at pH 7.4 and 9.5. We used the ID26 beamline at the ESRF to obtain direct structural data on bisulfide solutions of copper at pH 7.4, 0.5M NaHS and pH 9.5, 0.7MNaHS. The solutions measured were prepared under nitrogen, using NaOH, H₂S and sodium borate buffer. To this powdered covellite was added, which was allowed to equilibrate for one week before the data were recorded.. To raise the Cu concentration to a measurable level, the samples were spiked with excess Cu shortly before the data were

collected. ICP-MS studies have showed that this raises the ppm Cu to 1.2 and 4.4 from 1.16 and 0.8 in the pH 7.4 and 9.5 solutions. The solutions were injected into PVC cells with 25 micron PEEK windows through a 5 micron syringe filter. The cells were sealed with epoxy resin and the data collected in fluorescence mode using a 9 element Si drift detector with an Ni filter. 24 spectra of the pH 9.5 solution and 12 of the pH 7.5 solution were collected scanning at equal energy steps in the EXAFS region for 4 seconds a point. The spectra were initially examined individually before being summed to check for sample degradation due to radiation or oxidation. None was found for either sample. Data was collected up to the zinc edge at 9 523 eV though the useful data range was to 9 k for the pH 7.4 and 10k for pH 9.5 solutions. The k^3 -weighted EXAFS was analysed using EXCURV98. One shell fits indicate 2 S atoms at 2.22Å from Cu in the pH 9.5 solution and 3 S at 2.25 Å from Cu in the pH 7.4 solution. The fit to the pH 9.5 data is shown in the figure. These are lower coordination numbers than those found in the Helz study but are in agreement with recent UV work by T.M. Seward (personal communication).

It is believed that these data represent some of the lowest concentration solutions studied by XAS and with the full development of the DRIFTS detector the potential to study systems at even lower (sub ppm levels) concentrations exists. This will be particularly useful for studying the speciation of metals in real systems and for looking at changes in that speciation as the temperature of the solutions is raised.



Reference

Helz G.R., Charnock J.M., Vaughan D.J. and Garner C.D. (1995) Multinuclearity of aqueous copper and zinc bisulfide complexes: An EXAFS introduction. *Geochim. Cosmochim. Acta.* 57, 15-25.