A SWELLING CHLORITE MINERAL

by

H. H. Sutherland and D. M. C. MacEwan

Carnegie Laboratory of Physics, Queen's College, Dundee, Scotland

ABSTRACT

A green chloritelike material exfoliates on heating, and gives a series of complexes with amines. Its structure is explained in terms of a 1:1 interstratification of chlorite and swelling chlorite.

INTRODUCTION

Some time ago we got a sample of material from Messrs. Cape Building Products Ltd., London, which was known as "green vermiculite" and labeled "suspected Rhodesian origin." A few trials convinced us that the mineral was not vermiculite, although it exfoliated on heating. It proved in fact to be of considerable interest, and forms the subject of the present study.

The sample consisted of two types of material intimately intergrown, one being opaque, brittle and microcrystalline, and the other transparent and very soft. X-ray data on the microcrystalline material, before and after treatment with organic compounds, suggested that it contains vermiculite and a mineral of 7 Å basal spacing, presumably related to antigorite. This material did not exfoliate on heating, whereas the transparent material did.

This paper is concerned therefore with the second material.

EXPERIMENTAL RESULTS

This material before heating gave a regular series of basal $00l$ reflections, corresponding to $d_{001} = 14.46$ Å. The intensities were nearer to those of chlorite (penninite) than of vermiculite, although the 001 reflection was the strongest. The $0kl$ reflections with $k = 3n$ were diffuse. The $h0l$ series of reflections were nearly, but not quite, orthorhombic in character, and corresponded to a 001 spacing of 3×14.46 Å. This was true of $20l$ and $40l$, but $60l$ showed only the fundamental spacing of 14.46 Å. Higher-order row lines have not been observed so far.

451

The $h0l$ reflections can be regarded as due to the superposition of two sets of reflections, each due to a monoclinic lattice, with $a/3$ translations in opposite directions, and one set of reflections being slightly stronger than the other. This will give a doubling of the reflections along the $(20l)$ and $(40\ l)$ row lines, whereas for the $(60l)$ row line the two sets of reflections will superpose exactly. This process is illustrated for the $(20l)$ row line
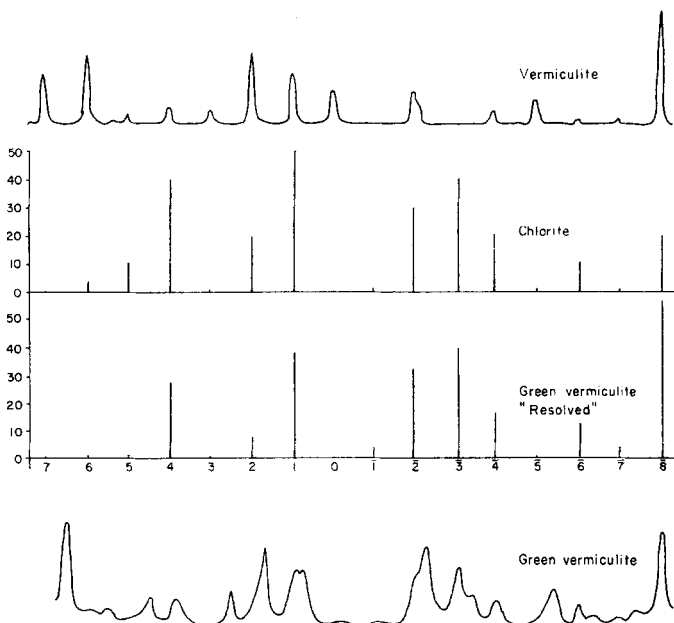

FIGURE 1.—Intensities of $(20\ l)$ row line for green vermiculite, compared with those for vermiculite and chlorite.

in Fig. 1, the experimental intensities being derived by photometering the row line on a Buerger-type precession photograph of the $(h0l)$ plane. Here once again the intensities follow in general the chlorite pattern.

Effect of Heat

The 14 Å series of reflections was very stable, remaining virtually unchanged up to 700 °C. They were still present after heating to 800 °C, although accompanied by diffuse scattering at low angles. The material had started to exfoliate at this temperature, taking on a golden color. A one-dimensional Fourier synthesis using the data from a specimen heated to 600 °C for 24 hr shows the same modification as Brindley and Ali (1950) found with penninite (Fig. 2).

Complex Formation

The complexes with neutral amines gave a regular series of basal $00l$ reflections, which were approximately 14 Å higher in spacing than those obtained with the Irish and West Chester vermiculities using the same amines (Fig. 3).

The intensities of the $00l$ reflections for vermiculite–amine complexes are similar to those predicted by the $|F|^2$ curve for vermiculite. There are some differences but the zeros and minima of the intensites for the com-
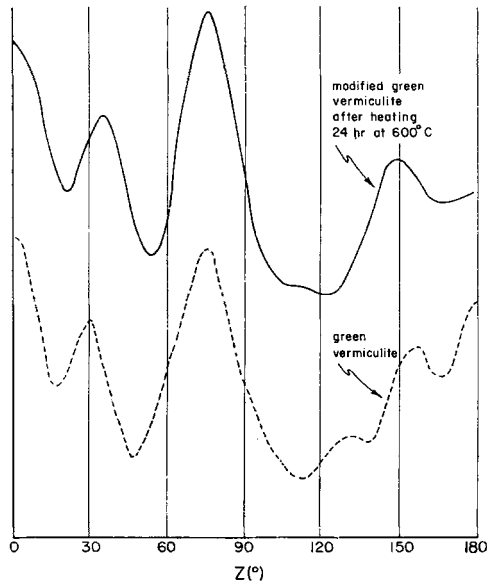
FIGURE 2.—One-dimensional Fourier syntheses of the green vermiculite, before and after heating to 600 °C for 24 hr.
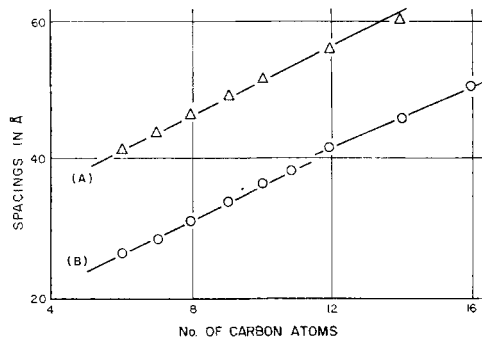
FIGURE 3.—d(001) values for complexes of straight chain amines with the green vermiculite (A), compared with those for complexes with West Chester vermiculite (B).

plexes occur in approximately the same position as the zeros and minima on the $|F_l|^2$ curve for vermiculite.

On comparison of the intensities of the complexes of green vermiculite with amines against the $|F_l|^2$ curves for vermiculite and penninite, there are several values of spacing where the intensities are markedly different. For example, at about $r = 0.3$ Å^{-1} both vermiculite and penninite curves have a maximum value. In the complexes the intensities around this point are zero or very very low. Reflections occurring at $r = 0.29$ Å^{-1} and $r = 0.35$ Å^{-1} are very intense.

The intensities of the orders 1–5 should decrease regularly if the structure were vermiculite or penninite, but this does not happen. The intensities
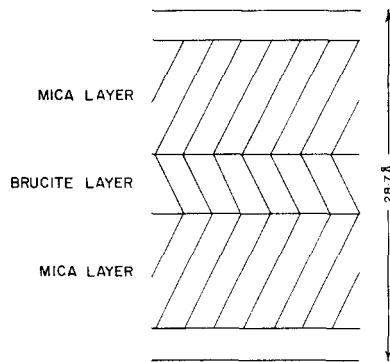

FIGURE 4.— One type of assumed structure.

reach a minimum value in the region $r = 0.035$ Å^{-1}, or $d = 28$ Å. This together with the fact that the 001 spacings for the complexes are about 14 Å higher than those of the corresponding vermiculite–amine complexes leads to the conclusion that there is an interstratification of swelling layers and nonswelling layers.

In this case, the fundamental unit of structure consists of two layers. The $|F|^2$ curve for the single layer will thus be modified by interference between the layers. Such a two-layer unit will behave like a minute crystallite and will show maxima and minima superposed on those due to the single layer.

Both the vermiculite and penninite curves of $|F|^2$ were modified to take account of a double layer. The intensities were then compared with the $|F|^2$ values. The modified penninite curve gave better agreement. A $|F|^2$ curve for a lattice consisting of a mica layer, brucite layer, and another mica layer was calculated (Fig. 4). This gave good qualitative agreement with the observed intensities of the 00l reflections for $l = 1$ to 5. A comparison of the $|F|^2$ values with intensities is given in Tables 1 and 2, and the $|F|^2$ curves in Fig. 5.

Optical Data

Optical determinations on this material were kindly performed for us
by Mr. A. R. Newton of the Geological Survey Department, Ridgewy,
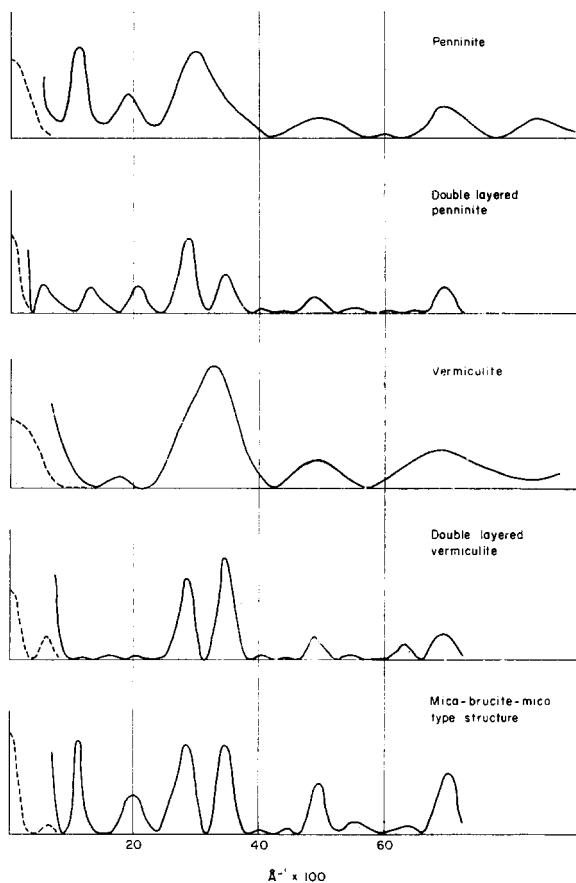
FIGURE 5.—Calculated structure factor curves F_l^2 for various types of structure.

Lusaka, Northern Rhodesia, and also by Mr. Hedley Wright of the Geology
Department, Queen's College, Dundee.

The material has $n = 1.5$ which is in the range for both vermiculite and
penninite. There are, however, no anomalous interference patterns which
are characteristic of penninite. Basal sections show a very small $2V$ ($< 10°$)
and negative sign.

TABLE 1.—VALUES OF $|F|^2$

n	$|F_0|^2_1$	$|F_0|^2_2$	Vermiculite (M)[1]	Vermiculite (−)[2]	Penninite (1)[3]	Penninite (2)[4]	M–B–M[5]
1	83	43	180	103	6	23	140
2	37	40	8	3	45	20	4
3	60	77	27	1	66	37	60
4	*100*	*100*	*100*	*100*	*100*	*100*	*100*
5	152	121	262	140	45	59	120
6	−	--	8		0	0	0
7	103	42	25	40	14	27	64
8	6	9	12	5	12	7	20
9	14	8	17	33	12	2	16

[1] Mathieson and Walker's values.
[2] Vermiculite less Mg ions + water molecules.
[3] Values obtained by Brindley and Ali (1950).
[4] Our values.
[5] Mica–brucite–mica type structure.

TABLE 2.—$|F|^2$ FOR AMINE COMPLEXES

n	$|F_0|^2$	Vermiculite	2-Layer Vermiculite	Penninite	2-Layer Penninite	M–B–M	Complex
1	179	258	62	220	50	220	$C_6H_{13}NH_2$
2	22	150	35	35	9	30	
3	59	30	30	5.5	5.5	65	
4	a	9.8	0	20	0	0	
5	33	2	0.5	24	10.5	20	
1	94	264	80	230	70	300	$C_8H_{17}NH_2$
2	10	190	5	75	4	25	
3	39	60	60	8	7	75	
4	6	16	4	7	2.1	2	
5	9	4	0.5	35	2.8	50	
1	400	268	140	250	100	420	$C_{10}H_{21}NH_2$
2	a	210	0	120	0	0	
3	110	93	93	13	9	80	
4	113	25	20	5.5	4.9	38	
5	40	10	1.5	20	1.4	2	
1	490	270	140	260	120	420	$C_{12}H_{25}NH_2$
2	30	220	20	150	0	30	
3	34	120	80	22	11	55	
4	77	40	40	6	6	70	
5	a	3	0.5	8	2	0	
1	vvs	270	148	263	140	450	$C_{14}H_{29}NH_2$
2	a	235	0	170	1	20	
3	a	140	50	30	10	40	
4	w	50	50	7.2	7	80	
5	a	20	9	5.7	3	18	

The values of $|F|^2$ are not absolute values.   All these values are based on our calculations.

TABLE 3.—CHEMICAL ANALYSIS
"GREEN VERMICULITE"
(Analysis by B. Mitchell, Macaulay
Institute for Soil Research,
Aberdeen)

	Percent
SiO_2	41.2
TiO_2	—
Al_2O_3	10.31
Fe_2O_3	3.10
FeO	3.66
MnO	—
CaO	1.83
MgO	20.09
Na_2O	0.03
K_2O	—
H_2O^-	5.78
H_2O^+	9.78
Total	101.78

C.E.C.: 36.6 meq/100 g (Ca saturated specimen).

TABLE 4.—ION CONTENTS OF "GREEN VERMICULITE,"
PER $\frac{1}{2}$ UNIT-CELL-LAYER, AS CALCULATED FROM
ANALYSIS, ON TWO SUPPOSITIONS

	No. of Atoms in Cell	
	(a)	(b)
Si	3.259	4.148
Al	0.961 $\begin{cases} 0.741 \\ 0.220 \end{cases}$	1.223
Fe^{3+}	0.184	0.235
Fe^{2+}	0.242	0.308
Ca	0.155	0.197
Mg	2.367	3.013
Na	0	
H_2O^-		
H_2O^+	(5.157)	(6.563)

(a) Assuming vermiculite-type structure—22 charges.
(b) Assuming chlorite-type structure—28 charges.

Formula

(a) $[Si_{3.259}Al_{0.741}]^{IV}[(Al_{0.220}Fe^{3+}_{0.184})(Fe^{2+}_{0.242}Mg_{2.367}Ca_{0.155})]^{IV}(OH)_2O_{10}$.
(b) More than four silicons.

CCM 30

Chemical Analysis

The result of a chemical analysis, kindly carried out by B. W. Mitchell, of the Macaulay Institute for Soil Research, Aberdeen, on selected material, is shown in Tables 3 and 4, together with an allocation of ions to layers, on the assumptions of (a) a vermiculite-type structure, and (b) a chloritelike structure. It will be seen that a satisfactory allocation on the latter basis cannot be made, the sum of ions on 4-coordination being greater than 4, but it would be possible to assume a structure of intermediate type.

CONCLUSIONS

There can be no reasonable doubt that this material consists essentially of double chlorite layers, each alternate one being capable of swelling. The exact nature of these layers, however, is still uncertain. The chemical analysis rules out the possibility that they could consist of normal chlorite; on the other hand the stability under heat treatment is incompatible with normal vermiculite or even with a 1:1 vermiculite–chlorite interstratification. On the whole therefore, this must be a 1:1 chlorite–swelling-chlorite interstratification.

The material is thus very close to corrensite. It is distinguished from corrensite by the absence of multiple spacings. As a matter of fact, a weak and diffuse 28 Å spacing has been observed with certain samples. It seems, however, to be much less marked than with the corrensite samples hitherto described. Also the heat stability of this material seems be, on the whole, rather greater than that of corrensite, being in fact quite comparable with that of penninite.

This material seems as if it might be similar to the chloritic mineral associated with vermiculite, which was described by Shimane and Sudo (1958).

REFERENCES

Brindley, G. W. and Ali, S. Z. (1950) X-ray study of thermal transformations in some magnesian chlorite minerals: *Acta Cryst.*, v. 3, pp. 25–30.
Shimane, Hidetoshi and Sudo, Toshio (1958) A chloritic mineral found associated with vermiculite: *Clay Min. Bull.*, v. 3, pp. 297–301.