Grazing-incidence XAFS investigations of Cu(II) sorption products at α-Al₂O₃–water and α-SiO₂–water interfaces

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Grazing-Incidence XAFS was used to study the local atomic structure of Cu-containing species that form at the oxide-water interface of oriented single crystals of α-Al₂O₃ and α-SiO₂. Cu(II) forms edge-sharing bidentate complexes on both α-Al₂O₃ (1-102) and (0001) surfaces. However, polarization-dependent XAFS measurements suggest that the binding sites of the surface complexes are different on the two surfaces. The distance to Si backscatterers is consistent with both monodentate and bridging bidentate Cu surface complexes on the α-SiO₂ (0001) surface, but the absence of structural information in the EXAFS spectra beyond ~3Å suggests that Cu complexes do not bond to a single well-ordered surface site. The structural information is used to explain the relative extent of Cu uptake on the three oxide surfaces studied.

Keywords: GI-XAFS; Cu(II); sapphire; quartz.

1. Introduction

Copper(II) contamination of natural waters as a result of mining, wastewater discharge, and other human activities poses a serious threat to biota in a variety of ecosystems. Natural and engineered pathways of Cu removal from aqueous solutions typically involve surface reactions (sorption and precipitation) on Fe- and Al-hydroxide colloids or mineral coatings (Karthikeyan, et al., 1997). Chemical models used to predict both the extent of Cu removal and the stability of reaction products require a detailed description of the composition of relevant surface species, how they bind to mineral surfaces, and the nature of precipitate phases, if any, containing Cu.

EXAFS spectroscopy is one of the few direct probes available for studying the structure of metal ion complexes at the oxide-water interface, and for distinguishing among the dominant types of chemical reactions that control the fate and transport of metal ions in natural systems. Many previous EXAFS investigations of metal ion sorption have used slurries of high surface area Fe- and Al-hydroxide particles as model systems (Brown, et al., 1995). The present work is an extension of previous studies in our lab of metal-ion reactions at oriented single crystal oxide-water interfaces using grazing-incidence EXAFS spectroscopy (Bargar, et al. 1996, 1997; Towle, et al., 1995, 1998a, 1998b). This approach reduces the complexity of powder EXAFS studies by reducing the number of different types of potential surface sites to which a metal ion may bond. Here we discuss the Cu(II) surface species that form at the α-Al₂O₃- and α-SiO₂-water interface.

2. Experimental

The orientation (Laue diffraction), surface roughness (synchrotron X-ray reflectivity), and composition (XPS) of 50mm diameter sapphire (Union Carbide) and quartz (Princeton Scientific) single-crystal wafers were determined prior to reaction. Metal-ion uptake on the wafers was measured by XPS (Surface Science Instruments, Al-kα) after two hours of reaction in low-CO₂ solutions at different pH, ionic strength, and [Cu]ₜ to determine optimal coverage for EXAFS measurements. Uptake was achieved for EXAFS samples by reacting the wafers in 30μM Cu(II) (0.01M NaNO₃) solutions for 2-12 hours. The wafers were removed from solution under an N₂ jet. Cu K-edge EXAFS were collected on SSRL beamlines IV-2 and VI-2 using a 13-element Ge detector (Canberra) and SSRL's GI-XAS rail for sample manipulation. The vertical height of the focused incident beam was limited to 150μm in order to keep the X-ray footprint on the crystal and avoid excess scattering. The sample was maintained in a humidified (>80%) N₂ atmosphere during data collection, which results in multiple monolayers of water on the surface (Yan, et al., 1987). Polarization dependent data were collected with the E-vector parallel and normal to the substrate (horizontal and vertical modes, respectively) with the angle between the incoming beam (dimensions 0.15x5.0 mm) and the crystal surface fixed just below the critical angle of the substrate (~0.2°).

The raw data were averaged (15-30 sweeps for each sample) and analyzed with EXAFSPAK (George and Pickering, 1995) and k^3-weighted EXAFS were fit (k-range=3 to 11Å⁻¹) with phase and amplitude functions generated by FEFF7 (Zabinsky, et al., 1995). Fits of the EXAFS and the Fourier-filtered EXAFS of each shell were used to arrive at the final fit numbers. The accuracy of parameters varied during a least-squares fit (N_{eff}±10%, R±0.02Å 1ˢᵗ shell, and N_{eff}±30%, R±0.05Å for more distant shells) was derived from fits of spectra of crystalline model compounds. The Debye-Waller term (σ^2), was fixed based on fits of model systems. Models of sorption complexes were proposed based on geometric constraints (distances to and identities of backscattering atoms) and the polarization dependence of a shell's effective coordination number (N_{eff}) (Towle, et al., 1998a). In cases where two or more models of Cu surface species yielded satisfactory fits of the data, the results were compared with local coordination environments of Cu(II) crystalline model compounds and solutions in order to narrow down the possible geometries.

3. Results and Discussion

Contaminant concentration on the pre-reacted substrates was below the detection limit of the XPS instrument (~0.05μmole/m²). Therefore, we assume that Cu uptake is a result of an interaction between hydrated Cu atoms and Al/Si-hydroxy surface functional groups. Furthermore, as determined by X-ray reflectivity measurements between EXAFS spectral collection, the surface roughness (~2-5Å rms) did not increase after multiple cycles of cleaning and reaction with metal solutions, suggesting that significant dissolution did not occur (c.f. Chiarello, et al., 1993). Under equivalent solution conditions and exposure times, Cu(II) uptake follows the trend: α-Al₂O₃ (0001) > α-Al₂O₃ (1-102) > α-SiO₂ (0001). The solution conditions reported in Table 1 were chosen to ensure that solutions were sub-saturated with respect to basic Cu(II) salts, and that Cu(II) surface coverage was less than 1μmole/m².

3.1. α-Al₂O₃ (0001) and (1-102)

The EXAFS spectra and Fourier transforms of Cu(II) sorbed on the α-Al₂O₃ (1-102) and (0001) surfaces are shown in Figure 1D-G and the fit parameters are shown in Table 1. The distance to the 1st shell of oxygen atoms (1.92-1.94Å) is characteristic of four equatorial oxygen atoms of a tetragonally distorted Cu(H₂O)₆²⁺ octahedron. The two more distant axial oxygen atoms, which have been included in fits of EXAFS spectra of aqueous Cu(II) (Filiponi, et al. 1994), did not affect the final fit parameters of the other shells. Therefore, this shell was not included in the final analysis in order to minimize the number of fit parameters. The consistently larger 1st shell Neff with the E-vector parallel to the oxide surface suggests that the Cu(O,OH,H₂O)₆ octahedral complexes are preferentially oriented with the plane of equatorial oxygen atoms parallel to the surface. The multiple frequencies evident in the EXAFS are indicative of 2nd and higher shells.
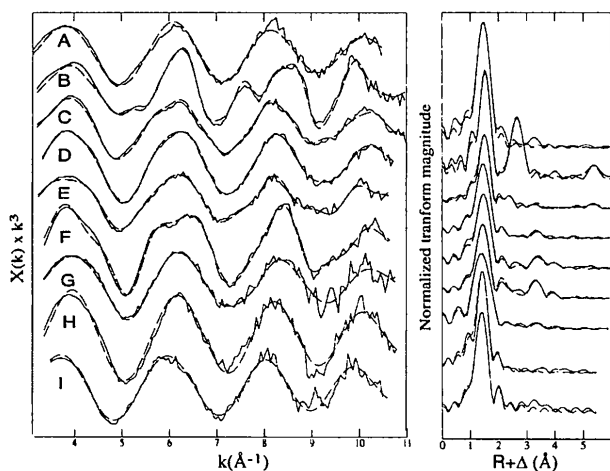

Figure 1

EXAFS data and least-squares fits of the spectra, and Fourier transforms uncorrected for phase shift of (A) Cu(II) nitrate solution at pH4, (B) Cu(OH)₂ model compound, (C) Cu(II) adsorbed on high surface area alumina powder, and Cu(II) adsorbed on α-Al₂O₃ (1-102) single crystal with the E-vector (D) parallel and (E) normal to the surface, α-Al₂O₃ (0001) with the E-vector (F) parallel and (G) normal to the surface, and α-SiO₂ (0001) with the E-vector (H) parallel and (I) normal to the surface.

Distances to near-neighbor Al atoms (2.78-2.93Å) are consistent with edge-sharing bidentate Cu(II) complexes on both α-Al₂O₃ (1-102) and (0001) surfaces. The orientation of the equatorial oxygen atoms relative to the surface and the Cu-Al 1st shell distances, which are slightly longer than previously observed for edge-sharing bidentate Cu complexes (Cheah, et al., 1998), suggest that the Cu complex is attached to the surface through an equatorial and an axial oxygen when bonded to a terrace site (see below). If a monodentate complex bonded to the surface through an axial oxygen did dominate Cu sorption on the two α-Al₂O₃ surfaces, then we would not expect to observe structural order beyond the 1st shell of Al atoms. Furthermore, the narrow range of distances to the next shell of Al atoms (3.91-4.06Å) suggests similar coordination spheres surround Cu(II) atoms on both surfaces. However, we are unable to reconcile the distances to 3rd and 4th shells of Al atoms with a model of a bidentate Cu complex sorbed on the idealized surfaces. Therefore, either the connectivity of Al(OH)₆ octahedra at the reacted surface does not reflect the bulk termination, or the more distant shells are not Al atoms. Cu-Cu phase and amplitude functions alone do provide reasonable fits of 2nd, 3rd and 4th shell features in the EXAFS spectra (Fig. 2), raising the possibility that Cu-hydroxy clusters or precipitates may have

formed. However, backscattering from Cu atoms at 2.6-2.7Å and 4.0-4.7Å is not consistent with Cu-Cu near-neighbor distances in Cu oxides, Cu hydroxides (Fig. 1B), hydrotalcite-like phases, or basic Cu nitrates (2.9-3.4Å and 5.3-6.0Å). Therefore, if we assume that the 2nd and more distant shells are Al atoms, then the polarization dependence of the contribution from Al shells provides indirect evidence that the distribution of Cu species is different on the two surfaces.

Table 1

Fit parameters, corrected for phase shift, from overall fits of EXAFS spectra. (*) Denotes a parameter that was fixed

Substrate Sample conditions	E-vector orientation	Shell	Cu-O	Cu-Al/Si	Cu-Al	Cu-Al
		σ²	0.007	0.01	0.01	0.01
α-SiO₂ (0001) 30µM Cu. pH5.5, 0.01M NaNO₃	Vertical	Neff	4.3(1)	1.0(2)		
		R	1.95(1)	2.90(2)		
	Horizontal	Neff	5.1(1)	0.3(2)		
		R	1.95(1)	2.86*		
α-Al₂O₃ (0001) 30µM Cu pH5.5, 0.01M NaNO₃	Vertical	Neff	5.1(1)	1.0(2)	1.0(4)	
		R	1.93(1)	2.78(2)	3.98(4)	
	Horizontal	Neff	6.5(2)	2.6(3)	5.4(6)	2.3(8)
		R	1.92(1)	2.88(2)	3.91(1)	4.58(2)
α-Al₂O₃ (1-102) 30µM Cu pH5.5, 0.01M NaNO₃	Vertical	Neff	4.4(1)	0.7(3)	2.4(6)	1.7(8)
		R	1.94(1)	2.97(3)	4.06(2)	4.82(4)
	Horizontal	Neff	6.0(1)	0.9(2)	1.9(4)	
		R	1.93(1)	2.93(2)	4.01(2)	

The Fourier transforms of the EXAFS of Cu sorbed on α-Al₂O₃ (1-102) and (0001) surfaces with the E-vector parallel to the surface are compared in Figure 2. The strong backscattering amplitude in the highlighted region of Figure 2A suggests that well-ordered shells of atoms are present in the plane of the α-Al₂O₃ (0001) surface. In contrast, when Cu is adsorbed to the α-Al₂O₃ (1-102) surface, backscattering from well-ordered shells of neighboring atoms is more pronounced in the EXAFS in the vertical orientation (Fig. 1G). If Cu sorbs on both α-Al₂O₃ surfaces to sites at the edge of terraces (strong backscattering in the horizontal orientation) and sites on the terraced surface (strong backscattering in the vertical orientation), then a possible explanation for these observations is that Cu is bound to a greater number of terrace edge sites on the (0001) surface. Furthermore, stronger Cu uptake on the (0001) surface relative to the (1-102) surface could be a result of a higher density of terrace edge sites
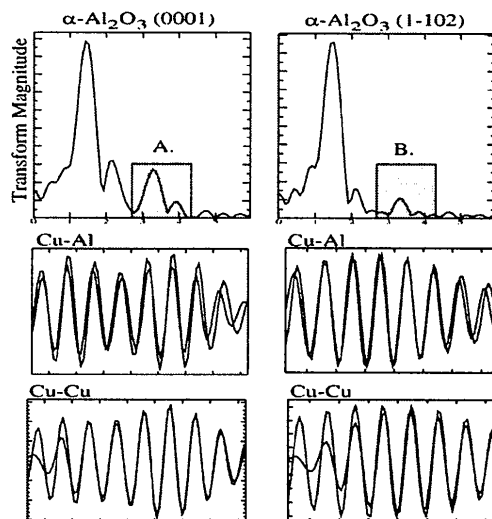
on the (0001) surface.

Figure 2

Fourier transforms of the EXAFS of Cu sorbed on α-Al₂O₃ (1-102) and (0001) surfaces collected with the E-vector parallel to the surface. The

back-transformed 3rd and 4th shell features highlighted in the Fourier transforms are fit with Al and Cu phase and amplitude functions below.

3.1. α-SiO$_2$ (0001)

Cu coordination with 1st shell oxygen atoms when sorbed on the α-SiO$_2$ (0001) surface is consistent with tetragonally distorted Cu(O,OH,H$_2$O)$_6$ octahedral complexes oriented with the equatorial oxygen atoms parallel to the surface. Backscattering from Si atoms at 2.91Å is consistent with both a monodentate and bridging bidentate surface complex. Bridging bidentate coordination of Cu to two apical oxygen atoms of adjacent Si tetrahedra is observed in Cu-containing silicate minerals (e.g. dioptase). However, the relatively low uptake of Cu on the α-SiO$_2$ (0001) surface, and the absence of backscattering from neighboring atoms beyond the 2nd shell Si atoms suggests that Cu forms a weakly bound monodentate surface complex. These observations are consistent with the bonding proposed for Cu(II) species sorbed on am-SiO$_2$ colloids (Cheah, et al., 1998).

4. Conclusions

Tetragonally distorted Cu(O,OH,H$_2$O)$_6$ octahedra sorb as bidentate edge-sharing complexes to both α-Al$_2$O$_3$ surfaces investigated. However, polarization-dependent measurements provide indirect evidence that the extent of Cu uptake on the two α-Al$_2$O$_3$ surfaces investigated may be correlated with a higher density of terrace edge sites on the (0001) surface. Cu and Al phase and amplitude functions provide equally satisfactory fits to 2nd and 3rd shell features for the Cu(II)/α-Al$_2$O$_3$ spectra, and therefore, the formation of Cu hydroxide polymers or precipitates cannot be ruled out. Cu sorbs to the α-SiO$_2$ (0001) surface as monodentate or bridging bidentate surface complexes, with the former being more likely. In general, the proposed structure of Cu complexes sorbed on α-Al$_2$O$_3$ and α-SiO$_2$ substrates investigated in this study are consistent with the observation that Cu sorption complexes are more tightly bound to the surface of α-Al$_2$O$_3$ powders than Cu sorption complexes on am-SiO$_2$ (Cheah, et al., 1998). High-resolution AFM or TEM images of the single crystal surfaces are required to determine if surface morphology is consistent with the proposed structure and distribution of Cu sorption species.

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