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Characterization of Cu-complexes in smectite with different layer charge location: Chemical, thermal and EXAFS studies

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Abstract—The retention of Cu and Cu-amino acid complexes by montmorillonite and beidellite, before and after repeated acidified aqueous solution treatments, was studied using X-ray diffraction, chemical and thermal analyses, mass spectrometry and synchrotron-based X-ray absorption spectroscopy (XAS).

The results indicate that the extraction of metal complexes from smectites depends on the nature of the layer charge and on the kind of organic species. Cu-cysteine complexes are strongly retained in the interlayer position, whereas Cu-glycine complexes are mostly adsorbed in cationic form which can be easily removed from the silicate layer. The layer periodicity for Cu-smectites treated with glycine shows little or no layer expansion, whereas significant swelling of the layer periodicity is observed in smectites treated with cysteine.

Thermal decomposition of both smectites with sorbed Cu-amino acid species shows the evolution of H₂O, NO, CH₃CH₃, and CO₂. In Cu-cysteine treated smectites, the release of H₂S, NO₂, SO₂, and N₂O₃ also occurs.

X-ray absorption spectroscopy (XAS) was used to assess the relationships between the structure of the Cu complexes and their desorption from smectites. In Cu-exchanged smectites, the first coordination shell agrees with the hypothesis that the Cu coordinates to oxygen atoms to form monomer and/or dimer complexes. The first coordination shell of Cu in smectites treated with glycine shows four atoms at distances of ~2 Å. Two of these bonds are with nitrogen and two with oxygen atoms. For copper-cysteine complexes XAS data are compatible with the existence of Cu-N clusters, thus suggesting that Cu links to the amino acid by the aminic group. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Cu is a common constituent of runoff from mining operations, of urban stormwater runoff, and of industrial and agricultural effluents. Although in low concentrations it is essential to life, excessive copper levels may be detrimental. Thus, reactions that remove Cu species from the aqueous phase rendering them immobile and limiting their bioavailability are desirable. Previous studies have demonstrated that Cu mobility depends on its speciation (Goodman et al., 1984; Brand et al., 1986; Knauer et al., 1997; Xia et al., 1997) which is determined, among other factors, by complexation with organic ligands and sorption to colloidal phases. Among organic compounds, the importance of protein amino acids (the natural degradation products of organic matter) in controlling environmental pollution has been widely reported, and several studies in different fields (e.g., chemical, medical, biological, and mineralogical) have been carried out (e.g., Brigatti et al., 1999; Benincasa et al., 2000, and references included therein). Protein amino acids can bind metal cations by different functional groups: by amino (-NH₂) and carboxylic (-COOH) groups, which characterize all species, and by sulfur-containing groups (-SH and -SCH₃), which are specific for cysteine and methionine. Fine-particle materials that present a large surface area such as oxides, hydroxides, oxyhydroxides and clay minerals are among the principle sorbents of the metal species. For metal interaction with smectite surfaces, several studies indicate that

the metal uptake is dependent on the magnitude and the location of the layer charge (McBride et al., 1975; McBride, 1976). According to the HSAB theory of Pearson (Pearson, 1963, 1968) the hydrated interlayer cations and the layer of smectites can be considered Lewis acids and bases, respectively (Xu and Harsh, 1992). The location of the layer charge determines the strength of the Lewis base: smectite behaves as a soft base when the layer charge is located in the octahedral sites, whereas it behaves as a hard base when the charge is located in the tetrahedral sites. Because hard bases link preferentially with hard acids and soft bases with soft acids, the smectite layer charge location strongly affects the sorption processes.

The interactions between Cu or Cu-organic complexes and montmorillonite have recently been studied by Brigatti et al. (1999), Benincasa et al. (2000), and Morton et al. (2001). These studies indicate that at the edge sites of montmorillonite, Cu forms dimers or a combination of monomers and dimers which are linked by hydroxyl groups or oxygen atoms at the mineral surface. Cu adsorbed on the permanent charged sites of montmorillonite develops an outer sphere complex where the metal is surrounded by a shell of at least one layer of water molecules (Morton et al., 2001). They also show that Cu forms a stable chelate complex with the amino acid cysteine in the interlayer sites, by linking carboxylic and thiol functional groups (Brigatti et al., 1999), and that cationic Cu-glycine complexes exchange the interlayer cation of smectites (Benincasa et al., 2000).

To gain insight into the relationship between the structure and composition of the sorbed phases and the Cu desorption behavior, we carried out a study on Cu-exchanged smectites characterized by different layer-charge location (montmorillon-

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ite and beidellite) and treated with two different α -amino acids (glycine: $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$, and cysteine: $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$). The experimental method can be divided into the following steps: (1) adsorption of copper and copper amino acid complexes by the smectites; (2) extraction of sorbed species from the smectite layer, in aqueous solution, at pH 5.0; (3) determination of Cu adsorbed species and of their reaction products; (4) application of Extended X-ray Absorption Fine Structure (EXAFS) analysis to gain insight into the nature of adsorbed Cu species.

2. MATERIALS AND METHODS

2.1. Samples and Model Compounds

Montmorillonite, reference clay Saz-1, from Cheto Apache County, Arizona, USA (nominal Cation Exchange Capacity [CEC] = 120 meq/100 g) and beidellite from Rasta, Vicenza, Italy (CEC = 78 meq/100 g) were used. Montmorillonite derives its layer charge mostly from low-charge cations sited in the octahedral sheet, whereas the beidellite layer charge is mostly related to Al for Si tetrahedral substitutions. Thus, montmorillonite can be considered a soft Lewis base whereas beidellite a hard Lewis base. Details of the mineralogical, chemical and surface properties of the samples under examination can be found in van Olphen and Fripiat (1979) and Brigatti et al. (1996). Both samples were pretreated to remove organic and inorganic impurities using methods based on those described by Kunze and Dixon (1986).

Synthetic model compounds containing Cu^+ and Cu^{2+} ions and Cu-amino acid complexes, cuprite (Cu_2O), spertiniite ($\text{Cu}(\text{OH})_2$), tenorite (CuO), covellite (CuS), bis(glycinato)copper(II) monohydrate, glycyglycinatocopper(II) dihydrate and Bis(S-methyl-L-cysteinato)copper(II) were used in the EXAFS study.

2.2. Solutions

Cu(II) 1 N stock aqueous solutions were obtained by dissolving CuCl_2 analytical grade reagent. Glycine and cysteine 0.1 mol/L solutions were prepared using a commercial reagent with declared impurity of < 1%.

2.3. Cu- and Amino Acids Sorption-Desorption Procedures

Before starting experiments, a calculation of Cu speciation at 1 N solution concentration of CuCl_2 were carried out by the MINTEQA2 program, to exclude the formation of precipitated Cu-phases on the smectite surface (Allison et al., 1991). Theoretical calculation suggests that below a pH value of 3.3, no precipitated phases occur and that most Cu species in solution are Cu^{2+} , CuCl^+ and CuCl_2 . Precipitation of small amounts of atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) starts at pH 3.3, with Cu^{2+} , CuCl^+ and CuCl_2 still remaining in solution. Tenorite (CuO) precipitation begins only at weakly alkaline pH (7.7).

Cu-rich smectites (Cu-exchanged montmorillonite and Cu-exchanged beidellite, hereafter referred to as Cu-m and Cu-b, respectively) were prepared by mixing 10 g of each smectite sample with 1 L of Cu(II) 1 N solution. The suspensions were stirred overnight at room temperature and at a pH of 3.0, and then centrifuged. The solution was then aspirated off and fresh solution was added. The sequence was repeated three times. Excess salt was removed from the homoionic clays by dialysis until the aspirated solution tested negative with AgNO_3 . Finally, filtrates were analyzed by atomic absorption spectrophotometry to check for the presence of metal cations used in the exchange.

Adsorption of amino acid by smectites was carried out by suspending 2 g of each Cu-rich sample with 100 mL of 0.1 mol/L aqueous solution of glycine or cysteine, respectively. The starting pH values were determined to be: Cu-montmorillonite glycine = 5.2; Cu-montmorillonite cysteine = 4.20; Cu-beidellite glycine = 4.7; Cu-beidellite cysteine = 3.90. At the end of the experiments four samples were obtained: Cu-montmorillonite and Cu-beidellite treated with glycine and cysteine, respectively, referred to as Cu-m-gly (Cu-exchanged

montmorillonite with glycine), Cu-m-cys (Cu-exchanged montmorillonite with cysteine), Cu-b-gly (Cu-exchanged beidellite with glycine) and Cu-b-cys (Cu-exchanged beidellite with cysteine). The suspensions were stirred at room temperature for 48 h. The solids were separated from the solutions by centrifugation.

Clays previously obtained, containing Cu and α -amino acids, were repeatedly treated with a fixed amount of distilled water (100 mL) acidified with CO_2 up to pH 5.0. The input fluid was stored in a polyethylene cylinder and CO_2 was injected by a peristaltic pump at a flow rate of 7×10^{-3} atm. This flow rate was calculated using the MINTEQA2 code (Allison et al., 1991). The suspensions were shaken for 1 h at 25°C and then centrifuged. The treatments were repeated thirteen times and, after each treatment, a portion of the minerals was separated, air-dried and characterized.

2.4. Characterization Procedures

Elemental analysis (Elemental Analyzer, Carlo Erba 1106) was performed to check the amount of amino acid sorbed. An atomic absorption spectrophotometer (Perkin Elmer Analyst 100) was used to analyze the amount of metal retained.

Basal d_{001} spacings were determined by X-ray powder diffraction (XRD) analysis at room temperature ($T = 25^\circ\text{C}$, relative humidity [RH] = 60%) and in the temperature range $25 \leq T(^{\circ}\text{C}) \leq 500$, on oriented mineral aggregate mounts, using a Philips PW 900 diffractometer ($\text{CuK}\alpha$ radiation; quartz as standard) equipped with a monochromator and an in situ heating apparatus.

Thermal analyses were performed with a Seiko SSC 5200 thermal analyzer equipped with a quadrupole mass spectrometer (ESS, Gene-Sys Quadstar 422) to analyze the gases evolved during thermal reactions. Gas sampling by the spectrometer was via an inert, fused silicon capillary system, heated to prevent gases condensing. Gas analyses were carried out in Multiple Ion Detection mode (MID) which allows the qualitative determination of evolved masses vs. temperature or time. Background subtraction was performed to obtain the point zero conditions before starting MID analysis.

A synchrotron-based X-ray absorption spectroscopy (XAS) technique was used to obtain information on the local chemical environments of Cu-sorbed species.

Cu K-edge X-ray absorption experiments were performed at the European Synchrotron Radiation Facility (ESRF) at GILDA beamline. High energy resolution is ensured by using Si(311) and Si(511) monochromating crystals. Spectra were collected in transmission mode on powder-pressed disks obtained by mixing an appropriate amount of clay sample with cellulose. Energy calibration was performed using a Cu-metal foil for all samples, with the first inflection point of the K-absorption edge assigned as 8979.1 eV.

The experimental EXAFS spectrum ($\chi(k)$) is built up from the contribution of the photoelectron waves scattered back from the shells of atoms neighboring the central atom (Cu) excited by the incident synchrotron radiation. The frequencies of the photoelectron scattered waves can ideally be isolated one from the other using a Fourier transform. After correcting for phase shift effects, each backscattering atom can thus be identified and its distance from the Cu atom calculated by taking into account the intensity and frequency of each elementary wave constituting the EXAFS spectrum. In practice, in real and complex systems the contribution from different backscattered atoms can partially or completely overlap; thus, a Fourier transform (FT) previously calculated from the EXAFS experimental spectrum was back transformed to generate a Fourier filtered EXAFS spectrum (FT^{-1}).

The Fourier filtered EXAFS spectrum is compared with theoretical EXAFS spectra, calculated from the FEFF-8 program (Ankudinov et al., 1998). Theoretical spectra refer to structurally well-determined model compounds, which are assumed to present Cu coordinations similar to the sample under examination. The difference between computed and filtered spectra is optimized after a least-squares approach.

To fit the experimental Cu K-edge spectra, a number of assumptions were made. Firstly, in Cu-exchanged smectites, it was assumed that Cu^{2+} atoms can link water molecules and/or can form oxide and hydroxide precipitates. The experimental spectrum obtained for Cu-exchanged montmorillonite and beidellite was thus fitted using $\text{Cu}(\text{OH})_2$ and CuO as reference compounds, starting from atomic

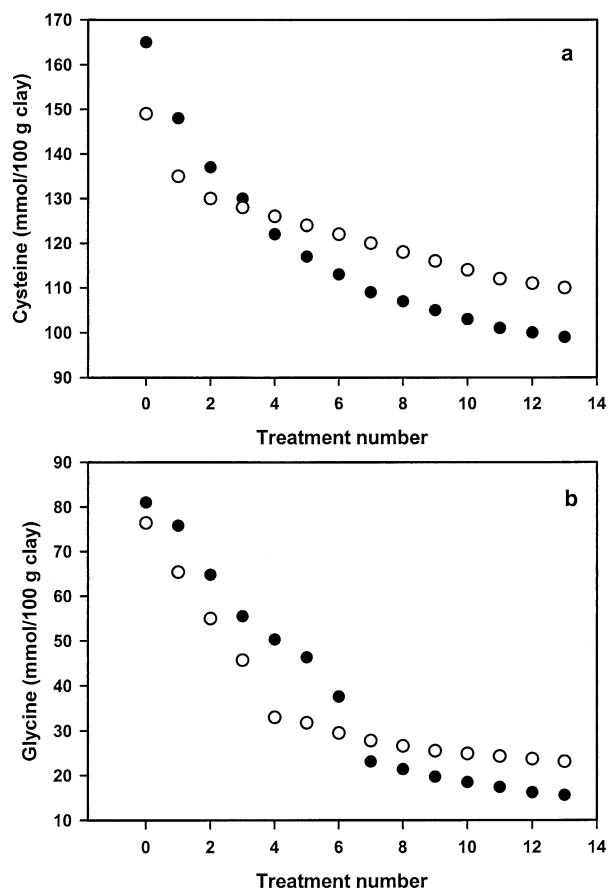


Fig. 1. Amount of (a) cysteine and (b) glycine released by montmorillonite (filled circles) and beidellite (open circles), after repeated washing with acidified water treatments (pH = 5.0). The treatment number zero refers to Cu-exchanged smectites treated with amino acid.

coordinates reported by Åsbrink and Norrby (1970) and Oswald et al. (1990). Secondly it was assumed that cysteine ($\text{H}_2\text{NCH}[\text{CH}_2\text{SH}]\text{CO}_2\text{H}$) can complex copper by using amino ($-\text{NH}_2$), carboxylic ($-\text{COOH}$) and thiol ($-\text{SH}$) groups. The experimental data obtained for Cu-smectite-cysteine complexes were, therefore, fitted using the following structures: CuS , CuS_2 , $\text{Cu}(\text{OH})_2$, Bis(S-methyl-L-cysteinato)copper(II), (Evans and Konner, 1976; King and Prewitt, 1979; Dubler et al., 1986; Oswald et al., 1990). Thirdly it was assumed that glycine ($\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$) can link transition metals by $-\text{NH}_2$ and $-\text{COOH}$ groups; the experimental data obtained for Cu-smectite-glycine complexes were therefore compared with the calculated profiles of bis(glycinato)copper(II) monohydrate, glycyglycinatocopper(II) dihydrate and $\text{Cu}(\text{OH})_2$ (Freeman et al., 1964; Kistenmacher and Szalda, 1975; Oswald et al., 1990).

3. RESULTS AND DISCUSSION

3.1. Desorption Experiments

Figure 1 shows the release of amino acid species (cysteine and glycine) from Cu-rich smectites as a function of the number of washing treatments, as previously detailed. It can be observed that a slight larger quantity of sorbed amino acids was found for montmorillonite than for beidellite, as regards both glycine and cysteine. Cysteine can be sorbed in greater quantity by Cu-rich smectites than can glycine, both in montmorillonite and beidellite. The release of the sorbed Cu and amino acids,

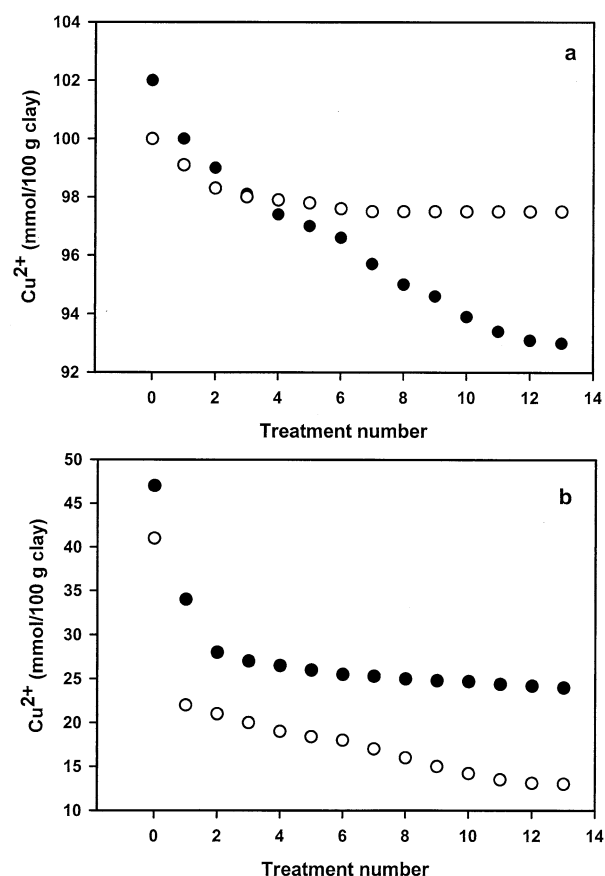


Fig. 2. Amount of Cu released by (a) Cu-exchanged smectites treated with cysteine and (b) Cu-exchanged smectites treated with glycine, after repeated washing with acidified water treatments (pH = 5.0). Filled circles: montmorillonite; open circles: beidellite. The treatment number zero refers to Cu-exchanged smectites treated with amino acid.

evaluated at constant pH (pH 5.0) as a function of the amount of water, indicates that both smectites quickly release a fraction of sorbed cysteine, but at the end of the experiment a considerable amount of the amino acid (~ 100 mmol/100 g clay) is still retained in the mineral layers (Fig. 1a). These data also indicate that glycine is significantly and almost completely removed from both smectites (Fig. 1b) and that both Cu-m-cys and Cu-b-cys (Fig. 2a) release very little Cu even after repeated washing. Cu-m-cys decreases very slowly, whereas Cu-b-cys is slightly affected only by the first washings. Figure 2b shows the release of Cu from Cu-m-gly and Cu-b-gly. The first washings are very effective in reducing the metal content retained in the mineral, whereas the following washings are much less effective. The amount of final Cu (i.e., after 13 washings) is higher for montmorillonite than for beidellite, while washing is more effective for beidellite than for montmorillonite (Fig. 2b).

3.2. X-ray Diffraction Characterization

X-ray diffraction data obtained for Cu-exchanged montmorillonite and beidellite show that d_{001} values at room temperature are very similar for montmorillonite ($d_{001} = 14.5 \text{ \AA}$) and beidellite ($d_{001} = 14.7 \text{ \AA}$) and that the d_{001} value de-

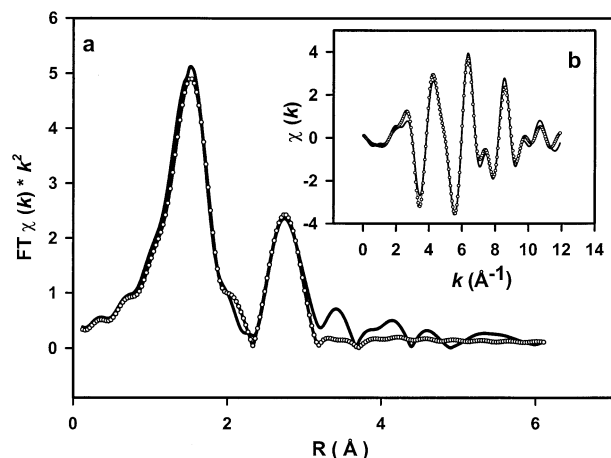


Fig. 3. Cu K-edge EXAFS data for Cu-exchanged montmorillonite. (a) Fourier Transform (FT) and (b) associated inverse Fourier-filtered scattering curve (FT^{-1}) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using $Cu(OH)_2$ as reference compound.

creases to 10.0 Å as the temperature is increased to 340°C for montmorillonite and to 320°C for beidellite. This can be related to the decrease in the interlayer separation produced by the progressive loss of H_2O molecules and is in good agreement with thermogravimetric analysis results.

This XRD study of Cu-m-cys and Cu-b-cys proves that swelling of the structures occurs on uptake of the organics (d_{001} values of 19.2 and 19.0 Å for montmorillonite and beidellite, respectively). The expansion of the smectite interlayer is consistent with the formation in the interlayer of a Cu-cysteine or a Cu-cystine complex. The oxidation reaction cysteine-cystine is catalyzed by Cu(II), and the interlayer cation can therefore be easily complexed by both molecules (McAuliffe and Murray, 1972; Cody, 1985; Cakir et al., 2001).

Compared with Cu-exchanged smectites, both Cu-m-gly and

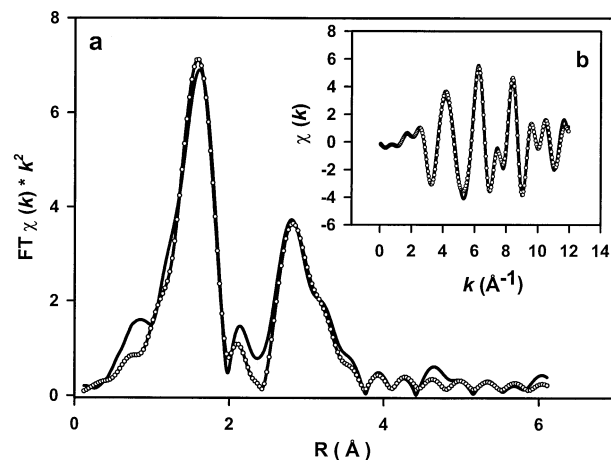


Fig. 4. Cu K-edge EXAFS data for Cu-exchanged beidellite. (a) Fourier Transform (FT) and (b) associated inverse Fourier-filtered scattering curve (FT^{-1}) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using $Cu(OH)_2$ as reference compound.

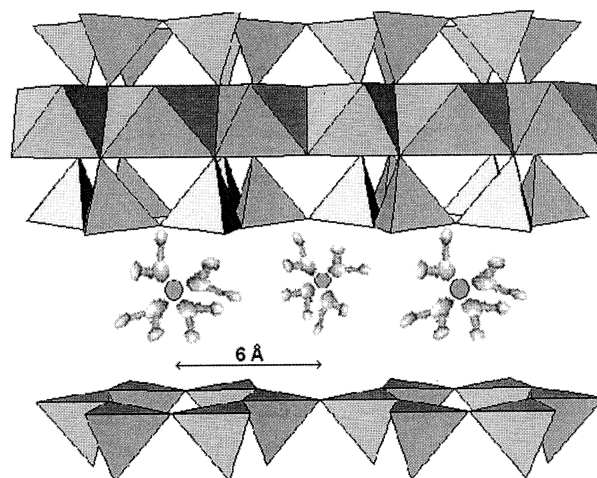
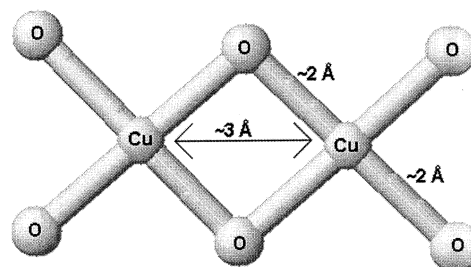


Fig. 5. (a) Sketch of the planar double-bridged structure of copper dimers with Cu-Cu distances of ~ 3 Å. (b) Hydrated structure of copper characteristic of complexes formed in the smectite interlayer with Cu-Cu distances at ~ 6 Å. Modified after Morton et al. (2001).

Cu-b-gly show a broad (001) peak and only a slight increase in the d_{001} value ($d_{001} = 15.5$ Å for both samples). This behavior is consistent with an increase in layer-stacking disorder, without any significant increase in layer periodicity.

3.3. Thermal Behavior and Evolved Gas Analysis

Thermal analyses for Cu-m and Cu-b samples show an endothermic reaction at $\sim 100^\circ C$, related to weakly bonded water molecules. Then, in the temperature range 100 to 350°C, endothermic reactions occur at 170, 180, and 350°C for the Cu-m sample and at 150 and 318°C for the Cu-b sample. Further endothermic reactions occurring in the temperature range 400 to 700°C are due to the dehydroxylation of the octahedral sheet (Brigatti et al., 1999; Benincasa et al., 2001).

Thermal behavior of Cu-smectite treated with amino acids and obtained from TGA and MS-EGA analyses shows that in the temperature range 25 to 150°C, the percentages of observed weight loss (Cu-m-gly = 8.9 wt.%, Cu-b-gly = 6.8 wt.%, Cu-m-cys = 5.0 wt.%, Cu-b-cys = 5.3 wt.%) correspond to the release of H_2O molecules ($m/z = 17$ and 18, where m/z is the dimensionless ratio between the mass number and the charge

Table 1. Result of EXAFS analyses. Aa-Sa: relationship between central absorber and scattering atom; *N*: coordination number; *R*: refined interatomic distance, σ^2 ; Debye-Waller factor; ΔE_0 : energy shift

Aa-Sa	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0	Aa-Sa	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0
Cu montmorillonite					Cu beidellite				
Cu-O	3.8	1.93	0.0145	-6.5	Cu-O	3.7	1.98	0.0087	-4.5
Cu-Cu	0.9	3.03	0.0079		Cu-Cu	0.9	3.07	0.0042	
Cu-Cu	1.9	6.02	0.0033		Cu-Cu	1.9	6.03	0.0054	
Cu-glycine montmorillonite					Cu-glycine beidellite				
Cu-N	1.4	1.90	0.0016	-4.8	Cu-N	0.8	1.93	0.0005	-7.9
Cu-O	1.4	1.95	0.0389		Cu-O	0.8	1.95	0.0060	
Cu-O	1.4	1.97	0.0000		Cu-O	0.8	1.97	0.0248	
Cu-N	1.4	2.03	0.0984		Cu-N	0.8	2.03	0.0001	
Cu-O	1.4	3.27	0.0232		Cu-O	0.8	3.05	0.0014	
Cu-Cu	1.4	3.75	0.0098		Cu-Cu	0.8	3.78	0.0034	
Cu-cysteine montmorillonite					Cu-cysteine beidellite				
Cu-O	0.9	1.91	0.0028	-8.1	Cu-O	0.9	1.96	0.0050	-7.7
Cu-O	0.9	1.95	0.0000		Cu-O	0.9	1.97	0.0050	
Cu-N	0.9	2.04	0.0028		Cu-N	0.9	1.99	0.0050	
Cu-N	0.9	2.06	0.0052		Cu-N	0.9	1.99	0.0050	
Cu-O	1.1	2.67	0.0234		Cu-O	0.9	2.70	0.0190	
Cu-O	1.1	2.68	0.0207		Cu-O	0.9	2.73	0.0000	

number of an ion). In the temperature range $150 \leq T$ (°C) ≤ 400 , the weight loss of Cu-rich smectites complexed with both amino acids (Cu-m-cys = 17.2 wt.%, Cu-b-cys = 15.5 wt.%, Cu-m-gly = 6.8 wt.%, Cu-b-gly = 6.5 wt.%) is linked to the emission of H₂O ($m/z = 17$ and 18), NO (or CH₃CH₃, $m/z = 30$), and CO₂ ($m/z = 44$). In Cu-rich smectites complexed with cysteine, the release of H₂S ($m/z = 34$), NO₂ ($m/z = 46$), SO₂ ($m/z = 64$) and N₂O₃ ($m/z = 76$) was also identified. The TGA data, together with the MS-EGA curves, indicate that the thermal decomposition of Cu-cysteine complexes mostly occurs in the temperature range between 150 and 400°C, and that the shape of these curves varies between smectites. In montmorillonite, CO₂, NO₂, and SO₂ emission extends over wide temperature intervals (150 to 400°C), resulting in broad peaks, whereas in beidellite the intervals are narrower (160 to 250°C).

At temperature of 400°C, the TGA curves indicate weight losses (Cu-m-cys = 5.5 wt.%, Cu-b-cys = 5.9 wt.%, Cu-m-gly = 4.3 wt.%, Cu-b-gly = 3.5 wt.%) usually attributed to the complete dehydroxylation of the smectite layer ($m/z = 17$ and $m/z = 18$). The greater weight loss values obtained for both Cu-cysteine smectites can be explained from the overlap of dehydroxylation effects and of emission of residual molecules present in Cu-cysteine complexes. The emission of SO₂ ($m/z = 64$) at $\sim 600^\circ\text{C}$ may be attributed to the oxidation of these residual molecules.

The above results suggest that the smectite-metal complexes are stable at room temperature and decompose progressively during heating. The thermo-analytical results prove that the evolution mainly occurs over the temperature range between 180 and 400°C. The location of the smectite layer charge seems to affect the interlayer Cu species. The different dehydroxylation behavior can be related to a greater structural disorder in the beidellite octahedral sheet, thus releasing (OH) groups over

a wider temperature range and leading to less defined peaks in the MS-EGA curves.

3.4. EXAFS Spectroscopy

The FT and the associated FT⁻¹ functions generated from the Cu K-edge EXAFS spectra of Cu-exchanged smectites are reported in Figures 3 and 4. There is a good match in the peak positions and peak intensities between the experimental spectra of both smectites and the Cu(OH)₂ model compound, whereas the fits derived using CuO as model compound are poorer in both cases. Four oxygen atoms at Cu-O distances < 2.0 Å and one Cu atom at 3.03 Å relevantly contribute to the first peak of the montmorillonite spectrum, thus indicating that Cu is surrounded by four neighboring oxygens. The Cu-Cu distances at 3.03 Å is consistent with the formation of monomers and/or dimers (or mixture of them) at the surface, whereas longer Cu-Cu distances at 6.02 Å can be attributed to interlayer water complexes. As in the case of montmorillonite, the beidellite spectrum is best interpreted in terms of four Cu-O distances of < 2 Å, and Cu-Cu distances at 3.07 and 6.03 Å (Table 1). In agreement with Morton et al. (2001), these spectra agree with a first-shell coordination to four oxygen atoms surrounding Cu at distances of < 2 Å, with neighboring Cu atoms at ~ 3 Å. Morton et al. (2001) also suggested that the Cu-Cu distance is ~ 3 Å in monomers and dimers adsorbed on the mineral edge sites (Fig. 5a), and ~ 6 Å for hydrated Cu cations in the interlayer (Fig. 5b).

The FT and FT⁻¹ of Cu K-edge spectra for Cu-exchanged smectite treated with glycine at the end of the extraction experiments with acidified distilled water, are reported in Figures 6 and 7. The goodness of the fits between experimental and theoretical data is better when Cu is taken to form complexes like glycylglycinatocopper(II) dihydrate. Although the agree-

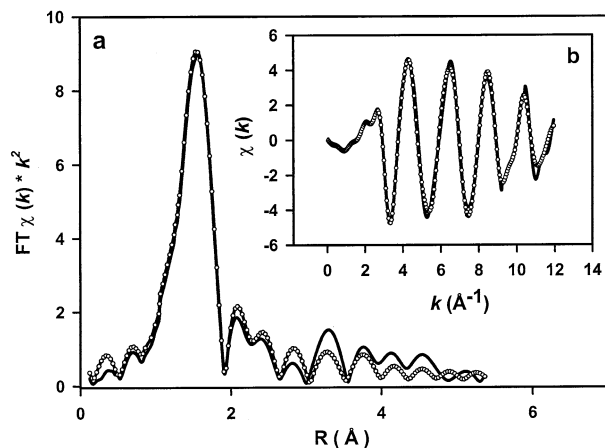


Fig. 6. Cu K-edge EXAFS data for Cu-exchanged montmorillonite treated with glycine. (a) Fourier Transform (FT) and (b) associated inverse Fourier-filtered scattering curve (FT^{-1}) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using glycyglycinatocopper(II) dihydrate as reference compound.

ment between experimental and calculated spectra is poorer considering $Cu(OH)_2$ as model compound, the presence of this species cannot be completely excluded. Glycyglycinatocopper(II) dihydrate is confirmed also for beidellite. Anyway, for this sample the poor signal/noise ratio does not allow further insight. The montmorillonite spectrum shows several contributions from atoms surrounding Cu centers (Table 1), namely: (1) two oxygen atoms at Cu-O distances of 1.95 and 1.97 Å, respectively; (2) two nitrogen atoms at Cu-N distances of 1.90 and 2.03 Å, respectively; (3) a Cu-O at 3.27 Å; (4) a Cu-Cu distance at 3.75 Å. The distances found here suggest a five-fold coordination for Cu atoms, and are in good agreement with the crystal structure of glycyglycinatocopper(II) dihydrate (Kistenmacher and Szalda, 1975). This molecule is characterized by an equatorial plane defined by four Cu bonds: (1) a

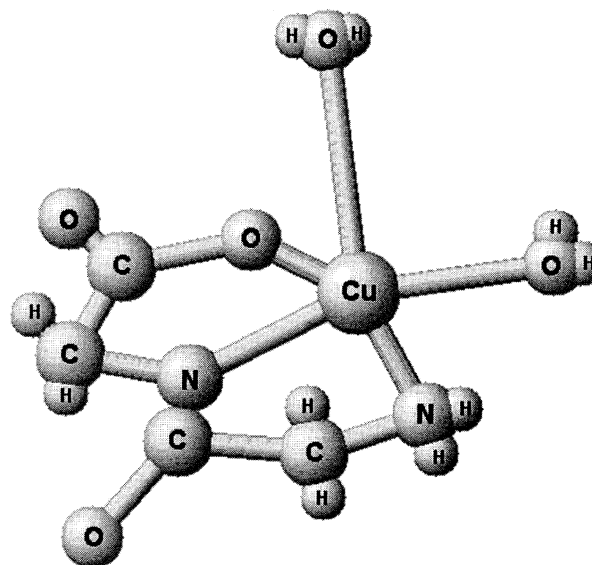


Fig. 8. Schematic illustration of the structure of the glycyglycinatocopper(II) dihydrate complex.

tridentate glycyglycine dianion and (2) a strongly-bonded water molecule (Fig. 8). The five coordinate sphere around Cu is completed by a loosely-bonded axial water molecule. The Cu-Cu distance at 3.75 Å can be related to the formation of glycyglycinatocopper(II) dihydrate dimers produced by sharing oxygen atoms of the two water molecules inside the complex. The same conclusions can be also drawn for beidellite.

Two different situations are observed for Cu-smectites treated with cysteine and are illustrated in Figures 9 and 10, which compare the FT and FT^{-1} curves of the experimental Cu K-edge EXAFS spectra of montmorillonite and beidellite, respectively, with spectra theoretically calculated using Bis(S-methyl-L-cysteinato)copper(II). Table 1 and Figure 9 suggest

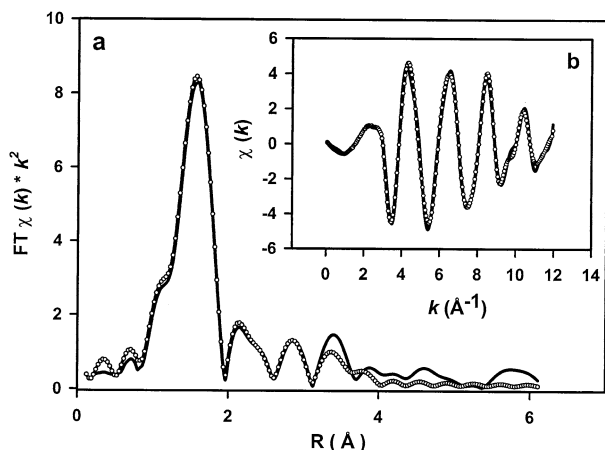


Fig. 7. Cu K-edge EXAFS data for Cu-exchanged beidellite treated with glycine. (a) Fourier Transform (FT) and (b) associated inverse Fourier-filtered scattering curve (FT^{-1}) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using glycyglycinatocopper(II) dihydrate as reference compound.

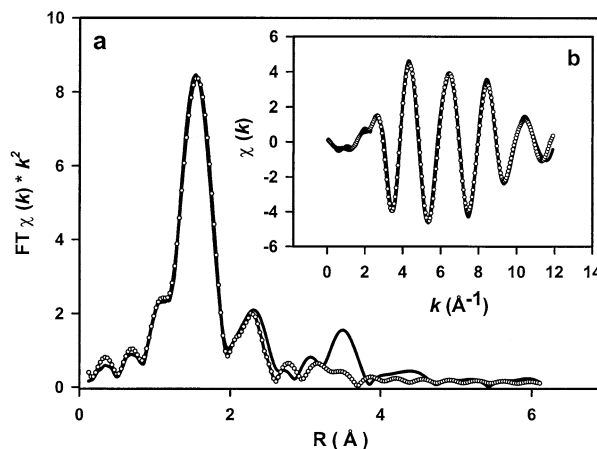


Fig. 9. Cu K-edge EXAFS data for Cu-exchanged montmorillonite treated with cysteine. (a) Fourier Transform (FT) and (b) associated inverse Fourier-filtered scattering curve (FT^{-1}) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using Bis(S-methyl-L-cysteinato)copper(II) as reference compound.

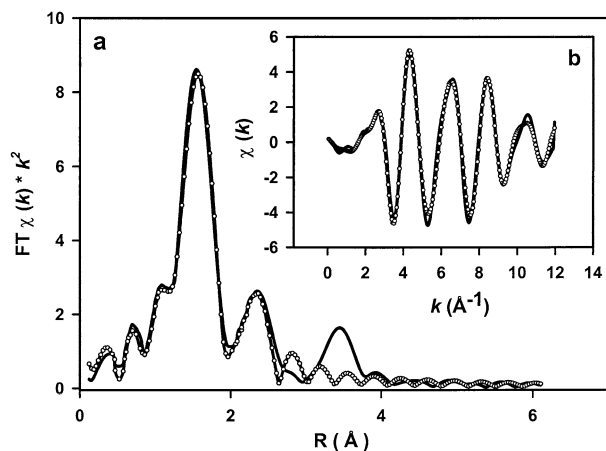


Fig. 10. Cu K-edge EXAFS data for Cu-exchanged beidellite treated with cysteine. (a) Fourier Transform (FT) and (b) associated inverse Fourier-filtered scattering curve (FT^{-1}) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using Bis(S-methyl-L-cysteinato)copper(II) as reference compound.

that in montmorillonite Cu is always six-fold coordinated by four oxygen and two nitrogen atoms with Cu-O distances of 1.91, 1.95, 2.67 and 2.68 Å and two nitrogen atoms with Cu-N distances of 2.04 and 2.06 Å, respectively. Table 1 and Figure 10 indicate that six atoms contribute significantly to the beidellite spectrum, and they are: (1) two oxygen atoms at Cu-O distances of 1.96 and 1.97 Å, respectively; (2) two nitrogen atoms at a Cu-N distance of 1.99 Å; and (3) two oxygen atoms at longer Cu-O distances of 2.70 and 2.73 Å, respectively. The crystal structure of Bis(S-methyl-L-cysteinato)copper(II) (Dubler et al., 1986) consists of an approximately square planar trans coordination of the central copper atom with two O atoms belonging to carboxylic groups (Cu-O = 1.936 and 1.951 Å), and two N atoms belonging to amino groups (Cu-N = 1.995 and 2.001 Å) (Fig. 11). Above and below the plane containing the square planar coordinated Cu, two oxygen atoms at distances from the central Cu of 2.703 and 2.728 Å, respectively, complete the 4+2 Jahn-Teller distorted coordination.

The square planar coordination of Cu shown by EXAFS analysis is significantly distorted in montmorillonite, whereas Cu is nearly at the center of the square in beidellite. The results

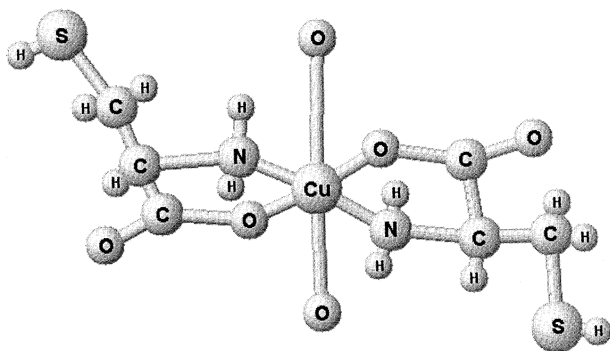


Fig. 11. Schematic illustration of the structure of the Bis(L-cysteinato)copper(II) complex.

for beidellite are in close agreement with X-ray diffraction results (Dubler et al., 1986), showing that copper is nearly at the center of the square. Furthermore, the Jahn-Teller octahedral distortion is confirmed for both smectites.

The fits obtained using sulfides as model compounds (CuS_2 and CuS) show poor agreement with respect to Bis(S-methyl-L-cysteinato)copper(II). These results suggest that Cu links with the amino acid aminic group.

These conclusions partially disagree with the results proposed by Brigatti et al. (1999) based on infrared spectroscopy. In this study cysteine was found to complex Cu by thiol and aminic group, whereas the bound by thiol group is excluded by EXAFS analysis results.

The substrates used in the adsorption/desorption experiments appear to have a substantial effect on the amount and the retention of Cu-amino acid complexes, and on the geometry of the coordination polyhedra, whereas the layer charge location does not appear to affect the chemical speciation of the inter-layer.

4. CONCLUDING REMARKS

Copper can be sorbed by layer silicates with a 2:1 expandable layer structure, in different ways, and this chiefly depends upon the different complex that the cation can form in the interlayer position. The 2:1 layer charge has a greater effect on the amount of sorbed metal than on the metal speciation. When Cu is complexed by water molecules, monomers and dimers occur at the edge sites, as well as Cu-water complexes in the interlayer positions. The cation environment is different when organic molecules are involved in the complexation of Cu in the 2:1 layer. When Cu is complexed by glycine, it is octahedrally coordinated; here, two adjacent glycyglycinatocopper(II) dihydrate complexes are shared by the two water molecules.

The structural environment of Cu is similar in the presence of cysteine; in this case, Cu coordination is again octahedral, with two bonds to N and four to O. However, by comparison with glycine-Cu complexes, the cysteine-Cu complexes appear to be differently bonded in the 2:1 layer, as suggested by the smaller amounts of Cu released after repeated washing treatments.

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