NOTE

Spectroscopic study on the anion exchange behavior of Cu chloro-complexes in HCl solutions and its implication to Cu isotopic fractionation

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The mode of coordination about Cu(II) adsorbed on a strongly basic anion exchange resin equilibrated in HCl aqueous solutions was determined using extended X-ray absorption fine structure (EXAFS) and Raman spectroscopies. EXAFS spectra of the adsorbed Cu chloro-complexes were constant over a wide range of HCl concentrations in contrast to stepwise Cu–Cl complexation in the solutions. The adsorbed anion species was estimated to be $[\text{CuCl}_4]^{2-}$. Its Raman spectra suggested the most plausible coordination structure of $[\text{CuCl}_4]^{2-}$ was 4 Cl coordination without H_2O ligands. The change from sixfold coordination $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to fourfold coordination $[\text{CuCl}_4]^{2-}$ in stepwise chloro-complexation in the aqueous phase and preferential adsorption of $[\text{CuCl}_4]^{2-}$ to the resin through ion-exchange reactions in elevated HCl concentrations will result in larger mass fractionation of Cu compared to Zn, which has a tendency to form tetrahedral Zn chloro-complexes in the presence of chloride ions.

Keywords: Cu chloro-complexes, stepwise complexation, ion exchange resin, X-ray absorption fine structure (EXAFS), Raman spectroscopy

INTRODUCTION

Recent developments in inductively coupled plasma mass spectrometry with multiple-collector configuration (MC-ICP-MS) have revealed isotopic variations in transition elements such as Fe, Cu, Zn, and Mo in natural samples (Johnson *et al.*, 2004). In equilibrium isotope exchange reactions, the heavy isotopes of an element tend to be concentrated in substances where the element forms the most rigid bonds, and large equilibrium fractionations are most likely to occur at low temperatures between substances with different coordination numbers (Schauble, 2004) based on the Bigeleisen-Mayer algorithm (Bigeleisen and Mayer, 1947).

With the development of MC-ICP-MS, isotopic fractionation by chemical purification of samples has also been widely recognized. Maréchal and Albarède (2002) carried out Cu and Zn isotopic fractionation experiments with an anion exchange resin eluted with HCl solutions

to determine their fractionation coefficients. The resultant Cu isotope fractionation was one order of magnitude greater than that for Zn, but the origin of the large isotopic fractionation was not fully explained. This is because of the stepwise Cl complexation from Cu^{2+} up to CuCl_4^{2-} (Ramette, 1986 and references therein) and from Zn^{2+} up to ZnCl_4^{2-} (Ruaya and Seward, 1986 and references therein) in aqueous solutions, and thus only the average coordination of more than three species can be estimated. The coordination structure of Cu in chloride solutions is not well resolved despite a number of investigations (D'Angelo *et al.*, 1997 and references therein), in contrast to the well-known distorted octahedral coordination of hydrate Cu^{2+} ion in aqueous solutions.

Here, we applied extended X-ray absorption fine structure (EXAFS) analysis to this equilibrium reaction system. EXAFS is a powerful technique that can be applied to multiple component structures, such as high ionic strength solutions and biological molecules, because it can determine the local environment (such as interatomic distances and coordination numbers) surrounding an X-ray absorbing atom separately from other atoms. We present here the result of an EXAFS study in combination with Raman spectroscopy for a better understanding of the relationship between the coordination of the Cu–

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Cl complexes and isotopic fractionation in the ion-exchange equilibrium reaction.

EXPERIMENTAL

Sample preparation

Three 0.1 M Cu aqueous solutions containing 12, 7.0, and 3.0 M HCl were prepared by weight from analytical reagent grade HCl, Milli-Q water, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and used for analysis. Cu-adsorbed resin samples were prepared from AG MP-1 (Cl-form, Bio-Rad Laboratories, Inc.) by the batch method with the solutions above. AG MP-1 is a strong basic anion exchange resin with $-\text{N}^+(\text{CH}_3)_3$ groups as anion-exchange sites attached to a styrene divinylbenzene copolymer lattice. About 0.3 g dry AG MP-1 (100–200 mesh) was added to the 0.1 M Cu solutions of 0.8 mL. After being shaken gently for 30 minutes the mixtures were left overnight. The resins were then filtered and the remaining interstitial solutions were twice removed by centrifugation (3000 rpm $\times$ 10 min). The intact residual resins were sealed with polyethylene film and preserved for analysis. As the ion exchange capacity of dry AG MP-1 is 4.2 mmol/g, about 6% of the total exchange sites would be occupied in the case of all ions converting to monovalent ions (i.e., 13% occupation for divalent ions).

Spectral measurements

EXAFS XAFS spectra at the Cu K-edge were taken in the fluorescence mode with a Lytle detector using station BL-12C (Nomura and Koyama, 1996) at Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan. Cu K-edge spectra were calibrated using the lowest energy inflection point in the spectrum of copper metal foil fixed at 8980.3 eV. Data were analyzed using the REX2000 program (Rigaku Co.). The pre-edge background of the XAFS spectra was fitted with linear functions and then cubic spline functions were used to extract the EXAFS function $\chi(k)$ (Cook and Sayers, 1981). All experimental procedures were performed at ambient temperature.

Raman Raman spectra were recorded with the T64000 (Horiba Jobin-Yvon Inc.) spectrometer at Kochi Core Center, Japan. Liquid samples were packed in quartz cuvettes and solid samples in quartz tubes and their spectra taken at room temperature.

RESULTS AND DISCUSSION

EXAFS spectra

The presence of divalent copper was confirmed in the pre-edge region by a weak transition near 8976 eV (e.g., Pickering and George, 1995) that corresponds to a $1s \rightarrow 3d$ transition (data not shown). EXAFS spectra of the so-

Fig. 1. Cu EXAFS k^3 -weighted $\chi(k)$ plots for (a) Cu solution in 12 M, 7 M, and 3 M HCl and (b) Cu-adsorbed AG MP-1 anion exchange resin equilibrated in 12 M, 7 M, and 3 M HCl solutions.

lutions and resins in k -space are shown in Figs. 1(a) and (b) as $k^3\chi(k)$. Radial structural functions (RSF) obtained as the Fourier transforms of $k^3\chi(k)$ from $k = 3.8$ to $13.0 \text{ \AA}^{-1}$ are given in Figs. 2(a) and (b). The Fourier transform peaks were not corrected for phase shifts.

Major peaks for samples were found at $\sim 1.4 \text{ \AA}$ and $\sim 1.8 \text{ \AA}$, as for solid hydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, shown in Fig. 2. An X-ray crystallographic study of the solid hydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ shows that the Cu^{2+} has a $4 + 2$ configuration of two oxygens at $1.96 \text{ \AA}$, two chloride ions at $2.29 \text{ \AA}$ at the equatorial sites and a further two chloride ions at $2.94 \text{ \AA}$ in the axial positions due to Jahn-Teller distortion (Engberg, 1970). A previous EXAFS study of the solid indicates that the two observed peaks are the contribu-

Fig. 2. The Fourier transform of the weighted $\chi(k)$ data for (a) Cu solution in 12 M, 7 M, and 3 M HCl and (b) Cu-adsorbed AG MP-1 anion exchange resin equilibrated in 12 M, 7 M, and 3 M HCl solutions. A spectrum of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was measured with instrumental settings identical to those used for the other spectra and inserted in the figures. The Fourier transform of Cu solution in 3 M HCl is in good agreement with that by D'Angelo *et al.* (1997).

tion of O (~ 1.4 Å) and Cl (~ 1.8 Å) at the equatorial sites (Pascal *et al.*, 1984). In the chloride solutions, the peak at ~ 1.4 Å decreases and the peak at ~ 1.8 Å increases with increasing molarity of HCl from 3 M to 12 M (Fig. 2(a)), confirming these peaks correspond to the contributions of O and Cl. The absence of detectable pronounced peaks from the axial positions is not unexpected for such long interactions due to large Debye-Waller factors (Pickering and George, 1995), which is consistent with the previous Cu EXAFS result in chloride solutions (D'Angelo *et al.*,

1997). It should be emphasized that the change in the equatorial coordination of samples is an averaged structural change among the several chloro-complexes dissolved in the solutions. Structural changes between individual complexes are not distinguishable from the RSF of the Cu complexes dissolved in the solutions (Fig. 2(a)).

In contrast to the solution spectra, EXAFS spectra and the Fourier transform peaks of the adsorbed Cu chloro-complexes on the resins were identical despite different HCl concentrations used for equilibrium adsorption reactions (Figs. 1(b) and 2(b)). The uniformity of EXAFS spectra of Cu adsorbed on the resin despite the variation in Cu complexes in HCl solutions (Figs. 1(a) and 2(a)) indicates a preferential adsorption of one species among anionic Cu chloro-complexes.

The candidates for the adsorbed Cu anionic complex are $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$. Among them, the latter is suggested as the adsorbed species from an RSF comparison between Cu solution in 12 M HCl and Cu adsorbed on the resin in 12 M HCl (Fig. 2). In 12 M HCl Cu solution, $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ species account for almost 90% of the total Cu-Cl complexes (Maréchal and Albarède, 2002). The RSF around Cu in 12 M HCl solution in Fig. 2(a) therefore approximately reflects an averaged structure of the two species, and the peaks of ~ 1.4 Å (Cu-O bond) and ~ 1.8 Å (Cu-Cl bond) mentioned above can be recognized. In contrast, we observed no significant contribution from the ~ 1.4 Å peak in the Cu-adsorbed resin (Fig. 2(b)). This demonstrates that the Cu complex adsorbed on the resin is a species with a lower degree of hydrated H_2O , that is, $[\text{CuCl}_4]^{2-}$. Furthermore, the amount of adsorbed Cu increased with Cl molarity, which was calculated from a rough ICP-AES analysis of Cu concentration remaining in the equilibrated aqueous phases to be about 50% for 3 M HCl solution and about 80% for 7 and 12 M HCl solutions, respectively. This trend is more consistent with the distribution of $[\text{CuCl}_4]^{2-}$ species than that of $[\text{CuCl}_3]^-$ (Maréchal and Albarède, 2002). These phenomena indicate the most plausible adsorbed complex is $[\text{CuCl}_4]^{2-}$. Possible coordination geometries of $[\text{CuCl}_4]^{2-}$ were estimated by curve-fitting the EXAFS spectra using FEFF calculations (Rehr and Albers, 2000). The first shell of the Fourier transform (1.17 Å– 2.27 Å in Fig. 2(b) adsorbed in 12 M HCl) was used for the curve-fitting. FEFF calculations were carried out using models of Cu-O (1.96 Å and 2.23 Å) and Cu-Cl (2.29 Å). Four-fold Cl coordination around Cu was fitted well, but 4 Cl + 2 H_2O coordinations were also fitted sufficiently as shown in Table 1. The coordination geometry of $[\text{CuCl}_4]^{2-}$ was not determined solely from the EXAFS results.

Raman spectra

Raman spectra are sensitive to different modes of coordination as changes in symmetry. Raman spectra of the

Table 1. FEFF fitting results for the adsorbed Cu–Cl complexes on resin equilibrated in 12 M HCl solution

First shell	N	R (Å)	ΔE_0 (eV)	σ (Å)	Residual (%)
Fourfold Cl coordination Cu–Cl	3.8	2.24	–0.8	0.064	0.4
4Cl + 2H ₂ O octahedral coordinations (with two Cu–Cl in the second shell at axial positions)					
Cu–O	1.9	2.06	3.2	0.045	0.3
Cu–Cl	2.0	2.26	3.2	0.036	
(Cu–Cl planar with Cu–H ₂ O at axial positions)					
Cu–O	1.9	2.18	0.8	0.061	0.1
Cu–Cl	3.8	2.23	0.8	0.063	

N: coordination number, R: interatomic distance, ΔE_0 : threshold E_0 shift, σ : Debye-Waller factor. Fitting residuals are calculated by the REX2000 software and represented in percent. Uncertainties of the resultant parameters are estimated to be $\pm 20\%$ for N, ± 0.02 Å for R, and $\pm 20\%$ for σ , respectively (O'Day et al., 1994).

Cu-adsorbed anion resin equilibrated in 12 M HCl and the Cu solution in 12 M HCl are shown in Fig. 3 with those of analytical grade 12 M HCl, AG MP-1 (Cl-form), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ powder as references. The reference spectrum of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is consistent with that reported in the literature (Tanaka et al., 1987). A specific peak at 280 cm^{-1} is found only in the samples (both Cu solution and Cu-adsorbed resin), which demonstrates this peak is due to Cu-related Raman scattering. This band is far from the stretching modes of Cu–O at $\sim 400\text{ cm}^{-1}$ and Cu–Cl at 216 cm^{-1} in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in octahedral coordination, but is similar to those of Cu–Cl in $[\text{CuCl}_4]^{2-}$ square-planar (248 cm^{-1}) and tetrahedral (280 cm^{-1}) Cl coordinations in $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ and Cs_2CuCl_4 (Beattie et al., 1969). The frequency difference between tetrahalo species and tetrahedral halide solutions is usually within 10 cm^{-1} (e.g., Quicksall and Spiro, 1966). This indicates tetrahedral coordination is the most plausible symmetry for $[\text{CuCl}_4]^{2-}$ but further investigations are necessary to exclude the other possible symmetry.

The origin of isotopic fractionation through ion-exchange resin

In the calculated distribution of Cu chloro-complexes in HCl solutions by Maréchal and Albarède (2002), the fraction of $[\text{CuCl}]^+ : [\text{CuCl}_2]^0 : [\text{CuCl}_3]^- : [\text{CuCl}_4]^{2-}$ is 16:30:42:10 for 3 M HCl solution, 4:16:51:29 for 7 M HCl solution, and 1:8:46:44 for 12 M HCl solution. As a consequence, the average coordination number of Cl around Cu is 2.4, 3.1, and 3.3 in 3 M, 7 M, and 12 M HCl solutions, respectively. The results are qualitatively consistent with the variation of the RSF in Fig. 2(a). Based on the current results, on the other hand, it is suggested that $[\text{CuCl}_4]^{2-}$ is preferentially adsorbed on to the ion-exchange resin in 3 M, 7 M, and 12 M HCl solutions.

Fig. 3. Raman spectra of Cu solution in 12 M HCl and Cu-adsorbed resin equilibrated in 12 M HCl solution (top) and related reference materials (bottom).

The EXAFS and Raman spectra obtained here indicate a coordination change in Cu–Cl complexation in elevated HCl concentrations from 6 to 4, in contrast to the tendency of tetrahedral Zn chloro-complexes to form in

the presence of chloride ions (Silber *et al.*, 1984). We therefore assume the vibrational energy of $[\text{CuCl}_4]^{2-}$ may be higher than those of 6 coordinate Cu–Cl complexes, resulting in the enrichment of the lighter Cu isotope in $[\text{CuCl}_4]^{2-}$ according to the Bigeleisen-Mayer algorithm (Bigeleisen and Mayer, 1947). Anion exchange resin only extracts $[\text{CuCl}_4]^{2-}$ and this preferential adsorption and separation of $[\text{CuCl}_4]^{2-}$ from HCl solutions will be the origin of larger mass fractionation of Cu compared to Zn. Exact determination of structural parameters through further experiments will help to calculate fractionation coefficients theoretically for a quantitative understanding of the mass fractionation (e.g., Fujii *et al.*, 2006).

Ion exchange resin preferably adsorbs one species among several electrolytic complexes in a stepwise complexation system of elements in an aqueous equilibrium reaction. Application of the spectroscopies to other stepwise ligand substitution reactions in a similar manner, and comparisons of the spectra with previous thermodynamic data, will verify the validity of this approach. This kind of equilibrium chemical reaction in aqueous solution is a natural analogue of elemental adsorption on clay minerals under an aqueous environment. Spectroscopic evaluation of the adsorbed species will provide significant information regarding the mass fractionation mechanism of heavy elements in nature.

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REFERENCES

- Beattie, I. R., Gilson, T. R. and Ozin, G. A. (1969) Single-crystal Raman spectroscopy of 'square-planar' and 'tetrahedral' CuCl_4^{2-} ions, of the ZnCl_4^{2-} ion, and of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. *J. Chem. Soc. A*, 534–541.
- Bigeleisen, J. and Mayer, M. G. (1947) Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* **15**, 261–267.
- Cook, J. W., Jr. and Sayers, D. E. (1981) Criteria for automatic x-ray absorption fine structure background removal. *J. Appl. Phys.* **52**, 5024–5031.
- D'Angelo, P., Bottari, E., Festa, M. R., Nolting, H.-F. and Pavel, N. V. (1997) Structural investigation of copper(II) chloride solutions using x-ray absorption spectroscopy. *J. Chem. Phys.* **107**, 2807–2812.
- Engberg, Å. (1970) An x-ray refinement of the crystal structure of copper(II) chloride dihydrate. *Acta Chem. Scand.* **24**, 3510–3526.
- Fujii, T., Moynier, F., Telouk, P. and Albarède, F. (2006) Isotope fractionation of iron(III) in chemical exchange reactions using solvent extraction with crown ether. *J. Phys. Chem. A* **110**, 11108–11112.
- Johnson, C. M., Beard, B. L. and Albarède, F. (eds.) (2004) *Geochemistry of Non-traditional Stable Isotopes*. Reviews in Mineralogy and Geochemistry Vol. 55, The Mineralogical Society of America.
- Maréchal, C. and Albarède, F. (2002) Ion-exchange fractionation of copper and zinc isotopes. *Geochim. Cosmochim. Acta* **66**, 1499–1509.
- Nomura, M. and Koyama, A. (1996) Design and performance of a new XAFS beamline at the Photon Factory; BL-12C. KEK Report 95-15.
- O'Day, P. A., Rehr, J. J., Zabinsky, S. I. and Brown, G. E., Jr. (1994) Extended x-ray absorption fine structure (EXAFS) analysis of disorder and multiple-scattering in complex crystalline solids. *J. Am. Chem. Soc.* **116**, 2938–2949.
- Pascal, J.-L., Potier, J., Jones, D. J., Rozière, J. and Michalowicz, A. (1984) Structural approach to the behavior of ClO_4^- as a ligand in transition-metal complexes using EXAFS, IR, and Raman spectroscopy. 1. A perchlorate-bridged copper chain with short copper-copper distances in $\text{Cu}(\text{ClO}_4)_2$. *Inorg. Chem.* **23**, 2068–2073.
- Pickering, I. J. and George, G. N. (1995) Polarized x-ray absorption spectroscopy of cupric chloride dihydrate. *Inorg. Chem.* **34**, 3142–3152.
- Quicksall, C. O. and Spiro, T. G. (1966) Raman spectra of tetrahalozincates and the structure of aqueous ZnCl_4^{2-} . *Inorg. Chem.* **5**, 2232–2233.
- Ramette, R. W. (1986) Copper(II) complexes with chloride ion. *Inorg. Chem.* **25**, 2481–2482.
- Rehr, J. J. and Albers, R. C. (2000) Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621–654.
- Ruaya, J. R. and Seward, T. M. (1986) The stability of chlorozinc(II) complexes in hydrothermal solutions up to 350°C. *Geochim. Cosmochim. Acta* **50**, 651–661.
- Schauble, E. A. (2004) Applying stable isotope fractionation theory to new systems. *Geochemistry of Non-traditional Stable Isotopes* (Johnson, C. M., Beard, B. L. and Albarède, F., eds.), 65–111, The Mineralogical Society of America.
- Silber, H. B., Simon, D. and Gaizer, F. (1984) Octahedral-tetrahedral geometry changes for zinc(II) in the presence of chloride ions. *Inorg. Chem.* **23**, 2844–2848.
- Tanaka, H., Henning, J., Luts, H. D. and Kliche, G. (1987) Infrared and Raman spectra of $\text{CuCl}_2 \cdot (\text{H}, \text{D})_2\text{O}$ and $\text{K}_2\text{CuCl}_4 \cdot 2(\text{H}, \text{D})_2\text{O}$. Vibrational modes, assignment and coupling of the water librations. *Spectrochim. Acta Part A* **43**, 395–400.