Mineralogical Magazine, October 1999, Vol. 63(5), pp. 769–772

EXAFS of copper in hydrosulfide solutions at very low concentrations: implications for the speciation of copper in natural waters

J. F. W. MOSSELMANS[1], R. A. D. PATTRICK[2], J. M. CHARNOCK[1,2] AND V. A. SOLÉ[3]

[1] CCLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK
[2] Department of Earth Sciences, University of Manchester, Manchester M13 9PL, UK
[3] ESRF, BP-220, 38043 Grenoble Cedex, France

ABSTRACT

Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra have been obtained for two very dilute solutions of copper in hydrosulfide solutions using beamline ID26 at the ESRF. The concentrations of the solutions (4.4 ppm {69 μM} pH 9.5, 1.2 ppm {19 μM} pH 7.4) are such that the experiments illustrate that, with the advent of third generation synchrotron sources, natural systems can now be studied by EXAFS. Analysis of the data indicates an average environment for the copper of 2.3 S atoms at 2.22 Å in the pH 9.5 solution of 2.5 S atoms at 2.23 Å in the pH 7.4 solution. These results are in accord with the solubility study of Mountain and Seward (1999), who conclude that $Cu(HS)_2^-$ and $Cu_2(HS)_2S^{2-}$ are the principal copper species in such solutions.

KEYWORDS: EXAFS, hydrosulfide solutions, copper speciation.

Introduction

IN studies of the metal transport in natural systems, knowledge of the speciation is critical to a comprehensive understanding of metal behaviour. Many investigations have been based on thermodynamic models or 'indirect' analysis of the species present, such as solubility studies. Where spectroscopic techniques are employed, solutions are often at unrealistically high metal concentrations. This is particularly true of sulfidic solutions in which solubilities are at a micromolar level in natural waters, and extreme values of pH are needed to obtain measurable metal concentrations. Extended X-ray absorption spectroscopy fine structure (EXAFS) can provide unique, element specific, structural information on metals in solution (Mosselmans *et al.*, 1996) and is providing definitive structural information on metal-sulfur species in solution, complementary to other work (Mosselmans *et al.*, 2000). This investigation reveals the value and current limits of this technique in the study of Cu speciation in hydrosulfide solutions.

Copper is important in bio-geochemical cycles and this has resulted in much research into its speciation in natural waters. In anoxic waters, hydrosulfide and polysulfide complexes of Cu are expected to be dominant (Gardner, 1974; Jacobs and Emerson, 1982). The total amount of dissolved Cu rarely exceeds 100 μM except at very high sulfide concentration. This has resulted in a paucity of direct structural studies and the only previous EXAFS study of copper speciation (Helz *et al.*, 1993) in hydrosulfide solution used 9 M NaHS solution to dissolve enough Cu to obtain copper EXAFS spectra. Helz *et al.* (1993) provided evidence for multinuclearity of the copper bisulfide species present but this was in solutions containing 3–16 mM Cu, 100–1000 times more concentrated than the solutions described in this study. Recent solubility studies (Mountain and Seward, 1999) on naturally relevant Cu concentrations have indicated that two-coordinate monomeric and dimeric hydrosulfide copper complexes are the most common in dilute solutions. This is in contrast to Thompson and Helz (1994) who suggested the principal copper species to be $Cu(HS)_3^{2-}$ and $Cu_2S(HS)_2^{2-}$, or $Cu_3S(HS)_3^{2-}$ *and* $Cu_4S_2(HS)_2^{2-}$.

The advent of third generation synchrotron sources (such as the European Synchrotron Radiation Source – ESRF) has, by producing higher photon fluxes, lowered the minimum concentration that is required for EXAFS spectroscopy. Spectra can, potentially, be obtained on solutions of 10 μM concentrations, within the range of natural waters. This study reports on the EXAFS analysis using beamline ID26 at the ESRF to study the speciation of Cu in 0.5 and 0.7 M hydrosulfide solutions, where the concentration of copper is between 10 and 40 μM (Shea and Helz, 1988), and at pH 7.4 and 9.5, respectively.

Experimental method

A 0.7 M NaOH solution was saturated with H_2S gas to produce a 0.7 M NaHS solution, and a pH of 9.5 was maintained *using a* 0.1 M *sodium* borate buffer. A 0.5 M NaHS solution was prepared in similar fashion and a pH of 7.4 maintained by excess H_2S. Fine grained, poorly crystalline CuS was added to each solution, which was then sealed in a polythene bottle, and held in a N_2 atmosphere for two weeks before the experiment. All solutions were deoxygenated with N_2 prior to starting, and the solutions were prepared in a N_2 glove box.

EXAFS measurements were conducted in 1 mm thick cells made from polyvinylchloride with 25 μm PEEK windows fixed by epoxy resin. Approximately 30 min before the data were collected, the solutions were supersaturated by adding a few grains of $Cu(NO_3)_2$. The solution was injected into the cell through a 0.20 μm filter in an N_2 glove bag and the holes used for injection sealed with epoxy resin. The copper concentration of the filtered solutions was determined using inductively coupled plasma mass spectroscopy (ICP-MS) both before and after supersaturation. The concentration of Cu was raised to 1.2 and 4.4 ppm (19 and 69 μM) from 0.8 and 1.16 ppm (13 and 18 μM) in the pH 7.4 and 9.5 solutions, respectively. The samples were at ambient temperature during data collection, though the intensity of the photon beam may have caused some localized heating.

The EXAFS data were collected using a Si(220) double crystal monochromator with a silicon mirror to reject harmonics. The monochromator was calibrated using a Cu foil, defining the top of the pre-edge peak as being at 9883.3 eV. The I_o was recorded using a photodiode to measure the scatter from a filter in the beam; the data were collected using a 12 channel Silicon Drift detector. A 5 μm Ni foil was used to reduce the number of scatter counts in the detector. Blanks were run with the cell empty and full of deionized water to ensure that the Cu signal collected was from the solution. Twenty-four spectra of the pH 9.5 solution and twelve of the pH 7.4 solution were collected, scanning at equal energy steps in the EXAFS region for 4 s for each point. The spectra were initially examined individually before being summed to check for sample degradation due to radiation or oxidation; no evidence of beam induced changes was found. Data were collected up to the Zn edge at 9523 eV for the pH 9.5 solution and to 10.5 k ($Å^{-1}$) for the pH 7.4 solution. The data were summed and then reduced in the normal way (Pattrick *et al.*, 1998). The useful data range was to 10.5 k ($Å^{-1}$) for the pH 9.5 solution and 9 k ($Å^{-1}$) for the pH 7.4 solution. The k^3-weighted EXAFS was simulated using the program EXCURV98 (Binsted, 1998). Phase shifts were calculated using *ab initio* methods with Hedin-Lundquist exchange and von Barth ground state potentials. The fit index, *R*, quoted is defined by

$$R = \Sigma_i[(1/(\sigma_i))(|\text{experiment(i)-theory(i)}|] \,.100\%$$

$$\text{where: } 1/(\sigma_i) = [k(i)]^3/(\Sigma_i[k(i)]^3.|\text{experiment(i)}|)$$

Results and discussion

The spectra from the two solutions are similar. The higher pH solution data are of better quality, the result of more summed spectra and a higher concentration of Cu. The EXAFS data and fits are shown in Fig. 1. The data for both solutions can be simulated by one shell of S atoms. The pH 9.5 solution spectra were fitted to 2.3 atoms at 2.22 Å with a Debye-Waller Factor ($2\sigma^2$) of 0.013 $Å^2$ ($R = 55$), while those of the pH 7.4 solution indicate 2.5 S atoms at 2.23 Å with a Debye-Waller factor of 0.018 $Å^2$ ($R = 60$). The first of these bond lengths is shorter than those seen in trigonally-coordinated CuS species (typically 2.23–2.27 Å) and, although the restricted data range may have contributed to the absence of a significant second shell, there is no evidence of Cu at the distances expected for multimeric complexes. The short bond distances and low coordination numbers, thus indicate that linear-coordinated monomeric Cu(I) is the main species present. This finding is in accord with Mountain

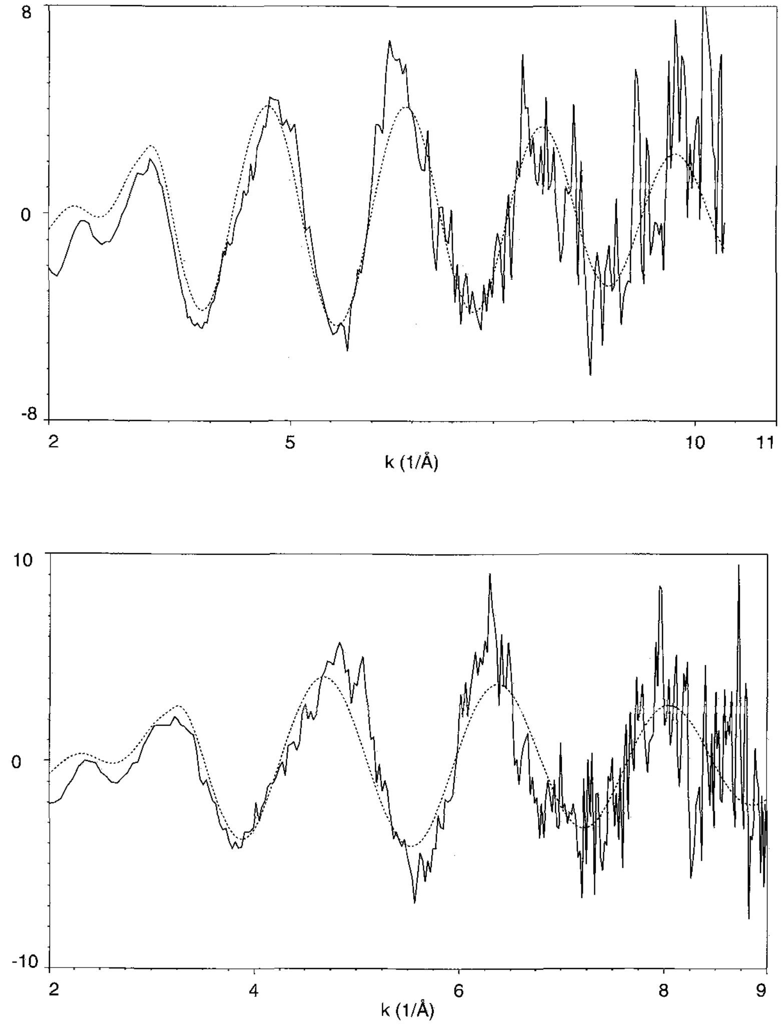

FIG. 1. (*a*) Cu K-edge k^3 – weighted EXAFS of 4.4 ppm Cu in a 0.7 M NaHS solution pH 9.5 solution (— experimental data, - - - simulation). (*b*) Cu K-edge k^3– weighted EXAFS of 1.2 ppm Cu in a 0.5 M NaHS solution pH 7.4 solution (experimental data, - - - simulation).

and Seward's (1999) solubility study which indicated that the major Cu species in these solutions will be $Cu(HS)_2^-$ and $Cu_2(HS)_2S^{2-}$.

Thus, we have demonstrated the feasibility of using EXAFS to investigate the complexation in hydrosulfide solutions containing very low concentrations of Cu by obtaining structural parameters on the linear Cu complexes. These are the first such structural data on two-coordinate Cu species in solution and have allowed discrimination between two possible models presented in previous work (Thompson and Helz, 1994; Mountain and Seward, 1999). Multiple scans are seen to provide data on the inner coordination shell on solutions containing ~1 ppm Cu. Further improvements in data quality can be expected with a 30 channel Silicon Drift detector, which would enable variable temperature EXAFS studies to be undertaken on these solutions and also EXAFS spectra to be recorded on systems with metal concentrations as low as 0.2 ppm. Synchrotron instrumentation now allows metal speciation to be determined on concentrations relevant to natural hydrous environments, and therefore, analysis of metals in natural waters becomes possible.

Acknowledgements

We are grateful to the Director of the ESRF for providing access to the facility (Beamtime award number Ch-532). We also appreciate the use of the Material Science Laboratory at the Daresbury Laboratory for the preparation of the samples and thank Professor Seward for providing details of his work (Mountain and Seward, 1999) prior to publication. Mr P. Lithgoe is thanked for assistance with the ICP-MS analysis.

References

Binsted, N. (1998) *EXCURV98*. CCLRC Daresbury Laboratory computer program.

Gardner, L.R. (1974) Organic versus inorganic trace metal complexes in sulfide marine waters – some speculative calculations based on available stability constants. *Geochim. Cosmochim. Acta*, **38**, 1297–302.

Helz, G.R., Charnock, J.M., Vaughan, D.J. and Garner, C.D. (1993) Multinuclearity of aqueous copper and zinc bisulfide complexes: An EXAFS introduction. *Geochim. Cosmochim. Acta*, **57**, 15–25.

Jacobs, L. and Emerson, S. (1982) Trace metal solubility in an anoxic basin. *Earth Planet. Sci. Lett.*, **60**, 237–52.

Mosselmans, J.F.W., Schofield, P.F., Charnock, J.M., Garner, C.D., Pattrick, R.A.D. and Vaughan, D.J. (1996) X-ray absorption studies of metal complexes in aqueous solution at elevated temperatures. *Chem. Geol.*, **127**, 339–50.

Mosselmans, J.F.W., Helz, G.R., Pattrick, R.A.D., Charnock, J.M. and Vaughan, D.J. (2000) A study of speciation of antimony in bisulfide solutions by X-ray absorption spectroscopy. *Appl. Geochem.*, (in press).

Mountain, B.W. and Seward, T.M. (1999) The hydrosulphide sulphide complexes of copper(I): Experimental determination of stoichiometry and stability at 22°C and reassessment of high temperature data. *Geochim. Cosmochim. Acta*, **63**, 11–29.

Pattrick, R.A.D., Mosselmans, J.F.W. and Charnock, J.M. (1998) An X-ray absorption study of doped sphalerites. *Eur. J. Mineral.*, **10**, 239–49.

Shea, D. and Helz, G.R. (1988) The solubility of copper in sulfidic waters: Sulfide and polysulfide complexes in equilibrium with covellite. *Geochim. Cosmochim. Acta*, **52**, 1815–25.

Thompson, R.A. and Helz, G.R. (1994) Copper speciation in sulfidic solutions at low sulfur activity: further evidence for cluster complexes? *Geochim. Cosmochim. Acta*, **58**, 2971–83.

[*Manuscript received 9 August 1999: revised 6 September 1999*]