

in air in an electric furnace for intervals of approximately 24 hours at temperatures varying from 460 to 985° C. After cooling, x-ray powder pictures were taken. It was found that the material inverted to a new form between 560 and 570°. At 925° the material seems to have melted and recrystallized; at least it is very strongly sintered. At 985° a light brown glass formed, but it recrystallized, giving a powder pattern not significantly different from those produced from any of the samples heated to 570°. Table 1 contains the powder data on this high-temperature form. The two forms of natrophilite yield powder data that appear to tie in with those for low ( $\beta$ ) and high ( $\alpha$ ) forms of Ca Na PO<sub>4</sub> which have a transition point of 680° as determined by Bredig (1942), who lists other materials that are isotypous with each of these.

Both lithiophilite and triphylite were heated in similar fashion to about 900°. At 885° the South Dakota (Custer Mt. Lode) lithiophilite became thoroughly sintered, but the resulting material yielded powder diffraction data not significantly different from the same unheated material. At 880° the Rochester, New Hampshire triphylite was slightly sintered; at 925° it appeared to have been completely melted, but had recrystallized. The films of the triphylite heated to 600° or above showed minor differences from the unheated material; these were chiefly the production of doublets for the 5.2, 3.95, and 2.79 lines.

## REFERENCES

- BREDIG, M. A. (1942) Isomorphism and allotropy in compounds of the type A<sub>2</sub>XO<sub>4</sub>. *Jour. Phys. Chem.* **46**, 747-764.
- BYSTRÖM, A. (1944) The structure of natrophilite, Na Mn PO<sub>4</sub>. *Ark. Kemi*, **17B** (4), 1-4.
- LINDBERG, M. L. (1950) Arrojadite, hühnerkobelite, and graftonite. *Am. Mineral.* **35**, 72.
- PALACHE, C., H. BERMAN AND C. FRONDEL (1951) *The System of Mineralogy of the Danas*, Vol. 2, 671, John Wiley & Son, N. Y.

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THE FORMATION OF VERMICULAR PELLETS IN NEW ZEALAND  
GLAUCONITES

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## INTRODUCTION

Since the paper by Galligher (1936) on the transformation of biotite to glauconite in Monterey Bay, California, this method of formation has been given credence, though seldom enthusiastically as a method of forming large greensand deposits.

In a recent investigation into the structural properties of some New Zealand glauconites, large numbers of vermicular pellets (Fig. 1) were found in the greensands of the South Canterbury-North Otago area in the South Island of New Zealand. Greensands are a prominent feature of the Tertiary deposits in this region which, during the Cretaceous, had been uplifted, folded and subsequently eroded to reveal extensive metamorphic rocks. Peneplanation continued until towards the end of the Cretaceous when the first marine transgressions took place. Shallow seas with periods of local emergence were to be common until the end of the Oligocene, and in most of the area sequences of marine beds can be traced.



FIG. 1. Vermicular pellet of glauconite, usual form.

Commonly these marine beds, many of which are glauconitic, lie above coal beds. This is also true of many other major greensand deposits in New Zealand, and it is probable that the gases evolved during the formation of coal may have contributed largely to the production of conditions suitable for glauconite formation.

Five greensands collected from the South Canterbury-North Otago region had a glauconitic component of from twenty per cent to sixty per cent, with fifty to ninety per cent of the glauconite present as vermicular pellets, other grains being of the more usual irregularly rounded morphology. A few vermicular pellets showed continuation of a whorl (Fig. 2), but these were extremely rare.

Chemical analyses were available for three of the samples, two of which, 6035 and 5392, had been fully analysed and reported on by Hutton and Seelye (1941). A third, RT, was analysed by Chemistry Division, N. Z. Department of Scientific and Industrial Research. The remaining

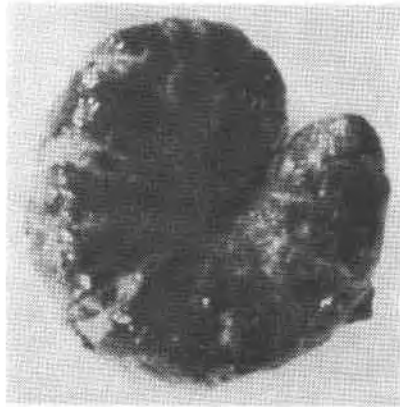


FIG. 2. Whorl shaped vermicular pellet of glauconite, an unusual occurrence in these sediments.

samples, RCW and FF, were analysed for iron, potassium and sodium by the author. Major constituents of analyses are given in Table 1.

All samples show iron, potassium and sodium contents consistent with those of a disordered glauconite and no similarity to a typical biotite

TABLE 1. CHEMICAL ANALYSES OF GLAUCONITES (PER CENT)

	5392	6035	RT	RCW	FF
SiO <sub>2</sub>	43.33	48.54	51.0		
Al <sub>2</sub> O <sub>3</sub>	7.27	7.82	6.1		
Fe <sub>2</sub> O <sub>3</sub>	24.87	17.50	21.5	23.5	20.0
FeO	2.90	3.07	0.9	3.3	
MgO	2.95	3.26	2.3		
CaO	0.10	0.68	<0.2		
Na <sub>2</sub> O	0.02	0.22	0.15	0.1	0.1
K <sub>2</sub> O	6.00	5.87	5.0	6.7	6.2
TiO <sub>2</sub>	0.20	0.10	0.04		
P <sub>2</sub> O <sub>5</sub>	0.15	0.14	0.19		
H <sub>2</sub> O <sup>+</sup>	6.22	6.00	5.65		
H <sub>2</sub> O <sup>-</sup>	5.94	6.71	6.02		

RCW Road cutting near Waihao Forks River Bridge, Waimate Survey District, Canterbury.

RT Disused railway cutting, Rakis Tunnel, Awamoko Survey District, Otago.

FF Five Forks, Kauroo Survey District, Otago.

5392 Abandoned railway cutting, Elephant Hill Survey District, Canterbury. (Hutton and Seelye, 1941)

6035 Kakaho Creek, Otepopo Survey District, Otago. (Hutton and Seelye, 1941)

analysis. Galligher found that firm vermicular pellets such as those shown in Fig. 1 were biotites, which after going through a spongy intermediate stage were moulded by passage through marine worms into coprolites thereafter having a glauconitic constitution and a shape which only barely suggested their vermicular origin. The glauconites considered in this paper have suffered no such intermediate stage and are glauconitic in the plain vermicular form. Nevertheless, it was at first considered that the vermicular pellets might be the result of the passage of clay sized glauconite or other clay material through the digestive tract of a marine mud eater, ciliations in the organs of the animal aligning the flaky material in the  $c$  direction, with subsequent hardening completing the process. Such a mechanism could be envisaged where many polychaetes flourished. Even if fecal pellets had not survived, material remaining in the animal after death would have a good chance of preservation and glauconitisation.

However, flakes of clay material formed in this way would certainly be randomly oriented in the  $a$  and  $b$  directions. If proven, the existence of alignment in these directions would eliminate this origin, and indicate that the glauconite was formed by the alteration of some other single micaceous crystal.

To check the existence of single crystals and simultaneously the order of these, a Buerger  $x$ -ray precession camera was used. Samples were flakes of about 0.05 mm in the  $c$  direction, from vermicular pellets of between 60 mesh and 35 mesh sieve size. Initially these flakes were mounted in the goniometer head of the camera on a glass fibre, with the  $x$ -ray beam perpendicular to the (001) plane. On alignment, zero level photographs of the reciprocal lattice plane containing the  $a$  and  $b$  axes were obtained. Figure 3a shows the reasonably clear lattice pattern of RCW which contains 6.7%  $K_2O$  and is relatively well ordered. In Fig. 3b is shown the pattern from 5392, to which those from RT, FF and 6035 are similar, where the smeared spots indicate some disorder and disalignment of the  $a$  and  $b$  axes. Comparison of this pattern with that of Fig. 3c obtained from a flake of glauconite formed by random sedimentation of a suspension of less than one micron material shows clearly the difference between random orientation and alignment in the  $a$  and  $b$  directions. All of these vermicular pellets can therefore be considered as having been formed by the alteration of some pre-existing crystal and not by the random accumulation of clay sized particles.

#### CRYSTAL DIMENSIONS

Precession photographs were also obtained for the plane containing the  $b$  and  $c$  axes, enabling measurements of the  $c$  dimensions to be made. Two types of photographs were obtained.

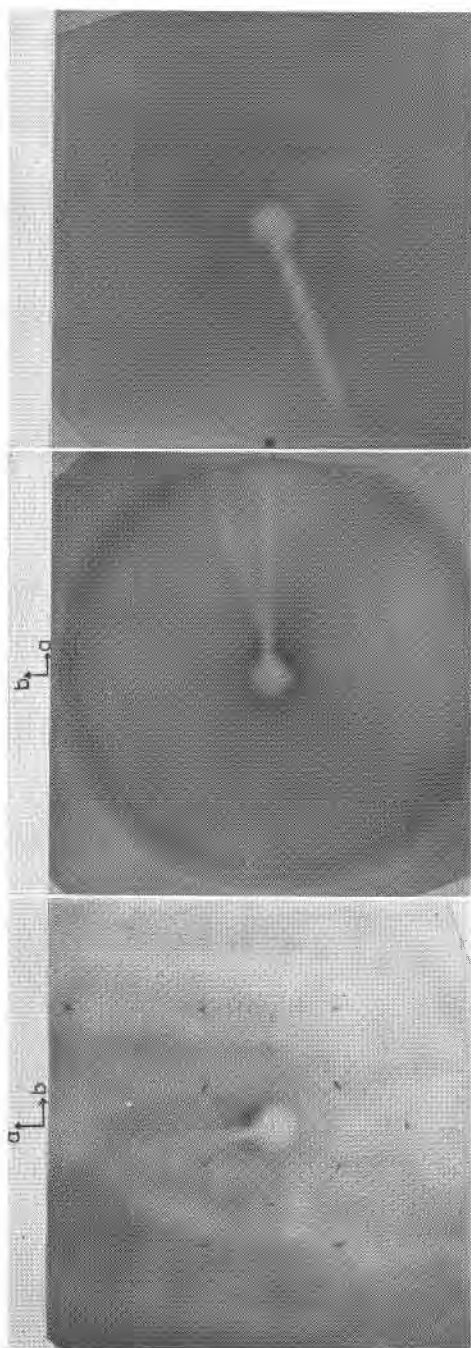


FIG. 3a. Zero level photograph of a glauconite flake with little disorder (*a* and *b* axial directions as marked).  
FIG. 3b. Zero level photograph of a glauconite flake with greater disorder indicated by smearing (*a* and *b* axial directions as marked).  
FIG. 3c. Zero level photograph of an artificial flake of glauconite formed by sedimentation from a suspension of less than one micron particles—random orientation.

- (i) Figure 4a shows the more common result. In the  $c$  direction 10 Å reflections with strong (001) and (003) and weaker (005) are present; and weak 14 Å reflections, (002) and (004), appear when the 10 Å reflections are overexposed (18 hours with Cu radiation). The  $b$  dimensions measured from these photographs were from 9.07 to 9.11 Å, which lie within the range for glauconites, 9.08 Å being usual for a well ordered glauconite.
- (ii) Figure 4b is characteristic of two thin flakes from RCW and 5392. The lines are sharper than those of Fig. 4a, though still elongated into an arc, and other reciprocal lattice points are present. In the  $c$  direction, as well as weak 10 Å reflections and a strong 14 Å (004) reflection, there is a regular spacing of 24.6 Å due to regular

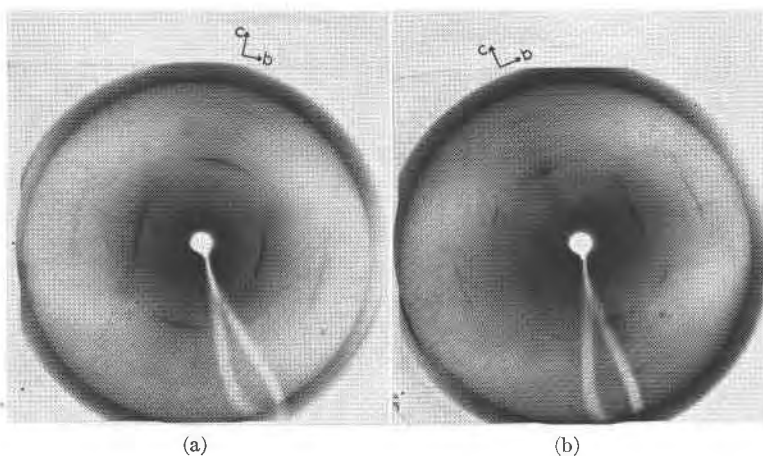


FIG. 4a. Most usual zero level photograph containing the  $b$  and  $c$  axes, in which 10 Å and 14 Å reflections occur independently (axial directions marked)

FIG. 4b. Zero level photograph containing the  $b$  and  $c$  axes of regularly interlayered 10 Å and 14 Å material; a much less common result than that shown in Fig. 4a.

interlayering of a 10 Å lattice-glauconite, and a 14.6 Å lattice-vermiculite or chlorite. Reflections are: (002) strong; (003) medium; (004) very very weak; (005) medium; (006) very weak; (007) weak (but this almost coincides with the strong (004) reflection for the 14 Å dimensions). The  $b$  unit direction for these two flakes were larger, between 9.18 and 9.21 Å and are typical of a vermiculite or chlorite. It was possible to measure the  $b$  dimension quite accurately from the clear sharp (060) reflection common to micas, but the  $a$  dimension which was not as clearly defined could only be measured as being between 5.21 and 5.30 Å.

In addition, x-ray diffractograms were obtained from oriented slides of magnesium saturated samples of RT and RCW ground to less than one micron in size. A broad 10 Å reflection was present on traces for both samples; in both cases these were sharpened with glycerol saturation and a small 18 Å peak typical of an expanding montmorillonitic lattice appeared. This expanding component accounts for the broadness of the 10 Å reflection on the precession photographs. Other reflections showed

on treatment with acid and by reaction to heat treatment that RCW contained a small amount of chlorite and kaolinite, whereas RT showed slight evidence of vermiculite only.

Diffractometer traces were also recorded from oriented slides of magnesium saturated samples of the less than one micron material in the sediments from which the glauconites RCW, RT and FF were separated. All showed a strong 7 Å reflection, a weak 10 Å reflection, and other low angle reflections which expanded to about 18 Å when treated with glycerol. These last indicate an expanding montmorillonite type lattice. From acid and heat treatment the 7 Å reflection in all cases was deduced to be mainly kaolinite with a little chlorite. No vermiculite was found.

#### ORIGIN OF VERMICULAR PELLETS

These glauconite samples from localities up to forty miles apart, in each case were found in the earliest glauconitic sediments deposited at these points after the marine transgression which began in the late Cretaceous, most of them being deposited in the Upper Eocene. Later glauconites in the same area contain few, if any, pellets of the vermicular type, but are of a microcrystalline nature, some obviously casts of foraminifera or echinoid spines, some tending to a framboidal morphology, but most being worn to a greater or lesser degree. Very smooth discs and pellets are not as common in the glauconites of the South Island of New Zealand as they appear to be in glauconites reported elsewhere, and many of the glauconites can be considered to be authigenic.

If the vermicular glauconites are considered as altered micas it is necessary to look to the metamorphic rocks below them for source material. Petrographic study of these rocks by Amies (1952) showed that sericite, muscovite and chlorite are ubiquitous, but that biotite is rare.

It is known that many 10 Å micas can be converted to a 14 Å lattice and biotite-vermiculite and biotite-montmorillonite clays (Walker, 1949, 1950), and dioctahedral vermiculite-like clays apparently formed from muscovite (Rich and Obershain, 1955; Hathaway, 1954), have been reported. Weaver (1958) studying clays derived from micas found that vermiculites and montmorillonites derived from muscovite will contract to 10 Å when potassium-saturated at room temperature, and that heating for some time will produce the same effect for montmorillonites and vermiculites derived from biotites. Clays derived from non-micaceous minerals will not contract below 11 to 12.4 Å.

Muscovite is known to be a very stable lattice (Bassett, 1960). Bronson *et al.* (1960) state that leaching of potassium ions from muscovite with aqueous salt solutions or potassium complexing solutions has not

proved satisfactory, and that potassium ions have been removed from it in any quantity only by treatment with molten salts. In the area in which vermicular pellets of glauconite were found there is evidence of vulcanism at about the time when these glauconitic sediments were deposited, some of them being intruded by sills and dikes. Under these circumstances it could be postulated that the muscovite present might have been degraded into a form receptive to the entry of excess iron and subsequent recollapse to 10 Å.

A source of biotite, which is easily degraded (Barshad, 1948), can only be found many miles inland in the potassic green schists of the Wakatipu region. The biotites in these schists are rich in ferrous iron (Hutton, 1940), and introduces the doubt that a dioctahedral mica (glauconite) could be obtained from them. However, it was found that on attempting to strip the ions from a biotite by heating in hydrochloric acid, pH 3, at 80° C. for 240 hours to simulate accelerated weathering under acid conditions, that the biotite lost not only 58 per cent of its total potassium but also 46 per cent of its total iron content. X-ray diffractograms of this final substance showed a 10 Å peak of considerably less sharpness than that due to the original biotite and a peak at 14.6 Å of about one third the height of the 10 Å peak. The process of conversion was obviously not completed but the octahedral layer was being drastically affected. Perhaps too much emphasis has been given in the past to changes in the interlayer cations and the effect of these, and not enough to the changes in the octahedral layer. It was noted by Ehlmann *et al.* (1963) that the pale immature forms of glauconite forming at present on the ocean bottom contain a substantial amount of iron. In the present survey this was found also to be true of glauconites which are now forming on the ocean floor off the East Coast of the North Island of New Zealand, where whitish grains forming inside foraminifera already contained 16.5 per cent total iron oxides. This leads to the conclusion that the original material from which these glauconites were formed had either (1) a large trivalent iron content or (2) an octahedral layer highly degraded by weathering, that is a very high initial charge deficiency which could have been brought into greater equilibrium by absorption of, say, colloidal ferric hydroxide. Ferrous iron content of these recent glauconites is consistently low, less than two per cent FeO, and does not favour a mechanism which initially introduces the iron into the lattice in ferrous form. Introduction of the iron in ferric form as a colloidal hydroxide also obviates the necessity for highly reducing conditions for formation, the necessity for which has proved embarrassing when so many recent glauconites have been found in obviously oxygenated environments.



## SUMMARY

It has been found that vermicular pellets of glauconite from the South Canterbury-North Otago region of New Zealand can be considered to be single crystals, disorder being due to interlayering of other clay minerals both of an expanding montmorillonite type and a 14 Å chlorite or vermiculite type. These glauconites are components of the earliest greensands formed after marine transgression over a peneplain formed of metamorphic rocks and it is thought that they are the result of alteration of muscovite or chlorite, perhaps degraded by vulcanism, or of biotite from a source much further to the west, inland. The mechanism of alteration proposed here involves the creation of a high charge deficiency in the octahedral layer to which large numbers of ferric ions are then attracted, probably in the form of colloidal ferric hydroxide. It is not suggested that the alteration of micas of the size suggested in this paper has been responsible for the bulk of glauconitic deposits, as the vermicular pellets are considered to be a special case.

It is suggested, however, that a similar mechanism requiring high charge deficiency could have been responsible for most glauconitic deposits. In this case the parent material must be considered to be highly degraded clay sized material or even unstable silicates precipitated from solution.

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## REFERENCES

- AMIES, A. C. (1952) Petrological features of the rocks of the Marewenua district, North Otago. *Trans. Roy. Soc. N.Z.* **79**, 376-85.
- BARSHAD, ISAAC (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions,  $x$ -ray analyses, differential thermal curves, and water content. *Am. Mineral.* **33**, 655-78.
- BASSETT, W. A. (1960) Role of hydroxyl orientation in mica alteration. *Bull. Geol. Soc. Am.* **71**, 449-56.
- BRONSON, R. D., J. M. SPAIN AND J. L. WHITE (1960) Potassium depleted muscovite. Part I. Preparation using filtration process for treatment with molten lithium nitrate. *Proc. 8th. Natl. Conf. Clays Clay Minerals*, 39.
- EHLMANN, A. J., N. C. HULINGS AND E. D. GLOVER (1963) Stages of glauconite formation in modern foraminiferal sediments. *Jour. Sed. Pet.* **33**, (1), 87-96.
- GALLIGHER, G. W. (1936) Glauconite genesis. *Bull. Geol. Soc. Am.* **46**, 1351-66.

- HATHAWAY, J. C. (1954) Studies of some vermiculite-type clay minerals. *Proc. 3rd Natl. Conf. Clays Clay Minerals*, 74-86.
- HUTTON, C. O. (1940) Metamorphism in the Lake Wakatipu region, Western Otago, New Zealand. *N.Z. D.S.I.R. Geol. Mem.* 5.
- AND F. T. SEELYE (1941) Composition and properties of some New Zealand glauconites. *Am. Mineral.* 26, 595-604.
- RICH, C. I. AND S. S. OBERSHAIN (1955) Chemical and clay mineral properties of a red-yellow podzolic soil derived from muscovite schist. *Proc. Soil Sci. Soc. Am.* 19, 334-9.
- WALKER, G. F. (1949) The decomposition of biotite in the soil. *Mineral. Mag.* 28, 693-703.
- (1950) Tetrahedral minerals in the soil-clays of northeast Scotland. *Mineral. Mag.* 29, 72-84.
- WEAVER, CHARLES E. (1958) The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material. *Am. Mineral.* 43, 839-61.

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THE EFFECT OF  $Mg^{2+}-Fe^{2+}$  SUBSTITUTION ON THE CELL DIMENSIONS OF CUMMINGTONITES

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INTRODUCTION

Recently Klein (1964) has determined optical properties, chemical compositions and cell dimensions of nine cummingtonites and suggested that a linear relationship exists among cell dimensions:  $a \sin \beta$  and  $b$  and the composition. He has shown that  $b$  varies considerably with composition, whereas  $a \sin \beta$  and  $c$  vary very little.

Previous to the publication of this paper, we started work on the cummingtonite-grunerite series, with a view to determine the influence of  $Mg^{2+}-Fe^{2+}$  substitution on the cell dimensions. Though our results are similar in nature to those of Klein, they show slight discrepancies. Klein's figures, expressing the variation in the cell dimensions, are based on the data of only 6 grunerites, whereas the figures presented in this paper depend upon the data of 21 specimens. Hence we decided to publish our results and offer a structural explanation for the anisotropic expansion of the cell dimensions due to  $Mg^{2+}-Fe^{2+}$  substitution.

EXPERIMENTAL

The cummingtonites studied came from the metamorphosed iron formation of east-central Quebec and were obtained through the courtesy of Dr. R. F. Mueller. The iron formation has been investigated by