

## Characterization of Cu-amino acid complexes in the interlayer of smectites by EXAFS spectroscopy.

Maria Franca Brigatti, Daniele Malferrari, Luca Medici, Luciano Poppi

### Introduction

Cu is a common constituent of runoff from mining operations, of urban stormwater runoff, and of industrial and agricultural effluents. Reactions that remove Cu species from the aqueous phase rendering them immobile and limiting their bioavailability are desirable. Previous studies demonstrated that Cu mobility depends on its speciation which is determined, among other factors, by complexation with organic ligands and sorption to colloidal phases.

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 (montmorillonite and beidellite) and treated with two different  $\alpha$ -amino acids (i.e., 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 ideally divided into the following steps: *i*) adsorption of copper and copper amino acid complexes by smectites; *ii*) extraction of sorbed species from smectite layer, in aqueous solution, at  $\text{pH} = 5.0$ ; *iii*) determination of Cu adsorbed species and of their reaction products; *iv*) application of Extended X-ray Absorption Fine Structure (EXAFS) analysis to gain insight into the nature of adsorbed Cu species. We expected from EXAFS analysis a detailed information about the Cu local environment changing both the neighboring smectite environment and the interlayer species.

### Experimental aspects

Montmorillonite, reference clay Saz-1, from Cheto Apache Country, 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 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. Synthetic model compounds containing  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions and Cu-amino acid complexes, cuprite ( $\text{Cu}_2\text{O}$ ), spertiniite [ $\text{Cu}(\text{OH})_2$ ], tenorite ( $\text{CuO}$ ), covellite ( $\text{CuS}$ ), bis(glycinato)copper(II) monohydrate, glycyglycinatocopper(II) dihydrate and Bis(S-methyl-L-cysteinato)copper(II) were used as model compounds in the EXAFS study.

Cu-rich smectites (Cu-exchanged montmorillonite and Cu-exchanged beidellite), were prepared by mixing approximately 10 g of each smectite sample with 1 L of Cu(II) 1N solution. Adsorption of amino acid by smectites was carried out by suspending 2 g of each Cu-rich sample with 100 mL of 0.1 M aqueous solution of glycine or cysteine, respectively. Clays previously obtained, containing Cu and  $\alpha$ -amino acids, were repeatedly treated with a fixed amount of distilled water (100 mL) acidified with  $\text{CO}_2$  up to  $\text{pH} 5.0$ . The treatments were repeated thirteen times, and after each treatment a portion of the minerals was separated, air-dried and characterized.

Cu K-edge X-ray absorption experiments were performed 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.

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, the following assumptions were formulated: *i*) in Cu-exchanged smectites,  $\text{Cu}^{2+}$  atoms can link water molecule 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  $\text{CuO}$  as reference compounds; *ii*) cysteine [ $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$ ] can complex copper from 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:  $\text{CuS}$ ,  $\text{CuS}_2$ ,  $\text{Cu}(\text{OH})_2$ , Bis(S-methyl-L-cysteinato)copper(II); *iii*) 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) monohydrated, glycyglycinatocopper(II) dihydrate and  $\text{Cu}(\text{OH})_2$ .

## RESULTS

The EXAFS results are summarized in the following figures and table.

Table 1. Result of EXAFS analyses. Aa-Sa: relationship between central absorber and scattering atom; *N*: coordination number; *R*: refined interatomic distance,  $\sigma^2(\text{\AA}^2)$ : Debye-Waller factor;  $\Delta E_0$ : energy shift.

Cu-beidellite					Cu-cysteine Beidellite				
Aa-Sa	N	<i>R</i> (\AA)	$\sigma^2(\text{\AA}^2)$	$\Delta E_0$	Aa-Sa	N	<i>R</i> (\AA)	$\sigma^2(\text{\AA}^2)$	$\Delta E_0$
Cu-O	3.7	1.98	0.0087	-4.5	Cu-O	0.9	1.96	0.0050	-4.8
Cu-Cu	0.9	3.07	0.0042		Cu-O	0.9	1.97	0.0050	
Cu-Cu	1.9	6.03	0.0054		Cu-N	0.9	1.99	0.0050	
					Cu-N	0.9	1.99	0.0050	
					Cu-O	0.9	2.70	0.0190	
					Cu-O	0.9	2.73	0.0000	

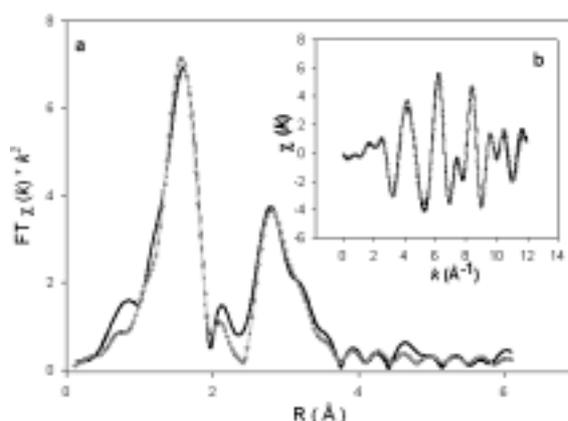


Fig. 1. Cu-exchanged beidellite. a) Fourier Transform (FT) and b) associated inverse Fourier-filtered scattering curve ( $\text{FT}^{-1}$ ) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using  $\text{Cu}(\text{OH})_2$  as reference compound.

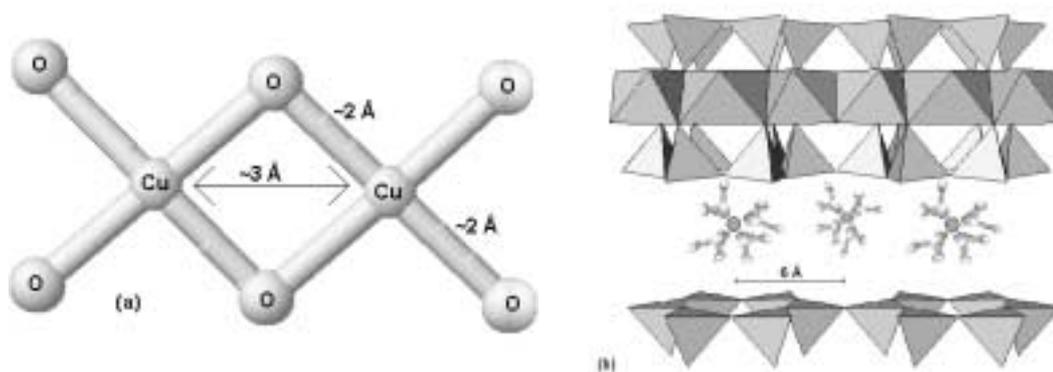


Fig. 2. (a) Sketch of the planar double-bridged structure of copper dimers with Cu-Cu distances of about 3 Å . (b) Hydrated structure of copper characteristic of complexes formed in the smectite interlayer with Cu-Cu distances at about 6 Å.

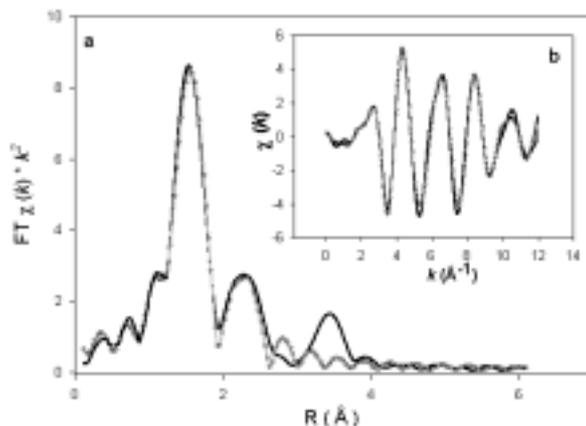


Fig. 3. Cu-exchanged beidellite treated with cysteine. a) Fourier Transform (FT) and b) associated inverse Fourier-filtered scattering curve ( $FT^{-1}$ ) spectra. Solid lines indicate experimental data and circles indicate the fit curve obtained using Bis(S-methyl-L-cysteinato)copper(II) as reference compound.

## References

Ankudinov A. L., Ravel B., Rehr J. J. and Conradson S. D. (1998) Real Space Multiple Scattering Calculation and Interpretation of X-ray Absorption Near Edge Structure. *Phys. Rev.* **B58**, 7565.

## Publications

Benincasa E., Brigatti M.F., Malferrari D. & Poppi “XAFS study of Cu sorption products on smectites treated with  $\alpha$ -aminoacids”, ICAM 2000, 6<sup>th</sup> International Congress on Applied Mineralogy, Göttingen, Germany, 17-19 July 2000.

Brigatti M.F., Benincasa E., Malferrari D., Medici L. & Poppi L. “X-ray absorption spectroscopy of Cu-rich smectites treated with  $\alpha$ -amino acids”, MID-EUROPEAN CLAY CONFERENCE '01, Stará Lesná, Slovakia, 9-14 September 2001

Brigatti M.F., Malferrari D., Medici L. & Poppi L. “Characterization of Cu-complexes in smectite with different layer charge location: chemical, thermal and EXAFS study”. Clay meeting of France Clay Group, Orleans, March 22, 2002.

Brigatti M.F., Colonna S., Malferrari D., Medici L. “Structural modifications induced by metal complexation with organic matter in smectites: a multi-analytical approach” “Decimo Convegno S.I.L.S.”, Rome, 11-13 July 2002.

Brigatti M.F., Colonna S., Malferrari D., Medici L. & Poppi L. “Metal-organic Cu complexes in smectites with different layer charge location: chemical, thermal and EXAFS study”, Mineralogy for the New Millenium, XVIII General Meeting of the International Mineralogical Association, Edinburgh, 1-6 September 2002.

Brigatti M.F., Malferrari D., Medici L. & Poppi L. Low cost sorbent for Cu polluted areas remediation: EXAFS spectroscopy investigation. Environmental Engineering Science, in press.