Studies of the Solid State

THE MINERAOLOGY AND ENVIRONMENT

OF

SOME NEW ZEALAND GLAUCONITES

A Thesis presented for the
degree of Doctor of Philosophy.

University of Canterbury
1964

D. P. Seed.
That which is far off, and exceeding deep,
who can find it out?

Ecclesiastes. 7
I wish to thank . . .

Professor R. S. Allan and the staff of the Geology Department for accepting me as a Ph. D. student.
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and especially - my husband and family.
ABSTRACT

Glaucnite occurs as the major constituent of late Cretaceous and Tertiary greensand and deposits formed in New Zealand during periods of marine transgression. These glauconites are generally found to be high in potassium content, and X-ray studies show them to be well ordered, some of them falling into the highest classification group for this mineral (1M). These 1M glauconites are not restricted to any particular period, and are usually found associated with calcareous or quartzose sediments.

Recent glauconites, now forming off the East Coast of New Zealand, have not yet fully developed the glauconitic structure and are extensively interlayered with an expandable montmorillonitic clay. They form mainly as foraminiferal casts, in sediments which often contain very little clay sized material.

Glaucnites from different deposits are shown to react differently to both mechanical and chemical weathering, the effects being largely due to the manner of cementation of the glauconite crystallites. The change in glauconite structure on heating has been studied both by X-ray diffraction and infrared absorption methods. On heating to 1000°C a spinel is formed; the order of crystallisation of this spinel is found to depend on the Fe: Mg ratio in the glauconite.

The origin of glauconite is discussed. X-ray investigation of vermicular pellets, which occur in large quantities in South Canterbury and North Otago, upholds an existing theory of the change of biotite - or other mica - to glauconite. Many other deposits from these areas suggest foraminiferal casts, formed by either the alteration of existing degraded clay particles, or by a method of precipitation from solution. This latter method is found to be possible by synthesis on a laboratory scale, and is suggested as a highly probable method of formation for some greensand deposits.
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A1 Microwave Spectrum of Glauconite.
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1. INTRODUCTION

The study of glauconite is not new. Indeed, for almost a century investigators have tilted at the problems associated with these microscopic grains of quaint morphology and uncertain origin. A lively account of work undertaken prior to 1932 is given by Hadding, showing how interest has been stimulated by approaches from two schools; that studying recent sediments retrieved by oceanographic expeditions, and that studying fossil glauconites. No agreement as to origin has been found, then or now, although most workers now cautiously uphold a theory of multiple origin. More success has been achieved in the study of the grains themselves, making it currently possible to classify glauconites quite rigidly.

1.1 Structure of Glauconite

Glauconite, the mineral, belongs to the mica family, being a layered silicate of general formula

\[
R_y^M_x [(\text{OH})_2 Si_{4-x} Al_x O_{10}] \cdot nH_2O. \quad \text{Gruner, (1935)}
\]

where \( R \) is mainly potassium, sodium or calcium but many other monovalent or divalent ions are also found, 
\( M \) is usually \( Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+} \) with small amounts of other ions usually present.

The distinguishing features of glauconite are its green colour and its large proportion of \( K_2O \) (5–8%) and of \( Fe_2O_3 \) (15–25%), making it easily distinguishable in its normal forms from other green minerals such as chlorite.

Crystal sizes in glauconite are usually of the order of 1 \( \mu \) (\( \mu = \)micron) or less, so that it is most easily studied by methods of clay technology. Indeed, as clay minerals are usually found associated with, and often interlayered with, glauconite, any
investigator of this substance soon becomes very "clay minded".

The two basic structural units for layered silicates are ideally:

(1) a unit in which a silicon ion is tetrahedrally co-ordinated to four oxygen ions, and

(2) a unit in which an aluminium ion is octahedrally co-ordinated to six oxygen or hydroxyl ions.

From these basic units the micas and clays are formed, the individual features of each mineral being governed by:

(a) substitution of other ions for the aluminium and silicon in the ideal structure.

(b) stacking of units.

It is common in these substances for aluminium to substitute for silicon in the tetrahedral layer, leaving this layer negatively charged. In the octahedral layer many other ions, both trivalent and/or divalent, of similar radius may substitute for aluminium, the divalent ions furthering the charged state of the unit cell. To restore neutrality large positive ions are attracted between the layers - usually K⁺ or Na⁺, but also Ca²⁺, Sr⁺, Sr²⁺, Ba²⁺. These have hexagonal co-ordination with the outermost layer of oxygen atoms in the tetrahedral layer.

The phyllosilicates can, therefore, have a varied structure, ranging in micas from the relatively simple ideal structure of muscovite, K₂[Al₂[(OH)₂Si₃AlO₁₀]̅, through a complexity of ion combinations, to give many distinctive minerals, which in turn may have a variety of forms and composition. Initial points of distinction and classification are however, charge deficiency in both layers, and the valencies of octahedral cations; trivalent occupancy giving a dioctahedral mica and divalent occupancy a trioctahedral mica. Glauconite is classified as a dioctahedral mica, but it can be seen from the structural formula below, (Gruner, 1935), that there is considerable charge deficiency in the
Octahedrally coordinated cations; mainly MgAl or Fe  o Additional hydroxyl ions
O X ions below bottom layer (K, Na, Ca)  O X ions above upper layer (K, Na, Ca)
Thick lines: bottom Si₂O₅ layer  Thin lines: upper Si₂O₅ layer
octahedral layer, as well as a deficiency due to aluminium substitution in the tetrahedral layer. Gruner's formula is

\[(\text{OH})_6 \cdot 10^7 \cdot 2 \cdot 3(MgFe^{2+}Ca)_{1-3}(Fe^{3+},Al,\text{Si})_{3-6}(Si_{1-3}Al_{2-3})_0 3-4 \cdot \]

By studying the diagram in Fig. 1 of the tetrahedral-octahedral-tetrahedral stacking of the mica family, the repetition of a unit cell can be determined. The Si-O distance in silicates is about 1.62 Å, giving for a hexagonal array of regular tetrahedra based on this distance a calculation of \(D = 9.16 \) Å and \( \varphi \) being equal to \( \frac{\sqrt{3}}{2} \), then becomes 5.2 Å. The \( \varphi \) dimension being dependent on the interlayer cations is variable, but for micas is about 10 Å, or a multiple of this, depending on stacking. Owing to the hexagonal co-ordination of the interlayer cations the unit cell can be stacked basically on four different rotations about these cations. Smith and Yoder (1956) have determined and labelled the six different polymorphs of micas obtained for a constant stacking angle. These are:

- 1M, for which \( \varphi = 10 \) Å.
- 2M, 2M, 20, " " \( \varphi = 20 \) Å.
- 3M, " " \( \varphi = 30 \) Å.
- 6M, " " \( \varphi = 60 \) Å.

Ordered glauconite has the 1M structure. However, these basic polymorphs assume a constant stacking angle which is not always favoured in the growth of natural minerals. This results in a disordered crystal. Furthermore, micaceous minerals may form interlayered growth giving irregular \( \varphi \) spacings, or may form mixed minerals with other clays. There are then four possibilities in the growth of glauconites; these were defined by Darst (1958) and are accepted generally as a classification:

- Ordered, denoted by 1M.
- Disordered, " 1Md.
- Interlayered,
- Mixed mineral,

any of which should be possible, and all of which are found in
nature. Disorder is more common than order in glauconites, as they are formed at low temperatures from complexes approaching colloidal dimensions. Under these circumstances surfaces are large and ion attraction great, so that stoichiometric proportions are not maintained.

1.2 Nomenclature

The mineral classifications above have facilitated international comparisons of glauconite structure, especially, as is shown later, by the manner in which classifications are tied to the results of X-ray analysis, but the term glauconite still remains a maid of all work, often applied indiscriminately in the field to all green sedimentary grains. It could be suggested that the old terms "greensands" and "green clays" be retained for description of assemblages of green grains whose mineral content has not been ascertained, and that the "mixed mineral" classification of Burst be changed to "mixed clay mineral" without the implication of glauconite. It could then be used extensively as a general classification. There is definite lack of rigour in classifying a mixture whose composition is mainly of 14 Å clay minerals, as a glauconite, merely because it is green.
Outline of Research

It is proposed in this thesis to present the results of study of some of the glauconitic sediments of New Zealand, and to consider the origin of glauconite. Although on occasions it may be necessary to make cross reference between sections, to provide coherence to this narrative, it is desirable to itemise the work as follows:

Section 2 Sample collection and preparation - general.
Section 3 Morphology of grains.
Section 4 Detailed description of glauconites and accompanying sediments from each locality sampled.
Section 5 Chemical analyses and discussion of these.
Section 6 Structural analyses.
Section 7 Colour, refractive index, magnetic susceptibility, density.
Section 8 Effects of weathering.
Section 9 X-ray diffraction studies.
Section 10 Electron microphotographs.
Section 11 Absorption in the infrared.
Section 12 Changes in glauconites on heating.
Section 13 Recent glauconites.
Section 14 A discussion of the origin of glauconite.
Appendix Paramagnetic resonance.
Fig. 2 Middle and Upper Eocene Geography, showing main types of sediment of Bortonian Stage and transgression in Kaitan and Runangan times.

Fig. 2 Oligocene Paleogeography, based on the distribution of sediments of the Whaingaroan and Duntruoian stages. Oligocene penguins, though nominally in North Otage, are known as far north as Kowhai in the North Island. Corrigendum: The panel marked 'Limestones (shallow facies)' should show coarse dots in a brickwork pattern.
2. SAMPLE COLLECTION AND PREPARATION

2.1 Distribution of Glaucocnitc Sediments in New Zealand

Greensands are a relatively common geological feature in New Zealand, but here they cover a more restricted period of time than is reported elsewhere. Early Paleozoic glauconites are found extensively in the United States, Sweden and the U.S.S.R., and some, probably Precambrian, is reported in N.E. Greenland by Schaub (1955), who considers that glauconitic sediments could have been formed at that time, but in most cases would have suffered subsequent metamorphism. The first Precambrian glauconites from the United States were studied by Gulbransen, et al. (1963), who report that glauconites of this age have also been found in China and the U.S.S.R.

To the author's knowledge, no pre-Jurassic glauconite has been found in this country, although all N.Z. Geological Survey Offices in New Zealand were contacted on this matter. This is not perhaps surprising as pre-Devonian sediments are present only in N.Z. Nelson and Fiordland and these are highly altered, while post-Devonian geology consists largely of the filling of a rapidly subsiding geosyncline to the east of these older rocks. It is not until after the early Cretaceous with a period of uplift and folding followed by erosion, that conditions became suitable for the deposition of glauconite. In the late Cretaceous the first great marine transgression occurred, flooding the peneplains present with shallow seas. These marine transgressions were a feature of the next sixty million years, being at their maximum during the Bortonian and Duntroonian stages; these then are periods of the great greensand deposits in New Zealand. Fig. 2 (C. A. Fleming, N.Z. Biogeography) shows the probable coastline during the Middle Eocene and Lower Oligocene. It is seen that the present coastal Canterbury and Otago areas contain extensive greensand deposits from these times. After the Lower Miocene the tempo of
FIG 3a
SAMPLING LOCALITIES

NEW ZEALAND

Auckland
Great Barrier Island
Wellington

Hawkes Bay

Greytown
Hawke

Otago
Dunedin
Oamaru
Waipara River
Canterbury

100 miles
Fig. 3b Location of South Canterbury and North Otago Samples.
disturbance and sedimentation again quickened and the record of greensands was practically finished except for small local deposits. It is interesting to note, however, that glauconite is at present forming off the coasts of New Zealand on the Chatham Rise, and these deposits are at present being considered as a possible source of agricultural fertiliser.

The Canterbury and Stago greensands, then, afford excellent deposits for study of the structure and composition of New Zealand glauconitic sediments.

2.2 Sampling Localities

To study possible correlation of physical properties and age, material from thirteen main localities was obtained, as listed below, and referenced on the map opposite. Of these the first four are of particular significance, in that they enable a detailed study of glauconite in vertical sequences of beds - an approach not previously reported in the literature.

(1) Middle Waipara River, North Canterbury, where twenty samples were collected from over five hundred feet of vertical section. Denoted W

(2) Waihao, South Canterbury, where five samples were collected from a road cutting Denoted RC

(3) Earthquakes, near Duntroon, where five samples were taken representing thirty feet of deposition Denoted EC

(4) Old Rifle Butts, Oamaru, whence seven samples from thirty feet of sediment were collected Denoted ORB

(5) Pinnacle Gully, Waihao, three samples Denoted EF

(6) Five Forks, Oamaru district, three samples. Denoted FF

(7) Cobden Limestone, Greymouth, three samples, from D. Young, Geological Survey. Denoted COB

(8) Broken River, two samples from Dr. M. Frost, Canterbury University. Denoted BR
(9) Weka Pass, North Canterbury. ......... Denoted WEKA
(10) Coal Creek, North Canterbury .......... Denoted CC
both from Dr. W. Sevon, Canterbury University.
(11) Raki's Tunnel, Ohara district ........ Denoted RT
(12) Kaimaiar River, Hurunui district,
from P. Maxwell, Canterbury University .... Denoted TT
(13) Mauriceville, Kaketahuna Road,
supplied by P. Vella, Victoria University. .... Denoted V

These samples plus seven samples previously analysed by Button and Seelye (1941) and generously provided by Geological Survey, Lower Hutt, were the fossil glauconites which were studied fully in this project.

Some observations were also made on sediments from the following localities:-

Paukumara Peninsula, N 86/977664.
from Dr. Kingma, Geological Survey, Christchurch. Denoted BP
Akatore Formation,
from Geological Survey, Dunedin ........ Denoted AK
Hurunui River, North bank, Lowry Hills S.D.,
(about ½ mile S.W. Trig. B)
from P. Maxwell, University of Canterbury
Otai Greensand Junction Opahi-Pokapu Road and
Waipakino Road ........ Denoted CTAI
Pa Greensand near Opahi Railway Station . . . . Denoted IA
both near Kawakawa, North Auckland.

More exact information of the main sampling sites is given with the detailed account of beds and sediments in Section 4, page 13 et seq.
2.3 Separation of Glaucconite

This is by nature a laborious task. All sediments were separated into six weighed sieve fractions, >1 mm., >0.4 mm., >0.2 mm., >0.062 mm., >0.02 mm., <0.02 mm. Distilled water only was used to break down the sediments. Each size fraction was examined under a binocular microscope in order to ascertain the nature and amount of glaucconite present, and the range of accompanying minerals. These size fractions most rich in glaucconite, usually the >0.4 mm. and >0.2 mm. portions, were then washed and separated magnetically using a Franz Isodynamic separator. Where several grain types were present in one sample, separation was made at several different current values. This provided a good separation, except where oxides of iron were also present. These, and other minor impurities, were removed by handpicking as the need arose. All glaucconite samples were washed at least six times with distilled water and dried at a temperature of less than 50°C.

Records were made of all current ratings of separation so that a general comparison of magnetic susceptibility could be made.

More accurate measurements were later obtained by the Cooney method.)

2.4 Visual Examination

As a general indication of the proportion of glaucconite in the various size fractions of the sediments the percentage of glaucconitic material was estimated by eye to within about ten per cent. This could give a key to the subsequent weathering of the material.

Accompanying minerals were found to be most commonly quartz, calcite and feldspar with small amounts of muscovite, biotite and pyrite sometimes present. It was hoped that the asphericity of the accompanying minerals might give an account of weathering, but this was rarely satisfiable in the main greensand deposits since other minerals were often present in grain sizes
which were not easily observable under the microscope.
3. MORPHOLOGY OF GLAUCONITE

It is soon realised when working with glauconites, that their morphology cannot be judged in the same way as that of other sedimentary minerals. It is, for instance, quite possible to find a perfect sphere of glauconite. This is not usually an indication of prolonged weathering, but is likely to be authigenic, the cast of a simple globigerina (Fig. 4).

At first sight it would seem difficult to classify grain types owing to diversity of form, but, keeping possible origin as a significant factor, a pattern of grain types can be established:

1. Grains with framboidal or botryoidal surfaces - little worn Foraminiferal casts.
2. Torn and broken samples of (1), but still showing strong veining.
3. Smooth worn discs and elongate pellets similar to fecal pellets. However, long smooth crescent shaped glauconite grains (Fig. 5) were found in a recent sediment (P.155). These had definitely separated from the cast of Quinqueloculina. Care must therefore be taken in assigning an origin to these elongate grains. It was interesting to see that Hermund (1961) found many grains of this shape in only the Sabine (Lower Eocene) and Midway (Paleocene) sediments in a study of American glauconites. To me this is an indication that quinqueloculina (or similar genus) flourished at this time in these localities. Hermund also mentions a cap shaped pellet prevalent in the upper Eocene. These have been found in only one sample in this investigation, that from North Tank Murunui River, dated as Foranqan (Lower Eocene) by P. Maxwell, University of Canterbury. There could be a correlation here of microfossil population.
4. Verrucular pellets (Fig. 6) usually elongate and often curved
which have perfect cleavage perpendicular to the long axis of the grain.

(5) Other microfossil casts, e.g., echinoid spines (Fig. 7).

(6) More angular grains with pitted surfaces, which appear to be the result of surface chemical weathering.

(7) Glauconites which are formed by the replacement of other minerals.

(8) Pigmentary glauconite present as fillings in cavities, or as encrustation of other minerals, often quartz.

Of these types in the larger grain sizes, type (2) was predominant in the samples studied, most grains being definitely lumpy and irregular, but not angular, and often strongly veined. Very smooth worn discs and ovoidal pellets occurred less often than they appear to do in many of the reports on glauconites. In the small grain sizes, < 62μ, most grains seem angular and broken, and are often pale and glassy in appearance.
Fig. 8  Middle Waipara.
<table>
<thead>
<tr>
<th>N. Z. Series</th>
<th>Stage</th>
<th>Denoted</th>
<th>Climate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATA</td>
<td>Piripauan</td>
<td>Mp</td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>Haumurian</td>
<td>Mh</td>
<td></td>
</tr>
<tr>
<td>Cretaceous</td>
<td>Teurian</td>
<td>Mt</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wangaloan</td>
<td>Mw</td>
<td></td>
</tr>
<tr>
<td>Paleocene</td>
<td>DANNEVIRKE</td>
<td>Waipawan</td>
<td>Dw } Temperate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mangaorapan</td>
<td>Dm { rather</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heretauanan</td>
<td>Dh } than warm.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Porangan</td>
<td>Dp</td>
</tr>
<tr>
<td>Lower Eocene</td>
<td>ARNOLD</td>
<td>Bortonian</td>
<td>Ab Temperate to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>subtropical.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kaiatan</td>
<td>Ak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Runangan</td>
<td>Ar</td>
</tr>
<tr>
<td>Mid. Eocene</td>
<td>LANDON</td>
<td>Whaingaroan</td>
<td>Lwh Not fully</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tropical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Duntroonian</td>
<td>Ld Warm, subtropical</td>
</tr>
<tr>
<td>Upper Oligocene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Waitakian</td>
<td>Lw</td>
</tr>
<tr>
<td>Lower Miocene</td>
<td>PAREORA</td>
<td>Otaian</td>
<td>Fo</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hutchisonian</td>
<td>Ph Temperate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Awamoan</td>
<td>Pa</td>
</tr>
<tr>
<td>Mid. Miocene</td>
<td>SOUTHLAND</td>
<td>Altonian</td>
<td>Sa</td>
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<tr>
<td></td>
<td></td>
<td>Clifdenian</td>
<td>Sc</td>
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<td></td>
<td></td>
<td>Lilburnian</td>
<td>Sl</td>
</tr>
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<td></td>
<td></td>
<td>Waiauan</td>
<td>Sw</td>
</tr>
<tr>
<td>Upper Miocene</td>
<td>TARANAKI</td>
<td>Tongaporutuan</td>
<td>Tt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kapitean</td>
<td>Tk</td>
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<tr>
<td></td>
<td></td>
<td>Opoitian</td>
<td>To</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Waitotaran</td>
<td>Tw</td>
</tr>
</tbody>
</table>
4. DETAILED DESCRIPTION OF GLAUCONITIC SEDIMENTS

In the following pages a detailed account is given of samples from each site including information on:- locality including grid references, positions of samples, age, size analysis of sediments, percentage of glauconite in each size fraction, other minerals present, general nature of the sediments and obvious differences between the beds.

In the size analyses and subsequent pages,

\[ >1 \text{mm. means } >1 \text{mm.} <\frac{1}{2} \text{mm.} \]
\[ >\frac{1}{2} \text{mm. means } >\frac{1}{2} \text{mm.} <\frac{1}{4} \text{mm.} \]
\[ >\frac{1}{4} \text{mm. means } >\frac{1}{4} \text{mm.} <\frac{1}{16} \text{mm.} \]

4.1.1 Middle Waipara Section


From the late Cretaceous to the Lower Miocene, about 2500 feet of sediment were laid down in this area. At the base of these are coal measures formed as a consequence of marine advance over a low lying surface. Conformably above these are the Saurian Sands, sandstones containing large concretions, topped by finer siltstones and sandstones concluding five hundred feet of sediment laid down in the Raurian Stage. (Table 1, opposite, lists the New Zealand series and stages with their symbols, and also climates thought to be prevailing.)

Above these are the Teurian deposits, the first hundred feet being a continuation of the Saurian Sands; above this are the Waipara Greensands which are sands and glauconitic sandstones through which hard cemented bands are interspersed (see Fig. 8). It is from this 500 feet of sediment that most of the Middle Waipara samples were collected. One was also taken from the Raurian deposits below, and five from sediments above the Teurian beds, as far up as the Amberley limestone - see lithological column opposite,
White argillaceous limestone with cuboidal jointing and a mottled weathering appearance. (Amberley limestone)

Coral and foraminifera with distributed borings, grading up into the overlying limestone

Brown-green, mucky mudstone with grains of glauconite

Grey calcareous bentonitic mudstone with considerable glauconite near base, decreasing in quantity towards top

Red mudstone, dark mudstone with pyritic nodules and sulphur efflorescence

Alternating dark grey and greenish-grey sandstone and lenticular green, concretionary, grey mudstone. Less sulphur efflorescence than in underlying and overlying beds. Barnacle peduncles at 560.73 m.

Blue-grey and purple, mucky mudstone with vitrinite weathering, thin and slightly glauconitic, towards the top. Sulphur efflorescence towards top sand on concretions with radiating calcite veins at Grid ref

12 ft yellow sandstone. Dark glauconitic sandstone, small benthos, and sawmill teeth

Creams, banded fine and medium sandstone with sulphur efflorescence. Thin bands with bioclastic cement. Light grey fragments. Ventral concretions up to 12 ft diameter with sawmill teeth and shells, abundant from 80 ft above base to 100 ft below top

6 ft grey-yellow mudstone with thin lignite bands

12 ft yellow sandstone, with yellow-red sandstone parting

Medium grey, fine, loose sand with thin bands of grey wacke, grit and lenses of lignite and carbonaceous mudstone. Sulphur efflorescence

Carbonaceous mudstone with thin lignite seams

Compacted sandstone (greywacke) with rare quartz veins and compacted mudstone (argillite) with abundant quartz veins. Laminated for 15 ft below contact

Fig. 9 Middle Waipara.
Details of sampling are given below.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Nature of Sediment</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-LINE</td>
<td>Amberley limestone</td>
<td>Lwh</td>
</tr>
<tr>
<td>MW 1</td>
<td>Bentonitic mudstone, light grey 15 ft. above base of bed</td>
<td>Dw</td>
</tr>
<tr>
<td>MW 2</td>
<td>Glaucnctic mudstone below base of MW 1</td>
<td>Dw</td>
</tr>
<tr>
<td>MW 3</td>
<td>Light grey glauconitic siltstone 15 ft. below MW 2</td>
<td>Dw</td>
</tr>
<tr>
<td>MW 4</td>
<td>Light grey compacted glauconitic siltstone, bed 2 ft. thick, below MW 3</td>
<td>Dw</td>
</tr>
<tr>
<td>MW 5</td>
<td>Dark brown glauconitic siltstone 10 ft. below MW 4</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 6</td>
<td>Dark brown glauconitic siltstone 30 ft. below MW 5</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 7</td>
<td>Sulphurous</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 8</td>
<td>First hard band, compacted glauconitic siltstone</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 9</td>
<td>Glauconitic mudstone, 20 ft. below MW 7</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 10</td>
<td>Total 25 ft.</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 11</td>
<td>Hard band compacted glauconitic mudstone</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 12</td>
<td>10 ft. below MW 9, six bands down, between bands</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 13</td>
<td>Limonitic, glauconitic siltstone</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 14</td>
<td>Hard green band 15 ft. below MW 10</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 15</td>
<td>Sulphurous on weathered face</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 16</td>
<td>Loosely compacted grey, glauconitic siltstone</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 17</td>
<td>10 ft. below MW 11</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 18</td>
<td>Hard band below MW 12</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 19</td>
<td>Sulphurous</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 20</td>
<td>Vein filling associated with MW 13</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 21</td>
<td>Soft greensand immediately below hard bands</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 22</td>
<td>Brown mudstone 30 ft. below MW 15</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 23</td>
<td>Similar to, and 30 ft. below MW 16</td>
<td>Mt</td>
</tr>
<tr>
<td>MW 24</td>
<td>Mudstone 40 ft. below large concretions</td>
<td>Mt</td>
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</tbody>
</table>
### Size analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;1mm %</th>
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<th>&gt;1mm %</th>
<th>&lt;1</th>
<th>&gt;1mm %</th>
<th>&lt;1</th>
<th>&gt;62µm %</th>
<th>&lt;62µm %</th>
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<td>&lt;1</td>
<td>3</td>
<td>&lt;1</td>
<td>97</td>
<td>&lt;1</td>
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<td>WW 2</td>
<td>3 100</td>
<td>9</td>
<td>100</td>
<td>6</td>
<td>60</td>
<td>28</td>
<td>20</td>
<td>54</td>
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<tr>
<td>WW 3</td>
<td>2 100</td>
<td>20</td>
<td>95</td>
<td>40</td>
<td>70</td>
<td>10</td>
<td>70</td>
<td>30</td>
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<tr>
<td>WW 4</td>
<td>3 80</td>
<td>20</td>
<td>90</td>
<td>20</td>
<td>70</td>
<td>10</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>WW 5</td>
<td>&lt;1</td>
<td>1</td>
<td></td>
<td>40</td>
<td>50</td>
<td>30</td>
<td>10</td>
<td>30</td>
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<td>60</td>
<td>50</td>
<td>50</td>
<td>20</td>
<td>50</td>
<td>20</td>
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<td>WW 7</td>
<td>&lt;1</td>
<td>3</td>
<td>80</td>
<td>30</td>
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<td>30</td>
<td>40</td>
</tr>
<tr>
<td>WW 8</td>
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<td>10</td>
<td>60</td>
<td>55</td>
<td>40</td>
<td>10</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>WW 9</td>
<td>&lt;1</td>
<td>10</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>WW 10</td>
<td>&lt;1</td>
<td>5</td>
<td>30</td>
<td>50</td>
<td>30</td>
<td>20</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>WW 11</td>
<td>not weighed</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>WW 12</td>
<td>&lt;1</td>
<td>2</td>
<td>50</td>
<td>40</td>
<td>40</td>
<td>30</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>WW 13</td>
<td>not weighed</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WW 15</td>
<td>&lt;1</td>
<td>10</td>
<td>70</td>
<td>50</td>
<td>40</td>
<td>20</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>WW 16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>WW 17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2 few</td>
<td>30 few</td>
<td>70 few</td>
<td></td>
</tr>
<tr>
<td>WW 18</td>
<td>-</td>
<td>-</td>
<td>&lt;1 few</td>
<td>1</td>
<td>few</td>
<td>30</td>
<td>70</td>
<td>few</td>
</tr>
</tbody>
</table>

where: - few = a few grains

%G = percentage of glauconite in that size fraction.

As size analysis becomes unreliable in compacted muds and silts owing to the difficulty in separating the grains, figures in the list above are given mainly to the nearest ten per cent. It is clear however that the mudstones WW 16 to WW 18 lying below the greensands have a much finer nature than the siltstones above, and also have a negligible glauconitic content. The almost constant glauconite content of the beds WW 4 to WW 15 would not be expected from their appearance, as the lower beds are the only ones which appear green in situ. The grains of WW 5 to WW 8 are embedded in a brown matrix which proved to be mainly quartz with some pyrophyllite and alumina present. In WW 7 some feldspar appears also
and persists in most of the lower beds, including MW 15. In MW 7 also a calcareous component enters which was not present in MW 2 to MW 6. This becomes very large in MW 9 but disappears in MW 13 and MW 15.

The glauconite in the Middle Waipara beds can only be termed as "nobbly", such terms as botryoidal being too definite for such an array of shapes. Most of it is a very dark green, usually encrusted with a coating of paler material. In MW 2 and MW 3 the grains are pitted, and strong veining is present on all grains, sufficient to trap the enclosing matrix as impurity. However all grains are worn enough to have lost any original surface ornament present on most foraminiferal casts - if this is considered as their origin. Most fine fractions are quite highly glauconitic, to a greater degree than the greensands from obviously calcareous beds which have suffered little movement.

This means that either the Waipara beds have been considerably weathered, or that their origin was not that of foraminiferal casts. The presence of much surface sulphur in places would indicate that pyrite was deposited with the glauconite and has since oxidised; this leads one to speculate that this glauconite might have been precipitated directly from solution, the fine grains being a direct result of precipitation, and the "nobbly" ones due to the impression of existing quartz grains on the colloidal precipitate. The mechanism of such an origin is discussed in the section on "Origin of Glauconites" on page 122.
Samples RCW 1 to 5 represent different stages of weathering of the same glauconitic mudstone. The unweathered area containing RCW 4 to 5 is bonded by a calcareous cement, which is replaced by a ferruginous material as weathering proceeds.

Size Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;5mm %</th>
<th>&gt;2mm %</th>
<th>&gt;1mm %</th>
<th>&gt;62μm %</th>
<th>&lt;62μm %</th>
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</thead>
<tbody>
<tr>
<td>RCW 1</td>
<td>-</td>
<td>1 100</td>
<td>13 50</td>
<td>38 10</td>
<td>48 10</td>
</tr>
<tr>
<td>RCW 2</td>
<td>-</td>
<td>-</td>
<td>14 50</td>
<td>36 30</td>
<td>50 10</td>
</tr>
<tr>
<td>RCW 3</td>
<td>-</td>
<td>few</td>
<td>13 60</td>
<td>29 30</td>
<td>56 10</td>
</tr>
<tr>
<td>RCW 4</td>
<td>-</td>
<td>few</td>
<td>18 60</td>
<td>41 40</td>
<td>40 15</td>
</tr>
<tr>
<td>RCW 5</td>
<td>-</td>
<td>few</td>
<td>18 60</td>
<td>47 40</td>
<td>31 10</td>
</tr>
</tbody>
</table>
These samples proved to be some of the most interesting in the collection due to the nature of the glauconite grains, about half of which were the usual rounded type, but the remainder being the vermicular type, composed of stacks of parallel plates which cleaved easily from the grain. All of these portions were full of flakes from these grains, as demonstrated in Fig. 10, a photograph of a thin section of BCW 5. These vermicular grains were separated from the rounded grains and considered separately. The vermicular grains were either:

(1) straight stacks of flakes,

(2) often slightly rounded.

Some of them, Fig. 11, show continuation of a whorl and look like the cast of some microfossil, but these are rare and types (1) and (2) are characteristic.
Further samples examined later (from McCullough's Bridge in the same area) contain a great deal of this type of glauconite, which must have formed in vast quantities at this time. This type is considered fully later in this thesis (page 76).

In the RCW sediments loose muscovite and biotite are also present, and in the weathered portions flakes of all shades of brown are found. Further study showed that the glauconite is interlayered with other clay minerals, and thin sections indicate interlayering with other micas. X-ray diffraction patterns of the <62μm fraction of the accompanying sediment show mainly quartz and feldspar, also clays with a strong 7A reflection but only a small 10A reflection, i.e., very little material of a micaceous or illitic nature. Powder X-ray photographs of the glauconite in RCW 5 have h lattice spacings typical of glauconite, but those of the weathered RCW 1 give h lattice spacings typical of both glauconite and a mica with larger h dimension. In this sample it does seem possible that glauconite could be changing to biotite as a result of weathering. X-ray diffractometer studies of the flakes from RCW 1 show these to be 10A material interlayered with an expandable clay, which could account for the increased h dimension. Also present, however, is a small but definite 20A peak which is not altered by treatment with glycerol or by heating. This indicates that a 2M mica is now present - but in very small quantities.

A mechanism that alters glauconite to biotite would be unusual as all other reported transformations have been in the opposite direction, i.e., biotite to glauconite. The most likely product of weathering is an expandable clay which has been shown to be a strong component of RCW 1, but the possibility of a glauconite-biotite transformation cannot be ignored.
4.1.3 Earthquakes EQ

Kokoamu Greensand  Age: Dunroonian.
Earthquakes Road near Dunroon, Camaru, S.D.
S 43/243932

![Diagram of stratigraphy]

**Size Analysis**

| Sample | >

\(\frac{1}{2}\)mm | % | >\(\frac{1}{4}\)mm | % | >\(\frac{1}{8}\)mm | % | >62µ | % | <62µ | % |
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>EQ 1</td>
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<td>EQ 2</td>
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<tr>
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<td>90</td>
<td>20</td>
<td>50</td>
<td>21</td>
<td>50</td>
<td>25</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>EQ 5</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>1</td>
<td>39</td>
<td>10</td>
<td>30</td>
<td>10</td>
<td>29</td>
</tr>
</tbody>
</table>

Matrix material contained in the samples is nearly all calcareous except for up to 20% quartz in the <62µ portion. Recognisably foraminifera, whole and broken, were present in all but EQ 1, where the matrix was crushed and cemented - this is a region of strongly bored sediment. Once again the glauconite is present in the \(\frac{1}{2}\)mm. and \(\frac{1}{4}\)mm. sizes, but the presence of a number of \(\frac{1}{8}\)mm. grains indicates a lack of movement in most of these layers.
Grains generally are of the more botryoidal type, many tending to frambooidal, and show every sign of being derived from foraminiferal deposits.

Gage (1957) states that Kokoamu Greensand invariably rests on a corroded, bored and usually phosphatised surface. In most places the underlying formation is McDonald limestone, but at Raki's Table the greensand rests on the bored surface of Raki Silt, indicating that sedimentation had been interrupted, and the lower strata eroded, before the greensand was laid down; i.e., slight emergence caused shallowing sufficient to prevent deposition, and to permit erosion at some places.

Kokoamu Greensand and Gee Greensand, of which the next samples referred to, from the Old Rifle Butts are an example, are in contact in the upper part of Landon Creek. These are indistinguishable without microfaunal evidence, yet the two sections studied here show distinct differences in morphology of the glauconite, and could not be confused.
Old Rifle Butte Oamaru ORB

Gee Greensand Age: Awamoan.
On the coast about 2 miles south of Oamaru.
S 43/540629

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
</table>

blue sandy clay

3ft. shells and fossils (glauc.)
1ft. finely broken shells (glauc.)

10ft. current cross bedded sandstone, glauconitic.

3ft. glauconitic sandstone
greensands, brachiopods

4ft. white rubbly limestone

10ft. adulterated McDonald limestone

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;(\frac{1}{4} \text{mm})</th>
<th>%</th>
<th>&gt;(\frac{1}{16} \text{mm})</th>
<th>%</th>
<th>&gt;(\frac{1}{32} \text{mm})</th>
<th>%</th>
<th>&gt;(62\mu)</th>
<th>%</th>
<th>&lt;(62\mu)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORB 1</td>
<td>4 &lt;1</td>
<td>32 95</td>
<td>31 95</td>
<td>18 30</td>
<td>18 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORB 2</td>
<td>36 3</td>
<td>13 30</td>
<td>19 30</td>
<td>10 30</td>
<td>22 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORB 3</td>
<td>4 30</td>
<td>36 70</td>
<td>31 50</td>
<td>18 10</td>
<td>11 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORB 4</td>
<td>1 few</td>
<td>26 30</td>
<td>26 40</td>
<td>14 20</td>
<td>33 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORB 5</td>
<td>32 20</td>
<td>25 30</td>
<td>18 20</td>
<td>15 10</td>
<td>10 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORB 6</td>
<td>50 1</td>
<td>10 40</td>
<td>10 10</td>
<td>10 5</td>
<td>20 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORB 7</td>
<td>1 90</td>
<td>2 50</td>
<td>9 25</td>
<td>39 &lt;10</td>
<td>50 &lt;10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From ORB 1 to ORB 6 inclusive, the matrix material is all calcareous except for a little quartz in the fines of all samples, and limonite coating (actually goethite) in ORB 1 to ORB 4. The large amount of $>\frac{1}{2}$ mm. material in some samples is due to brachiopods in ORB 2, to finely broken shells in ORB 5, and to larger shell fragments in ORB 6. From ORB 1 to ORB 4 inclusive, whole foraminifera are present but none are present in ORB 5 and ORB 6, all the calcareous material being very broken before being cemented together.

ORB 7 differs strikingly from the rest of the samples in this section in having 50% of its sediment less than 62 $\mu$ and only 10% greater than 62 $\mu$. ORB 7 is also spectacular for the wealth of foraminifera in this portion and for the obviously foraminiferal
shapes of the glauconite grains. Fig. 12 shows a beautifully preserved foraminiferal glauconitic cast.

The other deposits in this section are notable for the large number of glauconite grains obviously developed from echinoid spines. These are prevalent in all samples except ORB 7, and the grains tend to be a paler yellow colour, contrasting strongly with the bright green grains from ORB 7. Fig. 13 shows a thin section through one of these grains from an echinoid spine. The structure can be clearly seen as the replacing glauconite is of different opacity in the originally empty parts of the echinoid spine.

Gee Greensand here overlies, and is mixed with, a thin layer of heavily corroded McDonald limestone which overlies Deborah volcanic tuffs, both Whaingaroan. Accumulation was slow and discontinuous with little net gain in thickness: breaks in this region have far less diastrophic significance than in thick geosynclinal sediments (Gage 1957). Note that the tuffs and limestone do not contain iron in any great quantity to contribute to glauconite formation, but phosphatic deposits are often present below the Gee Greensands, indicating animal life and remains which could supply some iron.
4.1.5 Pinnacle Gully, Waiau Forks WP

Age: Duntroonian-Waitakian.

About two miles up the Mt. Harris Road from Waiau River Bridge. Loosely compacted dark green greensand lying unconformably below limestone.
Current cross bedding present.
Size Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;\frac{1}{2} \text{mm}</th>
<th>%</th>
<th>&gt;\frac{1}{16} \text{mm}</th>
<th>%</th>
<th>&gt;\frac{1}{16} \text{mm}</th>
<th>%</th>
<th>&gt;62 \mu</th>
<th>%</th>
<th>&lt;62 \mu</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>WF 1</td>
<td>-</td>
<td>-</td>
<td>19</td>
<td>40</td>
<td>55</td>
<td>80</td>
<td>9</td>
<td>10</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>WF 2</td>
<td>1</td>
<td>-</td>
<td>9</td>
<td>50</td>
<td>76</td>
<td>80</td>
<td>7</td>
<td>40</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>WF 3</td>
<td>-</td>
<td>-</td>
<td>9</td>
<td>10</td>
<td>84</td>
<td>80</td>
<td>4</td>
<td>50</td>
<td>3</td>
<td>40</td>
</tr>
</tbody>
</table>

There is very little clay sized material in this section, the matrix being calcareous with limonitic staining; foraminiferal content mostly broken; a little quartz in the fines. The glauconite present is largely ovoidal, or discoidal apparently from wear but many are tending to betyroidal; a few vermicular. Veining is prominent on even the most worn. The higher percentage of glauconite in the <62 \mu portion reflects greater wear in the current bedded section.

4.1.6 Five Forks, Oamaru. Kauru Formation

Downstream from bridge. Age: Wangaloan.

These are the oldest glauconites taken from the Waitaki district. Samples were obtained from two members, the Five Forks Glauconitic Sands and the underlying member, the Dixon Silt. The latter consists of a finely ground mixture of quartz, illitic material, and a clay with medium 7A reflection on a powder pattern. The small h measurement from (060) would suggest kaolin. No glauconite was found in this member. From the glauconitic sands above, the >\frac{1}{16}\text{mm.} and >\frac{1}{16}\text{mm.} portions contained about 50% of pale pitted glauconite of originally vermicular form.

Beneath the Kauru Formation is the lowest sedimentary deposit in this area, the Papakaio Formation which consists largely of sorted quartz sands often topped with coal beds. Beneath these are the strongly leached schists of the Cretaceous peneplain.
4.1.7 Cobden Limestone COR Age: Dunroonian–Waitakian
from Cobden Quarry, Greymouth
S 46°7'49.9"

COB 1. Plain Cobden limestone.
COB 2. Glaucosnitic filling in borings in limestone.
COB 3. Glaucosnitic limestone near the top of the quarry.

No size analyses could be made owing to the nature of the
samples.

COB 1

Hard limestone with only a few grains of glauconite, also a
few grains of mica. Rod-like inclusions of pyrite or
marcasite are also present.

COB 2

Large grains up to 2 mm., frequency about 10 per cm², in
fillings of borings. Under the microscope these grains are
seen to be of composite form, as in Fig. 15, which is a
x 100 enlargement of the surface of one of them, showing a
network of veins and small foraminifera filled with the
darker glauconite. These grains are formed of foraminifera
and pieces of limestone, often replaced by glauconite
or pyrite, and often held together by a ferriferous cement.
X-ray investigation shows a large amount of siderite to be
present. In some cases the glauconite is present only as
foraminiferal casts, but in others it is filling in cracks,
and in a very few grains glauconitisation has proceeded
space until the whole grain is a uniform green. Fig. 16
shows a thin section of foraminifera replaced by glauconite
and rimmed by pyrite. These grains would indicate that the
finished grain is due to a very local environment, which,
from the presence of both pyrite and siderite, is reducing.
Smaller grains of glauconite are also present in this
sample. These are clearly of foraminiferal origin.

COB 3

About one per cent glauconite, grain sizes 0.125 to 0.25 mm.,
showing foraminiferal shapes in thin section. A few
vermicular pellets also present.

**A.R.6 Broken River BR**

Greensands upstream from the bridge on the Main West Coast Road.
S 55/200980

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;1mm %</th>
<th>&gt;1mm %</th>
<th>&gt;1mm %</th>
<th>&gt;62μ %</th>
<th>&lt;62μ %</th>
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</thead>
<tbody>
<tr>
<td>BR 1</td>
<td>1 80</td>
<td>17 80</td>
<td>42 40</td>
<td>19 30</td>
<td>21 much</td>
</tr>
<tr>
<td>BR 2</td>
<td>7 80</td>
<td>52 80</td>
<td>24 70</td>
<td>9 40</td>
<td>8 much</td>
</tr>
</tbody>
</table>

**BR 1**
The glauconite in this sample is very pale, soft and pitted, the only other mineral being present at first sight is quartz. When stirred with water this glauconite crumbles easily. From the paleness of this sample one might predict an iron deficiency, but this did not appear initially on analysis. However a deficiency of 3.2% in total analysis is almost certainly due to the presence of minute inclusions of marcasite in the grains, and can be attributed to the sulphide radicle. This then, would account for about 4% Fe₂O₃. It is interesting that the analysed amounts of iron are almost identical with those for BR 2 which was obtained from the same locality but has grains of the more usual dark pelletal nature.

**BR 2**
The glauconite content is high, as in BR 1, but in different form. Pellets rounded and well worn, smaller aises being broken forms of larger grains. In both samples the glauconitic content of the fines is very high.
6.1.9 Weka Pass, North Canterbury

Loose greensand.  
Age: Duntroonian.  
S 56/08-21.

Size Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;1 mm</th>
<th>%</th>
<th>&gt;1/4 mm</th>
<th>%</th>
<th>&gt;1/8 mm</th>
<th>%</th>
<th>&gt;62 μ</th>
<th>%</th>
<th>&lt;62 μ</th>
<th>%</th>
</tr>
</thead>
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<tr>
<td>WEKA</td>
<td>1</td>
<td>10</td>
<td>23</td>
<td>10</td>
<td>56</td>
<td>40</td>
<td>17</td>
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<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>

In this sample larger grains of quartz were found, some of them stained pale green, most of them rounded. About 70% of the other material is quartz, the remainder being calcareous and stained with limonite. This sample is very similar in composition to that from

6.1.10 Coal Creek CC

Loose greensand containing lumps 2–3 cms. across bonded with iron oxides.  
UW = unweathered  
W = weathered

Size Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;1 mm</th>
<th>%</th>
<th>&gt;1/4 mm</th>
<th>%</th>
<th>&gt;1/8 mm</th>
<th>%</th>
<th>&gt;62 μ</th>
<th>%</th>
<th>&lt;62 μ</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>CCUW</td>
<td>39</td>
<td>few</td>
<td>26</td>
<td>20</td>
<td>16</td>
<td>40</td>
<td>9</td>
<td>40</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>CCW</td>
<td>24</td>
<td></td>
<td>20</td>
<td>few</td>
<td>16</td>
<td>20</td>
<td>14</td>
<td>30</td>
<td>26</td>
<td>much</td>
</tr>
</tbody>
</table>

The quartz in the larger sizes is well rounded and shows no tendency to glauconitic staining. In the smaller sizes all the components are more angular and the glauconite more broken and pitted. More large grains of quartz are present in this sample than in the Weka Pass greensand.

6.1.11 Raki's Tunnel ET

Tapui Formation, Age: Bartonian.  
Disused railway tunnel, Raki's Table, Camarua  
S 43/341795
Size Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>$&gt;\frac{1}{2}$mm %</th>
<th>$&gt;\frac{1}{4}$mm %</th>
<th>$&gt;\frac{1}{16}$mm %</th>
<th>$&gt;2\mu$ %</th>
<th>$&lt;2\mu$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>1 15</td>
<td>15 20</td>
<td>40 20</td>
<td>25 1</td>
<td>19 few</td>
</tr>
</tbody>
</table>

The glauconite in this sample consists mainly of vermicular pellets, very pale green in colour, and broken chips of these in the smaller sizes. Quartz, feldspars, and a 7A clay are the other components. Non-calcareous. A bored surface separates Tapui from the Kauru Formation at the Eastern tunnel portal.

4.1.12 Hurunui, North Canterbury, Ti

Kaiwharva Stream left bank
Age: Tongaporutuan.

From sectipeetan bed, near Athol Glen homestead.

The over $\frac{1}{2}$mm portion contains 80% glauconite, the remainder quartz and broken sectipeetan.

The over $\frac{1}{4}$mm portion contains 40% glauconite, the rest quartz and small calcareous grains.

4.1.13 Mapua—Ekakuna Road, V, V₂

N 158/206882

V 1 Mid grey glauconitic mudstone immediately below
Te Aute limestone: streaks of iron oxidation.

V 2 Yellowish grey muddy shell bed at base of limestone.

Age: Waitotaran.

V 3 Mid grey glauconitic mudstone at base of Opoitian.
White Rock Road cutting, 1 mile S of Mangaopari-Makara stream ju.

Size Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>$&gt;\frac{1}{2}$mm %</th>
<th>$&gt;\frac{1}{4}$mm %</th>
<th>$&gt;\frac{1}{16}$mm %</th>
<th>$&gt;2\mu$ %</th>
<th>$&lt;2\mu$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>V 1</td>
<td>2 -</td>
<td>2 40</td>
<td>4 40</td>
<td>4 5</td>
<td>88 few</td>
</tr>
<tr>
<td>V 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V 3</td>
<td>16 90</td>
<td>15 90</td>
<td>22 90</td>
<td>6 40</td>
<td>41 10</td>
</tr>
</tbody>
</table>
V 1 is distinguished by the presence of large green glassy grains up to 1 mm. in diameter. Glassiness persists to some extent in the smaller grains, but they are often very dark and subvitreous. X-ray powder patterns of the 1/4 mm. glassy grains show mainly quartz, with a little feldspar and faint glauconite lines, also a faint 7A line. A thin section of one of these grains shows quartz (transparent) interlaced by a glauconitic network (Fig. 17).

In V 2 some large grains of glauconite are present. The sediment is mainly calcareous with enough ferruginous cement to give a yellow colour.

The sediment V 3 is highly glauconitic, with more pure grains than V 1 and V 2. X-ray powder patterns of the >1/2 mm. grains give much the same picture as for V 1, but for the >1/4 mm. grains the lines are predominantly those of a disordered glauconite.
4.2 General Considerations on Samples and their Localities

(1) In the greensand localities the sand portion >62μ is predominantly glauconite. Quartz is rare in these sizes, the remainder of >62μ fraction being usually calcareous. This could mean that the sediments were previously of a much finer type, the coarser element being introduced by colonies of benthonic foraminifera, and planktonic skeletons, with subsequent formation of glauconite - if the glauconite is authigenic. That is, the greensands are sands due only to the introduction of glauconite, and not by the mechanism of initial deposition; therefore they would rate as silts and muds without the glauconitic and fossiliferous content.

(2) Many of the main greensand localities in New Zealand are underlain by coal seams and conditions of great organic change. From late Cretaceous to Southland times coals were formed as marine transgression progressed over the Cretaceous peneplain. These coals are usually highly sulphurous. In the Oamaru district the coal seams of the Papakaio formation appear to vary in age, since they underlie sediments varying in age from Tangaloan to Duntroonian. During the change of organic material to coal, CO₂, S₂S, CH₄ and NH₃ are evolved, which, passing through the upper sediments can create unusual local conditions and could easily account for the reducing conditions usually thought necessary for a growth mechanism for glauconite.
### TABLE 2A

**CHEMICAL ANALYSES OF GLAUCONITE**

(Hutton and Seelye 1941) *

<table>
<thead>
<tr>
<th></th>
<th>4640 *</th>
<th>6034 *</th>
<th>5392 *</th>
<th>6035 *</th>
<th>5621 *</th>
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<tr>
<td></td>
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<td>percent</td>
<td>percent</td>
<td>percent</td>
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<td>percent</td>
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<tr>
<td>SiO₂</td>
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<td>49.29</td>
<td>43.33</td>
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<td>Al₂O₃</td>
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<tr>
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<td>n.d.</td>
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<td>n.d.</td>
<td>n.d.</td>
<td>n.f.d.</td>
<td>n.f.d.</td>
<td>n.f.d.</td>
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<td>6.00</td>
<td>6.07</td>
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<td>H₂O⁻</td>
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<td>5.94</td>
<td>6.71</td>
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</tr>
<tr>
<td></td>
<td>RT</td>
<td>ORF 3</td>
<td>EQ 2</td>
<td>HR 2</td>
<td>MW 15</td>
<td>4895*</td>
</tr>
<tr>
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* HR 1 which was also analysed by Chemistry Division has been excluded from this list because of the large marcasite impurity found in it.
5. CHEMICAL ANALYSES

Seven samples which had been fully analysed chemically and discussed by Rutton and Seelye (1941) were gratefully received from Geological Survey Office, Lower Hutt. A further six samples were fully analysed (1963) by Chemistry Division, D.S.I.R., Petone. These thirteen samples, for which the analyses are given in Table 2A, form a stable basis for comparison with other properties. In addition, the author analysed sixty samples for potassium, sodium and total iron content, and thirty of these for ferrous iron.

These analyses were done by standard methods on small samples of 25 or 50 milligrams, owing to the difficulty of separating large amounts of pure material. This is recognised practice for glauconites.

The samples were readily soluble in a mixture of sulphuric and hydrofluoric acids. Sodium and potassium contents were measured using an EEL flame photometer, interfering ions being precipitated by addition of ammonium sulphate. Total iron was measured with a Bausch and Lomb Spectronic 20 spectrophotometer at 522 mμ, using fresh solutions of ferrous ammonium sulphate as standard and a colour developing reagent of dipyridyl solution plus sodium acetate plus hydroxylamine hydrochloride. (Riley 1958)

Ferrous iron was measured volumetrically by the classical method of titration with potassium dichromate, with barium diphenylamine sulphonate as indicator.

These chemical measurements were made so that any sudden change in the important potassium and iron contents could be traced as the sampled sections were traversed, and also to note differences from locality to locality. Although the author was not an experienced analyst, it is felt that consistency of method should ensure consistency of error and that results should offer reliable comparison between samples.
Results were checked by comparison with the analyses from Chemistry Division, whose potassium results were in general about five per cent higher than mine, due perhaps to a different method of eliminating interfering ions. Therefore a correction of plus five per cent of the measured $K_2O$ component has been applied to results quoted in Table 3. The only serious discrepancy is in the ORP 3 sample which is shown in the Chemistry Division's analyses as having 7.4 per cent $K_2O$. My analyses (corrected by five per cent) for the six samples, ORB 1 to ORB 6 give values 6.9, 6.8, 6.7, 6.7, 6.7, 6.7 per cent $K_2O$. With this consistency of value I am loathe to relinquish these readings. Subsequent diffractograms of these samples also indicate that they were in the <7.0 per cent $K_2O$ group.

Results for total iron cannot be considered consistent as iron oxide contamination is an ever present hazard. Results compared with those of the professional analyst within $\pm 5$ per cent (usually well within these limits). This makes the decimal place doubtful, but the results are quoted as being correct for a sample from what can only be termed as a very variable host.

Table 3 lists the results of these analyses for the various sections and single samples, and are arranged in groups of the same geological age for purposes of comparison. Beds from the same section are given with the youngest first with age increasing downwards.

5.1 Discussion of Results

Doubts as to the purity of 4835, 6034 from the Hutton collection, and BR 1 led to their exclusion. For the other samples variations in analyses are:

* Table 3, pages 43, 44.
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</table>

None of these shows any extreme of values such as have been reported by Smulikowski (1936) in establishing a new mineral skolite, a glauconite with a very high percentage of $\text{Al}_2\text{O}_3$. Total $\text{Si}_2\text{O}_4\text{Fe}_2\text{O}_3\text{Al}_2\text{O}_3$ varies only slightly - from 73.8 to 78.6 per cent, seven out of ten samples lying between 74.8 and 76.1 per cent inclusive. None of the new analyses contains a high percentage of aluminium in the octahedral layer, structure analyses (page 48) showing that at least half of the aluminium which is present is in the tetrahedral layer if this is assumed to be complete. It is also to be noticed that a low value of $\text{SiO}_2$ is not necessarily compensated by a high $\text{Al}_2\text{O}_3$ content, as evidenced in the analysis of ORB 3, where to completely populate the tetrahedral layer it is necessary to allow some of the $\text{Fe}^{3+}$ ions to be accommodated there. It is not usual for iron to substitute for silicon although a little may do so at high temperatures. However, there is precedence for iron substitution for silica at low temperatures in a chlorite mineral, cronstedite (Goldschmidt 1954).

5.1.1 Potassium Content

Percentage of $\text{K}_2\text{O}$ varies from 5.0 to 7.6. Correlation of potassium content with ordering of crystalline structure will be seen in the section on X-ray diffraction. The low potassium content of ORB 7 is surprising when the appearance of the grains is considered, as these are a bright clear green and look in an advanced state of glauconitisation, which again indicates that appearance is a most misleading characteristic. The only other
sample with a very low $\text{Fe}_2\text{O}_3$ content is RT (5.0%), a very pale vermicular glauconite with well formed platelets, and probably of special origin (page 78).

5.1.2 Sodium Content

There is a consistently low sodium content, usually less than 0.2 per cent $\text{Na}_2\text{O}$, but again there is a noticeable difference in the Old Rifle Butts sediments. ORB 1 to ORB 6 have a high amount of $\text{Na}_2\text{O}$ for glauconite, 0.4 to 0.6 per cent, but ORB 7 has only 0.1 per cent. It is felt that perhaps the different grain form has a bearing on this difference, there being many of the grains from echinoid spines in ORB 1 to ORB 6.

The only other sample with a high sodium content is V 3, (0.7%).

5.1.3 Magnesium Content

Magnesium oxide ranges from 2.3 to 5.0 per cent, but in some cases low $\text{MgO}$ is compensated for by a higher FeO content, so that $\text{FeO} + \text{MgO}$ varies between 5.5 and 7.9 per cent.

5.1.4 Titanium Content

There is a very small titanium content in all samples, less than 0.2 per cent $\text{TiO}_2$. This component has been used by Allen (1937) to trace the possible derivation of glauconite from biotite which is often titanium rich. Allen believed that the glauconite should retain a significant amount of titanium, but Sutton and Seelye found no evidence of rutile needles in their samples, and the new analyses show even less titanium.

5.1.5 Ferric to Ferrous Iron Ratio

This is discussed in detail under COLOUR, page 50. As many grains show obvious oxidation effects on the surface, the outside 10 per cent (by weight) was ground from WR 1-5 to check on ferrous content. This was found to be 10 per cent less for the outside layer than for the remainder of the grain, a small but
measurable difference, showing that oxidation has taken place on
the outside. The ferrous iron content of the outside portion is
however still considerable at 3.0 per cent FeO.

5.1.6 Total Iron Content

This varies from 17 to 27 per cent, the lowest
values being found in glauconites from COE 3 (19%), MW LIME (18%),
EQ 5 (18%) — all three of which are separated from limestones —
and in glauconites from the Waihao Forks section (18.5%) and the
Earthquakes area in general (max. 20%). Both of these areas are
highly calcareous, with thick greensand deposits and are topped
closely by limestones. There is no other coarse material present
in any of these sediments. All of these are also in the Landon
series, but there are other samples of this age which have a greater
iron content.

5.1.7 Iron Content, Middle Waipara

Beneath the topping Amberley limestone, where the
glaucconite contains 18 per cent iron oxides, the total iron content
of the underlying beds gradually increases from 19.5 per cent in
MW 2 and MW 3 through MW 5 (20%), MW 7, 8, 9, (22%), to 23 per cent
in the lower greensand beds. Ferrous iron content of these Middle
Waipara beds was measured at 3.2, 3.5, 3.2 per cent for lower beds,
an average value for Tertiary glauconites — Takahashi (1939) gives
an average value for seven Tertiary glauconites of 3.2 per cent FeO.

5.1.8 Iron Content of Other Sections

Another glauconite which contained about this average
amount of FeO was that from the Waihao road cutting in the
unweathered state (RCW 5, 3.3%). Beds above this were progress-
ively weathered, the total iron content becoming progressively less,
from 23.5 to 20.4 per cent. The ferrous iron content also
diminished from 3.3 to 1.5 per cent, showing that half of the iron
lost has been of the divalent form.

The only other glauconite of the new collection with such
a high ferrous iron content was ORB 7, with 3.0 per cent ferrous oxide. With this high ferrous iron content and a very low potassium content (4.9%), this sample is unique among the Old Rifle Butts collection, as the other ORB samples have a low ferrous iron content (0.9%), and a high potassium content (6.7%). Here the strongly contrasting nature of the accompanying sediments, a blue clayey siltstone for ORB 7 versus a highly calcareous medium for all the others, is reflected in the highly contrasting chemical composition of the glauconites. Total iron for ORB 7 however, is very low, 19.8 per cent, as compared with 25 per cent for the others.

Later, when measuring the ferrous iron content of glauconites from present day marine deposits, it was noticed that these had an almost constant ferrous iron content (page 110), though from sediments hundreds of miles apart. This was rather a disquieting discovery, as the ferrous iron content had been thought to be the manifestation of very local oxidation-reduction conditions.

Inspection of the results from the vertical sections shows a remarkable constancy in the ferrous iron content, except in the RCW section which is obviously weathering, and the sudden change in ORB 7. This constancy, together with that of other components over tens and hundreds of feet of sediment, poses another question. Does this mean (1) that conditions for formation of glauconite have been constant over this period, or. (2) that the lower glauconites have been sufficiently well ordered to withstand a great deal of reworking without much change to their composition?

Considering this:—

5.1.9 The Middle Waipara Section

Sample M 15 consists of a mature well ordered glauconite, above which similar glauconites occur throughout the section. This glauconite was found to be very resistant to weathering, either mechanical or chemical (page 117), and the upper
beds are probably reworkings of the lower ones. It is not conclusive that any of these No. 15 glauconites was formed in place, as all show the effects of wear. If their origin is considered to have been foraminiferal casts, then the surface ornament has disappeared. Light (1952), in attempting to distinguish between surface features of authigenic and detrital glauconites, states that authigenic glauconites show very little breaking or irregularity, are usually rough and pitted, having a dull to subvitreous lustre, and an ovoid to subspherical surface. The most important criterion which he lists is probably that the structural shapes persist even in the finer fractions. Such features as pitting and cracking can be the result of chemical weathering, (Section 8.2), while smoothness can be assigned either as an initial property of the grain, or due to the usual processes of abrasion.

The finer size fractions of No. 15 are highly glauconitic. Some of this glauconite is of the same general outline as the larger grains, but some is glassy and angular. Surface properties indicate that the Middle Waipara glauconite has been transported, and all beds have a calcareous or feldspathic content which acts as a cement rather than existing as individual grains of calcite or feldspar. The presence of hard bands in the section show changes in compaction, and conditions of deposition, but the glauconitic grain type remains similar. It is thought, therefore, that they are of the same origin and that the top beds at least, are redeposited.

5.1.10 Earthquakes

Again there is a great similarity of the glauconites in the beds. From inspection of the sediments, No. 4 has a little more glauconite in the smaller grain sizes, and is a sugary paler green. In No. 1, in which the accompanying foraminifera are broken, there is strong evidence of borings and downward mixing. The beds containing No. 2 and No. 3 therefore appear to be the main greensand beds and may be considered to be authigenic. However, the
glaucnite in the beds above has not moved far, as the grains which are greater than $\frac{1}{2}$ mm. are still intact, and they in general are of an easily broken, composite nature.

5.1.11 Pinnacle Gully

Morphology and chemical composition all point to these glauconites having been derived from the same deposition as those at Earthquakes. However strong current bedding in these deposits indicate that they are detrital.

5.1.12 Old Rifle Butte

Here the glauconites are undoubtedly of microfossil origin. On inspection, ORB 1 and ORB 3 are the least worn, and ORB 4, ORB 5, and ORB 6 appear to be derived from ORB 3, but none of them have moved far, as the larger grains, which are greater than $\frac{1}{2}$ mm. are still intact and numerous.
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6. STRUCTURAL ANALYSES

From the chemical analyses the number of ions per unit cell was calculated, assuming,
(a) Twenty oxygen ions and four hydroxyl ions per structural unit, as for ideal mica structure,
(b) a full tetrahedral layer,
(c) the excess water over that required for four hydroxyl ions is present as interlayer oxonium ions, H$_2$O$^+$, (Brown and Norrish 1952).

From thermal analyses (page 94), it is seen that interlayer water is lost by glauconites at about 130°C. This is the pattern for hydrous micas and clays. It is obvious, therefore, that some of the water, denoted H$_2$O$^+$ (i.e., evolved at above 100°C) in the chemical analyses, is held between the layers by attraction due to charge deficiencies in the lattice. On these assumptions, structural analyses were made for ten glauconites known by personal examination to have been relatively pure. These are tabulated in the following pages (Tables 4 and 5). As well as the number of ions per unit cell, the totals for octahedral, tetrahedral, and interlayer occupancy are given, also the total charge deficiency in the octahedral plus tetrahedral layers, for comparison with the calculated interlayer occupancy.

In most cases the octahedral layer is slightly deficient in ions necessary to complete the quota for a dioctahedral mica, the greatest deficiency being 0.29 ion in a total of four ions (ideal), i.e., 7 per cent deficiency. This is an immediate contradiction of the analyses made by Hendricks and Ross (1941) on forty samples. Their analyses disregarded the water content of the grains entirely, and gave an octahedral occupancy of between 4.0 and 4.18 for all but five of thirty-two samples. It does not seem unreasonable to me to expect a deficiency in this layer, considering the sluggish ion mobility at low temperatures of formation. The
Fig. 18
only one of the present samples which shows an occupancy greater
than four is 5392, which has also a very high amount of aluminium
replacing silicon in the tetrahedral layer. (This fact is supported
by infrared spectroscopy, page 90.)

6.1 Interlayer Cations

Without H$_3$O$^+$, interlayer cations vary in number between
1.01 for RT and 1.52 for MW 15. When H$_3$O$^+$ is included, all
but RT have an interlayer occupancy of two or greater (Column 4,
Table 5). When the charge deficiency for each glauconite is
calculated from the tabulated ion occupancy of the layers, it is
seen that not all the charge deficiency is accounted for by the
amount in Column 4. These figures are, however, derived from
chemical analyses, by taking into account only the water content
driven off above 100$^\circ$C and neglecting the water content below this
temperature. Other water molecules would certainly be held below
100$^\circ$ C. Indeed, glauconite does slowly adsorb atmospheric water at
room temperature.

In Fig. 18 total charge deficiency is plotted against
interlayer ions, against both potassium ions only, and total inter-
layer ions including H$_3$O$^+$. The total interlayer ions are much
more linearly related to total charge deficiency than are the
potassium ions alone.

Hower (1961) has endeavoured to link the amount of
potassium to the amount of total iron present. Certainly both
potassium and iron content are low in the immature forms, but
consideration of the more mature forms shows no correlation.
(See Fig. 19) It is difficult to follow Hower's logic in pro-
posing this idea. A degraded layer lattice with low net lattice
charge, which he postulates as an initial state for glauconites,
can have few vacant octahedral sites and little substitution of
divalent for trivalent ions. For the lattice charge to increase,
greater substitution of divalent for trivalent ions must occur, or
more vacancies must be created. More substitution of \( \text{Fe}^{3+} \) for \( \text{Al}^{3+} \) in the octahedral layer will not, as Power suggests, alter the charge on the layer, and therefore will have no effect on the force securing potassium ions. If divalent iron or magnesium were to replace the aluminium however, there would be a deficiency which could attract potassium ions.
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Average (without RT) 3.83 2.14
7. MACROSCOPIC PROPERTIES OF GLAUCONITE SAMPLES

7.1 Colour of Grains

Glauconite grains vary in colour from a light yellowish green to a dark greenish black. These colours in minerals containing a significant amount of iron substituting for aluminium are attributed by Fersman (1937) to the presence of both divalent and trivalent iron in the lattice; the combination of the greenish yellow due to the divalent ion and the reddish brown due to the trivalent ion producing a greenish black. Chemically, the colour changes in an iron hydroxide precipitating from solution are as follows: the divalent hydroxide precipitating in an air-free solution with alkali is a white flocculent material which absorbs oxygen with great avidity, turning to a dirty green; this darkens with oxidation and passes into the red brown colour of trivalent iron compounds.

Colour, therefore, should vary not with the total amount of iron, but rather on the ratio of ferric to ferrous ions. In the fully analysed samples of glauconite this ranges from 5:1 for 5618, to 25:1 for ORB 3. Many grains have a coating of lighter material which makes colour assessment difficult, but in general those grains which have a high ferric to ferrous iron ratio tend towards a paler shade of green. This is evidenced by the ORB samples which have a high ferric/ferrous ratio, all greater than 20:1, and are all a yellowish green, compared with ORB 7, which has a lower ferric/ferrous ratio of 7:2, and contains grains of a darker colour. All of the Middle Paipara grains, which have a low ferric/ferrous ratio throughout the section, are consistently a dark green tending towards black.

Ferric/ferrous iron ratios are shown in the sectional chemical analysis data in Table 3, pages 43, 44. The only really pale glauconites, PT and the ORB samples, all have a ratio greater
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than 20:1, while the darker glauconites have a ratio considerably less than this. It is not possible to develop this correlation to any greater degree of accuracy.

Of the cap shaped glauconite grains from Murunui River (page 11), about fifty per cent are iron black in colour. These were checked for phosphate content, using ammonium molybdate as indicator, but no reaction was found. No lines due to impurities were found on the X-ray powder photographs. The extreme colour must then be due to a trace element.

7.2 Refractive Index $\mu$

This was measured by comparing crushed grains with a selection of oils, by observation of the Becke line with a polarising microscope. The refractive indices of the oils were measured with a Leitz-Jelley refractometer using sodium light.

As individual grains vary widely in the same sample it is difficult with these measurements — as with the density measurements (page 53) — to obtain representative results, but it is possible to establish trends.

In general it is noted that:

(a) All measurements lie between 1.560 and 1.614.
(b) Glauconite grains which are brown in transmitted light have a lower refractive index than those which are bright green.
(c) Samples with higher iron content usually have a higher refractive index. In the Middle Waipara section both $\mu$ and iron content increase as the main greenstone beds are approached from each side. The refractive index decreases suddenly for the ORB beds as ORB 7 is encountered. Here the iron content decreases suddenly from 25% to 20% (see chart opposite). It would however be more convincing if the $\mu$ specimens had a much lower value of $\mu$ to agree with their very low total iron content (18.5%). Hutton and Seelye, after a detailed
measurement of the optical properties of seven glauconites, found a reasonable correlation between Fe$_2$O$_3$ content and refractive index with the exception of one sample.

(d) FCW samples have the same refractive index for both the round and the platy grains. The refractive indices of both are in the intermediate range, the iron content about 22 per cent.

(e) The Earthquakes beds have a very wide spread of values of $\mu$, all of which are less than or equal to 1.510.

(f) No correlation of refractive index with potassium content can be obtained.

7.3 **Density Measurements**

Density of all samples was measured by comparing the weight in air and in toluene on a density balance (Bethlehem Instrument Co.).

For thirty five samples from all sources, size $> 0.25$ mm, the mean density was $\rho = 2.70$ with a standard deviation $\sigma$ of 0.02.

For thirty five samples, size $> 0.125$ mm, mean density was $\rho = 2.69$, with a standard deviation $\sigma$ of 0.12. This shows a uniformity of material in the two grain sizes. From the variance of the difference of the means, statistically, the two size fractions are of the same origin. These samples which a density value lying outside one standard deviation from the mean were:

(a) All the samples from the Five Forks area. These grains - of the angular type with pitted surfaces - have a mean density of 2.5. However from chemical analyses they do not appear to be deficient in iron.

(b) Some of the grains from the zone of weathering in the road cutting at Taihao (50F) have a density as low as 2.52, but values for unweathered grains lie close to the mean. There was no significant difference in density between rounded and platy grains in these samples.

(c) In the Middle Waipara (MW) section samples from the top of
the section - marl, glauconitic siltstone, bentonitic mudstone - have $\rho = 2.70$, while samples from the lower green-sand beds have $\rho = 2.80$. This correlates with the increase in total iron content of these lower beds.

No particular colour significance has been found relative to the density measurements, colour having been found to vary with the ratio of ferric to ferrous iron present. For example, some of the darkest glauconites are from the Earthquakes (00), but these are found to have one of the lowest total iron contents (20%), and density measurements at, or below, the mean. Consider also the WF samples which have a low iron content (13.5%), a mean density of $\rho = 2.70$, and a dark colour.

Valetton (1958) found that, in general, a low refractive index correlated with a low density. This would of course be so if refractive index varied as iron content, and density also varied as iron content, but in this survey the awkward exceptions such as the FF samples preclude a definite correlation.

### 7.4 Magnetic Susceptibility $\chi_m$

On separating the grains of glauconite magnetically with the Franz Isodynamic separator it is observed that the current required for separation varies from sample to sample: there is however often a greater variation in the grains in the same sample than between different samples, making it difficult to compare samples by this method. From measurements taken during magnetic separation and using the equation

$$\text{mass susceptibility} = \frac{2 \sin \phi}{I^2} \times 10^{-5} \text{ c.g.s.u.}$$

where $\phi = \text{side slope of magnet}$

$I = \text{r.m.s current (amps.)}$

$\chi_m$ was found to lie between $2 \times 10^{-5}$ and $4 \times 10^{-5}$ c.g.s.u. for all samples.

More accurate measurements were taken using the Gouy
Fig. 20
method in which a glass tube of internal cross section A, filled with the finely powdered specimen, is suspended in a magnetic field so that one end is in a position of maximum field $H$ and the other in a minimum field $H_0$. Then the force on the sample is

$$F = \frac{1}{2} A (H^2 - H_0^2) \chi_m$$

Corrections are applied for the susceptibility of the glass tube and the volume susceptibility of the air displaced by the sample. By the use of a standard sample, Co$_2$Hg(CNS)$_4$, with known susceptibility ($\chi_m = 16.44 \times 10^{-6}$ c.g.s. units), the measurement of $(H^2 - H_0^2)$ is eliminated. The field in this case was of the order of 8000 gauss and the force on the sample measured by the displacement of a "settler balance capable of measuring to $10^{-5}$ gm.

Uniform packing of the powder sample, of < 50 $\mu$ grain size, is the weakness of this method, making it necessary to repeat all measurements many times until satisfactory repetition within 3 per cent is obtained. All measurements for this project were repeated at least five times, to obtain good statistics. Susceptibility of eight samples, each of which had been fully analysed, was measured and the results plotted against the iron Fe$^{3+}$ content, Fe$^{2+}$ having no unpaired electronic spins.

It is seen from Fig. 20 that apart from 0RP 3 the points fall on two nearly parallel lines.

Regression analyses of $\chi_m$ on Fe$^{3+}$ concentration (c) for these gives

$$\chi_m = 11.84 + 9.41 c$$

and

$$\chi_m = 9.80 + 8.93 c$$

for the samples 4640, MW 15, 6035, 5621

and

Kc 1, RT and 5392, respectively.

The corresponding correlation coefficients are

$$r = 0.99845$$

and

$$r = 0.99899.$$ 

The difference between these regression lines is effectively only that of the additive constant.
Attempts to account for the discrepancy physically, by consideration of the effects of other ions, bonding, etc., have been unsuccessful, as were similar efforts to include CRB 3.

Making the unlikely assumption that the parallelism of the lines is merely fortuitous, a regression line

\[ \chi = 15.3 + 7.25 c, \]

with correlation coefficient 0.99599 provides a reasonable fit to the data, with the exception of CRB 3.
8. EFFECTS OF WEATHERING

It was obvious on working with glauconites that the hardness varied considerably from sample to sample, greater hardness being generally attributable to grains of better ordered glauconite. Some simple weathering tests were made on a few samples to ascertain the differences in breakdown rates.

8.1 Mechanical Weathering

Four grams each of >\(\frac{1}{2}\)mm : <\(\frac{1}{2}\)mm grains of samples BR 1, BR 2, RT and WR 15 were each stirred by a milk shake mixer with 10 grams of glass balls ( >\(\frac{1}{4}\)mm ; <\(\frac{1}{4}\)mm) for (a) 10 mins. (b) a further 30 mins., and dried and sieved and weighed after each operation, with the following results:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sieve sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;(\frac{1}{2})mm</td>
</tr>
<tr>
<td>All initially</td>
<td>4.00 gms.</td>
</tr>
<tr>
<td>BR 1</td>
<td>10 mins.</td>
</tr>
<tr>
<td></td>
<td>further 30 mins.</td>
</tr>
<tr>
<td>BR 2</td>
<td>10 mins.</td>
</tr>
<tr>
<td></td>
<td>further 30 mins.</td>
</tr>
<tr>
<td>RT</td>
<td>10 mins.</td>
</tr>
<tr>
<td></td>
<td>further 30 mins.</td>
</tr>
<tr>
<td>WR 15</td>
<td>10 mins.</td>
</tr>
<tr>
<td></td>
<td>further 30 mins.</td>
</tr>
</tbody>
</table>

Great differences are apparent. The grains of BR 1 have been composed of loosely bound smaller particles. During disaggregation microscopic grains of quartz and calcite were also released.

Sample BR 2 was found to contain about 5 per cent free
quartz: a quarter of the total has been broken to smaller size, surprisingly more than for RT, which is a very soft material. Only Wi 15 has suffered very slight breakdown.

The main disaggregation was achieved in all cases in the first ten minutes of mixing.

8.2 Chemical Weathering

The glauconite grains of BR 2, RT, and Wi 15, remaining greater than 1 mm. in size after the above treatment, were divided into portions of 0.6 grams and left for twelve months in each of the following solutions:

(1) HCl at pH 3.4.
(2) phosphate solution, a mixture of 158.4gm. of $\mathrm{KH}_2\mathrm{PO}_4$ and 89.7gm. of $\mathrm{Na}_2\mathrm{HPO}_4\cdot2\mathrm{H}_2\mathrm{O}$, at pH 6.50
(3) 0.05 M. $\mathrm{Na}_2\mathrm{BO}_3\cdot10\mathrm{H}_2\mathrm{O}$, at pH 9.2.
(4) $\mathrm{NaOH}$ at pH 10.5.

The pH values were remeasured at three monthly intervals and if necessary the solutions replaced.

After the first three months, solution (1), initially at pH 3.4, had increased to 7.7 in Wi 15, 7.5 in BR 2, 4.3 in RT. This was replaced by a stronger acid solution, pH 1.7, which remained for the rest of the year.

Solution (2), phosphate, turned slightly yellow with RT, and solution (3), borate, very yellow with RT.

Solution (4), pH 10.5, needed continual replacement as the pH had dropped each time especially with RT whose initial drop was to pH 4.6. (As this solution and solution (1) were not buffered, changes in pH were to be expected.)

After a year in these solutions the glauconites were removed, washed and dried, and surveyed under the microscope for surface changes.
MW 15. The surface shape of all samples was unchanged, but there was pale material on each sample, being most prominent on the phosphate and borate soaked grains. MW 15 was the least susceptible to chemical attack.

PR 2. This showed much more reaction. Only with the acid solution was the surface smooth and intact, and even with this, the colour change to a pale apple green was pronounced. In all the other solutions the grain surface was pitted and completely covered with paler material, the effect being strongest with the phosphate treated grains which were beginning to disintegrate, and least with the borate treated grains.

RT. The acid and phosphate soaked grains appeared unchanged in form or colour. The alkaline solution had not changed the outward appearance of the grains but cracks were developing across the cleavage faces. The grains soaked in borate solution had disintegrated completely.

These results illustrate the non-uniform behaviour of glauconites. MW 15 and PR 2 have very similar chemical compositions (page 33) and are both well ordered glauconites, yet PR 2 has suffered very much from chemical attack while MW 15 is almost immune. Either the crystallites of MW 15 must be larger and more firmly bound together, or the cement which initially bound them more completely replaced by glauconite in this sample. It was surprising that the surface of RT was so little changed by all but the borate solution. RT is very soft, impure, and full of cleavage planes, and would seem a good subject for attack.

8.3 Chemical plus Mechanical Weathering

To conclude this test the grains, which had been tested as in 8.1 and 8.2, were once more stirred in the milk shake mixer with the glass balls for ten minutes.
Little change. Six per cent of the borate soaked grains and two per cent of the grains from the other solutions were now less than \( \frac{1}{2} \) mm. (All grains initially were \( > \frac{1}{2} \) mm.)

About ten per cent of the grains from all solutions were now less than \( \frac{1}{2} \) mm.

About ten per cent of the acid and borate soaked grains were now less than \( \frac{1}{2} \) mm.

Eighty five per cent of the borate soaked grains were now less than 62 microns.

Fifteen per cent of the grains soaked in NaOH were less than 62 microns and forty per cent less than \( \frac{1}{2} \) mm.

### 8.4 Changes in Chemical Composition due to Weathering

MW 15 was chosen as a sample of a mature glauconite and submitted to the following tests. Half gram samples, ground to \( < 62 \mu \) were put in solutions of

1. **Borax**, \( \text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O} \) 0.05 M

2. **Phosphate solution**, \( \text{H}_2\text{PO}_4 \) 158.4 gm., \( \text{Na}_2\text{HPO}_4 \) 89.7 gm., pH 6.50,

3. **0.2N NaOH**, and kept at 70°C for 240 hours, then left for two months to stabilise at room temperature. Potassium, sodium and total iron contents, for both the \( < 2 \mu \) and the \( > 2 \mu \) fractions of the glauconite, were then measured by the methods described in the section on chemical analysis.
<table>
<thead>
<tr>
<th></th>
<th>Potassium (K₂O)</th>
<th>Sodium (Na₂O)</th>
<th>Iron (total oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Borax solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2μ fraction</td>
<td>6.6</td>
<td>1.2</td>
<td>21.6</td>
</tr>
<tr>
<td>&gt;2μ &quot;</td>
<td>6.7</td>
<td>0.7</td>
<td>22.2</td>
</tr>
<tr>
<td>(2) Phosphate solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2μ &quot;</td>
<td>7.0</td>
<td>0.7</td>
<td>21.7</td>
</tr>
<tr>
<td>&gt;2μ &quot;</td>
<td>7.8</td>
<td>0.7</td>
<td>23.0</td>
</tr>
<tr>
<td>(3) NaOH solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2μ &quot;</td>
<td>5.9</td>
<td>1.8</td>
<td>17.1</td>
</tr>
<tr>
<td>&gt;2μ &quot;</td>
<td>6.6</td>
<td>1.6</td>
<td>18.5</td>
</tr>
<tr>
<td>MW 15 initial</td>
<td>7.6</td>
<td>0.2</td>
<td>23.0</td>
</tr>
</tbody>
</table>

The smaller grain sizes are more affected by each solution than the larger ones, and the sodium content has risen in all cases. To remove spurious sodium and potassium readings due to the solutions, all the samples were washed six times in distilled water using a centrifuge for precipitation. Iron content has been reduced by all solutions but most drastically by the strong NaOH solution. In general the results show that the final chemical composition of a glauconite, especially of the finer grains, could be due to the nature of percolating ground water.
9. X-RAY DIFFRACTION STUDIES

Like the clays, glauconite has in general a very small crystal size - less than one micron - making optical examination of the mineral very uncertain. X-ray diffraction methods have, however, proved to be a powerful tool for the investigation and identification of this type of material, and by their application much reliable X-ray data is now available on most clays and micas. Much of this is readily accessible, published in "The X-ray Identification and Crystal Structures of Clay Minerals" (edited G. Brown).

Burst (1958) classified four types of glauconites as follows:

- Ordered, denoted 1M
- Disordered, denoted 1Nd
- Interlayered
- Mixed mineral

The polymorphic classification follows that of Smith and Yoder (1956) for micas, the identification of these types being made from X-ray diffractograms.

Much investigation has been made into the nature of glauconite using X-rays, leading to the following conclusions, summarised from Hower (1961), upon which there has been general agreement.

1. All glauconites are interlayered to some extent.
2. Interlayering is between non-expandable 10A illitic layers and from 5 to 40 per cent expandable montmorillonitic layers.
3. Vermiculite and chlorite layers are not usually found (but this may be due to lack of identification of chlorites, which, when poorly crystallised, decompose on heating, and do not give the characteristic X-ray lines by which they are recognised).
4. The percentage of expandable layers varies inversely with the potassium content.
Ordered 1M glauconite has <10 per cent expandable layers.
Disordered 1Md glauconite has 10 to 20 per cent expandable layers.
Interlayered glauconite has >20 per cent expandable layers.

2.1 Methods of X-ray Investigation

It is now standard practice to study clay minerals with an X-ray diffractometer giving quickly on a chart recorder a measure of position and intensity of the diffracted X-ray beam. Two types of sample are used,

(a) a random powder mount for investigation of the general structural characteristics of the clay.

(b) an oriented slide upon which clay particles of the order of their crystal size (<1μ) settle from a suspension with their flat sides parallel to the slide, thus enhancing (001) reflections.

With the addition of glycerol, KCl, and by heat treatment of these slides, observation of the subsequent changes in position and intensity of lines, permits the nature and amount of expandable material to be ascertained. These were in general the methods used by workers on glauconites to obtain the conclusions listed in the previous section.

As no X-ray diffractometer was available here, most of the X-ray work was restricted to powder photography, using two 114.33mm. diameter Debye-Scherrer powder cameras with a Philips P.W.1010 generator. However, by the courtesy of the Geology Department, University of Otago, Dunedin, and the Geological Survey Office, Lower Hutt, the author was able to use their diffractometers to obtain the results in Section 9.3.
9.2 Powder Photographs

Glauconite grains were ground to pass through a 270 mesh sieve, and loosely packed in a Lindemann glass tube. This does not give a completely random distribution of crystallites, as the flakes of glauconite tend to lie parallel in the tube, thereby enhancing the (h00) and (0k0) reflections. However, this was thought to be the best compromise, as any form of rolling enhances the (001) reflections, and these are adequately measured from the diffractograms obtained from oriented slides.

Two pair of powder patterns are given in Fig. 21, two patterns each for Cu and Fe radiation. Iron fluorescence from the sample makes the photographs taken with Cu radiation very dark, but as it takes two days or more with the less intense Fe radiation to bring up the weaker lines, most of the exposures were made with Cu radiation.

The reflection from the (001) plane shows as a strong clear line on the well ordered glauconites, Figs. 21a and 21c, but becomes broad and indeterminate on the less ordered glauconites, as in Figs. 21b and 21d, due to the 10A layers being inter-stratified with other clay minerals. The (003) reflection tends to be broad, probably due to the proximity of (022) at 3.36A; a reflection due to (002) is discernible only on the films from the well ordered glauconites.

It is seen that reflections from (020) and (060) are sharp and clear on all films. Reflection from (060) is forbidden for two layer micas with space group C2/c (Hendricks and Jefferson, 1939). Consideration of this fact has led Badoslovich (1961) to the conclusion that dioctahedral muscovite is distorted by rotation to ditrigonal instead of hexagonal symmetry in the tetrahedral network.

A weak sharp line at 2.26 to 2.27A can be attributed to (040) as it is present on all films regardless of the sharpness of
(001), therefore it cannot be due to (221). With increasing order in the crystals other reflections become more clear, such as (112) and (112). The (200) reflection is present in all patterns, but always tends to be broad.

While these powder photographs do not give reflections of a true random powder, and are of doubtful use in comparing true intensities, they can be readily used to check variations in unit cell dimensions, especially the \(a\) and \(b\) dimensions.

2.2.1 Measurement of the \(a\) dimension

From measurements of the (400) reflections and rarely present (600) reflections, from well ordered glauconites, the unit dimension in the \(a\) direction was found to be between 5.22 and 5.23A; with increasing disorder the \(a\) dimension increases to 5.26A for the samples FF 5 and BR 1. However, as in the case of the \(b\) dimension, other factors must come into play, since samples such as 6035 and RT have small \(a\) dimensions despite their disorder.

2.2.2 Measurement of the \(b\) dimension

Measurements of the clear reflection of (060) were taken giving a determination of the unit length in the \(b\) direction. It is believed that this length is dependent on the nature of the cation in the octahedral layer. Brindley and MacEwan (1953) considered the \(b\) dimension as the arithmetic mean of (1) the tetrahedral \(b\) dimension calculated from the known Si-O and Al-O bond lengths, and (2) the octahedral \(b\) dimension based on the observed changes in this dimension in aluminium, magnesium and iron hydroxides. The resulting formulae gave good results for most clays and micas, but it was pointed out by Radoslovich and Norrish (1, 1962) that the model proposed was too simple and among other omissions did not allow for the effect of interlayer cations. In a series of six papers, (denoted I - VI), Radoslovich and coworkers have set out to elucidate the structure of the layer lattice silicates. Paper II gives formulae connecting the \(b\) dimension with
chemical composition. These formulae were obtained by the multiple regression analyses of X-ray data and ionic proportions as given by the structural formulae. These analyses indicate that the value of \( p \) does not depend on the amount of Al substituting for Si in the tetrahedral layer, but only on the interlayer and octahedral cations, a significant difference from the ideas of Brindley and MacEwan.

The formula given by Radoslovich and Norrish for micas is:

\[
p = (8.925 + 0.099K - 0.069Ca + 0.062Mg + 0.116Fe^{2+} + 0.096Fe^{3+} + 0.166Ti) \pm 0.03 \text{ Å}
\]

This formula was used for three well ordered glauconites whose structure had been calculated (page 49), namely MW 15, FR 2 and 5621, the results being:

<table>
<thead>
<tr>
<th></th>
<th>( p ) observed (Å)</th>
<th>( p ) calculated (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW 15</td>
<td>9.08</td>
<td>9.15</td>
</tr>
<tr>
<td>FR 2</td>
<td>9.08</td>
<td>9.17</td>
</tr>
<tr>
<td>5621</td>
<td>9.09</td>
<td>9.16</td>
</tr>
</tbody>
</table>

showing a discrepancy of 0.07 Å between observed and calculated values. It is only fair to say that the formula recognised that these differences exist, and the paper states that celadonites do not conform, as their octahedral layer is charge deficient, and the layer probably disproportionately thick. This deficiency of octahedral charge is also present in glauconites and the observed \( g \) dimension is - for these well ordered samples - about 10.05 Å (cf. 9.99 Å muscovite, 9.98 Å illite). Thus the octahedral layer could be expanded by 0.06 Å in the \( g \) direction and in consequence contracted in the \( b \) direction.

Table 7 gives the \( b \) dimensions of twelve other glauconites as calculated from the (060) dimension.
Also given are the sum of percentages of total iron and potassium oxides in the glauconites. Magnesium, the only other significant cation in the formula of Various, is considered as a constant. Ionic proportions were not available for many of the samples, therefore, actual percentages had to be used in this instance. It is seen that the \( b \) dimension is not directly dependent on the cations alone, but that some with small total Fe plus \( K \) content do also have a small \( b \) value.

Comparison of the \( b \) dimension with the charge deficiency in the lattice was also attempted, but no correlation was found.

It is evident that a complex situation exists and governs the unit cell dimensions in this mineral. This is not at all surprising when one considers both the lack of purity and probable multiplicity of origin.

In the following pages, in Table 8, are listed reflections observed on powder photographs for a number of glauconites. The powder photograph has the advantage over the diffractometer in that the weaker reflections are much more easily recognisable and measurable. Intensities are given and, where possible, reflections are classified.
**Abbreviations used in defining intensities**

<table>
<thead>
<tr>
<th>L.H.S</th>
<th>R.H.S</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>m</td>
<td>b</td>
</tr>
<tr>
<td>w</td>
<td></td>
</tr>
<tr>
<td>vw</td>
<td></td>
</tr>
<tr>
<td>vvw</td>
<td></td>
</tr>
</tbody>
</table>

\[ + \text{ or } - \] above a letter denote a greater or lesser degree.
<table>
<thead>
<tr>
<th>(hkl)</th>
<th>FF 5</th>
<th>IR 1</th>
<th>5392</th>
<th>4640</th>
</tr>
</thead>
<tbody>
<tr>
<td>020</td>
<td>4.55 s s</td>
<td>4.55 s s</td>
<td>4.55 s s</td>
<td>4.53 s s</td>
</tr>
<tr>
<td>101</td>
<td>4.38 w s</td>
<td>4.42</td>
<td>4.34 w s</td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>3.68 w b</td>
<td>3.66 w b</td>
<td>3.69 vw b+</td>
<td>3.64 m b-</td>
</tr>
<tr>
<td>003</td>
<td>3.34 m s</td>
<td>3.36 m s</td>
<td>3.33 w b+</td>
<td>3.33 m b-</td>
</tr>
<tr>
<td>112</td>
<td>3.13 w b-</td>
<td>3.10 vw b</td>
<td>3.10 w b</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.60 s b-</td>
<td>2.60 s b-</td>
<td>2.60 s b-</td>
<td>2.59 s b-</td>
</tr>
<tr>
<td>201</td>
<td>2.40 m b-</td>
<td>2.42 m s</td>
<td>2.43 m b+</td>
<td>2.40 m b-</td>
</tr>
<tr>
<td>040</td>
<td>2.28 w s</td>
<td>2.29 w s</td>
<td>2.28 vw b+</td>
<td>2.27 w s</td>
</tr>
<tr>
<td></td>
<td>2.22 vw s</td>
<td>2.22 vw s</td>
<td></td>
<td>broad band</td>
</tr>
<tr>
<td>005</td>
<td>1.99 w b+</td>
<td>2.00 w b+</td>
<td>2.00 vw b</td>
<td>1.99 vw b+</td>
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<td>1.80</td>
<td>vw s</td>
<td>1.72 w s</td>
<td>1.72 vw s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.66 w b+</td>
<td>1.65 w b</td>
<td>1.66 w b+</td>
<td>1.60 vw s</td>
</tr>
<tr>
<td>060</td>
<td>1.520 m+ s</td>
<td>1.526 m+ s</td>
<td>1.520 m s</td>
<td>1.515 s s</td>
</tr>
<tr>
<td>1.504</td>
<td>vw s</td>
<td>1.51 w b-</td>
<td>1.506 vw</td>
<td>1.501 vw s</td>
</tr>
<tr>
<td>1.315</td>
<td>w b-</td>
<td>1.314 m b-</td>
<td>1.308 m b-</td>
<td></td>
</tr>
<tr>
<td>1.26</td>
<td>vw</td>
<td>1.27 w s</td>
<td>1.263 vw</td>
<td>1.256 w b-</td>
</tr>
<tr>
<td>0.986</td>
<td>w s</td>
<td>0.990 vw</td>
<td>0.873 vw</td>
<td></td>
</tr>
</tbody>
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### Table 8

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>Mw 13 Uw</th>
<th>Ccuw</th>
<th>EG 2</th>
<th>VF 1</th>
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<tbody>
<tr>
<td>020</td>
<td>4.54 s</td>
<td>4.54 s</td>
<td>4.53 s</td>
<td>4.54 s</td>
</tr>
<tr>
<td>101</td>
<td>4.35 w</td>
<td>4.36 w</td>
<td>4.35 w</td>
<td>4.33 w</td>
</tr>
<tr>
<td>112</td>
<td>3.65 w b^-</td>
<td>3.66 w b</td>
<td>3.65 w b</td>
<td>3.66 m b</td>
</tr>
<tr>
<td>003</td>
<td>3.32 w+ b^-</td>
<td>3.33 w b</td>
<td>3.33 w b</td>
<td>3.33 m^- b</td>
</tr>
<tr>
<td>112</td>
<td>3.09 w b^-</td>
<td>3.10 w b</td>
<td>3.07 w b</td>
<td>3.08 w b</td>
</tr>
<tr>
<td>200</td>
<td>2.59 s b^-</td>
<td>2.59 s b</td>
<td>2.58 s</td>
<td>2.59 s b^-</td>
</tr>
<tr>
<td>201</td>
<td>2.41 m b^-</td>
<td>2.41 m^- b</td>
<td>2.42 m b</td>
<td>2.40 m b^-</td>
</tr>
<tr>
<td>040</td>
<td>2.27 w s</td>
<td>2.27 w s</td>
<td>2.26 w s</td>
<td>2.27 w s</td>
</tr>
<tr>
<td></td>
<td>2.21 vv s</td>
<td>2.21 vv s</td>
<td>2.21 vv s</td>
<td>2.21 vv s</td>
</tr>
<tr>
<td></td>
<td>2.15 w b+</td>
<td>2.17 vv b</td>
<td>2.14 w b</td>
<td>2.15 vb w</td>
</tr>
<tr>
<td>005</td>
<td>2.0 w b+</td>
<td>1.98 w vb</td>
<td>2.0 w vb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.79 vv s</td>
<td></td>
<td>1.72 vv</td>
<td>1.71 w s</td>
</tr>
<tr>
<td></td>
<td>1.67 w b+</td>
<td>1.66 vv</td>
<td>1.65 vv</td>
<td>1.66 w b+</td>
</tr>
<tr>
<td></td>
<td>1.592 vv s</td>
<td></td>
<td></td>
<td>1.60 vv s</td>
</tr>
<tr>
<td>060</td>
<td>1.515 s s</td>
<td>1.516 m</td>
<td>1.509 m s</td>
<td>1.514 s s</td>
</tr>
<tr>
<td></td>
<td>1.496 vv s</td>
<td>1.498 vv s</td>
<td>1.493 vv s</td>
<td>1.494 w s</td>
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<tr>
<td>(400)</td>
<td>1.308 m s</td>
<td>1.309 w b</td>
<td>1.309 w s</td>
<td>1.308 m s</td>
</tr>
<tr>
<td>(260)</td>
<td>1.260 vv</td>
<td>1.255 w</td>
<td>1.252 vv</td>
<td>1.260 w s</td>
</tr>
<tr>
<td></td>
<td>1.211 vv</td>
<td></td>
<td></td>
<td>1.206 vv</td>
</tr>
<tr>
<td></td>
<td>0.985 vv</td>
<td>1.054 vv</td>
<td>0.981 vv</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.873 vv</td>
<td>0.882 vv</td>
<td>0.869 vv</td>
<td></td>
</tr>
</tbody>
</table>
9.3 Oriented Aggregates

Electron microscope photographs (page 86) indicate that the crystal size of most glauconites is $< 1 \mu$, and therefore to obtain well oriented slides for use in an X-ray diffractometer particles of this size should be used. Oriented slides of this size fraction of glauconites were accordingly prepared by grinding, and diffractograms for these obtained on the Philips X-ray diffractometer at the Geology Department at the University of Otago, using quartz as a standard for the 3$\alpha$ region and a zeolite, Linde 4A powder (synthetic) with (100) at 12.32$\alpha$ and (110) at 8.706$\alpha$ as a standard for the lower angle region. Diffractometer settings were: rate meter 8, time constant 4 sec., for all but MW 15 and IR 2 where the rate meter setting was 16. Scanning rate was 1$^\circ$ per minute.

Traces were obtained for twenty four glauconites with known chemical differences. Diffractometer patterns of oriented slides enhance basal reflections and are important in determining degree of crystallinity and interstratification with other minerals. Where these are present - and Hower (1961) states that all glauconites contain both 10A illitic layers and expandable montmorillonitic layers to some extent - the (001) 10A peak becomes less sharp and more asymmetric. With increasing clay content asymmetry is a feature of the low angle side of this peak when montmorillonite clays are present, and of the high angle side of the (003) peak. Burst (1958) published diffractograms showing clearly (1) the sharp symmetrical peaks at 10A and 3.3A and the presence of a 5A (200) peak for ordered 1Md glauconites; (ii) weakening, broadening and asymmetry of the peaks and the resurgence of the 4.54A (020) peak in the 1Md disordered type; and (iii) curves for interlayered glauconites in which the 10A peak is smeared to a greater $d$ value, indicative of a swelling material, while the other peaks are small, broadened and irregular.
Fig. 22

X-ray diffraction patterns of oriented glauconites.
9.3.1 Diffractometer Traces for Glaucconites

Fig. 22 shows traces obtained for six glauconite samples, together with their measured potassium content. It must be remembered that peak intensities are comparable only in the same trace and not from sample to sample owing to varying thickness of scattering material on the slides.

It is clear that sharpness and symmetry fall off with decreasing potassium content. Those samples with broader asymmetric peaks were treated by saturating with glycerol, left overnight, then X-rayed again. In most cases, although the (001) peaks were considerably sharpened, there was only a slight difference in the low angle side of the peak and no pronounced 17.7A peak typical of glycerol saturated montmorillonites. Heating to 550°C, however, always collapsed the layers of samples not treated with glycerol until a sharp symmetrical peak occurred.

The poor response to glycerol treatment in some of the low potassium glauconites raised the question as to whether there could also be chlorite or vermiculite interlayered with the glauconites. Vermiculite was considered most likely as well ordered chlorites do not collapse to 10Å on heating, although some disordered chlorites will break down completely above about 450°C.

Galligher (1937) proposed a theory of glauconite formation by the alteration of biotite, which necessitates a change via vermiculite if the observed pattern of biotite weathering is adhered to. To check for the possible presence of vermiculite, oriented slides were made of Mg saturated RCM 5, RT and ORB 7, the first two being of particular interest with regard to the biotite theory, as they occur in laminated vermicular pellets which suggest biotitic (or other micaceous origin). As ORB 7 was the only low potassium glauconite of obviously microfossil origin in the survey — disregarding recent sediments — this sample was also chosen for investigation. Only for Mg saturated sediments is the non-swelling property of vermiculite treated with glycerol fully substantiated.
2.3.2 Results for Mg Saturated Glaucnites

With an Mg saturated slide, clays are differentiated as follows:

(1) Mg-montmorillonites, (a) expand on treatment with glycerol to about 17.7A.
    (b) Collapse on heating to 550°C, to about 10A.

(2) Mg-vermiculites, (a) initially give a strong 14A peak and a very weak 7A peak.
    (b) do not expand beyond 14.5A when saturated with glycerol.
    (c) Collapse to less than 10A on heating to 550°C.

(3) Chlorites, (a) initially give a medium 14A reflection and a strong 7A reflection.
    (b) do not expand with glycerol saturation.
    (c) on heating above 550°C, the 14A is enhanced.
    (d) Treatment with HCl will dissolve the chlorite, thus removing the reflections from it.

(4) Kaolinites, (a) initially give a strong 7A reflection, which
    (b) disappears on heating to 550°C.

ORB 7: Initially, gives a very broad peak, 9.9 to 11.1A, very asymmetric on the low angle side. No 7A or 14A peak is present.

Glycerol saturation shifts the broad peak to cover 9.5 to 10.1A. There is no appreciable peak in the 17.7A region, but most of the trace between 10A and 17A is brought down to background level.

Heating to 550°C gives a sharp peak at 10.05A.

Most of the clay interlayered with the glauconite ORB 7 is therefore of the expanding type, probably montmorillonite.
RCW 5: Initially, has a broad peak 10.5 to 11.2A, asymmetric on the low angle side; and a small peak at 7A. Glycerol saturation creates only a small peak at about 18A. The main 10A peak is considerably sharpened at 10.05A, and the 7A peak remains. Acid treatment was applied to test for chlorites, by adding 1:1 HCl at 80°C for 15 minutes. The integrated intensity of the 7A peak was reduced by one third. Heating to 550°C intensifies the sharpness of the 10A peak and eliminates the 7A peak.

The clay interlayered with the glauconite in RCW 5 is partly of the expanding montmorillonitic type, partly chloritic, and partly kaolinitic.

RT: Initially, shows a peak at 10.5 to 10.8A. A very small 14A reflection is present but none at 7A. Glycerol saturation shifts the broad peak to cover 9.8 to 10.1A. A small 17.6A peak appears. Heating to 550°C sharpens the 10A peak to 10.0A, cutting out small peaks which were present on the low angle side of this peak.

Most of the clays interlayered with RT are of the expanding type, with a small amount of vermiculite.

These glauconites were saturated with magnesium to detect the presence of vermiculite. A positive reflection at 14A was found only for RT, and this was very small. However, some chlorite was present in RCW 5. Therefore both the glauconites in the vermicular pellet form do have some 14A material present.

2.4 Classification of Glauconites from Oriented Slides

In general it was found that the slides used were well oriented, suppression of other than basal reflections being almost complete. None of the glauconites examined contained a greater amount of expandable material than of illitic material, and
most qualify for the 1st classification, i.e., 10 to 20 per cent expandable layers. The only ones which could be classified as 2nd, i.e., <10 per cent expandable layers are:

(1) Tt, from Hurunui, a Tongaporutuan glauconite.
(2) Coal Creek sample, CCW; COB 2 from the Cobden limestone, and 4640 (on the lower limit) ... all Duntroonian deposits
(3) HR 2, from Broken River.
(4) Sample 5621, probably Mangaloan.
(5) Upper Cretaceous deposits MW 5, MW 11 and MW 15 - for which diffractograms were made - and probably the other Middle Waipara beds of high potassium content, but definitely excluding beds above MW 5.

These show that high crystal order is not confined to any special era, but is a function of conditions in the locality concerned.

A great deal of effort has been made by previous workers to correlate variations in glauconitic composition with time of deposition. Smulikowski (1954) and Conway (1942) agree that Tertiary and Recent glauconites are deficient in potassium and have attributed this to changes in the chemistry of the ocean as a whole. The results obtained above, showing that ordered glauconites occurred over widespread times in the Tertiary, do not support this theory. They do, however, further the ideas of Hower (1961), that results have been misconstrued through inadequate sampling, and that the lithology of the accompanying sediments is of greater importance and has more bearing on the final state of glauconitisation. The 1st glauconites cited above, except those from the Middle Waipara, are found in quartzose or calcareous sediments. The lower greensand beds in the Middle Waipara, from which most of the upper ones are presumably derived, are mixed with mainly quartzose material, but also have some other argillaceous sediment present, especially feldspars.
Hower correlates order of crystallisation of glauconites with the lithology of the accompanying sediments and finds that 1M glauconites and those of the highest 1Md classification occur almost exclusively in sandstones in which the detrital grains are mainly quartz, quartzite, or chert and the cement is silica or carbonates; he also asserts that disordered glauconites occur with argillaceous sediments, often feldspathic, and with marls. This again leads to the conclusion that the Middle Taipara deposits may not be authigenic.

2.4.1 Basal spacings for 1M Glauconites

From the results obtained these can now be said to consist largely of illitic material. Basal spacings for the samples above were calculated to be 10.05Å from the (003) measurements on the diffractograms.

2.4.2 Formula of a 1M Glauconite

Many formulae have been calculated for glauconite, most of which endeavour to encompass a large number of chemical analyses. As glauconites are now known to be interlayered with other clay minerals, it would seem reasonable to calculate a formula only for glauconites which can be classified as 1M.

Using the structural analyses (Table 4, page 42) for the samples BR 2, MW 15, 4640 and 5621, all well ordered glauconites, the structural formula for a 1M glauconite is

\[(\text{OH})_4(\text{K}_{1.4} \text{H}_{0.6-0.8})(\text{Mg,Fe}^{2+})_{0.9-1.4}(\text{Fe}^{3+}\text{Al})_{2.5-2.9}(\text{Si}_{7.1-7.6}\text{Al}_{0.6-0.9})_{20}\]

2.4.3 1Md Glauconites

Curves have been produced by Hendricks and Teller (1942), MacEwan (1958), and Weaver (1956) for expected intensities and migrations of basal reflections, due to random interstratification of clay minerals. Using these curves it is possible to estimate the proportion of each clay type present. Measurements were made from diffractograms of peak positions of some of the
glauconites classified as 1Md. These are given below in Table 9.

**Table 9** PEAK POSITION FOR 1Md GLAUCONITES

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>(001)A</th>
<th>(001) with glycerol A</th>
<th>001 heated A</th>
<th>(003)A</th>
</tr>
</thead>
<tbody>
<tr>
<td>WELA</td>
<td>10.05-10.30</td>
<td>-</td>
<td></td>
<td>3.32-3.36</td>
</tr>
<tr>
<td>EQ 2</td>
<td>10.05-10.2</td>
<td>-</td>
<td></td>
<td>3.34</td>
</tr>
<tr>
<td>V 3</td>
<td>10.2</td>
<td>10.05</td>
<td></td>
<td>3.35-3.36</td>
</tr>
<tr>
<td>WF 2</td>
<td>10.05-10.3</td>
<td>9.6-10.04</td>
<td></td>
<td>3.33-3.36</td>
</tr>
<tr>
<td>MV 2</td>
<td>10.3</td>
<td>-</td>
<td></td>
<td>3.32-3.34</td>
</tr>
<tr>
<td>ORB 2</td>
<td>10.3</td>
<td>10.0</td>
<td></td>
<td>3.34-3.36</td>
</tr>
<tr>
<td>ORB 5</td>
<td>10.3</td>
<td>9.7-10.0</td>
<td></td>
<td>3.33-3.35</td>
</tr>
<tr>
<td>6035</td>
<td>10.3-10.5</td>
<td>-</td>
<td></td>
<td>3.32-3.39</td>
</tr>
<tr>
<td>HR 1</td>
<td>10.2-10.8</td>
<td>10.05</td>
<td></td>
<td>3.30, 3.32, 3.34</td>
</tr>
<tr>
<td>ROW 1</td>
<td>10.4-11.3</td>
<td>10.03</td>
<td>10.05</td>
<td>3.33-3.40</td>
</tr>
<tr>
<td>ROW 5</td>
<td>10.5-11.2</td>
<td>9.6</td>
<td>10.05</td>
<td>3.30-3.36</td>
</tr>
<tr>
<td>ORB 7</td>
<td>9.9-11.1</td>
<td>9.7-10.0</td>
<td>10.05</td>
<td>3.30-3.35</td>
</tr>
<tr>
<td>RT</td>
<td>10.5-10.8</td>
<td>9.8</td>
<td>10.05</td>
<td>3.30-3.36</td>
</tr>
</tbody>
</table>

From the formulae of Hendricks and Teller, Weaver estimates that for a 10/12.4A random interstratification, 20 per cent of 12.4A material may be expected to shift a 10.0A peak to 10.3A, and a 3.33A peak to 3.31A.

Peaks for the first seven samples in Table 9 are all within these limits of peak shifting, and therefore contain less than 20 per cent of a 12.4A material. The other five show more complexity, many of them showing a broadening of the (003) line in both directions. This could be due to 10/14A mixtures. With water, montmorillonite takes up basal spacings of about 12.4, and 15.4A for most interlayer cations. Random mixtures of both these spacings with a 10A micaceous basal spacing tend to shift a 3.33A peak to smaller values. The broadening of the (003) line to a greater value typical of 10/14A interstratification, was an added reason for studying the vermicular pellets in ROW 5 and RT in the Mg saturated form, and for the further study of the structure of this type of grain by X-ray precession techniques.
9.5 X-Ray Studies of Vermicular Pellets

Since the paper by Galligher (1937) on the transformation of biotite to glauconite in Monterey Bay, this method of formation has always been given credence, though seldom enthusiastically, as a method of forming large greensand deposits. Pellets of the type referred to by Galligher have been found in generous numbers in some of the samples collected for this project, all in a restricted time range. These pellets of the vermicular type, pictured on page 62, by slight crushing, afford many cleavage flakes for further study.

At first, it was considered by the writer that these pellets could be the result of passage of clay sized glauconitic 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 a direction, and subsequent hardening completing the process. Such a mechanism could be possible where many polychaetes flourished. Even if faecal pellets had not survived, it was thought that material remaining in the animal after death would have a good chance of preservation.

However, clay material aligned in this way would certainly not be aligned in the a and b directions also, whether it were initially glauconite, or other clay sized grains subsequently altered to glauconite. Here, then, is a means of checking whether these particular pellets were formed from a collection of randomly oriented submicroscopic clay particles, or as Galligher suggests, by the alteration of some larger crystal form such as biotite.

9.5.1 Precession Camera Photographs

To check the existence of single crystals, and, simultaneously, the order of these, a Ruerger X-ray precession camera from the Physics Department, University of Canterbury, was used, samples being flakes split directly from the vermicular
pellets, and mounted with the X-ray beam perpendicular to the (001) plane. In the precession camera, (Buerger 1944), by the combination of two oscillation motions, at right angles and 90 degrees out of phase, the normal to the lattice plane being photographed always maintains a constant angle with the X-ray beam. By this means, the lattice plane always intersects the sphere of reflection in a circle of constant diameter, and when a photographic film is placed parallel to the reciprocal plane being photographed the pattern recorded on the film is that of the undistorted reciprocal plane. Flakes from the samples RT, RCW 5, 5392, 6035, and FF, from the > 4 mm. size fraction but measuring from 0.025 to 0.05 mm. in the c direction, were mounted on glass fibres and aligned on a goniometer head in the camera. On alignment zero level photographs similar to Fig. 23 were obtained. Fig. 23a shows the clear cut reciprocal lattice pattern of the (001) plane from the RCW 5 sample, which contains 6.7 per cent K₂O, and is relatively well ordered. Fig. 23b shows the pattern from 5392, to which those of 6035, RT and FF are similar, where the smeared spots indicate a certain amount of disorder and disalignment of the a and b axes. These samples are, however, lower in potassium content, and more highly disordered and interlayered than those of RCW 5. Comparing these results, however, with Fig. 23c which was obtained from a flake of glauconite formed by random sedimentation from a suspension of < 1 μ material, shows clearly the difference between random orientation, and alignment of the a and b axes. Flakes from these vermicular pellets can therefore be considered to be aligned in the a and b directions; it is therefore claimed that these particular glauconites were formed by the alteration of some other existing crystal, not from an accumulation of clay sized particles.

As these samples represent collection areas about forty miles apart, and this type of grain forms 50 to 90 per cent of the glauconite in prominent greensand deposits, it is felt that this definite pointer to their origin is of some importance. Significantly, all of these beds (except the Tungalooan sediments at Five
Forks) were deposited at about the same time, in the Bortonian-Kaiatan stages. Each is the first glauconitic deposit in its area, following the marine transgression after the peneplanation of metamorphic deposits in this area during the Cretaceous.

A specific source of materials to be changed into glauconite of this form is not so easy to envisage. The researches of Weaver (1958) show that biotite is the most likely initial material for this type of transformation. Petrographic studies by Amies (1952), of the metamorphic rocks, whose erosion formed the peneplain upon which Tertiary marine sediments were laid, showed that sericite and chlorite are universally present, also dense aggregates of white mica, but biotite is mentioned only in the phrases "sericite and chlorite also occur as pseudomorphs after clastic biotite, relics of which are sometimes preserved". If this glauconite is formed from sericite or muscovite or chlorite, which are ubiquitous, why is there little of this type of glauconite in the later greensands? If the source material is considered to be muscovite, it is known that a degraded muscovite will quickly collapse to 10Å when saturated with potassium ions from sea water (Weaver 1958). However, this collapse takes place very quickly - in fifteen hours - and does not allow for the more gradual transition to a 10Å lattice which is found in glauconites. Chlorite, too, presents problems when considered as a parent for glauconite, being a 14Å lattice, very stable to heat in its better crystallised forms. Little work has been reported on the decomposition of chlorites by various solutions, but this would be an interesting project as there is possibility in the area containing these glauconites, of contact with volcanism. The Tapui beds from which the PT samples were taken are intruded by many sills and dykes (Gage 1951). The Kaiarekan volcanics, thought to be Kaiatan in age, intruded extensively in the Camaru district, and volcanic action also took place at about this period in the environs of the Hampden Formation from which 6035 is taken. No evidence of volcanism is evident in the Vaihao area,
and the Waiarekan tuffs are missing, but Allan (1926) states that there is a marked palaeontological break above the greensand, and postulates a period of uplift during the time of the Waiarekan volcanics. Other micaceous minerals degraded by volcanism could therefore be the source material for widespread glauconites in the North Otago - South Canterbury area, the same volcanism assisting in providing of the reducing environment necessary to release iron from the sediments for incorporation in the crystal lattice.

If biotite is considered essential for transformation to glauconite, it is necessary to proceed further inland to the metamorphosed rocks of Central Otago as a source. Green biotites are most characteristic of the potassic green schists in the east of the Wakatipu region, and are often quite important constituents of these rocks. (Hutton, 1940) These biotites, by analysis were, however, found to be rich in ferrous iron, and would therefore be trioctahedral, necessitating a drastic change in octahedral occupancy to enable a dioctahedral glauconite to be formed. This could be achieved by removing the ferrous iron, which is not difficult in biotites (page 120), and refilling the layer with ferric ions, which would require more acid conditions, unless colloidal ferric hydroxide is attracted directly into the starved lattice. This is one of the enigmas of glauconite formation; why no tendency exists towards trioctahedral occupancy if some are formed from biotites, and points to the iron being taken in initially, mainly in the ferric form, rather than by a slow transition from ferrous to ferric. As the changes in biotites on weathering are seen to be substantial (page 121), and the octahedral iron to be loosely held, the original form of octahedral occupancy would, with this type of mechanism, be unimportant compared with the later history of the lattice.
2.6 Crystal Dimensions

From the X-ray precession photographs, measurements can be made of the unit cell dimensions of the crystals. This is the first recorded time that single crystal X-ray studies have been made of glauconites. Measurements of the \(a\) and \(b\) dimensions were made from photographs similar to those reproduced in the figures, and it is seen that some of the patterns do not produce clear lines capable of very accurate measurement. However, sufficient were able to be measured in the \(b\) direction to give a result as accurate as that from the powder photographs, as the \((060)\) reflection was sharp and narrow in these photographs also. The reflections in the \(a\) direction again lack definition, although \((200)\) is again strong as in the powder photographs.

2.6.1 Measurements in the \(a\) Direction

To include the \(a\) direction in the results necessitated lining up one of the other axes with the camera spindle axis, by a number of setting photographs, then rotating the crystal about this axis until the \(a\) axis and the other axis required either \(a\) or \(b\) were both perpendicular to the X-ray beam. Two types of photograph were obtained from these settings and are reproduced in Fig. 24. Again the spots are spread into lines, due to disorder, but two types of result are clear and interesting.

(a) Fig. 24(a) shows the most common type of result, from ten of twelve flakes. In the \(a\) direction strong 10A lines, \((001)\), \((003)\), and a weaker \((005)\); with weak 14A lines appearing as \((002)\) and \((004)\) when the 10A lines are overexposed (18 hours with Cu radiation).

(b) Fig. 24(b) is characteristic of two very thin flakes, from 5392 and RCN 5. Here the lines are sharper but still spread, and some of the other reciprocal lattice points are appearing forming a criss-cross pattern. In the \(a\) direction there is a regular spacing of 24.6A, due to regular interlayering of a 10A (illite) lattice and a 14.6A 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 strong (004) of the 14.6Å lattice); (008) medium. These intensities agree with the structure factors for regular 10/14Å interlayering. Also discernible are faint reflections for a 10Å lattice and the strong (004) reflection for the 14Å lattice.

2.6.2 Measurements for the b Direction

For the thinner flakes with regular interlayering, the b dimension was 9.18 to 9.21Å, but for the more normal flake of mainly 10Å layers, the b dimension was 9.07 to 9.11Å. The larger b dimensions are typical of a vermiculite or chlorite, but are too large for even an iron-rich montmorillonite.

The a dimension, which was not as precisely defined, varied between 5.21 and 5.30Å.

2.7 Fine Material in the Sediments

Accompanying these Glauc nites

Powder photographs were also made of the <62μ portion of the accompanying sediments from RT, RTC 5, and FF. This could not be done for 6035 and 5392 as only the glauconite from these samples had been received. For the other three samples, however, the fine materials gave a constant pattern, with lines due to quartz, feldspars, and a definite 7Å clay line. When the RTC 5 fines were heated to 600°C and X-rayed, the 7Å line disappeared, and more definite evidence of diffuse reflection in the 10Å region was present, but not as a sharp line. As a further check on the components of these clays, oriented slides were made of the <1μ portion of the Mg saturated fines of these three samples for study on the diffractometer at Geological Survey Office, Lower Hutt.

Using the main criteria for clay recognition given on
page 73, the clay minerals were assessed as follows:

**FF:** A strong 7A reflection is present, with a weak 10A peak. Also present are reflections about the 12 and 15A region, which expand to 18A with glycerol treatment, thereby sharpening the 10A peak. Acid treatment has little effect on the 7A peak, but it disappears on heating to 550°C.

This clay mixture is, then, largely kaolinite, with montmorillonite and illite also present. The term "illite" is intended here to include 10A micas.

**RCW 5:** Again a strong 7A peak is dominant, with a weak 10A peak. Reflections in the low angle region, which are expanded to 18A with glycerol treatment, are present. A very weak 14A peak also appears. The 7A peak is not reduced by acid treatment, but disappears on heating to 550°C.

Again the clay is largely kaolinitic, with montmorillonite and illite present.

**BT:** Once more there is a strong 7A peak with a weak 10A peak, and low angle reflections which are expanded by saturation with glycerol. No 14A peak is present. The 7A peak is only slightly reduced by acid treatment, but disappears on heating to 550°C.

This clay also consists mainly of kaolinite, with montmorillonite and illite.

All three clays, then, are basically the same in composition, having kaolinite, montmorillonite and illite as the main constituents. Clays with 14A basal spacing are present but only as minor components. From the powder photographs measurement of (060) gives a d spacing of from 8.9 to 9.1A for the clays present. These figures confirm the results above.

The presence of 14A clays in the accompanying glauconites cannot be attributed to the fine materials of the sediments in
which they have developed, but must be a function of the alteration product of the micaceous crystals from which the glauconite originated.
10. ELECTRON MICROSCOPY

The electron microphotographs presented here, of glauconite grains finely ground and suspended in distilled water, were recorded from the electron microscope at Physics and Engineering Division, D.S.I.R., Lower Hutt, by Miss Marie Packwood.

Previous microphotographs of glauconites published by Burst (1958) indicate a lath-like grain shape in well ordered glauconites, and more equidimensional shapes in the disordered types. In the photographs reproduced here there is some tendency to elongate shapes of irregular dimensions. Individual grain sizes are not greater than about half a micron.

Figures 25 (a), (b) and (c) show photographs of grains of decreasing order of crystallinity. Single flakes are larger in UF 15 which is the best ordered glauconite of these samples and the small grains in this sample have a lath-like shape. Consideration of Figs. 25 (d) and (e), however, makes one cautious in interpretation. These are both photographs of finely ground grains which proved subsequently to consist of stacks of flakes which were single crystals — see previous section. The sample RT which is interlayered with montmorillonite and a little vermiculite gives an indeterminate picture, but RCW 5 has a large proportion of long sharp lath like grains. On page 74 RCW 5 has been shown to be interlayered with montmorillonite, kaolinite and chlorite. Most montmorillonite crystals are irregular in outline but nontronite, the iron rich montmorillonite, tends to occur in elongate lath-shaped units (Grim, 1953). Kaolinites do not usually occur in lath shapes, but favour a hexagonal outline. Lath like grains are not usually found in either vermiculites or chlorites — private communication, Soil Bureau, Wellington — and photographs published by Whitehouse, et al. (1958), show vermiculites to be large, very thin, equidimensional plates, and some
chlorites to be similar to vermiculites but smaller, thicker, and with ill defined edges. The quantity of this lath-like material in RGW 5 leads to the conclusion that this is due to cleaving of the larger glauconite crystals into needle shaped laths on grinding. This may also account for the results of Burst's investigations and it would seem worth while for some research to be carried out into exact crystal sizes in some of the better ordered glauconites... They may well prove to be larger than has been thought.
11. INFRARED ABSORPTION SPECTRA

Absorption of wavelengths in the infrared region of 1 - 25 microns signifies the use of absorbed energy in promoting vibrations of a molecule, and can therefore give information about the bonding between the atoms.

Absorption spectra of many rock forming minerals were recorded and published by Keller and Pickett (1948, 1949, 1952). These included carbonates, phosphates, and many silicates, including clay minerals, and it is evident that minerals of the same structural group have similar spectra, dominant features being due to bonds between oxygen and the cations present. With the main trends of the absorption spectra for mineral groups established, study soon turned to variations within groups of similar minerals, with the intention that this would be a simpler method of analysis than say chemical analysis. It was found for carbonates (Adler and Ferr, 1963), and sulphates (Miller and Wilkins, 1952), that change of the positive ion in a molecule causes a slight, but measurable shift of the absorption band.

In spectroscopy, theoretical investigations invariably lag behind experimental work, but a consideration of crystal symmetry and the use of group theory (Bethe 1929) will give a qualitative picture of expected vibrations and degeneracies...

Further understanding of the meaning of spectra can be gained from the physical properties of the ions involved; their mass, radius, charge and interatomic distances being important in the calculation of the force constant $k$ which is a measure of the binding energy involved. This has been demonstrated for simple atoms by Adler (1963). With silicates however, which consist mainly of coupled molecular groups, the situation is much more involved, although group theory has been applied to $\alpha$ and $\beta$ quartz (Saksena, 1940, 1949) and to various silicon oxygen groups.
Fig. 26  Typical Infrared Spectrum of Glaucnite.
(Matossi, 1949), showing how change in symmetry alters the expected vibrations.

### 11.1 Infrared Absorption Spectra of Glauconites

Initial spectra for glauconites previously chemically analysed by Hutton and Seelye (1944), were obtained on a Perkin-Elmer recording infrared spectrophotometer, Model 221, using NaCl optics. Samples consisted of powdered glauconite - 230 mesh - incorporated in a half inch KBr disc under a pressure of 10 tons p.s.i.

A typical infrared absorption spectrum is shown in Fig. 26. All the glauconite spectra are similar, showing absorption peaks at: 2.85 to 2.95 μ, weak: 6.15 μ, weak: 9 - 11 μ, very strong: 12.3 μ, weak: and probably at 14.4 μ at the end of the trace. A slight absorption at 11.4 μ in sample 6034, and the tendency for this to be present in other specimens, was taken to be an indication of the known strong absorption in this region of the better ordered members of the mica family. (Hunt et al. 1950).

#### 11.1.1 9 - 11 μ Region

There is a very strong absorption in this region in all silicates due to the vibration of the Si-O bond, α quartz having absorptions at 8.6 and 9.2 μ. Keller, Spotts and Biggs (1952) state that the absorption in this region shifts to longer wavelengths as the number of Al and other ions replacing Si in the tetrahedral assemblage increases. Milkey (1960), plots absorption peaks versus Al replacing Si in various silicates, and shows that this is so. The greater electronegativity of the silicon has more influence on the force constant than does the greater mass of the aluminium atom, causing the frequency of vibration to be less for aluminium than for the silicon which it replaces...The Si-O bond was calculated by Smith (1954), by the refinement of atomic parameters by successive Fourier series, to be 1.60 ± 0.02A, while that of Al-O was 1.78 ± 0.02A. The longer
Variation of infrared absorption with Al(tetrahedral)
bond would vibrate at a lower frequency, (longer wavelength).

Lyon and Tuddenham (1960) state that the shape of the absorption curve of micas in the 9 to 10μ region depends on the Al for Si substitution in the tetrahedral layer, and give curves to illustrate this. Unfortunately some of the crucial curves lacked supporting chemical analysis, and it was felt that further evidence was desirable. It was therefore of great interest to be able to test this theory on these analysed glauconites, still keeping in mind doubtful purity of glauconite samples. Fig. 27 shows this portion of the glauconite spectrum for three samples with different replacements of Al for Si, as derived from structural analyses. These samples were chosen as having the same percentage transmission at non absorbing frequencies, since it is impossible to compare curves under other circumstances. It is seen that the sample with the most Al ions replacing Si has the sharpest peak, and is less absorbing at the lower wavelengths, and that this set of curves gives some support to the theory above.

However, absorption in this region is also confused by the presence of the octahedral layer. The major bands in gibbsite Al(OH)₆ are at 9.78μ and 10.30μ (Nahin, 1955), and alumina absorbs with a weak peak at 8.6μ with progressively stronger absorption, till a maximum is reached at 13μ (Branc et al., 1957). To check the wavelength of the vibration of the Fe-O bond, absorption spectra were obtained of haematite, FeO, and magnetite, Fe₂O₄, which both absorbed weakly at 8.6μ and 10.3μ, with an extra very weak absorption at 9.25μ for haematite. Fresh iron hydroxide Fe(OH)₃ absorbed weakly and broadly at about 10.6μ and weakly at 13.9μ. It would be reasonable to allow that some of the absorption in the 9 to 10μ region in micas is due to all of these bonds. Substitution of other ions for Fe and Al would affect this only slightly, but distortions due to imperfect fitting of the tetrahedral and octahedral layers might be expected to alter these distances. Recent work by Radoslovich in pointing
out the great variation in cation-oxygen bond length in layer silicates in both the tetrahedral and octahedral layers, due to adjustments necessary to maintain equilibrium, makes the picture very complex indeed.

Adding to this the lack of knowledge of the ordering of replacement in both these layers, in nearly all phyllosilicates, there would appear to be much work to be done before this area of the infrared spectrum of these materials is fully understood.

11.1.2 2.8 - 2.9 μ Region

Absorption in this region is due to the OH stretching vibration which varies in frequency according to location and surroundings. While in vapours and liquids the direction of the OH bond is randomly oriented, the closer packing and symmetry imposed by crystals restricts the bond direction. By varying the angle of incidence of infrared radiation on mica flakes it has been deduced (Serratosa and Bradley, 1958, Bassett, 1960) that the OH bond in trioctahedral micas is perpendicular to the cleavage, but that the OH bond in a dioctahedral mica is inclined by the presence of holes until it is at a small angle to the cleavage. Furthermore, dioctahedral muscovite, which has trivalent aluminium as the octahedral cation, has a single absorption peak at about 2.78 μ, while trioctahedral phlogopite with divalent magnesium absorbs at about 2.70 μ. Some biotites intermediate between these two contain both divalent and trivalent ions, and absorb near both these wavelengths; the longer wavelength peak being constant with angle of incidence, as is found in muscovite, but the shorter wavelength peak altering in intensity with angle of incidence as in phlogopite. It is therefore suggested that these criteria indicate the different types of occupancy. (Serratosa and Bradley, Bassett).

Glaucophane has been accepted by all writers as a dioctahedral mica consisting of a ratio of about three trivalent octahedral cations to one divalent ion. It would then be expected
from the above to give two peaks in the 2.9μ region, both of longer wavelength than those due to muscovite and phlogopite, as

\[
\text{radius Fe}^{3+} > \text{radius Al}^{3+} \\
\text{radius Fe}^{2+} > \text{radius Mg}^{2+}
\]

This region has very poor resolution on the Perkin-Elmer Model 221 spectrophotometer but absorption at 2.65 and 2.95μ is clearly present in all samples, broadening to 3.5μ on the long wavelength side being due to hydrogen bonding. On the Model 421 grating spectrophotometer, with much greater resolution, the broadening is much more apparent as the wavelength scale is much expanded at this end. To ascertain whether this absorption and/or the hydrogen bonding was due to interlayer water - as free water absorbs at 2.7 to 2.9μ - a sample was heated to 180°C for two days, after which it gave the same spectrum as before. After heating at 210°C for a further 30 days the spectrum still showed considerable broadening due to hydrogen bonding. It is considered that all of the interlayer water should have been driven out at 210°C over 30 days and that the hydrogen bonding is not due to the interlayer water, but is present in the octahedral layer of the glauconite.

11.1.3 6.1μ Region

Absorption at 6.1μ was interpreted as the CH deformation vibration. Grim (1953) states that it is believed to be due to adsorbed water, but results from taking infrared spectra of heated samples (page 100) show that this absorption is still present at 900°C, and its disappearance coincides with the breakdown of the layered lattice structure. Therefore it is due to structural CH.
Interpretation of infrared absorption in clay materials is not simple, and their final meaning will not be determined until much more work is done on a high resolution instrument, on all types of fully analysed samples, whose structural distortion are fully known and understood. At the moment these requirements are out of reach.
12. DIFFERENTIAL THERMAL ANALYSIS, D.T.A.

Equipment for differential thermal analysis consists basically of a furnace in which the mineral under investigation and an inert material are heated side by side at a uniform rate, and a recorder upon which differences in temperature between the two substances are plotted with respect to time (i.e., temperature). These differences in temperature are due to a production or absorption of heat during a reaction within the sample.

In order to carry out this work it was necessary for the author to construct a differential thermal analysis unit, and develop it into reliable equipment. The following components were used:

Tube furnace, FS-700, 1 kw., with ceramic block and heating cell of type specified by Grimes, Heaton and Roberts (1945). This furnace is rather underpowered and lags the controller slightly, above 900°C.

Controller. This is an Ether Ltd. Transitrol which both controls and indicates temperature. Control is achieved by means of a motor driven cam which moves an arm in the indicating head of the instrument, at a uniform rate. When this arm coincides with the position of the temperature recording pointer an optical system is interrupted whose output is fed to a photocell. Variation in the output from this photocell is fed via a servo amplifier to the control winding of a saturable reactor, whose load windings are in series with the furnace heating element. The reactor presents either a very large or very small impedance to the mains supply, according as the control current is zero or finite, effectively switching the furnace off or on. "Funting" of the pyrometer needle can be made very fine by suitable adjustment of the controls, and the furnace control was measured to be linear.
within \( \pm 5^\circ C \) up to \( 900^\circ C \) for the D.T.A. results about to be described. Temperature differences were measured on a Cambridge recording millivoltmeter, \( \pm 1 \text{mv} \), using chromel - alumel thermocouples.

### 12.1.1 Sample Preparation

All samples were ground to pass a 230 mesh sieve and diluted with powdered calcined alumina - the inert material used - initially in the proportion of one part of sample to two parts of alumina. This dilution helps counteract base line drift, and was also thought necessary as some glauconites bake hard. The samples were kept in vacuo over saturated calcium nitrate solution for at least a week.

**Heating rate** was controlled at \( 10^\circ C/\text{min} \). The controller was found to hunt more efficiently when the controlling thermocouple was placed outside the heating block next to the furnace wall. This necessitated a separate thermocouple for reading the actual sample temperature as in a ceramic block large temperature gradients are present. The sample temperature was read on a potentiometer using a 35swg chromel - alumel thermocouple, placed at the centre of the sample. These operating conditions comply with those recommended as standard practice, as tabulated by Mackenzie (1957).

**The difference temperature** was also measured using 35swg chromel - alumel thermocouple wires. Use of this fine wire minimised heat conduction from the samples, but the thermocouples have a short life. This, however, is tolerable where only a few samples are under investigation.

Many initial difficulties were encountered. Spurious voltages, attributable to conduction in the ceramic block at high temperatures, were eliminated by placing an earthed nickel shield between the ceramic block and the furnace element. It was also found necessary to earth the equipment to the water supply, as the mains earthing was not sufficiently reliable.
FIG. 28a  Differential Thermal Analyses
12.1.2 Results of D.T.A.

With the dilution of the sample material by two parts of alumina, as originally intended, the recorder was not sensitive enough to give an accurate measure of peak temperature, but four samples were run through with this dilution to estimate the general trend of the response. Typical results are seen in Fig. 28(a) in the traces for Tt and ECW 1. Consideration of these traces shows three regions of change;

(1) 50 to 200°C., with a peak at about 120 to 140°C. This is the first endothermic peak, attributable to the gradual loss of interlayer water.

(2) 300 to 700°C., with peak at about 520 to 530°C. This, the second endothermic peak, is a very broad peak attributed to the loss of hydroxyl ions in the octahedral lattice. This peak is asymmetric, being sharper on the high temperature side.

(3) 800 to 1000°C. It is in this region that different glauconites responded differently, two giving an endothermic peak at about 900°C and two others an exothermic peak. These were however so small, that, added to the slight thermal drift results were uncertain. The remaining traces in Figs. 28 (a) and (b) were obtained with the samples diluted in the proportion of two parts glauconite to one part alumina, increasing the peak heights considerably, although it was felt that a more sensitive recorder would have been desirable for a material with such broad peaks.

All the glauconites show the first endothermic peak at 130 to 140°C, and the second at 530 to 540°C, all the peaks being broad. This uniformity is probably due to uniform sample preparation and packing, and makes the results of one operator, comparable. However, with D.T.A. work, comparison with results from other workers is not often possible, unless operating conditions are well known.
FIG. 28b  Differential Thermal Analyses

- RT
- 5621
- RCW 5
- S.A.G

Temperatures: 135°, 540°, 880°

Degrees C.: 0 to 1000
Major differences in results would not be expected for the first two peaks, but the region above 550°C is likely to show deviations, as this is the region of bond adjustment in the octahedral layer where occupancy varies greatly. At these higher temperatures great structural changes take place in the micas, previous dehydration having made slight differences to interatomic distances, but not to crystal structure. Structural breakdown commences above 800°C and is complete at about 900°C, a spinel being formed.

Samples MW 15, ORB 3, and Tt. all show the third endothermic peak at about 920°C. Both MW 15 and Tt were baked hard and consolidated at 1000°C and shrink in the holder, but ORB 3 was still soft and unconsolidated, as were all the remaining samples which were heated. These were also much softer initially, than the better crystallized MW 15 and Tt. It would seem from this that the better ordered glauconites either form better ordered spinels, or that the glassy phase due to silica plus alkalis appears at a lower temperature in these samples, binding them together. Subsequent hardness does not seem to be a function of iron present in the sample, and cannot be due to initial ordering alone, as 5621 with a high potassium content is also soft after heating, and has a higher endothermic peak at 965°C. As well as being low in magnesium this sample is lower in silicon and higher in aluminium than, say, MW 15.

There is no peak for RCW 5 in the high temperature range, and the overall curve approaches those given for hydrobiotite in Mackenzie (1957). Sample RT has a slight exothermic peak at 880°C. This is a characteristic peak position for vermiculites and is a further indication of interlayering. This sample also has a tendency for a second peak in the low temperature region, just above 200°C, which is also characteristic of vermiculites. The last trace in Fig. 28 is for the South African glauconite, discussed in Section 4, and shows marked differences from our
### Table 10 X-ray Powder Lines for Glaucnite Heated to 1000°C.

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(Å) I</th>
<th>d(Å) I</th>
<th>d(Å) I</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
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<td>4.04</td>
<td>3</td>
<td>4.84</td>
<td>3.36</td>
</tr>
<tr>
<td>022</td>
<td>2.96</td>
<td>6</td>
<td>2.98</td>
<td>2.97</td>
</tr>
<tr>
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<td>2.53</td>
<td>10</td>
<td>2.53</td>
<td>2.52-2.53</td>
</tr>
<tr>
<td>222</td>
<td>2.42</td>
<td>1</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>2.09</td>
<td>7</td>
<td>2.10</td>
<td>2.095</td>
</tr>
<tr>
<td>224</td>
<td>1.712</td>
<td>4</td>
<td>1.712</td>
<td>1.711</td>
</tr>
<tr>
<td>(1 1 5)</td>
<td>1.611</td>
<td>8</td>
<td>1.617</td>
<td>1.615</td>
</tr>
<tr>
<td>(3 3 3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>1.441</td>
<td>9</td>
<td>1.424</td>
<td>1.483</td>
</tr>
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<td>1.327</td>
<td>2</td>
<td>1.328</td>
<td>1.326</td>
</tr>
<tr>
<td>3 3 5</td>
<td>1.280</td>
<td>4</td>
<td>1.281</td>
<td>1.275</td>
</tr>
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<td>1</td>
<td>1.266</td>
<td>1.275</td>
</tr>
<tr>
<td>114</td>
<td>1.211</td>
<td>1</td>
<td>1.212</td>
<td>1.209</td>
</tr>
<tr>
<td>24 6</td>
<td>1.122</td>
<td>4</td>
<td>1.122</td>
<td>1.121</td>
</tr>
<tr>
<td>(1 3 7)</td>
<td>1.094</td>
<td>8</td>
<td>1.093</td>
<td>1.088-1.091</td>
</tr>
<tr>
<td>(3 5 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>006</td>
<td>1.050</td>
<td>5</td>
<td>1.049</td>
<td>1.048</td>
</tr>
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<td>0.990</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
fossil glauconites. The first endothermic peak is at a lower temperature, the second at a higher temperature, and the high temperature peak is much sharper. Reported peak temperatures for glauconites recorded by Mackenzie and Grim (1953) do show wide differences in peak temperatures for both glauconites and celadonites, but the differences shown here are nevertheless interesting, when the constancy of peak temperatures for other samples is taken into account.

Micas are reputed to have also an exothermic peak at 900 to 1000°C. A tendency towards this is shown by NW 15, but other samples do not exhibit an exothermic peak within the 1040°C upper limit of the furnace. As this peak has been associated with the appearance of spinel, four samples, NW 15, RT, 5621, and RCW 5 were X-rayed after heating to 1000°C. The powder patterns (Fe radiation) for NW 15 and RT are shown in Fig. 29.

12.1.3. Sample NW 15 after heating to 1000°C

This becomes consolidated to a hard dark brown mass which gives the values of \( \chi \), for Fe radiation, shown in Table 10. Comparison with \( \chi \) values and intensities for magnetite \( \text{Fe}_3\text{O}_4 \), and magnesioferrite \( \text{MgFe}_2\text{O}_4 \) (Berry and Thompson), show that the resulting mineral is of spinel structure. Intensities for the narrower spacings are much lower than those for the standard minerals, and the lines tend to be broad, but the heated glauconite closely approaches magnesioferrite. This was a well ordered potassium rich glauconite and the structural analysis gave an \( \text{Fe} : \text{Mg} \) ion content approaching 2:1, the ratio for magnesioferrite. This then would seem to be the criterion for a well ordered spinel after heating; a ratio of \( \text{Fe} : \text{Mg} \) compatible with that necessary for filling the spinel lattice in an ordered fashion.

12.1.4. Sample 5621 after heating to 1000°C

This gives only weak diffuse lines of spinel structure, though not quite as diffuse as those of RT in Fig. 29. This
Fig. 30
sample, though potassium rich and well ordered, has only a small quantity of MgO, and both RT and 5621 have a Fe: Mg ratio of about 5:1. In X-ray powder photographs for both RT and 5621 (heated) faint haematite lines are present, this apparently being the disposal mechanism for the excess iron. Sample RCW 5, interesting because of its different origin, gave a pattern similar to RT, but the haematite lines were very faint. As this sample has not been fully analysed chemically in this case no conclusions could be made about the significance of the Mg: Fe ratio.

12.1.5 Infrared Absorption Spectra of Heated Glauconite

To tie in with this work, a sample of WW 15, an example of well ordered 1M glauconite, was heated and an infrared absorption spectrum obtained at each of five different temperatures, 270, 600, 800, 950, and 1000°C, pertinent to the D.T.A. results. The breakdown of the cation-OH bonds and the change in the Si-O bonds were of great interest. These samples were also X-rayed as powder samples.

For the infrared spectra the sample was heated to the required temperature, maintained at this temperature for ten minutes, mixed with Nujol on being taken from the furnace, and the spectrum recorded immediately on the Perkin-Elmer 221 infrared spectrophotometer. The change in the hydroxyl bonds on heating is illustrated in Fig. 30 for both the OH stretching vibration at 2.9 μ and the OH deformation vibration at 6.1 μ. Consideration of the shape of each trace as the wavelength is increased shows that there is still some evidence of these bonds at 800°C, showing that they are present at a much higher temperature than was thought previously. Grim and Bradley (1948), presenting differential thermal analyses of clay minerals, which have been heated to various temperatures, and allowed to stand at room temperature for different periods of time, attribute the presence of the second endothermic peak (about 500 to 600°C) to rehydration of the lattice. Unfortunately they do not appear to
Fig. 31

Transmittance vs. microns for temperatures:
- 1040 °C
- 950 °C
- 800 °C
- 600 °C
- 270 °C
have done a D.T.A. run on the samples immediately after heating. It is possible, especially for the illite samples, that some of the water attributed to rehydration had never, in fact, left the lattice.

Absorption in the 8 to 13 μ region, Fig. 31, shows a gradual flattening of the peak in the 9.5 to 10.5 μ portion, and the additional distinction of a 12.8 μ absorption as the temperature increases. It is not easy to compare traces of infrared spectra, but transmission conditions for these were reasonably constant, and it is felt that a true picture is shown here of the changes in this region. In the powder patterns of the 15 heated to 1040°C, faint quartz lines are present. This will account for the increased absorption in the lower wavelengths in this spectral range, and also for the ascendancy of the 12.8 μ absorption peak, as a very small amount of quartz has a very high absorption in this region.

### 12.1.6 X-ray Powder Photographs of Heated Glaucconites

From X-ray powder patterns of these heated samples (Fig. 32), it is seen that only at 900°C is the structure showing signs of change. By the time 600°C has been reached the p unit cell dimension has decreased from 9.08 to 9.03Å and the g dimension is also decreased by 0.01Å. The (001) line is still very strong and sharp, and the layered silicate lattice is still supreme. The (112) and (112) reflections, which by their sharpness in the original sample helped to define it as a well ordered glauconite, are now missing, however. At 900°C the lines are beginning to broaden, especially (200), and by the time 950°C has been reached the change over to the spinel structure is complete. At this temperature the sample is still soft and powdery, but when it has reached 1000°C, it is hard, and very dark in colour. The X-ray powder patterns are still the same and the hardness probably caused by the fusing of the silica.
12.2 The Effects of Natural Heat Treatment

In the Broken River district, 1½ miles downstream from the bridge over Broken River, on the Main West Coast Road, a basalt dyke about twelve feet wide intrudes a bed of glauconitic quartz sand. This offered an ideal opportunity for investigating the effect of such an intrusion on the structure of glauconite for comparison with the effects of heating only, as examined in the laboratory, and described in the previous section.

**Sampling**: Continuous sampling of the first twelve inches from the western contact of the dyke with the quartz sand was carried out. Three samples were taken at one foot intervals from the outermost of these, and a control sample of the glauconitic bed taken at a distance of twenty five feet from the dyke. All samples were sieved into size fractions, and inspected with the binocular microscope. The control sample of the original glauconitic bed consists of unconsolidated fine quartz, ninety per cent of which is less than 1 mm., and glauconite of the same size. Not more than ten per cent of the sample is glauconitic, although this, like many other samples, appears very green to the eye. X-ray powder photographs of this glauconite show typical glauconite lines with no obvious impurities.

12.2.1 Effect of Heating by the Basalt Dyke

For the first six inches from the dyke the loose quartz sand has been welded into a sandstone with a calcareous cement. Instead of the green glauconite a blackish material is present. Further out from the dyke the bed was less firmly compacted, with less black material and more green glauconite, until, at three feet from the dyke the calcareous component is very small, there are few dark grains and in content the bed approaches that of the original greensand. Near the dyke the quartz and other materials are partly fused together. The grain size of the quartz in the altered beds is less than that of the
unaffected beds.

Thin sections of the samples show a considerable amount of calcite in the region affected by the dyke. As there is no calcareous material in the original greensand the calcium and the $\text{CO}_2$ must have been provided by the intrusive material of the dyke.

The dark material was separated from each sample with the Franz magnetic separator and was seen under the microscope to vary in colour from dark grey to black.

X-ray powder photographs were taken of this dark material. It was surprising to see on these, that the 10A reflection was weak, but a strong line was present at 7A, indicating a change in the basic structure of the glauconite. Weak lines for pyrite, and strong lines for quartz were also present.

Diffractometer traces were made of the dark material from a sample six inches from the dyke. From an oriented slide of less than 1 $\mu$- particles, the results were:

Untreated: A strong broad reflection is present at about 14A; also medium peaks at 10A and 7A.

Glycerol treatment: The strong peak shifts to about 18A; a weak peak is isolated at 14A. The 7A and 10A peak remain as before.

Acid treatment: The 7A peak disappears.

This material is identified as an iron rich chlorite which dissolves easily in HCl, plus an expanding montmorillonitic clay, plus some original 10A material. From measurements of broad lines on the powder photographs,

\[ a = 5.12 \text{ to } 5.22 \text{A}, \text{ and } b = 9.04 \text{ to } 9.12 \text{A} \]

which generally cover the values for ferric chamosite,

\[ a = 5.25 \text{A} \quad b = 9.10 \text{A} \]

(Brindley and Youell, 1953).
and nontronite, an iron rich montmorillonite

\[ a = 5.14 - 5.26 \text{Å} \quad b = 9.12 \text{Å} \]

(quoted by MacGowan, 1961),

and also a glauconitic lattice.

As it has been demonstrated in the previous section that heat alone will not produce these changes, they must be due to the vapours and solutions from the intrusive magma. The 7Å line is a feature of powder photographs for material up to at least two feet from the dyke. Material from the contact with the dyke shows a very, very weak 7Å line and a weak 10Å line plus diffuse radiation at lower angles. The strong lines on the film are due to quartz, calcite and feldspars, and a little pyrite is also present.

The results above, which are as comprehensive as can be obtained with the facilities available, show that under conditions which promote metamorphism in rocks, the pre-existence of glauconite in a sediment before metamorphism would not be suspected, as it would have been changed into iron rich forms of other clay minerals, particularly chlorite, at temperatures lower than it can withstand when subjected to heating alone.

Much interesting and possibly informative work could be done with this line of study, were an X-ray diffractometer available for detailed analyses of the clays successively out from the dyke.
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Latitude South</th>
<th>Longitude East</th>
<th>Depth in Fathoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 107</td>
<td>35° 58.0'</td>
<td>176° 5.0'</td>
<td>124</td>
</tr>
<tr>
<td>B 12</td>
<td>39° 22.2'</td>
<td>177° 42.5'</td>
<td>37</td>
</tr>
<tr>
<td>B 151</td>
<td>39° 32.1'</td>
<td>177° 46.9'</td>
<td>63</td>
</tr>
<tr>
<td>B 155</td>
<td>40° 01.2'</td>
<td>177° 22.0'</td>
<td>177</td>
</tr>
<tr>
<td>B 154</td>
<td>40° 20.8'</td>
<td>177° 11.6'</td>
<td>100</td>
</tr>
<tr>
<td>B 153</td>
<td>40° 38.2'</td>
<td>177° 01.6'</td>
<td>88</td>
</tr>
<tr>
<td>C 508</td>
<td>40° 39.0'</td>
<td>177° 03.5'</td>
<td>410</td>
</tr>
<tr>
<td>C 512</td>
<td>40° 40.0'</td>
<td>176° 56.9'</td>
<td>390</td>
</tr>
<tr>
<td>C 506</td>
<td>41° 14.4'</td>
<td>176° 09.2'</td>
<td>75</td>
</tr>
<tr>
<td>C 505</td>
<td>41° 15.3'</td>
<td>176° 11.6'</td>
<td>420</td>
</tr>
<tr>
<td>C 488</td>
<td>41° 37.0'</td>
<td>175° 39.2'</td>
<td>260</td>
</tr>
<tr>
<td>C 487</td>
<td>41° 39.6'</td>
<td>175° 35.2'</td>
<td>260</td>
</tr>
</tbody>
</table>
Fig. 33 Location of Recent sediments.
13. RECENT GLAUCONITES

Initially four samples from the present ocean bottom were supplied by Oceanographic Institute, Wellington, numbered by the Institute, A 107, B 151, B 154, and B 155. Later, eight further samples were received which gave a greater coverage of East Coast sediments. The locations of these samples are shown in the map, Fig. 33, and detailed in Table 11. A 107, which is not shown on the map is from farther north, east of Great Barrier Island.

All of these samples from off the East Coast were divided into two portions, > 62μ, and < 62μ and the amounts in each fraction weighed as given below.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Depth (fathoms)</th>
<th>%wt &lt;62μ</th>
<th>%wt &gt;62μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 12</td>
<td>37</td>
<td>62</td>
<td>18</td>
</tr>
<tr>
<td>B 151</td>
<td>63</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>B 155</td>
<td>177</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>B 154</td>
<td>100</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>B 153</td>
<td>88</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>C 512</td>
<td>390</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>C 508</td>
<td>410</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>C 505</td>
<td>420</td>
<td>94</td>
<td>0</td>
</tr>
<tr>
<td>C 506</td>
<td>75</td>
<td>57</td>
<td>43</td>
</tr>
<tr>
<td>C 487</td>
<td>260</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>C 488</td>
<td>260</td>
<td>67</td>
<td>13</td>
</tr>
</tbody>
</table>

It is seen that the amount of fine material varies greatly in samples from the same depth, and that a sediment from a greater depth does not necessarily contain more fine material than sediments from shallower locations.
FIG. 34 Location of Recent glauconitic sediments.


13.1 Examination with the Microscope

Under the microscope great variation in sediment content was found. B.151 - the furthest north of the East coast sediments - is about 50% pumice and glass, the remainder being foraminifera, many of which are filled with glauconite and in the process of peeling from it, and free glauconite, some dark green and some brown (phosphatic).

B.153, B.154, C.512, C.508 represent sediments from more complicated bottom contours (Fig. 32).

B.153 contains large calcareous sediments with large grains of glauconite, some brown and phosphatic. Many small foraminifera are present. B.154 has smaller grain size than B.153, many small foraminifera filled with green material, a few phosphatic grains; all glauconite is clearly of foraminiferal origin.

C.508 and C.512, both from about 400 fathoms, show large differences. C.508 has about equal amounts of dark green glauconite, foraminifera and broken glassy siliceous material, including pumice and sponge spicules, whereas C.512 has very little glauconite, and this is small in grain size and glassy in appearance. There is more pumice present in this sample and many small foraminifera.

C.506 (75 fathoms) and C.505 (420 fathoms) from the same coastal region differ mainly in grain size, C.506 being full of large lumpy glauconite, and C.505 mainly containing small broken pieces clearly redistributed. In both, the accompanying sediments are similar, being quartz, foraminifera and echinoid spines.

C.487 and C.488, from the same area and depth show differences in glauconitic content. Both are highly glauconitic. C.487 contains dark green, highly veined, large grains of glauconite with a background mainly consisting of quartz, a few large
foraminifera, and a few pieces of pumice. The fines are glaucono-nitic and calcareous. C 486 on the other hand, contains all pale and earthy glauconite, none of it veined, and smaller than that of C 487. Other material present consists of many small foraminifera, sponge spicules, echinoid spines, and many broken glassy fragments. The fines are glauconitic, but not as calcareous as those of C 487.

A study of the first four samples obtained, showed further that there is considerable variation in glauconites, and that it does definitely form inside foraminifera and other micro-fossils. Treatment with dilute HCl shows that even those solid forams which are outwardly unperturbed are completely filled inside with a non-calcareous solid, sometimes of a flaky nature, ranging from white to a pale yellowish green in colour. This was present even in A 107, a highly glauconitic sediment in which the glauconite is very dark rounded and polished, probably attributable to globigerina casts, and surrounded by clean glassy fragments and other small fossils giving the impression that the glauconite was not formed among this particular sediment, but is the finished product of some other environment which has been transported from its original site. The material from inside the A 107 foraminifera was isolated and X-rayed as a powder photograph, and found to consist of a mixture of low plagioclase feldspars. The (11T) and (711) for albite were not present and (040) was broad. The presence of a line at 4.54A, (020) for clays, and the smearing of radiation in the low angle region indicates the presence of some clays also.

13.2 Composition of Recent Glauconite

As samples B 154, B 154a, B 155 are all taken from off the East Coast of the North Island where glauconite is a prominent component of the land mass, the glauconite in these samples could be either authigenic or detrital. However, one
particular sample B.155 can safely be considered as containing authigenic glauconite. This sample consists of about half pumice and glassy material, the other half being foraminifera and echinoid spines filled with glauconite, together with free glauconite obviously of foraminiferal origin (see frontispiece). The glauconite freed from the enclosing fossil is a dark green, but that still enclosed is of a paler colour, some being almost white. The whitish grains, when released from the fossil with dilute HCl, are distinctly paramagnetic and separate out with the green grains in the Franz magnetic separator.

Measured iron contents were:

<table>
<thead>
<tr>
<th>Total iron oxides</th>
<th>Paler immature grains</th>
<th>16.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mature green grains</td>
<td>24.4%</td>
</tr>
</tbody>
</table>

A number of single whitish grains were also tested singly for the presence of iron and gave a strong positive reaction.

Although the iron content of the pale grains is less than that of the mature ones it appears that a substantial iron content is an initial component of glauconite. This agrees with the findings of Fhlman, Hulings and Glover (1963), and indicates that the iron is not attracted slowly to replace aluminium, as the low lattice charge theory of Hower (1961) predicts, but that a large amount of the iron is attracted to the lattice immediately the degraded structure finds itself in a new environment to which it must adjust.

Potassium content decreases from 4.0 to 3.6 per cent K₂O in the paler grains. It was thought that the pale colour of the immature grains could have been due to a large ferric/ferrous iron ratio, but the measured percentage of ferrous oxide present was 1.7 per cent, giving a ferric/ferrous iron ratio of 10:1, which is usual for a dark mature glauconite.

Ferric iron content was also measured for three other recent samples from which sufficient glauconite could be separated to provide the half gram needed for this
untreated.

glycerol saturated.

heated 550°C

14.7 Å

17.7 Å

10 Å

Fig. 35
Diffractograms of B155.
measurement. The results were remarkably constant, being:

- C 487, 1.7 per cent; A 107, 1.8 per cent; C 508, 1.6 per cent.

These measurements, plus that of 1.7 per cent for B 155, led to the conclusion that ferrous iron content must be a function of the ocean as a whole rather than of the very local conditions. It would be interesting to be able to compare this result with the ferrous iron content of other glauconites from the ocean bed in other parts of the world.

13.3 X-ray Results for the Glauconite in B 155

Samples of B 155 were first X-rayed using the Debye-Scherrer powder cameras. Basal reflections were diffuse, but others were positive. The (200) reflection was very broad, but both (020) and (060) were quite sharp for both the whitish and the darker green material. Measurements of the (060) lines gives a \( d \) value of 9.16A, rather greater than that of a matured glauconite, for which \( d \) is 9.08A. Also present in the powder photographs of the immature grains were faint lines due to plagioclase feldspars. No 7A reflections were present.

Diffractometer traces for oriented slides of the portion of the immature material were also obtained, and can be seen in Fig. 35. Untreated material gave a large peak at 14.7A, and a small 10A peak. On treating with glycerol the 14.7A peak expanded to 17.7A peak, which, on heating, collapsed to 10A. Clearly most of the less fraction of this sample is an expanding clay of montmorillonitic dimensions. If, as it appears from this evidence, glauconite originates as an expanding type lattice, it is advisable at this point to consider what adjustments are necessary to encompass the change to the illitic structure typical of glauconite. If the expanding clay is considered as montmorillonitic, a change to glauconite would involve great changes in ion occupancy. In the montmorillonite lattice there is little replacement of Si by Al in the tetrahedral layer. Most
of the charge deficiency is found in the octahedral layer, and the interlayer cations, K\(^+\), Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), are less strongly bound than tight fitting K\(^+\) ions which are present between illitic layers. It has been shown (Hutton and Seelye) that a glauconite treated with progressively stronger HCl at last breaks down to gelatinous silica, any calcium present being lost easily, and the magnesium ions more easily than the iron. It can be envisaged that a degraded clay in an acidic environment iron would be retained more strongly than magnesium, and potassium more strongly adsorbed than other interlayer cations. It would, however, be hard to see how there could be further replacement of Si by Al in a montmorillonite at a pH of 6 or 7, as aluminium is at these values practically insoluble and therefore not available as a replacing ion.

This leads one to the view that the expanding material is not a true montmorillonite, but is as suggested by Burst (1958), and currently believed to be, a degraded mica. However, the degraded mica theory does not account for:

1. the fact that glauconites are dioctahedral — one could also expect trioctahedral ones on this theory,
2. the large amount of iron present,
3. the fact that all of the 10A clays in these recent sediments have a distinct (002) reflection (see page 115\(^-\)), as it seems reasonable to conclude that other degraded micas, not housed in microfossils, would adjust to the marine environment with a degree of disorder approaching that of the glauconites, and, like disordered glauconites, would not give an (002) reflection,
4. pigmentary coating of glauconite on other minerals.
13.4 Nature of Clays in the Recent Sediments

It was considered that examination of the nature of the fines present in some of these recent sediments might give some information as to the environment best suited to the formation of glauconite.

From seven of these samples, the \(<1\mu\) fraction was separated with a centrifuge. Portions of these were saturated with \(\text{FeCl}_3\) and \(\text{MgCl}_2\), shaken at regular intervals during the day and left overnight, then washed six times using the centrifuge for precipitation. From these suspensions potassium and magnesium saturated slides of the clays were prepared, from which X-ray diffractometer traces were made by the Soil Bureau, Lower Hutt. Three traces for each sample were made, namely, X-saturated, untreated; X-saturated, heated to 550°C; and Mg-saturated, treated with glycerol.

Criteria for the recognition of various clays have been given on page 73. Added to these are the distinction of vermiculites of different origin, as follows:-

**K-saturated:** Highly charged vermiculites derived from micas have a basal spacing of \(10.4\AA\). Low-charge vermiculites derived from non-micaceous minerals do not contract to \(10.4\AA\). (Weaver, 1958).

To determine the ratio of montmorillonite to illite, the intensities of the \(10\AA\) and \(17\AA\) peaks of the samples treated with glycerol are used. The result for illite has to be multiplied by four to compensate for the greater scattering power of three-layer clay minerals at the lower angle, corresponding to \(17\AA\), (Bradley, 1953). Comparison of the other clays is effected by comparing the intensities of the \(3.3\AA\) and the \(3.5\AA\) peaks, taking into account the effects of glycerol expansion and heat treatment. The state of crystallisation being uncertain, heating to 550°C will not certainly show the difference between kaolinites and
chlorites, so that initially the results are given as a ratio of illite : montmorillonite : kaolinite + chlorite + vermiculite. To differentiate positively between kaolinite, chlorite, and vermiculite, it would be necessary to X-ray the samples at several different temperatures, and apply acid treatment. As this was not possible, these components are given only relative quantitative assessment, assuming perfect crystallisation for all three.

Ratios of amounts present were estimated from integrated intensities shown in the diffractograms, subject to the qualifications stated above, with the following conclusions -- the samples being listed as progressing from the southernmost latitudes northwards: --

**C 457**

- **Illite:** strong (002) reflection
- **Montmorillonite:**
- **K + C + V:** 14Å medium; 7Å strong;
  - both reduced by heating
- **K > C > V**
- **Glaucogne:** large, veined, none in foraminifera.

**C 512**

- **Illite:** (002) present and sharp
- **Montmorillonite:**
- **K + C + V:** strong 7Å and 14Å peaks,
  - reducing on heating
- **K > C = V**
- **Glaucogne:** small, glassy and infrequent.

**A 153**

- **Illite:** (002) present, (003) very strong
  - major component
- **Montmorillonite:** very little
- **Chlorite:**
- **Glaucogne:** large, lumpy grains, phosphatic.
B 154
Illite: (002) present 2
Montmorillonite: 1
K + C + V: 14A strong, 7A strong; 2
both much reduced on heating
K > C > V
Glauconite: infilling in foraminifera.

B 155
Illite: strong (002) 3
Montmorillonite: 2
K + C + V: strong 14A, strong 7A; 3
both reduced considerably on heating
K = C > V
Glauconite: infillings in microfossils.

B 12
Illite: (002) indeterminate 3
Montmorillonite: 2
K + C + V 1
Nearly all chlorite
Glauconite: very few grains.

A 107 - not a very clear trace.
Largely illitic, small (002).
Very little montmorillonite.
Small 14A peak; larger 7A
C > V > K
Glauconite: free, smooth dark green, rounded.

In no place is the amount of montmorillonite present greater than the illitic content, which is particularly large for the southernmost sample. In Hawke Bay the montmorillonite content increases, as might be expected from the large amount of volcanic glass present which provides a source of silica. But in the sample B 12, with a higher amount of montmorillonite,
there is practically no glauconite, and the same holds for sample C.512. Both of these samples also have over 80 per cent of their material in the <62μ fraction, giving an ample supply of source material of an alterable size, yet it is in the other Hawke Bay sediments containing very little fine material that the glauconite is found as infillings of microfossils. It does seem that a host in the form of a microfossil favour glauconite formation, and that from the little fine material available a precipitation method of formation can be envisaged.

Note has been taken of the presence of a (200) reflection at 4.98A for the illites present. If this were finely divided glauconite, the presence of this peak is not likely, as it indicates a mica with much better ordering. The glauconite present in these samples is not therefore considered to be due to the redistribution of finely disseminated glauconite from the mainland, but rather, to be an authigenic mineral.

The provision of iron in sufficient quantities is a problem, but the presence of heavy minerals such as magnetite in reasonable quantities in B.155 is encouraging, and the possibility of iron capture by bacteria is also possible. This is enlarged upon in the next section, on the origin of glauconite.

It is also to be noted that larger numbers of foraminifera are found in the samples from the shallow ridges in this area than from those in the deeper water. This was also found to be so by Revelle and Shepard (1937) on the California coast, where ridge sediments were almost entirely calcareous and glauconitic. These situations would certainly not be un oxygenated. Correns (1937) also found it true for the sediments of the North Atlantic Ocean that on submarine ridges large numbers of foraminifera were found. Trask (1937) states that organic material on ridges is small in quantity and the decomposition of organic matter in oxygenated waters is rapid, so that slow decomposition of organic material often postulated as necessary
for glauconite formation cannot hold here.

These glauconitic sediments off the East Coast of the North Island are, like many Recent glauconites, found in an area where warm and cold currents meet, being from the region of Subtropical Convergence. Measurements by Garner (1955) show that offshore from Hawke Bay, in the colder seasons, the subantarctic waters intermingle with the subtropical waters, causing complex layering and temperature dispersion in this area. It is interesting to note that from the findings of the "Challenger" expedition of 1873-6, and the "Gauss" expedition of 1901-3, Murray and Philippi, as quoted by Hadding (1932), state that "glauconite occurs preferably where cold and warm currents meet."

Summary

Results from this section are summarised as follows:-

(1) Glauconite in recent sediments from off the East Coast of New Zealand originates as an expandable montmorillonitic type clay lattice with an appreciable iron and potassium content.

(2) Ferrous iron content is constant for samples hundreds of miles apart.

(3) It is not necessary to have a large amount of fine material present in the sediment to promote glauconite formation. In fact, many glauconitic localities have very little less than 52 micron material present.

(4) A large montmorillonitic content in the fine material is not necessary for glauconite formation. In most of the localities there is a larger component of 7 and 14A clay minerals present.

(5) Glauconite formation is prominent on ridges where foraminifera flourish. This is an oxygenated area.

(6) A theory of precipitation from solution, see page 123, in more consistent with the above results than that of alteration of a degraded mica.
14. THE ORIGIN OF GLAUCONITE

In the course of this thesis comment has been made from time to time on the possible origin of various glauconites. Methods of glauconite formation have been a source of speculation and discussion for at least a century, but the whole answer to this problem has remained elusive. Hadding (1932) records the opinions of earlier workers, and intimates that great controversy was centred around this subject in the latter part of the nineteenth century, over the parent materials and the environment necessary.

Broadly speaking there are only two ways in which a glauconitic material could be formed:—

(1) By the alteration of some other silicate.
(2) From solution, by the aggregation of attractive ions, i.e., by precipitation.

From chemical analyses it is evident that glauconite has a greater than average content of both iron and potassium. That these two requirements be met, condition (1) above dictates either (a) a parent lattice rich in Fe and K which readjusts to its local environment, or

(b) a silica lattice into which Fe and K are attracted by charge deficiencies, the final result being again dependent on the chemistry of the environment.

Theory (a) has found support from the observations of Galligher (1935) in Monterey Bay, California, where glauconite is forming by the alteration of biotite, which swells along its cleavage planes along which glauconite develops. During this research, the finding of this type of grain, obviously formed by the alteration of single crystals of some other mica, lends support to this theory.
Theory (b), expounded by Burst (1958), is currently popular. It does not in fact differ too greatly from (a) in that it postulates glauconite formation from clay particles which have been degraded by loss of ions into a state of greater charge deficiency. "Degradation" was not rigidly defined, but appears, like "stripping", to consist of the removal of mainly interlayer cations. The question of the state of the octahedral ions was not referred to by Burst, but is shown later in this text to be significant. Hower (1961) believed that the degraded clay lattice should have a low charge, and that glauconitisation should take place by slow replacement of Al by Fe in the octahedral layer.

It has long been realised that glauconite can be formed by the alteration of other materials. In 1937 Takahashi stated that glauconite is formed from volcanic glass, opaline silica, clayey materials, faecal pellets, etc., which have become gelatinous by hydration and are converted to glauconite by the adsorption of K and Fe and loss of Al. Moore (1937) also reports that transition from mud to glauconite has been traced in pellets with progression into deeper waters, and is of the opinion that faecal pellets can survive in sediments. Takahashi and Yagi (1929) carefully studied the "glauconization" of coprolites, and state that in this case the presence of a ferri-siliceous gel as an intermediate stage is important.

With more research on glauconites, reports have been made of its presence under a variety of circumstances. Hodgson (1962) reports muscovite changing into glauconite in Western Australia. Muscovite is known to be a very stable lattice (Bassett, 1960). Bronson et al., (1960) state that leaching of potassium ions with aqueous salt solutions or potassium complexing solutions has not proved satisfactory for muscovite, and potassium ions have been removed from it only by treatment with molten salts. It is for this reason that muscovite as a
source material for the vermicular pellets found in this survey, is not favoured unless it has been degraded by volcanic activity.

Interlayering of glauconite with muscovite could, however, take place by the impregnation of glauconite in a colloidal form between the layers of muscovite. Bailey and Courtney-Pratt (1954) found that although mica has an almost perfect basal cleavage, steps occur on the surface which are a multiple of the lattice spacing, and that on applying tangential forces to mica sheets in contact, shearing occurred, until another junction was formed at a lower tangential force, a continuous track joining the two junctions. Under weathering conditions grains are subjected to many shearing forces, and the sequence of layers must contain many such steps and tracks. On these steps, under the right conditions, another micaceous lattice could progress. This is a likely mechanism for the interlayering of glauconite with muscovite.

Carozzi (1961) states that glauconite has a great affinity for siliceous sponge spicules. This has not been found to be so in the present research, although sponge spicules were abundant in some of the recent sediments. Some quartz grains have been found to be thickly impregnated with glauconite (see page 37). In the East Coast recent sediments, which in places contain a large proportion of pumice, a few pumice grains have glauconite formed in the vesicles, (see frontispiece), but the occurrence is rare.

14.1 Alteration of Micas

It is well recognised that potassium is easily leached from biotite by aqueous solutions, giving an expanded vermiculite type lattice. Barshad (1948) found that complete conversion of particles of biotite less than one micron in size, took three months in a magnesium saturated solution. Occurrence of biotite-vermiculite clays in soils has often been reported
Vermiculite-chlorite and biotite-chlorite mixtures can also occur.

Although, as just mentioned, potassium ions are not easily removed from muscovites, several occurrences of dioctahedral vermiculite-like minerals believed to have been formed by the alteration of muscovite are reported, (Hathaway, 1954; Rich and Obershain, 1955). Weaver (1958) studying clays derived from micas, found that vermiculite and montmorillonite derived from muscovite will contract to 10Å when potassium saturated at room temperature, and that heating for some time will produce the same results in montmorillonites and vermiculites derived from biotites, whereas expanded clays derived from non-micaceous minerals will not contract below 11 to 12.4Å. These "stripped" micas are not often found in marine sediments as the potassium present in sea water is sufficient to contract them. If a ferriferous medium can be found to influence them, here are the degraded lattices specified by Burst as the source of glauconite. However, in order to achieve a dioctahedral lattice from a trioctahedral biotite, it will be necessary to remove most of the ferrous iron and place the lattice in a source of trivalent iron.

14.2 Alteration of Biotite

To investigate more fully the changes in biotite it was decided to simulate the weathering of this mineral under acid conditions. This artificial weathering was accelerated by heating biotite particles of less than one micron in size in hydrochloric acid of pH 3 at 80°C for 240 hours. After this time the potassium in solution was measured with the flame photometer, and the total iron spectrophotometrically. It was found that the biotite had lost 58 per cent of its total potassium and 46 per cent of its total iron content.

Oriented slides of the material before and after treatment were examined on the Otago University diffractometer,
(a) Biotite before acid treatment.

(a) after treatment.

(c) (b) heated 600°C.

Fig. 36

ALTERATION OF BIOTITE.
and show, in Fig. 36:—

(1) lowering and broadening of the basal peak,
(2) slight broadening of the basal spacing from 10.10 to 10.20Å,
(3) a new small peak at 14.15Å.

On treating with glycerol the small peak at 14.15Å does not move, but the main peak at 10.20Å shifts to 10.66Å.

On heating to 600°C the 14.15Å peak collapses and new triple peaks appear at 9.93, 10.16 and 10.28Å. It is concluded that part of the biotite has been converted to vermiculite.

Debye-Scherrer powder photographs of these samples show (001) reflections much reduced in sharpness. The strong reflection at 1.67Å due to (204),(1 3 5) becomes very weak; (060) loses its sharpness but (200) remains sharp. The (202),(1 3 3) reflection at 2.18Å and the (201),(1 3 2) reflection at 2.45Å also lose their clarity. Measurements of (060) show that the material still has octahedral occupancy of the octahedral layer. This is not surprising as much of the material has not yet departed from the 10Å mineral structure. However, the loss of so much iron leads to the conclusion that the degradation of biotite affects the octahedral layer as drastically as the interlayer cations, and if the process were taken to completion there would be many vacancies available in the octahedral layer for entry of other ions. It would be reasonable too, to postulate that it is the excess charge deficiency in this layer which causes the lattice to expand through repulsion between the layers.

14.3 Alteration of Illite

Because it was suggested by Furst that glauconite has been formed by the entry of ions into degraded illitic lattices, it was decided to try to degrade an illite. This was attempted under the same conditions as those used for biotite. It was found that this illite was not easy to degrade, only two per cent of the total potassium being released into solution.
Diffractometer traces of the illite before and after treatment show exactly the same curve shape at the 10A region. This substance then is not as easy to degrade as biotite.

14.4 Glauconite formed by Precipitation

While glauconite may be formed by the alteration of other minerals, it is also possible that it is formed from the ions present in sea water being combined and precipitated due to local variations in chemical conditions. Sea water contains sufficient potassium in solution at all pH values. Iron presents a greater problem, being only slightly soluble in sea water. Indeed, iron is deposited in alkaline waters after being carried in solution in acid fresh waters.

\[ \text{At pH 6 iron solubility is } 5 \times 10^{-3} \text{ mg./m}^3 \]
\[ \text{At pH 7 } \quad \text{"} \quad \text{"} \quad \text{"} \quad 4 \times 10^{-5} \text{ mg./m}^3 \]
\[ \text{At pH 8 } \quad \text{"} \quad \text{"} \quad \text{"} \quad 8 \times 10^{-7} \text{ mg./m}^3 \]
\[ \text{At pH 8.5 } \quad \text{"} \quad \text{"} \quad \text{"} \quad 3 \times 10^{-8} \text{ mg./m}^3 \]

and the ions in solution are then mainly $\text{Fe}^{2+}$ and $\text{FeOH}^{2+}$ (Cooper, 1937). At a pH of 7.6, which is general for bottom sediments of the Central Pacific Ocean at present (Bordovsky, 1961), very little iron would be expected to be in solution. In the early Tertiary however, in the Otago and Canterbury areas, there would have been a great deal of iron produced by the weathering of the rocks of the Cretaceous peneplain. This iron would have been precipitated as ferric hydroxide on contact with the alkaline marine waters and finally accumulate in the sediments as ferric oxide. Under reducing conditions iron can go back into solution, when a low oxidation potential is caused by

(a) actual lack of oxygen at depth,

(b) reducing agents such as $\text{H}_2\text{S}$ liberated by the decomposition of proteins by anaerobic bacteria,

(c) carbon dioxide, produced by the oxidation of carbon by
oxygen from some plants, plus that produced by the reduction of sulphates by bacteria.

Reducing gases may also percolate from buried sediments, especially under conditions such as those in which the main greensand deposits were formed in New Zealand, where lower beds contained terrestrial deposits turning to coal. Further, Shepard (1959) states that it is suggested by Revelle of the Scripps Institution, that, at the end of the Cretaceous great extrusions of lava brought up vast quantities of gas (this theory purporting to account for the presence of submerged guyots and the large quantities of limestone formed since the Cretaceous). Here again is a source of reducing gases, or at least an inert atmosphere by the presence of large quantities of CO₂.

14.5 Synthesis of Clauconite by Precipitation

The synthesis of clay materials by precipitation from solution has been studied for the last thirty years, but as the crystals obtained are so small, it is only since the electron microscope has been available that substances formed by these methods can be studied with assurance. As early as 1930, Mattson (1930), as part of an exhaustive research into colloidal solutions included the AlCl₃-SiO₂ system and the FeCl₃-SiO₂ system in his studies, determining the isoelectric point for these and many other systems. At about the same time Noll (1935), quoted by Grim (1937), was examining the Al₂O₃-SiO₂-H₂O system, noting the formation of different clay types as the ratios of the constituents were varied, as other ions, particularly potassium, were added, over a range of temperatures. Lately, more refined investigation of the properties of clays formed by these methods has been undertaken by such workers as De Vospe et al. (1961), who determined base exchange properties, and measured surface areas for clays produced from AlCl₃-SiO₂ and MgCl₂-SiO₂ systems in solution. Although the precipitates which they produced from
the AlCl₃-SiO₂ mixture gave no X-ray lines they were able to identify them with an electron microscope and measure the aluminium co-ordination numbers for them.

Introducing iron into such an alumino-silicate system immediately presents a problem as there are two valencies to consider. A study of the chemistry of iron shows many intricacies. In sea water the dominant anion is Cl⁻, so that for precipitation in sea water, the iron can be taken to be initially present as a chloride. X-ray examination has shown that hydrolysis of trivalent iron chloride has FeO(OH) - goethite - as its end product at ordinary temperatures. There are two significant facts about the conversion of chlorides to goethite;

(1) It is a slow process and may take months,
(2) The conversion takes place by way of Fe₂O(OH) - lepidocrocite - so that to start with there is a mixture of chlorides and hydroxides.

These give a picture of great instability over a long period of time, and indicates that the incorporation of iron into an introduced silicate lattice will be by the adsorption of iron hydroxide and will initially form a complex substance.

14.6 Iron Bearing Silicates Grown from Solution

As ferric hydroxide precipitates at a pH of 3, and the presence of ferrous iron is more compatible with the pH values of a marine environment, it was decided to attempt the synthesis of a ferro-alumino-silicate by the use of a ferrous salt as an iron source, and to keep the solutions in a nitrogen atmosphere during the period of growth.

Aluminium, potassium, magnesium and ferrous iron were provided in the form of chlorides in solution, and silicon by the addition of sodium silicate solution. Ferrous chloride was added in excess, but the other ions were supplied to be as nearly as possible in the ratios present in an average glauconite.
The chlorides were mixed together, the silicate added quickly, and the pH of the solution adjusted by the addition of NaOH. The mixtures were left with nitrogen gas bubbling through them for a period of two months, after which the precipitates were filtered, dried at 50°C, and X-rayed in the Debye–Scherrer powder cameras.

Details of solutions:

### Solution

<table>
<thead>
<tr>
<th></th>
<th>Si : Al</th>
<th>pH</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7 : 1</td>
<td></td>
<td>pH 8.2 at the end of the growth period.</td>
</tr>
<tr>
<td>2</td>
<td>14 : 1</td>
<td></td>
<td>pH 8.2</td>
</tr>
<tr>
<td>3</td>
<td>30 : 1</td>
<td></td>
<td>pH 9.3</td>
</tr>
</tbody>
</table>

These mixtures started to form dense green gelatinous precipitates at a pH of about 6. The density of these intensified as the pH was increased. In the one with excess silica, a milky white constituent was also noticeable due to the precipitation of excess silica. On drying at 50°C the precipitates remained green but oxidised slowly on exposure to the atmosphere, turning a yellowish-brown after about two weeks. This was also found by Birdsall (1951) who also synthesized a "glaucnite" from solution.

On X-ray powder photographs, the samples from solutions (1) and (2) both had broad diffuse lines at about 4.50, 2.60, and 1.52Å. These are the main reflections shown by a true glauconite, being (020), (200), and (060) reflections. Very faint but sharp quartz lines were also present. Solution (3) with an excess of silica and a higher pH, showed only quartz lines in the X-ray powder photograph. A repeat set of solutions was mixed, but the precipitates formed gave no additional information. These were of greater quantities of material, for a growth period of only six weeks. The only effect of excess NaCl solution added to the mixture was to flocculate the gel more compactly, but did not cause better crystallisation. The presence of crystalline quartz in these products shows that authigenic quartz can form in marine sediments and that some silicate–quartz mixtures
may have been formed in this way. However, the initial programme has shown that a silicate of \( a \) and \( b \) dimensions approaching those of a mica can be formed from solution, but it would take a much longer time than was available to reach stability.

In this respect it is interesting to note that research workers, endeavouring to find better methods of precipitation as an aid in chemical analysis, have found that substances which usually form a gelatinous colloidal complex, such as aluminium hydroxide, formed a dense precipitate if very dilute ammonium hydroxide is added at a very slow rate. This, in 1937, led to the technique of homogenous precipitation (Gordon, 1956) in which slow decomposition of urea was used to release ammonia to precipitate aluminium in the presence of a suitable anion — for aluminium, a sulphate. This process has been used for many other ions. There could be a relation between this type of precipitation, and that of a substance such as glauconite, especially as our glauconites were formed in sediments overlying others which were changing into coal and evolving ammonia and other gases. This may account for intense precipitation in the early Tertiary sediments.

11.7 The Role of Foraminifera in the Formation of Glauconite

From the study of New Zealand glauconites it is apparent that a great many glauconite deposits are in the form of foraminiferal casts. Considering this as one positive environment for glauconite growth, necessitates the following conditions:

1. Requisite temperature and food supplies for the support of a flourishing foraminiferal colony.

2. Presence in solution or other form, of ions necessary for glauconite structure.

Temperature conditions at the periods of greatest green-sand deposits in New Zealand were subtropical. Phleger (1960) states that in present day foraminifera, reproduction is greatest
at temperatures between 20 and 30°C and that fine grained sediments usually contain a greater amount of organic matter - potential food for foraminifera - and may support a much greater population than clean sand. From the results of size analyses, which show that in the main greensand deposits most of the coarser material is glauconitic, it seems quite reasonable that these were foraminiferal colonies living among fine grained silts and muds.

How then does the glauconite form inside a foraminifera or other organism? It is likely that the microfossil merely provides a sheltering environment for the aggregation of glauconite. The first problem is that of the choice of the source material for glauconite formation, i.e., between an accumulation of degraded clay particles which have drifted into the empty microfossil, and a mechanism of precipitation from colloidal solution. It was seen in the study of recent sediments, that where glauconite is forming in foraminifera there is little fine clay sized material in the accompanying sediments, and yet the foraminifera were found to be full of a clayey material turning to glauconite. Formation from precipitation is, then, a reasonable concept, the colloidal material formed initially being consolidated by imprisonment in the microfossil, and any formed outside being unstable and easily dispersed, unless the surroundings are very calm. An iron source is the most difficult component to provide for glauconite, but if the precipitation mechanism is adopted, the iron could be readily taken into the embryonic lattice as a hydroxide, either ferrous or ferric, stability being gained as the silicate becomes more crystalline. Whatever the valency of the initial iron content, there is no doubt that the majority of the iron is finally ferric and that therefore conditions have been oxidising, even if only slowly. Iron brought into solution by reducing conditions a few centimeters below the sediment surface, could easily be reprecipitated as a colloidal hydroxide at the surface and incorporated there in
a silicate lattice, without introducing extreme values of reducing conditions.

Changes in oxygen supply, and therefore in iron solubility can also be brought about by the seasonal sinking of cold water. Glaucophites have been noted to occur where warm and cold waters meet, and layering of water at different temperatures occurs. This too could provide changes in the solubility of the iron in the bottom muds, and facilitate the release of iron necessary for glauconites.

It may well be that the foraminifera themselves assist in glauconite formation, as well as providing a host. Some globigerina are credited with having up to 2 per cent of iron in the test, (Vinogradov, 1953), while some arenaceous foraminifera are known to use a ferruginous cement in their skeletons. The silt in regions dominated by the latter type of organism becomes enriched in iron, apparently biochemically. It is also known that some bacteria concentrate iron, the iron bacteria Gallionella which contains a concentration of iron oxides being first found in silts in the sea, in 1928. Other iron bacteria are also known and some of them are found to concentrate silica as well as iron, and these may play a large part in concentrating the right constituents for a glauconite. It has long been known that pyrite is often present inside foraminifera, the general supposition being that this was formed by the products of decomposition of the protoplasm, the iron being supplied from the surrounding muds. Le Calvez (1951) however, considers that the iron, already a part of the metabolic processes of the foraminifera, was pyritised "in vivo", causing disturbances of great magnitude - which he cites - to these metabolic processes. Until more research has been carried out on the living and dead forms of foraminifera, one cannot be sure how great a role they play in iron contribution, or whether one must depend on the sediments themselves as the only iron source.
It was seen from study of sample E 155, that the foraminiferal cast fills the test at all times, from the initial whiter grains through to the darker green more mature grains. Finally the foraminiferal shell breaks off, leaving a dark green cast. This has often been attributed to increased expansion and pressure from the glauconite. However, as glauconite contracts from an expandable clay to a 10A lattice with maturity the grains themselves are not likely to expand, and the loss of the foraminiferal shell is attributable to mere mechanical agitation. From study of the peeling foraminiferal shells, they appear thinner than those of foraminifera unfilled with glauconite.

It must not be thought that foraminifera alone provide a host for glauconite. In E 155 are many examples of glauconite forming in echinoid spines - see frontispiece. In these specimens it is quite evident that the glauconite first forms in the central duct of the spine and works its way outwards, the outer layers being often quite free from glauconite or any other filling. Specimens from echinoid spines are also quite clearly recognisable in the samples from the Old Rifle Butts, from the replica of the echinoid spine structure. These specimens are also noticeably a paler green than other mature glauconites. Also in E 155 were lumps of aragonite - see frontispiece - (detected by staining) which, on dissolving in hydrochloric acid, left the green thread-like networks which had been filling up all the available minute spaces. No dependence on the presence of organic matter can be detected in this case, although decomposition of organic matter is often postulated as necessary for producing a reducing environment for the growth of glauconite.

It is obvious from the preceding pages that many factors, chemical, biological and geological play their part in the formation of glauconite. The most significant of these is, however, the chemistry of the environment, but the probability that some of this chemistry is provided biologically confuses the problem.
There is no doubt that other micas such as biotite will change into glauconite, but where no significant clay fraction can be found in the sediments to account for an alteration process of other degraded clay micas, the mechanism of precipitation from colloidal solution, although not generally favoured, must be seriously considered.

14.8 Non-Marine Glauconites

Over the years, glauconite has assumed an importance in the mineralogical world as an indicator of marine origin of the sediments in which it is found. However, there are now recorded exceptions to this postulate of marine origin of glauconites.

In 1956, Dyadcheno and Khatuntzeva reported a non-marine glauconite among alluvial deposits on the terraces of the Irab River in Russia. These glauconites, which consisted of irregular grains and also pigmented coating on feldspars, apatite and other minerals, were found in the sands and muds overlying crystalline rocks consisting of calcium feldspar, plagioclase, quartz, apatite and pyroxene, plus other minerals due to the changes of these by solutions. These authors considered that this glauconite had originated as precipitation from colloidal solutions in the ground water in a faintly oxidising medium, and that pH and oxidation potential are the primary factors to be considered in the formation of glauconite.

Keller, (1958) explains the presence of a glauconitic mica in known non-marine deposits in Colorado, U.S.A., as due to the alteration of montmorillonites forming from volcanic ash, by downward moving solutions. During this alteration magnesium was leached from the montmorillonite and replaced by potassium. It has been suggested that the potassium was supplied by an abundance of saline solutions. Here again the environment was believed to be slightly oxidising.
14.3.1 South African Glaucnite

It was with sincere gratitude that a sample of non-marine "glaucnite" was received by the author from Mr. L. Engelbrecht, Geological Survey, Pretoria, South Africa. Quoting from his letter: "It is found in Heuningvlei Pan (+23°9′E, 26°19′S), situated in the Heuningvlei Bantu Reserve in the district of Vryburg, Cape Province. The pan is dry for most of the year but contains salt water and in all probability lies partly on banded ironstone and partly on dolomite; its floor consists of a light greenish clay with patches of greenish silcrete on or near the surface. The age of the pan is probably Quaternary, but that of the glauconite has not been determined yet. The glauconite is found in isolated patches in the light greenish clay, and is everywhere associated with patches of banded ironstone rubble occurring in the light green clay".

This was a welcome addition to a collection of marine glauconites. The sample consisted of a fine green powder most of which passed easily through a 62 micron sieve. Some gritty larger grains were found to be quartz. Most of the sample was of clay size. A portion of grains, size less than one micron, was separated and washed several times, dried and X-rayed. On the powder photographs, in addition to the lines seen for the other glauconites, a line at 1.999Å (005) was clear and sharp. The b dimension was measured on (060) to be 9.07Å, and the g dimension measured on (600) was 5.23Å. From the clarity of the X-ray lines this was interpreted as a mica of high order.

An oriented slide of this material was scanned by the X-ray diffractometer at the University of Otago, showing a g dimension of 9.96Å. Basal reflections were found to be very sharp and more symmetrical than for any other glauconites studied. Reflections from (001) to (005) were all present, that from (003) being of one third the intensity of that from (001). The other basal reflections were of low intensity.
Differences in the infrared spectrum of this sample also point to its being different from our Tertiary glauconites. The OH stretching vibration is at 2.70 μ instead of 2.85 μ, and is less broadened by hydrogen bonding. The OH deformation vibration is at 6.0 μ instead of 6.1 μ. The greatest difference, however, was in the 9 to 11 μ region where two distinct peaks emerged, one of medium intensity at 9.0 to 9.3 μ, and a strong peak at 10.2 to 10.3 μ. These indicated also that this material is probably better ordered than the glauconites previously studied.

Chemical analysis. Potassium, sodium, total iron and ferrous iron contents were measured for the <1 μ portion of the sample, with the following results:—

K₂O, 9.6%; Na₂O, 0.2%; Total iron oxides, 23.0%; FeO, 3.5%.

Subsequently Mr. Engelbrecht sent a full chemical analysis, but stated that he was doubtful of the purity of the sample analysed and that it was being redone. No further information has been received. Two points stand out in the analysis supplied:—

(1) The low aluminium content (2.08% Al₂O₃). A structural analysis, deduced from the total analysis, shows that all the aluminium present would be used in completing the tetrahedral layer, leaving only iron and magnesium to fill the octahedral layer.

(2) The high potassium content, confirmed by my analysis as given above. The highest potassium content of our New Zealand glauconites was 7.6 per cent and a substance with greater than 9 per cent K₂O is likely to fall into the class of a well ordered micas, perhaps that of an iron bearing muscovite.

This material is different from our fossil glauconites and our recent marine glauconites in many respects, and raises the question - is it truly a glauconite at all? From the hypothesis of degraded micas or illites being the source material of
glauconites, there is no reason why glauconite should not form in a terrestrial environment. Should a degraded micaceous sediment settle in a lake, it will depend entirely on what ions are available as to what its final composition will be. If aluminium is available this will re-enter the lattice, which should then regain its initial structure and probably pass unnoticed. It is only when an unusual feature like glauconite occurs that these sediments are taken note of.

In this case, in the pan in South Africa there is available: Mg from dolomite, Fe from ironstone, and an acid environment from excess NaCl, and probably KCl also, as a component of the salt solutions. In this environment a degraded mica could easily fill its octahedral layer with iron and magnesium and the interlayer positions with potassium ions.

It would be more difficult to postulate a precipitation mechanism for this particular material, as acid conditions are most likely to prevail. However it was the fine ordering of this "glauconite" that led to the inclusion in the glauconite synthesis programme (page 125) of one mixture to which a great deal of NaCl had been added. Dekimpe, et al. (1961), experimenting on the growth of alumino-silicates from solution found that "high salt concentration favours gel flocculation, but evidence of preferential orientation was not found".

To me this was an exciting sample. The generous quantity supplied indicated no shortage of this material, and the thought that glauconitic material could form in these very special conditions is certainly stimulating.
15. CONCLUSION

The pleasure and the frustration of investigating natural minerals is that deposits in different localities are individuals. Nevertheless, the general structure of glauconite has been studied by chemical, X-ray and infra-red absorption methods, the latter being particularly valuable for the study of the hydroxyl ions. With a polarised infra-red source this could be taken further, but there is still a great deal of accompanying theoretical work required in the infra-red region. Specific siting of the ions in the octahedral layer of the mica lattice can best be studied by resonance methods, as described in the Appendix to this thesis.

It has been possible to classify many of the New Zealand glauconites, and to show that conditions favourable to glauconite formation either, (i), were extreme enough, due to the percolation of gases from the underlying sediments, or (ii), persisted long enough, to form great quantities of well ordered glauconites. They are marine in origin, and many have obviously formed from foraminiferal casts. However, under conditions existing in the areas of great green sand deposits in the late Cretaceous and early Tertiary, a precipitation mechanism could account for many other grains, whose shape can best be envisaged as the result of the impression of other sedimentary minerals on a flocculating gel.

Vermicular pellets have been found to be single crystals, often deformed by expansion, and interlayered - in a few cases, regularly - with 14A clay minerals. Biotite, from which ions are easily leached, is thought to be the most likely source materials for these glauconites, but further research into the alteration products of chlorites, which abounded in the schists of the peneplain beneath these sedimentary deposits, would be a worthwhile contribution to our knowledge of these glauconites. The clays associated with the vermicular pellets are found to consist
of montmorillonites, illites and kaolinites, with only a small 14A clay component. With an X-ray diffractometer available, assessment of the clay component of other glauconitic sediments would give information about the environment in which the glauconites were formed.

If the idea of degradation of micas is enlarged to include loss of ions in the octahedral layer, and not only the interlayer cations, the theory of glauconite formation from degraded illites or other clays, differs from that of the alteration of biotite only in the size of crystal involved. It is my opinion that glauconite forms from a depleted lattice of high charge deficiency, into which an initial large quantity of iron is attracted, completion of the process being more gradual. If the process of degradation of any mineral is carried to completion, so that most of the ions are lost into solution, and only a skeletal lattice remains, this provides the constituents for re-precipitation from a colloidal gel. The method of glauconite formation could then be considered as dependent only on the initial state of materials present and the environment to which they are subjected.

During the course of this research, it has been shown that in addition to geology, the study of glauconites requires the application of chemistry, physics and biology. It would, for instance, be interesting to measure the potentials developed in decaying organisms, and the effects of sudden water temperature changes on foraminiferal colonies. It is increasingly obvious that an interdisciplinary attack on many scientific problems such as this one would greatly facilitate and hasten their solutions.
BIBLIOGRAPHY

Allen V.T., Amer. Miner. 22 1180 1937.
Barshad I., Amer. Miner. 33 655-78 1948.
Bordovsky O.V., Abstracts of Symposium papers, 10th Pacific Science Congress 1961.
Brindley G.W. and Youell R.F., Min. Mag. 30 57-70 1953.


De Kimp C., Gastuche M.C. and Trindley G.W., Amer. Miner. 46 1370-81 1961.


Feiman A.E., Comptes Rendus (Doklady) de l'Academie des Sciences de l'URSS 17 No. 4 201 1937.


" " in "Recent Marine Sediments", Published A.A.P.G. 1937.


" " in "Recent Marine Sediments" 1937.


Hendricks B.S., Foss C.S., Amer. Miner. 26 683-708 1941.


Keller W.D. and Pickett E.F., Amer. Miner. 34 855-64 1949.
Le Calvez J., Vie et Milieu 2 335-7 1951.
MacEwan D.M.C., Kolloidschr. 156 61-67 1958.
" " Amer. Miner. 47 617 1962. II.
Saksena B.D., Proc. Ind. Acad. Sci. 12A 93 1940
Smith J.V. and Yoder H.S., Min. Mag. 31 209 1956.
Takahashi J., in "Recent Marine Sediments", 1937.
Takahashi and Yagi T., Econ. Geol. 24 838-52 1929.
Trask P.D. in "Recent Marine Sediments" 1937.
Vinogradov A.P., Memoir 2, Sears Foundation for Marine Research 1953.
Weaver C.E., Amer. Miner. 41 202-21 1956.
APPENDIX

**Microwave Spectroscopy**

As with optical and infrared spectroscopy, microwave spectroscopy is used to measure energy level changes within the atom, but the changes in this case are very small compared with atomic transitions giving optical spectra. Microwave absorption in solids is related to the forces and interactions inside the crystalline lattice, and a study of spectra obtained in this region will give detailed information concerning interatomic binding forces, and about the magnitude and symmetry of fields present with the solid. This method can furnish more specific results than infrared spectroscopy as the microwave frequencies used can be measured very accurately, better than 1 in $10^5$. By the study of the hyperfine structure of the spectrum, much information can also be derived about the nuclear properties of the atom.

Not all solids can be studied by microwave spectroscopy, however. The atom being studied must have a resultant electronic magnetic moment, i.e., be paramagnetic. In this category lie the ions with partially filled electron shells, one group of which, the iron transition group comprising ions of Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, has incompletely filled 3d shells. Not all ions of these elements are able to be studied by microwave spectroscopy, as the method depends on the fact that an external magnetic field can lift from energy levels, degeneracy still remaining after the influence of the internal electric atomic fields. It is transitions between levels split by the external magnetic field which are observed by microwave methods. If no degeneracy remains for the magnetic field to lift, these methods will give no results. However, it is known that, by
Kramer's Rule, if an ion has an odd number of unpaired electrons, no electric field can completely remove the degeneracy, so that results from microwave absorption methods can always be expected for such ions.

When an ion with a resultant magnetic moment is placed in an external magnetic field the energy levels of the atom are split. Absorption of microwave radiation causes transitions between these levels. This phenomenon, known as paramagnetic resonance, is observed by recording the absorption of a microwave signal of frequency $\nu$ at a magnetic field setting, $H$.

At resonance

$$h\nu = g\beta H$$

for the free ion.

$h = \text{Planck's constant}$

$\beta = \text{Bohr magneton}$

The "spectroscopic splitting factor", $g$, is a measure of the coupling of the spin angular momentum of the ion to its own orbital angular momentum, and is equal to 2.0023 where no such coupling exists, (including the relativistic correction).

Where $g$ has values other than the free electron value, this is due to the electric crystal field of the ions surrounding the paramagnetic ion causing the coupling referred to above, and several other interactions, which are allowed for by additional terms in the spin Hamiltonian, which gives a quantum mechanical description of the energy states of the paramagnetic ion.

Solution of the Hamiltonian equation (Bleaney and Stevens, 1953; Bowers and Owen, 1955) gives the energy levels, which in turn reflect the symmetry of the ion site; thus the microwave spectrum is highly sensitive to the angular variation of the ion site in relation to the external magnetic field when the sample is a single crystal, allowing an accurate evaluation of the ion environment. For a powdered sample the angular variations are averaged over $4\pi$ radians, thus losing valuable information.
Fig. A1. Microwave spectrum of glauconite.

d.p.p.h. = α-α diphenyl picryl hydrazyl g marker.
The quantity of material required for paramagnetic resonance study is very small, about $10^{-8}$ gram, and dilution of the paramagnetic ions by diamagnetic ions is commonly needed to reduce the unwanted effects of spin-spin coupling and exchange interaction. This makes paramagnetic resonance an ideal method for studying the structure of natural minerals, where ions of the iron transition group commonly replace such diamagnetic ions as aluminium, often in small quantities.

**Paramagnetic resonance of glauconite**

Microwave spectra of powdered glauconites were obtained on the X-band spectrograph in the Physics Department, which operates at a microwave frequency of 9.423.5 Mc/s. For technical reasons the curves produced are the first derivatives of the absorption line shapes. Figure A1 shows a typical microwave spectrum of Fe$^{3+}$ in powdered glauconite (ORB 3), which is characterised by a single very broad line (1400 Gauss), due to the large number of Fe$^{3+}$ ions, and $g = 2.03$, which is close to the free electron value. Transitions due to Fe$^{2+}$ cannot be observed except at low temperatures ($4^\circ$F), and a higher frequency (35,000 Mc/s), which is not available.

As the sample is a powder and only one line is present in the spectrum, little information about the sites of the iron ions in glauconites can be gained without the availability of another microwave frequency. However, a macroscopic mica, fuchsite, containing the ion Cr$^{3+}$, gives a spectrum containing more than one line and shows variations with respect to the angle of the external magnetic field (Fig. A2).

The author now proposes to study the symmetry of the octahedral layer in crystalline micas by means of paramagnetic
Fig. A2. Microwave spectra of fuchsite.

d.p.p.h. = < diphenyl picryl hydrazyl g marker.

$\phi = $ crystal angle. $\theta = $ angle of external magnetic field. $G =$ Gauss.
resonance of the ions replacing aluminium in muscovites. This should effect a final solution to this problem.