

INFLUENCE OF SORBED COPPER(II) ON THE DYNAMICS OF $\text{Al}(\text{OH})_3$ PRECIPITATION IN HYDROXY-AL-MONTMORILLONITE

Key Words—Adsorption, Aluminum, Copper, Gibbsite, Hydroxy-Al-montmorillonite.

The formation of gibbsite from synthetic hydroxy-Al interlayers in montmorillonite has been shown to depend upon the initial OH/Al molar ratio of the interlayer material and the quantity of precipitated Al (Barnhisel and Rich, 1963; Turner and Brydon, 1965, 1967). These workers showed that gibbsite forms after several months if the amount of Al exceeds about 8 eq Al^{3+} /kg montmorillonite and/or the initial OH/Al molar ratio exceeds about 2.8. Kittrick (1983) pointed out that in such preparations the solubility product, $(\text{Al}(\text{OH})_3)$, exceeds that of gibbsite and, therefore, these interlayered clays must be considered thermodynamically unstable systems.

Chemisorption of copper to interlayer Al-OH sites in a synthetic hydroxy-Al-montmorillonite complex exceeded adsorption on microcrystalline gibbsite (Harsh and Doner, 1984). Transmission electron micrographs and phosphate sorption studies of the complex (to be reported elsewhere) suggested that its high sorption capacity was due to the high specific surface area of the $\text{Al}(\text{OH})_3$ precipitated on the surface. In light of evidence that trace metals coprecipitated with iron(III) hydroxides inhibit growth of the microcrystals (Nalovic *et al.*, 1976), it is likely that sorbed species might retard crystal growth in the hydroxy-Al-montmorillonite system. Specifically, the rate of gibbsite formation at the expense of interlayer $\text{Al}(\text{OH})_3$ was examined in a hydroxy-Al-montmorillonite complex as a function of sorbed Cu(II).

EXPERIMENTAL

A hydroxy-Al-montmorillonite complex was prepared from Wyoming montmorillonite (sample SWy-1, obtained from the Source Clays Repository of The Clay Minerals Society) by titrating 9.28 eq $\text{Al}(\text{ClO}_4)_3$ /kg of montmorillonite with NaOH to an OH/Al molar ratio of 2.38. The suspension was aged at 25°C for five weeks. The solid phase was then washed five times each with 1 M NaClO_4 and 0.01 M NaClO_4 and stored ten weeks in the latter solution. Subsamples were then aged in 0.01 M NaClO_4 suspensions to which Cu(II) had been added. Copper(II) concentrations ranged from 0 to 4×10^{-3} M in the subsamples. The pH was adjusted over three days to 5.3. Further details of the preparation of the complex and the nature of the interlayer material have been previously published (Harsh and Doner, 1984).

Subsamples from the 0.01 M NaClO_4 suspensions were taken 5 weeks before and 9.5 months after the Cu(II) was added. These aliquots were saturated with potassium, smeared on glass slides, and air-dried or dried at 110°C overnight. X-ray powder diffraction (XRD) patterns were obtained using Ni-filtered, $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Initial and final Cu(II) concentrations and the amount of Cu(II) sorbed are reported in Table 1. XRD patterns for these samples are shown in Figure 1. The XRD patterns of subsamples taken before adding Cu(II) to the suspensions showed no evidence of the formation of gibbsite and are not shown.

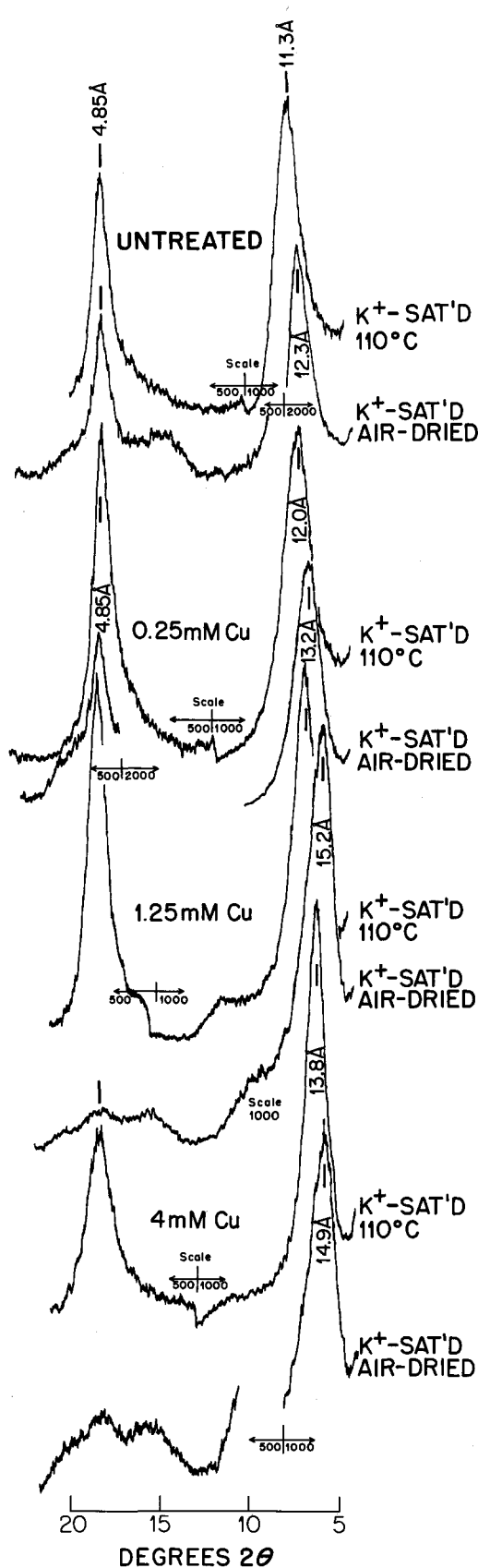
Copper sorption markedly influenced the crystal growth of gibbsite. In the presence of 0.25 mM Cu(II) the interlayer spacings of the complex were 13.2 Å (25°C) and 12.0 Å (110°C) compared to 12.3 Å (25°C) and 11.3 Å (110°C) in the untreated sample. The formation of gibbsite was indicated by an XRD peak at ~4.8 Å. As Cu sorption increased, the interlayer spacing also increased indicating that less material was lost from the interlayer and that gibbsite crystallization had been inhibited. This interpretation is supported by the fact that the 4.8-Å peak was not present in the XRD patterns of the air-dried samples which initially contained 1.25 and 4.0 mmole Cu. No correlation was found between pH and the observed structural changes (Table 1); hence, the presence of Cu(II) was predominantly responsible for the inhibition of crystal growth of gibbsite.

Table 1. Cu(II) sorbed on 0.01 g hydroxy-Al-montmorillonite suspended in 30 ml of 0.01 M NaClO_4 .

Initial Cu concentration (mM)	Final Cu concentration ¹ (mM)	Final pH ²	Quantity Cu sorbed (mole Cu(II)/kg clay)
0	0	5.54	0
0.25	0.16	5.12	0.08
1.25	200	5.12	0.33
4.0	2200	5.27	0.60

¹ Final concentration refers to that after five weeks of Cu sorption.

² Final pH was taken the same day the samples were prepared for X-ray powder diffraction.



The most likely mechanism of the observed inhibition is that Cu(II) occupied edge sites of the interlayer Al(OH)₃ clusters and inhibited agglomeration and crystal growth. Octahedral positions in an Al(OH)₃ precipitate apparently do not accommodate Cu ions as shown by electron spin resonance (ESR) experiments. ESR spectra of Cu(II) coprecipitated with Al³⁺ and OH⁻ have shown that Cu(II) occupied only surface sites (McBride, 1982). Complexation of Cu(II) at edge Al-OH groups was proposed on the basis of ESR spectra of Cu(II) on microcrystalline gibbsite (McBride *et al.*, 1984). Continued growth of a Cu-substituted gibbsite is, therefore, not energetically favorable, and much of the Al(OH)₃ precipitate was probably retained in the interlayer when Cu(II) was sorbed. An increase in surface positive charge on the Al(OH)₃ due to sorbed Cu(II) may also have led to relative stabilization of the hydroxy-Al-montmorillonite complex.

In nature, hydroxy-Al interlayered silicates commonly contain trace metal contaminants (Barnhisel, 1977). Thus, traces of some metals could conceivably have inhibited the formation of a separate Al(OH)₃ solid phase at the expense of the interlayer material. Two differences must be noted, however, between the experimental conditions of this study and the expected conditions in a natural system. First, solution Cu(II) levels would normally be much lower than 4×10^{-3} M where minimal inhibition of the formation of gibbsite was seen. Second, the pedogenic formation of hydroxy-Al interlayers takes place over much longer periods of time than were used in this laboratory preparation. It is possible that, coupled with the slow formation of the interlayer material, even trace levels of metals, continuously adsorbed at the Al(OH)₃ surface, could have influenced the rate of formation of more stable solid phases.

Department of Plant and
Soil Biology
University of California
Berkeley, California 94720

J. B. HARSH¹
H. E. DONER

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¹ Present address: Department of Agronomy and Soils, Washington State University, Pullman, Washington 99164.

Figure 1. X-ray diffractograms of untreated and Cu(II)-treated hydroxy-Al-montmorillonite. Scale values indicate extent of full scale.

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