

CATALYTIC ACTION OF COPPER ON THE OXIDATION OF STRUCTURAL IRON IN VERMICULITIZED BIOTITE

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Abstract—The ferrous iron content of two vermiculitized biotites decreased by treatment with 0.1 N salts of copper at 70°C from 9.1–14% to 1.8–2.6%. Presumably, interlayer copper ions acted as a catalyst (here, an electron carrier) for the oxidation of iron by dissolved oxygen. The oxidized iron was ejected from the structure and formed crystalline iron minerals, such as hematite and goethite. Weight loss determinations, chemical, and X-ray powder diffraction data suggest that Cu(II) ions were polymerized to hydroxy-hydrous compounds in the interlayer space. Poor exchangeability of the resultant complex is attributed to the formation of strong electrostatic attractions between OH groups of the interlayer complexes and silicate oxygens.

Key Words—Biotite, Catalyst, Copper, Iron, Oxidation, Vermiculite.

INTRODUCTION

In 1958 Bassett synthesized copper vermiculites from biotites and vermiculitized biotite and compared the reaction products with copper-bearing vermiculites from Rhodesia. He observed that after a 6-day treatment with 1 M CuCl₂, the natural samples changed from black to golden brown. He further found, by X-ray powder diffraction, that potassium from 1 M solutions could not replace the copper. Although he studied the samples by various physical means, he failed to realize that structural iron is strongly oxidized in copper solutions. The aim of the present study is to investigate the exchange properties and the nature of interlayer copper ions and to suggest a catalysis mechanism involving copper ions for the oxidation of structural iron in vermiculitized biotite.

EXPERIMENTAL

Clean flakes of biotite from Bamle, Norway, and East Africa (from F. Krantz Co., Bonn) were wet ground and separated into various particle-size fractions. Small portions (25 mg) of the 5–20 μm size fractions were vermiculitized by replacing interlayer potassium with hydrated barium ions three times with one liter of 0.1 N BaCl₂ solution. Refluxing the products three times with 0.1 N MgCl₂ replaced the interlayer barium with magnesium ions. Further exchange with Cu, Ni, and Zn was carried out by using one liter of 0.1 N salt solutions. For exchange of interlayer copper, the products were treated with one liter of 0.1 N chloride salts of K, Mg, Ca, and Ba. All exchanges were carried out for a period of 8 hr on a sand bath at 70°C.

Mg and Cu contents were determined by atomic absorption spectrophotometer after HF/HClO₄ treatment. Interlayer Mg was calculated by subtracting octahedral Mg (found in the Na-saturated form) from total

Mg. Dry samples were prepared by heating at 700°C for 6 hr. H₂O₂ consumptions were found by mixing 10–20-mg samples with 20 ml of 4.5 N H₂SO₄ and 1 ml of 0.05 N FeSO₄ using a Metrohm automatic titrimeter (Multi-Dosimat). Ferrous iron percentages were calculated from H₂O₂ consumptions. Ferrous iron was oxidized by treating 50–100-mg samples with 1 ml of 10% H₂O₂ in one liter of 0.1 N Mg(NO₃)₂ solution. This overnight treatment oxidized iron completely as shown by the analysis procedure described above.

X-ray powder diffraction (XRD) diagrams were obtained with a Seifert diffractometer using Ni-filtered CuKα radiation. Infrared (IR) spectra were recorded by the KBr disk technique on a Beckman IR-spectrophotometer (Model 4220). Weight-loss determinations on 30-mg samples were carried out in platinum crucibles, using a period of 8 hr for each consecutive heating.

RESULTS AND DISCUSSION

Iron oxidation in copper solutions

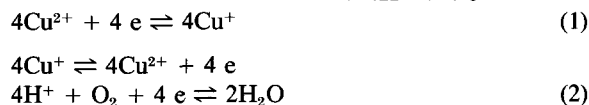
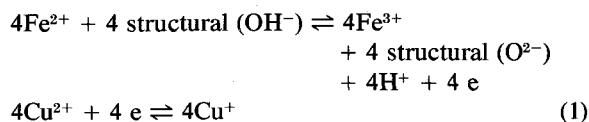
When Cu solutions came in contact with the vermiculitized biotites, a strong oxidation of iron occurred (Table 1). No oxidation took place in the Ni and Zn solutions. Although Cu²⁺ hydrolyzes more readily than either Ni²⁺ or Zn²⁺, and generates more interlayer acidity than the other two metal ions, such reactions do not explain the strong oxidation of iron. Unlike Ni and Zn, Cu has a relatively unstable valence state of +1, which is involved in a number of catalytic reactions (Chaltryan, 1966). Catalytic action of Cu²⁺ in the Wacker process, in which alkenes are converted to aldehyde, is well known (Cotton and Wilkinson, 1974, p. 977). Cu-treated kaolinite and montmorillonite strongly catalyze the oxidation of ethyl alcohol to aldehyde (Albareda *et al.*, 1954). Similarly, copper ions may take part in an

Table 1. H₂O₂ consumptions and Fe²⁺ contents of vermiculitized biotites (air-dry) saturated with various ions.

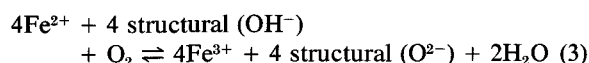
Exchange ion	Salt used	H ₂ O ₂ consumed (meq/100 g)	Fe ²⁺ (wt. %)
Bamle, Norway			
Mg ²⁺	MgCl ₂	162	9.05
Cu ²⁺	CuCl ₂	31.6	1.76
Cu ²⁺	CuSO ₄	46.4	2.59
Ni ²⁺	Ni(NO ₃) ₂	162	9.05
Zn ²⁺	ZnSO ₄	167	9.32
East Africa			
Mg ²⁺	MgCl ₂	234	13.5
Cu ²⁺	CuCl ₂	43.2	2.41

oxidation-reduction cycle and act as a catalyst in the oxidation of iron. Recently, Rozenson and Heller-Kallai (1978) observed by Mössbauer spectroscopy that copper treatment leads to the strong oxidation of iron in Wyoming montmorillonite. The oxidation of structural iron by Cu²⁺ is electrochemically possible as shown by standard reduction potentials (Cu²⁺ + e ⇌ Cu⁺, 0.158 V; Fe³⁺ + e ⇌ Fe²⁺, 0.770 V) (Hunsberger, 1977). However, monovalent Cu does not persist in vermiculite. First, cuprous chloro complexes are rapidly oxidized to cupric compounds by oxygen in air (Cotton and Wilkinson, 1974, p. 845). Second, low H₂O₂ consumptions (Table 1) indicate that, except for structural ferrous iron, there is no ion to be oxidized in the material. Hence, cuprous ions probably formed during the reaction as transitory electron carriers, electron acceptors being the dissolved oxygen. As ferrous iron was oxidized, electroneutrality was maintained by deprotonation of octahedral OH groups (cf. Newman and Brown, 1966; Veith and Jackson, 1974) and by ejection of octahedral iron (Farmer *et al.*, 1971) and other ions (Veith and Jackson, 1974).

Based on these reactions, the following oxidation scheme is proposed:



The overall reaction is:



Copper ions do not appear in the overall reaction, thus acting as a catalyst in the oxidation of iron by oxygen.

Infrared spectroscopy

A strong IR absorption near 3550 cm⁻¹ after Cu treatment of the starting material indicates that octahedral

Table 2. Copper content (water-free basis) and basal spacing (air-dry) of Cu-vermiculite from Bamle, Norway, after treatment with various ions.

Exchange ion	Cu (%)	d(001) (Å)
Without ascorbic acid		
Cu ²⁺	12.1	14.4
K ⁺	11.2	14.4
Mg ²⁺	11.2	14.4
Ca ²⁺	11.8	14.4
Ba ²⁺	9.5	14.3
With ascorbic acid		
K ⁺	5.5	12.3
Ba ²⁺	4.0	13.0

iron was ejected from the structure (Farmer *et al.*, 1971; Sayin *et al.*, 1979). This band is ascribed to hydroxyl groups associated with Fe³⁺-Fe³⁺ pairs (Vedder, 1964). The ejected iron hydrolyzed and precipitated on the surfaces of the mineral as noncrystalline oxides (Farmer *et al.*, 1971), causing absorption in the 3400–3200 cm⁻¹ range without a definite peak, after elimination of adsorbed water. Microcrystalline hematite and goethite detected by Bassett (1958) as red and yellow inclusions in the Cu-containing micaceous vermiculites seem to be the crystallized successors of such noncrystalline iron.

Nature of interlayer copper

After treating a synthetic Cu-vermiculite (10% by weight) with 1 M KCl at 100°C, Bassett (1958) observed that potassium did not replace copper and no collapse of the structure took place. To study the same phenomenon, Cu-vermiculite was treated with 0.1 N chloride solutions of potassium, magnesium, calcium, and barium. Almost no change in the XRD basal spacing and little change in intensities were observed. However, chemical analysis revealed that some exchange did occur, the strongest being with barium (Table 2). These data are in accordance with the proposed deprotonation reaction by which copper ions are strongly held as a result of the elimination of the screening effect of structural hydrogens. The treatment in the presence of a reducing agent, ascorbic acid (0.5 g), resulted in a much stronger but still incomplete exchange. It seems that a limited reconversion of oxygens to hydroxyls occurred and that a more positive environment was created for interlayer copper. Increases in K re-absorption were also noted with completely oxidized vermiculites (unpublished data).

In addition, the prevention of "water" loss upon heating (Table 3) suggests the existence of strong bonds between oxygens of the silicate layers and water molecules surrounding the copper ions. Sorption of copper in excess of magnesium (Table 4) suggests that not all

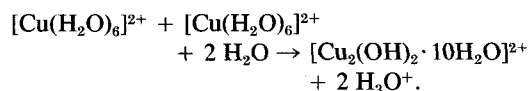
Table 3. Weight loss¹ of vermiculite from Bamle, Norway, saturated with Mg and Cu.

Temperature (°C)	Weight loss (%)	
	With Mg ²⁺	With Cu ²⁺
110	5.8	0.0
220	9.1	0.0
300	12.8	3.5
400	14.6	2.5
500	14.6	12.0
600	17.8	12.0
700	14.6	10.0

¹ Preheated to 50°C.

of the copper was present as the simple hexa-aquo ion. In contrast to the Mg-saturated sample, 002, 003, and 004 reflections of the Cu-saturated sample intensified at the expense of 001 and 005 reflections. Bassett (1958) interpreted similar changes as due to increased electron density in the interlayer space. The increase of the 002/001 ratio indicates that the vermiculite became similar to chlorite ($I_{002}/I_{001} = 1.3-3.3$) with respect to the amount of cations per unit cell. High "saturation" of the East African vermiculite with copper ions is reflected by a relatively high 002/001 ratio (Table 4). These data suggest the formation of hydroxy-aquo complexes of copper.

Because almost no reduction of layer charge occurred during the H₂O₂ oxidation of iron in vermiculite (Veith and Jackson, 1974; unpublished data by the author), no change of interlayer charge was expected when the amount of interlayer copper increased, probably because of hydrolysis and polymerization of hexa-aquo copper, with first step being:



Water hydrogens have associated with the negatively charged oxygen ions of silicate layers, and OH ions may have been electrostatically attracted to the tetrahedral silicate layers; consequently, the interlayer complex was stabilized. A similar reaction occurs with aluminum (Rich, 1960) and is expected to occur with the ions of transition elements which form coordinate bonds in aqueous solutions. The high charge of vermiculite is probably a great advantage over the low charge of smectites in stabilizing the interlayer complex. Complete polymerization with elimination of water eventually leads to chloritized vermiculite.

The interlayer spacing of Cu-treated vermiculite is 14.4 Å, hence, the interlayer space is equivalent to two layers of water molecules. Heating a Cu-treated sample to 220°C caused a collapse to 11.3 Å. On further heating to 700°C, the layers contracted to 9.5 Å, showing com-

Table 4. Intensity ratios of basal reflections (air-dry) of vermiculites as related to Mg and Cu content (water and cation-free basis) in the interlayer space.

Treatment	Structural Fe ²⁺ (%)	Interlayer ions		I_{002}/I_{001}
		Mg ²⁺ (meq/100 g)	Cu ²⁺ (meq/100 g)	
Bamle, Norway				
Untreated	18.8	214	nd	0.105
Cu	1.85	15.6	291	0.425
H ₂ O ₂ , Cu	0	21.4	245	0.300
H ₂ O ₂ , Cu (20-50 μm)	0	65.8	247	0.258
East Africa				
Untreated	19.9	221	nd	0.135
H ₂ O ₂ , Cu	0	0	563	1.264

nd = not detected.

plete dehydration of copper ions. The similar amounts of copper in the 5-20-μm and the 20-50-μm fractions indicates that the formation of interlayer complexes was the only important sorption reaction in silt-size vermiculites (Table 4).

Retention of Cu²⁺ ions in excess of the cation exchange capacity in H-montmorillonite can be explained by the precipitation of Cu(OH)₂ on the surface of the mineral (see, Bingham *et al.*, 1964). An equivalent exchange of copper with ammonium was found when the solubility product of Cu(OH)₂ was not exceeded. In the present study the pH of the 0.1 N CuCl₂ solution is ~4—too low to precipitate copper from the solution.

CONCLUSIONS

Cu²⁺ catalyzes the oxidation of structural iron by dissolved oxygen in vermiculitized biotite. Cu²⁺ polymerizes in the interlayer space, creating strong electrostatic attractions between the interlayer complex and the silicate sheets forming a chlorite-like material. Chloritization of vermiculite, with hydroxy aluminum as the interlayer material, is also expected to take place in nature in a similar manner. Percolating copper solutions in contact with Fe²⁺-rich minerals should oxidize the iron and lead to the accumulation of iron minerals, such as hematite and goethite. Copper is a hazardous pollutant in many natural waters, but it is strongly held by vermiculitic minerals and "deactivated" in soils unless reducing conditions are encountered. These same reducing conditions are employed in the commercial recovery of copper from the sheet silicates in copper deposits.

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REFERENCES

- Albareda, J. M., Alexandre, V., and Fernandez, T. (1954) Influence of the mineralogical composition of clays and of exchange cations on the catalytic oxidation of ethyl alcohol in the vapour phase: *Clay Miner. Bull.* **2**, 107–110.
- Bassett, W. A. (1958) Copper vermiculites from northern Rhodesia: *Amer. Mineral.* **43**, 1112–1133.
- Bingham, F. T., Page, A. L., and Sims, J. R. (1964) Retention of Cu and Zn by H-montmorillonite: *Soil Sci. Soc. Amer. Proc.* **28**, 351–354.
- Chaltykyan, O. A. (1966) *Copper Catalytic Reactions*: (trans. from Russian by A. E. Stubbs), Consultants Bureau, New York, 68 pp.
- Cotton, F. A. and Wilkinson, G. (1974) *Anorganische Chemie*: (trans. from English by H. P. Fritz), Verlag Chemie, Weinheim, 1235 pp.
- Farmer, V. C., Russell, J. D., McHardy, W. J., Newman, A. C. D., Ahlrichs, J. L., and Rimsaite, J. Y. H. (1971) Evidence for loss of protons and octahedral iron from oxidized biotites and vermiculites: *Mineral. Mag.* **38**, 121–137.
- Hunsberger, J. F. (1977) Electrochemical series: in *CRC Handbook of Chemistry and Physics*, 58th ed., R. C. Weast, ed., CRC Press Inc., Cleveland, Ohio, D-141–D-146.
- Newman, A. C. D. and Brown, G. (1966) Chemical changes during the alteration of micas: *Clay Miner.* **6**, 297–309.
- Rich, C. I. (1960) Aluminum in interlayers of vermiculite: *Soil Sci. Soc. Amer. Proc.* **24**, 26–32.
- Rozenson, I. and Heller-Kallai, L. (1978) Reduction and oxidation of Fe³⁺ in dioctahedral smectites—III. Oxidation of octahedral iron in montmorillonite: *Clays & Clay Minerals* **26**, 88–92.
- Sayin, M., Beyme, B., and Graf von Reichenbach, H. (1979) Formation of metallic silver as related to iron oxidation in K-depleted micas: *Proc. Int. Clay Conf., Oxford, 1978*, M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 177–186.
- Vedder, W. (1964) Correlations between infrared spectrum and chemical composition of mica: *Amer. Mineral.* **49**, 736–768.
- Veith, J. A. and Jackson, M. L. (1974) Iron oxidation and reduction effects on structural hydroxyl and layer charge in aqueous suspensions of micaceous vermiculites: *Clays & Clay Minerals* **22**, 345–353.

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Резюме—Содержание железистого железа двух вермикүлитуризованных биотитов уменьшалось после обработки 0,1 N медными солями при 70°C и концентрациях от 9,1–14% до 1,8–2,6%. Возможно, что межслойные ионы меди действовали как катализатор (в этом случае как носитель электронов) при окислении железа растворенным кислородом. Окисленное железо было выброшено из структуры и образовало кристаллические минералы, такие как гематит и гетит. По определению потери веса и данным химического анализа и порошковой рентгеновской дифракции можно предположить, что ион Cu²⁺ был полимеризован в гидрокси-водные соединения в межслойной области. Плохая обменная способность полученного комплекса приписывается образованию сильного электростатического притяжения между группами OH межслойных комплексов и атомами кислорода силиката, а также присутствию протоноотобранных групп OH. [E.C.]

Resümee—Der Fe²⁺-Gehalt von zwei vermiculitisierten Biotiten nahm nach der Behandlung mit 0,1 n Cu-Salzlösungen bei 70°C von 9,1–14% auf 1,8–2,6% ab. Es wird angenommen, daß die Kupferionen in den Zwischenschichten als ein Katalysator (in diesem Fall als Elektronenträger) für die Oxidation des Eisens durch gelösten Sauerstoff wirkten. Das oxidierte Eisen wurde freigesetzt und bildete Eisenminerale, wie z. B. Haematit und Goethit. Gewichtsverlustbestimmungen, chemische Untersuchungen, und Röntgenpulverdiffraktometeraufnahmen deuten darauf hin, daß das Cu²⁺ zu Hydroxy-Aqua-Verbindungen in der Zwischenschicht polymerisierte. Die geringe Austauschbarkeit des entstehenden Komplexes wird auf die Bildung einer starken elektrostatischen Wechselwirkung zwischen der OH-Gruppe der Zwischenschichtkomplexe und den Sauerstoffen des Silikates zurückgeführt und außerdem auf das Vorhandensein deprotonierter OH-Gruppen. [U.W.]

Résumé—Le contenu en fer de deux biotites vermiculitisées a diminué de 9,1–14% à 1,8–2,6% après traitement avec 0,1 N sels de cuivre à 70°C. On présume que les ions de cuivre intercouche se sont comportés comme un catalyste (ici un porteur d'électrons) pour l'oxidation du fer par oxygène dissolu. Le fer oxide était éjecté de la structure et a formé des minéraux ferreux cristallins tels l'hématite et la goethite. Des déterminations de perte de poids, et des données chimiques et de diffraction poudrée aux rayons-X suggèrent que Cu²⁺ a été polymérisé en composés hydroxy-aquo dans l'espace intercouche. La capacité d'échange du complexe résultant est attribué à la formation de fortes attractions électrostatiques entre les groupes OH des complexes intercouche et les oxygènes silicates, et à l'existence de groupes OH déprotonés. [D.J.]