

ASPECTS OF THE CHEMISTRY
OF MINERAL - TYPE COMPOUNDS

by

Lynton W. R. Dicks, M.Sc.

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Department of Chemistry,
Imperial College,
London, S.W.7.

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SUMMARY

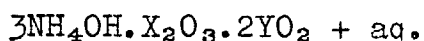
In this work the results of an investigation of the synthesis of layer-lattice silicates of the mica and montmorillonite type are presented.

Hydrous gels of general composition $R_4\text{NOH} \cdot \text{Al}_2\text{O}_3 \cdot n \cdot \text{SiO}_2 + \text{aq.}$ where $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{etc.}$, were subjected to hydrothermal treatment in stainless steel bombs at temperatures between 130 and 450°C.

Montmorillonite compounds containing alkylammonium cations in the interlayer region were prepared at 200-450°C. In this temperature range breakdown of the alkylammonium ions was found to occur and well crystallized montmorillonites containing quaternary ammonium ions could not be prepared.

To avoid breakdown of the alkylammonium cations subsequent synthesis studies were made at low temperatures with gels of the following composition: $\text{Li}(\text{F}, \text{OH})_x \cdot \text{MgO}_{6-x} \cdot 8\text{SiO}_2 + \text{aq.} + x\text{R}_2\text{O}$, where $R = \text{Li}^+, (\text{Me})_4\text{N}^+, (\text{Et})_4\text{N}^+, (\text{Prop.})_4\text{N}^+, (\text{Bu})_4\text{N}^+$. Using these gels, hectorite-like compounds containing quaternary ammonium cations between the 2:1 lamellae could be prepared. These hectorite-like compounds were characterized by X-ray diffraction, ion-exchange, D.T.A., thermogravimetric, infra-red and sorption studies.

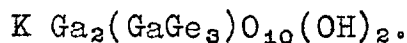
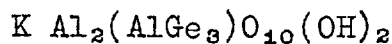
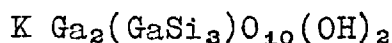
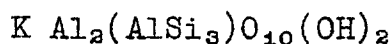
Some ammonium micas were synthesized from gels of the following composition:



where X = Al, Ga, Y = Ge, Si.

Attempts to prepare the ammonium aluminogermanate mica were unseccessful; instead two aluminogermanate phases were prepared, one of which could not be identified with any previously reported compound.

The extent of solid-solution between the following four potassium micas was investigated



Analysis of the synthetic potassium micas indicated complete solid-solution in three of the systems, although X-ray studies showed that two of these systems exhibited polytypism. One composition in the $\text{K}_2\text{O}-(\text{AlGa})_2\text{O}_3\text{-SiO}_2$ system always produced a 2nd phase in addition to a mica. Separation of the micaceous phase for analysis was not achieved and thus the extent of solid solution in this system remains uncertain.

Acknowledgements.

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1. INTRODUCTION

Recent work by Denny (1959) showed that by using alkylammonium bases in the alumina-silica system, layer silicates of the montmorillonite type and some diverse framework structures could be prepared. The use of the ammonium base in his studies showed that an ammonium mica could be readily synthesized.

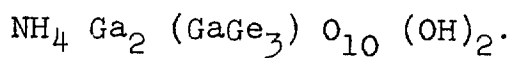
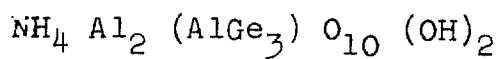
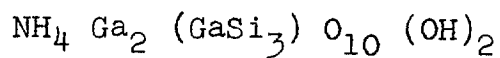
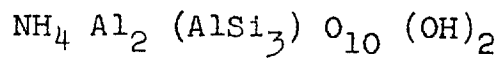
As a result of this work on the ammonium, alkylammonium-alumina-silica system and in view of the importance of the chemical relationship between many nitrogen compounds and soil minerals the system:

$N(R)_4OH - Al_2O_3 - SiO_2 - H_2O$, where $R = H, CH_3, C_2H_5$, etc., was selected for further study.

The areas of investigation, providing the basis for the study were as follows:

1. The synthesis of layer lattice silicates of the montmorillonite type containing quaternary ammonium ions and their characterization in some detail.
2. The extension of the study previously made by Denny on the ammonium micas and investigation of the effect of isomorphous substitution of gallium and germanium for aluminium and silica respectively in the ammonium mica structure. Thus, with a view to obtaining further knowledge

of the ammonium micas containing Al, Ga, Ge and Si it was decided to investigate the extent of solid solution between the four end member micas:



2. STRUCTURES OF SILICATES AND ALUMINOSILICATES

2.1. General Principles

The chief characteristic of silicate structures is the way in which complex structures are built up by linking together in various ways the simple basic units formed by the co-ordination of large anions around small cations. Goldschmidt's rules, deduced from a study of a wide variety of mineral types, state that the co-ordination number of any ion is governed by the ratio of the radius of the central ion to the radius of the anion surrounding it. For fourfold co-ordination of the central ion this ratio must lie between 0.22 and 0.41, and for sixfold coordination between 0.41 and 0.73. The radius ratio of silicon to oxygen is 0.37 and so silicon is always found in tetrahedral coordination with oxygen, whereas the aluminium:oxygen radius-ratio is 0.40 and as a consequence aluminium may form either tetrahedral or octahedral groups with oxygen. The size of the AlO_4 tetrahedron is close to that of the SiO_4 tetrahedron and isomorphous replacement of AlO_4 for SiO_4 may take place provided that an additional cation can be introduced into the structure to neutralize the additional negative charge produced by such a substitution.

This type of isomorphous replacement cannot occur indefinitely however since the third of Pauling's rules, Pauling (1929) states a further requirement if a stable structure is to be achieved. This is that shared edges or shared faces of groups in a coordinated structure decrease the stability, and this effect is particularly great in a case where the radius ratio approaches the lower limit of stability for that coordination number. This rule may be applied to the aluminosilicates in the form:- when two similar atoms are both neighbours of a given atom, the most stable configuration is achieved when one of them is in its highest coordination state. Hence no two adjoining tetrahedra in a silicate structure may both contain aluminium as the central atom. From this Lowenstein (1954) has deduced that in a three-dimensional aluminosilicate framework based on fully linked tetrahedra of AlO_4 and SiO_4 the ratio of aluminium to silicon can never be greater than 1:1, and that in structures which do have this maximum substitution the SiO_4 and AlO_4 tetrahedra must occur alternately in an ordered fashion throughout the structure.

2.2. Classification of Structures

The most satisfactory general classification of

silicate structures is that first formulated by Bragg and based on the way in which the SiO_4^{4-} tetrahedra are linked. The silicon-oxygen bonds are so strong that the tetrahedra themselves are found to be of nearly constant shape and dimension whatever the rest of the structure may be.

The orthosilicates. The four oxygen ions surrounding each silicon are not bound to any other silicon atom and so the structure is built up of units each having four negative charges which are neutralized by the cation in the structure. An example of this type of structure is the olivine group, $(\text{MgFe})_2\text{SiO}_4$, where for example in forsterite every O^{2-} anion is situated at the apices of a SiO_4 tetrahedron and a MgO_6 octahedron. Minerals of the garnet group are also built up from isolated SiO_4 tetrahedra with the charge neutralized by iron or aluminium ions in six-fold coordination.

The sorosilicates. The SiO_4 tetrahedra may be linked together in a number of ways to form finite groups from which the structure is built. For instance, two tetrahedra may be linked together through a common apex to give an $\text{Si}_2\text{O}_7^{6-}$ group as in thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$. Tetrahedra can also link together to form rings of three tetrahedra as in benitoite, $\text{BaTi}(\text{Si}_3\text{O}_9)$, and a well known

example of rings composed of six tetrahedra is beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. An unusual example in this class of structures composed of finite groups is zunyite, $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$, where the unit $\text{Si}_5\text{O}_{16}^{12-}$ consists of a central SiO_4 tetrahedra linked to another tetrahedron at each apex.

The inosilicates. Structures composed of infinite chains of SiO_4 tetrahedra are typical of such common minerals as the pyroxene group, for example diopside, $(\text{CaMg})(\text{Si}_2\text{O}_6)$, where the chains are held together by the calcium and magnesium ions which satisfy the free valencies of the oxygen anion in the chains. The closely related mineral group, the amphiboles, are built up from double chains since alternate tetrahedra in a pair of adjacent chains point towards each other and share the apical oxygen. An example of this type is tremolite, $\text{Ca}_2\text{Mg}_5(\text{Si}_8\text{O}_{22})(\text{OH})_2$.

The tectosilicates. When all four corners of each tetrahedron are shared by neighbouring tetrahedra a three dimensional framework is produced and this is the basis of the structures of the crystal varieties of silica, and of the feldspars, feldspathoids and zeolites. In the feldspars cations are accommodated in the interstices of the structure to neutralize the charge produced by the replacement of some of the silicon by aluminium. This replacement also takes

place in the feldspathoids and zeolites but the very much more open structures of these types often enable them to contain in addition to the cations considerable quantities of inorganic salts, e.g. cancrinite $\text{Na}_6\text{Ca}_2(\text{SiAlO}_4)_6(\text{CO}_3)_2$ or water, e.g. chabazite $(\text{Ca},\text{Na}_2)\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$.

Phyllosilicates. Due to the emphasis in this thesis on layer-lattice silicates of the mica-montmorillonite type, a detailed discussion of this group follows.

General:

The types of layer lattice minerals discussed are:

2 layer 1:1 Silicates

3	"	2:1	"	Pyrophyllite - Talc
3	"	2:1	"	Expanded 2:1 Minerals
3	"	2:1	"	Micas

If three corners of each tetrahedron are linked to neighbouring tetrahedra then sheet structures $n\text{Si}_2\text{O}_5$ can be formed.

The largest class of this group are the clay minerals mica and montmorillonite.

The structures of these minerals are based on the work of Pauling (1930), West, Radoslovich (1960) and many others.

Fundamental Structural Scheme Common to Layer Silicates.

The fundamental structural units in layer silicates are silica layers and brucite (or gibbsite) layers. The former consist of Si-O tetrahedra connected at three corners in the same plane so that a two dimensional network of hexagonal rings is obtained. The fourth, unjoined oxygen corners all point in the same direction. The silica, or tetrahedral layer is shown in fig. 1. The brucite or gibbsite layers consist of hydroxyl ions in two planes, above and below a plane of magnesium or aluminium ions which are octahedrally co-ordinated. The difference between the brucite and gibbsite layers lies in the fact that in the former all the octahedral cation positions are filled, whereas in the latter only two-thirds of these positions are filled. A gibbsite layer is shown in fig. 2.

The dimensions of the hexagonal units are essentially the same as those of the tetrahedral layer. Nearly all the clay minerals can be generated by a very simple combination of these two units. The two layers are combined in such a way that the unlinked oxygens of the tetrahedra replace two-thirds of the hydroxyls in one plane of the octahedral layer. The remaining hydroxyls in this plane assume positions at the centres of the hexagons formed by the oxygen of the tetrahedra as shown in fig. 2.

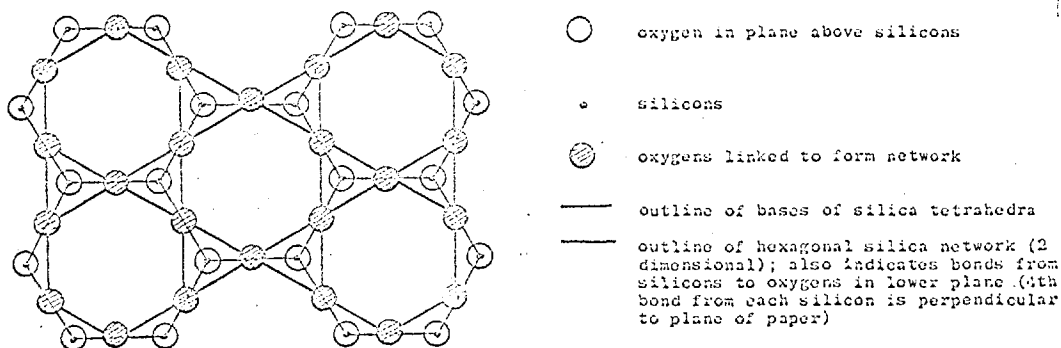


Fig : 1.
Silica or tetrahedral layer,
viewed from above.

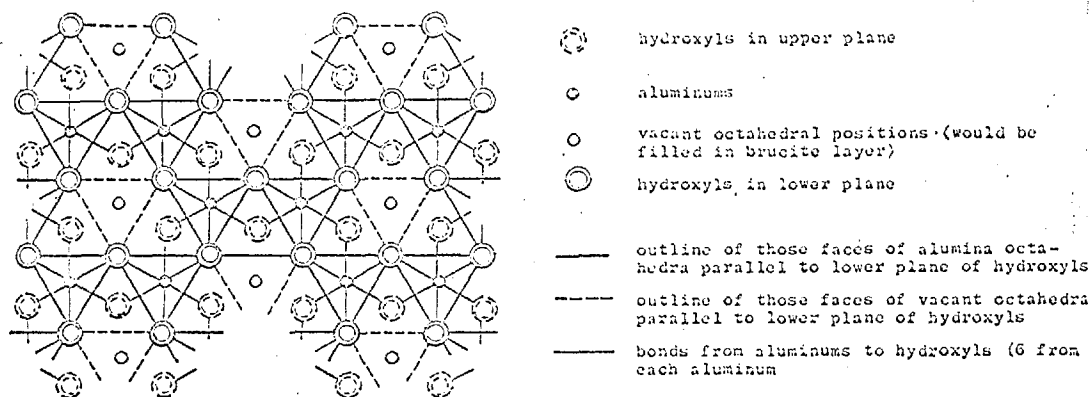


Fig : 2.
Gibbsite, or octahedral layer,
viewed from above.

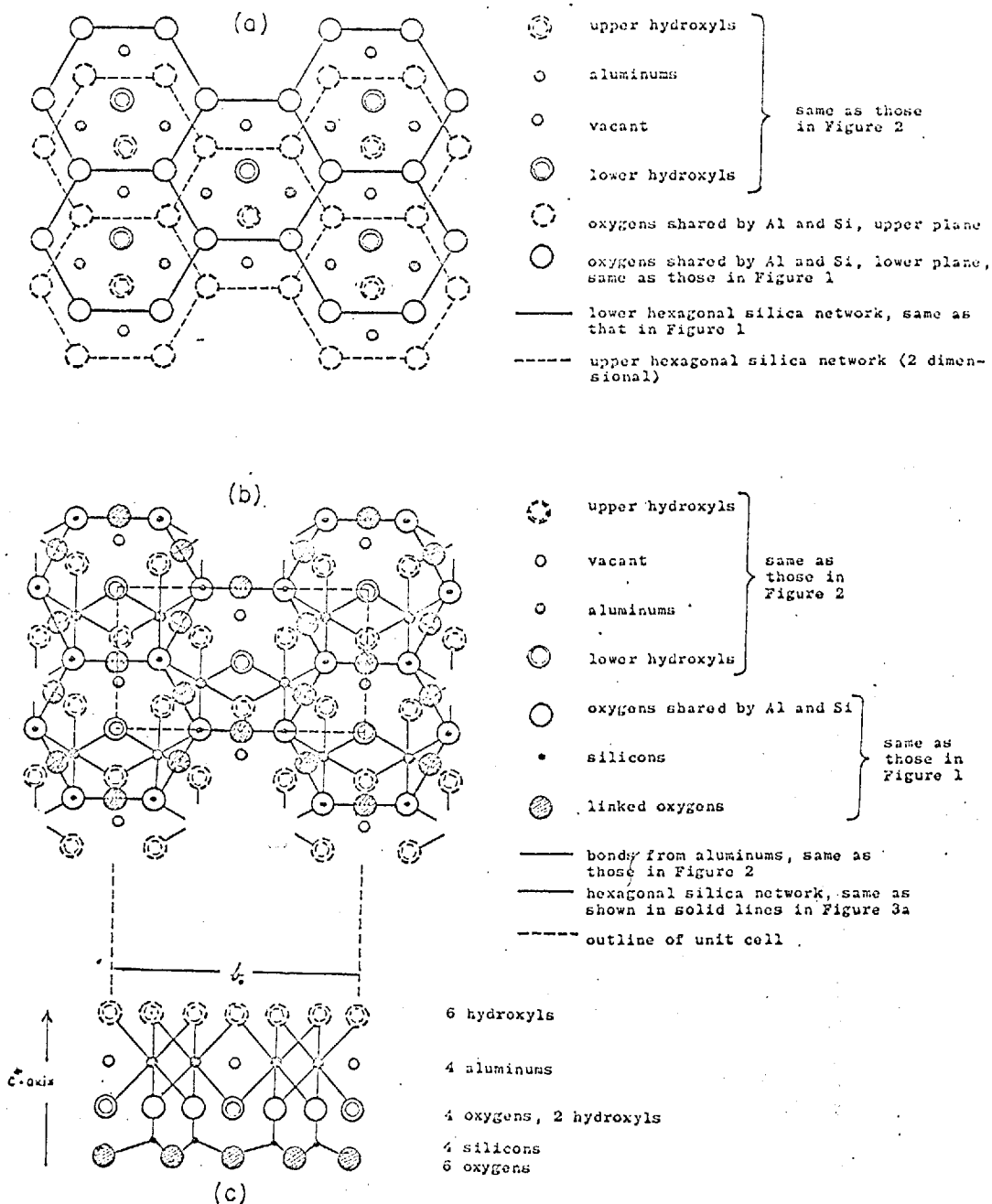


FIG : 3. Combinations of octahedral and tetrahedral layers.

a. Octahedral layer when part of a 2:1 mineral, for example pyrophyllite or muscovite.

b. Combined tetrahedral and octahedral layers. 1:1 (001) projection. (the diagram shows no distortions and the unit cell is monoclinic rather than triclinic like kaolinite.)

c. (100)* projection of unit cell shown in 3b.

The combination of one of each type of layer is shown in fig. 3.

Examination of the unit cell outlined in fig. 3c shows that a unit cell of a silica sheet plus a gibbsite layer contains the following ions in sequential layers, 6 O, 4 Si, 4 O plus 2 OH, 4 Al, 6 OH. The layer lattice silicates are subdivided on the basis of three main criteria, two basically structural and one basically compositional.

- (1) The type of combination of the tetrahedral silica layers with the brucite or gibbsite layers. 1 tetrahedral:1 octahedral or 2 tetrahedral:1 octahedral.
- (2) The cation content of the octahedral layer, either 2 cations per half unit cell (dioctahedral) or 3 cations per half unit cell (trioctahedral).
- (3) The manner and perfection of stacking of the fundamental unit (2:1 or 1:1) packets upon each other.

Table 1 and figures 4 and 5 illustrate how the first criterion divides the clay minerals into three main groups and figures 4 and 5 illustrate the combination of layers in those groups.

The simplest combination of one octahedral layer and one tetrahedral layer yields the so-called "kaolinite-septechlorite" group, which is aptly described by the term

1

Groups	2-layer = 1:1 = 7 Å		3-layer = 2:1 = 10 Å						4-layer = 14 Å
	KAOLIN-SEPTICHLORITE		PYROPHYLLITE-TALC		EXPANDED 2:1 MINERALS		MICA		CHLORITE
	dioc.	trioc.	dioc.	trioc.	dioc.	trioc.	dioc.	trioc.	trioc.
Mineral or mineral families*	Kaolinite	Chrysotile (SERPENTINES)	Pyrophyllite	Talc	Montmorillonite	Hectorite	Celadonite	Polyolithionite	
	Dickite					Stevensite			
	Nacrite								
	Halloysite								
	Endellite								
increasing tetrahedral substitution ↓	↑				BEIDELLITES	SAPONITES	PHENGITES	LEPIDOLITES	
	↑				nontronite				
	↑				dioc. vermiculites	VERMICU- LITES	Muscovite	Phlogopite	CHLORITES
	↑						Margarite	BIOTITES	
Common heteropolytypes	SEPTICHLORITES				mixed layers		mixed layers		

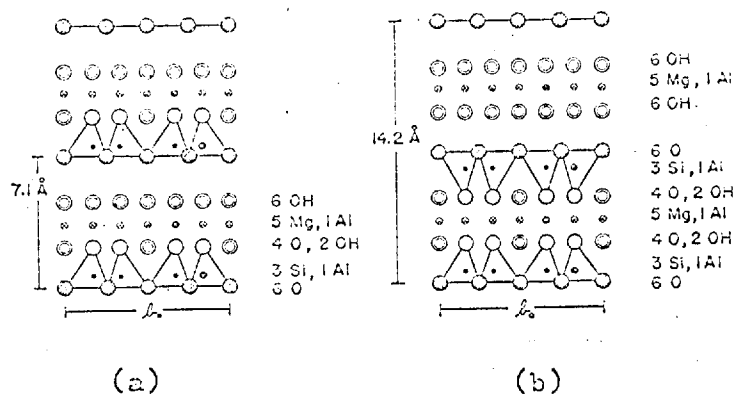


FIG : 4. Diagrammatic (100)* projections of septechlorite (a) and normal chlorite (b) of clinocllore composition. Compare fig:4a. with the dioctahedral analogue shown in fig:3c. The exact locations of the aluminium ions shown in the octahedral and tetrahedral layers are not significant.

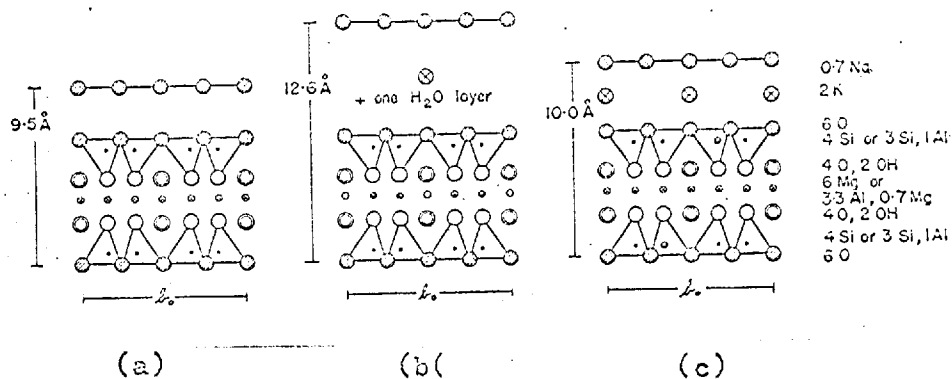


FIG : 5. Diagrammatic (100)* projections of 2:1 layer silicates.

a. talc, b. montmorillonite c. phlogopite. Variations in the thickness of unit layers (not thickness of unit cells, which may contain more than one unit layer) are indicated.

1:1 clay mineral group. It is also referred to as the $7\text{\AA}^\circ$ group from the fact that $7\text{\AA}^\circ$ is approximately the thickness of the combined layers and this corresponds to the largest spacing observed on the X-Ray diffraction pattern. See fig. 4.

Next is the talc-mica-montmorillonite group which is also referred to as the 2:1 or $10\text{\AA}^\circ$ group, the former in reference to the fact that there are two tetrahedra layers for each octahedral layer in the unit. The $10\text{\AA}^\circ$ refers to the height of such a 2:1 combination. Fig. 5c.

The chlorites or $14\text{\AA}^\circ$ group, consists of a regularly alternating sequence of 2:1 or talc units and complete brucite layers. The sequence of layers is therefore (2:1)(1)(2:1), fig. 4(b).

The group known as mixed layer minerals which will be described later consists of combinations of fundamental units of more than one main group.

Composition of layer Silicates. The compositional relationship among and within the main families of the clay minerals can be shown in a ternary compositional diagram having as apices SiO_2 , R^{2+}O and $\text{R}^{3+}_2\text{O}_3$. The minerals and families plotted on fig. 7 show no alkalis, and the anhydrous composition are plotted on a ternary diagram that is actually the anhydrous base of the tetrahedron with H_2O as the fourth apex.

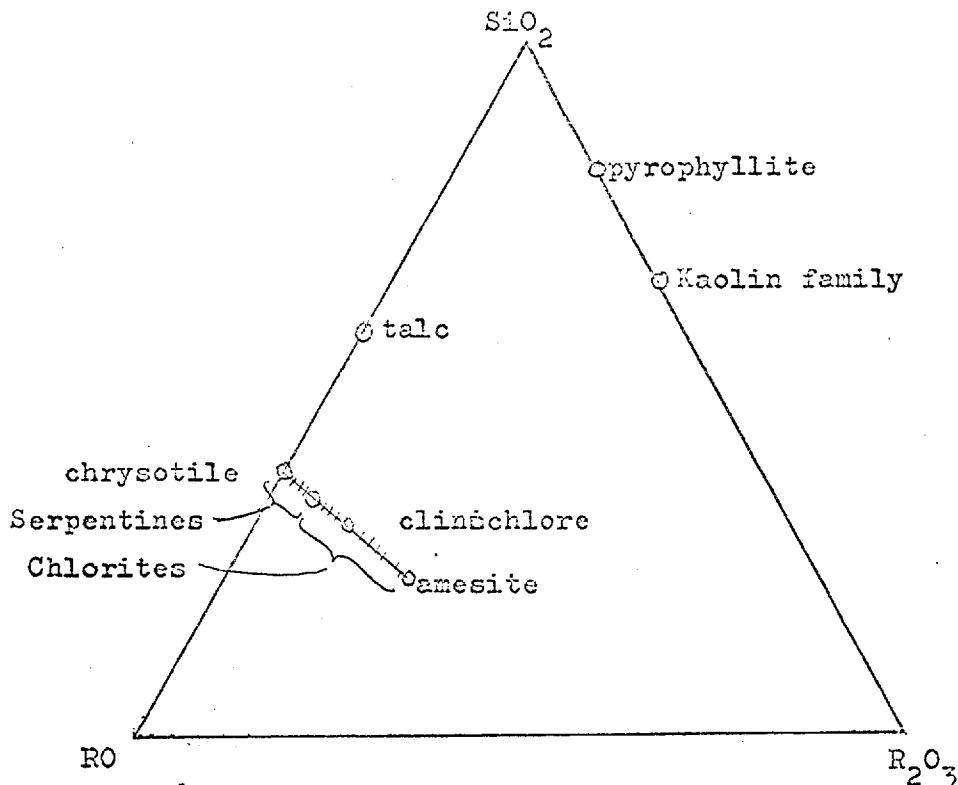


Fig : 6 Diagram showing composition of aluminium, magnesium, and iron layer silicates containing no alkalis. Diagram shows projection of hydrous phases onto anhydrous base.

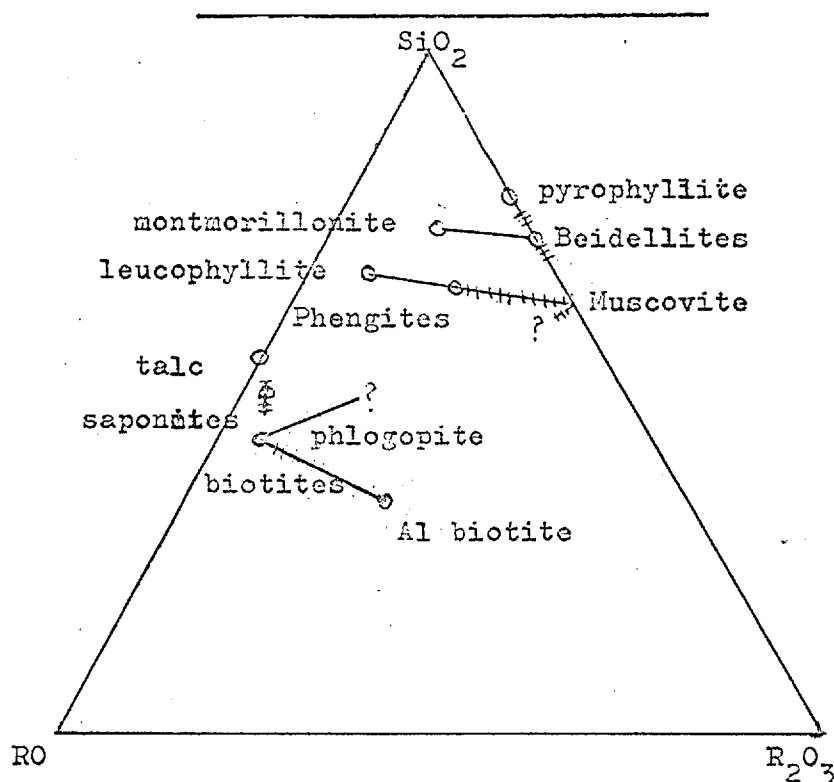


Fig : 7 Diagram showing compositions of the aluminum, magnesium and iron 2:1 layer silicates. Diagram represents projection of mica and montmorillonite composition planes onto anhydrous, alkali-free base.

In the plotting of figure 7 both water and alkali oxides were subtracted from the mineral compositions so that this diagram actually represents the composition planes of both the micas and expanded 2:1 minerals in the anhydrous tetrahedron $R_2O - RO - R_2O_3, SiO_2$.

Talc and pyrophyllite are also shown in fig. 7. The crossed lines indicate the extent of solid solution found experimentally by hydrothermal synthesis. Compositional variations in the clays are controlled by simple crystal-chemical principles.

The simplest substitutions involve the replacement of an ion by another of similar ionic radius but identical charge e.g. Fe^{2+} replacing Mg^{2+} . However many more combinations are possible by balanced substitution in the various positions in the layer lattice. Thus a very common substitution is Mg^{2+} (in 6 fold coordination) + Si^{4+} (4 fold) being replaced by Al^{3+} (in 6 fold) + Al^{3+} (4 fold). The charge lost in one "layer" is compensated for by an identical gain in another.

In micas, expanded 2:1 minerals and chlorites with three types of positions, several combinations are possible. Silicon is commonly replaced by aluminium or ferric ion, and the ions commonly substituting for one another in the octahedral layer are aluminium, magnesium,

ferrous and ferric iron and lithium. Hydroxyl ions are replaced by fluorine or chlorine ions but these substitutions do not require accompanying substitutions in other positions.

The ions that may occur in the interlayer positions are commonly potassium, sodium, calcium, magnesium, aluminium and hydronium. Many other cations have been substituted for these by direct synthesis and nearly completely by ion-exchange methods. Much of the theory concerning ionic substitutions has been verified by syntheses of the various layer silicates under controlled conditions of composition, temperature and pressure.

Figures 6 and 7 show that the various structural families are also clearly represented by compositional ones. Thus the trioctahedral and dioctahedral 1:1 families (fig. 6) are widely separated. The presence of 2:1 families is also shown although here the compositional tendency to merge into one another is also apparent.

With regard to the expanded 2:1 minerals considerable idealization is involved in the representation of the compositional variation as straight lines. Both work on synthetics and analyses of natural materials suggest much greater latitude in compositional variation, reflecting various possible combinations of structural 'defects'.

Three layer (2:1) Silicates

Pyrophyllite-Talc.

Only three minerals fall into this group; no polytypic variations have been found. Pyrophyllite, the dioctahedral mineral is a pure hydrous aluminium silicate. A small amount of ~~aluminium~~ in talc, the trioctahedral magnesium mineral, has been found, Brindley (1960). Minnesotaite is the ferrous iron analogue of talc, (Gruner (1944)).

Expanded 2:1 Minerals

These minerals are intermediate in the structural scheme between pyrophyllite-talc minerals and the micas (see fig. 5.) This concept is known as the Hofmann-Edell-Wilm-Marshall-Hendricks structure of montmorillonite.

The work of Maegdefrau and Hofmann showed that generally the unit layers are stacked without any fixed periodical arrangements in the a and b directions. Although **Vermiculite** is included in this group it does, like a number of other trioctahedral expanding 2:1 minerals, show hkl reflections demonstrating considerable order of stacking.

The expanded minerals unlike the other 2:1 layer

silicates include loosely bound cations and layers of water between the silicate sheets. The water can be partially or completely replaced by polar organic molecules.

The physical swelling and the variability of the basal spacing is the property all expandable 2:1 silicates share and in general these minerals have an interlayer cation population of less than two-thirds of the maximum possible interlayer cation population. The number of interlayer cations is commonly but not invariably approximately one third that found in micas.

The various expandable 2:1 layer silicates are listed in Table 2. The interlayer cations are represented by M_x as they may be varied by simple cation exchange.

Of the minerals listed in this table, montmorillonite, hectorite, and stevensite show less variation in composition than do the other minerals in this group, because only minor amounts of substitution occur in the tetrahedral layer. Montmorillonite is by far the most common of these three minerals. Minerals having both octahedral and tetrahedral substitution fall into three families, beidellites, saponites and vermiculites.

In general all the minerals in the upper portion of Table 2 should be grouped together as the minerals of this group can be distinguished from the vermiculites,

TABLE : 2.

Diocahedral			Triocahedral		
Name	* Formula of 2:1 layer	Seat of charge	Name	* Formula of 2:1 layer	
MONTMORILLONITE GROUP	Montmorillonite	octahedral only (essentially)	Hectorite	$Mg_{3-x}Li_xSi_4O_{10}(OH)_2$	MONTMORILLONITE GROUP
	$Al_{2-x}Mg_xSi_4O_{10}(OH)_2$	$x > y,$ $y \text{ near } 0$	Stevensite	$Mg_{3-x}Si_{4-y}O_{10}(OH)_2$	
		octahedral dominant	Saponite	$Mg_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$	
		$x > y.$	pimelite	$Ni_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$	
	(Beidellite)		sauconite	$Zn_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$	
	Nantronite		Nedmonite	$Cu_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$	
	$(Fe,Al)_2Si_{4-y}Al_yO_{10}(OH)_2$	tetrahedral dominant	(Synthetic) saponite	$Mg_3Si_{4-y}Al_yO_{10}(OH)_2$	
	volchonskoite	$y > x$			
	$(Al,Cr)_2Si_{4-y}Al_yO_{10}(OH)_2$	tetrahedral only			
	(synthetic) beidellite	$y < 0.5$			
	$Al_2Si_{4-y}Al_yO_{10}(OH)_2$				
	diocahedral Vermiculite	tetrahedral dominant	Vermiculite	$Mg_{3-x}Fe_xSi_{4-y}Al_yO_{10}(OH)_2$	
	$(Al,Fe)_{2-x}Mg_xSi_{4-y}Al_yO_{10}(OH)_2$	$y \text{ near } 1.$			

* Idealized ; Interlayer cations omitted because variable.

which have larger amounts of tetrahedral substitution, by treatment with ethylene glycol.

In classifications of the clay minerals it is found convenient to have a sub-group name for this upper portion of Table 2. Most American clay mineralogists prefer the term montmorillonite, though the term smectite has been proposed by the Clay Minerals Group (British).

Micas.

The structural unit in the micas consists of two tetrahedral layers with a layer of octahedrally coordinated cations between them and with a layer of large cations (the interlayer cations) bonding this 2:1 unit to the next.

There is one interlayer cation per formula unit cell (two per unit cell of a single layer polytype). The interlayer positive charge is balanced by substitution of ions of smaller charge for some of those in the octahedral or tetrahedral layer or both. The bonding between the sheets is much stronger in the micas than in the other clay minerals, since the interlayer cations fill all possible positions and are not hydrated.

3. SOME PROPERTIES OF EXPANDING 2:1 TYPE CLAYS MINERALS.

3.1.1. Cation Exchange in Micaeous Type Layer Lattice Silicates

The montmorillonite type minerals have the property of sorbing certain anions and cations and retaining these in an exchangeable state i.e. these ions are exchangeable for other anions or cations by treatment with such ions in aqueous and non-aqueous environments.

Soil scientists have long been aware of the importance of cation-exchange, but it is only in recent years that exact quantitative studies of well defined clay minerals have been undertaken. Although the matter of cation replaceability is of great importance and a large amount of research on the problem has been reported it is not yet completely understood but it is known that it is controlled by a number of factors, and much has been learned about the influence of each of these. In the following discussion of some of the factors involved and survey of published work no attempt has been made to place them in order of importance.

Effect of concentration.

Since cation-exchange in clays is a stoichiometric

reaction and in general the laws of mass action would be expected to hold, any increase in the concentration of the replacing cation causes greater exchange by that cation. Many departures from these generalizations have been reported and Schachtshabel (1940) demonstrated conclusively that the effects of concentration depend on the kind of cation that is being replaced and also on the valency of the cation as well as on other factors.

The complexity of this factor of concentration is shown by the following data brought out by Kelley (1921). With cation pairs of about similar replacing power and of the same valency such as K^+ vs. NH_4^+ or Ca^{++} vs. Ba^{++} dilution has relatively little effect on exchange, while with cations of different replacing power and different valence, for example Na^+ vs. Ca^{++} or NH_4^+ vs. Ca^{++} , dilution produces a marked effect upon exchange. No fully satisfactory explanation of these facts has yet been made.

Population of Exchange Positions.

Jenny and Ayres (1939) and later Winklander (1946) have shown in considerable detail that the ease of release of an ion depends not only on the nature of the ion itself but also upon the nature of the complementary

ions filling the remainder of the exchange positions and on the degree to which the replaced ion saturates the exchange spots. Thus Winklander shows that as the amount of exchangeable calcium on the clay mineral becomes less, the calcium becomes more and more difficult to release. Sodium, on the other hand, tends to become easier to release as the degree of saturation with Na^+ ions becomes less. Magnesium and potassium are not affected by the degree of saturation to the same extent as calcium and sodium.

Effect of Heating.

The work of Hofmann and Endell (1939) and Hofmann and Kleman (1950) has indicated that heating to moderate temperatures not only reduces cation exchange capacity but changes the relative replaceability of the cations. See Table 3.

TABLE 3

MINERAL		Heating temperature °C.	Drying time (days)	Exchangeable cations meq./100gms.
Ca	montmorillonite	105	2	93
		300	2	41
		390	14	12
Na	montmorillonite	105	2	95
		300	2	90
		390	14	68
Li	montmorillonite	20	-	98
		105	2	56
		125	2	31
		200	2	20

The results shown above indicate that montmorillonite heated to 125°C tends to fix Li^+ in an unreplaceable form but does not affect the replaceability of Na^+ whereas at ordinary temperatures Li^+ is more easily replaced than Na^+ . Hofmann and Endell (1939) have interpreted their data to mean that when the clay is heated, the exchangeable cations tend to move inside the montmorillonite lattice. Since Li^+ is a small ion,

it can fit easily into the structure possibly in vacancies in the octahedral sheet, and consequently only a low temperature is required for the shift into the structure (see also section on Fixation of Cations).

Fixation of Cations.

It is well known by soil scientists that certain cations may be sorbed by the clay minerals in a non-exchangeable or difficultly exchangeable state. The ions held in a non-exchangeable manner are commonly described as being "fixed".

Potassium is the commonest ion that is 'fixed' to a considerable degree and the ion that has been most studied because of its importance in soil fertilization. Wood and De Turk (1941), Stanford (1947) and others have shown that illite will fix potassium and most of K^+ fixed in soils is probably due to this mineral. The potassium fixation in illite occurs by the emplacement of K^+ between the basal surfaces of the mineral in the position normally occupied by K^+ in this mineral. Much illite, particularly in soils which are undergoing leaching is somewhat degraded, i.e. it is potassium deficient in that leaching has removed some K^+ from positions between the layers. On the addition of potassium to such material K^+ goes

back into these normal positions and illite is rebuilt. A number of workers have noted the ability of potassium to 'fix' after dehydration of the clay. The clay becomes unexpandable even with water giving a mica like structure with a reduced base exchange capacity. Page and Baver (1939) related this to the similarity of size of the cavities in the sheets and the ionic size of K^+ . Jackson and Hellman (1959) noted that K^+ montmorillonite heated to $110^{\circ}C$ had a 'c' spacing of $10\text{\AA}$ and concluded that the K^+ ions must be sunk to some extent in the sheets. Partial fixation and a 'c' spacing of $9.4\text{\AA}$ was noted by Greene-Kelly for Lithium montmorillonite heated to $300^{\circ}C$. Similar results with Li^+ have been reported by Hofmann and Endell (See Section ^{on} Heating effects on ion-exchange) except that only moderate heating $105^{\circ}C$ was required to 'fix' the cations. Garcia (1949) noting a similar phenomena for Li^+ and Mg^{2+} suggested that fixation occurs with small ions having intense electrostatic fields after heating at temperatures low enough to remove only the water of hydration of the ions.

Some studies on the fixation of cations of various sizes in two montmorillonites have been made by Mackenzie (1964). After a process of repeated wetting and drying he found that ions with radii equal or less

than that of Lithium or greater than K^+ were fixed in amounts which increased with the number of wetting and drying cycles. The fixation of the small cations was explained by the penetration into the lattice of these ions, but no satisfactory explanation could be given for the behaviour of the large cations in montmorillonites which were considered from analytical data to have low layer charges. One tentative suggestion advanced to explain these fixation phenomena was the existence of localized spots of high charge density.

This brief outline of published work on the subject of ion fixation in montmorillonites indicates that although a large amount of research has been undertaken on the subject no satisfactory explanation for the phenomenon is yet forthcoming. In general however it can be said that ion size and temperature are two major factors in ion fixation.

Clogging of Cation-Exchange Sites.

It has been shown by a number of workers, such as Marshall (1934), Mukherjee (1942) and others that H^+ montmorillonites are in reality Hydrogen-aluminium systems because it is substantially impossible to prepare a clay in which all the exchange positions are occupied by H^+ ,

since H^+ moves from the lattice to exchange positions before saturation with H^+ becomes complete.

The development of Al^{3+} on exchange positions reduces the exchange capacity of montmorillonite clays. This is in part due to damaging of the montmorillonite lattice, but also in part to clogging of the exchange positions by aluminium. Numerous recent publications by Jackson (1959) (1960) (1961) have shown that the exchange capacities of clays containing $Al(OH)_2^+$ ions in the exchange positions can be considerably increased if the interlayer $Al(OH)_2^+$ ions are removed by treatment with a complexing agent such as sodium citrate.

A somewhat similar effect may be produced by organic ions. In a montmorillonite with a C.E.C. of 100 meq/100gms. and a unit cell weight of 720 and assuming that 80% of the exchange positions are on basal surfaces there would be 1 equiv for $1\frac{3}{4}$ unit cells. With a basal surface area of $92\text{\AA}^2$ per unit cell there would be a total surface area for each position on each basal plane surface of about $80\text{\AA}^2$. As a result of this limited area available per cation Hendricks (1941) has pointed out that large flat organic ions with areas $> 80\text{\AA}^2$ adsorbed on the basal surface would block more than one exchange position and thereby reduce the exchange capacity of the montmorillonite.

General.

Jenny and co-workers (1932) have determined the exchange isotherms for a number of cations on beidellite. The order of ease of entry by exchange was $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{H}$ and $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{La} < \text{Th}$. However in the divalent series the order depended to some extent upon the cation originally present whereas the monovalent series was entirely consistent. In the release of polyvalent cations irregularities were sometimes found.

Jenny considered that the two factors of greatest importance were valency and hydration though Marshall is of the opinion that comparative hydration figures for aqueous salt solutions may be somewhat misleading since the hydration of the cation which is anchored to the clay may be affected by the silicate structure itself. Giesecking (1939) exchanged H^+ and Ca^{++} montmorillonite for a large variety of organic ions. He found that with large ions the 'c' spacings were not significantly affected by variations in water content. The large ions were not easily replaced by H^+ but exchanged readily with ions of similar size to themselves. Hendricks (1941) showed that the interlamellar spacings depend on the size of the cations and suggested that the ions occupy their

minimum thickness between the sheets. Both amino groups of an organic diamine were found effective in ion exchange. He suggested that whilst only coulombic forces bind the inorganic ions the larger organic ions are held by van der Waals forces as well.

Jordan (1949) exchanged montmorillonites with n primary aliphatic amines. For chain lengths up to 10 C the separation corresponded to the diameter of one methyl group i.e. one layer of ions. Above 10 C. the separation was equivalent to a double layer of ions presumably since there is not sufficient interlamellar area to accommodate in one layer all the ions of higher chain length required for complete exchange. His organic derivatives with one layer of ions showed no swelling in organic liquids whereas those with two layers of ions did. This might be indicative of an increase in organophilic nature or increase in energetic ease of further separation with higher initial separation.

Weiss and co-workers have over the past ten years made a large contribution to the study of ion-exchange processes in mica-type layer lattice silicates. Their work is summarized in two recent reviews (Weiss (1963a) (1963b)) and the studies have included both inorganic and organic alkylammonium ions. The investigations

using alkylammonium ions of varying chain length are of particular interest. They found that the ion-exchange reaction of the layer silicates, mica, montmorillonite and vermiculite with n-alkylammonium depended on the change density of the silicate and the length of the n-alkyl chain.

3.1.2. Complex Formation and Interlamellar Sorption in Micas.

That water and other vapours may be held directly on the surfaces of the clay particles in a physical state different from that of the liquid has long been known.

Because of the polar character of the unit sheets, natural montmorillonite is capable of sorbing polar molecules including water and many organic molecules. Non-polar molecules are however only slightly sorbed on the external surfaces of the crystallites. The necessity for polar groups is no doubt associated with the fact that the montmorillonite sheets are charged and held together by positive ions between the sheets. The energy of formation of a purely van-der-Waals complex is insufficient to cause break-up of the sheet-ion-sheet complex. For convenience in describing some of the

complexes formed by montmorillonites they are divided into two main types

1. Liquids and inorganic cations.
2. Liquids and organic cations.

1. Complexes with inorganic cations and Liquids

Extensive studies of this type of complex have shown a marked influence of the cation on the layer separation and the common occurrence of mixed layer structures i.e. the interleaving of different hydrates with different spacings giving rise to non-integral series of orders and diffuse scattering.

Bradley, Grim and Clark (1937) found that water molecules are sorbed in monomolecular layers between the montmorillonite sheets. They concluded from experiments with H-montmorillonite that structures with one, two, three and four interlamellar water layers are possible. Other ions may not give quite the same sequence of layers but the occurrence of 'steps' is now accepted as a general phenomena. More recent investigations of the uptake of water as a function of vapour pressure show clear evidence of layer formation. (Mooney, Keenan (1952). Cornet (1943). Gillery (1959).) Curves relating the basal spacing to water vapour pressure

for various interlamellar cations are given in the paper by Mooney et al (1952) and the results show that for most cations, the two layer complex with an approximately $15.6\text{\AA}$ spacing has a wide range of stability. Ca^{++} montmorillonite tends to be more highly hydrated than Na-montmorillonite at all pressures.

The work which has so far been discussed is largely qualitative in nature because the experimental methods have not been either sufficiently accurate or reproducible to warrant quantitative analysis. More recently Barrer and co-workers have used more accurate methods in their investigations on montmorillonite-type clays.

Barrer and MacLeod (1954) in their measurement of the sorption properties of sodium rich montmorillonite found that non-polar species are not normally intercalated, but polar species may be. Methyl and ethyl alcohols, ammonia and pyridine for instance are all sorbed to an extent corresponding to the formation of a monolayer of sorbate between the lamellae. Water is sorbed more copiously corresponding to two layers of sorbate. This work was in agreement with that of Orchiston (1955) but whereas Orchiston observed only one step in the adsorption isotherm with water, Barrer

and MacLeod observed both steps in the isotherm corresponding to the first and second layers of sorbate on both the adsorption and desorption section of the isotherms. They found however that polar species may not penetrate the lamellae, where steric effects forbid e.g. tertiary-butanol. Norrish and Quirk (1954) have made a detailed study of the swelling of several clays in suspension. Lamellar separations up to $400\text{\AA}$ could be measured on a flat plate camera.

One flake of sodium bentonite was suspended in sodium chloride solution and the $d(001)$ spacing was found to increase as the salt concentration decreased. At high concentrations about $4N$, the spacing was $15.4\text{\AA}$. As the concentration was decreased, the spacing first increased suddenly to $19\text{\AA}$, then at $0.3N$ increased again suddenly to $40\text{\AA}$. Thereafter the increase with decreasing concentration was continuous until the X-ray pattern became diffuse and finally disappeared at a spacing of about $140\text{\AA}$. For the lithium and hydrogen clays a sudden increase in the lamellar separation was also observed. At a concentration of $0.5N$ with respect to the relevant chloride it jumped from 19 to $22.5\text{\AA}$. This was followed by a further jump to between 35 and $40\text{\AA}$. After this, the behaviour was the same as ~~the~~^{for} sodium

clay. Norrish points out that the variation in spacing below $22\text{\AA}^{\circ}$ is dependant on the cation, whilst above this value all three clays show a similar sudden increase in sheet spacing, which he suggests, may be due to a reversal of the forces holding the sheets together. Thus when the alumino-silicate sheets are close together, the positive charges on the cation pull the negatively charged sheets together, but as the cations become more heavily hydrated they are more effectively screened from the lamellae, which therefore repel one another.

A considerable variety of clay complexes with organic liquids have been studied. Greene-Kelly (1955) has prepared and examined by X-ray methods a number of complexes between sodium montmorillonite and polar liquids such as nitrobenzene, o-toluenitrile and pyridine. The nitrobenzene complex had a basal spacing of $15.2\text{\AA}^{\circ}$ or $12.5\text{\AA}^{\circ}$ depending on whether the nitrobenzene molecules were orientated in a flat or upright manner. Similarly the pyridine complex gave basal spacings of $12.5\text{\AA}^{\circ}$ and $14.8\text{\AA}^{\circ}$. Both the pyridine and nitrobenzene complexes had only one layer of organic molecules between the sheets.

The polar acetonitrile molecule was found by MacEwan (1948) to form a complex, having a $19.6\text{\AA}^{\circ}$ basal spacing with Ca^{++} montmorillonite. A one dimensional

Fourier projection of the acetonitrile complex indicated the presence of three molecular layers between the sheets.

The $17\text{\AA}$ ethylene glycol and glycerol complexes widely used in clay mineralogy as a qualitative test for the presence of expanding 2:1 clays has been extensively studied. With Na^+ and Ca^{++} saturated montmorillonites glycerol gives a basal spacing of $17.7\text{-}17.8\text{\AA}$ and a series of higher orders. The spacings reported for ethylene glycol with montmorillonite saturated with the same cations are in the range $16.9\text{-}17.1\text{\AA}$, also with higher orders. Both the glycol and glycerol complexes are of the two layer type, and are unaffected by water vapour.

2. Organic Cations with Liquids

When the cations in the natural montmorillonite are replaced by organic ions the sorptive and swelling properties of the clay often change markedly.

Jordan (1949) studied the change of montmorillonite from a hydrophillic to a hydrophobic material on replacement of the inorganic cations by organic cations. This would seem to indicate the importance of the ions as sorption sites, at least in the sorption of water. The organic complexes did not swell in water, nor in organic liquids unless two layers of ions were present. The

presence of two layers of organic ions may increase the organophyllic nature or may render further sheet separation more favourable, since there is a higher initial sheet separation.

The change in sorptive properties of montmorillonite when cations are replaced with small alkylammonium ions has been investigated by Barrer and co-workers over the past few years. Barrer and MacLeod (1955) replaced the sodium ions in montmorillonite by tetramethyl and tetraethylammonium ions and showed by X-ray examination of the organo-clays that expansion of the lattice in the 'c' direction had taken place. As a result of this lattice expansion free intercalation of many non-polar hydrocarbon vapours occurred, as indicated by a marked increase in the sorptive capacity.

Polar organic species were also freely intercalated, and the threshold pressure for intercalation having disappeared in some cases. Some 'sieve' action was apparent, both clays, for example, sorbing the pentanes in the order n-pentane > iso-pentane > neopentane. All results could be interpreted in terms of the interlamellar 'c' spacing and the shapes and sizes of the sorbate molecules and of the alkylammonium ions. Barrer and Reay (1957) extended this investigation to a study of

the mono, di-, tri, and tetramethyl ammonium montmorillonite, the 'c' spacings of the four clays increasing with the size of the ion. They again found that sorbates with initial dimensions less than the initial inter sheet separation of the outgassed clay were intercalated with the greatest ease and in substantial amounts. Certain sorbates with dimensions greater than the initial intersheet separation were also readily imbibed to give further expansion of the lattice, but the greater the lattice expansion required for intercalation, the less the net affinity for the clay.

Sorption by montmorillonite containing long chain organic cations has been less extensively studied although the swelling of such clays in a range of liquids has been investigated by Jordan (1949) and recently, more extensively by Weiss et al. Weiss has found that with the exclusion of a few still unexplained exceptions, Walker (1960) (1962) n-alkylammonium ions in montmorillonite do not build diffuse ionic double layers with water, since the alkyl groups are hydrophobic and the N-H --- O hydrogen bridges with the silicate sheet are too strong.

The swelling of n-alkylammonium montmorillonites in water is therefore completely different from that of unaltered montmorillonite. When the alkyl chains are short no swelling takes place. Surprisingly, however,

n-alkylammonium montmorillonites with longer alkyl chains do swell although here stronger hydrophobism is actually to be expected. The swelling behaviour in electrolyte solutions is also unexpected. In contrast to the situation with Na-montmorillonite where electrolyte limits the extension of the diffuse ionic double layer, the basal spacing of montmorillonite derivatives with long chain n-alkylammonium ions actually increase when an electrolyte is dissolved in the swelling agent. Weiss (1963b). The swelling of organo-montmorillonites follows a much simpler pattern in non-aqueous liquids than in water or aqueous electrolyte. With n-alcohols or n-alkylamines of the same chain length as the intercalated n-alkylammonium ions the charge density no longer has any effect on the interplanar distances. (See Ion-Exchange, n-alkylammonium montmorillonites). The similar behaviour of the minerals, montmorillonite, mica and vermiculite is according to Weiss due to the stoichiometry of the 'clathrate' compounds. The sum of the number of n-alkylammonium ions and the molecules of swelling liquid per $(\text{SiAl})_4\text{O}_{10}$ unit is nearly the same in all mica type silicates and amounts to 2.0 if compounds with unbranched alkyl chains are used as swelling agents.

In all of these 'clathrate' compounds the

alkylammonium ions and the molecules of swelling fluid are arranged in a trimolecular layer with their longitudinal axes perpendicular to the silicate layer.

The swelling of mica type layer-silicates with alkylene α -w diammonium ions depend largely upon the number of carbon atoms in the alkylene chain. If this number is even the two NH^+ groups are in direct contact with both the adjacent anion layers. With a cis-trans chain that is inclined at 56° to the basal plane surface all six N-Hydrogen atoms can form hydrogen bonds. Weiss and Michael (1960). The basal spacing that corresponds to this arrangement should therefore provide an upper limit to the swelling, since at least two hydrogen bridges per ion must be broken in order to exceed this distance.

3.1.3. Interstratification and Mixed-Layer Clay Minerals.

Due to structural similarities of the clay minerals, interstratified minerals can exist in which individual crystals are composed of elementary layers of two or more types. Interstratified, or mixed-layer minerals, represent a special case of intergrowths. We

should therefore expect to find a genetical relationship between the components. The simplest case is that of more or less hydrated layers. Montmorillonites and vermiculites are, for instance, essentially hydrated varieties of mica having interlamellar water molecules (i.e. neglecting differences in layer charges). Thus we would expect mica-vermiculite and mica montmorillonite interstratifications to be common as in fact they are.

Instead of water, hydroxide material of gibbsitic or brucitic nature may be present between certain layers, giving mica-chlorite interstratifications or, if hydration is also present, montmorillonite-chlorite, in addition to more complicated cases such as mica-montmorillonite-chlorite. Chlorite may also be interstratified with a kaolinite-like layer.

Interstratified systems may also be formed in montmorillonites and vermiculites by various treatments. Commonly one goes from one hydrate to another through an interstratified mixture of the two. Partial replacement of one interlamellar cation by another, and incomplete formation of organic complexes may also result in interstratification.

Types of Interstratification.

We can consider three ways in which the layers may be distributed in mixtures of this type, namely; regularly (type 1), randomly (type 2), or with segregation into zones in the crystallites (type 3). A regular interstratification has a definite periodicity, and may thus be considered to be a more of a well defined mineral species than the random types. An example is rectorite (Bradley (1950)) in which pyrophyllite-like (or mica-like) and vermiculite-like layers alternate quite regularly to give a structure having a repeat distance of $25\text{\AA}$ ($10\text{\AA} + 15\text{\AA}$). Even chlorites for instance may be regarded as regularly interstratified mica (or talc) brucites; but their importance accords them a separate classification.

In type 2 it should be noted that the word random is given a special meaning. It means with "no detectable influence of one layer on its neighbours". For instance, in a random interstratified mixture of minerals A + B, in equal proportions, the probability of any layer A or B occurring at any particular position is just equal to the probability of it occurring at all ($\frac{1}{2}$ in this case.) In a random mixed-layer structure of $10\text{\AA}$ and $15\text{\AA}$ layers, the first observed reflection will be a composite of (001) of both layers and will have a spacing

intermediate between 10. and $15\text{\AA}$, the exact position depending upon the relative abundance of the individual layers. A strong reflection at $5\text{\AA}$ will appear; this will be a composite of (002) of the $10\text{\AA}$ layers and (003) of the $15\text{\AA}$ layers. Only if the relative amount of the $15\text{\AA}$ layer is large will a slight reflection be found at about $7.5\text{\AA}$.

The position and relative of the composite peaks, or more properly bands, will vary with the relative abundance of the two layers, but it should be noted that the position and relative intensity of the composite peaks do not vary with the relative abundance of the constituent layers in a necessarily straight line relationship. An important diagnostic criterion of a random structure is that it gives a non-integral series of basal reflections.

The extreme case of type (3) is when separate crystallites of the minerals (say A and B) are present. Type (2) may grade into type (1), on one hand and type (3) on the other. The diffraction phenomena of these types of minerals have been dealt with in considerable detail by Hendricks and Teller (1942), Mering (1949), Brown and MacEwan (1951). The main problem with which we are confronted is, given the spacings and intensities of the

diffraction peaks, to deduce the nature of the layer succession.

Interpretation of Diffraction Patterns from Mixed-Layer clays Minerals.

Interpretation is straightforward for regularly interstratified materials. An integral sequence of 00 ℓ reflections is found from a periodicity representing the sum of the component layer thicknesses. Where layers have the same thickness as for example chlorite and vermiculite the interstratification may only reveal itself after treatment which alters the thickness of one kind of layer. In this case collapsing the vermiculite to $10\text{\AA}$ by dehydration will reveal a $24\text{\AA}$ spacing ($10 + 14\text{\AA}$). For regular interstratification of $14/14\text{\AA}$ material, if the layer structure factors of the two kinds of layer are sufficiently different, a reflection at $14 + 14 = 28\text{\AA}$ with higher orders will be observed.

With less regular mixed-layer materials, a considerable amount may be found without any calculation at all simply by examination and measurement of the diffraction pattern provided that the nature of the diffraction process is understood. The principle of a method adopted in many cases can be seen in fig. 8

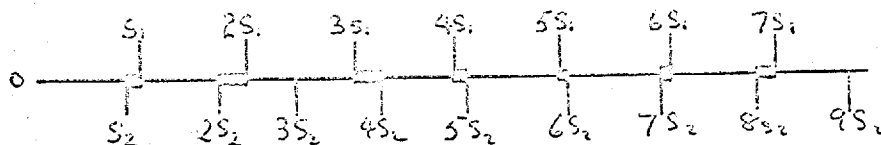


FIG : 8a. Mering's(1949) illustration of regions where reflections are to be expected from an irregularly interstratified mixed-layer material with reciprocal spacings s_1 and s_2

(after Mering (1949) which shows juxtaposed the 00ℓ reciprocal lattice rows of reciprocal spacing $S_1 = \frac{1}{d_1}$ and $S_2 = \frac{1}{d_2}$; the heavy lines indicate the regions in reciprocal space where reflections will occur from a non-regular two-component mixed-layer mineral whose fundamental spacings are d_1 and d_2 . As the fractional proportion of the material of spacing d_1 changes from 1 to 0, a reflection of the series S_1 moves towards the adjacent S_2 reflection.

In a preliminary analysis there will be no great error in assuming that the peaks move linearly from the position for one pure component towards the nearest position

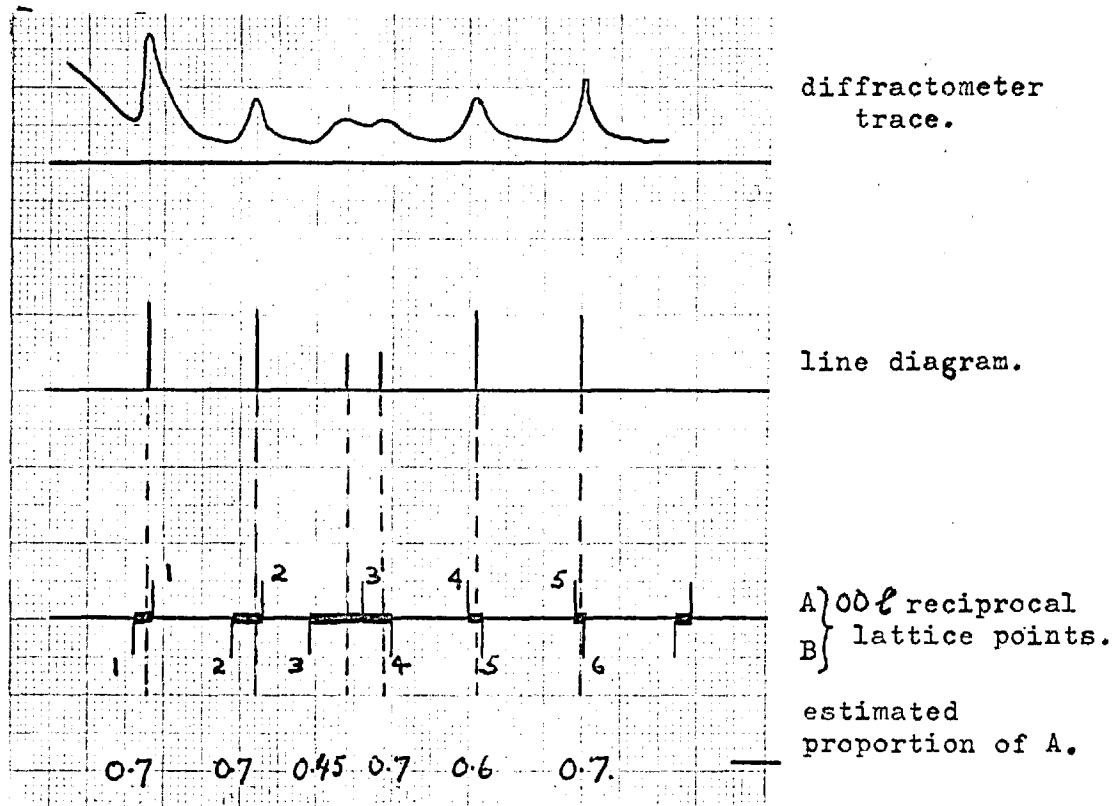


FIG : 8b. Diagrammatic illustration of visual inspection method of interpreting diffraction patterns from a mixed-layer structure.

of the other component as the proportion of the components alter. If a certain interstratification is thought to be present the positions of the 00ℓ reflections from the pure substances are marked off along a line beneath the diffraction diagram which may be in the form of a diffractometer curve, a microphotometer curve, or simply a line diagram of peak positions and intensities obtained from a powder photograph. No great error is involved in this, since the scale of the diffraction diagram and the scale of the reciprocal lattice θ and $\sin \theta$ respectively, are closely proportional below $\theta = 20^\circ$. The positions of the observed maxima are marked along the line beneath the diagram, and each of these is joined to the neighbouring reflection positions for the pure substances. It should be found that the observed reflections are situated at about the same relative distances from the nearest reflection positions of each pure substance and these distances indicate the proportions of the components. If the distances from neighbouring A and B positions are x and y respectively, the proportion of A is deduced to be $y/(x + y)$. If the interpretation is correct observed peaks will tend to be broad where the horizontal connecting line is long, and sharp when it is short. Figure 8 shows an idealized example of the process.

It is possible using methods developed by MacEwan (1956) to calculate the diffraction patterns to be expected for any assumed model; but this is essentially a trial and error method and for simple two component systems is unlikely to give much more information than the method of Mering (1949). However, curves can be calculated by MacEwan's method which takes into account differences in layer structure factors. Patterns from three component systems have been successfully interpreted by (Weaver (1956) Jonas (1959)). The approach adopted by Weaver is to reduce the system to several two component systems by suitable treatment of the specimen (heating, Mg^{2+} and K^+ saturation) and the diffraction patterns are then interpreted by the visual inspection method described by Mering. The results obtained by Weaver and other workers using this method shows that progress can be made in interpreting the diffraction effects from complex interstratification in a fairly straightforward manner.

For two component randomly interstratified layers with near equal structure factors the method of visual inspection combined with the many curves already calculated for specific instances (Brown (1961)) is generally considered to give satisfactory results. For more complicated systems with two or more components widely

differing layer structure factors, or less than completely random sequences interpretation is more difficult and is likely to give less conclusive results. When long sequences of diffraction maxima are available the direct method of MacEwan (1956) would appear to give the maximum information with the minimum effort.

3.2. Polymorphism in the Micas

Smith and Yoder (1956) have made a detailed experimental and theoretical study of mica polymorphism and it is from their paper that the following account is largely drawn. The structure of a mica polymorph was first established by Jackson and West (1933) from a two layer monoclinic muscovite. Hendricks and Jefferson (1939) demonstrated the existence of other polymorphs and determined their structures. They showed that all the polymorphs were based on the same sub-cell.

Polymorphism in the micas occurs because the atomic arrangement in the sub-cell has monoclinic symmetry, whereas the symmetry of the surface is hexagonal or pseudo-hexagonal. Rotation of a sub-cell by 60° does not affect the packing of the surfaces but does affect the position of the subcell.

The features of the mica structure have been

described earlier but are given again for the sake of convenience (see fig. 9).

All ions in the mica are in parallel pseudo-hexagonal arrays. In each mica layer there are two sheets of oxygen tetrahedra containing oxygen and silicon. Each sheet consists of tetrahedra linked at each of three corners to form an hexagonal array with all the bases parallel and all the vertices pointing the same way. The two silicon-aluminium sheets that are contained in each mica layer are parallel and have opposing vertices. They are held together by magnesium or other ions in octahedral co-ordination. For convenience, the basal oxygen ions of the Si and Al tetrahedra will be denoted O_B and the oxygen atoms at the apices, O_A , see fig. 9(B). The O_A atoms form a hexagonal array and the centres of the array are filled by OH or F ions, see (fig. 9(a)). Each magnesium ion is linked to $2, O_A$ and $1, OH$ from the upper silicon-aluminium sheet and $2, O_A$ and $1, OH$ from the lower sheet.

Although all the atoms are in hexagonal arrays, the linkage at the magnesium ions reduces the layer symmetry to monoclinic with a layer stagger of $1.7\text{\AA}$. Each layer has a vertical plane of symmetry passing through the OH ions, fig. 9(a) and the layer is face centred, giving

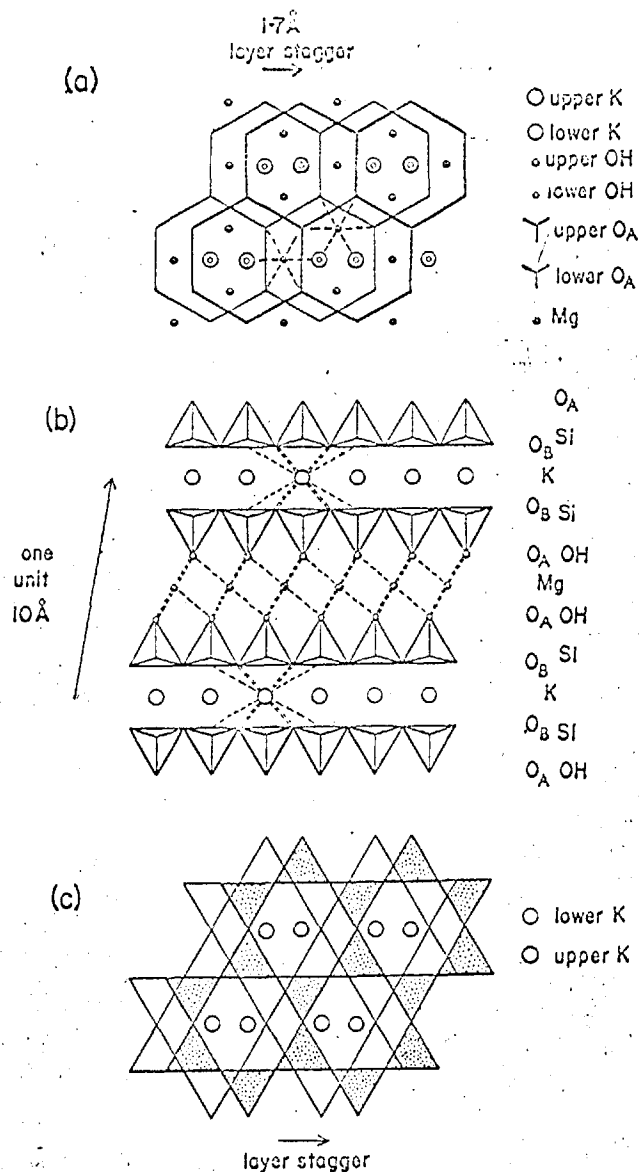


FIG : 9. (a) A projection normal to one mica layer showing the K (O), Mg (●), and OH (○) ions. The O_A oxygen atoms are at the corners of the hexagons. The thick and thin lines and circles in this figure and in fig. (c) represent the upper and lower layers of atoms in the unit. (b). A projection on (010) showing one layer together with the adjacent parts of the two adjoining layers. The O_A oxygen atoms overlap with the OH ions. The O_A and O_B oxygen atoms are at the vertices of the tetrahedra. The K, Si, Mg, and OH ions may be replaced by other ions. (c). projection normal to one mica layer showing only the K (O) and O_B atoms. The O_B atoms are at the corners of the Hexagons.

a symmetry of C_m . The layers are linked by K^+ ions in 12-fold co-ordination, six O_B atoms from each layer. The O_B atoms form two hexagonal arrays and each K^+ ion sits symmetrically in the centre of a hexagonal prism. The O_B atoms above and below the K^+ ions superpose exactly, giving no layer stagger at the interface.

The different ways of stacking two adjacent mica layers will now be enumerated. As the layer stagger is equal to the horizontal displacement of either the O_B atoms or the K^+ atoms and the interlayer stacking is concerned only with these atoms, it is only necessary to consider these atoms for the present purpose. When a new layer is added to the top of the first layer, the six lower O_B atoms of the new layer superpose directly on the six upper O_B atoms of the first layer. Because of the hexagonal symmetry of these oxygen sheets there are six possible orientations of the new layer which are related to 60° rotations. Correspondingly, the directions of stagger of the two layers may be at any one of the six angles 0° , 60° , 120° , 180° , 240° and 300° . Because of the plane of symmetry of the layer that is parallel to the layer stagger angles 60° and 300° are equivalent, as also are angles 120° and 240° . There are therefore four different ways of stacking two adjacent layers. The

simplest way of depicting the stacking sequence is to show the positions of the K atoms on a projection taken normal to the mica layer. It is convenient to draw vectors from one K atom to a K atom in the next layer with the arrowhead showing the direction of increasing height of the mica layers (fig.10.) From the positions of the K atoms the position of the other atoms may be reconstructed. The angle between two interlayer vectors, the interlayer stacking angle is measured in the counterclockwise direction in this discussion.

If there is no control over the choice of the interlayer stacking angle, disordered crystals will result, whose stacking angles occur in random sequence. Each layer will have its atoms in fixed positions: this is random stacking of whole layers, not of individual atoms.

Different sorts of disordered crystals may be obtained by restricting the possible stacking angles. For example, two extreme types of disordered crystals can be built; one containing a random mixture of 0° , 120° and 240° stacking angles, and the other containing a random mixture of 60° , 180° and 300° stacking angles. If there is complete control over the layer stacking, fully ordered crystals will result. By taking all combinations of the stacking methods an infinity of structures

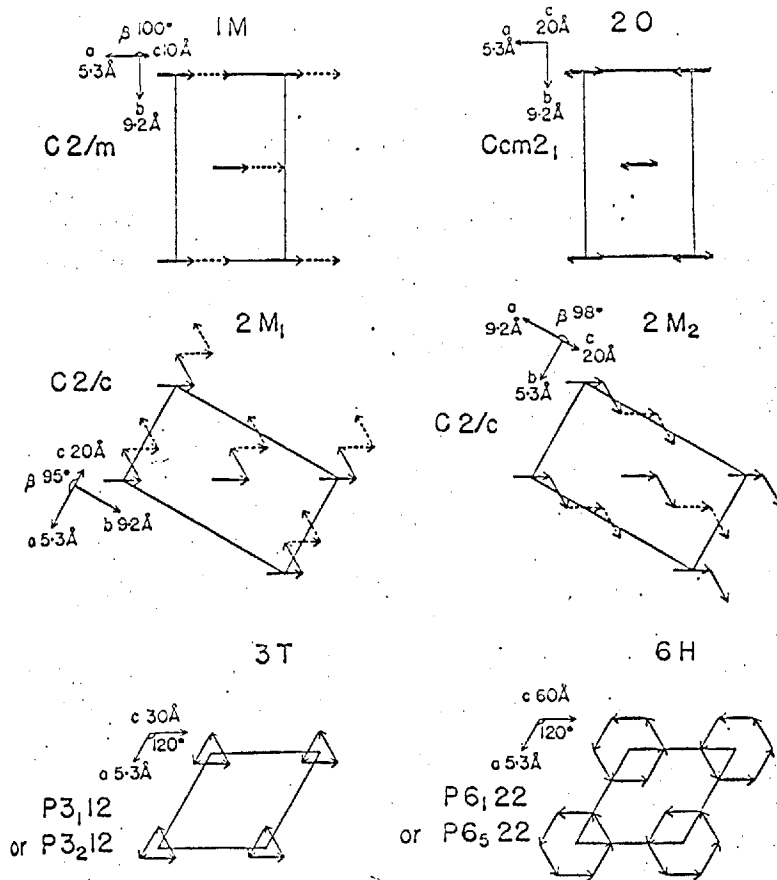


Fig : 10 The six simple ways of stacking Mica layers in an ordered manner. The arrows are the interlayer stacking vectors. Full lines vectors show the layer stacking in one unit cell, whereas the broken line vectors show the positions of layers in the next unit cell. The base of the unit cell is shown by thin lines, and the space group and lattice parameters are listed by the side of the diagram. Note that there are two possible directions of screw of the stacking vectors in the 3T and 6H polymorphs corresponding to the two space groups listed for each polymorph.

may be constructed. However it may be expected that if layers start growing with a particular stacking angle, additional layers will also have this stacking angle.

On the condition that only one stacking angle occurs, six polymorphs may be built as shown in fig.10. For convenience, a simple nomenclature has been adopted in which the first symbol gives the number of layers in the repeat unit and the second gives the symmetry. The polymorphs are 1M, $2M_1$, $2M_2$, 2O, 3T, and 6H. As there are two, two-layer monoclinic (2M) polymorphs, the subscripts 1 and 2 are used. The letter O represents orthorhombic; T, trigonal, and H, hexagonal. The derivation of the six simple polymorphs is as follows.

The only polymorph that can be built solely from the 0° stacking angle is the 1M structure. Similarly the 2O structure is the only one that can be built solely from 180° stacking angles. If 120° and 240° stacking angles are used, three simple arrangements can be found; two of which are merely mirror images. They are: a continuous sequence of 120° angles; a continuous sequence of 240° angles, which give rise to a mirror image of the 120° sequence; and a continuous alternative of 120° and 240° angles. The first two give the 3T polymorph and its mirror image; the third gives the $2M_1$ structure. The derivation

of the polymorphs based on the 60° and 300° angles is identical. The three structures formed are: a continuous sequence of 60° angles; a continuous sequence of 300° angles, which give rise to a mirror image of the 60° sequence; and a continuous alternation of 60° and 300° angles. The first two are the 6H polymorph and its mirror image and the remaining one is the $2M_2$ polymorph. It should be noted that the $2M_1$ and $2M_2$ polymorphs have quite different stacking arrangements even though they belong to the same symmetry system and have the same repeat unit.

If only an occasional stacking fault - that is, a mistake in the repeated sequence of layers, occurs in ordered crystals, twinned crystals result.

Factors governing the growth of Polymorphs:

If the stacking of the layers in the mica structure were uncontrolled, completely disordered structures should always result. In the majority of the natural and synthetic specimens examined so far, the structure is reasonably well ordered, thus demonstrating the existence of controlling bond forces. The presence of stacking disorder, either partial or complete, in some of the micas shows that the controlling bond forces may be weak and may

be rendered inactive under some thermodynamic conditions.

In this section an attempt is made to evaluate the relative dominance of the various structural factors which control the stacking of mica layers.

Observations on the mechanics of growth contribute to an understanding of the structural controls. Two mechanisms of growth have been recognized: growth of perfect crystals by secondary nucleation of each individual layer (Kossel 1927, Stranski 1928); and growth of imperfect crystals (Burton, Cabrera and Frank (1949)) by propagation of one nucleus into many layers of identical structure by spiral growth arising from a dislocation (cf. Frank (1952)).

Tolansky (1945) (1946) has shown that the surface of a mica sheet is violently contorted and crossed by cleavage steps, the heights of which appear to be multiples of the ~~lattice~~ spacing. He also found that muscovites exhibited large areas of uniform thickness and contained many inclusions. The absence of spirals is consistent with either secondary nucleation of perfect crystals or spiral growth with the original dislocation having extended themselves over all the examined faces of the crystal so that they can no longer be detected.

Amelinckx (1952) (1953) has demonstrated that cleavage faces of muscovite contain emerging screw dislocations and that growth spirals occur on a biotite crystal. It appears certain, therefore, that at least some micas have grown by the dislocation mechanism of Frank. The other micas may have grown by either method. If growth proceeds by secondary nucleation of each additional layer there is no necessity for the added layers to adopt a fixed orientation unless other factors control the orientation. However, if growth proceeds by the spiral mechanism, the added layers must adopt the orientation of the primary nucleus and the resultant crystal will consist of a single ordered type of stacking. The type of stacking will thus be governed by the structural bond forces of the primary nucleus.

The second consideration involves the nature of the mica structure itself, and some of its properties will now be examined for evidence of specific structural bond controls. The pseudo-hexagonal stacking of the atoms in the mica structure results in weak structural control between adjacent sheets. The larger the deviation from hexagonal symmetry of the sheets of atoms, the larger will be the structural bond forces that control the orientation of adjacent layers. It should be noted, however, that

even if all the atoms lie in arrays whose symmetry is exactly hexagonal there should still be a small controlling bond force, for the hexagonal sheets of atoms in any one layer are arranged in such a way as to give monoclinic symmetry. This bond force is probably quite small, for it arises in the stagger of the two halves of the mica layer that adhere at the octahedrally co-ordinated ions and it must operate through hexagonal arrays of SiO_4 and AlO_4 tetrahedra, which act as an electrostatic screen. In addition, asymmetry will arise from the distribution of Si and Al atoms in the tetrahedral sheet unless the Si and Al atoms are disordered.

Synthesis and Structural Studies related to Mica Polymorphism

Widely varying compositions in the trioctahedral mica group conform quite closely to the ideal a:b axial ratio of $\frac{\sqrt{3}}{3}$ and exist in several of the polymorphic schemes that depend on exact $\frac{1}{3}$ a displacements in the octahedral layer. Muscovite is of less variable composition with notable tendency towards exact 3:1 occupancy of tetrahedra by Si and Al, and exists in nature predominantly in one crystallization, the $2M_1$ with an 'a' displacement departing substantially from the exact $\frac{1}{3}$.

A survey of measured bond lengths in tetrahedra by Smith (1963) arrived at a consensus that Si-O bonds are $1.60 \pm .01\text{\AA}$ long and tetrahedral Al-O bonds are $1.78 \pm .02\text{\AA}$ long. These are the strongest bonds in the mica structure and they characterize the open hexagonally packed layers. It is logical to assume, that these scalar lengths are relatively fixed and that accommodation to octahedral lateral parameters are accomplished by closures (rotation of tetrahedra) in the open net. Ideal open packing of perfect silica tetrahedra of 1.60 Si-O bond length require a 'b' parameter of $9.05 \pm .06\text{\AA}$ i.e. $6 \times 2 \frac{3}{4} \times 1.60$.

Proportional allowance for $\frac{1}{4}$ Al occupants leads to about $9.3\text{\AA}$. In muscovites the $9.3\text{\AA}$ net is accommodated in a measured $9.02\text{\AA}$ period. The open packed silica net is subject to foreshortening (up to 15%) by rotation of tetrahedra towards close packed, and oversize members may be simply accommodated in the rotation.

From this evidence it is concluded that there is considerable bond control over the stacking of dioctahedral micas and smaller bond control (due to less misfit between octahedral and tetrahedral layers) in trioctahedral layers.

The synthesis of micas and the study of the relation between composition and polymorphic type enable

a contribution to the problem of the nature of controlling bond forces to be made. Yoder and Eugster (1953) found that at higher temperatures hydrothermal growth of synthetic micas is relatively rapid and equilibrium can be demonstrated. Synthetic muscovite crystallises with the $2M_1$ structure whereas phlogopite crystallises with the 1M, 3T or both 1M and 3T structures. Equilibrium at ~~the~~ high temperatures has been approached by converting a 1M and 3T muscovite into a $2M_1$ muscovite and a $2M_1$ phlogopite into a 1M, or 3T or both 1M and 3T phlogopite. These results are in agreement with those found by examination of natural micas from high-temperature environments.

According to Yoder and Eugster (1953), at low temperatures a different situation occurs with regard to the relative dominance of the polymorphs. In the laboratory, muscovite first crystallises with the completely disordered (1Md) structure which changes into the 1M structure during longer runs or at higher temperatures. On raising the temperature the 1M structure can be converted into a 2M structure. The reactions are so sluggish that equilibrium cannot be demonstrated. It is possible that the 1M structure is stable at low temperatures and it is probable that the transformation $1Md \rightarrow 1M$ depends upon the reaction rate.

At low temperatures phlogopite also grows with the lMd structure which transforms into the lM, 3T, or both lM and 3T structures in the course of time at higher temperatures. It is believed that in nature the progressive metamorphism of sediments leads to the transformation $lMd \rightarrow lM \rightarrow 2M_1$ for muscovite in accordance with the laboratory results. For phlogopite both lMd and lM structures have been found in low temperature environments.

In their study of mica polymorphism Yoder and Smith (1956) finally concluded that the growth of lMd phlogopites and muscovites at low temperature fits most easily with the hypothesis of secondary nucleation and no structural control. The $2M_1$ muscovites at higher temperatures with absence of disorder and polymorphism is explained by complete structural control and growth by either mechanism. The growth of phlogopites and biotites at high temperatures with the observed tendency to give lM, 3T, or both lM and 3T polymorphs suggests a moderate structural control that can often be overwhelmed.

The relative importance ascribed to structural control by Smith and Yoder has been rejected by Amelinckx and Dekeyser (1953) who consider order results from crystal growth by the method of Frank (1952) and disorder from high temperature and supersaturation.

A final answer to the problem of mica polymorphism will probably only be settled by more detailed investigations into mica synthesis and accurate structure determinations of a variety of mica polymorphs to determine the interatomic forces operating in the various structures.

4. SOME PREVIOUS SYNTHESSES

4.1. Montmorillonite Type

Information on the composition of the montmorillonite group of minerals obtained by chemical analyses provide a basis for the interpretation of their syntheses in the laboratory.

Ewell and Insley (1955) Noll (1936), Norton (1939). Hauser and Reynolds (1939) all succeeded in carrying out syntheses of montmorillonite type clays. Ewell and Insley (1935) using slightly alkaline co-precipitated gels of Al_2O_3 and SiO_2 in which the mole ratios were $1\text{Al}_2\text{O}_3:2\text{SiO}_2$, succeeded in preparing beidellite at 380° and 390°C and 167 and 260 atmospheres of water vapour pressure respectively. Their material was probably a true beidellite with the composition near $\text{Al}_{2.17}(\text{Al}_{0.87}\text{Si}_{3.17})\text{O}_{10}(\text{OH})_4\text{X}_{0.33}$ which would approximate the $1:2 \text{Al}_2\text{O}_3:\text{SiO}_2$ ratio and in which the exchangeable base X was probably sodium or $\text{Al}(\text{OH})_2^+$. When aluminium and silica were used in the absence of bases only kaolin and pyrophyllite were obtained.

The most elaborate early work on clay^{mineral} synthesis was that of Noll (1936). He used mixtures of hydrated alumina and silicic acid gels in which the mole ratios

were $\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:4$. All experiments were carried out at 300°C and a water vapour pressure of 87 atmospheres. A wide variety of bases were investigated and he systematically varied the base/alumina ratio $(\text{R}_2\text{O}, \text{RO}):\text{Al}_2\text{O}_3$ from $.002 \rightarrow 2:1$ where $\text{R} = \text{Na}, \text{K}, \text{Cs}, \text{Mg}, \text{Ca}$ and Be . In general, when strong bases were used, kaolin was obtained at low base:alumina ratios, montmorillonite from intermediate ratios and analcite at the high base:alumina ratios. His syntheses using magnesium hydroxide base showed that montmorillonite type minerals could be prepared over a very wide range of magnesia concentrations; a factor which is in harmony with their compositions and with the genetic relationship within the group. The experiments of Noll overemphasize the importance of alkaline conditions in the formation of minerals of the montmorillonite group; the presence of bases being of more importance than alkalinity as such.

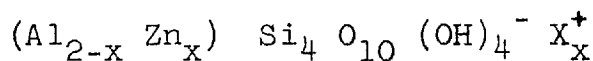
Stresse and Hofmann (1941) prepared a clay-like magnesium silicate by a process involving the slow addition of magnesium chloride to a boiling potassium silicate solution and by modifications of this process with various bases. Their product is described as a "two dimensional gel" having the a-b characteristics of hectorite. When they employed high concentrations of

potassium hydroxide, they reported the formation of mica-like minerals.

Hauser and Reynolds (1939) studied the devitrification of obsidian and of glass approximating Wyoming bentonite in composition, in the presence of acids and bases at 300°C. Both glasses gave montmorillonite type minerals, but the obsidian was much the more stable of the two and altered only in acid solution. Basic conditions were not found to be necessary and in agreement with Noll (1936) a wider range of concentrations were effective when magnesium hydroxide was used.

Using gels of initial composition

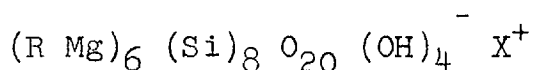
(0.2 - 3.0) ZnO, Al₂O₃, 4SiO₂ + aq, Otsubo and Kato (1954) synthesized a number of zinc smectites. From their results they concluded that the zinc smectite was dioctahedral and could be represented by the following structural formula:



With an emphasis upon low temperature (c.u. 100°C) and dilute solutions the French clay mineralogists, Caillere, Gastuche, Henin, Esquevin et al (1953) (1953) (1964) have synthesized a wide range of clay minerals of the 2:1 and 1:1 layer types.

The cations employed in these syntheses in

addition to silica were Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , Co, and Al^{3+} . The R^{2+} , $\text{R}^{3+}:\text{Si}^{4+}$ ratio was varied in many syntheses over wide ranges to see what effect this would have on the course of the reaction and the nature of the products. Their success in obtaining montmorillonite type clays from alkaline solutions containing the divalent Co, Mg, Ni cations led them to suggest that the brucite-like structure common to all the hydroxide of these cations acted as a nucleus for the formation of the 2:1 clay. When using aluminium in their syntheses they were never able to synthesize 2:1 type clays; instead kaolin and hydrated alumina phases were obtained. Granquist (1961) has carried out a detailed investigation into one of the synthesis of hectorite which can be represented by the general formula:



where R = Li, (Na, K). By using gels having the general composition as shown above he was able to synthesize magnesium clays with properties very similar to those of natural hectorite. He found that if he lowered the pH of the reacting solution by using lithium fluoride in place of the hydroxide he could obtain a marked increase in the rate of hectorite synthesis. Differential thermal

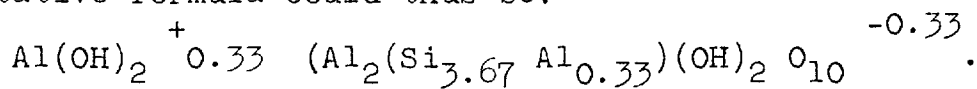
analysis of his products showed that the fluoride ion, as well as catalyzing the clay synthesis, also resulted in a more stable structure being formed. The material synthesized in the presence of lithium hydroxide showed a marked endothermic→exothermic peak at 650°C which was not present on the D.T.A.'s of the material containing fluoride ions.

A considerable amount of work on the conditions for synthesis and the possible range of smectite composition has been carried out by Roy and collaborators in recent years using hydrothermal techniques. Roy and Roy (1955) carried out syntheses in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system which resulted in a variety of montmorillonites from compositions high in silica. Using the following mole ratios for $\text{MgO:Al}_2\text{O}_3\text{:SiO}_2$ of 25:10:65; 22:22:56 and 9.5:12.5:78 they were able to prepare both trioctahedral and dioctahedral montmorillonites. Systematic studies of the variations in properties of expanded 2:1 layer silicates with different types and amount of substitution have been made by Karsulin and Stubican (1954), Koizumi and Roy (1959) and Gillery (1959). Koizumi and Roy (1959) synthesized a number of beidellites with base exchange capacities varying from $\frac{1}{2} N \rightarrow 2N$ (where N = exchange capacity of an ideal beidellite having a b.e.c. of .

90 meq./100 gms. The phases they obtained were reported to be homogeneous, all expanding to $17\text{\AA}^0$ with glycol. These workers also investigated the compositional range of the saponites but found that only the N and 2N members could be prepared as a single phase. Optimum conditions for smectite synthesis in this work were at 300°C for seven days.

The experimental evidence afforded by the studies of Mumpton and Roy (1956) has indicated that solid solution between synthetic dioctahedral and trioctahedral minerals is incomplete. This conclusion ^{which is} ~~being~~ in agreement with the observations of Foster (1951) on natural minerals.

Some interesting syntheses of 'montmorillonites' in the absence of any alkali-metal ions have been reported in the NiO-SiO_2 , MgO-GeO_2 , $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{Ga}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ systems. Roy and Osborn (1954), investigating the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system, reported the synthesis of a pure aluminium end-member of the smectite family (viz. beidellite). The structure however only swelled to $14\text{\AA}^0$ w. glycol. A possible explanation for this diminished expansibility has been put forward by Ross and Hendricks (1941) who suggest that the exchangeable base could be $\text{Al}(\text{OH})_2^+$. A tentative formula could thus be:



The ideal composition then approaches an alumino-silica ratio of 1:3. ($\text{Al}_2\text{O}_3, \text{SiO}_2$)

In the $\text{Ga}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system Roy (1954) synthesized a gallium smectite containing essentially no other cations except Ga^{3+} and Si^{4+} . It expanded to $17\text{\AA}$ with glycol (cf. Al-beidellite) and gave a fairly sharp diffraction pattern. As with the alumina-silica system the exchangeable base is assumed to be $\text{Ga}(\text{OH})_2^+$.

If this smectite synthesized in the $\text{Ga}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system was in fact completely alkali free the results are particularly interesting in view of the fact that no crystalline gallosilicates have previously been reported in the literature although Gehlensdorf (1957) and Toropou (1960) specifically attempted syntheses in this system.

In the $\text{NiO-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO-GeO}_2\text{-H}_2\text{O}$ system Voorthuijsen (1951) and Pflugmacher (1958), respectively, were able to synthesize material having the characteristic smectite X-ray pattern.

As it is unlikely that Ni or Mg would substitute for Si or Ge in the tetrahedral layers the charge is considered to arise from vacancies in the octahedral layer.

4.2. Micas

As part of his general investigation into the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system Noll (1936) was able to prepare both muscovite and paragonite from alumino-silica gels containing potassium and sodium respectively.

Gruner (1942) reported the synthesis of paragonite, but it was not until recently (Yoder (1955b)) that the stability field of paragonite was established.

Roy and collaborators have made a massive contribution to the chemistry and mineralogy of many members of the mica family. The extent of solid solution between the dioctahedral (muscovite) and trioctahedral (phlogopite) was examined by Crowley (1959) and this work was followed by a wide variety of syntheses in the muscovite, phlogopite, celadonite and phengite-type mica fields, (Roy (1964) Roy (1965)). The effect of boron substitution in the muscovite structure and of nickel and gallium in the phlogopite structure are examples of studies of the effect of isomorphous substitution upon stability that have been made by these workers (Roy (1957) Stübican (1962)).

Yoder and Eugster (1955) investigating the $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system were able to synthesize both the 1M and 2M type polymorphs from oxide mixes of the

muscovite composition. They found that whereas the 2M polymorph could be readily synthesized at 600°C it required some 200 days at 250°C-300°C to obtain the transformation of the 1M → 2M type structure. These results led them to suggest that the 2M polymorph widely found in nature, is the stable form of the two muscovite structures.

Warshaw (1960) also studied the $K_2O-Al_2O_3-SiO_2-H_2O$ system but did not obtain the 2M type structure under the conditions of her investigation. Warshaw's investigation was extended to include those mica compositions deficient in alkali and was able to show that where the composition was deficient only in K_2O , mixed layer structures were formed. When the aluminium content of the gels was reduced simultaneously with the potassium, illitic micas were formed. Syntheses with very low $K_2O:Al_2O_3$ ratios gave rise to montmorillonites.

The synthesis of an ammonium mica directly from ammonium-alumina-silica gels was first reported by Barrer and Denny (1961). Gruner (1939) had previously reported the synthesis of an "ammonium mica" by the hydrothermal treatment of vermiculite with ammonium hydroxide but his product was in effect vermiculite with interlayer ammonium ions. One point of considerable interest in the ammonium mica synthesis of Barrer and Denny (1961) was the

fact that they were synthesized from gels with very high base:alumina ratios. Similar high base:alumina ratios in the K_2O or Na_2O -alumina-silica systems give rise to analcite and other sodium/potassium rich phases.

These reported syntheses show that the mica structure is able to accommodate a wide variety of ions and although not directly related to hydrothermal synthesis the solid state synthesis of fluormicas containing such ions as Co, Mn, Fe, B, Ge, Ni further illustrates the compositional diversity of the micas.

5. EXPERIMENTAL APPARATUS AND METHODS

5.1 Chemicals

(a) Silica:

The silica used in all the experiments was in the form of a stable suspension of amorphous silica in water, supplied by Monsanto Chemicals Ltd. under the trade name of Syton 2X. This contained 29.7% by weight of silica, had a S.G. of 1.2, a pH of ~ 10 , and contained a trace of chloride.

(b) Alumina:

Two types of alumina were used in these investigations.

b(i) Aluminium hydroxide amorphous to X-rays: The aluminium hydroxide was prepared by the method of Wislicenus (1904). Aluminium foil was divided into small pieces and amalgamated lightly by contact with a 2% solution of mercuric chloride for about 15 seconds. It was then well washed and allowed to stand overnight in a large volume of distilled water maintained at 0°C. The precipitated gel was separated from any unreacted foil by washing with water, alcohol and ether and sucked dry. It was then sieved through

an 85 mesh sieve and allowed to stand overnight in an open vessel. The light grey powder was then analyzed by igniting a sample to constant weight and kept in a closed bottle.

It was normally found to contain between 50 and 58% Al_2O_3 ; and when freshly prepared was amorphous to X-rays. The gel was not used after about 3 weeks from the date of its preparation because of its tendency to age and crystallize.

b(ii) Aluminium nitrate solution: An 8-10% solution of aluminium nitrate was made up by dissolving the approximate amount of AnalaR $\text{Al}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in a standard volume of water. The accurate aluminium nitrate content of the solution was then determined by conventional gravimetric procedures utilising 8-hydroxyquinoline as precipitant (Hillebrand (1953)).

Gallium: The gallium-nitrate was obtained as a deliquescent solid from Johnson and Matthey. The amount of gallium oxide present in the solid was determined by ignition of a small amount of the solid, after which an amount sufficient to give an 10% solution was weighed out and dissolved in a standard volume of water. The accurate determination of the amount of gallium present in the solution was made complexometrically using E.D.T.A. and galloicyanine as an indicator.

(c) Bases:

The organic bases, tetra-alkylammonium hydroxides were supplied by B.D.H. in the form of solutions which were suitably diluted and standardised. The ammonia was diluted AnalaR 0.88 ammonia. The potassium hydroxide solutions were made from AnalaR potassium hydroxide pellets and standardised against 0.1N, HCl after suitable dilution.

(d) Lithia:

The lithium used was either in the form of a solution of AnalaR lithium hydroxide, or in the form of lithium fluoride powder supplied by Hopkins and Williams Ltd.

(e) Magnesium:

The magnesium used was in the form of freshly precipitated magnesium hydroxide. The magnesium hydroxide was precipitated by the addition of dilute ammonia to a hot dilute magnesium chloride solution. The precipitate was thoroughly washed to remove all trace of Cl^- and NH_4^+ ions.

The magnesium content of the powder dried at room temperature in a desiccator, was determined, after dissolution in 0.1N HCl, by titration with ethylene-diamine-tetra acetic acid. Distilled water was used in all preparations.

(f) Germanium:

The germanium oxide was supplied by Johnson and Matthey as a very fine grain powder which was used for synthesis work without any additional grinding. X-ray examination showed the powder to be the hexagonal form of the oxide, commonly known as soluble germanium oxide.

5.2 Preparation of gels

5.2.1 Hydrothermal crystallizations using alkylammonium or ammonium bases.

From the chosen formula of the gel the quantities of base, alumina (gallia) and silica reagents required to give a dry weight of 0.5 gms of oxide in 7 ml of water were calculated. The calculated amounts of organic or ammonium base and Syton 2X were added to a 250 ml conical flask by means of a graduated pipette. The weighed amount of alumina or gallium hydroxide was then added together with the calculated amount of distilled water to make up a total volume of 7 ccs per autoclave. The mixture was then stirred for 1-2 hours to obtain a homogeneous suspension.

When stirring was complete, 7 ml aliquots of the

suspension were transferred to the autoclaves; care being taken that no settling out of solids occurred during the withdrawal.

5.2.2 Hydrothermal crystallizations using potassium hydroxide.

As the silica was used in the form of a colloidal suspension and the germanium as a fine powder the usual method of gel preparation used in these laboratories (see previous section) tended to result in autoclaves charged from the same initial mixture giving products which varied both in the nature of the micaceous phase and the amount of second phase present. In view of the nature of the study (investigating extent of solid solution) it was essential to obtain an initial gel-oxide mixture which was homogeneous.

The method finally found suitable and adopted was that proposed by Roy (1956), and was as follows. The silica was in the form of the colloidal suspension and the germanium as a fine powder. The aluminium and gallium were introduced in the form of nitrate solutions and the alkali as a solution of the hydroxide or nitrate. The required amounts of aluminium and/or gallium nitrate solution were added to the colloidal silica and/or germanium oxide powder followed by

the addition of the alkali. If the alkali was added in the form of the hydroxide, a few drops of HNO_3 were usually added to prevent precipitation of the hydroxides. The mixture was diluted sufficiently to enable it to be well-stirred after which the solution was evaporated slowly to dryness on a hot-water bath. The gel obtained in this manner was ignited at 450°C - 500°C overnight to get rid of the nitrate ions. After firing the powder was ground up very finely in an agate mortar and introduced in weighed amounts to the autoclaves. The required amount of water was then added, the autoclave sealed and placed in the furnace in the usual manner.

5.2.3 Low temperature syntheses at atmospheric pressure. (Hectorites).

From the chosen formula, the quantities of lithium and magnesium required to give $\sim 5\%$ solids in a reacting solution of 450 mls. was weighed out and transferred to a 500 ml. conical flask. The calculated amount of Syton 2X or germanium oxide was then added to the lithia and magnesia together with approximately 300 mls. of hot water. This was followed by the addition of the inorganic or organic base (or fluoride) and the mixture thoroughly stirred for one hour. After stirring was completed, the contents of

the flask were transferred to the 3-necked reaction vessel and the total volume of solution made up to ~ 450 mls.

5.3 Reaction Vessels

5.3.1 Hydrothermal syntheses.

For the hydrothermal syntheses in the temperature range $200-450^{\circ}\text{C}$ stainless steel tube autoclaves supplied by Messrs. Baskerville and Lindsay were used. These had a capacity of 14 ml. and were sealed with silver washers (figure 11) which flowed slightly on closing the autoclave and also expanded more than the steel on heating. This form of seal was very satisfactory provided that the seals were renewed from time to time. A molybdenum sulphide anti-scuffing paste was used on the threads so that they would not seize up at high temperatures.

5.3.2 Low temperature syntheses at atmospheric pressure.

For these syntheses a 500 ml. capacity 3-necked round-bottomed flask was fitted with a reflux condenser, a stopper and a mechanical stirrer. The flask was heated by means of a heating mantle controlled by a sunvic regulator.

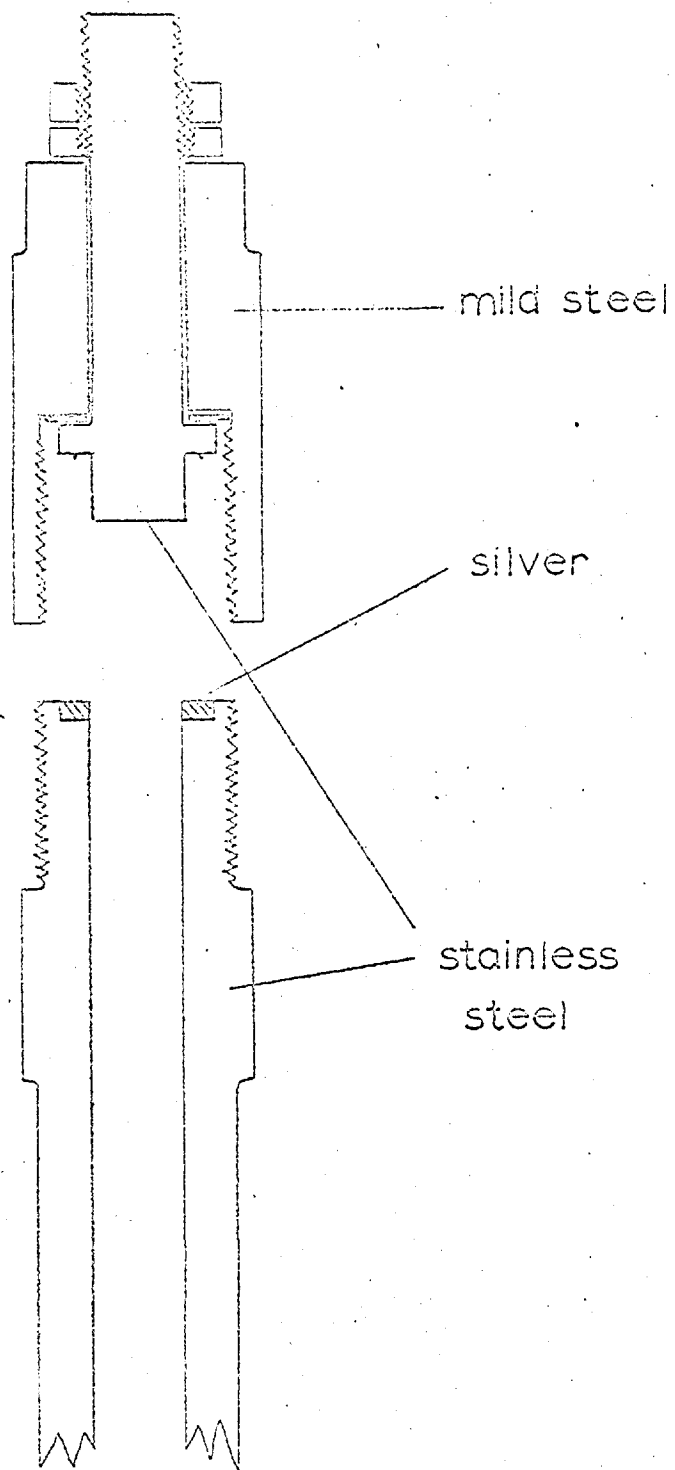
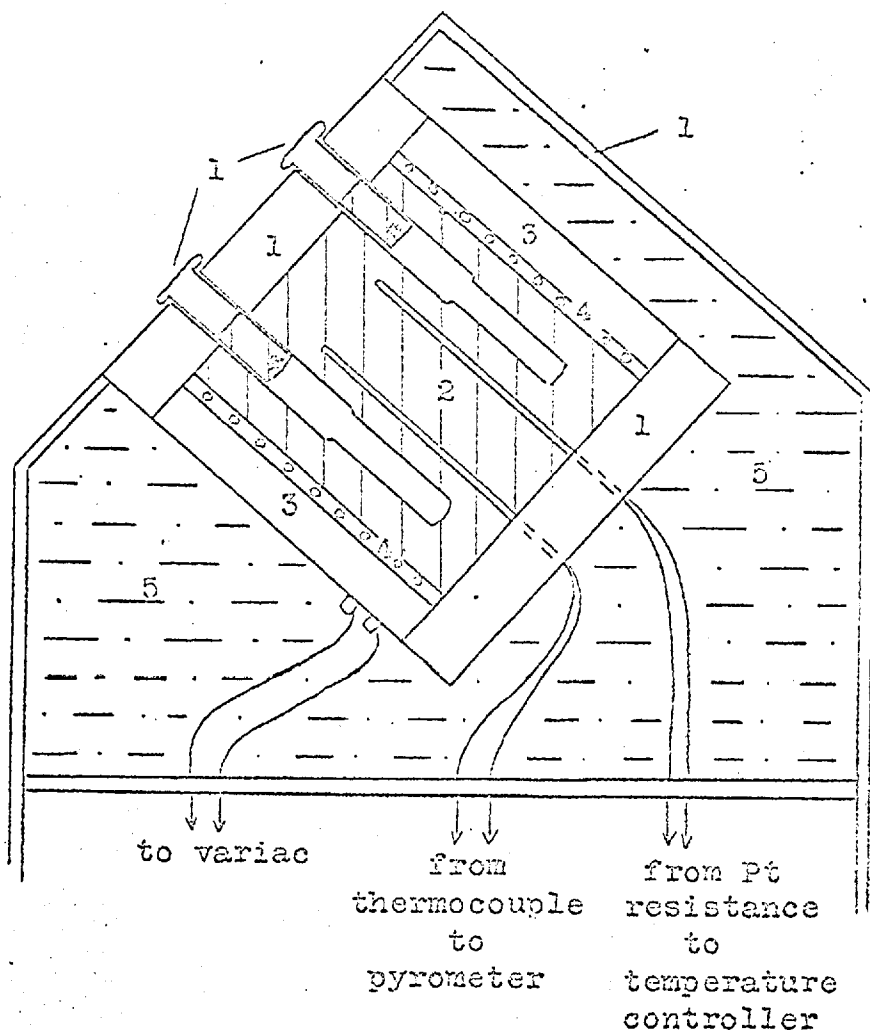


Fig. 11. Autoclave Closure.

5.3.3 Ovens and Furnaces.

Electrically heated air ovens, thermostatically controlled to $\pm 3^{\circ}\text{C}$ were used for runs at temperatures between 200°C and 300°C inclusive. For runs at temperatures above 300°C a specially constructed furnace was used (figure 12). This consisted of a large copper block having nine holes drilled in it to closely fit the autoclaves, and packed around with asbestos wool inside a Sindanyo case. The electrical circuit was as shown in figure 13. The control relay was operated by the amplified out of balance signal from a Wheatstone bridge, one arm of which was a platinum resistance inserted into the copper block of the furnace. This could maintain a given temperature $\pm 2^{\circ}\text{C}$ over a long period. The temperature was measured directly with a pyrometer, using chromel/alumel thermocouples also inserted into the copper block, but each time that the furnace was adjusted to a fresh steady state the temperature was checked using a Pt/Pt 13% Rh. thermocouple placed in one of the autoclave sockets and a Cambridge pontentiometer, with the cold junction at 0°C .



1. Sindanyo.
2. Copper.
3. Alumina Cement.
4. Nichrome Windings.
5. Asbestos.

FIG. 12 The Large Furnace.

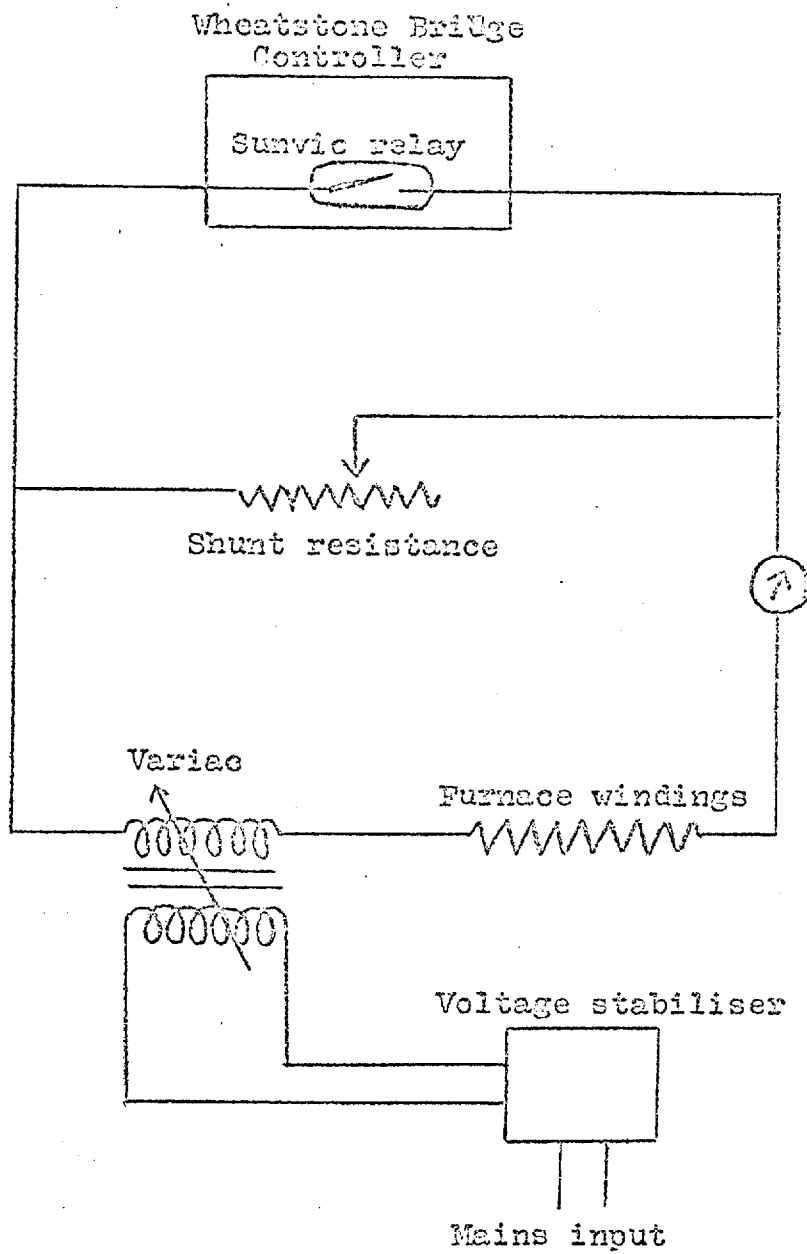


FIG. 13. Circuit of large furnace.

5.4 Recovery of products from hydrothermal runs

On completion of the desired period of treatment the autoclaves were removed from the oven or furnace and normally quenched in cold water. In some cases the autoclaves were allowed to cool down in air at room temperature, since preliminary tests had revealed no difference in the products whether the autoclaves were quenched or not. When cold, the autoclaves were opened, the mother liquor decanted and its pH measured to the nearest 0.5 unit with universal Indicator paper. The product was washed out of the autoclave, filtered off and washed with cold water and alcohol and finally dried at 105°C.

Where the final product was removed from the autoclave in the form of a stiff gel as in the case of the hydrothermal alkylammonium syntheses, centrifugation was usually employed to ensure a well washed product.

5.5 Examination of products

5.5.1 Optical Microscopy.

A drop of water suspension of each product was taken, dried out on a microscope slide and examined under a

Leitz III c polarising microscope. A Vickers projection microscope capable of magnification up to 4000 X was used for further examination and for taking photomicrographs. In this way the crystal habit of the product could be studied and the purity of the preparation estimated.

5.5.2 Electron Microscopy.

Samples yielding crystals too small for study with the optical microscope or otherwise of interest were examined with a Philips 100 desk model electron microscope with the help of Dr. I. S. Kerr of this department. This means of examination was of particular importance in the estimation of the crystallinity of different clay and mica preparations.

5.5.3 X-ray diffraction.

Copper K α X-radiation was generated by means of either a Newton Victor Raymax 60 or a Hilger and Watts Microfocus X-ray set, operating at 40 KV with a water or oil cooled copper target. A Nickel filter was used except with the Guinier camera. Two types of X-ray powder camera were used in this work.

(a) A Guinier camera supplied by "Nonius" of Delft.

This camera was fitted with a curved quartz monochromator. Because of the self-focussing action of this camera which causes the $K\alpha_1$ and $K\alpha_2$ copper radiation to be coincident for a wide angle around 15° , no doublets were observed and so the weighted mean value of $1.542 \text{ \AA}$ for the two wavelengths was used. The camera was designed to record the diffraction pattern of four samples simultaneously. The specimens were mounted in a flat plate with four apertures, each containing a thin layer of powder held in place with 'sellotape'. This plate could be given a translatory motion in its own plane, but this was seldom used as the size of the grains produced in the syntheses was such that smooth diffraction lines were obtained without it. The dispersion factor of this camera was 4 mm per degree and it was thus equivalent to a Debye-Scherrer camera of 22.9 cm diameter. However because of the shrinkage of the film on processing and storage it was necessary to calibrate the camera in some way and this was done by putting a dusting of synthetic quartz in one of the apertures. The spacings thus obtained were compared with those for quartz in the A.S.T.M. file and the apparent dispersion factor calculated.

The camera printed the image of its two fixed notches at the bottom of each film, and once these had been calibrated with a quartz pattern it was possible to use this

method also to calculate the apparent dispersion factor for any film. When using the Guinier camera the distance of the diffraction lines from the zero mark was measured to 0.005 cm using a film measuring rule with a Vernier scale, supplied by Hilger and Watts Ltd. These distances were converted into values of θ and looked up in graphical tables of θ vs. d . (Parrish (1953)).

The intensities of the lines were estimated visually.

(b) The second camera, was a flat plate camera used when large d spacings, such as occur in the clays, were required. The specimens were mounted in sealed off capillary tubes and were accurately centred in the X-ray beam.

The diffraction pattern consisted of concentric rings whose radii gave the desired d spacings. Longer exposures of 12-24 hours were usually required in order to obtain satisfactory results. To measure the d spacings from the pattern recorded on the flat plate camera the distance between centres of the arcs of the diffracted beams and the position of the mark made by the undiffracted main beam can be measured accurately on the film using the vernier rule mentioned above. The value of T can be easily related to the d spacing to give the equation:

$$d = \frac{\lambda}{2 \sin \frac{T}{2R}}$$

where R = radius of camera.

5.6 Interpretation of X-ray photographs

Once a list of observed d spacings had been drawn up attempts were made to index these lines and so deduce the unit cell of the compound. For cubic, tetragonal and hexagonal crystals this can be done by quite simple graphical and analytical procedures using the equations

$$Q_{hkl} = \frac{1}{a^2}(h^2+k^2+l^2) \quad \text{Cubic}$$

$$Q_{hkl} = \frac{1}{a^2}(h^2+k^2)+\frac{l^2}{c^2} \quad \text{Tetragonal}$$

$$Q_{hkl} = \frac{4}{3a^2}(h^2+hk+k^2)+\frac{l^2}{c^2} \quad \text{Hexagonal}$$

where $Q_{hkl} = 1/d_{hkl}^2$. If the compound was known to fall into one of these systems, or was suspected to do so on account of its crystal habit then the d spacings were converted to Q values from tables and one of the following procedures was adopted. (Azaroff (1958))

5.6.1 Cubic.

It can be seen that all the Q values will be integral multiples of $1/a^2$ which can therefore be determined by inspection. Indices can be assigned to all the lines and the most accurate value of the unit cell parameter computed from a series of carefully measured higher lines.

5.6.2 Tetragonal.

In this case all the Q_{hk0} values will be integral multiples of $1/a^2$ and it should be possible to find a set of Q values which satisfy this requirement and so deduce a . However it was often more profitable to use a graphical method to determine the indices first, the chart used for this purpose being that devised by Harrington (1938). The principle of this chart can be derived from the tetragonal equation as follows. Two special cases of this equation are

$$Q_{hk0} = \frac{h^2 + k^2}{a^2}$$

and

$$Q_{00l} = l^2 / c^2$$

by addition

$$Q_{hk0} + Q_{00l} = \frac{h^2 + k^2}{a^2} + l^2 / c^2$$

$$Q_{hkl} = Q_{hk0} + Q_{00l} .$$

From this we see that the interplanar spacing of an hkl plane is asymptotic to the interplanar spacing of the corresponding $hk0$ or $00l$ plane as either a^2 or c^2 becomes very

large. Therefore if the $hk0$ and $00l$ curves are drawn as families of parallel straight lines, the hkl curves, being asymptotic to them, have the same shape and the chart is easy to construct from a single template. This condition was realised by plotting the axial ratio c/a on a logarithmic scale, when all $hk0$ curves have a slope of -2 and all $00l$ curves a slope of $+2$. To use this method the observed d spacings were plotted on a slip of paper using a logarithmic scale, and this strip of paper was moved up and down the chart parallel to the horizontal axis until a satisfactory fit of at least all the lower angle lines was obtained. The axial ratio and the indices of the lines were noted and these values used to compute the unit cell which gave the best fit to the experimental data.

5.6.3 Hexagonal.

It can be seen from the hexagonal equation that there is a very close similarity between this system and the tetragonal one, and hence the same methods are applicable. Thus, although analytical methods are possible in theory, whenever hexagonal symmetry was known or suspected an attempt was made to index the lines using a large scale Harrington chart. If consistent indices were obtained these were used

to compute the unit cell which gave the best fit to the observed data.

5.6.4 Orthorhombic.

The corresponding equation for the orthorhombic system is

$$Q = h^2/a^2 + k^2/b^2 + l^2/c^2 ,$$

and graphical methods similar to those above can be used if one of the axial ratios is known. However when it was possible that the species being studied was orthorhombic analytic methods were attempted, but without success in the present work. The two approaches attempted were the Hesse-Lipson procedure and Ito's method. The Hesse-Lipson procedure, Lipson (1949), is based on the assumption that if all possible combinations of the observed values of $\sin^2\theta$ are used to form equations of the type

$$\sin^2\theta_{0k_10} = \sin^2\theta_{h_1k_10} - \sin^2\theta_{h_100}$$

$$\sin^2\theta_{00l_1} = \sin^2\theta_{h_1k_1l_1} - \sin^2\theta_{h_1k_10}$$

$$\sin^2\theta_{00l_1} = \sin^2\theta_{h_2k_2l_1} - \sin^2\theta_{h_2k_20}$$

then the $\sin^2\theta$ values which will be obtained most frequently

from such equations will be those of the pinacoid reflections $h00$, $0k0$, and $00l$. Thus if the observed $\sin^2\theta$ values are calculated and the difference between each possible pair is tabulated, then the differences which occur most often, within the limits of ~~experimental~~ error, can be tested as possible values for the pinacoid reflections by attempting to index all the observed reflections by means of them.

Ito's method can be applied regardless of the symmetry of the crystal and is based on the fact that each reflection on the powder photograph corresponds to a vector in reciprocal space, Ito (1948). If ~~six~~ appropriate lines can be chosen from the powder pattern then a reciprocal unit cell can be obtained and it will be possible to index all the lines observed. The two chief difficulties with this method are that reciprocal lattice points which correspond to weak or absent reflections will not be available, and hence the reflections selected to represent Q_{100} , Q_{010} , Q_{001} may not account for all the observed reflections. This can be overcome by trial and error but the other requirement of this method is that in order that it may be applied with reasonable success it is necessary to know the value of Q accurately to at least three and preferably four figures. This requires that the d spacings must be known to at least three places to the right of the decimal point, and this was not always possible with the samples studied.

5.6.5 Monoclinic and Triclinic.

Ito's method is also applicable to these crystal systems but is very lengthy. The only monoclinic species encountered in this work were the micas and preliminary indexing of the X-ray pattern for these specimens was aided by comparing the pattern with indexed mica patterns available in the literature, (Brown (1961), Yoder (1955)).

5.7 Analytical Methods

5.7.1 Magnesium.

Magnesium was determined complexometrically using E.D.T.A. as tritrant and Eriochrome Blue Black indicator. Magnesium in magnesium hydroxide was determined after dissolution of a weighed portion in hydrochloric acid and the solution buffered with ammonium chloride-ammonium acetate buffer to pH.9. The end-point was shown by a sharp colour change from blue to red. When magnesium was determined in the synthetic clays the sample was first dissolved in concentrated hydrochloric acid and then evaporated to dryness. The residue was taken up with a small amount of 0.1N HCl and heated gently to obtain solution

of the magnesia, leaving the silica which was filtered off. The magnesium in the filtrate was then determined in the manner previously described.

5.7.2 Aluminium.

Aluminium was determined gravimetrically with good precision by precipitation as the 8-hydroxy quinolate Hillebrand (1953). A complexometric method using E.D.T.A. was tried, but was found to be unsatisfactory because of poor end-points in titrations using Eriochrome Blue Black as an indicator.

5.7.3 Gallium and Germanium.

Gallium by a complexometric method.

The gallium nitrate stock solutions were standardised by complexometric titration using E.D.T.A. and gallo-cyanine as indicator. The end-point was denoted by a colour change from **blue to red**.

Gallium and germanium by an X-ray fluorescence method.

The gallium and germanium contents of mica samples were determined by means of an X-ray fluorescence method

whereby the intensity of the K α fluorescence of gallium and germanium was measured. The apparatus used was a Phillips PW.1051 X-ray generator fitted with Phillips X-ray fluorescent apparatus. In samples which contained both gallium and germanium the $\frac{\text{Ga}}{\text{Ge}}$ intensity ratio was determined. Since the amount of only one of the heavy elements was varied in a system at any one time the gallium and germanium contents of the micas relative to the end-member containing both the heavy elements could be determined by utilising the second heavy element as an internal standard. This method of determining gallium or germanium was found to give satisfactory results with a precision of $\pm 1\%$. In samples containing only one element with an atomic number > 16 , e.g. the $(\text{K}_2\text{O}-\text{GaAl}-\text{Si})$ and $(\text{K}_2\text{O}-\text{Al}-\text{GeSi})$ systems the determination of the amounts of gallium and germanium could not be determined by the above method. To determine the gallium and germanium contents of these samples a series of standards was prepared by taking a gallium and germanium free aluminosilica mica and adding to it known amounts of gallium or germanium. Provided that due care was taken to see that the heavy element and mica sample were well mixed, satisfactory results could be obtained. By preparing comparison standards in this manner errors due to matrix effects could be avoided.

The intensity of the X-ray fluorescence from gallium and germanium in the samples was determined by the fixed time-count method, the average number of counts from four, one-minute intervals being taken as the intensity of the fluorescence emission under standard conditions of generating voltage and amperage.

Difficulties due to the fact that only a limited amount of material was available and the area of irradiation in the specimen holder large, were overcome by compressing the sample into small, 3 mm diameter pellets of identical thickness. This method of sample preparation ensures that the sample area irradiated was the same for all specimens.

5.7.4 Nitrogen.

The nitrogen determinations were carried out by the Dumas method or a modified Kjeldal method (Stevenson (1960)) in which the sample was heated at 430° in a thick walled sealed tube with sulphuric acid and mercuric oxide catalyst. The conventional Kjeldal method does not give good results with quaternary ammonium compounds unless mercuric oxide is used together with sulphuric acid and there are long heating periods of 6-10 hours. Furthermore reaction temperatures cannot be allowed to exceed 330°C

without low results, due to loss of ammonia. In enabling higher temperatures to be used, without fear of ammonia loss, the sealed tube method results in a much more vigorous reaction taking place and the quantitative conversion of the quaternary nitrogen to ammonium sulphate, completed in 1-2 hours.

After reaction the tube is cooled and opened by applying a very small sharp flame to one end and allowing the internal pressure to blow out a small hole. After opening the tube is placed in an oven at 100°C for 1 hour to get rid of any carbon dioxide, after which the contents are carefully transferred to the conventional distillation apparatus and distilled in the usual way.

The main possible source of error in the method was found to be in transfer of the contents of the reaction tube to the distillation apparatus; with due care however this error could be eliminated and results with an accuracy similar to those found with the Dumas method could be obtained.

5.7.5 Carbon and Hydrogen.

The carbon and hydrogen contents of the clay samples were determined by the organic microanalytical laboratory of this Department using conventional apparatus.

5.8 Differential Thermal Analysis

5.8.1 General Principles.

The method of d.t.a. is widely used in the investigation of minerals, particularly of clays, and a good review on this subject has been edited by Mackenzie (1957). The principle of d.t.a. is to heat the sample at a steady heating rate under conditions identical to those of an inert reference material, and to measure the difference in temperature between the two samples. Thus if any reaction involving a heat change takes place in the sample under study, such as chemical reaction, dehydration or phase change, then the temperature of the sample will change with respect to that of the inert reference. Ideally a plot of ΔT vs T will show a horizontal base line with peaks corresponding to those temperature ranges over which some reaction takes place, and the direction, shape and position of these peaks will be characteristic of that particular substance and also provide information on its thermal stability or the occurrence of phase transformations. In practice however a number of factors may operate to cause considerable base line drift. There may be a variation of the specific heat or thermal conductivity with temperature, or a variation in packing density or thermal contact which may result from

such reactions as gas evolution, or shrinkage on dehydration. Such effects are most serious when quantitative data is sought from the d.t.a. record since it makes it very difficult to draw a base line so as to calculate the area under a peak, but in severe cases these effects may sometimes make the qualitative interpretation of the record uncertain. Sewell (1958) has developed a method for calculating a more accurate base line when the drift is due to differences in specific heats and thermal conductivity. However the method is complicated and requires knowledge of the thermal properties of the materials which was not available in this work. In order to get reproducible and consistent results with different samples the rate of heating must be constant and the thermocouples must be carefully centered in each sample.

5.8.2 Apparatus used.

The apparatus used was based on the design of Mackenzie (1952) and was fully described by Langley (1957). Ceramic cell holders and cells were used, of the Roberts and Grimshaw type. The cell was a block about 19 x 9 x 8 mm in size with two cylindrical wells 7 mm in diameter, one for the sample and one for the reference material. Chromel/alumel thermocouples were used, and the temperature measuring

thermocouple was situated in the inert sample. The furnace consisted of a metal and Sindanyo case packed with alumina insulating powder and having the heating element wound on a central horizontal porcelain tube into which the cell holder just fitted. This tube was lined with an earthed sheet of nickel foil to screen the thermocouples from the furnace windings. A temperature controlling thermocouple, also chromel/alumel, was brought through the back of the furnace case and rested closely against the wall. The thermocouple wires were connected to the recorder leads through thermostatted mercury connections.

The temperature and differential temperature were recorded on Kent "Multilec Moving Chart Potentiometers". These recorders balance the signal received by means of a mechanically driven sliding contact on a potentiometer wire which is automatically standardised against a standard cell at regular intervals. The sensitivity of the differential temperature recorder could be adjusted by a simple potential divider to give a full scale deflection ranging from $\pm 2\text{mV}$ to $\pm 10\mu\text{V}$.

The furnace temperature was recorded on a similar Kent Multilec recorder fitted with a programming cam which had been cut by trial and error to give a rate of heating of $10^{\circ}\text{C}/\text{min}$. The heating element of the furnace was fed from

a pair of concentrically mounted Variacs set about 10 volts apart whose output was slowly raised by a suitably geared motor. The programming cam operated a relay which switched the output to the furnace from the higher to the lower setting when the temperature rose above the program value, and vice versa. The slight change in heating rate which was thus caused could be picked up by the differential temperature recorder on its more sensitive settings, and so gave rise to "hunting" which at higher temperatures could obscure or distort the true curve. This could be minimised by adjusting the starting voltage of the variacs but only at the expense of loss of linearity in the rate of heating.

All the recorders were situated in an air thermostat maintained at 25°C . The switches for all the parts of the apparatus were mounted on a control panel and subject to a single master switch, so that all the recorders and the furnace could be started simultaneously. From the automatically recorded curves of differential e.m.f. vs. time and temperature vs. time the graphs of differential temperature could be plotted by converting the thermocouple e.m.f. to temperature ($40\text{ }\mu\text{V} = 1^{\circ}\text{C}$) and making allowance for the small but definite difference in the speeds of the two charts.

The inert reference material used in all the experiments was ignited kaolin. The cells were filled with equal volumes of reference material and sample, and tightly packed down by hand using as nearly as possible identical conditions each time. All the samples were pretreated by being allowed to stand for several days over a saturated solution of magnesium nitrate (84% relative humidity).

5.8.3 Thermogravimetry.

In order to provide further information on those samples which showed peaks on the d.t.a. curves, thermogravimetric studies were carried out, which made it possible to distinguish between peaks due to phase changes and those due to dehydration or dehydroxylation by plotting graphs of percentage weight loss vs. temperature. In order that the comparison with the d.t.a. results might be as close as possible an identical furnace was used, mounted vertically, and controlled by the same programming recorder. The bucket used was half a d.t.a. cell, suspended on 55 cm of platinum wire from an air-damped Stanton balance so that it hung freely in the centre of the furnace. A series of baffle plates and screens minimised the effects of draughts and hot air currents on the suspension and the balance.

The temperature was measured with a chromel/alumel thermocouple mounted in the furnace and previously calibrated by comparison with another thermocouple fixed in a cell containing ignited kaolin and held at the position which would be occupied by the suspended bucket. A dummy run was also carried out with a bucket of ignited kaolin to determine the buoyancy correction. All the samples were pretreated as for the d.t.a. experiments.

5.9 Infra-Red Spectrophotometry

The infra red spectra of the potassium and ammonium mica samples were obtained on a Grubb-Parsons double-beam grating spectrometer. The potassium bromide disc method was used for recording the spectra of the micas.

Samples were prepared by adding 1 mg. of mica to 100 mg. of finely ground anhydrous potassium bromide. After thorough mixing the powder was pressed into clear 15 mm diameter discs by using a Perkin-Elmer screw press.

The instrument drew a graph directly of transmittance vs. linear wavelength from 5-25 microns.

5.10 Sorption Experiments.

The sorption capacity of a number of clay samples was investigated with nitrogen at 78°K in the standard volumetric sorption apparatus shown in Figure 14. In order to calculate the volume of nitrogen sorbed by the samples the following volumes were determined.

(a) The gas burette volumes were found by filling the burette to each mark in turn and weighing.

(b) Even bore tubing was used for the manometer and the volume per cm was found by weighing the amount of mercury required to fill a measured length.

(c) The doser volume is the volume between the taps A, D, E, F, and the marks B and M on the gas burette and the manometer respectively. This volume was calculated by admitting a dose of helium into this system and measuring the pressure as it was expanded into each bulb of the gas burette in turn and then applying the ideal gas laws.

(d) The cold volume is the volume of the sorption bulb below the etch mark C and was determined by weighing the bulb, filled to the mark with mercury, before sealing it into the tap and socket assembly S-H. The volume of the sorbent was afterwards deducted.

(e) The volume between the tap E and the mark C is

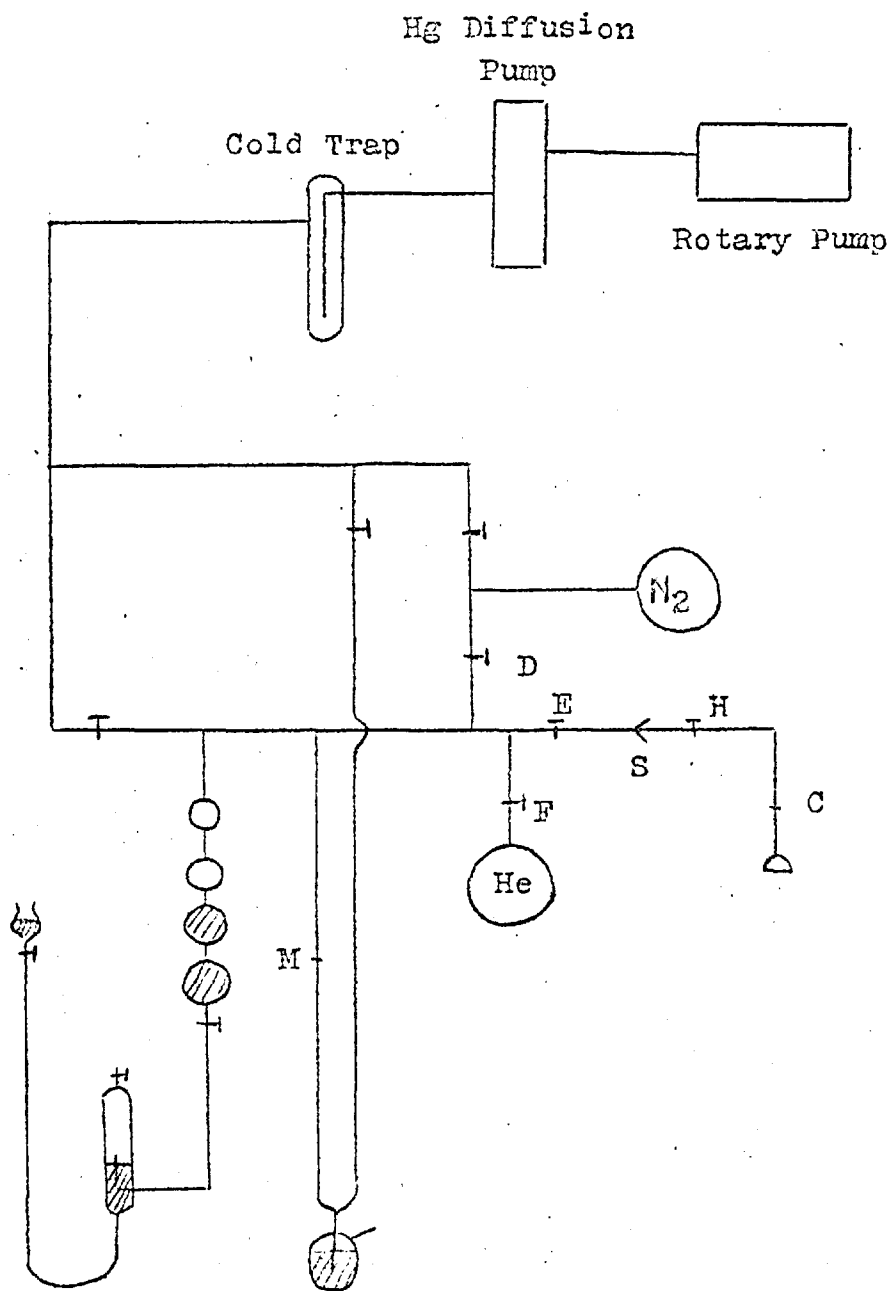


FIG. 14. The Sorption Apparatus.

also required and this was obtained by admitting a dose of helium to the whole system and then calculating the total volume from which the doser volume and the cold volume were subtracted.

The rest of the experimental procedure was as follows. A sample of about 0.5 g of the species to be studied was equilibrated over a saturated magnesium nitrate solution and then weighed into the calibrated sorption bulb which was sealed on to the tap H and connected to the system by means of the ground glass cone and socket joint S. It was evacuated for several hours, and then surrounded by a suitable furnace and the temperature was raised slowly to 100°C, held there for about twenty-four hours, and then allowed to cool under high vacuum.

With tap E closed a dose of nitrogen was admitted to the system and the volume, pressure and ambient temperature were measured, the height of the manometer being read to ± 0.001 cm with a cathetometer. The bulb was surrounded with liquid nitrogen to the mark C and tap E opened. After allowing time for the system to come to equilibrium, the pressure was again read, then tap E was closed and the process repeated. The volumes of nitrogen present with the tap E shut and open could be calculated and reduced to N.T.P. The difference between them was a measure of the

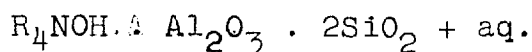
amount of gas sorbed by the sample. An isotherm could be obtained by plotting the amount sorbed against the equilibrium pressure. The saturation capacity was obtained from the slope of the straight line obtained by plotting P/x vs. P .

6. RESULTS AND DISCUSSION

6.1 SYNTHESIS OF ALKYLAMMONIUM SMECTITES:

Introduction:

The object of this section of the work was to investigate the products of hydrothermal synthesis using gels of general formula:-

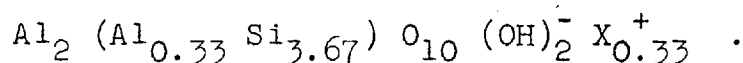


The work of Barrer and Denny (1961) showed that a number of nitrogenous alumino-silicates could be synthesized in which an organic base provided the cations necessary to neutralize the charge on the structural framework or layer. The pH. of the reacting solutions was kept high by the strongly basic organic hydroxides. An important product obtained in this work, in the temperature range 200-300°C was the layer lattice mineral montmorillonite with large organic cations between the layers.

It was therefore hoped that a general investigation using similar gels would result in the synthesis of montmorillonites containing even larger cations such as the tetra-ethyl and tetra-butyl ammonium ions, between the layers.

With this in mind it was hoped to synthesize a

series of montmorillonites with their layer charges dependent upon the cation incorporated. This might be done by using sufficiently large ions whose equivalent areas exceeded that available unit charge on the ideal beidellite structure,



Experimental Results:

Tetra-methyl ammonium alumino-silicates:

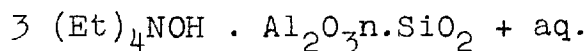
The work of Denny was repeated, particular emphasis being placed on trying to synthesize montmorillonites containing the tetra-methylammonium ion.

Although it is possible to make these montmorillonites the yields are small and duplicate syntheses often produce montmorillonites with different basal spacings, indicating that hydrolysis occurs to varying degrees in gels of the same initial composition.

Attempts to improve yields of the low temperature products from these gels, such as Linde sieve type zeolites by addition of small quantities of sodium, as suggested by work carried out by Linde Air Corporation (1962) proved unsuccessful.

Tetra-ethylammonium aluminosilicates:

Crystallisations have been attempted in the temperature range 136-340°C using gels of initial composition:-



where n is between 1 and 10. The products and their approximate crystallisation fields are indicated in **Figure 15** and Tables 4, 5, and 6.

With reference to the montmorillonite crystallization field much the same pattern exists as for the field obtained by Denny using the tetra-methyl base. In the temperature range 200-340°C montmorillonite is the main product, the ammonium mica occurring at 340°C when times greater than one day are used. Of particular note in this diagram is the absence of any low temperature products, other than boehmite. Even where hydrolysis has been extreme, no phase other than the ammonium mica appears.

Crystallisations at 210°C are poor and are probably related to the tendency for the starting mixtures to form stiff gels. Any attempts to increase the time or temperature factor only serves to increase the extent

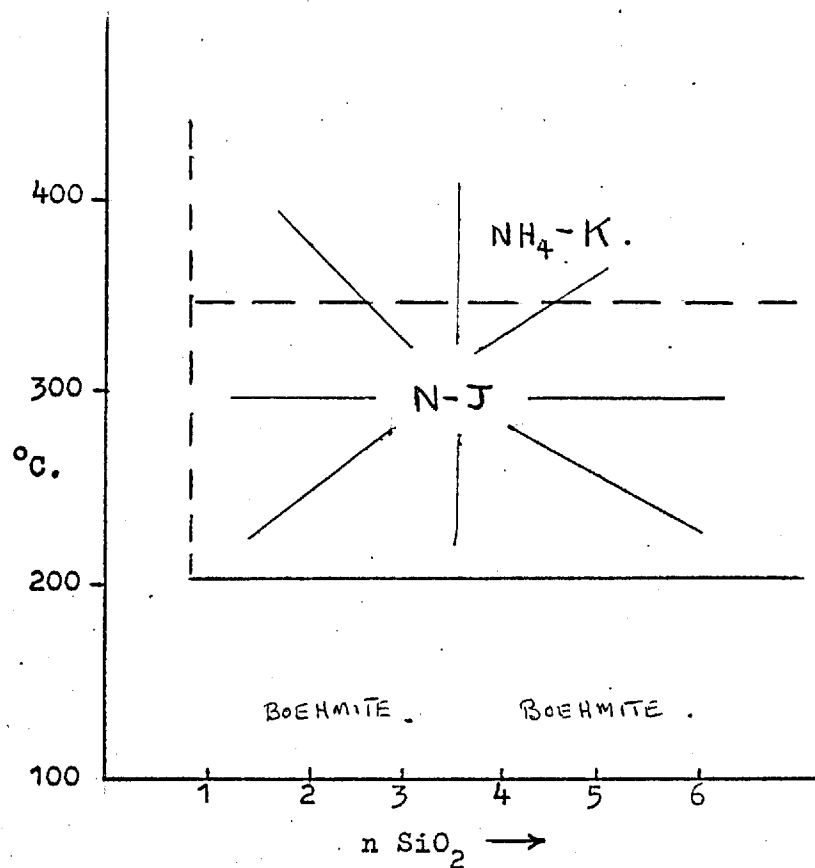


Fig : 15.

Crystallization diagram for the system
 $(Et)_4NOH, Al_2O_3, nSiO_2 + aq.$

N - J = alkylammonium montmorillonite.

NH₄ - K = ammonium mica.

Table 4.

<u>Gel composition:</u> <u>Ratio:</u>	<u>Time</u> <u>(days)</u>	<u>Temp.</u> <u>°C</u>	<u>Products.</u>
$(\text{Et})_4\text{NOH}:\text{Al}_2\text{O}_3:\text{SiO}_2$			
3:1:4	20	136	U
3:1:4	5	210	mod-good M.
3:1:4	6	240	good M.
3:1:4	6	300	good M
3:1:4 + 20% alcohol	4	210	mod-good M
3:1:4	7	210	good M
3:1:4	6	300	good M
3:1:4 + 30% alcohol	5	210	good M
3:1:4	5	300	good M
3:1:4	7	300	good M
3:1:4	2	340	mod M + mica
$(\text{Et})_4\text{NOH}:\text{Al}_2\text{O}_3:\text{SiO}_2$	4	340	good M + mica
3:1:4 + 40% alcohol	5	210	mod-good M
3:1:4	6	240	mod-good M
3:1:4	4	340	mod M + mica
3:1:4 + 1% Na_2O	17	136	boehmite
3:1:4	25	136	boehmite
3:1:4	17	210	mod M + analcite
3:1:4	24	210	mod M + analcite
3:1:4 + 2% Na_2O	17	136	boehmite
3:1:4	25	136	boehmite
3:1:4	17	210	mod M + mica
$(\text{Et})_4\text{NOH}:\text{Al}_2\text{O}_3:\text{SiO}_2$	24	210	mod M + mica

M = montmorillonite,

U = uncrystallized gel,

mod = moderate crystallinity.

Table 5.

<u>Gel composition:</u> <u>Ratio:</u>	<u>Time</u> <u>(days)</u>	<u>Temp.</u> <u>°C</u>	<u>Products.</u>
(Et) ₄ NOH:Al ₂ O ₃ :SiO ₂			
3:1:2 + solid amine	6	210	poor M tr. kaolin
3:1:2 + hydrochloride	6	210	poor M + tr. kaolin
3:1:6	14	136	U
3:1:6	26	136	U
3:1:6	8	210	mod-good M
3:1:6	14	210	mod-good M
3:1:6	6	240	mod M
3:1:6	12	240	good M
3:1:6	5	300	mod-good M
3:1:10	15	136	trace M
3:1:10	5	210	U
3:1:10	15	210	mod M
3:1:10	30	210	mod M
3:1:10	5	240	mod M
6:1:2	6	210	mod M
6:1:2	9	210	mod M
6:1:2	14	210	good M
6:1:2 + 80% alcohol	5	210	U
6:1:2	11	210	poor M
1:1:4	16	136	U
1:1:4	27	136	U
1:1:4	15	210	poor M
1:1:4	23	210	mod - M
1:1:6	16	136	poor boehmite
1:1:6	23	136	poor boehmite
1:1:6	7	210	poor M
1:1:6	20	210	mod - M
1:1:6	4	240	mod - M
1:1:6	7	240	mod - M
1:1:6	2	300	poor-mod M

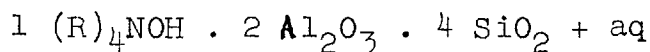
Table 6.

<u>Gel composition:</u> <u>Ratio:</u>	<u>Time</u> <u>(days)</u>	<u>Temp.</u> <u>°C</u>	<u>Products</u>
$(Et)_4NOH:Al_2O_3:SiO_2$			
1:2:4	16	210	poor-mod M
1:2:4	7	240	good M
1:2:4	3	300	good M
1:2:4	10	300	good M
1:2:4 + 30% ethanol	5	240	very good M
1:2:4 + 30% methanol	5	240	very good M
$(Prop)_4NOH:Al_2O_3:SiO_2$			
3:1:2	2	210	U
3:1:2	5	210	very poor M
3:1:2	8	210	poor-mod M
3:1:2	12	210	poor-mod M
3:1:2	5	250	mod M
1:2:4	6	210	boehmite
1:2:4	11	210	boehmite
1:2:4	20	210	poor boehmite
1:2:4	6	250	good M
$(Bu)_4NOH:Al_2O_3:SiO_2$			
3:1:2	5	210	U
3:1:2	8	210	poor M
3:1:2	14	210	poor-mod M
3:1:2	6	250	poor-good M
3:1:2 + 10% alcohol	4	250	mod M + tr kaolin.

U = uncrystallized gel,

M = montmorillonite.

of hydrolysis, resulting in montmorillonite products containing the di-or tri-substituted ions. When gels having the initial composition of:-



were used it was found that in contrast with the earlier syntheses where the base:alumina ratios were kept constant at 3:1 the yields as estimated only from the bulk of material obtained, were almost doubled. Nevertheless, as it is virtually impossible to determine the amount of amorphous material present in the final yield, it may be that due to a decrease in the amount of base used, an increasing proportion of amorphous material is being obtained.

In all the smectites synthesized none had basal spacings exceeding 13.6-13.9 $\text{\AA}$. The ammonium base breaks down progressively according to the following equation:



Attempts to suppress this hydrolysis were made by suitable additions of the corresponding alcohols and in two runs the addition of solid tetra-ethyl ammonium hydrochloride was also made.

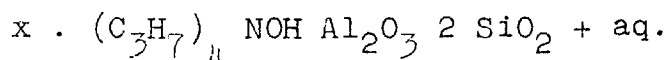
Table 7 indicates the effects on the position of the 001 ~~reflections~~ of the final products of alcohol additions to the starting gels of base:alumina ratio of 3:1:2.

Table 7.

Temperature	Aqueous	95% Alcohol	46% Alcohol	28% Alcohol
210-220°C	13.4-12.5	U	12.5-11.5	13.2-12.7
	2 Samples			
	13.8			
	13.9			
240-250°C	12.8-12.2	13.0	12.6	---
300°C	12.6 and mica	13.0	12.5	12.5
340°C	13.0 and NH ₄ mica	13.0-12.9	13.1-12.5	12.2

Tetra-propyl ammonium alumino-silicate gels:

Crystallisations at 210°C and 250°C were attempted using gels of general formula:



In these syntheses the alumina/silica ratio was kept constant

whilst the base:alumina ratio was varied from 3:1 to 0.5:1. Again hydrolysis appears to occur fairly rapidly. At 250°C no tetrapropyl-ammonium gels gave products with basal spacings greater than 13.4⁰Å. At 210°C and with heating times of 11 and 20 days only boehmite was produced.

One sample, to which an addition of methanol had been made to the initial gel, gave a ~~14.1~~ spacing of 14.2⁰Å.

Additions of the corresponding alcohol were made in a few cases, but no improvement was observed.

Tetrabutylammonium alumino-silicate gels:

Crystallisations using tetrabutylammonium hydroxide as base were effected in the same manner as that used for the tetra-propyl base. Products obtained from syntheses at 210°C had broad basal spacings in the 13.2-14.5⁰Å range. Crystallisation at 250°C with small additions of butanol produced montmorillonites with basal spacings at 13.2⁰Å. Kaolin also occurred as a product of crystallisation at 250°C, though only in small amounts.

Alkylammonium gallosilicate gels:

In view of the improved crystallinity of the micas synthesized, when aluminium was replaced by gallium

(see Section on Micas) it was decided to see whether gallium would have the same effect in systems involving the use of alkylammonium bases.

A limited number of experiments with the tetramethyl and tetra-ethyl ammonium ions were carried out and are summarized in Table 8 .

Tetramethylammoniumgallosilicate gels:

The results using these gels indicated that good yields of crystalline smectite could be obtained at temperatures of 210°C for 5 days, and at 250°C 1 day. In nearly all of the products the 1st order of the basal spacing was strong and slightly broad in the $13.1\text{-}13.5\text{\AA}$ region.

In duplicate experiments however, the products did not always have the same basal spacings e.g. 300°C x 2 days produced a product with a very diffuse 001 reflection, whereas a duplicate run gave a product with a strong, relatively sharp 001 reflection.

These tetramethylammonium gallo smectites readily exchange their interlayer cations with potassium or sodium and there is a corresponding reduction of the basal spacing from $13.5\text{\AA}$ to $9.8\text{\AA}$ (outgassed)

The carbon and nitrogen analyses for some of these smectites are given in Table 12 .

Table 8.Tetramethylammonium gallosilicate gels.Gel composition: $3(\text{Me})_4\text{NOH}, \text{Ga}_2\text{O}_3, 2\text{SiO}_2 + \text{aq.}$

<u>Temp.</u>	<u>1 day</u>	<u>2 days</u>	<u>5 days</u>
175°C			no crystalline material
210°C	V-good M	V-good M	V-good M
250°C	V-good M	V-good M	V-good M

Tetraethylammonium gallosilicate gels.Gel composition: $3(\text{Et})_4\text{NOH}, \text{Ga}_2\text{O}_3, 2\text{SiO}_2 + \text{aq.}$

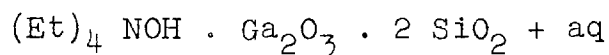
<u>Temp.</u>	<u>2 days</u>	<u>3 days</u>	<u>6 days</u>
250°C		v-good M	good M
300°C		v-good M ^x 001 10Å (illitic)	good M ^x 001 10Å (illitic)
250°C (50 cc autoclave)	Good M ^x		
	001 10Å (illitic)		

M = montmorillonite.

^x These products showed some hkl reflections and are probably better described as illites.

Tetra-ethylammoniumgallosilicate gels:

Using gels of general formula



crystallizations were effected in both small and large autoclaves (14 and 50 ml capacity respectively). The large autoclaves tended to produce smectites with more diffuse basal reflections, but the ion-exchange characteristics of the smectites, produced in both the large and small autoclaves were the same. The products synthesized at 240°C had basal spacings in the $12.5\text{--}13\text{\AA}$ region which became sharp and moved to $10.0\text{\AA}$ after treatment with potassium chloride solutions.

In contrast with the tetramethylammonium gels, the gels reacted at 300°C to give products which had basal spacings of $10\text{\AA}$ and showed no tendency to exchange their interlayer cation with inorganic or organic cations. These products appeared from the X-ray pattern to be more illitic than the other gallosmectites and this is confirmed by the fact that the $10\text{\AA}$ product showed no tendency to swell with glycol.

The ~~was~~, repeat distance of $10.0\text{--}10.1\text{\AA}$ is the same as that obtained for the ammonium micas and this

similarity indicates that the predominant ion present in the structure is the ammonium ion resulting from complete hydrolysis of the tetra-ethylammonium ions.

Description and Characterization of Alkylammonium
Smectites.

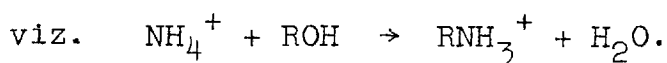
Alkylammonium Alumino Silicates:

X-Ray diffraction analysis of the samples produced in the syntheses previously described has shown that using alkylammonium bases 'smectite like' compounds having a crystallinity as good as that of many natural specimens can be obtained.

Of note in the X-Ray patterns of these smectites is the constancy of the maximum basal spacings irrespective of whether the initial gel contained the tetra-ethyl or tetra-butyl ammonium bases. No reduction in these basal spacings ~~was~~^{is} observed on outgassing at less than 10^{-5} cm. and 60°C . and little or no swelling is observed when the smectites are treated with ethylene glycol.

The absence of swelling when the crystals are treated with glycol is not unusual, however, since Greene-Kelly (1955) has shown that organo-philic smectites are not affected by treatment with glycol or glycerol.

Alcohol additions have been shown to have little effect upon hydrolysis of the alkylammonium ions though addition of alcohol to $\text{NH}_4\text{OH-Al}_2\text{SiO}_5$ gels often results in smectites being formed in preference to micas. (Barrer and Denny) (1961). This suggests that substitution of the ammonium ion may be occurring: viz.



The most notable general characteristic of these organo-smectites is however the fact that the interlayer cations are resistant to ion-exchange with inorganic or other organic cations. The increased basal spacings of the alkylammonium clays ($\sim 13.5\text{\AA}^0$ -13.9) and the results of the carbon and nitrogen analyses (see table 13) were considered sufficient evidence that the clays contained substituted ammonium ions, located between the layers of the 2:1 sheets.

The ion-exchange, thermal and other treatments are given in Tables 9, 10, and 11.

Due to the small amount (~ 0.25 gms) of product synthesized no quantitative results on the nitrogen contents before and after treatments with alkali metal chloride solutions were obtained.

Table 9.

Gel composition: $(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$

<u>Sample no.</u>	<u>Temp./ Time</u>	<u>orig $d(001) \text{ \AA}$</u>	<u>Solutions used for ion exchange</u>	<u>Observed effects on 001 of treatments</u>
74	250/7	13.85	CaCl ₂ NaCl Na citrate (Et) ₃ NHCl Na O Et (refluxed)	no change no change no reduction in 001 no change 001 = 13.86 $\text{\AA}$ (outgassed)

Gel composition: $(\text{Bu})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$

73	250/6	14.5 (outg.)	CaCl ₂ (3 mths. at 60°C) C ₁₂ NH ₂ HCl Na O Et (refluxed)	001 = 13.86 $\text{\AA}$ (outgassed) 001 = 14 $\text{\AA}$ air dried diffuse 001 on outgassing broadening of 001 (outgassed)
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Table 10.

<u>Gel composition:</u> $3(\text{Me})_4\text{NOH}.\text{Ga}_2\text{O}_3.2\text{SiO}_2$				
Sample no.	Temp./ Time	Position orig. 001	Solutions used for ion-exchange	Observed effects of treatment
69-5	210/5	13.5	KCl	basal spacing decreases from 13.5-10.5
69-6	210/6	13.5	MgCl_2	basal spacing = 10.2 Å 14.2 (air dried)
88-4	250/6	13.5	KCl	basal spacing = 10.2 Å
<u>Gel composition:</u> $3(\text{Et})_4\text{NOH}.\text{Ga}_2\text{O}_3.2\text{SiO}_2$				
89-2	250/3	broad diffuse	KCl	sharp basal reflection at 10.5 Å
89-3	300/6	10.4	KCl	no change
98-1	250/2	10.4	$(\text{Et})_3\text{NHCl}$	no change
<u>Gel composition:</u> $0.5(\text{Me})_4\text{NOH}.2\text{Al}_2\text{O}_3.4\text{SiO}_2$				
91-2	300/6	13.2	KCl	after 14 days at 65°C basal spacing = 12 Å (outgassed)
<u>Gel composition:</u> $3(\text{Et})_4\text{NOH}.\text{Al}_2\text{O}_3.2\text{SiO}_2$				
99-1	250/3	very diffuse	NH_4Cl	no change, still very diffuse
99-2	250/7	broad 11-13 Å	KCl	very faint, diffuse 001 at 11-13 Å outgassed spec. still diffuse
86-1	300/5	broad 13-13.5	KCl	001 becomes weak and diffuse no change to 001 on outgassing

Table 11.

Gel composition: (Prop)₄NOH.2Al₂O₃.4SiO₂

<u>Sample no.</u>	<u>Temp./ Time</u>	<u>Position orig. 00l</u>	<u>Solutions used for ion exchange</u>	<u>Observed effects on 00l of treatments</u>
60	250/7	13.65 Å ^o (outg.)	NaCl	basal reflection becomes diffuse
			further NaCl treatments	outgassed spec. 00l = 13.6
			C ₁₆ NH ₂ HCl (after NaCl)	air dried spec. sharp 00l = 13.8
			C ₁₆ NH ₂ HCl (2 mths.)	outgassed spec. sharp 00l = 13.8
			(C ₆ H ₁₃) ₂ NHHCl	outgassed spec. 00l = 13.8 Å ^o
				outgassed spec. 00l = 13.6 Å ^o

Gel composition: (Prop)₄NOH.2Al₂O₃.4SiO₂

20-3	250/6	13.8 (outg.)	CaCl ₂	outgassed spec. 00l = 12.4 Å ^o
			glycolated	air dried spec. 00l = 14.5 Å ^o
				00l = 17.2 Å ^o

Gel composition: 0.5 Na₂O Al₂O₃.2SiO₂

72-3	300/5	10.0 (outg.)	C ₁₂ NH ₂ HCl	air dried 00l = 17 Å ^o
			glycolated	00l = 17.2 Å ^o

In experiments 99-2, using tetra-ethylaluminosilicate gels, the smectite produced had an initial broad basal spacing of 11.5-13.0 Å (air dry) which showed an increase in width after treatment with KCl solutions, indicating that some exchange of the interlayer cations had taken place. The very diffuse nature of the basal reflection prevented measurements on the outgassed product being determined successfully.

The various ion-exchange treatments given to sample 60, a 'tetra-propylammonium' smectite, are shown in Table 11 and the results seem to indicate that only limited exchange has occurred. Repeated treatments with sodium chloride solutions gave a specimen whose basal spacing after outgassing differed only slightly from that of the original sample. Treatment of a sample (previously treated with NaCl solutions) with hexadecylamine hydrochloride solutions gave a smectite which after outgassing had a basal spacing of 13.85-13.9 Å. This spacing has a value greater than the original and the Na⁺ treated forms and indicates that partial replacement by the C₁₂NH₃⁺ ions of ions present in the smectite had taken place.

The basal spacing of a smectite with a b.e.c. of 0.85 meq/gram fully exchanged with C₁₂NH₃⁺ would be ~ 16.5 Å. (Weiss (1961)). Sample 74 a tetra-ethyl

alumino-smectite was treated with various chloride solutions and the results are shown in Table 9. In the absence of any quantitative results and assuming that any exchange of the original organic ions with Na^+ or Ca^{++} would bring about a decrease in the basal spacing, the results indicate that no exchange has occurred. In experiment 91-2 where the base/alumina ratio was reduced to 0.25:1, the product had an initial basal reflection at $\sim 13.2\text{\AA}^{\circ}$ which on repeated treatments with potassium chloride solutions decreased to $\sim 12\text{\AA}^{\circ}$. As this basal spacing was obtained on a well outgassed specimen the final value of $12\text{\AA}^{\circ}$ would indicate that the sample was probably a mixed-layer type of clay (i.e. with some expanding layers and some non-expanding, but both of the 2:1 type).

The formation of a mixed layer smectite from a gel having a base/alumina ratio of 0.25/1 is in agreement with work carried out by Warshaw (1960) who investigated the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system where the K/Al ratio was less than one. She found that when this ratio was reduced below 0.3, a mixed layer (mica-montmorillonite) type mineral was formed.

The treatments with sodium citrate were undertaken because it was thought that some of the interlayer material could be $\text{Al}(\text{OH})_2^+$, which might not be readily exchanged in

the usual way, but might be removed by complexing plus exchange. Treatment of Sample 74 with sodium citrate solution did not produce any observable alteration of the X-Ray pattern and the results of subsequent ion-exchange experiments were the same as those on the untreated sample.

Sample 20-3, a tetrapropylammonium smectite showed a decrease in the basal spacing from $13.8\text{\AA}$ to $12\text{\AA}$ after treatment with CaCl_2 solutions. The same sample, after treatment with CaCl_2 , was solvated with ethylene glycol and expanded to give a basal reflection at $17.2\text{\AA}$ which is the value expected for a homionic Ca^{++} specimen.

Treatment of Sample 73, a 'tetra-butyl ammonium' smectite with CaCl_2 solutions gave a product whose basal reflections had decreased from the original $14.5\text{\AA}$ to $13.8\text{\AA}$. Treatment of the same sample with $\text{C}_{12}\text{NH}_2\text{HCl}$ gave a product having a basal spacing of $14.5\text{\AA}$.

The results of experiments with sample 73 are similar to those found with sample 60, and indicate that ion-exchange is taking place only to a limited extent.

The results discussed above show peculiar anomalies. In one case a short treatment with CaCl_2 solutions was sufficient to remove some of the interlayer ions incorporated during synthesis whereas with another sample vigorous and sometimes extensive (3 months) treatment

with concentrated chloride solutions failed to give any exchange (observable on X-Ray pattern) of the interlayer ions.

Table 12.

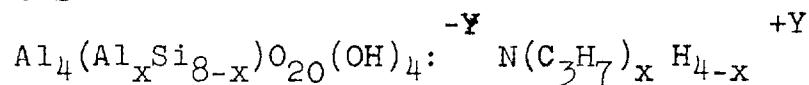
The carbon and Nitrogen Analyses for a few Samples are given below.

Sample	Temp. Time	Composition:	C%	N%	H%	$\frac{C}{N}$
60-A	250/7	$1(\text{Prop})_4\text{N} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	5.42	1.2	2.31	5.2
60-B	250/7	" " "	3.19	<1.0	2.05	3.72
88-1	300/1	$3(\text{Me})_4\text{N} \cdot \text{Ga}_2\text{O}_3 \cdot 2\text{SiO}_2$	2.38	1.17	1.43	2.37
88-3	300/2	"	1.64	1.22	1.40	1.57
88-6	300/6	"	1.27	0.66	1.51	2.23
69-A	300/5	"	3.53	1.52	1.93	2.72
88-2	250/1	"	2.56	1.13	1.40	2.66
88-4	250/2	"	3.34	1.09	1.97	3.57
88-7	280/6	"	1.80	1.11	1.52	1.89
69-6	210/12	$3(\text{Me})_4\text{N} \cdot \text{Ga}_2\text{O}_3 \cdot 2\text{SiO}_2$	4.43	1.73	2.36	3.00

The carbon/nitrogen ratios are much lower than the ideal (for tetrapropylammonium it would be 12, and for tetra-methylammonium, 4) and indicate that hydrolysis of the alkylammonium ions has occurred to varying degrees. Table 13 shows the

value of the exchange capacity, Y^+ , calculated from the nitrogen content, assuming the following ideal formulae for the two structures.

60-A and 60-B



88-1 - 69-6

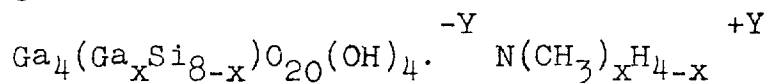


Table 13.

Average cation composition from C/N ratio.	Y^+ value from analysis	Sample no.
$(N(C_3H_8)_{1.7} \cdot H_{2.33})^{Y+}$	0.69	60-A
$(N(C_3H_8)_{1.24} H_{2.76})^{Y+}$	0.56	60-B
$(N(CH_3)_{2.37} H_{1.63})^{Y+}$	0.78	88-1
$(N(CH_3)_{1.57} H_{2.43})^{Y+}$	0.81	88-3
$(N(CH_3)_{2.23} H_{1.77})^{Y+}$	0.44	88-6
$(N(CH_3)_{2.72} H_{1.28})^{Y+}$	1.02	69-A
$(N(CH_3)_{2.66} H_{1.34})^{Y+}$	0.76	88-2
$(N(CH_3)_{3.57} H_{0.43})^{Y+}$	0.75	88-4
$(N(CH_3)_{1.89} \cdot H_{2.11})^{Y+}$	0.74	88-7
$(N(CH_3)_{3.00} H_{1.00})^{Y+}$	1.17	69-6

Table 14.

	H% (Interlayer Cation)	H% (Interlayer + Structural)	H% Analysis
60-A	1.96	2.45	2.31
60-B	1.60	2.10	2.05
88-1	0.93	1.34	1.43
88-3	0.77	1.19	1.40
88-6	0.89	1.32	1.51
69-A	0.99	1.41	1.93
88-2	0.98	1.40	1.40
88-4	1.16	1.57	1.97
88-7	0.83	1.25	1.52
69-6	1.05	1.47	2.36

Table 14 shows the percentage hydrogen content of the specimens calculated (i) from the hydrogen present in the "postulated ion" (table 13) and (ii), (i) above, plus the hydrogen present in the structural (OH)'s in the clay structure. These are compared with the total percentage of hydrogen present attained from analysis. The difference between calculated and experimental values was taken as the hydrogen present as molecular water.

In the foregoing calculations, it must be emphasized

that the "postulated ion" is an average ion as it was estimated from the C/N ratios obtained by analysis, i.e. a C/N ratio in these cases probably reflects the mean of a number of possible substituted ammonium ions, both more and less substituted than would be indicated by a C/N ratio.

The basal spacings of a number of outgassed specimens are listed in Table 15 where they are compared with those of the corresponding dehydrated ion-exchanged natural bentonites.

These results confirm in most cases that hydrolysis has occurred giving rise to smaller (less substituted) ions which when intercalated give basal spacings less than those expected if the 'original' ions had been present between the layers.

Any further conclusions on the basis of the basal spacing values are complicated by the fact that interstratification could have taken place.

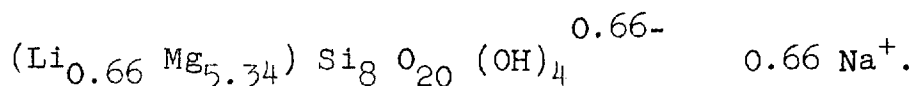
The results shown in the lower portion of Table 15 i.e. for samples 15-3, 15-5, 15-4 and 15-6 are listed here in order to show the effect that additions of methanol and ethanol had upon the basal spacings of the final product. Of particular importance in this series of products is the rational series of basal reflections which rule out (in this case) the possibility of random interstratification.

Table 15.

Sample no.	Temp. Time	Composition	<u>Basal Spacing 001.</u>		
			Synthetic Sample.	Wyom B (EXC)	
9	$\frac{250}{6}$	$1(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	14.24	13.95	
DD3	$\frac{250}{7}$	$1(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ + (eOH)	14.40	13.95	
27-3	$\frac{250}{6}$	$3(\text{Prop})_4\text{NOH} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	13.45	15.70	
13-4	$\frac{300}{5}$	$3(\text{Bu})_4\text{NOH} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	13.80	17.0	
24-1	$\frac{250}{4}$	$3(\text{Bu})_4\text{NOH} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	14.08	17.0	
73	$\frac{250}{7}$	$1(\text{Bu})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	14.50	17.0	
			<u>001</u>	<u>002</u>	<u>004</u>
15-3	$\frac{250}{5}$	$+(\text{EtOH})(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	13.4	6.65	3.31
15-5	$\frac{250}{5}$	$+(\text{EtOH})(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	13.20	6.65	3.31
15-4	$\frac{250}{5}$	$+(\text{MeOH})(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	14.08	7.0w	
15-6	$\frac{250}{5}$	$+(\text{MeOH})(\text{Et})_4\text{NOH} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	14.10	7.0w.	

6.2 SYNTHESIS OF ALKYLAMMONIUM HECTORITE-LIKE COMPOUNDS

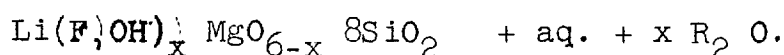
In their classification of the montmorillonite minerals Ross and Hendricks (1945) listed hectorite (Hector, California) as a trioctahedral montmorillonite having the formula



MacEwan (1951) in his discussion of the montmorillonite minerals includes hectorite, and establishes the criterion that the 06 spacing for the trioctahedral montmorillonite should be slightly greater than $1.5\overset{\circ}{\text{Å}}$. The main diagnostic criteria for a hectorite are:-

- (a) montmorillonite diffraction pattern
- (b) 06 spacing $> 1.5\overset{\circ}{\text{Å}}$
- (c) D.T.A. curve and analytical and cation-exchange results in reasonable accord with the general formula.

As a result of the detailed investigation into the synthesis of hectorite made by Granquist (1960) the syntheses carried out in this work were confined to using starting gels of the following general composition:-



where $R = \text{Li}, \text{Na}, (\text{Me})_4\text{N}^+, (\text{Et})_4\text{N}^+, (\text{Prop})_4\text{N}^+, (\text{Bu})_4\text{N}^+, \text{NH}_4^+, (\text{CH}_2)_x(\text{NH}_2)_2$. In three separate runs the silica was replaced by germania.

In most of the experiments the $\text{R}_2\text{O}:\text{lithia}$ ratio was kept constant at one, as this would provide just sufficient ~~ex~~ quaternary ammonium ions to occupy all the exchange sites between the anionic layers assuming all the lithia in the starting gel had substituted for Mg^{2+} in the octahedral layers of the hectorite formed.

The reactions took place in three necked 500 ml round bottomed flasks fitted with mechanical stirrers and heated by means of heating mantles.

The total volume of the reacting solution and the weight of solids present in this solution was kept constant at 400 mls. and 1% respectively.

All reactions were carried out at 100°C . Granquist (1960) found that it was possible to follow the rate of hectorite synthesis by observing the rate at which the diffraction lines due to one of the components of the starting gel ($\text{Mg}(\text{OH})_2$) became less intense, and eventually disappeared in the best syntheses.

This technique was found most useful in the present study and was used to estimate the approximate proportion of hectorite in a sample removed after a particular time interval.

When using a particular base the reactions were often repeated a number of times in order to get some idea of the reproducibility of the syntheses. After completion of a run the contents of the flask were filtered off and washed thoroughly with water and alcohol.

The gels which included organic bases gave products that settled out rapidly from solution and were easily filtered. In contrast to this behaviour the clays synthesized from inorganic gels without organic bases formed very stable suspensions which gave rise to stiff gels on filtering. In the latter cases centrifugation was often used to ensure a well washed product.

The results of syntheses summarized in Tables 16 and 17 show that hectorite-like compounds can be readily synthesized at low temperatures (c.a. 100°C) and that they crystallise just as readily in the presence of large organic alkylammonium cations as in experiments with inorganic ions only. Crystallisation was usually complete in five to seven days. The products obtained from longer runs of twelve to fifteen days did not show any improvement in crystallinity of the clay mineral.

Experiments with lithia-magnesia-silica gels in the absence of any organic cations produced typical expanding clays of the hectorite type. These synthetic

Table : 16

	<u>Gel composition:</u>	<u>synthesis time (days)</u>	<u>soln. pH.</u>	<u>Products.</u>
	$(Me)_4NOH:LiF:MgO:SiO_2$			
97B5	0.124:0.124:1:1.33	6	10	good hectorite
97B6	0.124:0.124:1:1.33	8	8	good hectorite + $Mg(OH)_2$
97B7	0.124:0.124:1:1.33	10	8.3	good hectorite +
97B8	0.124:0.124:1:1.33	9	9.5	mod hectorite + $Mg(OH)_2$
	$(Me)_4NOH:LiOH:MgO:SiO_2$			
97B9	0.124:0.124:1:1.33	7	9.5	$Mg(OH)_2$ + poor hectorite
97B9	0.124:0.124:1:1.33	14	9.5	mod hectorite + $Mg(OH)_2$
97B10	0.124:0.124:1:1.33	9	10.5	poor hectorite + $Mg(OH)_2$
	$(Me)_4NOH:MgO:SiO_2$			
104-1	0.248:1:1.33	17	10	$Mg(OH)_2$
	$(Et)_4NOH:LiF:MgO:SiO_2$			
102-2	0.124:0.124:1:1.33	1	9	mod hectorite + $Mg(OH)_2$
102-1	0.124:0.124:1:1.33	7	9	good hectorite + trace $Mg(OH)_2$
102-2	0.124:0.124:1:1.33	10	9.5	good hectorite
	$(Et)_4NF:LiF:MgO:SiO_2$			
109-1	0.124:0.124:1:1.33	11	8.5	mod hectorite + U
	$(Et)_4NF:LiOH:MgO:SiO_2$			
109-2	0.124:0.124:1:1.33	13	9.7	mod hectorite
	$(Et)_4NOH:LiF:Al_2O_3:SiO_2$			
106-6	2.0:0.124:1:1.33	18	10.3	U
	$(Et)_4NOH:Al_2O_3:SiO_2$			
106-2	3: 1 : 2	12	10	boehmite

Table : 17.

	<u>Gel composition:</u>	<u>synthesis time (days)</u>	<u>soln. pH.</u>	<u>Products.</u>
	(Prop) ₄ NOH:LiF:MgO:SiO ₂			
103-1	0.124:0.124:1:1.33	6	8.0	good hectorite + trace Mg(OH) ₂
103-2	0.124:0.124:1:1.33	4	9.5	mod hectorite
103-2	0.124:0.124:1:1.33	7	9.5	good hectorite
	(Bu) ₄ NOH:LiF:MgO:SiO ₂			
105-1	0.124:0.124:1:1.33	6	9.0	mod hectorite + Mg(OH) ₂
105-1	0.124:0.124:1:1.33	7	9.0	good hectorite trace Mg(OH) ₂
105-2	0.124:0.124:1:1.33	10	9.5	good hectorite + Mg(OH) ₂
105-5	0.124:0.124:1:1.33	3	10	good hectorite + Mg(OH) ₂
105-5	0.124:0.124:1:1.33	9	10	good hectorite + trace Mg(OH) ₂
	(Bu) ₄ NOH:LiF:MgO:SiO ₂			
105-6	0.124:0.124:1:1.33	3	9.1	good hectorite + Mg(OH) ₂
105-6	0.124:0.124:1:1.33	10	9.1	good hectorite
105-7	0.124:0.124:1:1.33 + 50% excess (Bu) ₄ NF.	12	8.8	mod hectorite + trace Mg(OH) ₂
	(Hex) ₄ NOH:LiF:MgO:SiO ₂			
108-1	0.124:0.124:1:1.33	2	9.5	Mg(OH) ₂
108-1	0.124:0.124:1:1.33	10	9.5	mod hectorite trace Mg(OH) ₂
108-2	0.124:0.124:1:1.33	9	8.8	mod hectorite

mod = moderate crystallinity.

clays^{minerals} had ion-exchange properties similar to the natural material and swelled to $17.2\text{\AA}$ in the presence of ethylene glycol. These synthetic hectorite-like compounds from inorganic-gels are subsequently designated IN-hectorites.

The experiments which included organic ions (except run 97B₇) yielded products which showed limited swelling with glycol and whose interlayer cations were peculiarly resistant to ion-exchange, using a large variety of both inorganic and organic ions in attempts to effect such ion exchange. These clays from gels containing organic cations are designated OR-hectorites.

Experiment 97B₇ which had only one third of the required amount of base, produced a hectorite-like compound which readily expanded with ethylene glycol to $17.2\text{\AA}$ and had a cation-exchange capacity of 78 meq./100 gms. This product is thus similar to the IN-hectorites.

In many runs the alkali metal and alkylammonium fluorides were used in place of the hydroxides to see whether the resulting lower pH. would increase the solubility of magnesium hydroxide and the rate of synthesis.

The use of lithium fluoride definitely resulted in an increase in the rate of clay^{mineral} synthesis and a general improvement in crystallinity. The use of alkylammonium fluorides did not have any pronounced effect upon the

crystallinity of the 'hectorite' produced though there tended to be less magnesium hydroxide visible on many of the X-Ray patterns of material from syntheses of short duration (3-4 days).

Excess additions of organic fluorides, in the case of runs 105-7, 109-1, appeared to have a retarding effect upon the clay crystallisation whereas a ten-fold excess of lithium fluoride in no way affected crystallisation from inorganic gel systems.

In the run 97, where an alkylammonium-magnesia-silica gel was used in the absence of any lithium, no hectorite was produced after ten days.

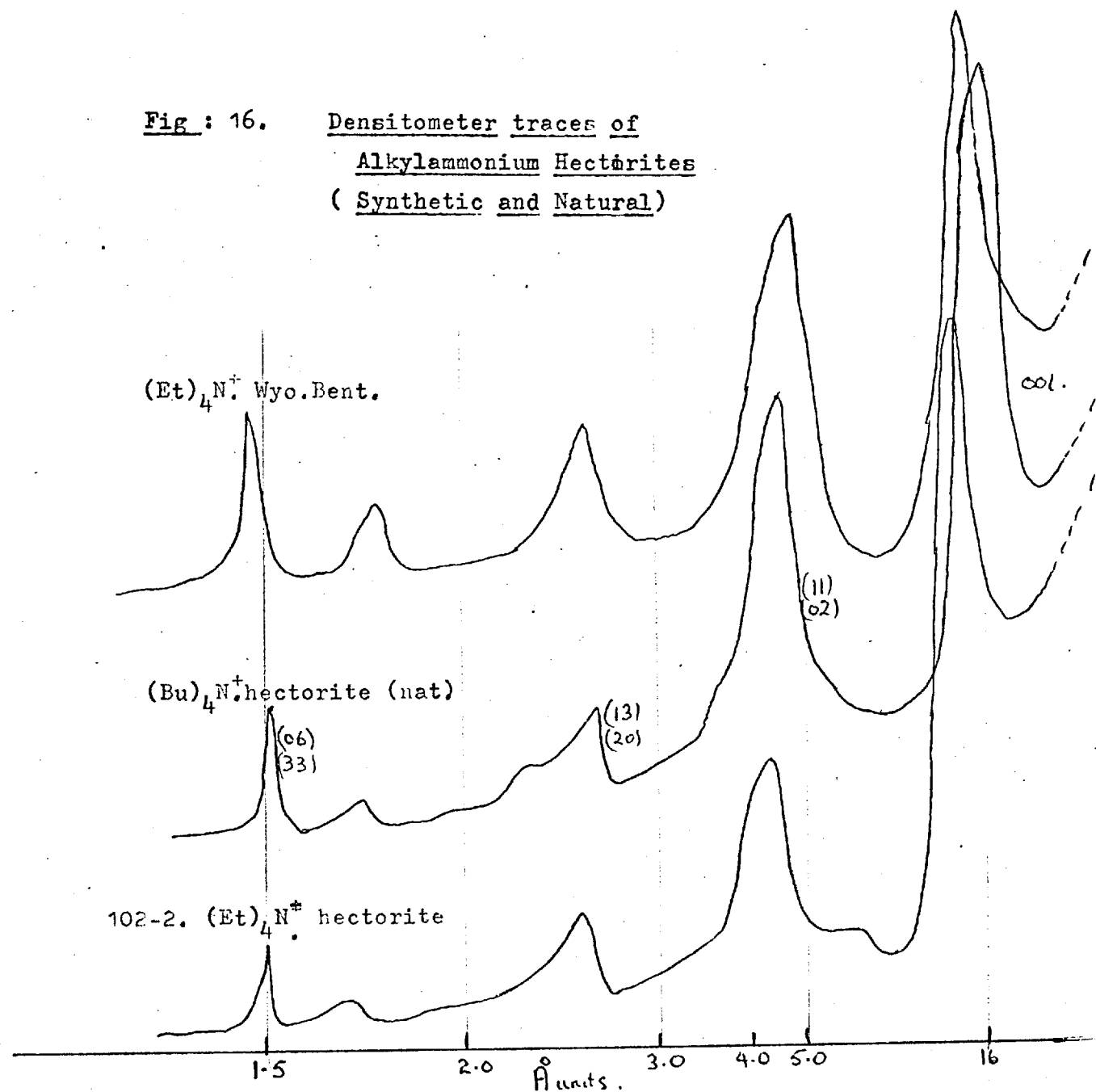
Characterization:

1. X-Ray diffraction:

X-Ray powder photographs of the materials prepared showed typical montmorillonite diffraction patterns. Densitometer traces of the X-Ray films of some of the clays are shown in fig. 16 where they are compared with that of a natural hectorite (Berk B.G.)

The hk reflections show the tailing towards high angles characteristic of the two dimensional disorder so common in montmorillonite-type clays. The 060 reflection

Fig : 16. Densitometer traces of
Alkylammonium Hectorites
(Synthetic and Natural)



is symmetrical and varies in value from 1.52-1.54⁰Å. The approximate unit cell sizes are as follows:

$$a = 5.26, b = 9.12, c = 9.8 \rightarrow 15.5^0\text{Å}.$$

The synthetic ~~2~~ OR-hectorites containing organic cations show very strong 1st order basal reflections but very weak 2nd and 3rd order reflections. The values of the 1st order basal reflection obtained from specimens outgassed at 10⁻⁴ mm and 50°C are shown in Table 18.

Table 18.

<u>Sample No.</u>	<u>Cation type</u>	<u>001 Value in Å ± 0.2Å</u>
97B ₅	(Me) ₄ N ⁺	14.6
97B ₈	"	14.5
102-1	(Et) ₄ N. ⁺	14.7
102-2	"	14.7
103-1	(Prop) ₄ N. ⁺	15.3
103-2	"	
105-1	(Bu) ₄ N. ⁺	15.5
105-2	"	15.4
105-3	"	15.3
110-1	(Bu) ₄ N. ⁺ (Ge sample)	15.2
110-2	" "	
154	Li ⁺ .	9.5

The results in Table 18 show that in the organic hectorites there is a small but definite increase in the basal spacings with increase in the size of organic cation added in the initial gel. These OR-hectorites showed no expansion in the presence of water vapour.

Although it is virtually impossible to estimate the amount of amorphous material present in a clay mineral especially those synthesised at a low temperature, the low background scatter and the results of some magnesium analyses suggest that amorphous material is not appreciable.

Electron Microscopy

The appearance of the inorganic and organic 'hectorites' under the electron microscope were markedly different.

The inorganic clays^{minerals} were easily dispersed and the micrographs plates 1-3 show thin particles which yield fairly sharp electron diffraction ring patterns. The OR-hectorites on the other hand have a 'crumpled paper' appearance and it was not possible to obtain electron diffraction patterns from these preparations.

The contrast in appearance noted above for the two types of synthetic clay, was also observed on natural

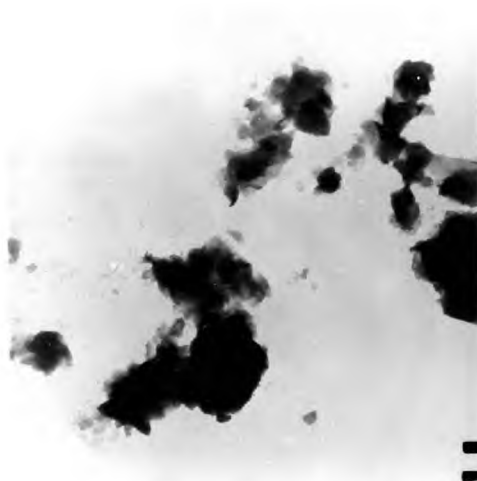


Plate : 1 x10,000
 IN - hectorite.
 Thin dispersed flakes
 yield electron diffraction
 ring patterns.

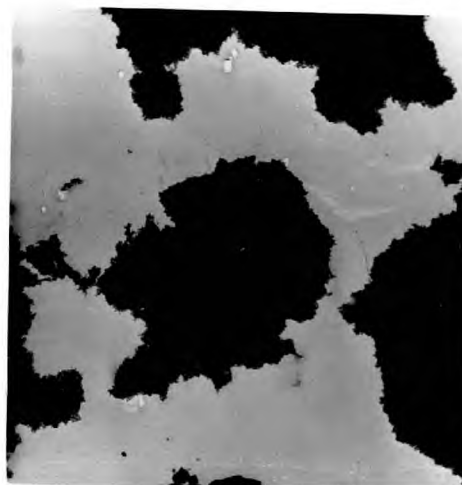


Plate : 2 x12,000
 IN - hectorite.
 Less well dispersed
 c.f. plate 1.

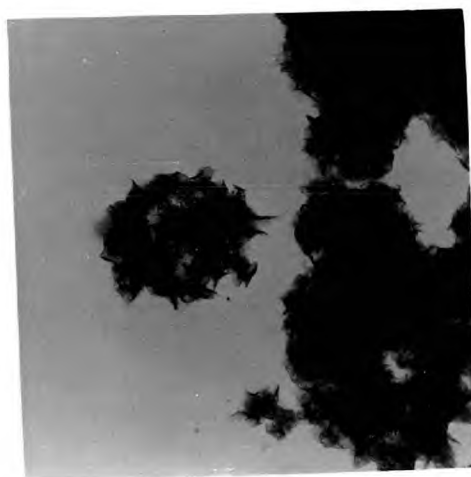


Plate : 3 x 15,000
 (Bu)₄N⁺ OR - hectorite.
 note 'crumpled paper' texture.

hectorite which had been dispersed in the natural sodium form and after treatment with alkylammonium ions.

Carbon and Nitrogen Analyses:

A number of the OR-hectorites were analysed for carbon, nitrogen and hydrogen using the Dumas and sealed tube combustion methods.

The clays chosen for the analyses had X-Ray patterns which showed that crystalline magnesium hydroxide was either absent or present in amounts < 10%. The results of the analyses are shown below.

<u>Sample No.</u>	<u>Cation type</u>	<u>C%</u>	<u>N%</u>	<u>H%</u>	<u>$\frac{C}{N}$</u>	<u>Ideal $\frac{C}{N}$</u>
97B ₅	(Me) ₄ N.	3.3	0.92	1.83	4.2	4
102-1	(Et) ₄ N.	6.06	0.85	2.27	8.3	8
103-1	(Prop) ₄ N.	7.21	0.81	2.24	10.5	12
105-1	(Bu) ₄ N.	10.20	0.81	2.81	14.7	16

Comparison of the calculated and experimentally determined C/N. ratios showed that hydrolysis of the alkylammonium ions is negligible and that the organic cations originally added to the gels are being incorporated into the lattice. The results of the carbon and nitrogen analyses together

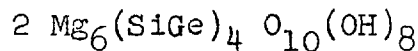
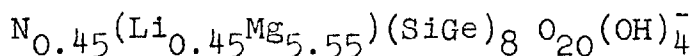
with the X-Ray measurements of the basal spacings of the OR-hectorites strongly support the view that the hectorites prepared do contain alkylammonium ions, which are located between the 2:1 layers.

In view of the difficulty experienced in effecting ion-exchange between the alkylammonium interlayer ions in the OR-hectorites with organic and inorganic ions (See next Section), an alternative interpretation of the 14-15⁰Å basal spacing was considered. Caillère (1949) and Slaughter and Milne (1959) found that brucite-like $\text{Mg}(\text{OH})_2$ layers could easily be precipitated between the 2:1 layers of an expanding clay by first saturating it with magnesium and then precipitating the magnesium hydroxide by addition of aqueous ammonia. These products showed a strong 14⁰Å basal spacing and the magnesium content was found to have increased by 12%.⁰

The magnesium content and the 14⁰Å basal spacing would thus give a product which by analysis and X-Ray methods would appear similar to that of a true chlorite. Thermobalance investigations by Caillère showed that the interlayer $\text{Mg}(\text{OH})_2$ in these artificially prepared "chlorites" was much more labile than the brucite layer in a true chlorite, and furthermore, unlike a true chlorite, they swelled to ~17⁰Å with ethylene glycol.

Some magnesium analyses were made on a few of the OR-hectorites and the results are shown below, where they are compared with the calculated magnesium contents for a clay containing $\text{Mg}(\text{OH})_2$ interlayers ("Mg chlorite") and a magnesium hectorite.

<u>Magnesium hectorite</u>	<u>Sample</u>	<u>MgO %</u>	<u>"Mg Chlorite"</u>
% MgO			% MgO
25.8 (Si)	105-6	24.1	43
27.3 (Si)	102-2	26.2	43
18.5 (Ge)	110-1	19.8	32.8



The results show that there is no excess magnesium present.

In all cases the initial basal spacing of the OR-hectorites was greater than the $14\text{\AA}$ obtained by Caillere et al on the clays with intercalated $\text{Mg}(\text{OH})_2$, but the samples did swell with glycol to give spacings which range from $16.8\text{\AA}$ - $18.4\text{\AA}$.

To make some further comparisons concerning the stability of clays with intercalated $\text{Mg}(\text{OH})_2$, a natural Wyoming bentonite was saturated with magnesium and interlayer

$\text{Mg}(\text{OH})_2$ precipitated as described by Slaughter and Milne (1959). The samples prepared in these laboratories showed a moderate to strong $14\overset{\circ}{\text{\AA}}$ basal spacing and had the same heat stability as that found by Caillère and Milne. Treatments of the clays with intercalated $\text{Mg}(\text{OH})_2$ and OR-hectorites with solutions of NH_4Ac or NH_4Cl at room temperature for 24 hours revealed a marked difference in stability.

The clays with magnesium-hydroxide intercalated, after treatment with ammonium acetate, showed a fall in the basal spacing to $\approx 11\overset{\circ}{\text{\AA}}$ in the air dry state, whereas the basal spacings of the OR-hectorites remained unaffected. On prolonged treatments, lasting three to six days, the OR-hectorites showed signs of structural breakdown by dissolution which is not unexpected when it is recalled that these **are** magnesium silicates^{hydrates} which have been prepared at low temperature.

The analytical, X-Ray, and ammonium acetate, investigations carried out provide substantial evidence to show that the OR-hectorites do not have significant intercalated $\text{Mg}(\text{OH})_2$ layers. In view of the fact that $14\overset{\circ}{\text{\AA}}$ material was never observed in synthesis from purely inorganic gels, even when the pH. was raised by addition of excess lithium hydroxide and precipitation might be

expected, it seems certain that the large basal spacings recorded from the OR-hectorites arise from the large interlayer organic cations and not from $\text{Mg}(\text{OH})_2$ layers.

Ion-Exchange:

In order fully to characterize a synthetic or natural hectorite it is essential to determine its cation-exchange capacity. The cation-exchange capacity of the clay would, in the ideal case, indicate the amount of ionic substitution present in the layers and thus the layer charge. The determination of the cation-exchange capacity of the synthetic IN- or OR-hectorites should allow any effect of starting materials, or in the case of the OR-hectorites, the size of organic cation incorporated, to be determined.

If quantitative exchange of the interlayer ions with di-n-alkylammonium ions can also be obtained then it should be possible to determine the layer charge by the method of Weiss (1963b).

Some qualitative ion-exchange experiments where X-Ray methods alone were used to interpret the results, were carried out in order to obtain some idea of the ion-exchange behaviour of the 'OR'- and 'IN'-hectorites.

The results of these experiments are summarized in Table 19.

Table 19.

Sample No.	Composition	Basal spacing. 001Å	Ion-Exchange Soln.	Observed Effect
154	LiFMgOSiO_2	$9.6\text{\AA}$ (outg.)	$(\text{Et})_3\text{NHCl}$ Glycol H_2O NH_4Cl	$001 \rightarrow 13.3\text{\AA}$ $001 \rightarrow 17.4\text{\AA}$ Swells detd. C.E.C. 84 meq/100gms.
97B ₅	$(\text{Me})_4\text{N} \cdot \text{LiMgSiO}_2$	$14.6\text{\AA}$	1) KCl 2) $\text{C}_{18}\text{NH}_2\text{HCl}$ 65°C x 11 days 3) Treated with H_2O_2 (100 Vol)	001 becomes slightly diffuse no change observed no effect on X-Ray pattern
102-1	$(\text{Et})_4\text{N} \cdot \text{LiMgOSiO}_2$	$14.7\text{\AA}$	1) KCl (42 days x 60°C) 2) H_2O_2 treated then KCl (42 days x 65°C)	no change in 001 no change in basal 001
103-1	$(\text{Prop})_4\text{N} \cdot \text{LiMgSiO}_2$	$15.3\text{\AA}$	1) KCl (42 days x 65°C)	no change in 001

The observations recorded above indicated that the interlayer organic ions showed little tendency to exchange their interlayer cations with potassium or octadecylammonium ions even when the exchange reaction was continued for 42 days at 60°C.

To check the conclusion arrived at from observations of the X-Ray patterns before and after treatment with inorganic and alkylammonium chloride solutions some quantitative determinations were made of the nitrogen content before and after treatment with sodium chloride solutions. The basal spacings of the outgassed clays were determined both before and after the ion-exchange reaction and are tabulated together with the results of the nitrogen analyses in Table 20.

Table 20.

<u>Sample No.</u>	<u>NITROGEN CONTENT</u>		<u>BASAL SPACINGS</u>	
	<u>BEFORE</u>	<u>AFTER</u>	<u>BEFORE</u>	<u>AFTER</u>
97B ₈ (Me) ₄ N.	1) 0.76%	0.58%	14.5	14.5
	2) 0.75%	0.57%		
102-2 (Et) ₄ N.	1) 0.62%	0.57%	14.7	14.7
	2) 0.62%	0.57%		
103-2 (Prop) ₄ N.	1) 0.64%	0.57%	15.2	15.1
	2) 0.60%	0.58%		
	3) 0.62%			
105-2 (Bu) ₄ N.	1) 0.66%	0.65%	15.3	15.2
	2) 0.65%	0.64%		

With the exception of Sample 97B₈ the absence of any marked exchange between the interlayer quaternary ammonium ions and sodium, confirm the qualitative observations.

Sample 97B₈ was given further treatment with NaCl solutions but the product showed no further loss of nitrogen, which suggests a certain degree of inhomogeneity in the original sample.

In view of the success achieved by Weiss (1963a) in removing potassium from mica by using long chain alkyl-ammonium ions, the OR-hectorites were treated with concentrated solutions of octadecylamine hydrochloride solutions.

The exchange reactions were carried out for 2-3 months at 60°C, the amine chloride solutions being replaced at weekly intervals. The basal spacing of a hectorite with $C_{18}NH_3^+$ ions between the layers has a value of $\sim 16\text{\AA}$. Thus any OR-hectorite in which exchange is taking place should show an increase in the basal spacing with increase in the amount of exchange.

X-Ray patterns of the $C_{18}NH_3HCl$ treated OR-hectorites were obtained after outgassing at 50°C and 10^{-4} cm Hg. Little change was observed in the positions of the basal spacings after treatment but in view of the proximity of the original basal reflection and the basal spacing expected for a fully-exchanged $C_{18}NH_3^+$ clay, small

changes would probably not be observed in view of the estimated error in measurement of the rather broad reflections of $\pm 0.2\text{\AA}$. For this reason small portions of the clays treated with $\text{C}_{18}\text{NH}_2\text{HCl}$ were further treated with MgCl_2 solutions for three days at 50°C . After treatment with magnesium chloride the samples were washed and dried and the basal spacing of the outgassed clay measured.

Within the limits of accuracy mentioned above the only specimen to show any change in basal spacing after these treatments was Sample 105-2, a $(\text{Bu})_4\text{N}^+$ hectorite. After Mg^+ saturation the outgassed clay had a basal spacing $0.8\text{\AA}$ less than the original spacing of $15.4\text{\AA}$.

In view of the better defined series of basal reflections shown by the OR-hectorites synthesized with germanium it was hoped that observation of the movement of the higher order basal spacings would give a more accurate estimation of the changes occurring in the inter-layer region.

The OR-hectorite, 110-1, was treated with successive aliquots of MgCl_2 , ammonium chloride and octadecylamine hydrochloride solutions. The samples treated with octadecylaminehydrochloride and MgCl_2 showed no change. The samples treated with ammonium chloride however resulted in a fall in the intensity of the original, very strong

1st order basal reflection, and disappearance of the higher orders of the basal reflection.

The change in position of the first-order reflection was approximately $0.3\text{\AA}$, which is however only a little greater than the experimental error in measuring the positions of these med-broad peaks.

A further unusual result was found when the tetraethylammonium ion-exchanged form of IN-hectorite 113-1 was treated with ammonium chloride and sodium chloride solutions. Repeated treatments with the chloride solutions failed to bring about any reduction in the basal spacing of the organic derivative. The only difference between this original IN-hectorite and the other IN-hectorites prepared was that this material contained germanium. The IN-hectorites prepared with silica and subsequently exchanged with organic ions all released their organic ions on treatment with ammonium chloride.

The layer charges calculated from the cation exchange capacity in the case of the siliceous hectorites and from the C/N results in the germanium containing sample show them to differ by only 14 meq/100 grams ; the germanium sample having the lower layer charge (Table 21).

Little previous work has been reported for the ion-exchange of symmetrical substituted quaternary ammonium

ions with inorganic ions in montmorillonites. MacAtee (1963) has successfully replaced dimethyldioctadecyl-ammonium ions on clays by inorganic and organic ions, but he did not use quaternary ammonium ions of the type used in this study. For this reason, a series of ion exchanged clays were prepared by treatment of the natural clays with tetramethyl-, tetraethyl- and tetrabutyl-ammonium chloride solutions.

These ion exchanged clays were then treated with sodium chloride, and ammonium chloride solutions to compare their ion-exchange properties with the OR-hectorites.

Complete exchanges of the tetraethylammonium, and tetramethylammonium interlayer ions were achieved with both hectorite and bentonite clays within four days. The tetrabutylammonium derivative released the butylammonium ions less readily than the derivatives containing smaller ions, but repeated treatments successfully removed all the tetrabutylammonium ions.

D.T.A. and Thermobalance Studies

The weight loss versus temperature are shown in fig.17a and are characterized by 4 maxima. The first peak at $\sim 150^{\circ}\text{C}$ can be attributed to the loss of molecular water, which is confirmed by the D.T.A. curve which has an endothermic peak in this region and by the X-Ray evidence which shows that no structure change occurs on heating to 150°C . Further weight losses occur in the 350°C - 500°C , 640 - 850 and $> 860^{\circ}\text{C}$ regions. The D.T.A. curves of these samples show large exothermic peaks at 375°C and 615°C ; (see fig.17b). The basal spacings of the OR-hectorites heated to 350°C are weak and very diffuse, but on being heated to 650°C the diffuse basal reflection previously present in the 10.5 - $12\text{\AA}$ region, disappears and is replaced by a fairly strong slightly broad peak at $\sim 9.8\text{\AA}$. The clay^{which is} initially white in colour ($< 200^{\circ}\text{C}$) turns blue-black in the 350 - 550°C range but becomes white again on heating to 650°C .

The above results taken together suggest that at $\sim 300^{\circ}\text{C}$ the alkylammonium ions begin to break down according to the equation:

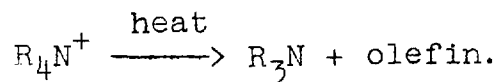


Fig: 17a.

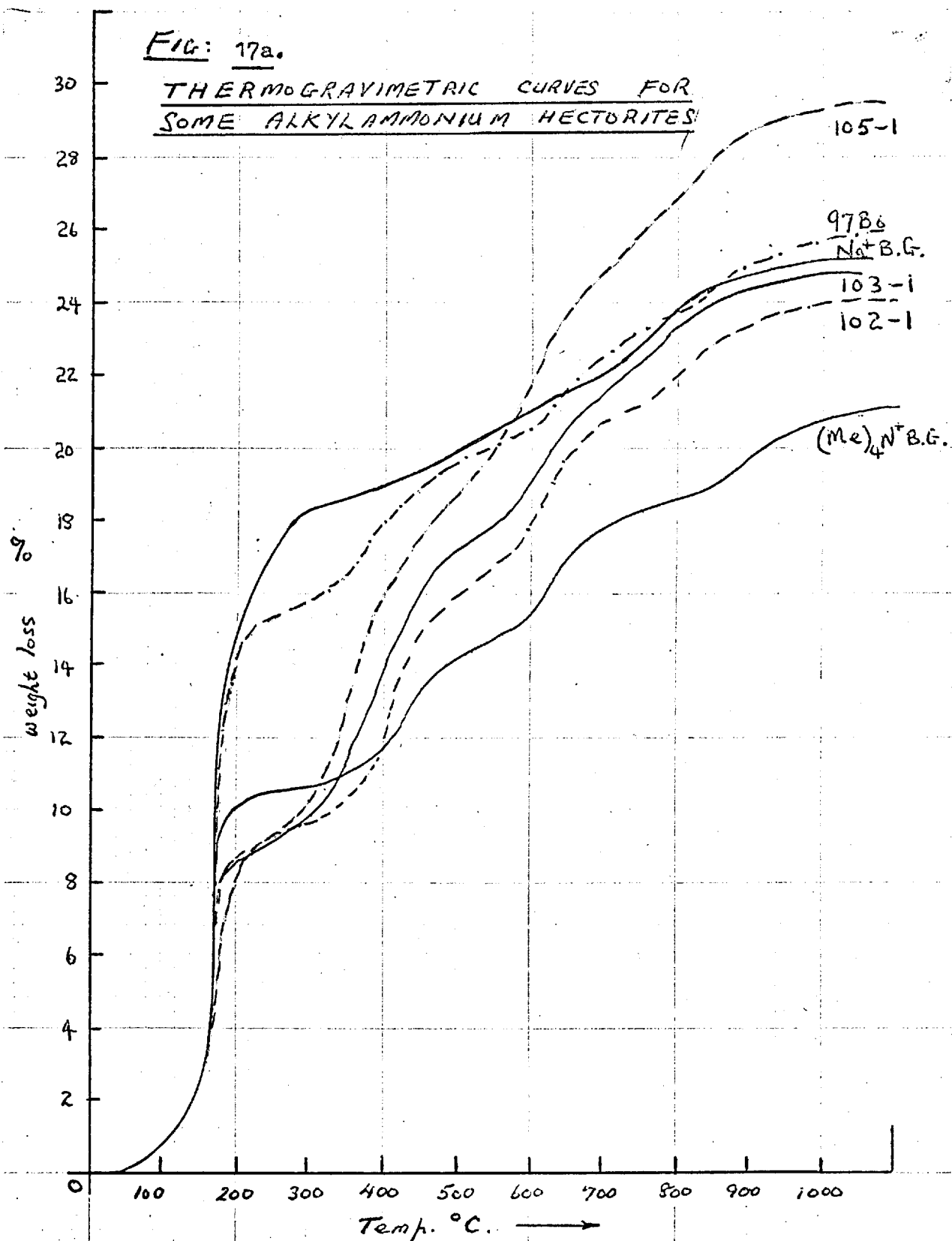
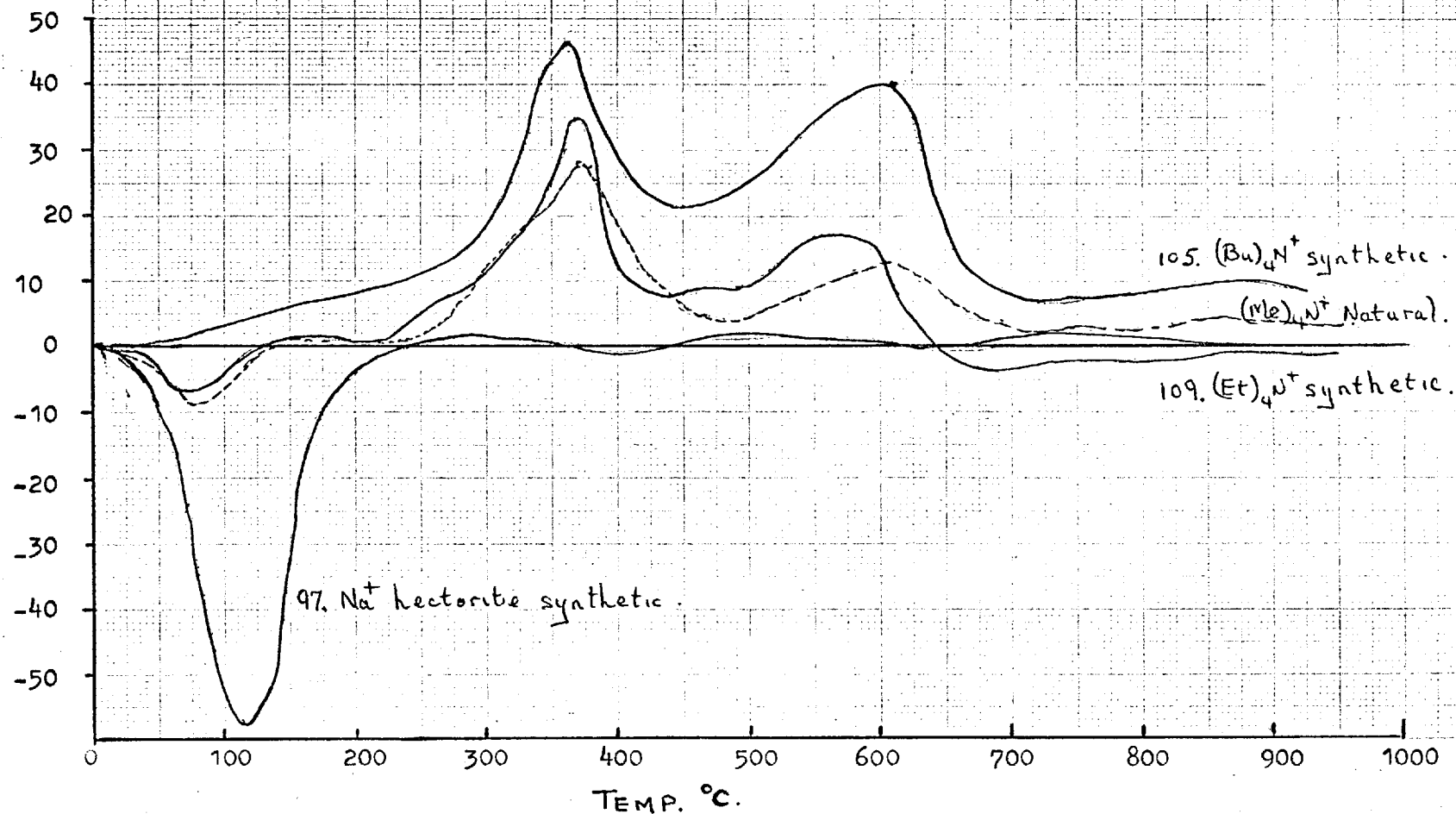
THERMOGRAVIMETRIC CURVES FOR
SOME ALKYLAMMONIUM HECTORITES

Fig. 17b.

Differential Thermal Analysis Curves for Organic
Derivatives of Synthetic and Natural Clays.

ΔT .



giving rise to an exothermic peak on the D.T.A. and a weight loss. This interpretation is supported by the diffuse nature of the basal spacing in this temperature region. The weight loss, colour change, and X-Ray results for samples in the 650-800°C range suggest that this particular weight loss can be attributed to the loss of organic matter by oxidation giving rise to a layer lattice having a repeat distance of 9.8⁰Å which is the same as that obtained for a hectorite having Na⁺ or Mg²⁺ between the layers and heated to the same temperature.

Above 650°C the X-Ray pattern indicates complete breakdown of the structure to give meso-enstatite and an amorphous phase.

Sorption Studies:

The sorption isotherms of a number of the OR and two synthetic IN- hectorites were determined by using nitrogen at 78°K. The surface areas for the various clays were calculated using the B.E.T. equation and their respective areas are shown below:

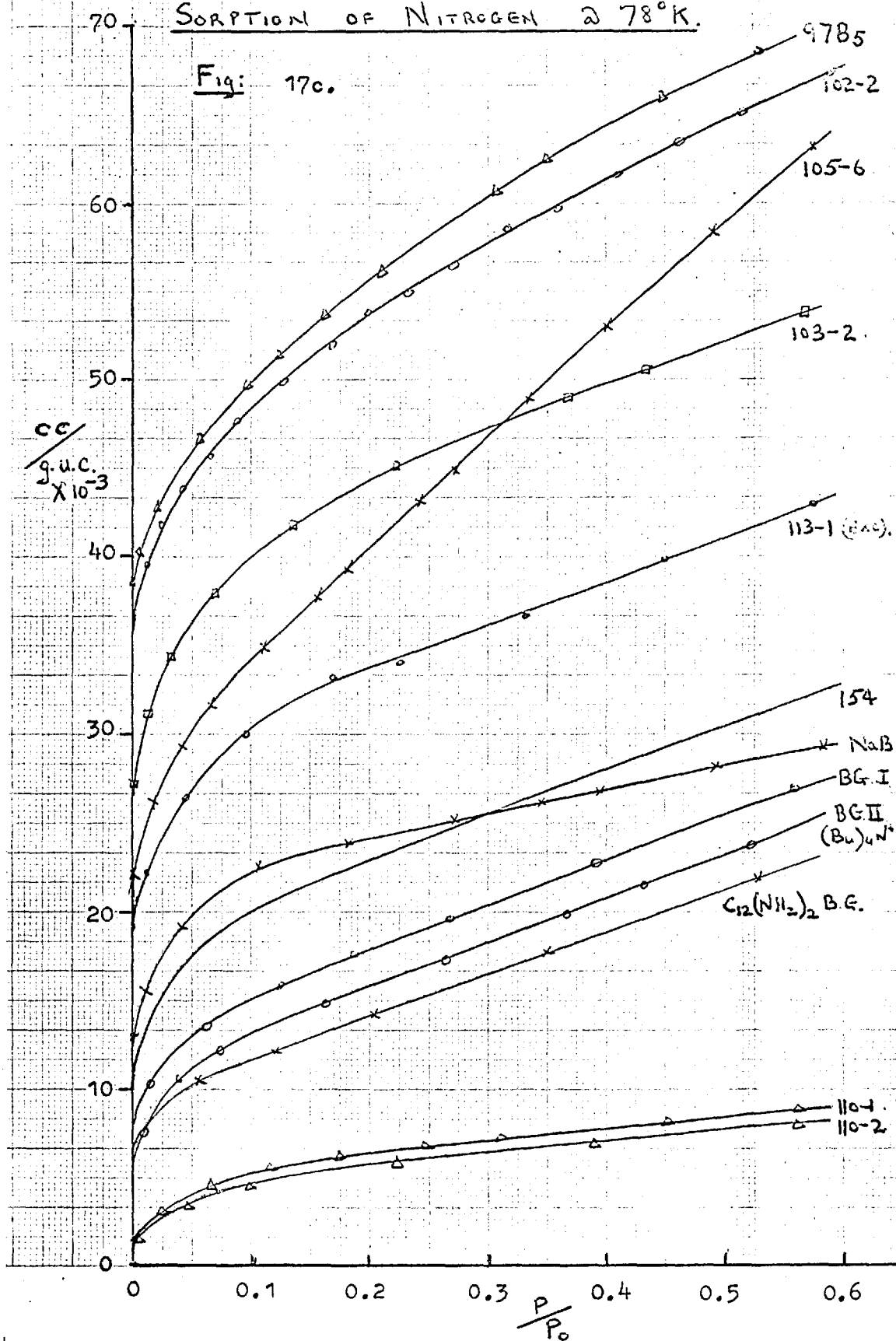
<u>Sample</u>	<u>Nitrogen</u>	<u>$m^2 \times 10^{-3}/g.u.c$</u>	<u>Cation</u>
	Area		Type
97B ₅	276		(Me) ₄ N.
102-2	271		(Et) ₄ N.
103-2	219		(Prop) ₄ N.
105-6	212		(Bu) ₄ N.
110-1	27		(Bu) ₄ N ⁺
113-1 (Exch)	166		(Et) ₄ N ⁺
154	124		Li ⁺

Samples, 154, 97B₅, 102-1, 103- , and 105 form a complete series in that clay 154, is an IN-type hectorite and the four other clays contain increasingly larger quaternary ammonium cations.

In view of the work by Reay (1957) the fall in nitrogen areas going from 97B₅ to 105-6 is to be expected as the internal area available to nitrogen between the organic ions becomes progressively less as larger cations are incorporated between the lamellae. From the calculated area available per cation and the estimated area of the tetra-butyl ammonium ion it is unlikely that in the OR hectorite with a tetra-butyl ammonium interlayer cations,

SORPTION OF NITROGEN at 78°K.

Fig: 17c.



there would be space available for nitrogen. A nitrogen area no larger than that obtained for a IN-hectorite is therefore to be expected. One explanation for the difference in surface area between the IN-hectorite and the tetrabutylammonium hectorite could be a difference in particle size from preparation to preparation.

For comparative purposes the isotherms for a natural sodium hectorite (Berk B.G.) and its tetrabutyl and tetra-propylammonium derivatives were determined in the same way as before. The surface areas for the three hectorites together with the area determined by Reay (1957) for a sodium Wyoming Bentonite are shown below.

Clay Type:		Surface area: $\frac{\text{m}^2}{\text{g.u.c.}} \times 10^{-3}$
Na^+	hectorite	128
$(\text{Prop})_4\text{N}^+$	hectorite	88
$(\text{Bu})_4\text{N}^+$	hectorite	80
$\text{C}_{12}(\text{NH}_2)_2$	hectorite (Millington (1965)).	80
Na^+	Wyoming Bentonite	28

The surface area determined for the Na^+ hectorite is greater than the areas of the corresponding hectorites with organic interlayer cations, which is unexpected considering that there is little or no penetration of nitrogen

between the layers in sodium or organo-hectorites with $(\text{Bu})_4\text{N}^+$ or $(\text{Prop})_4\text{N}^+$ ammonium ions.

Results similar to the above have been obtained by Millington who found that the $\text{C}_{12}(\text{NH}_2)_2^+$ derivative of the natural hectorite had an area of only $80 \times 10^{-3} \text{sq.m./g.u.c.}$

From these results on the natural organic ion-exchange forms, it is apparent that the organic ions are having a real effect in reducing the surface areas, as determined by nitrogen.

Samples 113-1, 110-2, 110-1 were all synthesized with germanium in place of silica. All the germanium samples were better crystallised than their silica counterparts. The organo-hectorites in this series all gave mod-strong well-defined series (001, 002, 003, 004) of basal reflections.

Sample 113-1, which was an inorganic hectorite, was treated with tetra-ethyl ammonium chloride to convert it to the $(\text{Et})_4\text{N}^+$ form. Nitrogen isotherms were determined on this exchanged form and samples 110-1 and 110-2. Samples 110-1 and 110-2 were tetra-butylammonium hectorites synthesized directly from the gels.

As the nitrogen isotherm of the 113-1 Li^+ form was not determined, no conclusions about a change of the surface area of the $(\text{Et})_4\text{N}^+$ form can be made. The areas

of 110-1 and 110-2 however are very low, and are similar to that found by Reay for a Na^+ Wyoming Bentonite. The appearance of the IN-hectorite 113-1 under the electron microscope indicated that the particle size for the germanium hectorites was larger than that of the silica-containing clays. It is likely therefore that the organo-hectorites containing germanium also have a larger particle size. The OR-Ge hectorites still have the texture of crumpled paper under the microscope.

Swelling Studies:

In view of the unusual properties shown by the OR-hectorites, some experiments to compare the swelling behaviour of these OR-hectorites with the organic derivatives of the natural hectorite and bentonite were carried out.

Samples were treated with solutions of ethylene glycol, acetonitrile and a very limited number with benzene.

Swelling in the presence of acetonitrile was carried out in two ways:

- 1) The sample was outgassed, followed by the introduction of acetonitrile into the system.
- 2) The sample contained in a capillary tube ~ 0.5 mm

diam was suspended in a test tube containing acetonitrile; the acetonitrile being drawn up by capillary action, providing the capillary was not too small. In both methods the sample was sealed off in the presence of excess acetonitrile.

Glycol treatments were carried out in a slightly different manner to that usually reported in the literature. The sample was placed in a capillary tube and with both ends of the tube open it was then placed in a beaker containing ~ 10 ml. of ethylene glycol. The beaker and contents were heated to approximately 60°C when the air in the capillary tube was expelled and the glycol able to enter and saturate the sample. The samples were again sealed carefully before X-Ray measurements were made.

The IN-hectorites and natural smectites containing inorganic ions.

The swelling behaviour in acetonitrile and glycol was the same for both the IN-hectorites and the natural material (see Table:21).

The large basal spacing obtained when samples were treated with acetonitrile has been explained by MacEwan as being due to the formation of a three layer acetonitrile complex between the lamellae. This

Table 20.

cation type	sample no.	C.E.C. meq/gram	orig. 001 Å	001 Å ^o glycol	001 Å ^o aceto- nitrile	001 Å ^o glycol	001 Å ^o aceto- nitrile	001 Å ^o benzene
(Me) ₄ N	97B ₅	0.66	14.6	15.7	19.8	1.1	5.2	15.5
(Me) ₄ N	97B ₈	0.57	14.5					
(Me) ₄ N	97B ₆	0.62	14.4	15.5		1.1		
(Et) ₄ N	102-1	0.61	14.7	16.7	16.8	2.0	2.1	15.8
(Et) ₄ N	102-2	0.45	14.7		16.8		2.1	
(Prop) ₄ N	103-1	0.59	15.3	17.4	17.6	2.1	2.3	16.2
(Prop) ₄ N	103-2	0.44	15.2	17.5	17.8	2.3	2.6	
(Bu) ₄ N	105-1	0.59	15.5					16.0
(Bu) ₄ N	105-2	0.47	15.4		18.3		2.9	
(Bu) ₄ N	105.6	0.52	15.3	16.4	17.3	1.1	2.0	
(Bu) ₄ NGe	110-1	0.43	15.1	15.4	18.4	0.3	3.3	
(Bu) ₄ NGe	110-2	0.53	15.2	15.0	18.4	3.2	3.2	
(Et) ₄ N	113-1	0.74	13.8	17.4	19.9			
L1 ⁺ (EXC).	154	0.89	9.6 outgassed	17.8	21.5	8.2	11.9	
(Me) ₄ N (EXC).	154E	0.89	13.5		20.7		7.2	

C.E.C. meq/gram. calculated from nitrogen content.

Table 21 M^+

Interlayer cation type	Sample no.	c.e.c. meq/gram	$M^+ \times$	Area available /cation $\text{\AA}^2$	Nitrogen surface area cc's $\times 10^{-3}$ /q.u.c.
$(\text{Me})_4\text{N}$	97B ₅	0.66	0.53	90.5	276
$(\text{Et})_4\text{N}$	102-2	0.45	0.36	133	271
$(\text{Bu})_4\text{N}$	105-6	0.52	0.45	106	212
$(\text{Bu})_4\text{N} \cdot (\text{Ge})$	110-1	0.43	0.53	90	27
$(\text{Et})_4\text{N}^+(\text{Ge})$ exchanged	113-1	0.74	0.80	60	166
Li	154	0.89	0.88	58	124

$\times$ M^+ calculated from the nitrogen content and assuming
the ideal formula:-

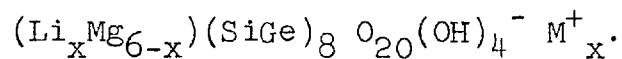


Table 22.Ion exchanged derivatives of natural clays:Wyoming Bentonite: C.E.C. 90 meq/100 gns.

Interlayer cation:	ORIG.	001 Å ^o	001 Å ^o
	001 Å ^o	Acetonitrile	Acetonitrile
(Me) ₄ N	13.6	21.1	7.5
(Et) ₄ N	13.9	19.9	6.0
(Prop) ₄ N	16.4	21.5	5.1
(Bu) ₄ N	17.2	24.8	7.6

Hectorite (Berk B.G.): C.E.C. 88 meq/100 gns.

(Me) ₄ N	13.9	20.7	6.8
(Et) ₄ N	14.1	20.5	6.4
(Prop) ₄ N	16.5	22.0	5.5
(Bu) ₄ N	17.1	23.0	6.0

interpretation would assign a thickness of $\sim 3.4\text{\AA}$ to each acetonitrile layer. Swelling with glycol gave 17-17.5 $\text{\AA}$ basal spacings which is typical of the two layer glycol complex formed with many members of the expanding clay group.

In their swelling behaviour as in their other properties reported earlier the IN-hectorites are very similar to the natural hectorites and bentonites.

The OR-hectorites and organic derivatives of natural clays:

The OR-hectorites and the analagous organic derivatives of the natural clays were treated with acetonitrile and glycol. The basal spacings recorded for these swollen samples are shown in Table:

Comparing the amounts of swelling ($\Delta s = (001\text{\AA}_{\text{swollen}} - 001\text{\AA}_{\text{orig.}})$) by the OR-hectorites and the natural clay derivatives it is evident that the synthetic material is swelling only $\frac{1}{3}$ to $\frac{1}{2}$ as much as the natural material.

The X-Ray pattern of the natural clay derivatives swollen in acetonitrile shows very strong 1st order basal reflections and med-weak 2nd and 3rd order reflections. In all cases where satisfactory X-Ray patterns were

obtained the basal reflections were found to form an integral series. The X-Ray patterns of the OR-hectorites swollen with acetonitrile were less sharp than those of the natural material and never showed higher orders of the basal reflection. The sample 113-1 $(\text{Et})_4\text{N}(\text{exch})$ (Table: 20) which was a synthetic IN-hectorite ion-exchanged with $(\text{Et})_4\text{N}^+$ ions, swelled $6.1\text{\AA}$ with acetonitrile, a value similar to the extent of the swelling shown by the ion-exchanged forms of the natural material. The non-exchangeable nature of the $(\text{Et})_4\text{N}^+$ ion (see Section on Ion-Exchange) apparently does not affect the degree of swelling of this particular hectorite.

Swelling with glycol was interesting in view of work by Greene-Kelly, Kinter et al (1961), who found that organic derivatives such as triethylammonium bentonites and tetramethylammonium bentonite did not form interlamellar complexes with glycol.

Samples 103-1 and 103-2 gave X-Ray patterns which showed higher orders of the basal spacing. These spacings formed an integral series, which indicates that the glycol complexes are regular throughout the structure. Randomly interstratified complexes would give X-Ray patterns showing non-integral higher order basal reflections. The thickness of a glycol layer in interlamellar

complexes has been shown to be $\sim 3.7\text{\AA}$. The Δs -values for swelling with glycol were with one exception less than this value. If however the Δs value is determined by subtracting the thickness of the lamellae ($9.5\text{\AA}$) from the swollen dimension the value found is very close to that found for hectorites with inorganic interlayer cations.

From 'available space' considerations it seems unlikely that there would be much room for glycol between the organic ions on the clay surface. The basal spacing recorded for the glycol-treated OR-hectorites is $17.4\text{\AA}$ or less, whereas for a OR-hectorite to form a single layer complex with glycol layer lying on top of the organic cations would require a basal spacing of $19\text{\AA}$. If, as the X-Ray results on samples 103 suggest, the complexes are regular, the orientation of the glycol molecule and the interlayer ion must be different from that found in other systems.

Conclusion.

The properties of those IN-hectorites synthesized from inorganic gels in the absence of any organic bases are similar to the properties of a natural hectorite (Hector, California), used for comparative purposes. None of the synthetic IN-Hectorites showed any indication of being mixed-layer type minerals. On the other hand the studies on the OR-hectorites have shown that whilst their X-ray patterns are similar to those of the organic derivatives of natural hectorites (so that in the structural sequence (2:1 layer; organic interlayer cation; 2:1 layer) they are basically the same) such properties as ion-exchange and swelling are dissimilar.

Many of the X-ray photographs of unswollen samples showed a regular but limited sequence of basal reflections (001, 002, 003). The regularity in the basal reflections suggests that all layers have the same dimensions in the 'd₀₀₁' direction and this in turn indicates that all layers probably have organic cations between them.

The layer charges of the OR-hectorites (see table 20) calculated from the carbon and nitrogen analyses are low by comparison with natural specimens of hectorite, but if the

organic cations were by virtue of their large size exerting some structural influence on the clay which is formed, a low value of the layer charge would be reasonable. Ready exchange of the interlayer cations of these OR-hectorites would however have been expected.

The lack of higher orders of the basal spacing in most swollen samples makes it difficult to say whether the swelling is regular or irregular. However the lack of similarity in swelling behaviour between the organic hectorites prepared from natural and from synthetic crystals coupled with the difficulty in relating the dimensions of the swollen layers to the thickness of monolayers of the liquids used, does suggest that some layers might be swelling more than others. This gives a first order basal reflection which is some kind of mean of the repeat distances in the swollen samples. Differences in the swelling as between different layers could arise if these layers have different charges. In view of the limited information obtainable from powder photographs showing only one basal reflection no attempt has been made to interpret the results further.

Finally it may be stated that whilst the synthetic IN-hectorites are similar to the natural material, the OR-hectorites although having the same basic structure have interlayer cations associated with the 2:1 lamellae in a manner which is not yet completely revealed.

6.3 MICA SYNTHESSES

6.3.1 Ammonium Micas

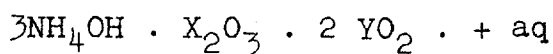
General

In view of the similarity in size between potassium and ammonium ions it seems likely that the dearth of ammonium containing minerals in nature can be ascribed, in many cases to the fact that during the process of mineral formation a source of ammonium cations was absent. The presence of the ammonium ion in the zeolite erionite, and the recent discovery of an ammonium feldspar (Erd, (1964) show that providing there is a source of ammonium cation structures containing these cations can be formed in nature.

The direct hydrothermal synthesis of an ammonium mica and two framework structures from ammonium aluminosilicate gels by Denny (1959) showed that ammonium aluminosilicates could be readily synthesized in the laboratory. Because of the lack of naturally occurring micas and the general interest of these laboratories in nitrogen containing minerals, a study was initiated to prepare and characterize the ammonium micas and to investigate the effect of introducing gallium and germanium into the structure in place of aluminium and silica.

Ammonium Mica Synthesis.

Syntheses using gels of the following composition were studied in the temperature range 210-450°C.



where X = Al, Ga,

Y = Ge, Si,

The predominant crystalline phase was the clay mineral mica.

The gels containing aluminium and silica were investigated in detail by Denny (1959) so only a few representative syntheses were carried out in this work. The pH,s of the cold mother liquor were greater than 10.5 in all cases, except where ammonium chloride or ammonium flouride was added to observe the effect of a lower pH. The products, synthesis times, and an estimate of the crystallinity of the phases prepared are given in table.23

Ammonium Aluminosilicate gels.

Crystallisations using these gels were carried out at 250-450°C. In all cases the predominant phase was a mica. The best conditions for synthesis were at 450°C and 2-5 days.

When base:alumina ratios of 1:1 were tried it

was found that, whereas the high temperature (450°C) still gave good micas the products of low temperature (250°C) syntheses were mainly boehmite and a poorly crystalline mica. Addition of ammonium fluoride in place of ammonium hydroxide did not result in any new species being formed even though the final pH of the cold mother liquor was 6-7.

Ammonium Gallosilicate gels.

In the temperature range 250 - 450°C these gels gave very good micas. At 250°C and 5 days the micas showed superior crystallinity to those obtained from the aluminosilicate ~~gels~~^{micas} under similar conditions. The X-ray pattern, when compared with that of the aluminosilica micas showed many differences in the intensities of the diffraction lines. Electron micrographs taken of these samples showed well formed hexagonal crystals with correspondingly clear diffraction patterns.

Ammonium Gallogermanate gels.

These gels have been investigated in the temperature range 300 - 450°C . The product obtained after five days at 350°C or 450°C was a well crystallised mica.

At lower temperatures the poorer crystallinity of the micas was indicated by a broadening of the lines on the X-ray pattern.

TABLE 23.

Gel composition:		$3\text{NH}_4\text{OH}.$ $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$3\text{NH}_4\text{F}$ $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$3\text{NH}_4\text{OH}.$ $\text{Ga}_2\text{O}_3 \cdot 2\text{SiO}_2$
Temp.	Time (days)			
250°C	5	mod-good M.		good M.
	10	good M.		V-good M.
	20	good M.		V-good M.
300°C	2	mod M.		
	5	mod M.		good M.
	11	good M.		
350°C	2	good M.		mod M.
	5	good M.	good M.	V-good M.
	10			V-good M.
450°C	2	good M.		mod M.
	5	good M.	good M.	good M.
		$3\text{NH}_4\text{OH},$ $\text{Ga}_2\text{O}_3 \cdot 2\text{GeO}_2$	$3\text{NH}_4\text{OH},$ $\text{Al}_2\text{O}_3 \cdot 2\text{GeO}_2$	$3\text{NH}_4\text{OH}, + (\text{Na}_2\text{O})$ $\text{Al}_2\text{O}_3 \cdot 2\text{GeO}_2.$
300°C	2	poor M.	V-good A.	mod M.
	5	poor-mod M.	V-good A.	
	11	mod M.		
350°C	2	mod M.	V-good A.	good M.
	5	good M.		V-good M.
450°C	2	mod M.	good A. good B.	good M.
	5	V-good M.	good B. mod A.	V-good M.
	10	V-good M.	V-good B.	
		$\text{Al}_2\text{O}_3, 2\text{GeO}_2,$ no base.		
450°C	2	mod B.		
	5	V-good B.		

M = Mica phase.

A = HEXAGONAL PHASE.

B = 'ANDALUSITE' PHASE.

At 450°C the mica crystallinity as shown by sharp X-ray diffraction lines and appearance under the electron microscope, was again superior to that of the aluminosilica micas.

Ammonium Aluminogermanate gels.

Crystallisations involving these gels were effected in the temperature range 300-450°C. In contrast to the three other systems investigated it was not possible to synthesize a mica containing ammonium, aluminium and germanium, although small additions of sodium to the gel resulted in a well crystallised mica with a 'c' parameter close to that of a sodium mica.

Comparison of the results using ammonium aluminium-germanium gels with the other systems shown in table 23 shows that in place of the expected mica in the temperature range 250-450°C two non-micaceous phases were formed. In the temperature range 250-450°C, phase A. was prepared whereas phase B. could only be prepared at synthesis temperatures of 440°C. In one run where ammonium hydroxide was omitted from the gel, phase B. was produced in good yield thus indicating that phase B. was essentially an aluminium-germanium compound.

Characterization of the Phases obtained from Ammonium-aluminium Germanate gels.

Phase A.

Under the microscope this phase appeared as thin large clear hexagonal plates averaging 0.04mm. in size. The relatively large size of the crystals allowed both single crystal and powder photographs to be obtained.

The single crystal investigation yielded the following data:

TRIGONAL

Space group: $P\bar{3}12$.

Observed density: 3.18 gm./cc.

By use of the hexagonal Bunn chart the powder pattern was subsequently indexed and the following accurate cell dimensions calculated by means of a least squares program (Rogers/Diamand 1980).

$$a = 4.832 \overset{\circ}{\text{\AA}} \quad c = 9.421 \overset{\circ}{\text{\AA}}$$

Analysis of this phase for aluminium and nitrogen gave the following results on pure material from two separate syntheses,

$$1) \quad \text{Al}_2\text{O}_3 = 32.46\% \quad \text{Nitrogen} = 1.06\%$$

$$2) \quad \text{Al}_2\text{O}_3 = 32.38\% \quad \text{Nitrogen} = 1.28\%$$

These aluminium analyses indicate a compound with an aluminium:germanium ratio of 1:1. A thermobalance run on this compound showed that there was a 3.4-3.7% weight loss at 560°C with no further loss even after heating to 1000°C.

An X-ray pattern taken of a sample heated to 600°C showed that no structural change accompanied this weight loss. Further X-ray patterns of this compound taken after heating to 850°C still showed no change, but on heating to 1000°C for 4 hours or 1150°C for half hour the X-ray pattern showed that transformation of the compound to the germanium analogue of mullite was almost complete.

Infra-red spectra were determined on samples heated to 300°, 600° and 800°C. The most striking change is that associated with the NH_4^+ , γ_3 band at $\sim 7\mu$ which disappears after heating to 600 but not 300°C.

With a total weight loss of 3.5% and an ammonium content of = 1.1% the results show that the structure contains approximately 2.4% of (non-ammonium) material volatile at 560°C. This weight loss can probably be associated with hydroxyl groups in the structure.

As part of a separate study, the detailed crystal structure determination of this hexagonal phase is at present under way.

Phase B.

This compound occurred as well formed prismatic crystals showing parallel extinction under crossed nicols.

The X-ray pattern was very similar to that of andalusite and was therefore indexed on an orthorhombic cell to calculate the cell parameters. The cell parameters chosen accounted for all the observed reflections and the accurate cell dimensions calculated by the least squares program were as follows

$$a = 7.693\text{\AA} \quad b = 8.287\text{\AA} \quad c = 5.718\text{\AA} \quad \text{all } \pm .004.$$

Allowing for the larger size of the germanium ion the cell dimensions are very similar to those of natural andalusite A.S.T.M. card No. 13-122 with which it is compared below.

On heating to 1150°C phase B. showed no loss in weight but transformed to the germanium analogue of mullite at 1050°C .

Natural ANDALUSITE:	$a = 7.79$	$b = 7.87$	$c = 5.58$	A.S.T.M. No. 13-122.
Al-Ge 'ANDALUSITE':	$a = 7.69$	$b = 8.28$	$c = 5.72$	this work.

Characterization of the Ammonium Micas.

The crystallinity of the gallium and germanium

micas as estimated from the sharpness of the diffraction lines and appearance under the electron microscope ~~was~~ superior to that of the alumino-silicate micas. The diffraction patterns were indexed by comparison with ~~the~~ published data (Brown (1961)) and the unit cells computed by means of a least squares program.

The unit cells of the three micas are shown below:-

	<u>NH₄, Al, Si,</u>	<u>NH₄, Ga, Si,</u>	<u>NH₄, Ga, Ge,</u>
a =	5.18 Å	5.22 Å	5.42 Å
b =	8.969 Å	9.18 Å	9.33 Å
c =	10.49 Å	10.67 Å	10.96 Å
β =	101.4°	101.3°	101.4°

Nitrogen analyses carried out on the three micas gave ammonium contents of: 4.6%, 3.4%, and 2.7%, respectively.

Further confirmation of the presence of the ammonium ion in the structure was shown by the occurrence of the NH₄⁺, γ₃ band at ~7.0 μ on the infra-red spectrum.

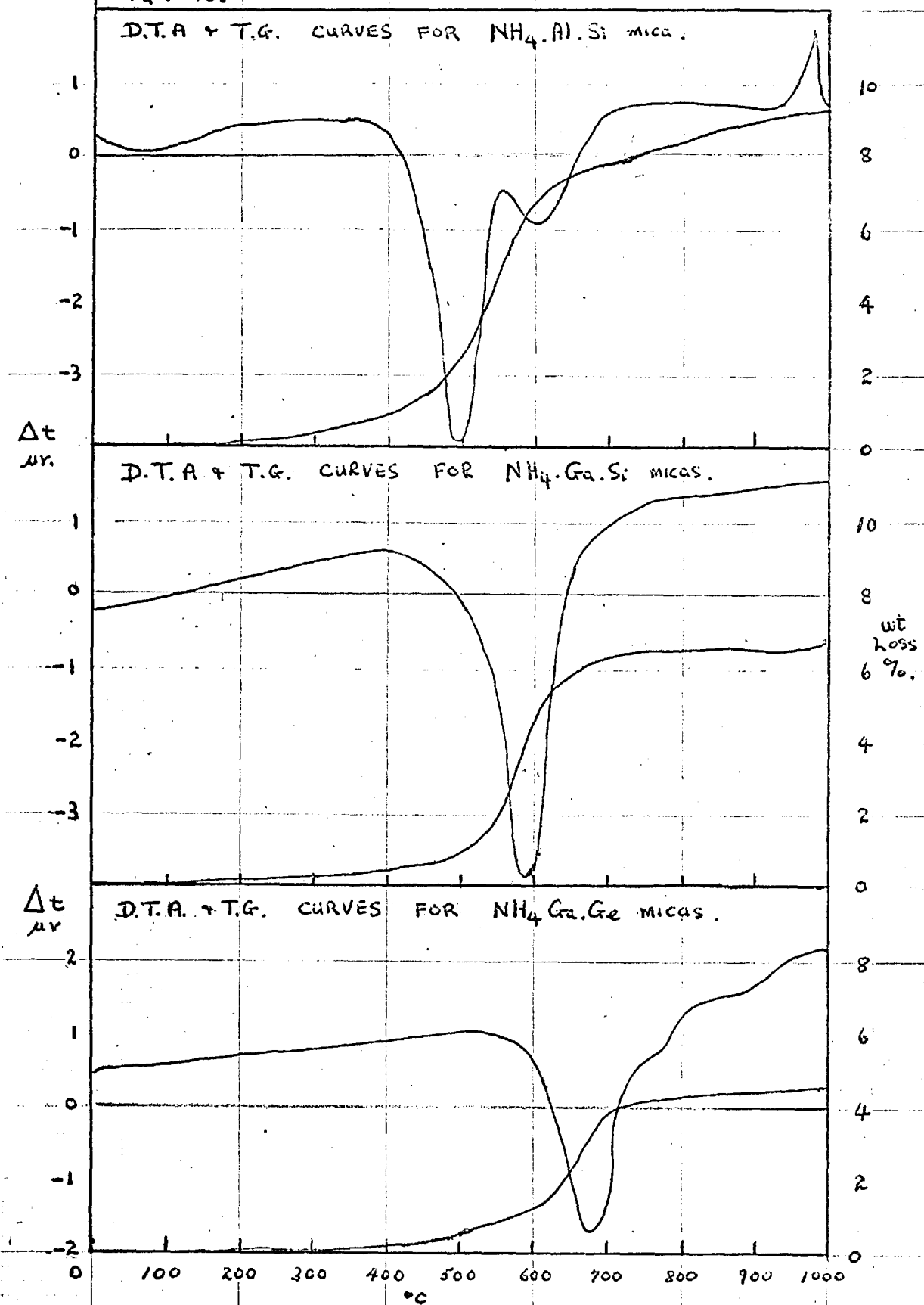
When heated to 550°C for half an hour all micas showed a decrease in the 'c' parameter in accordance with the breakdown of the ammonium ion and loss of ammonia from between the layers in the mica structure. The broad nature

of the basal reflection made it difficult to obtain accurate measurements of the 'collapsed' repeat distance but all were in the range 9.5-9.8 Å. The Infra-red spectrum of a mica heated to 500°C no longer showed the peak at 7.0 μ , although the spectrum of the mica structure itself remained unchanged.

D.T.A. and thermogravimetric studies were carried out on all the micas synthesized and the curves obtained from a plot of ΔT or weight loss versus time are shown in figure 18. The good correspondence of peaks between D.T.A. and thermobalance curves indicated that the endothermic peak observed in the 500°-600°C region was associated with a weight loss. This weight loss can be attributed to the dehydroxylation of the mica structure and ammonia loss on the breakdown of the ammonium interlayer ions. The weight losses, which occur almost completely in a single step over the region of ammonia loss and dehydroxylation, show a decrease as the mica composition was varied in the order Al-Si $\rightarrow$ Ga-Si $\rightarrow$ Ga-Ge.

This decrease in the weight loss, accompanied by a tendency for the micas to have better crystallinity as one goes from Al-Si, to Ga-Si to Ga-Ge, suggests that there is a gradual change from an illitic type mica in the case of the alumino-silica composition to a more well ordered mica in the case of gallo-silica and gallo-germanium preparations.

Fig: 18.



D.T.A.'s of specimens prepared using ammonium fluoride in place of ammonium hydroxide gave a typical mica curve, with no evidence to suggest that the hydroxyl groups in the octahedral layers had been replaced by a significant amount of fluoride ions.

Electron Micrographs.

Electron micrographs or projection microscope photos typical of all the phases prepared are shown in plates 1 - 6.



Plate : 1 x11,000
Ammonium alumino -
silica Mica.



Plate : 2 x12,000
Ammonium gallo -
germanate Mica.



Plate : 3 x 8000
Sodium aluminogermanate Mica.



Plate : 4 x 12000
Ammonium silico mica.



Plate : 5 x
Aluminogermanate
'Andalusite - Like'
phase.

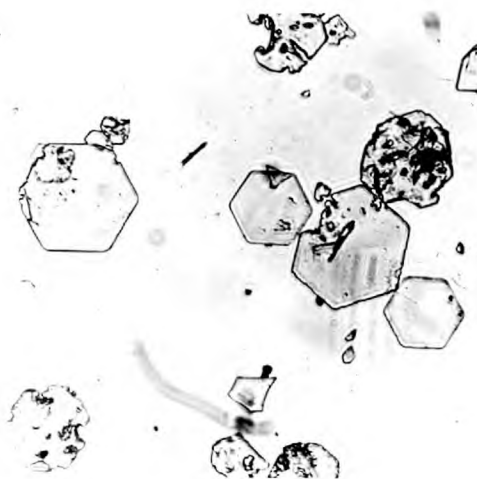
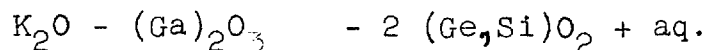
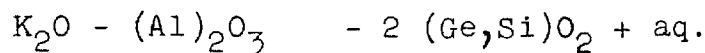
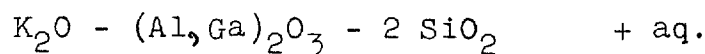


Plate : 6 x 500
Ammonium aluminogermanate.
'Hexagonal phase!'

6.3.2 Potassium MicasGeneral

It was originally intended to investigate the effects of isomorphous substitution of gallium and germanium in the $\text{NH}_4 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system but as the ammonium-alumino-germanate mica end member could not be synthesized the $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system was chosen for this study. A range of gels with the mica composition in the following four systems were prepared and synthesized in the manner described earlier.



In all four systems three gels of intermediate composition in addition to the gels of the particular end-members were prepared and treated hydrothermally in the usual way. The initial syntheses were carried out at 250, 350 and 450°C but in view of the poor crystallinity of the micas at 250°C the runs at 250°C were terminated. The micas prepared after 3 days had a fair to moderate crystallinity at both temperatures but with longer heating times the micas at 450°C had a crystallinity superior to those at 350°C.

With the exception of one composition in the $K_2O - (Al, Ga)_2O_3 - SiO_2$ system, the initial gels gave micas as single phases. The micas synthesized at $450^\circ C$ with their better crystallinity were used for measurement of the 'd' spacings and unit cell calculations as well as analyses for gallium and germanium utilising X-ray fluorescence methods. The measurement and unit cell calculations were carried out as follows: In a particular system one end-member mica and the three micas of intermediate composition were X-rayed simultaneously side by side on a Nonius Guinier Camera. Quartz powder was mixed with one of the four specimens and used as an internal standard for the calibration of all four samples.

After measurement of the 'd' spacings by means of a vernier measuring rule, a number of lines (approximately 8-10) were indexed by comparison with published data (Brown (1961) and Yoder (1955)) and the unit cells calculated by means of the least squares method described earlier. The unit cell calculated by this means was used in another program to index a further 4-5 lines. These newly indexed lines were then inserted together with the original 8-10 lines into the least-squares program and a new unit cell calculated. Scrutiny of the output where differences, θ , in degrees were given allowed an assessment of the indexing

procedure to be made. Where this difference was large ($\theta > 0.25^\circ$) the indexing of the lines was considered suspect and a lower weighting factor assigned to it. By the use of the two programs a good fit over a minimum of 12-15 lines could usually be obtained.

Since the 'b' parameter is related to the 'a' by the relationship $a = \frac{b}{\sqrt{3}}$ and the 'b' parameter can be accurately obtained from the 060 reflection, which can be unambiguously indexed, in most cases, it was only necessary to observe the position of this reflection to note the change in cell size with composition. Where the micas were X-rayed side by side the 060 reflections could be visually compared from one mica to the next.

The $K_2O - Al_2O_3 - 2(Ge, Si)O_2$ micas.

Well crystallized micas of the 1M type were obtained as single phases over the entire range of compositions studied. The potassium alumino-germanate micas had the best crystallinity and crystals up to .01 mm were obtained.

The unit cell parameters of the five micas are shown in table 24 and the plot of the 'b' dimensions against composition shown in figure 19. The 'b' dimension shows

TABLE 24.

$K Al_3(Ge_xSi_{1-x})_3O_{10}(OH)_2$. micas.

X =		C E L L D I M E N S I O N S				vol.
		a	b	c	B	
0.00	1M	5.214	8.994	10.278	101.69	472
0.25	1M	5.246	9.057	10.434	101.6	485
0.50	1M	5.294	9.088	10.507	101.5	495
0.75	1M	5.287	9.108	10.580	101.6	499
1.00	1M	5.313	9.139	10.673	101.4	508

$K Ga_3(Ge_xSi_{1-x})_3O_{10}(OH)_2$. micas.

X =		a	b	c	B	vol.
0.00	1M	5.308	9.150	10.358	101.8	492
0.25	1M	5.301	9.175	10.372	101.6	494
0.50	2M	5.327	9.241	20.621	95.6	1010
0.70	2M	5.330	9.263	20.748	97.7	1019
1.00	2M	5.377	9.313	20.677	93.2	1033

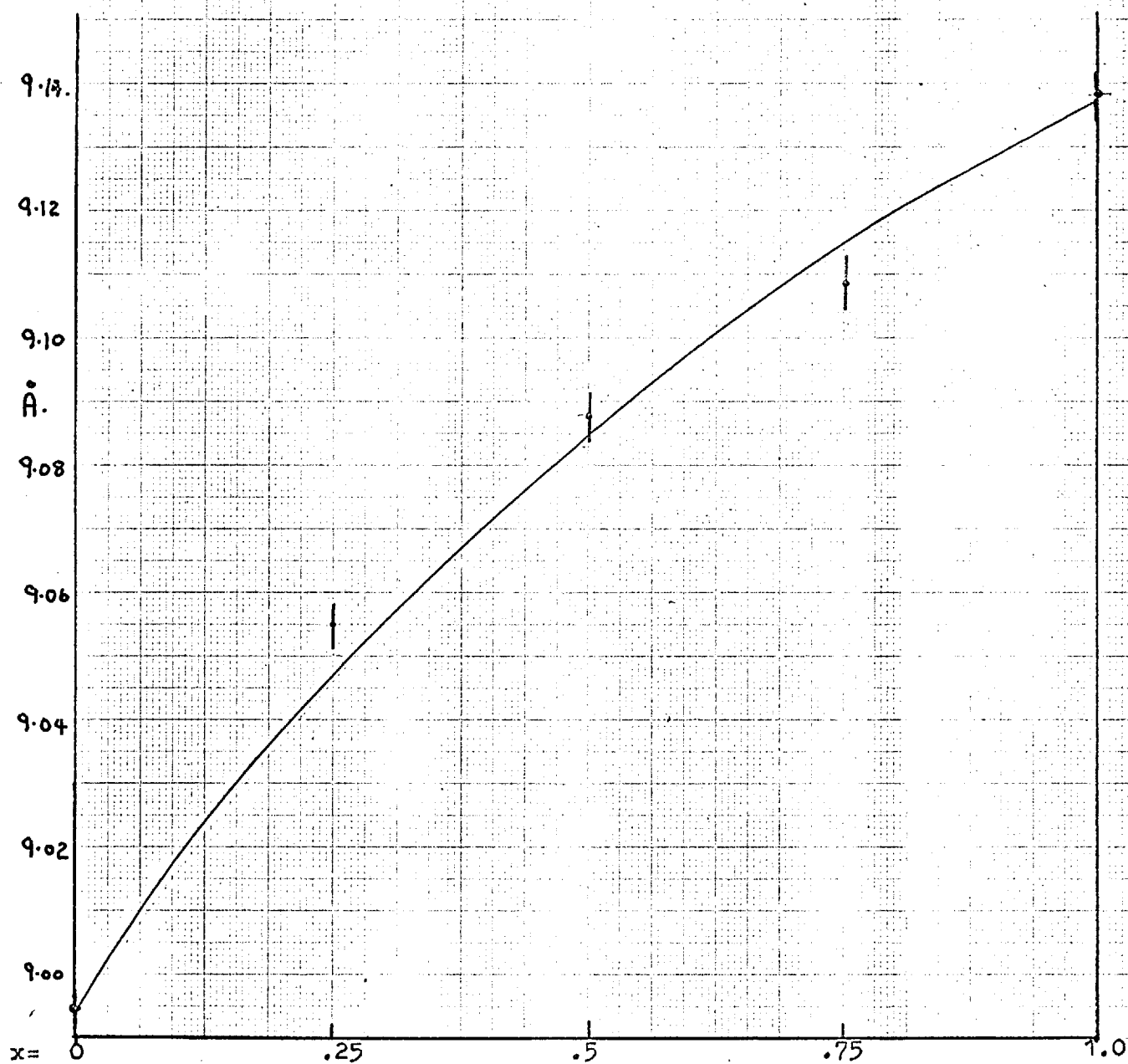
$K (Ga_xAl_{1-x})_3Si_3O_{10}(OH)_2$. micas.

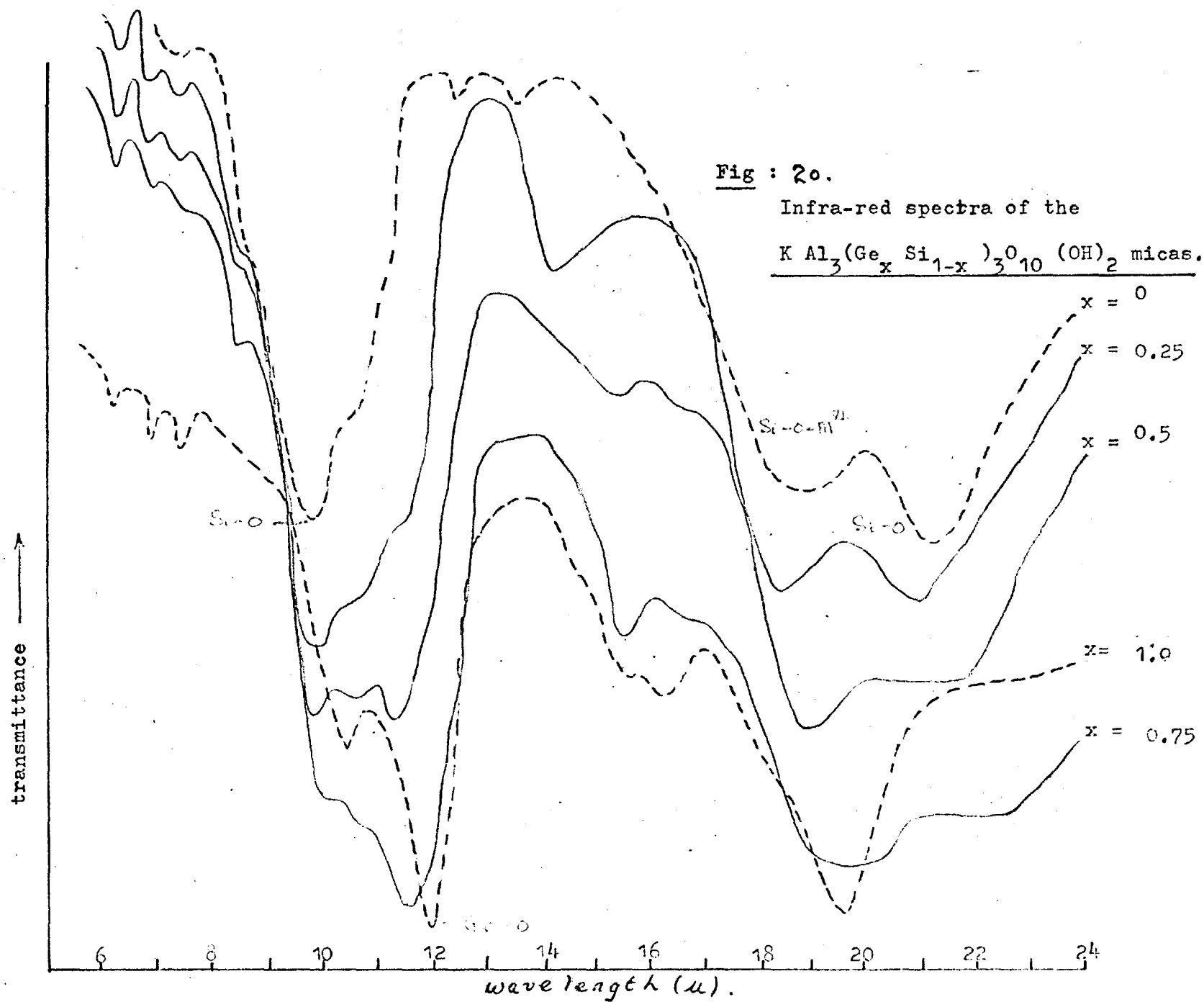
X =		a	b	c	B	vol.
0.00	1M	5.214	8.994	10.278	101.6	472
0.25	1M	5.274	9.069	10.281	101.7	481
0.50	1M	5.262	9.082	10.269	101.6	480
0.75	1M	5.297	9.143	10.293	101.5	488
1.00	1M	5.308	9.150	10.358	101.8	492

$K (Ga_xAl_{1-x})_3Ge_3O_{10}(OH)_2$. micas.

X =		a	b	c	B	vol.
0.00	1M	5.313	9.139	10.673	101.4	508
0.25	1M	5.337	9.197	10.699	101.6	512
0.56	1M	5.354	9.252	10.677	101.4	518
0.56	2M	5.348	9.254	21.023	95.5	1034
0.75	2M	5.345	9.269	20.895	95.6	1030
1.00	2M	5.377	9.313	20.677	93.3	1033

Fig: 19. $\text{K Al}_3(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{10}(\text{OH})_2$ micas.





a regular increase as the composition is varied from the potassium alumino silicate end-member to the potassium alumino germanate end-member.

The Infra-red spectra for all micas were determined and are shown in figure 20. The change in spectrum with changing germanium and silica content is particularly noticeable from the variation in intensity of the Si-O and Ge-O stretching frequencies in the $800-1100\text{ cm}^{-1}$ region.

The $K_2O - Ga_2O_3 - 2(Ge, Si) O_2$ micas.

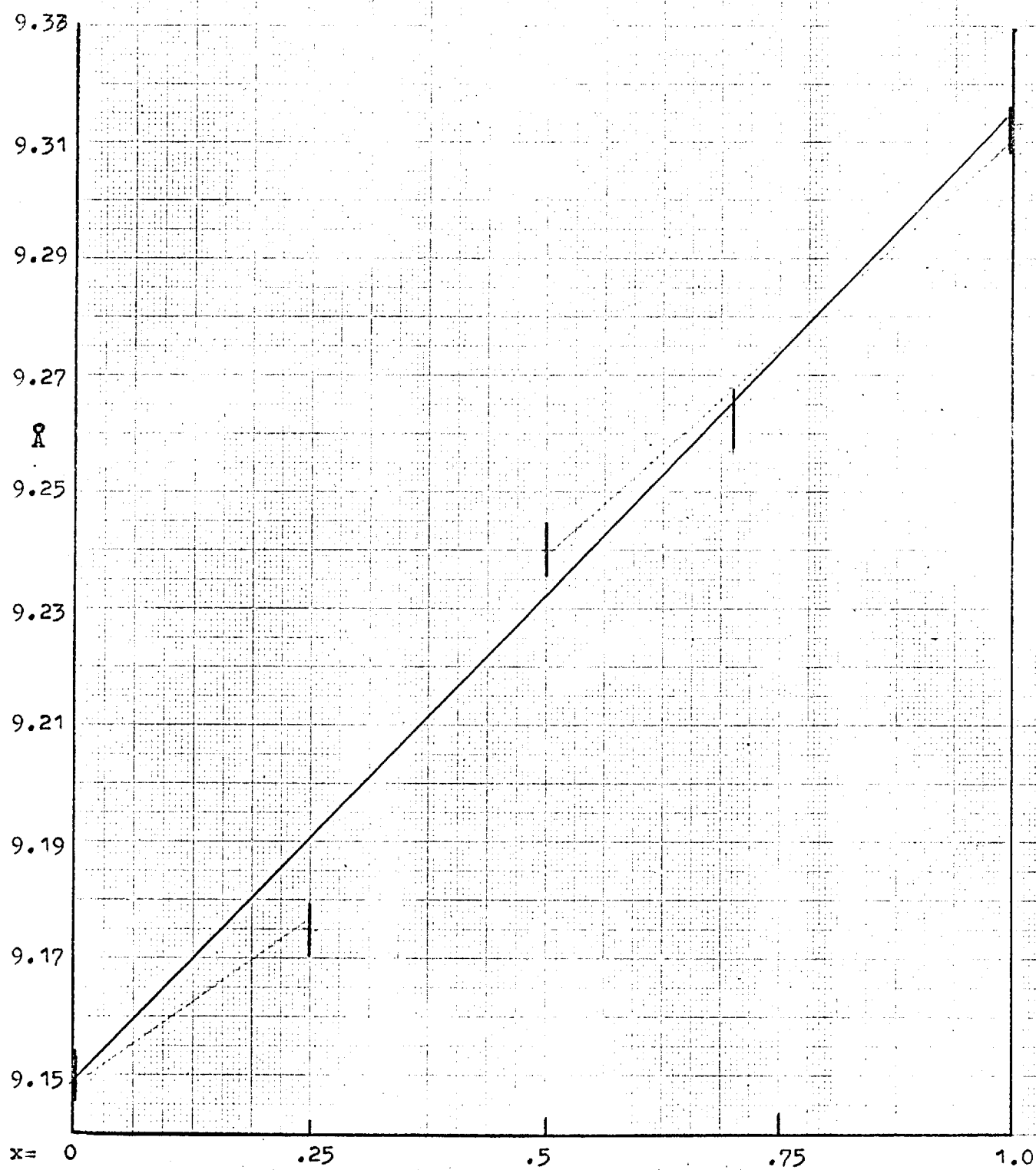
Well crystallised micas were obtained over the entire range of compositions studied. The most noticeable feature in this series of micas was the change in mica polytype with change in composition.

The potassium gallo-silicate end-member and mica with Ge:Si ratio of .33 had the 1M type structure whereas the remaining three micas of the series had the 2M type structure. The X-ray pattern of the mica from composition with Ge:Si ratio of 1 did show a small amount of the 1M polymorph to be present, (faint $11\bar{2}$ and 112 reflections).

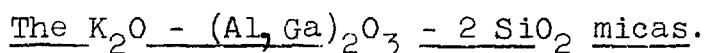
As all these micas were synthesized under the same conditions of temperature and pressure it would thus appear that composition is a controlling factor in the type of polymorph that is formed. The unit cells calculated for all the micas in this series are shown in table 24 and the plot of the 'b' dimension against composition is shown in figure 21.

The plot of the 'b' dimension versus composition shows a fairly regular increase in magnitude with increasing amounts of germanium entering the structure. Only those micas of the same polymorphic variety should be compared directly and this means that the first two points on the

Fig. 21. $\text{K Ga}_3(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{10}(\text{OH})_2$ micas.



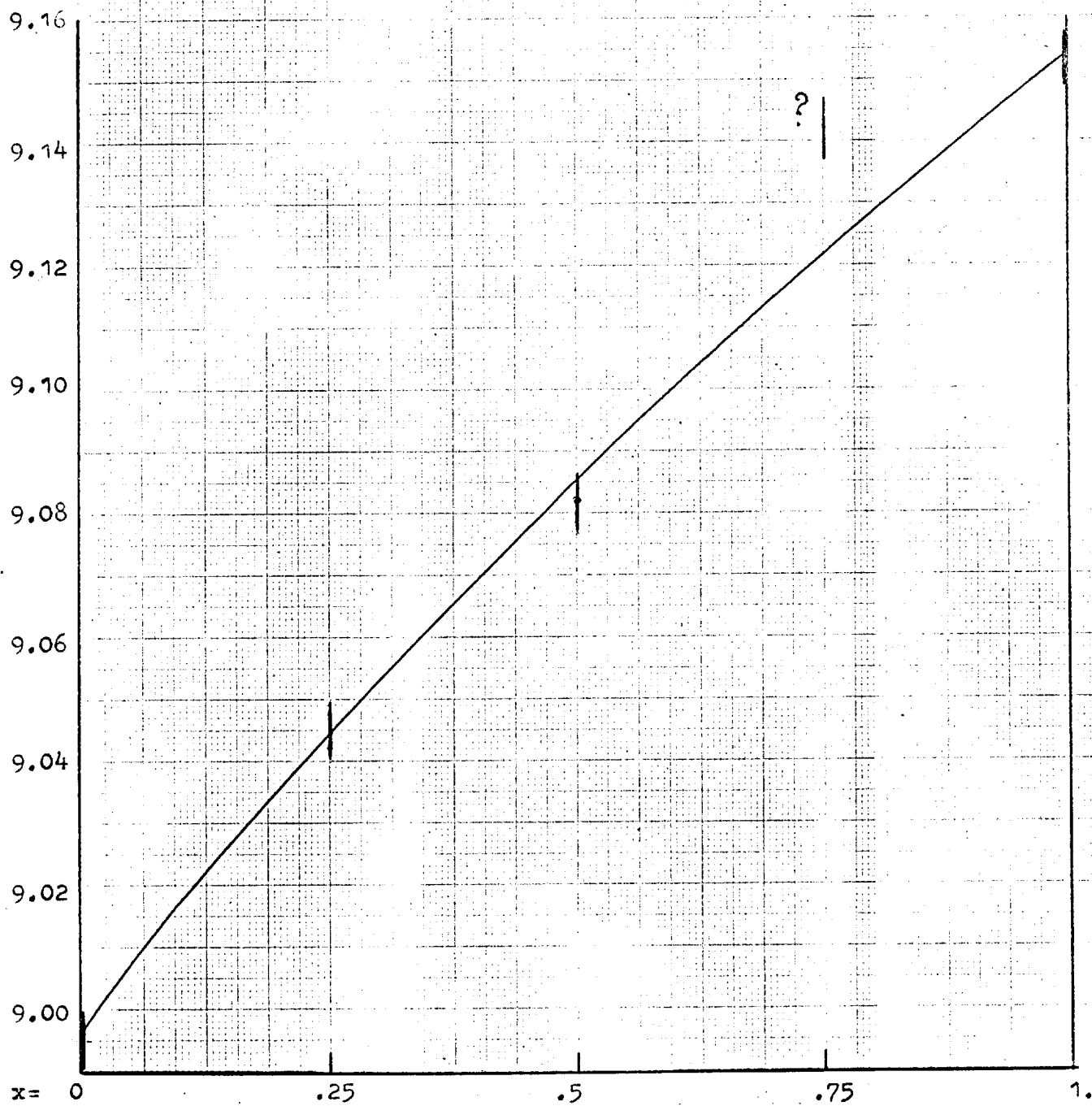
plot (end member and mica with Ge:Si ratio 0.33) should be considered as one group and the other three points as part of a second group having the 2M type structure. If this distinction is made the 'b' cell parameter can be considered to show a fairly regular increase with increasing amounts of germanium in the structure.



Good crystalline micas were obtained from all compositions studied. At 450°C the micas often occurred in the presence of a second phase, $\beta\text{-Ga}_2\text{O}_3$. This $\beta\text{-Ga}_2\text{O}_3$ phase was absent, except for mica composition (Ga:Al, 75:25) in micas synthesized at 350°C for times of five days.

For 'd' spacing measurement and unit cell calculation only micas that were prepared as single phases were normally used. An exception to this was made in the case of the mica of initial composition (Ga:Al = 75:25) where both the 450 and 350°C preparations contained 2-10% of $\beta\text{-Ga}_2\text{O}_3$. The unit cell dimensions of the micas in this system are shown in table 24 and the plot of the 'b' cell parameter against composition in figure 22. All micas synthesized in this system had the 1M type structure and therefore the cell parameter variation with composition may

Fig. 22. $\text{K}(\text{Ga}_x\text{Al}_{1-x})_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ micas



be directly compared over the entire range of compositions. If we ignore the 'b' parameter of the mica occurring in the presence of β Ga_2O_3 (initial Ga:Al ratio = 75:25) because of the uncertainty of the composition of the mica phase, the 'b' parameters of the remaining four micas show a fairly regular increase in size with increasing gallium content.

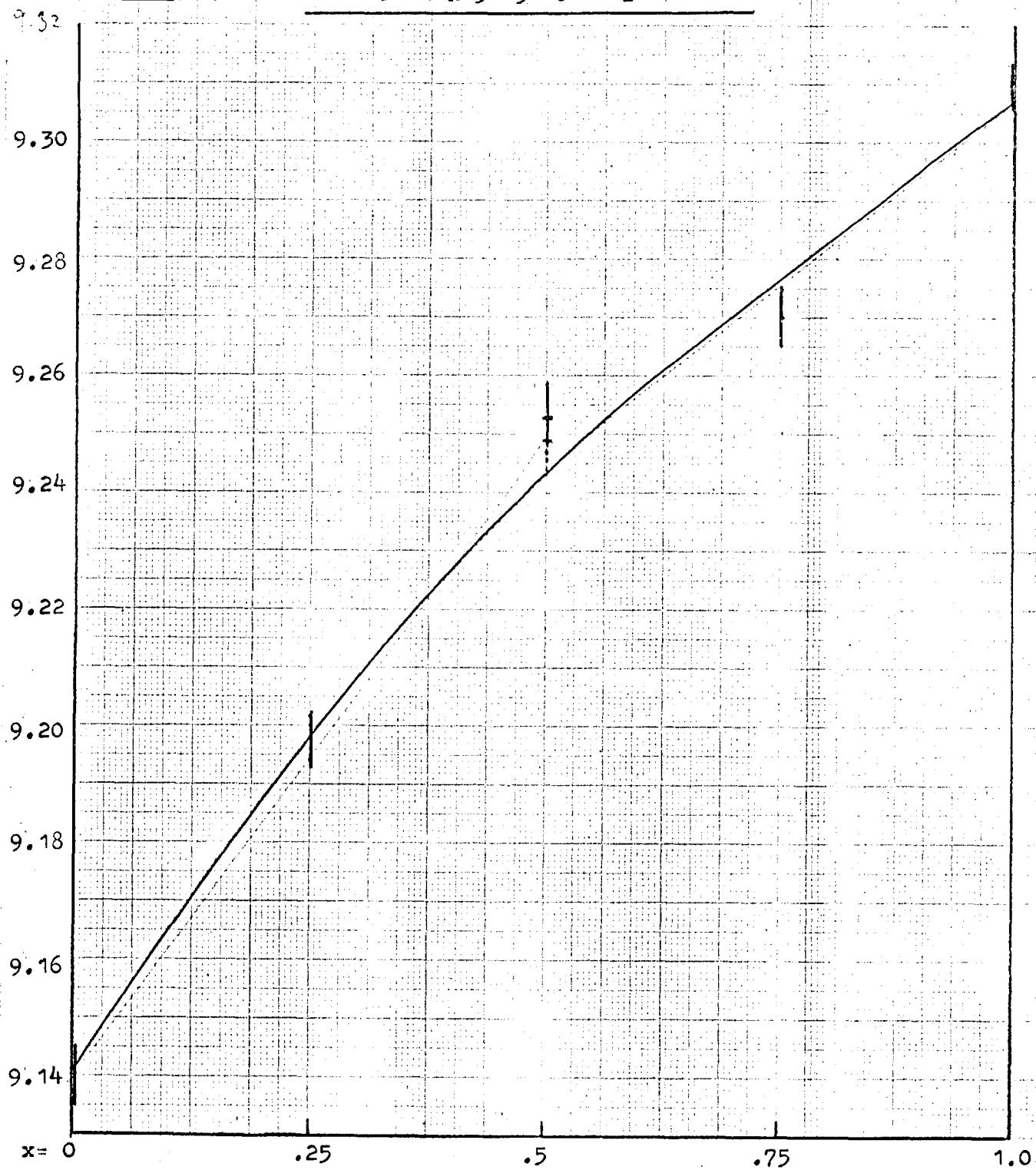
The mica represented by initial composition (Ga:Al, 75:25) has an X-ray pattern which shows 5-10% of β - Ga_2O_3 to be present. The presence of this β - Ga_2O_3 suggests that the mica phase has a final composition much less rich in Gallium than that of the initial oxide mix; however it seems unlikely that a mica of such low gallium content would have a 'b' dimension such as that calculated and shown in figure 23.

Further work is required with oxide mixtures of composition $\text{K}_2\text{O}(\text{Al}_{0.25}\text{Ga}_{0.75})_2\text{O}_3 - 2\text{SiO}_2$ to see whether the formation of this second phase is a result of immiscibility in the system or due to other factors such as gel preparation, or the high water:solids ratio used.

The $\text{K}_2\text{O} - (\text{Al},\text{Ga})_2\text{O}_3 - 2\text{GeO}_2$ micas.

Well crystallized micas were again obtained as pure phases over the entire range of compositions. When

Fig: 23.

 $K (Ga_x Al_{1-x})_3 Ge_3 O_{10} (OH)_2$ micas.

the Ga:Al ratio of the synthetic micas was approximately equal to or greater than one a 2M type mica was formed instead of the 1M structure found with lower gallium contents. This change in polymorphic type may be compared with that found in the $\text{Ga}_2\text{O}_3 - (\text{GeSi})\text{O}_2$ system where micas with Ge:Si ratios > 1 were of a different polytype (2M) to those containing less germanium (1M).

The X-ray pattern of the mica with Ga:Al ratio of 1.27 showed that both polymorphs were present though the 2M polytype was in greater abundance and better crystalline than the 1M polymorph, i.e. the $11\bar{2}$ and 112 reflections were both weaker and broader than the hkl reflections from the 2M polymorph. The unit cell dimensions calculated for all the micas are shown in table 24 and the plot of the 'b' dimension against composition is shown in figure 23.

Unit cells for both the 1M and 2M polymorphs in the mica composition with a Ga:Al ratio of 1.27 were calculated though the error in unit cell parameters for the 1M polymorph are greater as a result of the possible ambiguity in the assignment of indices to many of the lines in the mixture. If the 1M and 2M groups are considered separately (see figure 23) the plot of the 'b' parameter against final mica composition shows a regular increase with increasing amounts of gallium entering the structure.

General Discussion:

Micas crystallised from runs of long and short duration, i.e. three and fourteen days, always crystallised with the same polymorphic type of structure. The micas synthesized at 350°C and times of one to two days usually had X-ray patterns showing ~~many~~ fewer reflections. These structures would probably be more correctly described as having the 1Md or 2Md type of structure, (d denoting disordered form of the polymorph, following Yoder et al).

The intensity of the $11\bar{2}$ and 112 reflections in the 1M structure and the $11\bar{4}$ and 114 reflections in the 2M type structure were normally used to estimate the relative crystallinity of the mica phases synthesized for different periods of time. In general it may be stated that under the conditions of synthesis used in this investigation the end-member micas usually had better crystallinity than the micas of intermediate composition.

Of particular interest in four systems investigated was the formation of a 2M polymorph in the $\text{K}_2\text{O}-(\text{Al,Ga})_2\text{O}_3-\text{GeO}_2$ and $\text{K}_2\text{O} - \text{Ga}_2\text{O}_3 - (\text{Ge,Si})\text{O}_2$ system whenever the Ga:Al or Ge:Si ratio exceeded 0.5-0.6. In the aluminosilicate system only the 1M polymorph was found, but the work of Yoder (1955) suggests that over a sufficiently long period

of time $\sim$ 200 days the transformation 1M-2M will occur at 250-350°C. At the higher synthesis temperatures of 600-625°C Yoder (1955) was able to synthesize the 2M polymorph readily, but limitations of apparatus prevented a similar high temperature study of the potassium micas of this investigation.

On the basis of the X-ray and analytical results there seems little evidence of immiscibility in the four systems investigated although the appearance of β -Ga₂O₃ in the K₂O - (Al Ga)₂ O₃ - SiO₂ system needs further study. The small number of intermediate mica compositions studied might also have masked the observations of immiscibility over a narrow range of compositions.

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