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COPPER VERMICULITES FROM NORTHERN RHODESIA

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ABSTRACT

Vermiculite has been identified as the chief copper bearing mineral in samples of micaceous material from the copper belt of Northern Rhodesia. These samples range from 2% to 7% copper which is carried in the exchange position of the vermiculite. For comparison, copper vermiculite was synthesized from magnesium vermiculite and from biotite by simple base exchange procedures. The resultant materials give *x*-ray diffraction patterns with intensities for the 7 Å, 4.7 Å, and 3.5 Å reflections greater than those of a magnesium vermiculite, indicating that copper has entered the exchange position of the vermiculite lattice. The natural samples give *x*-ray diffraction patterns having a similar distribution of intensities. In some of the natural samples this intensity distribution must be attributed to the presence of chlorite but in others it is due to copper in the exchange position. Vermiculite has been distinguished from chlorite on the basis of differential thermal analysis, direct weight measurements of H_2O loss on heating, continuous *x*-ray diffraction during heating on the thermal increment diffractometer, and by exchanging large univalent ions for small bivalent ions in the exchange position. Copper appears to be firmly fixed in the vermiculite lattice and no simple base exchange procedure was found for its removal from either the natural or the synthetic material.

INTRODUCTION

Samples from the Roan Antelope mine of Northern Rhodesia were sent to the mineralogy laboratory at Columbia University for investigation. The samples consisted of micaceous material from the oxidation zone and had been found to contain up to 7% copper which was not recoverable by conventional methods of treatment. Later a bulk sample of similar material from the Banded Sandstone in the Nchanga mine of Northern Rhodesia was examined. The problem was similar to that encountered in the Roan Antelope samples.

The lack of ordinary copper minerals in an amount adequate to account for the copper content suggested the possibility that the copper might be carried in the micaceous material itself. The nature and extent of this association has formed the basis of a detailed mineralogical and *x*-ray study.

GENERAL DESCRIPTION OF THE ROAN ANTELOPE SAMPLES

Samples RA5, RA6, RA7, and G1 from the oxidation zone of the Roan Antelope deposit range from 2% to 7% copper (Table 1). Of these only one, RA5, has recognizable normal copper mineralization which is in the form of brochantite and constitutes about 1% of the sample. The chief constituents of all the samples examined are micaceous minerals. In RA5 the micaceous material is light green and represents about 90% of the sample. About 50% of RA6 is a light brown micaceous mineral. In RA7 light brown micaceous minerals constitute 65% of the sample, while G1 consists of nearly 95% colorless to light brown micaceous material. The optical properties of these micaceous minerals are variable even within the individual samples. The refractive indicies range from 1.575 to 1.605. All the flakes are biaxial negative but the axial angle ranges from 0° to 30° with a large majority of measurements in the range from 5° to 10°.

Quartz, tremolite, hematite, goethite, and limonite occur as secondary minerals in all the samples. The quartz appears as angular fragments ranging from less than 1% in G1 to nearly 20% in RA7. White tremolite needles range from less than 1% in RA5 to 40% in RA6. Hematite, goethite, and limonite are found both as discrete fragments and as inclusions in the micaceous minerals.

Table 1. Copper Content of the Samples Studied

Sample	%Cu (*X*-ray spectrometer)
Nchanga	1.5
RA5	7.2
RA6	2.6
RA7	2.4
G1	3.8
Synthetic Copper Vermiculite	10.0

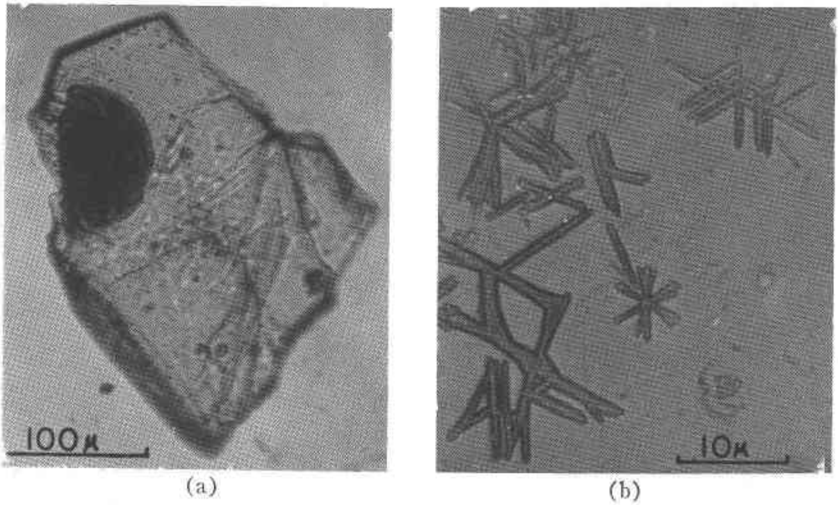
General Description of the Material from Nchanga

This material is granular with fragments that range from 28 mesh to fine dust. About 65% consists of micaceous minerals with optical properties similar to those of the Roan Antelope samples. Quartz, which is largely euhedral, constitutes about 25% of the sample. Recognizable copper mineralization consists of malachite, brochantite and chalcopyrite which together represent about 0.1% of the sample. A black iron-manganese wad-like material accounts for about 2% of the sample and carries a minor amount of copper. Accessory minerals are anthophyllite, apatite, and zircon.

When all the normal copper mineralization is considered, there is still far too little to account for the 1.5% copper content of the material. However, small red and yellow inclusions in the micaceous minerals offered a possible explanation for the copper content (Fig. 1). It had been suggested in an Anglo American Technical paper that the red inclusions might be cuprite. These inclusions are also present to a lesser extent in the other samples. Thus, a positive identification of the inclusions became desirable.

The red inclusions are round or irregularly shaped, range from 1 mm to submicroscopic, and are deep red. Under crossed nicols they show wavy extinction and sometimes yield false interference figures. This behavior under crossed nicols suggests that the inclusions are aggregates of elongate anisotropic crystals with a radial orientation. The individual crystals are not distinguishable under the highest power. The refractive index of the red inclusions is above that of the highest available refractive index media (sulfur and selenium; $n=2.7$).

The final identification of the red inclusions was accomplished by a recently developed x-ray technique for dealing with particularly small quantities of material. This technique is the micro x-ray camera. With this camera specimens 10–100 μ in diameter may be identified. The camera is mounted on a Norelco basic unit and is used with characteristic radiation.



(a) (b)

Fig. 1. (a) Photomicrograph of a vermiculite flake containing a semicircular inclusion of hematite; (b) Photomicrograph of yellow snowflake-like inclusions of goethite in a vermiculite flake.

The micro x-ray camera was well suited for the identification of the red inclusions since the inclusions consist of an aggregate of minute crystals with a large range of orientations resulting from the radial structure. With such a wide range of orientations, a single inclusion acts as if it were a powder having a random orientation. Three flakes containing red inclusions were hand picked under the polarizing microscope. These were first placed on a glass slide, then a drop of Duco cement was smeared over the fragments. When the Duco cement had dried it was easily floated off in water as a plastic sheet containing the fragments, which were then transferred to the camera.

The red inclusions in the flakes were exposed to characteristic copper radiation in the micro x-ray camera for six hours. The photographs show spots resulting from Laue type reflections produced by a single flake of micaceous material. Superimposed on the Laue pattern are rings characteristic of a powder type picture produced by the multi-oriented crystals of the red inclusions. The diameters of the rings were measured and the d(Å) values calculated by means of a nomogram provided with the microcamera. The values obtained are given in Table 2, where they are shown to compare favorably with the accepted values for hematite.

An exhaustive search was made in an effort to find red inclusions not showing birefringence which might be identified as cuprite. Only one such inclusion was found among the hundreds examined. It was too small to give a useful x-ray photograph and was probably a single crystal of hematite oriented in such a way as to show no birefringence.

Table 2. Micro X-ray Camera Data

Red Inclusions		Hematite		Yellow Inclusions		Goethite	
d(Å)	Int.	d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
3.7	2	3.68	2	2.70	2	2.70	4
2.7	10	2.69	10	2.60	1	2.58	2
2.52	9	2.51	8	2.45	10	2.45	8
2.22	1	2.20	2	2.25	1	2.25	1
1.85	1	1.84	6	1.80	1	1.80	1
1.72	1	1.69	6	1.74	1	1.72	4
				1.55	1	1.56	3

Yellow inclusions are a little more abundant than the red ones but are less noticeable due to their lighter color. They occur in three forms within the flakes of micaceous material.

1. As layers of fairly continuous yellow material sometimes showing needle-like crystals along the edges.
2. As snowflake-like aggregates (Fig. 1). Each "snowflake" is made up of six or more single crystals all of which have parallel extinction and are length slow. Occasionally red inclusions are found at the centers of these aggregates.
3. As rounded forms showing good false figures. None of the inclusions were observed to be more than 0.1 mm in diameter. These aggregates also are sometimes found intimately associated with the red material.

The index of refraction of the yellow inclusions was found to be above 2.00.

Micro x-ray photographs were taken of the yellow inclusions which seemed to show the largest number of crystals having different orientations. The resulting pictures yielded data comparing favorably with goethite (Table 2).

Thus scrutiny of the inclusions reveals iron minerals rather than copper. By a process of elimination, the existence of the copper in the micaceous material itself affords the most logical explanation. The diffraction and dehydration data which follow are offered as further proof.

DIFFRACTION DATA

The diffraction diagrams (Fig. 2) reveal the quartz and tremolite observed under the microscope. Nchanga, RA7, and G1 show the 10 Å reflections of biotite. All of the diagrams have 14 Å, 7 Å, 4.7 Å, and 2.8 Å reflections which may be attributed to either vermiculite or chlorite or both. Broad peaks at 12 Å, 8.5 Å, 4.85 Å, and 3.4 Å indicate interstratified biotite and 14 Å minerals. This corresponds to Gruner's hydrobiotite when the layers are biotite and vermiculite (Gruner, 1934).

Vermiculite may be distinguished from chlorite by the intensities of the x-ray reflections. Vermiculite has an intense 14 Å reflection and a weak 7 Å reflection, while chlorite has a 7 Å reflection which is about twice as intense as the 14 Å reflection (Fig. 3). RA5, RA6, and G1 give reflections with intensities intermediate between these two extremes (Nchanga and RA7 are complicated by mixed layer structure). The difference in structure between vermiculite and chlorite which is responsible for the distribution of intensities is to be found in the intersilicate magnesium. Because the intersilicate magnesium in chlorite (i.e. the brucite layer) is hydrated with OH^- ions, a high density of magnesium (approximately 3 ions per 10 oxygens) obtains, providing a high electron density at $z=0.5$ in the unit cell.

Vermiculite (Fig. 4), on the other hand, has an intersilicate layer (the exchange position) of magnesium hydrated with H_2O which permits only a relatively low density of magnesium (approximately 0.5 ion or less per 10 oxygen atoms) and hence a low electron density at $z=0.5$. The electron density of the intersilicate layer has a strong effect on the relative intensities of the 14 Å and the 7 Å reflections due to the fact that at $z=0.5$, $\cos 2\pi lz$ equals -1 for the 14 Å reflection and $+1$ for the 7 Å reflection.

When a material gives a diffraction pattern with intensities intermediate between those of vermiculite and chlorite, the material has an average electron density at $z=0.5$ intermediate between that found in vermiculite and that found in chlorite. This intermediate electron density in the intersilicate layer may result from four different circumstances:

1. A mechanical mixture of vermiculite and chlorite, (Weiss and Rowland, 1956).

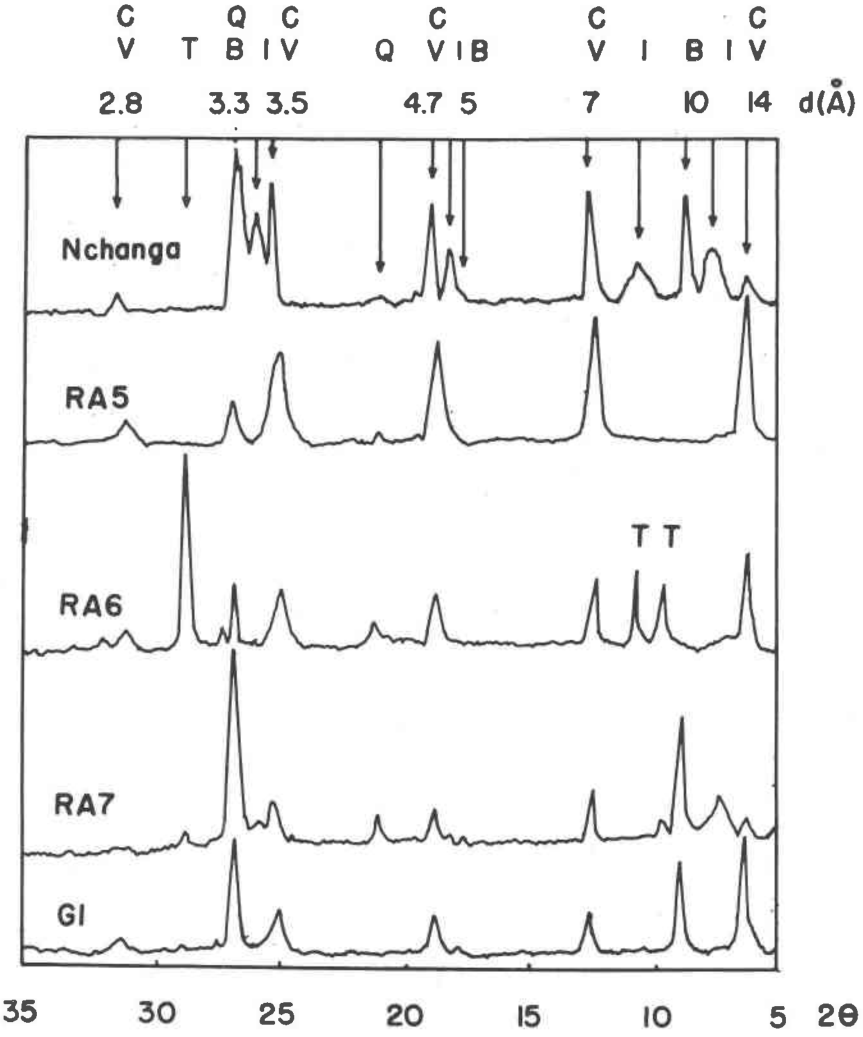


FIG. 2. *X*-ray diffraction diagrams of five copper-bearing micaceous samples from Northern Rhodesia. V = vermiculite, C = chlorite, B = biotite, I = interstratified 10 Å–14 Å material, Q = quartz, T = tremolite.

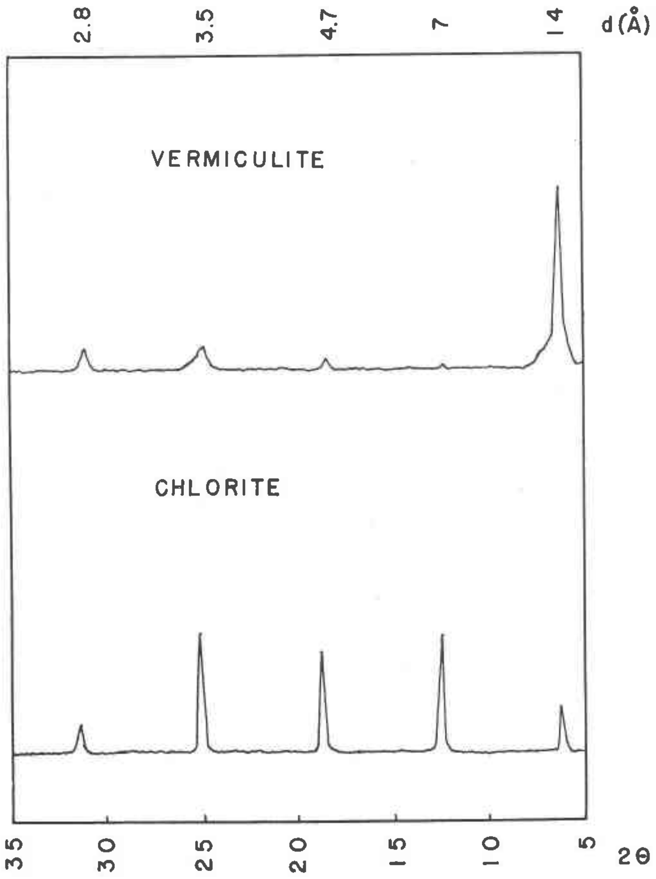


FIG. 3. *X*-ray diffraction diagrams of vermiculite and chlorite.

2. Mixed layer vermiculite-chlorite, (Weaver, 1956; Weiss and Rowland, 1956).
3. The presence of $Mg(OH)_2$ among $Mg \cdot H_2O$ in a chloritic vermiculite.
4. The presence of a high atomic number element (e.g., copper) in the intersilicate layer of a vermiculite.

Thus, the intermediate distribution of intensities observed in the diffraction patterns of the samples from Africa may result from either copper substitution in the exchange position of the vermiculite or the coexistence of chlorite and vermiculite. The problem of ascertaining the location of the copper in the samples becomes one of determining the rela-

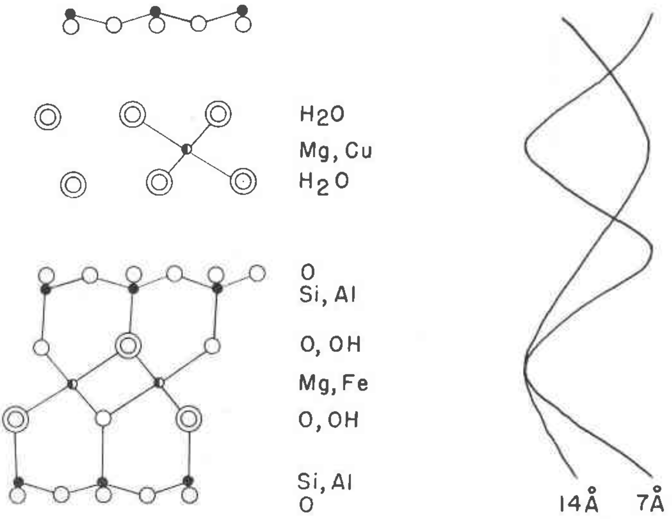


FIG. 4. Vermiculite structure and phase diagram.

tive amounts of chlorite and vermiculite, and of determining the effect on the diffraction pattern of copper substitution in the vermiculite exchange position. The former has been accomplished by various dehydration techniques; the latter, by the synthesis of copper vermiculite.

SYNTHESIS OF COPPER VERMICULITE

Copper vermiculite has been produced in the laboratory by two different procedures. First, by immersing a normal magnesium vermiculite from Corundum Hill, North Carolinia in a molar solution of ammonium acetate for 72 hours at 100° C., and then a molar cupric chloride for 120 hours at 100° C. The first stage reduced the lattice from 14 Å to 10 Å (Gruner, 1939). The second stage caused the lattice to expand to 14 Å again. The distribution of intensities in the *x*-ray pattern of the final product is quite different from the distribution observed in the *x*-ray pattern of the original material (Fig. 5). The intensities of the 7 Å, 4.7 Å, and 3.5 Å reflections have increased while those of the 14 Å and 2.8 Å reflections have decreased. Structure factor calculations show that this change represents an increased electron density in the exchange position which in this case can be attributed only to the substitution of copper for magnesium in the exchange position.

The second method for the preparation of copper vermiculite consisted of placing a normal biotite from Peekskill, New York in a molar solution of cupric chloride for 144 hours at 100° C. A hundredth of a gram of the

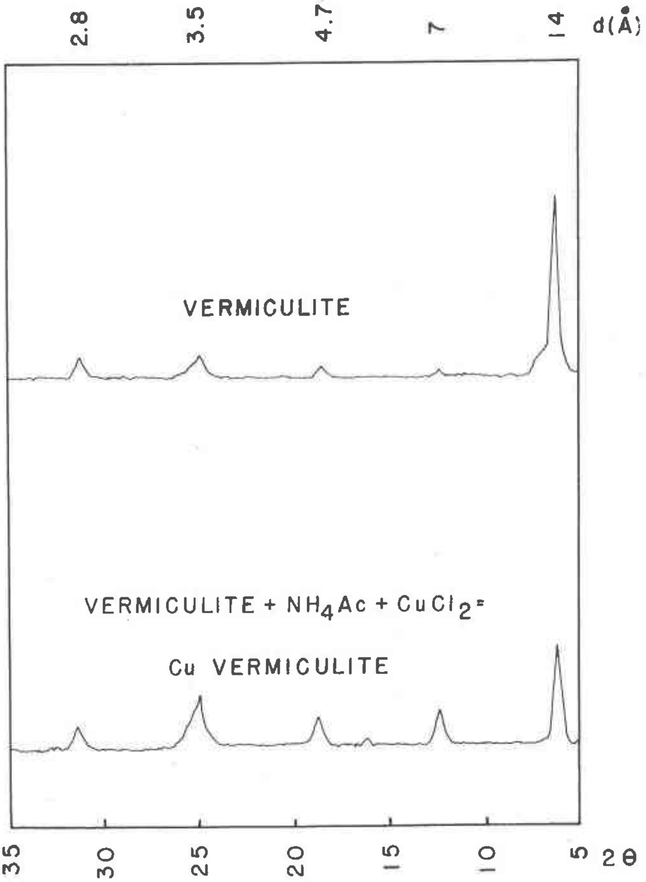


FIG. 5. *X*-ray diffraction diagrams of vermiculite and copper vermiculite synthesized from vermiculite.

biotite was used. At the end of the 144 hour period the biotite had turned from a vitreous black typical of biotite to a pearly, golden brown typical of vermiculite. It gave an *x*-ray pattern (Fig. 6) similar to that given by the material derived from the magnesium vermiculite by the method described above. Some residual biotite remained unaltered creating a pattern with striking similarity to G1 (Vermiculite and biotite from Roan Antelope).

When an attempt was made to repeat the synthesis of copper vermiculite from biotite using larger quantities of biotite, mixed layer biotite-vermiculite resulted giving an *x*-ray diffraction pattern (Fig. 6) with the broad hydrobiotite peaks mentioned earlier. When more biotite was used,

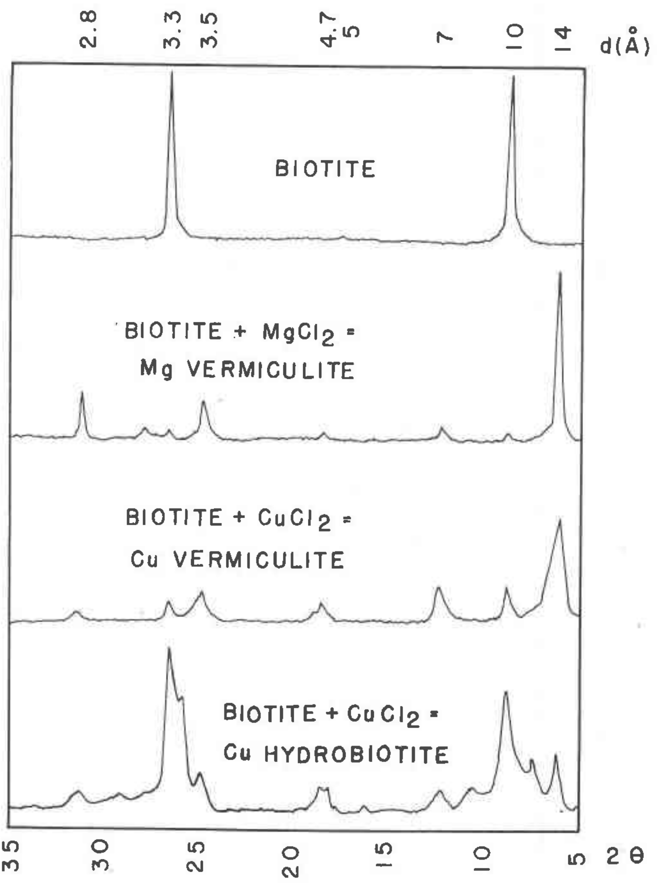


FIG. 6. *X*-ray diffraction diagrams of biotite and materials synthesized from biotite.

even more interstratified material formed at the expense of the discrete biotite and vermiculite. The formation of copper hydrobiotite, i.e., the interstratification of copper vermiculite with biotite seems to take place as readily as the formation of pure copper vermiculite from biotite. The resemblance between this mixed layer material and the natural mixed layer specimens, Nchanga and RA7, is also striking.

At the same time that the copper vermiculite was being prepared from the biotite, a magnesium vermiculite was synthesized from the same biotite for comparison with the copper vermiculite. The synthesized magnesium vermiculite gives a diffraction pattern (Fig. 6) with a 7 Å reflection only slightly more intense than the one observed in the natural magnesium vermiculite but a great deal less intense than the 7 Å reflections observed for copper vermiculites, either natural or synthesized.

Because the synthesized copper vermiculites were formed under closely controlled laboratory conditions from pure materials and give *x*-ray diffraction patterns completely reconcilable with the emplacement of the copper in the exchange position, they provide reference specimens against which the other materials may be compared.

DEHYDRATION STUDIES

As has been shown above, intensity distributions in *x*-ray diffraction patterns indicate merely the relative electron density of the intersilicate position $z=0.5$. It does not indicate whether the differences in electron density may be attributed to the presence of chloritic material, $Mg(OH)_2$, or to the presence of ions of high atomic number hydrated with H_2O. Because of the different bond strength with which the water is held in each case, one may distinguish the two types by studying dehydration characteristics. The following techniques were applied to the problem:

1. Exfoliation on rapid heating
2. Differential thermal analysis
3. Direct measurement of weight loss at 260° C.
4. *X*-ray diffraction during heating on the thermal increment diffractometer
5. Exchange of large univalent ions for small bivalent ions.

While this last method is carried out with the material entirely submerged in aqueous solution, it is considered a dehydration method here because the replaced small bivalent ions take with them the envelopes of H_2O molecules which accompany them in the vermiculite lattice.

Exfoliation

Perhaps the best known characteristic of vermiculite is its ability to exfoliate when rapidly heated to several hundred degrees. This exfoliation results from the puffing action of water vapor trapped between the layers. The water which is vaporized belongs to the H_2O hydration envelopes which surround the magnesium ions in the exchange position. The OH^- ions surrounding the magnesium in the brucite layer of the chlorite lattice are not driven off as readily and hence do not cause exfoliation. Thus, exfoliation may be used as an approximate indication of the amount of vermiculite and chlorite present in a sample.

A cubic centimeter of each sample from Africa was measured out and heated rapidly to red heat. The volumes of the samples were then remeasured. Table 3 gives the per cent increase in volume for each of the samples.

TABLE 3. VOLUME INCREASE ON HEATING

Nchanga	50%
RA5	70%
RA6	60%
RA7	100%
Gl	100%

It is not unusual for commercial vermiculites and hydrobiotites to expand to 20 times their volume or 1900%. When the heated samples were examined under the binocular microscope, long vermicules were observed indicating that the volume increase of some individual fragments had been far greater than the increase exhibited by the bulk samples.

Differential thermal analysis

Loss of either H_2O or OH^- is indicated on the differential thermal analysis apparatus as an endothermic reaction. Because the H_2O is held in the lattice by its polarity, while the OH^- is held by ionic bonding, there is a large difference in the temperature at which each is driven off. H_2O is lost from the vermiculite lattice in two stages at temperatures between 50° C. and 250° C. The first stage represents the removal of the hydration envelopes surrounding the magnesium ions in the exchange position and gives an endothermic peak between 150° C. and 200° C. The second stage represents the loss of a residual monomolecular layer of H_2O occupying space between the magnesium ions in the exchange position and gives an endothermic peak between 250° C. and 275° C. (Grim, 1953, p. 231). Removal of OH^- from the chlorite lattice requires a temperature of about 600° C. Both vermiculite and chlorite lose OH^- from the talc layer and decompose in the vicinity of 800° C. giving an endothermic reaction (Grim, 1953, pp. 231, 238).

The Roan Antelope specimens, G1, RA5, RA6, and RA7 give endothermic peaks at 150° C., 250° C., and 840° C. (Fig. 7) indicating vermiculite. RA5, RA6, and RA7 also show small peaks at 580° C. indicating the presence of some chlorite along with the vermiculite. G1, however, shows no peak at 580° C. and gives strong vermiculite reactions. The Nchanga specimen gives endothermic peaks at 300° C., 580° C., and 840° C. The endothermic peak at 300°–320° C. is pronounced in four of the samples but does not correspond with data that the author was able to find in the literature. Possibly this peak represents the loss of H_2O which is more tightly bound due to a high concentration of OH^- in the intersilicate layer. A high concentration of OH^- in this position would hold H_2O molecules entrapped making a higher temperature necessary for their removal.

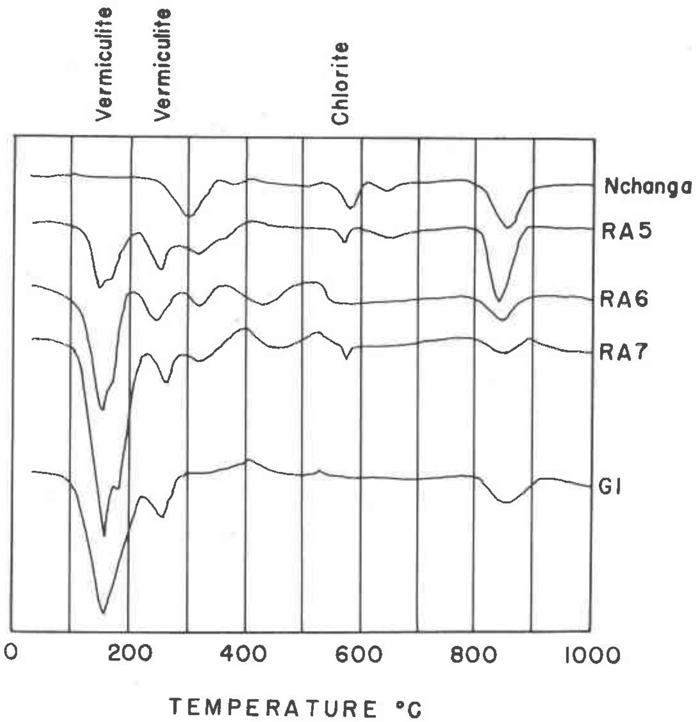


FIG. 7. Differential thermal analysis curves of five copper vermiculites from Northern Rhodesia.

Direct measurements of weight loss on drying

Table 4 shows the percentage weight loss of drying for each of the copper vermiculites and for a typical magnesium vermiculite from Corundum Hill, North Carolina. While the specimens from Roan Antelope lose from 3.85 to 5.90 per cent of their weight on drying at 260° C., the Nchanga specimen loses only 0.75 per cent. When the Nchanga specimen is heated just over 300° C. (exceeding the DTA peak at 300° C.), the

TABLE 4. WEIGHT LOSS ON DRYING

Sample	At 260° C.	At 300° C.
Nchanga	0.75%	1.2%
RA5	4.75%	
RA6	4.85%	
RA7	3.85%	
G1	5.90%	
Corundum Hill	13.5 %	

weight loss becomes 1.2 per cent which indicates that the material contains far less H_2O and more OH^- than the other samples and that the H_2O is lost at a higher temperature presumably because the greater OH^- content impedes the removal of the H_2O as suggested in the preceding section.

Thermal increment diffractometer

The thermal increment diffractometer (Bassett and Lapham, 1957) is designed to raise the temperature of a powdered sample while it is continuously subject to *x*-ray diffraction on a Norelco goniometer. The instrument makes it possible to chart the collapse of the vermiculite lattice as a function of temperature. A typical vermiculite from North Carolina shows two stages of dehydration, one just below 100° C and the other at about 200° C. (Fig. 8). Weiss and Rowland (1956) show a similar graph for jefferisite from West Chester, Pennsylvania. Walker recognizes six different stages of dehydration in vermiculite specimens from Kenya and from West Chester, Pennsylvania. They are 14.91 Å, 14.36 Å, 13.82 Å, 11.59 Å, 20.6 Å, and 9.02 Å. The shifts from 14.36 Å to 11.59 Å and from 11.59 Å to 9.02 Å are the most pronounced and unless the material is very pure and a great deal of care taken in its study, the other stages are difficult to observe. The two stages will suffice for the present purpose of distinguishing vermiculite from chlorite and recognizing mixed layer materials.

The Nchanga specimen shows no collapse during heating on the thermal increment diffractometer (Fig. 9). The 14 Å, 12 Å, and 10 Å reflections persist to nearly 500 ° C. with a gradual decline in intensity for the 14 Å and 12 Å peaks between 400° C. and 500° C. There is no change in either intensity or spacing at 300° C. to correspond with the DTA peak at that temperature. Apparently so much of the material is chlorite and mixed layer chlorite-biotite that no collapse is permitted.

The collapse in RA5 during heating from 25° C. to 200° C. is only from 14.48 Å to 14.13 Å. The intensity falls rapidly below 100° C., then gradually between 100° C. and 200° C. The fact that the 14 Å spacing does not collapse significantly but simply loses its intensity indicates the presence of a large amount of chlorite.

The 14 Å reflection of RA6 shows an immediate decrease in intensity and a rapid collapse of the 14 Å spacing indicating that the material is largely vermiculite. Unfortunately, the intensity decreases so fast that there is no opportunity to see if there is a second stage of dehydration.

RA7, also, has a 14 Å reflection which readily collapses and loses its intensity. The 12 Å reflection of the mixed layer material collapses also but its intensity increases and persists long enough to show a collapse be-

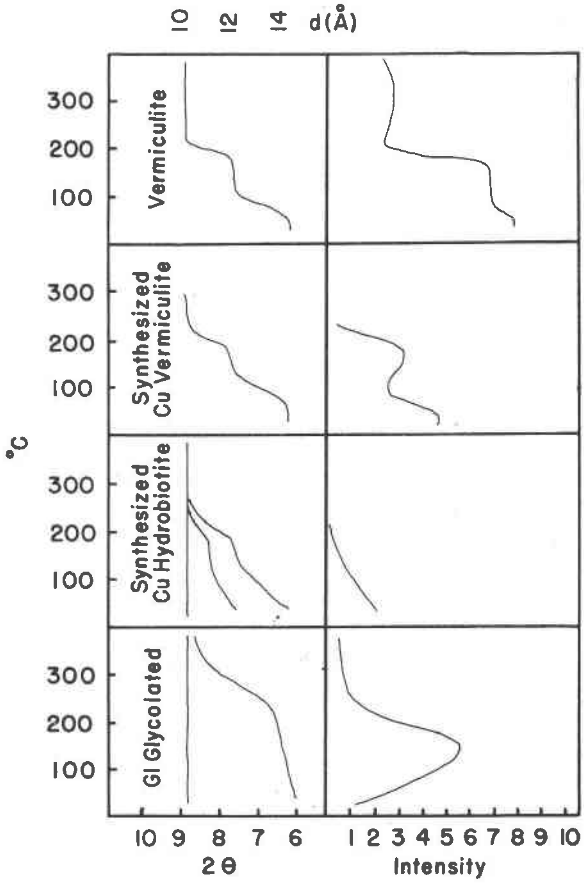


FIG. 8. Lattice collapse caused by dehydration on the thermal increment diffractometer.

low 100° C. and a leveling off at a constant spacing between 100° C. and 200° C. This is the behavior one should expect from vermiculite and hydrobiotite.

G1 gives the most satisfactory results on the thermal increment diffractometer. Its reflections persist to 200° C. and show the two stages of collapse found in the North Carolina specimen, the only difference being that the two stages of collapse seem to take place 20° C. or 30° C. lower in G1 than in the normal vermiculite. Also, the breaks are not as sharp as those in the normal vermiculite.

Because G1 gave reasonably good results, it was selected to be glycolated to determine if its behavior after glycolation would be similar to

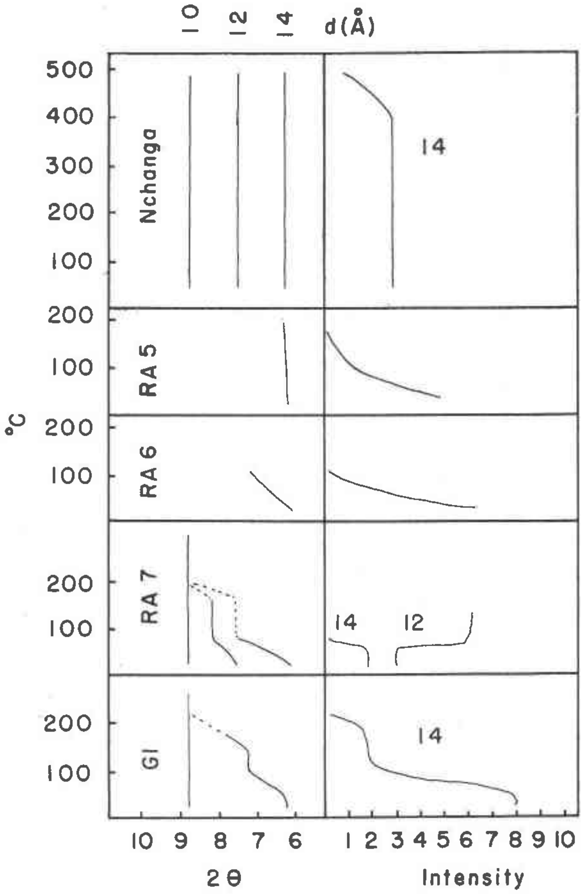


FIG. 9. Lattice collapse caused by dehydration on the thermal increment diffractometer.

that of abnormal vermiculite. According to Dr. Richards A. Rowland (personal communication), the glycolated material, if it is a true vermiculite, should have a more stable 14 Å spacing representing a single layer of glycol (in the place of two layers of H_2O) which should persist to a temperature well above 100° C. When G1 was glycolated and run on the thermal increment diffractometer, the 14 Å spacing shifted only slightly between room temperature and 230° C. (Fig. 8). Between these temperatures, the intensity rose and then fell. Between 230° C. and 400 °C., the 14 Å spacing collapsed to nearly 10 Å and the intensity fell to a low level.

Both copper vermiculite and copper hydrobiotite synthesized from biotite were run on the thermal increment diffractometer. The collapse exhibited in each case is very similar to the collapse observed in G1 and RA7 respectively (Fig. 8, 9).

Exchange of large univalent ions for small bivalent ions

When a pure vermiculite is placed in a potassium chloride or ammonium acetate solution and boiled for 80 hours, the potassium or ammonium enters the exchange position of the vermiculite and replaces the hydrated magnesium ions (Gruner, 1939). Since the hydrated magnesium ion is considerably larger than the unhydrated potassium or ammonium (they do not enter the exchange position in the hydrated form because they are too large to octahedrally coordinate six water molecules around them), the exchange causes a collapse of considerable proportions (14 Å to 10 Å). When potassium is used, the resultant material is a biotite.

When chlorite is submerged in potassium choride, there is no change in the spacing. The magnesium in the brucite layer is so tightly bound by the hydroxyl ions that no substitution can take place.

Mixed layer vermiculite-chlorite boiled in molar potassium chloride yields mixed layer biotite-chlorite which has a 12 Å spacing (Weaver, 1956). If a mechanical mixture of chlorite and vermiculite is boiled in molar potassium chloride, the vermiculite collapses leaving the chlorite pattern intact.

Each of the African specimens was boiled in molar potassium chloride for 80 hours. After this treatment they were run on the diffractometer (Fig. 10). Nchanga shows no sign of collapse indicating that the material is dominantly chlorite as was concluded from some of the other techniques. RA5, after treatment with potassium chloride shows a 14 Å reflection of diminished intensity but it shows no 10 Å reflection. Perhaps the 10 Å reflection is missing because the vermiculite does not collapse nicely to 10 Å, but instead collapses to a number of spacings in the vicinity of 10 Å. The pattern remaining after the potassium chloride treatment is that of chlorite.

After treatment with potassium chloride RA6 gives a far weaker chlorite pattern than the one encountered in RA5. A weak 10 Å peak appears indicating that at least some of the vermiculite was present as a mechanical mixture. The 14 Å and 12 Å reflections of RA7 both readily shift to 10 Å. Weak reflections at 7Å, 4.7 Å, and 3.5 Å indicate the presence of some chlorite in the original sample.

The potassium treatment causes the greatest change in G1. No 14 Å reflection remains and only weak ones persist at 7 Å, 4.7 Å, and 3.5 Å representing a minor amount of chlorite mechanically mixed with the vermiculite and biotite. The increased intensity of the 10 Å reflection results from nicely collapsed vermiculite indicating that there was no mixed layer structure in the original sample. The most interesting peak appearing in this run is at 17.52° 2θ (5.057 Å). Most normal biotites have a 5 Å reflection of zero or nearly zero intensity. In this run the intensity is 11 ($I_{10\text{Å}} = 100$). The author has attributed this to the presence of copper ions in the intersilicate position among the potassium ions. A 5 Å peak of 6 intensity appears in the diffraction pattern of RA7 after potassium chloride treatment suggesting a similar situation for that sample.

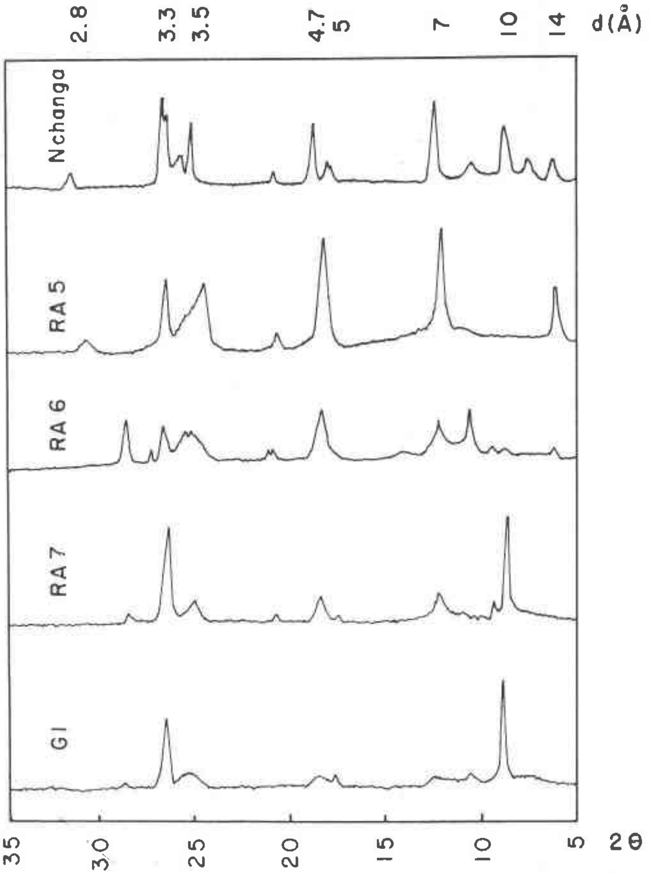


FIG. 10. X-ray diffraction diagrams of five copper vermiculites from Northern Rhodesia after treatment with potassium chloride.

When synthesized copper vermiculite was treated with molar potassium chloride at 100° C., the potassium did not replace the copper and no collapse took place. It is believed that some magnesium must be present along with the copper before potassium can enter the lattice and cause collapse. The synthesized copper vermiculite formed in a solution containing no cations but copper. Therefore, the material which resulted was a pure copper vermiculite with no magnesium. The natural copper vermiculites had access to magnesium and seem to have assimilated enough magnesium to permit collapse when subjected to the potassium chloride treatment.

COMPOSITION OF COPPER VERMICULITE

There are three specimens of copper vermiculite which are uncomplicated by chlorite or interstratification. They are the two synthesized copper vermiculites and G1. These three specimens have 7 Å reflections which are about one third the intensity of the 14 Å reflections (Table 5).

TABLE 5

Specimen	I_7/I_{14}
Mg Vermiculite	0.080
Vermiculite+Cu	0.346
G1	0.377
Biotite+Cu	0.380
RA6	0.625
RA5	0.877
Chlorite	2.500

According to structure factor calculations (Fig. 11), these three specimens have about 0.8 copper ions per ten oxygen atoms. This is corroborated by the 10% copper analysis for the synthesized copper vermiculites. G1 would probably have a comparable copper content were it not diluted by biotite.

Previous workers (Barshad, 1948; Walker, 1956) have found less than 0.5 magnesium ions per ten oxygen atoms in the vermiculite exchange position. One should expect 0.5 or less if magnesium or cupric copper is substituting stoichiometrically for potassium in biotite which has one potassium ion per ten oxygen atoms.

The high copper content of the specimens mentioned above is accounted for by the influx of hydroxyl ions with the cupric ions as they enter the exchange position. The hydroxyl ions attach themselves to the cupric ions leaving the solution acid. The molar cupric chloride used in the synthesis of copper vermiculite has a pH of 3.0 while the molar magnesium chloride has a pH of 6.1 (the pH of the distilled water used in the preparation of the solutions). The tenacity of the copper in the vermiculite lattice which makes the commercial recovery of the copper so dif-

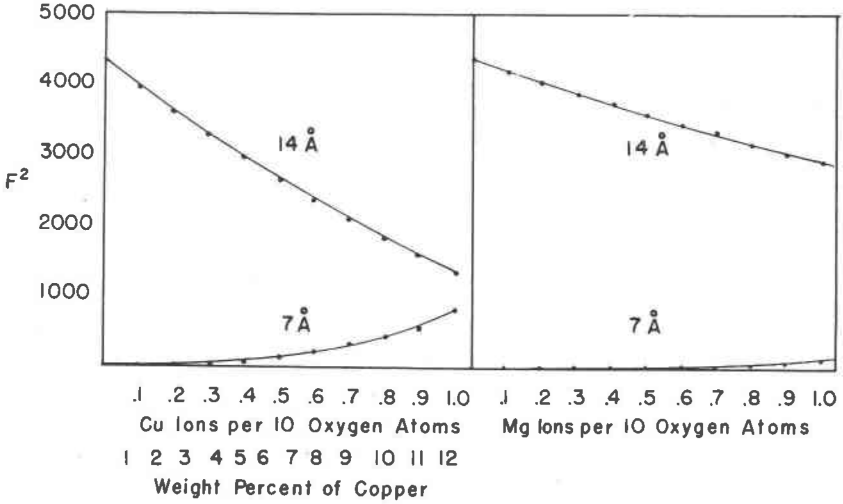


FIG. 11. F^2 (theoretical intensity) as a function of the copper and magnesium content of the exchange position of vermiculite.

ficult may be attributed to the presence of the hydroxyl ions.

The following general formula for simple copper vermiculite is suggested:

$$Cu_{0.8}(Mg, Fe)_3(Al, Si_3)O_{10}(OH)_2 \cdot xH_2O(OH)_{0.6}$$

It differs significantly from the general formula for magnesium vermiculite:

$$Mg_{0.5}(Mg, Fe)_3(Al, Si_3)O_{10}(OH)_2 \cdot xH_2O$$

Although it can be shown by differential thermal analysis, exfoliation, and direct weight measurements that both RA5 and Nchanga contain considerable amounts of H_2O, the other dehydration techniques indicate a large percentage of OH^- in the intersilicate position. In these samples the copper ions must be hydrated to a large degree by OH^- ions rather than H_2O, in which case they verge on being copper chlorites. Thus, there appears to exist a complete series from copper vermiculite which contains no more OH^- than is indicated by the formula given above to copper chlorite, in which the copper is hydrated by OH^- to the exclusion of H_2O. The samples dealt with have been termed copper vermiculites because they all contain significant quantities of loosely bound intersilicate water molecules.

CONCLUSIONS

X-ray diffraction studies and dehydration procedures have shown that the copper bearing micaceous materials from Africa contain vermiculite.

The flakes of vermiculite contain microscopic red and yellow inclusions which have been identified as hematite and goethite. The paucity of recognizable copper minerals even among the microscopic inclusions in the vermiculite flakes suggests that the copper is contained within the vermiculite lattice. Ion exchange experiments show that copper enters the exchange position of vermiculite. *X*-ray diffraction diagrams reveal certain similarities between synthesized copper vermiculite and the copper bearing micaceous materials from Africa which indicate that the samples from Africa contain copper within the exchange position of the vermiculite.

The ion exchange procedures used to synthesize copper vermiculite were carried out in molar solutions at 100° C. so that the reaction would take place in a reasonable length of time. These processes, however, would take place in more dilute solutions and at lower temperatures over longer periods of time. This and the fact that copper vermiculites are found in the oxidation zone suggest a low temperature supergene origin. Roy and Romo (1957) have indicated that vermiculite can form only under conditions of low temperature and pressure.

The samples of copper vermiculite from Northern Rhodesia are believed to have formed when copper solutions percolating through the oxidation zone encountered mixtures of biotite, chlorite, quartz, and tremolite reacting with the biotite to form copper vermiculite in varying mixtures with the other minerals.

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