

# Molecular–Structural Analysis of the Cu (II) Ion in Ordinary Chernozem: Evidence from XANES Spectroscopy and Methods of Molecular Dynamics

T. M. Minkina<sup>a</sup>, A. V. Soldatov<sup>a</sup>, G. V. Motuzova<sup>b</sup>, Yu. S. Podkovyrina<sup>a</sup>, and D. G. Nevidomskaya<sup>c</sup>

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## INTRODUCTION

Interest in metals occurring in natural environments is determined by their necessity for live organisms in optimal portions, but excess amounts of them have a toxic influence. The ecological importance of soil compounds of metals is determined by the composition of these compounds. Currently extraction methods are widely applied for analysis of the composition of metal compounds. However the influence of extractive agents is not selective and provides only indirect information on the relationships between metals and other soil components. The real forms of metal occurrence in soil are still unknown. During the last 20 years, development of methods of X-ray absorption spectroscopy provided information on the structural organization of soil metal compounds [1]. Application of the EXAFS and XANES methods allows us to determine the geometric structure of these compounds, reveal real phases carrying metals in soils, and establish chemical bond types.

This study is aimed at analysis of the spatial–structural organization of Cu (II) compounds in ordinary chernozem and at analysis of the relationship between metal ion and soil components. The tasks of investigation include obtaining XANES spectra for soil samples contaminated by CuO and Cu(NO<sub>3</sub>)<sub>2</sub>, calculation of the theoretical spectra of the initial copper-bearing compounds and construction of the model of copper ion absorption by montmorillonite on the basis of the methods of molecular dynamics, comparison of the experimental data with calculations, and establishment of the atomic structure of Cu (II) introduced into the soil in different forms and its links to sorption centers of the soil and minerals.

<sup>a</sup> Southern Federal University, Rostov-on-Don, Russia

<sup>b</sup> Moscow State University, Moscow, Russia

<sup>c</sup> Institute of Arid Zones, Southern Science Center, Russian Academy of Sciences, Rostov-on Don, Russia  
e-mail: minkina@sfedu.ru

## OBJECTS AND METHODS

The objects of investigation include samples of ordinary chernozem from Rostov region artificially contaminated in a model experiment by high portions of Cu(NO<sub>3</sub>)<sub>2</sub> (2000 ppm) and CuO (2000 and 10 000 ppm). The duration of metal incubation in the soils was 1 year. The composition of copper compounds in the soil was determined by the method of extraction fractionation by an original methodology [2].

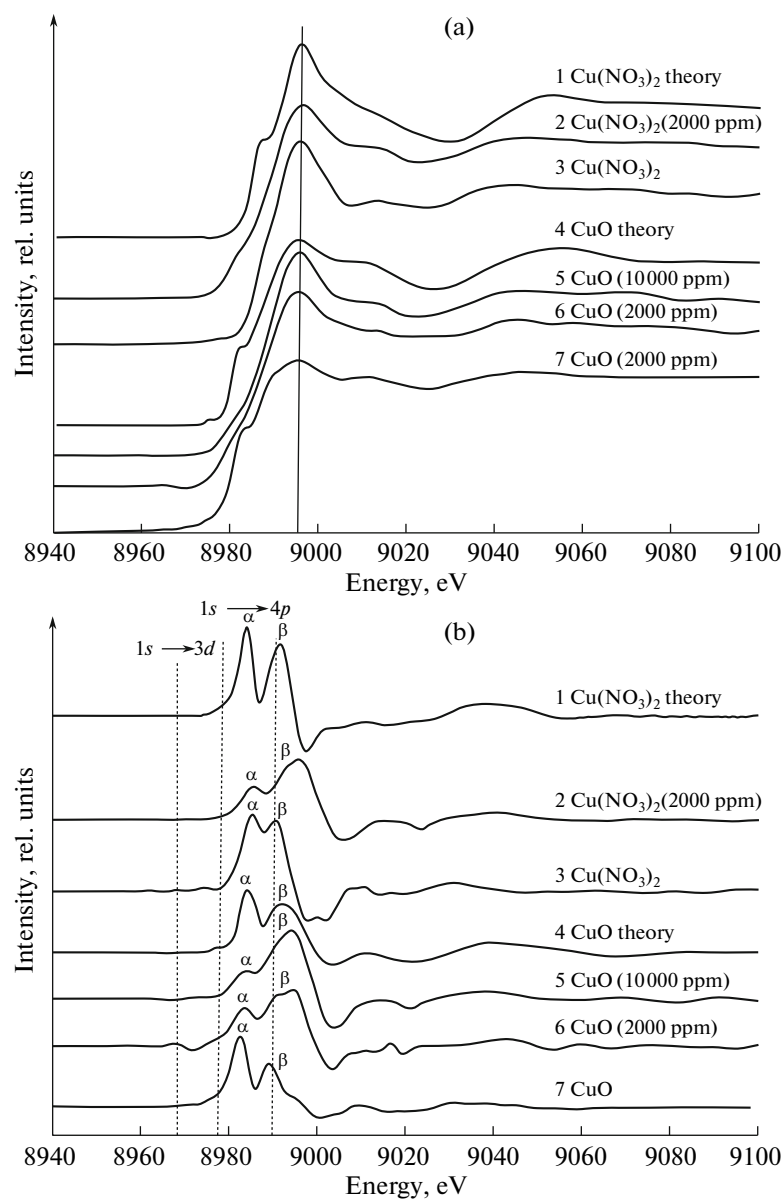
The XANES spectra (in the range of 8930–9250 eV) for the samples of soils were obtained on a Rigaku R-XAS Looper spectrometer using a Ge (440)-monochromator [3]. Theoretical modeling of the K-edge of spectra for CuO and Cu(NO<sub>3</sub>)<sub>2</sub> was carried out by the method of final differences for solution of the Schrödinger equation and by the method of full multiple scattering of photoelectrons using the FDMNES 2010 and FEFF9 software [4, 5].

In this study we compare (1) experimental spectra of soil samples treated with CuO and Cu(NO<sub>3</sub>)<sub>2</sub>, (2) experimental spectra of initial copper-bearing compounds Cu and Cu(NO<sub>3</sub>)<sub>2</sub>, and (3) theoretical spectra of the compounds mentioned.

## RESULTS OF THE STUDY

Extraction fractionation of copper compounds in the studied samples demonstrated that copper mainly (up to 83%) occurred in the framework of silicates in noncontaminated chernozem. Introduction of 2000 and 10 000 ppm copper compounds resulted in a decrease of the metal portion in the composition of silicates to 24–33% from the total concentration. The concentration of copper tightly bonded and poorly bonded by iron (hydro) oxides and organic compounds increased by factors of 8–10 and 4–8, respectively. These changes are more remarkable for the introduction of Cu(NO<sub>3</sub>)<sub>2</sub> than CuO [2].

Molecular–structural analysis was carried out in order to determine the type of metal bond with soil components. The parameters of the experimentally



**Fig. 1.** Experimental and theoretical spectra (a) and spectra of the first derivative (b) of X-ray absorption XANES for initial copper-bearing compounds and contaminated soil samples: (1) theoretical spectrum of  $\text{Cu}(\text{NO}_3)_2$  calculated using the FDMNES2010 software; (2) experimental soil spectrum saturated by 2000 ppm  $\text{Cu}(\text{NO}_3)_2$ ; (3) experimental spectrum of the initial compound  $\text{Cu}(\text{NO}_3)_2$ ; (4) theoretical spectrum of  $\text{CuO}$  calculated using the FEFF9 software; (5) experimental soil spectrum saturated by 10 000 ppm  $\text{CuO}$ ; (6) experimental soil spectrum saturated by 2000 ppm  $\text{CuO}$ ; (7) experimental spectrum of the initial  $\text{CuO}$  compound.

obtained XANES spectra for the studied samples and initial copper-bearing compounds are consistent with theoretical spectra of the studied copper compounds (Fig. 1a). The experimental spectrum of soil contaminated by copper occupies an intermediate position between the theoretical and experimental spectra of pure compounds, namely  $\text{CuO}$  and  $\text{Cu}(\text{NO}_3)_2$ . Both of them are characterized by the presence of a peak in the middle part of the main edge ( $\sim 8985$ – $8990$  eV) controlled by the presence of  $\text{Cu}(\text{II})$  ions.

We calculated the first derivatives of X-ray absorption spectra, which allowed us to reveal peculiarities of the

objects analyzed (Fig. 1b). The spatial–structural analysis of soil spectra was performed on the basis of diagnostics of the intensities of spectra in the near-edge and edge regions of spectra. The near-edge area ( $\sim 8975$ – $8980$  eV) of the K-edge of the copper spectra is characterized by a poor maximum, which is most likely controlled by the quadrupole  $1s \rightarrow 3d$  electron transition responsible for Cu bonding in the octahedral and tetrahedral sites.

The step structure as two peaks  $\alpha$  and  $\beta$  in the middle part of the spectrum ( $\sim 8980$ – $8995$  eV) characterizes the  $1s \rightarrow 4p_z$  transition. The intensity of the func-

Results of modeling of the montmorillonite structure by the method of molecular dynamics before and after Cu (II) ion absorption (confidence range of averages is calculated for  $n = 59$  and  $P = 0.95$ )

Atoms and their position	Bond distance, Å	Bond angle $O_{eq}-Al(Cu)-O_{ax}$ , deg
Montmorillonite, standard model		
Al–O <sub>eq</sub>	$1.929 \pm 0.004$	$105.92 \pm 18.25$
Al–O <sub>ax</sub>	$1.946 \pm 0.007$	
Montmorillonite, model with absorbed Cu (II) ions		
Cu–O <sub>eq</sub>	$1.916 \pm 0.008$	$105.15 \pm 18.10$
Cu–O <sub>ax</sub>	$1.931 \pm 0.004$	

tion of the near-edge transition  $1s \rightarrow 3d$  is sensitive to the presence or absence of a symmetry center. The function intensity increases with progressing distortion from the center of tetragonal symmetry in relation to an increase in  $p-d$  orbital mixing [6–8].

The similar intensities of near-edge peaks in spectra of soil samples treated by CuO and  $Cu(NO_3)_2$  pro-

vide evidence for the fact that copper ions absorbed by soil components occur in a low-symmetry environment analogous to that in pure copper-bearing compounds CuO and  $Cu(NO_3)_2$ .

The step structure represented by the  $\alpha$  and  $\beta$  peaks in the edge region of the experimental and theoretical spectra of the first derivate most likely reflects the Jahn–Teller effect providing evidence for tetragonal distortions of the centers of Cu bonding in octahedrons [6–9]. The distance between the energetic positions of the  $\alpha$  and  $\beta$  peaks is  $\sim 10$  eV. This parameter may be applied for qualitative estimation of the equatorial and axial Cu–O distances in copper-bearing octahedrons [10].

The intensity of the  $\alpha$  peak is controlled by the degree of bond covalence and characterizes the coordination environment and chemical bonds of the absorbed metal ion with its closest surroundings [11]. With a decrease in the  $\alpha$  peak energy, Cu complexes with soil components have predominantly the covalent character of the bond. The intensities of the  $\alpha$  and  $\beta$  peaks in the experimental spectra of the initial copper-bearing compounds are close.

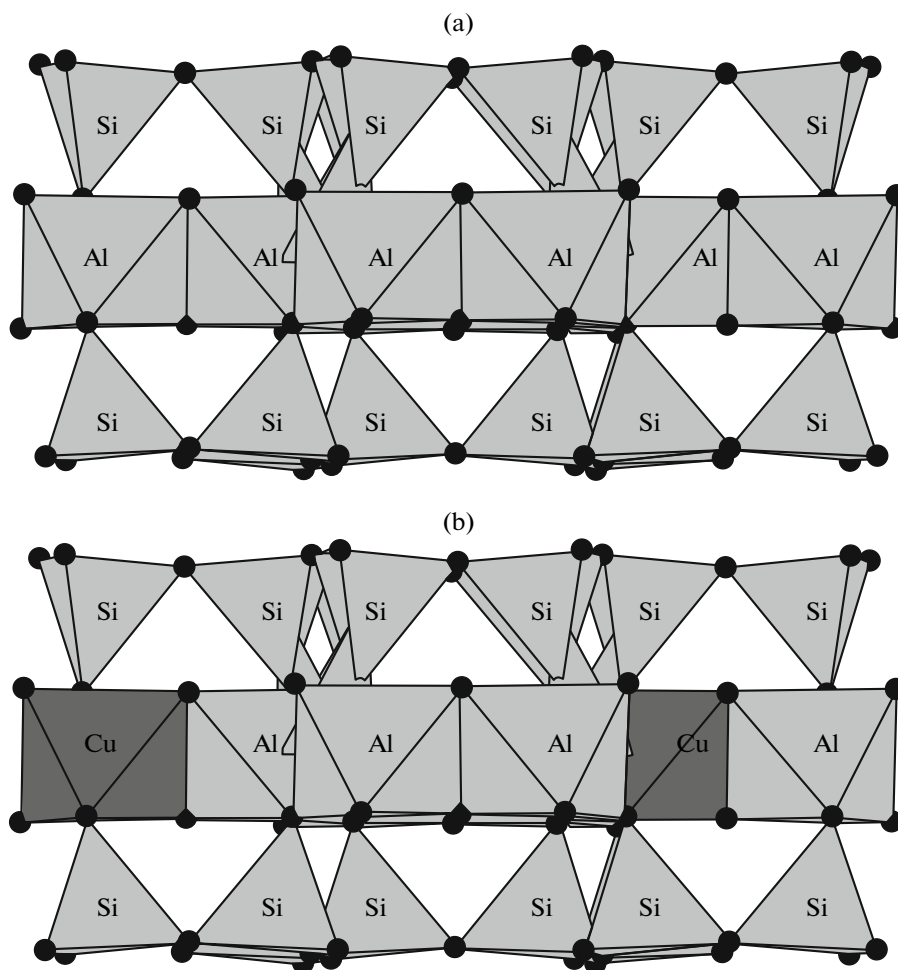


Fig. 2. Montmorillonite structure before (a) and after (b) Cu sorption.

The morphology, size, and peculiarities of edge and near-edge areas on XANES spectra of soil samples contaminated by CuO and Cu(NO<sub>3</sub>)<sub>2</sub> have clear differences mainly controlled by the differences in their local atomic structure around the central Cu ion. The spectra of soil samples contaminated by CuO demonstrate close similarity to experimental spectra of the initial copper-bearing compound CuO. By contrast, the spectra of soils treated by Cu(NO<sub>3</sub>)<sub>2</sub> differ significantly from the spectra of the initial copper-bearing compound providing evidence for transformation of the environment of the copper ion introduced into the soil. Copper nitrate is well-soluble in water; because of this, copper ions during the one year of incubation were sorbed by the soil and formed complexes with organic components.

The low intensity of the  $\alpha$  peak on the first derivative of the XANES spectra of soil samples contaminated by CuO and Cu(NO<sub>3</sub>)<sub>2</sub> is controlled by the electron transition  $1s \rightarrow 4p_z$  and provides evidence for electron transfer from the metal to a ligand [8]. This may lead to ion exchange in the tetragonal plane of water molecules with ligands. The interaction between copper ions and humic acid may result in the formation of multilateral 6-coordinated spatial structure Cu[H<sub>2</sub>O]<sub>2</sub>[RCO<sub>2</sub>]<sub>4</sub> of humate complex.

The intensity of the  $\beta$  peak energy on the XANES spectra is determined by the probability of the  $1s \rightarrow 4p_z/p_y$  electron transition [12]. It was previously established [11] that the highest intensity of the  $\beta$  peak was observed in spectra of the samples of humic acids and goethite containing adsorbed copper ions. As this takes place, triple complexes are formed; the central position in them is occupied by a copper ion bonded with organic and mineral components.

Based on modeling of the molecular and dynamic interaction between metal ions and montmorillonite, it was established that copper adsorption on the basal plane of the mineral mainly occurred at the expense of Coulomb forces (Fig. 2). Cu<sup>2+</sup> ions are incorporated in the positions of the inner-sphere complex replacing some aluminum ions in the octahedral sites. We may suggest that Cu<sup>2+</sup> is also sorbed by dimer (Cu–Cu) silicate and/or aluminum groups with incomplete coordination. The process may take place due to variations in the bond distances and the appearance of double bonds in the places of local defects of the crystal cell.

Table demonstrates variations of the main parameters of the montmorillonite structure caused by interaction with the metal.

Cu<sup>2+</sup> ions incorporated in the montmorillonite structure favor a decrease in the bond distances between Cu<sup>2+</sup> ions and O atoms in equatorial and axial coordination positions and decrease in the bond angle ( $O_{eq}-Al(Cu)-O_{ax}$ ) in copper-bearing octahedrons.

## CONCLUSIONS

XANES spectroscopy is an effective method for the study of bonds between metals and soil components. Application of this method demonstrated that the state of copper introduced in chernozem as CuO did not change after one year of incubation. Copper is absorbed after being introduced as Cu(NO<sub>3</sub>)<sub>2</sub>, and copper ions are incorporated in the octahedral and tetrahedral sites of minerals and bonded with humic materials at the expense of covalent bond and the formation of coordination humate copper complexes. Copper ions may be adsorbed on the basal plane of montmorillonite, and their incorporation in the inner-sphere complex with substitution of some aluminum ions in the octahedral sites is possible. This results in changes in the structure of octahedrons, namely the equatorial and axial Cu–O distances and bond angles in Cu-bearing octahedrons.

Changes in the structure of the metal ion, in particular breakdown of the symmetry of electron orbits of atoms, take place due to interaction with soil components.

## ACKNOWLEDGMENTS

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