Combined EXAFS and ab initio study of copper complex geometries adsorbed on natural illite

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SUPPORTING INFORMATION

Materials

Illite preparation.

The illite sample from the CMS repository is a greenish, easily disaggregated, shale with minor reddish oxy-hydroxides, especially along the foliation planes and small fractures. Two portions, each having 100 g, were gently ground to powder in a small agate mortar to further reduce the size of the small scale aggregated mineral grains. Both portions were then mixed and homogenized together to form a single 200 g sample.

Aliquots, each about 30 g of illite powder, were washed and further disaggregated for 45 minutes in glass columns with distilled water that was stirred with a continuous flow of compressed air from below. The columns were 50 cm tall and 8 cm diameter. Once the air-flow was stopped the suspended material was transferred into 1 L capacity measuring glass cylinder with a level mark above which the suspended particles with sizes less than 20 μm are kept in suspension after 5 minutes, according to Stokes’ law. The suspended material was then decanted and transferred into
beakers. The process was repeated for the remaining suspended material and for the material settled at the bottom, as many times as needed in order to retrieve the maximum amount of particles < 20 µm. These particles, once transferred into the beakers, were allowed to settle until most of them accumulated at the bottom. The unsettled particles were transferred into 80 mL tubes, and centrifuged for 30 min at 3000 rpm. The supernatant was decanted and filtered in a crucible with 0.4 µm Millipore membranes under vacuum. All fractions were dried in the oven, at a maximum temperature of 40°C. All the portions of dried material were gently disaggregated, mixed together, and homogenized. The final sample obtained corresponded to an illite with particles ranging from 0.4 to 20 µm in size. Observation of several aliquots of the separated fraction using a SEM showed that the particles had, in fact, dimensions lower than 20 µm. The total amount of illite recovered with this procedure was 91 g out of the initial 200 g, which corresponds to 45.5% efficiency.

Because clay minerals have characteristic impurities on their surfaces that can influence the sorption behavior of cations, the separated fraction of the IMt-1 illite was treated for soluble salts, carbonates, oxides, and organic matter, following the procedure from Kunze and Dixon (1986).

**Removal of carbonates and soluble salts**

Two portions of illite, each weighing about 45 g, were placed into a dialysis membrane closed at one end. The membrane was filled with a 0.5 M sodium acetate solution adjusted to pH 5 with acetic acid until the illite sample became wet. The membrane was then immersed into 1 L of the sodium acetate buffer solution with the open ending outside of the flask to allow the escape of the gases from the dissolution of carbonates. The sample was maintained in the solution for at least 24 h depending on the amount of carbonates and size of the particles, with a gentle but continuous stirring. When CO₂ release ceases, the dialysis membrane was transferred into a continuously stirred distilled water-filled flask. The water in the flask was replaced at least twice until an ionic concentration within the membrane was lower than 10 meq/L (monitored through conductivity). The sample was transferred
into centrifuge tubes and washed thoroughly with distilled water and then centrifuged at 2300 rpm for 20 min. After treatment, the sample was stored and dried in the oven at 40°C.

**Removal of organic matter**

The illite was mixed with distilled water in a 1:2 volume ratio in a beaker. Initially, aliquots of 5 to 10 mL of H₂O₂ (30% v/v) were added while stirring the suspension and controlling for any strong initial reaction. The beaker was then transferred into a water bath (65°C - 70°C), and H₂O₂ slowly added until a solution of circa 10% H₂O₂ was produced. Excess solution was evaporated between each H₂O₂ addition in order to maintain the 1:2 illite/solution volume ratio. The suspension was transferred into centrifuge tubes after oxidation of the organic matter was completed, and centrifuged at 2300 rpm for 15 min. The supernatant was decanted and rejected provided no clays particles remained in suspension. In case there was still suspended material in the tubes, a few drops of 0.5 M MgCl₂ were added and carefully mixed avoiding the disturbance of the settled illite, and centrifuged for 5 min. The sample was further rinsed filling about 1/3 of the centrifuge tubes volume with distilled water, and stirred continuously for 5 min. The suspension was centrifuged and the supernatant discarded.

**Removal of iron oxides**

Due to the Fe₂O₃ content of the Silver Hill illite, this procedure cannot be applied to more than about 8 g at a time. To each 8 g sample aliquot, 40 mL of 0.3 M sodium citrate and 5 mL of 0.5 M NaHCO₃ solutions were added and mixed into a beaker. The suspension was then heated to 80°C (±0.2°C) in a water bath, and 0.5 g of Na₂S₂O₄ was added. The suspension was stirred continuously for 1 min, and occasionally afterwards for a total of 15 min. If needed, a saturated solution of NaCl and acetone were added after the digestion to flocculate the suspension. The suspension was mixed and transferred to centrifuge tubes, and centrifuged for 15 minutes at 1600 rpm. The sample was washed at least twice with the sodium citrate solution, with NaCl and acetone added when necessary. Finally, the samples were thoroughly washed with distilled water having taken SEM images with
EDS and performed XRD and ATR-FTIR scans before and after treatment as can be seen in Figures S1, S2 and S3, respectively.
Fig. S1. SEM images with EDS spectra for the separated and treated illite aliquot (A) and coarser untreated illite aliquot (B).
**Fig. S2.** XRD scans before and after treatment. A: XRD patterns for the IMt-1 illite bulk sample (lower) and < 2 µm size (upper) before treatment; B: Glycol saturated illite showing no shift of the (001) reflection eliminating the possibility of a illite/smectite interstratified; C: Long-time acquisition XRD spectrum of the illite after treatment, with the indication of the illite (il), quartz (q) and kaolinite (k) peaks.
Fig. S3. ATR-FTIR spectrum of reacted illite at pH 6.5, HBEC, and 2.8 wt% Cu. Major absorption bands correspond to the Al and Si bands, and the noisy signal results from the atmospheric CO$_2$ correction. According to Du et al. (1997), if carbonate was in the system bands should have appeared in the range 3322 to 3451 cm$^{-1}$. 
Batch Sorption Experimental Data

**Fig. S4.** Adsorption isotherms of experimental data for pH 4.5, 5.5, and 6.5 with illites used for EXAFS spectra collection.
EXAFS Spectra and modelling

Fig. S5. FT of EXAFS spectra where a) represents the data at pH 4.5, b) at pH 5.5, and c) at pH 6.5.
Fig. S6. Relationship between bond-lengths (Å) and Cu concentrations (% Cu), where a) represents Cu-O_{eq}, b) Cu-O_{ax1}, c) Cu-O_{ax2} and d) Cu-Cu.
Fig. S7. Best fits of the FT EXAFS are given in dashed lines whereas the $k^2$-weighted normalized data is shown in solid lines, for the samples: a) pH 4.5; 0.27%, b) pH 4.5; 0.32%, c) pH 4.5; 0.36%, d) pH 4.5; 0.37%, e) pH 4.5; 0.43%, f) pH 4.5; 0.58%, g) pH 5.5; 0.12%, h) pH 5.5; 0.13%, i) pH 5.5; 0.32%, j) pH 5.5; 0.45%, k) pH 5.5; 0.57%, l) pH 5.5; 0.79%, m) pH 6.5; 0.27%, n) pH 6.5; 0.52%, o) pH 6.5; 1.13%, p) pH 6.5; 1.31%, q) pH 6.5; 2.76%, r) pH 6.5; 2.76%. Fit parameters are given in Table 1.
Modelling of the macroscopic batch adsorption experiments

Modelling of the adsorption experiments was done using the code PHREEQC (Parkhurst and Appelo, 1999), and the results are shown in Figure S8 (solution speciation in equilibrium with atmospheric CO₂) and Figure S9 (illite surface speciation). Surface complexation modelling and parameters measured or optimized with FITEQL (Herbelin and Westall, 1999) are shown in Table S1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sites (mol/g)</td>
<td>1.55 ± 0.11 × 10^{-4}</td>
<td>=SOH (refined; unpublished data)</td>
</tr>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>38.04 ± 0.04</td>
<td>Illite IMt-1</td>
</tr>
<tr>
<td>Model</td>
<td>DDL</td>
<td></td>
</tr>
<tr>
<td>Surface Potential (V)</td>
<td>−9.69 × 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>Surface charge (C/m²)</td>
<td>−1.20 × 10^{-1}</td>
<td></td>
</tr>
<tr>
<td>pK_a</td>
<td>3.98 ± 0.14</td>
<td>=SOH = =SO^{-} + H^+ (Gonçalves, 2006)</td>
</tr>
<tr>
<td>pK_{a3}</td>
<td>4.12 - 4.23</td>
<td>=SOH = =SO^{-} + H^+ (Du et al., 1997a)</td>
</tr>
</tbody>
</table>

Table S1: Parameters used in the chemical modelling of the batch adsorption experiments

Model equations for Cu adsorption on illite from Du et al. (1997b) (where =S represents a surface site):

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O} & \leftrightarrow \text{CuOH}^+ + \text{H}^+; \quad \log K = -7.7 \quad (\text{Eq. 1}) \\
\equiv \text{SOH} + \text{Cu}^{2+} & \leftrightarrow \equiv \text{SOCu}^+ + \text{H}^+; \quad \log K = -3.16 \quad (\text{Eq. 2}) \\
\equiv \text{SOH} + \text{Cu}^{2+} + \text{H}_2\text{O} & \leftrightarrow \equiv \text{SOCuOH} + 2\text{H}^+; \quad \log K = -8.51 \quad (\text{Eq. 3}) \\
\equiv \text{SOH} + 2\text{Cu}^{2+} + 2\text{H}_2\text{O} & \leftrightarrow \equiv \text{SOCu}_2(\text{OH})_2 + 3\text{H}^+; \quad \log K = -11.8 \quad (\text{Eq. 4}) \\
\equiv \text{SOH} + 2\text{Cu}^{2+} + 3\text{H}_2\text{O} & \leftrightarrow \equiv \text{SOCu}_2(\text{OH})_3(\text{sp}) + 4\text{H}^+; \quad \log K = -14.0 \quad (\text{Eq. 5})
\end{align*}
\]
Fig. S8. Copper speciation diagram in equilibrium with atmospheric CO₂ showing the relevant carbonate species at the highest Cu concentration used in the batch experiments. Data for Cu aqueous complexes from Du et al. (1997) and from the flnl.dat database (PHREEQC). Also shown is the saturation index (SI) for copper hydroxide Cu(OH)₂ (s); data from Hidmi and Edwards (1999). The phase of copper hydroxide (s) here is not to be confused with the copper hydroxide surface precipitate (sp) shown in Figure S9.
**Fig. S9.** Concentration of surface species (mol/g) and Cu in solution as a function of pH and at $10^{-3}$ M KNO$_3$ for a total Cu concentration of 0.05 mM using the equilibrium equations 1-5 and model parameters in Table S1. $\equiv$SOX represents surface complexes. The surface species $\equiv$SOCu$_2$(OH)$_3$(sp) represents a surface precipitate, and here was modelled as a regular surface species. The speciation diagram provides the pH for which the copper hydroxide surface precipitate is stable and starts to form.
Application of the Model of Alvarez-Puebla et al. (2005) to the macroscopic batch experiments

The model of Alvarez-Puebla et al. (2005) corresponds to a linear combination of 2 Langmuir isotherms and 1 Freundlich isotherm. The prevailing reactions for the pH range used in our study are the following

\[
\begin{align*}
\equiv SOH + [Cu(H_2O)_6]^{2+} & \leftrightarrow [Cu(H_2O)_6]^{2+} \quad \text{(Eq. 6)} \\
\equiv SOH + [Cu(H_2O)_6]^{2+} & \leftrightarrow [CuSO(H_2O)\text{O}_2]^{+} + H_3O^+ \quad \text{(Eq. 7)} \\
\equiv SOH + [Cu(OH)(H_2O)\text{O}_2]^{+} & \leftrightarrow [Cu(SO)(OH)(H_2O)\text{O}_2] + H_3O^+ \quad \text{(Eq. 8)} \\
[&Cu(H_2O)_6]^{2+} + 2OH^- \leftrightarrow Cu(OH)_2 \downarrow + 6H_2O \quad \text{(Eq. 9)}
\end{align*}
\]

and the model equation is

\[
n^e = n^e_1 + n^e_2 + n^e_3 = \frac{K_1n^e_{m(1)}C}{1 + K_1C} + \frac{K_2n^e_{m(2)}C}{1 + K_2C} + AC^b, \quad \text{(Eq. 10)}
\]

where \( n^e_1 \) is the amount of copper retained as \( [Cu(H_2O)_6]^{2+} \) according to equations 6 and 7, \( n^e_2 \) is the amount of copper retained as a surface complex from \( [Cu(OH)(H_2O)\text{O}_2]^{+} \) according to equation 8, and \( n^e_3 \) is the amount of copper retained as a surface induced precipitate according to equation 9.

Alvarez-Puebla et al. (2005) fitted parameters are as follows:

<table>
<thead>
<tr>
<th>( R_2 )</th>
<th>( b )</th>
<th>( A )</th>
<th>( K_1 )</th>
<th>( n^e_{m(1)} )</th>
<th>( K_2 )</th>
<th>( n^e_{m(2)} )</th>
<th>pH</th>
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<tbody>
<tr>
<td>0.9992</td>
<td>3.67</td>
<td>94.1</td>
<td>4.23</td>
<td>7.77</td>
<td>14.2</td>
<td>37.7</td>
<td>4.54±0.04</td>
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<tr>
<td>0.9987</td>
<td>4.53</td>
<td>6.95×10^3</td>
<td>13.9</td>
<td>60.7</td>
<td>4.98±0.03</td>
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<tr>
<td>0.9915</td>
<td>5.76</td>
<td>2.47×10^6</td>
<td>14.4</td>
<td>105</td>
<td>5.55±0.08</td>
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<td></td>
</tr>
<tr>
<td>0.9928</td>
<td>6.12</td>
<td>4.85×10^12</td>
<td>5.97±0.11</td>
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</tr>
<tr>
<td>0.9819</td>
<td>6.60</td>
<td>6.80×10^10</td>
<td>6.98±0.13</td>
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</tr>
</tbody>
</table>

**Table S2**: Alvarez-Puebla et al.’s model fitted parameters with regression coefficient values and pH conditions to be used in equation 10. Units are mM for solution concentration and mmol/kg for adsorbed copper.

Results of the model are shown in Figures S10 and S11 for pH 4.5 and 5.5, respectively. As it is clear from the model parameters for pH around 6 in Table S2, figure for pH 6.5 is unnecessary.
**Fig. S10:** Experimental data points for sorption batch reactions at pH 4.5 and results for the model of Alvarez-Puebla et al. (2005) for pH 4.54 and 4.98.

**Fig. S11:** Experimental data points for sorption batch reactions at pH 5.5 and results for the model of Alvarez-Puebla et al. (2005) for pH 5.55 and for the same pH but setting the $A$ and $b$ values from Table S2 to zero, which means no surface precipitation, in which case it does not occur before pH 6 according to Du et al. (1997b) model (Figure S9). Model with precipitation has been truncated.
DFT Calculations

<table>
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<tr>
<th></th>
<th>Charge (e)</th>
<th>CN a</th>
<th>Cu-O_{eq}</th>
<th>Cu-O_{ax}</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N b</td>
<td>R c (Å)</td>
</tr>
<tr>
<td>Cu(H_2O)_5</td>
<td>g</td>
<td>2</td>
<td>5</td>
<td>1.98(2)</td>
</tr>
<tr>
<td></td>
<td>l</td>
<td>5</td>
<td>4</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>Cu(H_2O)_5 + H_2O</td>
<td>g*</td>
<td>6</td>
<td>4</td>
<td>2.01 *</td>
</tr>
<tr>
<td></td>
<td>l</td>
<td>5</td>
<td>4</td>
<td>1.98(1)</td>
</tr>
<tr>
<td>Cu(OH)_2(H_2O)_4 trans</td>
<td>g</td>
<td>0</td>
<td>4</td>
<td>1.95(6)</td>
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<tr>
<td></td>
<td>l</td>
<td>4</td>
<td>4</td>
<td>1.95(7)</td>
</tr>
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</table>

a - Overall coordination number; b - Coordination number relevant to specific interaction; c - Interatomic distance; d - From calculations with the extra water molecule started at 2.3 Å; e - From calculations with the extra water molecule started at 2.8 and 3.3 Å. * Note that no standard deviation could be calculated for these cases as only one value was calculated.

Table S3: Structural results of DFT calculations in gas phase (g) and aqueous solution (l).
REFERENCES


