



**STRUCTURAL RELATIONSHIPS IN LAYER SILICATES
AND THEIR INTERCALATES**

PETER KASIMIR SCHULTZ B.A., B.Sc.(HONS.), M.Sc.

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DEDICATION

**This thesis is dedicated to my wife without whose
patience and understanding this work could never
have been completed.**

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SUMMARY

The main object of the work described in this thesis was to examine in detail some structural relationships between layer silicate clay minerals and interlamellar organic species. To that end three naturally occurring Mg-vermiculites from Llano County, Texas, Phalaborwa, Transvaal and Young River, Western Australia, possessing varying layer charge densities, were sodium saturated and then intercalated with anilinium cations. Electron microprobe and microchemical analyses were carried out on both the sodium saturated and the intercalated vermiculites. Their charges per unit cell, unit cell contents and the amounts of anilinium cations present in each cell were computed.

Single crystal X-ray structure determinations and refinements were carried out on the three anilinium intercalates. The positions of all atoms in the silicate layers and the anilinium ions in the interlayer region were successfully refined in the Llano material. The presence of inorganic cations with coordinated water was also detected in the interlamellar region. Complete structure solutions of the Phalaborwa and Young River intercalates were not accomplished as these structures showed excessive layer stacking faults.

Three other vermiculites from Texas (Llano County), Kenya and Nyasaland (now Malawi) were intercalated with triethylenediaminium cations, analysed and their charges and unit cell contents determined. An accurate structure of triethylenediamine dihydrochloride used to intercalate the Na-vermiculites, was also determined. Weissenberg and precession photographs of the three intercalated vermiculites showed that only the Nyasaland material was sufficiently ordered to make a full structure analysis feasible. The structure solution of the triethylenediaminium intercalated Nyasaland vermiculite was successfully accomplished and all the silicate layer atoms, the organic species plus remaining inorganic/water components present in the interlayer region were located.

The thermal stability of the three intercalates was also determined by heating them on the precession camera to 350°C. They were found to be thermally stable but for increased stacking disorders which disappeared on cooling.

The Llano, Kenya and Nyasaland vermiculites were also intercalated with p-phenylenediaminium cations, analysed, their unit cell contents computed and their thermal stability and degree of crystallinity determined. This intercalation, however, did not order the structures sufficiently to make full crystal structure determinations feasible.

Within the scope of the present work upon layer silicate structures, the crystal structure of ephesite, a sodium-bearing brittle mica, was re-determined as the space group Cc previously assigned to it was known to be incorrect. A new X-ray data set was collected and the structure was refined in C1 symmetry. The presence of previously noted additional reflections, forbidden in space group Cc, was successfully explained by a hitherto unrecognised mode of ordering of the aluminium and silicon ions across the interlayers.

DECLARATION

This thesis contains no material which has been accepted previously for the award of any degree or diploma in any university and to the best of my knowledge contains no material published or written by another person, except where due reference is made in the text.

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I wish to express many thanks to my supervisor Dr. S.W. Kennedy for his guidance and advice throughout this work.

My sincere gratitude goes to Dr. P.G. Slade of CSIRO, Division of Soils, Urrbrae, South Australia, who provided expert advice and sound guidance during the course of this study. Dr. Slade is also thanked for supplying all the vermiculite samples described in this thesis.

My colleague Dr. C. Dean is thanked for providing guidance in computing and for collaborating in crystal structure data collection and refinement of the anilinium vermiculites. I am indebted to Dr. E.R.T. Tiekink for his constructive advice in crystal structure solutions and in the writing of this thesis.

PUBLICATIONS

As a result of this work the following publications have been achieved :

KENNEDY, S.W., SCHULTZ, P.K., SLADE, P.G. AND TIEKINK, E.R.T.
(1987) Triethylenediamine Dihydrochloride. Z. Kristall.
180, 211-217.

SLADE, P.G., DEAN, C., SCHULTZ, P.K. AND SELF, P.G. (1987)
Crystal Structure of a Vermiculite-anilinium Intercalate.
Clays and Clay Minerals 35, 177-188.

SLADE, P.G., SCHULTZ, P.K. AND DEAN, C. (1987) Refinement of the
Ephesite Structure in C1 Symmetry. N. Jb. Miner. Mh. 6,
275-287.

SLADE, P.G., SCHULTZ, P.K. AND TIEKINK, E.R.T. (1989) Structure
of a 1,4-diazabicyclo[2,2,2]octane-vermiculite Intercalate.
Clays and Clay Minerals 37, 81-88.

CHAPTER 1

LAYER SILICATES: GENERAL INTRODUCTION



CHAPTER 1

LAYER SILICATES: GENERAL INTRODUCTION

1.1 Preliminary Remarks

Layer silicates include several groups of minerals of which the micas are the best known representatives. As the name implies they all consist of layers in which all the atoms are tightly bonded to each other with much weaker bonds between the layers; these arrangements result in large interlayer spacings and consequent easy cleavage into flakes. The layers themselves may carry a negative charge which is balanced by the presence of positively charged interlayer ions. The layer silicates mainly considered in this thesis are vermiculites, which in addition to carrying interlayer cations also contain water, some of which is coordinated to the interlayer cations and some of which is more labile. The total amount of water varies according to the temperature and humidity of the ambient atmosphere. This interlayer water can be removed by heating and the interlayer cations can be replaced by other cations, both organic and inorganic, so that the vermiculites are important natural materials capable of accumulating various compounds, such as pesticides which may be present in the soil. These pesticides can subsequently be released and may for example find their way into the food chain.

When the clay minerals are intercalated with appropriate materials they can find uses as heterogeneous catalysts. Active sites are formed for various chemical reactions (Thomas, 1982); and intercalated clays may act as molecular sieves to catalyse particular chemical reactions such as selective cracking of petroleum products (Pinnavaia, 1983).

The crystal structures of clay minerals and their intercalates are, therefore, of great practical importance, and especially the exact location of their interlayer components, which are responsible for the catalytical properties of these silicates. The knowledge of the exact positions of these intercalants, the distance between them and their thermal stabilities are essential if one wishes to understand and predict their suitability in producing catalysts for specific chemical reactions (Shabtai *et al.*, 1977; Tsvetkov and White, 1988).

1.2 Crystal Structure of Layer Silicates

1.2.1 Layer structure

The layer silicates discussed in this thesis consist of continuous two-dimensional tetrahedral sheets of composition T_2O_5 , where T stands for tetrahedral cations, normally Si, Al, or Fe^{3+} , found at the centre of each tetrahedron, with the oxygen atoms present at the corners of the tetrahedra. Individual tetrahedra are linked to neighbouring tetrahedra by each sharing three corners. The oxygens at these corners are called basal oxygens, since they are parallel to the sheets, and form a hexagonal mesh pattern when viewed normal to the sheets (Figure 1.1a). The fourth tetrahedral oxygen, called the apical oxygen, points in a direction normal to the sheet and at the same time forms part of an immediately adjacent octahedral sheet in which individual octahedra are linked laterally by sharing octahedral edges (Figure 1.1b).

The common plane formed by the tetrahedral and octahedral sheets consists of the shared apical oxygens plus unshared OH groups that lie at the centre of each tetrahedral six-fold ring at the same height as the apical oxygens. The octahedral cations usually are Mg, Al, Fe^{2+} and Fe^{3+} , but other medium-sized cations

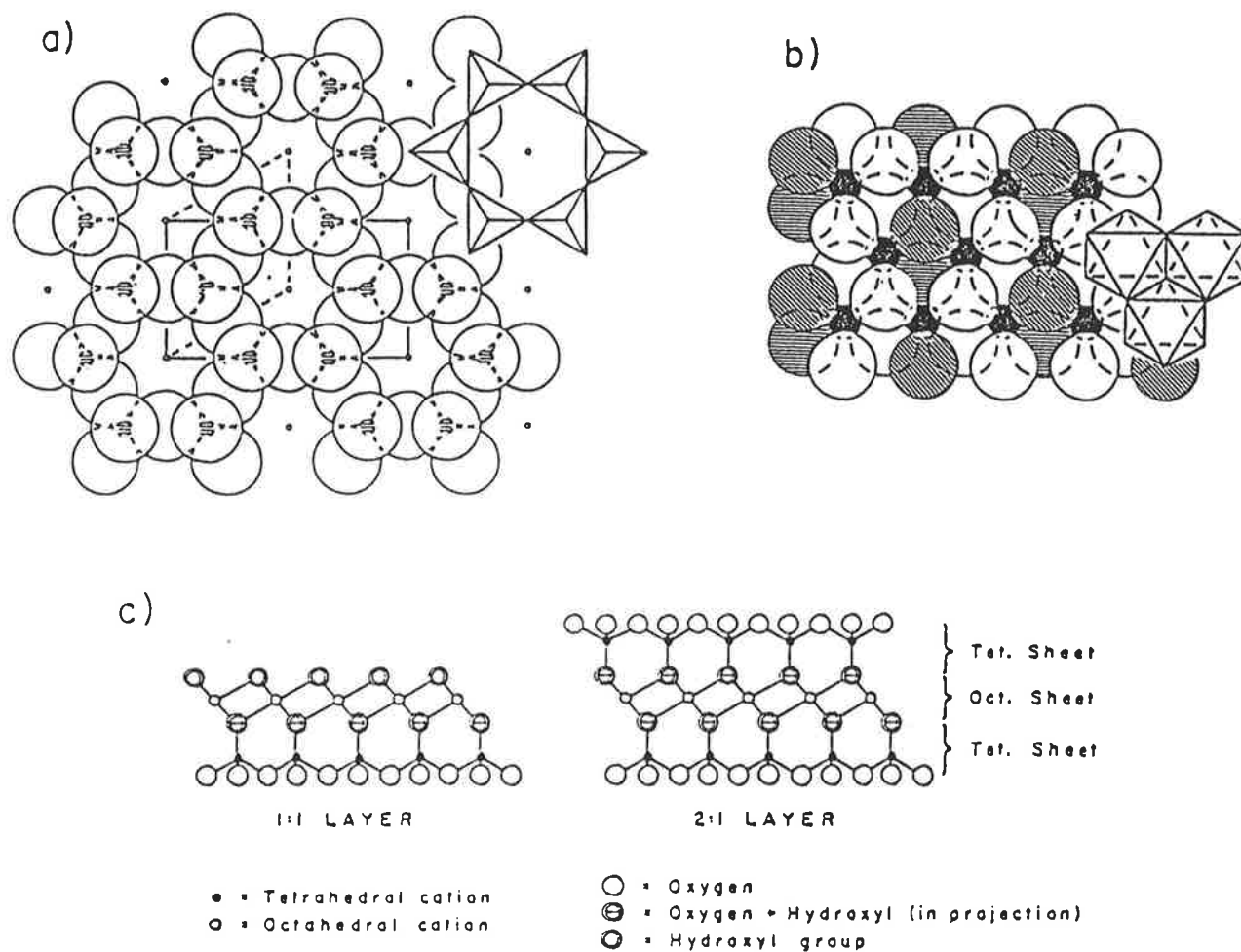


FIG. 1.1 (a) Plan view of ideally hexagonal tetrahedral sheet. Alternative hexagonal *P*- (dashed) and orthogonal *C*-cells (full lines) are shown connecting lattice points.

(b) Octahedral sheet with inner hydroxyl groups of 2:1 layer shown as shaded.

(c) Junction of sheets to form 1:1 and 2:1 layers.

From "Crystal Structures of Clay Minerals and their X-ray Identification", eds. G.W. Brindley and G. Brown.

such as Li, Ti, V, Cr, Mn, Co, Ni, Cu and Zn can also occur. The smallest structural unit contains three octahedra. If all three octahedra are occupied the sheet is classified as trioctahedral. If only two octahedra are occupied and the third octahedron is vacant, the sheet is classified as dioctahedral. The vermiculites are mostly trioctahedral.

The unit formed by linking one tetrahedral sheet with one octahedral sheet is known as a 1:1 layer. A 2:1 layer is formed by linking two tetrahedral sheets with one octahedral sheet. To accomplish this linkage, the upper tetrahedral sheet must be inverted so that its apical oxygens point down and can be shared with the octahedral sheet below (Figure 1.1c). The vermiculites are of the 2:1 type. If the 1:1 or 2:1 layers are not electrostatically neutral, the excess layer charge is balanced by various interlayer species, which may be simple inorganic cations, hydrated cations, organic cations or molecules. The total assemblage of a layer plus interlayer is referred to as a structure unit. It contains one or more formula units. The general formula can be written as $X_{0-1}Y_{2-3}Z_4O_{10}(OH)_2$ where X is the interlayer material, like K, Na, Ca or mainly Mg in vermiculites; Y are the octahedral cations, mainly Al, Mg, or Fe (2 for dioctahedral and 3 for trioctahedral sheets) and Z are the tetrahedral cations, mainly Si and Al, but they can also be Fe^{3+} or Ti. The symbols M and T are often used for octahedral and tetrahedral cations respectively.

The meanings given to the terms plane, sheet and unit structure are quite precise and refer to increasingly thicker parts of the layered arrangement.

The octahedral (Y) cations determine the positions of the two tetrahedral sheets within one layer, displacing them relative to each other by $a/3$ in the [100] direction. The composite layers are repeated on a rectangular network with dimensions approximately $5.3 \times 9.2\text{\AA}$. Often the layers have a negative

charge which is balanced by planes of cations (X), (K, Na, Mg, etc.) lying between them. In ideal cases these interlayer cations are in twelve-fold coordination, since they lie centrally on the line joining the centres of hexagons, formed by the basal oxygens of tetrahedral sheets, and no lateral displacement is introduced in going from the basal oxygens of one layer to the corresponding oxygens of its opposite layer. However the hexagons may be superimposed in six different ways. Thus one hexagon may be related to the next by rotation through 0 degrees or by a multiple of 60 degrees, and this, combined with the stagger of $a/3$ introduced by the octahedral sheet, determines the location of corresponding atoms in successive cells. Various sequences of layer rotations are possible, and when repeated regularly these build up unit cells with 1, 2, 3 or more layers. The most common stacking sequences lead to either one- or two-layer monoclinic cells (symbols $1M_1$, $2M_1$) or a different two-layer monoclinic cell ($2M_2$) or a three-layer trigonal cell ($3T$). Disordered crystals are common.

1.2.2 Layer distortion

The description of the fundamental layer structures given above is usually not realised in nature and in most materials the tetrahedra are twisted, so that the $(Si,Al)_2O_5$ sheets have di-trigonal instead of hexagonal symmetry. The twisting of the tetrahedra is caused by the different lateral dimensions of the tetrahedral and the octahedral sheets, which must fit together to form the common layer. The degree of fit between the tetrahedral and octahedral sheets can be determined by estimating the lateral dimensions such sheets would have in the free state. Free octahedral sheets occur in some hydroxide minerals, which can thus be used to estimate the ideal lateral dimensions for the octahedral sheets in layer silicates of similar composition. Thus gibbsite has $b=8.64\text{\AA}$, for the dioctahedral $Al(OH)_3$ composition and brucite has $b=9.36\text{\AA}$ for the trioctahedral $Mg(OH)_2$.

composition. Although tetrahedral sheets do not exist by themselves in minerals, it is possible to estimate their lateral dimensions in that hypothetical free state by assuming an average T-O bond length and ideal tetrahedral angles: $a = (4\sqrt{6}/3)(T-O)$; $b = a\sqrt{3} = (4\sqrt{2})(T-O)$. Thus for hexagonal geometry and $Si-O = 1.618 \pm 0.01 \text{ \AA}$ the resulting lateral dimensions are $a = 5.28 \pm 0.03 \text{ \AA}$ and $b = 9.15 \pm 0.06 \text{ \AA}$. Replacing silicon in the tetrahedral sites by the larger aluminium increases these values. Assuming $Al-O = 1.748 \pm 0.01 \text{ \AA}$, then $b = 9.89 \pm 0.06 \text{ \AA}$ or $b(Si_{1-x}Al_x) = 9.15 \text{ \AA} + 0.74x$. This relationship is only approximate because of uncertainties in the assumed bond lengths and also because the tetrahedral angles are known to vary a little from structure to structure.

Despite these uncertainties it is clear that tetrahedral sheets containing only Si have an ideal lateral b dimension that is intermediate between those of the ideal octahedral sheets containing only Mg or only Al. The degree of the misfit is approximately 3-5% for these compositions. Therefore some structural adjustments are necessary in order to eliminate this misfit and to fit the tetrahedral and octahedral sheets into layers containing a common interface.

In most of the layer silicates the ideal lateral dimensions of the tetrahedral sheet are larger than those of the octahedral sheet as a result of tetrahedral substitution of Al or Fe^{3+} for Si. Radoslovich (1961) has shown that it is relatively easy to reduce the lateral dimensions of a tetrahedral sheet by rotating adjacent tetrahedra in opposite directions in the (001) plane. The amount of rotation is given by $\cos \alpha = b(\text{obs})/b(\text{ideal})$, where α is the rotation angle. According to this formula, which is only approximate, because of the difficulty in estimating $b(\text{ideal})$, the lateral reduction varies from 1.5% for $\alpha = 10^\circ$ to 6.0% for $\alpha = 20^\circ$ and is 13.4% for a maximum possible rotation of 30° which would bring the basal oxygens into contact at the centre of each hexagonal ring. In reality the maximum rotation is smaller than

30° due to the increased repulsion between tetrahedral cations as they approach each other. Because adjacent tetrahedra rotate in opposite directions the symmetry of the network changes from hexagonal to approximately ditrigonal. Radoslovich and Norrish (1962) have subsequently shown that, for micas at least, the b-axis dimension is determined also by octahedral layer composition and by the interlayer cation type.

As the sheets are semi-elastic some adjustments can also be made by thickening the tetrahedral sheets and thinning the octahedral sheets, thereby decreasing and increasing respectively their lateral dimensions. These adjustments can be expressed as either the measured sheet thickness or as the T_{tet} and Ψ_{oct} angles. An ideal tetrahedron has an angle $T = (O_{apical} - T - O_{basal}) = 109^{\circ}28'$, which is increased by thickening and decreased by thinning. An ideal octahedron has an angle Ψ , which is defined as the angle between a body diagonal and the vertical, and for a sheet of linked octahedra is calculated as $\cos \Psi = \text{octahedral thickness} / 2(M - O, OH)$, where $M - O, OH$ is the mean of all octahedral cation-anion distances, including vacancies. The ideal Ψ angle is $54^{\circ}44'$, which increases with octahedral thinning.

1.2.3 Layer symmetry

As stated before, the individual sheets making up a layer have hexagonal symmetry when undistorted. In real crystals, however, the resultant three-dimensional symmetry may be lower, because of the faults in the stacking of successive layers along the Z direction, or because of layer distortions due to tetrahedral-octahedral sheet misfit, or because of cation ordering, or ionic interactions. However, if the symmetry remains hexagonal or trigonal, the smallest unit cell is primitive and has a hexagonal shape with three equivalent X-axes 120° apart lying in the horizontal plane of the layer and with the Z-axis normal to the layer. The axial repeat distances for

this cell are $a=b=5.1-5.4\text{\AA}$ and $c=n \times \text{unit structure thickness}$, where n =number of layers in the unit cell. A one-layer primitive cell of this shape contains one chemical formula unit (Z), provided there is no superperiodicity parallel to the layer.

A trigonal or hexagonal structure can also be described in terms of a larger C-centered orthogonal cell in which the Y-axis is chosen to be normal to the Z-axis and to one of the X-axes (Figure 1.1a). The axial repeat along this Y-axis is $b=a\sqrt{3}$, and the cell volume is twice that of the primitive cell for the same periodicity along Z. Because it is easier to index X-ray powder patterns on an orthogonal than on a hexagonal cell, the larger C-cell often is used for indexing. C-cells must be used to describe structures with orthorhombic, monoclinic, or triclinic resultant symmetries, although for the latter two cases the Z-axis is not necessarily normal to the layer.

The layer silicate minerals are classified on the basis of layer type (1:1 or 2:1), layer charge and type of interlayer. Further subdivision into sub-groups and species is made on the basis of the octahedral sheet type (dioctahedral or trioctahedral), chemical composition and geometry of superposition of individual layers and interlayers.

1.2.4 Interlayer structure

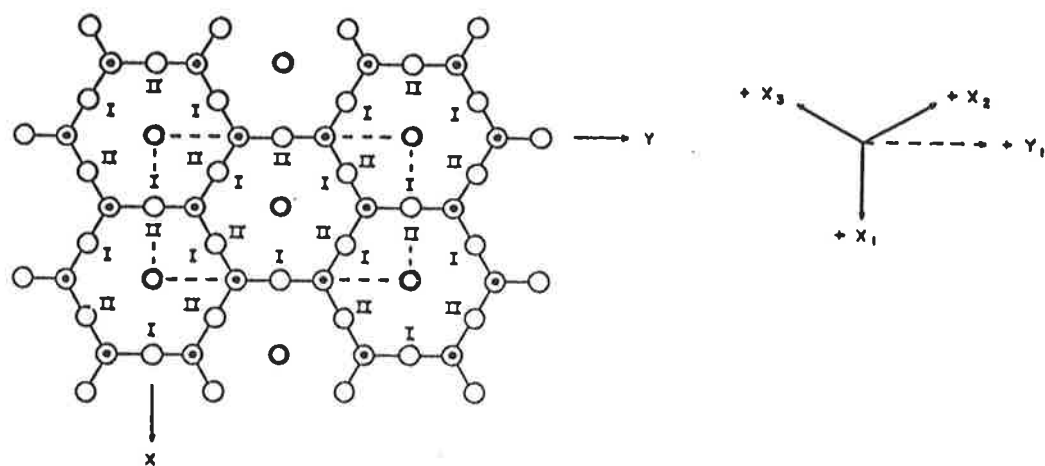
The negatively charged 2:1 layer trioctahedral layer silicates discussed in this thesis all contain interlayer cations. To accommodate these cations adjacent layers must superimpose so that the hexagonal rings formed by the basal oxygens line up and enclose them. Adjacent layers may often be propped apart somewhat by these interlayer cations because the tetrahedral rotation, necessary to fit the tetrahedral and octahedral sheets together, moves every other basal oxygen towards the centre of each ring thus reducing the size of the opening and increasing

the interlayer distance. Each interlayer cation then has only six nearest oxygen neighbours and not twelve, as is the case for ideal hexagonal geometry. Since adjacent 2:1 layers must line up to enclose the interlayer cations, the only movement possible is within a layer namely at the octahedral interface. Then the upper tetrahedral sheet must be staggered by $a/3$ relative to the lower tetrahedral sheet in order to maintain octahedral coordination around the octahedral cations, but it may do so along the positive or negative direction of any of the three pseudo-hexagonal axes X_1 , X_2 , or X_3 . Given a fixed set of initial axes, as defined in Figure 1.2a, the three octahedral cations can occupy either the three sites labelled I in each hexagonal ring or the three sites labelled II. If the I sites are occupied, then octahedral coordination about them can be provided by fitting the upper tetrahedral sheet in any of the three positions shown in Figure 1.2b. These correspond to shifts of $a/3$ along the negative directions of X_1 , X_2 , and X_3 . Conversely, if the II sites are occupied the upper tetrahedral sheet will be positioned as shown in Figure 1.2c, in which the $a/3$ shifts are along the positive direction of these same three axes. Because set I transforms to set II by rotation of the layer by $\pm 60^\circ$ or 180° , the only important difference is whether the same sites are occupied in each layer or whether there is an alternation between the I and II sites in successive layers.

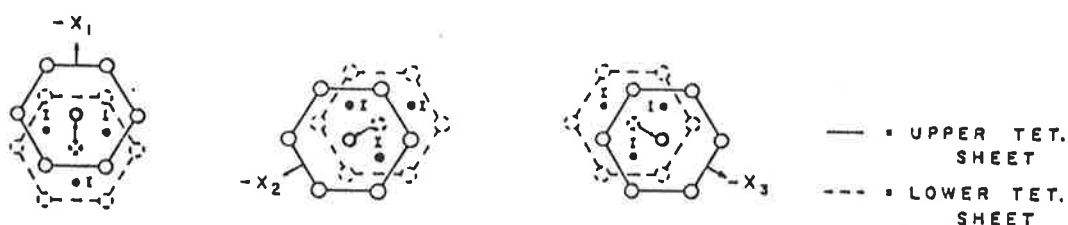
1.2.5 Polytypes

Smith and Yoder (1956) derived the six simplest polytypes that are theoretically possible assuming that the hexagonal rings are undistorted, that the octahedral positions are all occupied, that no cation ordering takes place and that in a given crystal the same interlayer stacking angle is found between all the layers. These possibilities are illustrated graphically in Figure 1.3. The structure with zero stacking angle, corresponding to successive $-X_1$ shifts, is the 1M polytype. The 20r polytype

a)



b)



c)

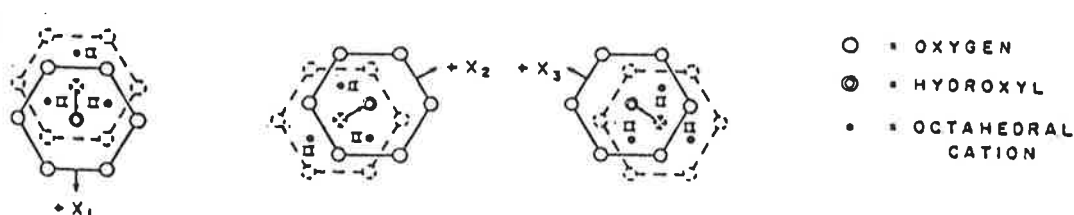


FIG. 1.2 (a) Definition of I and II sets of octahedral cation positions above a tetrahedral net relative to a fixed set of hexagonal axes for a 2:1 layer.

(b) Three possible directions of intralayer shift when octahedral cation set I is occupied.

(c) Three possible directions of intralayer shift when octahedral set II is occupied.

From "Crystal Structures of Clay Minerals and their X-ray Identification", eds. G.W. Brindley and G. Brown.

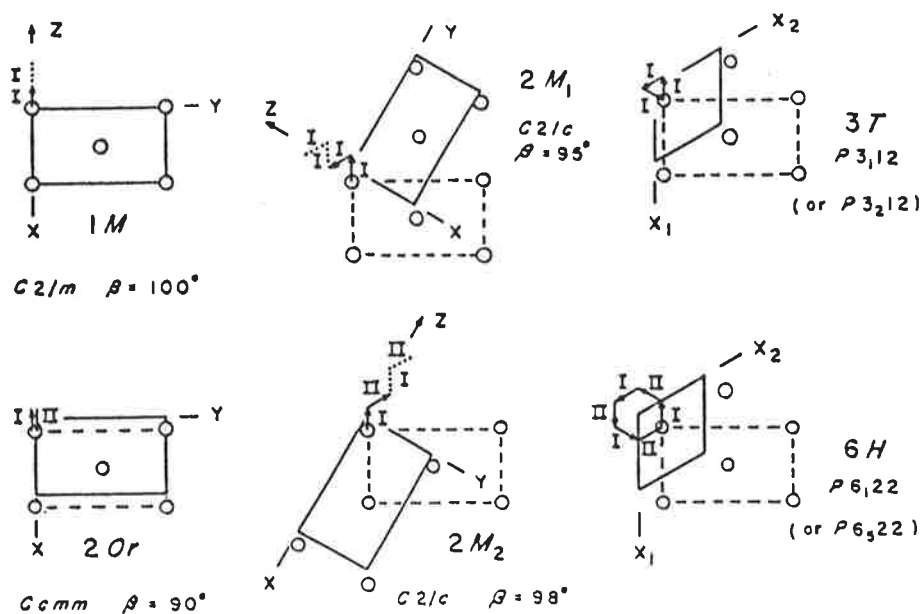


FIG. 1.3 Derivation of six ideal mica polytypes. The orientation of FIG. 1.2a is assumed for the first layer of each polytype with the I set of octahedral cation positions occupied and the intralayer shift $-a/3$. The base of the resultant unit cell (solid lines) may or may not coincide with the fixed cell (dashed lines) used for the first layer. The origin of each resultant unit cell has been placed as close to the centre (circles) of an hexagonal ring in the first layer as the symmetry permits.

From "Crystal Structures of Clay Minerals and their X-ray Identification", eds. G.W. Brindley and G. Brown.

results from 180° stacking angles, equivalent to alternate $-X_1$ and $+X_1$ shifts. These are the only polytypes that involve shifts along just one axis. If shifts are considered along two different X axes, then a continuous alternation of $\pm 120^\circ$ stacking angles yields the $2M_1$ polytype and the $2M_2$ polytype. In the $2M_2$ structure the X and Y axes must be reversed because the (010) symmetry plane is normal to the $5.2\text{\AA}$ axis. Any two X axes can be used and the same two structures would be derived differing only in the orientation of the resultant unit cell relative to the fixed starting axes. Finally, if all three X-axes are used for shift directions a continuous sequence of 120° angles along $-X_1$, $-X_2$ and $-X_3$ gives rise to the 3T polytype, or to its mirror image if 240° angles are used. In the same way continuous stacking angles of 60° or 300° along all three axes give two mirror image structures designated 6H. Hexagonal-shaped cells can be used for the resultant 3T and 6H structures, instead of the monoclinic- or orthorhombic-shaped cells necessary for the others.

To sum up, two polytypes result if shifts along just one X-axis are used. A second group of two polytypes results when shifts along two axes are employed and a third group involves shifts along all three axes. One member of each group relates to structures in which the same octahedral positions are occupied in each layer, whereas for the other member the octahedral sets I and II are occupied alternatively in successive layers (equivalent to layer rotation). More complex layer sequences can be derived if mixtures of different interlayer stacking angles are involved.

1.3 Crystal Structure of Vermiculites

Vermiculites possess a high layer charge, usually greater than 0.6 per formula unit. The high layer charge leads to their diagnostic physical property of spontaneous rehydration in the atmosphere after gentle dehydration at less than 300°C .

Vermiculites are of the 2:1 layer type. Most macroscopic vermiculites are trioctahedral and form by alteration of trioctahedral micas and chlorites. The original layer charge on the mica or chlorite may be reduced slightly during alteration to vermiculite by oxidation of octahedral ferrous iron or by hydroxylation of O to OH. The ideal composition for a trioctahedral vermiculite is $\text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2\text{Mg}_{0.5}(\text{H}_2\text{O})_{4.0}$ and the cell parameters are: $a \approx 5.35$, $b \approx 9.25$, $c \approx n \times 14.45 \text{ \AA}$, $\beta = 97.12^\circ$; space groups are Cc and C2/c.

The structure of vermiculite was first studied by Gruner (1934), who chose a monoclinic unit cell with $a = 5.3$, $b = 9.2$ and $c = 28.57\text{--}28.77 \text{ \AA}$, $\beta = 97.15^\circ$ and space group Cc or C2/c. Gruner concluded, using powder pattern intensities, that the structure consisted of trioctahedral 2:1 layers, between which lie double planes of water molecules occupying a space nearly equal to a complete interlayer sheet in the chlorite structure. Hendricks and Jefferson (1938a) confirmed Gruner's findings using single crystal diffraction, and proposed that vermiculites have partially random displacements of structural layers parallel to the Y-axis. Hendricks and Jefferson (1938b) further stipulated a hypothetical arrangement of the interlayer water molecules in planar hexagonal rings with the oxygen of each water being tetrahedrally bonded to four neighbouring oxygens through hydrogen atoms. Alternate water molecules in each of the two interlayer planes were assumed to bond to adjacent 2:1 layer surfaces. No provisions for exchangeable cations were made in these earliest studies, but these interlayer cations must be present in order to balance the negative charge on the 2:1 layers.

Walker (1956) showed that a Mg-saturated vermiculite in equilibrium with a humid atmosphere contains two slightly incomplete interlayer planes of water molecules as hydration shells around the exchangeable cations and gives a basal spacing of $14.36 \text{ \AA}$. When immersed in water the basal spacing increases to

14.81Å and it is assumed that two complete interlayer planes of water molecules are formed. Dehydration of the 14.36Å phase by gentle heating leads first to a 13.82Å spacing, which is believed to correspond to a structure containing two slightly incomplete planes of water arranged in a different way to those found in the 14.36Å phase. Further dehydration leads progressively to a 11.59Å phase, with a single plane of water molecules, a 20.6Å phase, consisting of roughly regular alternation of 11.59Å and 9.02Å components, and a 9.02Å talc-like phase that contains no interlayer water. The changes in the unit cell shapes and sizes during dehydration and the stacking sequences of layers postulated by Walker are shown in Figure 1.4.

1.3.1 Kenya vermiculite

Mathieson and Walker (1954) and Mathieson (1958) examined Mg-saturated vermiculite from Kenya by two-dimensional electron density and difference electron density maps. They found that the water molecules and exchangeable cations occupy definite sites in the interlayer region and that the 2:1 layer tetrahedral networks are distorted from regular hexagons by 5.5° planar rotations of the tetrahedra. They also determined that the exchangeable Mg^{2+} cations lie in a plane half-way between adjacent 2:1 layers and have a plane of water molecules on each side. Therefore the interlayer material takes the form of an incomplete octahedral sheet, similar to the interlayer sheet in chlorite, but with only 1/9 of the cation sites and 2/3 of the anion sites filled in the vermiculite examined. Their diffraction data did not specify which of the available sites are actually occupied in adjacent unit cells. Mathieson and Walker (1954) put forward a dynamic system which allowed the cation and water molecules to move between all available positions. They also suggested that there was a tendency to maintain a regular, hexagonal distribution of the occupied cation sites over three unit cells as a result of mutual repulsion, with the water

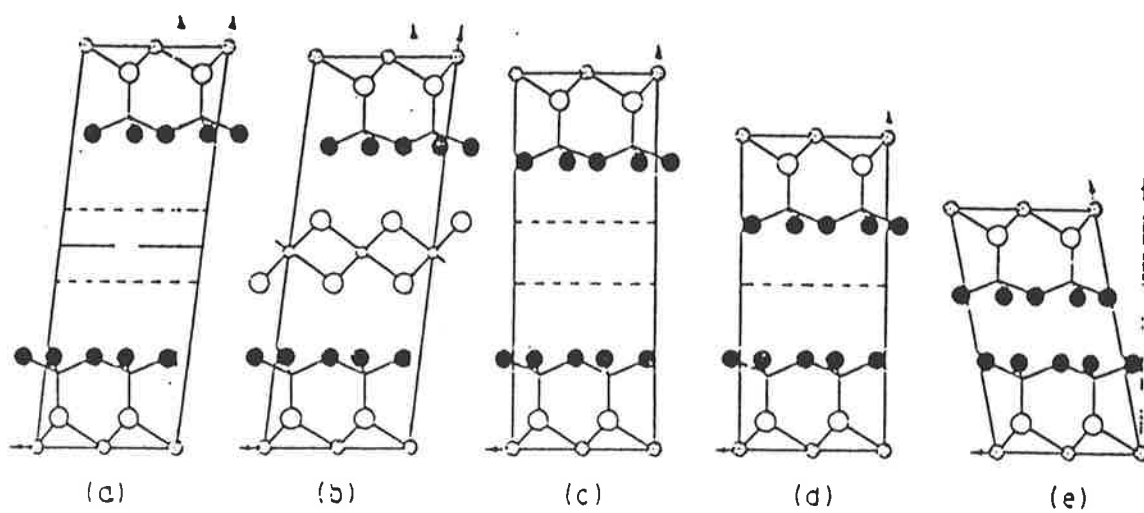


FIG. 1.4 [010] projections of Mg-vermiculite layer-interlayer assemblages in various stages of hydration (from Walker, 1956).

- (a) 14.81Å phase
- (b) 14.36Å phase
- (c) 13.82Å phase
- (d) 11.59Å phase
- (e) 9.02Å phase

clustering around the occupied cation sites as octahedral hydration shells. Every water molecule was found to be linked by a hydration bond to an oxygen in the nearest 2:1 layer surface, but no attraction was believed to exist between the exchangeable cations and the 2:1 layer surface. This postulated interlayer structure differs completely from the one proposed by Hendricks and Jefferson (1938b).

Mathieson and Walker (1954) established that two different two-layer stacking sequences, designated q and r, occur with equal probability in the Kenya vermiculite. In both structures the shift of $a/3$ within each 2:1 layer alternates along $-X_2$ and $-X_3$ in adjacent layers, relative to the resultant axes of the structure, and adjacent 2:1 layers are displaced alternatively by $\pm b/3$ relative to one another. If 2:1 layers with interlayer shifts along $-X_3$ are designated M layers and those with $-X_2$ shifts designated N layers, the q and r structures can be differentiated in terms of the relative displacement of the bottom of an N layer relative to the top of an M layer below. In the q structure this displacement is $-b/3$ along Y and in the r structure it is $+b/3$.

1.3.2 Llano vermiculite

Shirozu and Bailey (1966) determined in greater detail the vermiculite structure by a three-dimensional refinement of a specimen from Llano County, Texas, U.S.A. They used repeated cycles of least-squares refinement and electron density maps with 822 X-ray reflections to achieve a final R value of 9.1%.

The Llano vermiculite was found to have a two-layer structure of the type designated s by Mathieson and Walker (1954). In this structure the shift within each 2:1 layer is always along $-X_1$ (L layers) and successive 2:1 layers are displaced alternatively by $+b/3$ and $-b/3$ along the Y-axis.

Shirozu and Bailey (1966) established that in the Llano vermiculite the tetrahedral network is distorted by rotation of the tetrahedra by an average angle of 5.7° . The direction of rotation is such that each basal oxygen moves towards the position of the nearest water molecule in the adjacent interlayer space. They also determined that 0.41 atoms of Mg^{2+} occupy statistically one of the three available octahedral interlayer sites, and under the relative humidity conditions of the laboratory during the investigation 0.62 H_2O statistically occupy each of the six interlayer anion sites for a total of 3.72 H_2O per formula unit. The average position of each water molecule is appropriate for hydrogen bonding to an oxygen on the surface of the adjacent 2:1 layer. Large observed thermal parameters for the water were interpreted as due in the main to random displacements of the water molecules from their average positions.

Another structural feature described by Shirozu and Bailey was partial tetrahedral cation ordering with the resulting control of the exchangeable interlayer cation position by tetrahedral aluminium. Tetrahedral cation ordering was indicated both by the difference in average T-O bond lengths [$T(1)-O=1.673\text{\AA}$ and $T(2)-O=1.641\text{\AA}$] and by the difference in thermal parameters for these cations [$B=1.03$ for $T(1)$ and 0.83 for $T(2)$] when similar scattering factors were assumed for both. The exchangeable interlayer cations were found to be localised in only one of the three available octahedral interlayer positions. In this position they are immediately adjacent to the ordered Al in the $T(1)$ tetrahedra of the 2:1 layers above and below. The above ordering provides local charge balance which should make this structural arrangement especially stable.

De la Calle *et al.* (1976) have remarked that the actual structure of the Llano vermiculite is less perfect than the ideal structure given by Shirozu and Bailey (1966). They point out that the observed intensities and diffuseness of the $k \neq 3n$ reflections

indicate the presence of a large number of stacking faults. These faults break up the regular alternation of $+b/3$ and $-b/3$ interlayer shifts so that a $+b/3$ shift is as likely to be followed by another $+b/3$ shift as by $-b/3$ shift.

1.4 Intercalation of Layer Silicates

There are several distinct kinds of layer silicates which freely form intercalates; well known examples are montmorillonite, hectorite, vermiculite and kaolinite. The most important feature possessed by these layer silicates, as far as intercalation chemistry is concerned, is their ability to incorporate water and/or inorganic cations into the interlayer region and also to take up various organic species, sometimes as neutral molecules, sometimes as ionised entities, such as amino acids, and often both. Other important properties possessed by these layer silicates are their abilities to be converted from the hydrophilic to the organophilic state by for example exposing the parent water-rich intercalate to an appropriate organic reagent such as a primary amine. These silicates also exhibit strong acidity. Often Brønsted acidity predominates either because of the influence of the strong internal electric field exerted on the interlayer water molecules, which leads to detachment of protons by dissociation, or because of the additional influence of some hydrated interlayer cations, notably Al^{3+} . The layer silicates may also function as a Lewis acid in that there are identifiable sites, for example Fe^{3+} ions, which function as electron accepting centres. These silicates can be prepared in a variety of cation-exchanged forms, in which the original exchangeable cation usually Na^+ is replaced, as desired, by one, or more, of a whole range of inorganic or organic cations. When these ions are bulky and carry a multiple charge, they serve as fairly rigid, cross-linking rods or bridges. They can be converted to even more rigid, but open structures, less prone to swelling upon uptake of organic or inorganic guests; these are

then capable of exhibiting molecular sieve properties.

In some layer silicates the intercalate chemistry may be regarded as organic solid-state chemistry which involves selecting molecules according to their size, shape or stereochemistry and then inducing them to crystallise in certain desired crystallographic forms. Within those crystals, when they are stimulated for example with UV light, diffusionless intermolecular reactions will take place. The object is to select the parent molecules and crystal structures which will lead to a specific topochemically dictated product. In the majority of the organic layer silicate intercalates, however, the chemical reactions take place in contact with the solvent from which the guest molecules are initially introduced into the host silicate to form the intermediate intercalate. In some cases the reactions are difficult to sustain, and once the intermediate intercalate is converted to the product the reaction stops. But in many cases the parent layer silicate host can be utilised continuously and the intercalates form and react in specific fashions for long periods of time.

The catalytic properties of the layer silicates smectites and vermiculites do not extend to other layer silicates such as the micas. These widely differing properties may at first be considered paradoxical as all these minerals are layer silicates containing interlamellar cations and they all possess hexagonal (or ditrigonal) rings into which the interlayer cations are recessed. The surface charge density of the micas is however much higher than of the smectites and vermiculites so that all the hexagonal rings are occupied in the micas while only a small fraction of them are occupied in the smectites and vermiculites. As a consequence of this lower occupancy, or surface charge density, it is easier to separate the smectite and vermiculite layers than the mica layers; also due to substantial amounts of water present in the smectite and vermiculite interlayer regions the interlamellar cations are solvated and are therefore not as

firmly attached to the ditrigonal holes as in the micas. These interlayer cations have a greater degree of mobility and are therefore able to form cation exchange reactions with bulky organic species. An unfortunate consequence of the mobility of the interlayer cations is the loss of long-range order in the stacking of individual layers resulting in these layer silicates being virtually two-dimensional.

In order to select, identify and characterise the clay minerals and their intercalates a number of techniques can be employed. Firstly the cation exchange capacity of the layer silicates is a useful guide in determining the tendency of the silicates to form intercalates. The unit usually used is milliequivalents (mEq) of interlayer cations that may be exchanged per 100 g of silicate. The figures for vermiculites are about 100-170mEq per 100 g. Secondly the surplus electric charge on the surface layers, which is a measure of the number of cationic species that can be intercalated, can be determined by X-ray fluorescence or electron microprobe analysis of sodium or calcium intercalated layer silicates, as these two cations are only present in the interlayer regions. Thirdly X-ray powder diffractometry can be used to determine the progress of intercalation as intercalation is usually accompanied by a change in the c-axis repeat distance, i.e. the spacing between the layers changes. Finally, the actual amount of organic species intercalated can be determined by microanalysis for nitrogen, carbon and hydrogen.

Having established that intercalation has taken place, X-ray diffraction can be used to characterise precisely the silicate layers themselves and the interlayer species. One- and two-dimensional Fourier maps are usually used, but if the intercalate is sufficiently ordered three-dimensional X-ray structure determination may be attempted (Thompson and Cuff, 1985; Slade *et al.*, 1987). The X-ray diffraction studies can be supplemented by infrared and NMR techniques to establish the coordination number and the chemical environment of various

organic molecules and atomic species e.g., aluminium and silicon (Sanz and Serratosa, 1983 and Thompson, 1984).

1.5 Concluding Remarks

It is well known that a number of layer silicate minerals such as montmorillonite, hectorite, vermiculite and kaolinite can be easily intercalated with a variety of organic and inorganic species to form stable compounds which can act as catalysts for a great number of chemical reactions. But to understand and predict which chemical reactions are possible a detailed knowledge of the mechanisms, involved is necessary. In order to establish the mechanisms the exact positions of all the species in the interlayer and in the silicate layers themselves must be known.

The amounts of interlayer material intercalated can be determined by various microanalytical techniques (Tsvetkov and White, 1988). Solid state magic-angle spinning NMR spectroscopy and related techniques can also give some information on the chemical nature and environment of the interlayer species and atoms such as silicon and aluminium present in the layer silicates themselves (Thompson, 1984). X-ray diffraction techniques are widely used to identify the layer silicates, measure their interlayer spacings and in favourable circumstances determine the exact positions of both the layer silicate atoms and the interlayer materials (Thompson and Cuff, 1985).

The greatest difficulty with X-ray structure determination, however, is the nature of the clay silicates themselves which, with the exception of vermiculites, do not form crystals large enough for single crystal structure studies. These silicates also, as a rule, are not three-dimensionally ordered, so that only one and two dimensional structure work is possible. The layer silicate mineral vermiculite, however, does form large

crystal flakes which, when intercalated with some organic species, were found by Slade and co-workers to improve the three-dimensional order to such an extent as to make three-dimensional single crystal X-ray structure determination possible. This thesis describes the intercalation, chemical analysis and X-ray structure determination of a number of different vermiculites undertaken in collaboration with Dr. P.G. Slade of CSIRO, Division of Soils, Urrbrae, South Australia, at the suggestion of Dr. S.W. Kennedy. This work was supported in part by an equipment grant to Dr. S.W. Kennedy and Dr. P.G. Slade from the CSIRO University Collaborative Research Projects - Funding Scheme.

CHAPTER 2

ANILINIUM INTERCALATED VERMICULITES: PREPARATION AND ANALYSIS

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2.1 Introduction

The high cation exchange capacity of vermiculites results in a large variety of possible substitutions, not only of inorganic cations but also of a great number of organic species. Intercalation complexes involving vermiculites and some organic cations have been prepared and examined by X-ray diffraction techniques by Slade *et al.* (1976, 1978), Slade and Raupach (1982) and Slade and Stone (1983). One- and two-dimensional X-ray diffraction techniques were used as the intercalates lacked three-dimensional periodicity due to faults present in the stacking sequences of the silicate layers. However, Slade and Stone (1984) discovered that by intercalating sodium saturated vermiculite from Carl Moss Ranch, Llano County, Texas, U.S.A. with anilinium cations $[\text{C}_6\text{H}_5\text{NH}_3]^+$ an intercalate which was three-dimensionally ordered was obtained.

Further work was, therefore, undertaken in order to characterise the anilinium-vermiculite fully.

2.2 Preparation

Three naturally occurring Mg-vermiculites, from three different countries were used: these were from Llano County, Texas, U.S.A., Phalaborwa, Transvaal, South Africa and Young River, Western Australia. The three vermiculites were chosen as they possessed different cation exchange capacities. Their respective charges

per unit cell were 1.89, 1.58 and 1.46, as determined by Norrish (1973) using calcium saturated samples and X-ray fluorescence analysis.

The three intercalates investigated were prepared in the following manner: Mg-vermiculite flakes were cut into approximately 1-2 mm squares and refluxed with 2M NaCl solutions at 70°C for one week, renewing the solutions daily to achieve complete sodium saturation. Residual NaCl was removed by water washing and finally the vermiculite flakes were air dried.

The Na-saturated vermiculites were next refluxed in a 1% aniline hydrochloride solution for periods ranging from 2 to 10 weeks at 40°C. These solutions were changed every few days, at which time some flakes were removed for examination with an X-ray powder diffractometer. The powder diffractometry consisted of placing a number of flakes on their flat sides in a straight row on a glass slide cut to fit a Narelco powder diffractometer mount. A 1/4° divergence slit, a 0.2 mm receiving and a 1/4° scatter slits were used. The diffractometer trace was run from 4 to about 60° to obtain a set of 001 reflections starting from 001. In this way the exchange reactions were monitored by following the development of a new set of rational 001 reflections different from the original set of the Na-saturated vermiculites. As the intercalation reaction proceeded a new set of 001 reflections gradually appeared while the old set disappeared. To ascertain whether the new set of reflections belonged to the anilinium intercalated vermiculites and not to the original sodium intercalated kind, containing for example a different amount of water, the samples were heated on the diffractometer with a specially designed resistance heater which fitted under the glass slide containing the intercalated crystal flakes. The temperature was raised to about 80°C, the diffractometer set to the 001 reflection and its intensity monitored. The reaction was judged to be complete if no shift in this reflection occurred. Finally a complete diffraction trace was run and the d-spacings

calculated. The intercalation was then stopped and the flakes removed, washed with hot distilled water, until the filtrate was chloride free, and allowed to air-dry.

The anilinium intercalated vermiculites were also analysed for carbon, nitrogen and hydrogen by Australian Microanalytical Service, Melbourne, Victoria, Australia and/or Canadian Microanalytical Service Ltd., Vancouver, Canada, to determine the concentration of the organic complex and thus the degree of saturation achieved.

The results obtained showed that the Llano vermiculite was only about 60% saturated, even though it was intercalated for 10 weeks as opposed to 2 weeks for Phalaborwa and the Young River vermiculites, and therefore this intercalation reaction was continued for another 10 weeks at 60°C, but further microanalytical results did not reveal any increase of anilinium saturation, showing that the equilibrium was substantially achieved in the first 10 weeks of the reaction.

2.3 Chemical Analyses

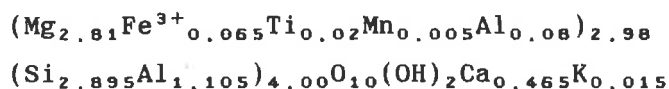
Chemical analyses of the three vermiculites were carried out by Dr. K. Norrish of CSIRO, Division of Soils, Urrbrae, South Australia, using X-ray fluorescence analysis and by the author, using electron microprobe analysis.

2.3.1 X-ray fluorescence analysis

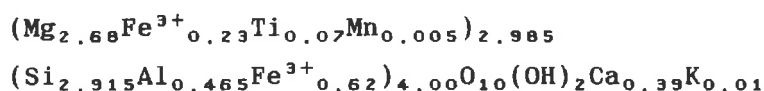
Norrish (1973) exchanged three naturally occurring Mg-vermiculites with calcium, using CaCl solutions, and with the X-ray fluorescence technique determined their composition and interlayer charge. Calcium was used as it only enters the interlayer region, while the original magnesium is present in

both the interlayer region and the octahedral positions of the silicate layers themselves. Norrish obtained the following structural formulae:

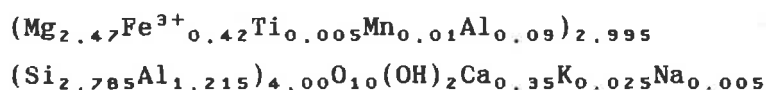
1. Llano vermiculite



2. Phalaborwa vermiculite



3. Young River vermiculite



Since two formula units are present in a unit cell, the interlayer charges for the three vermiculites are 1.89, 1.58 and 1.46 respectively.

2.3.2 Electron microprobe analysis

Selected flakes of sodium and anilinium intercalated vermiculites, from the three countries, were analysed using a JEOL 733 Superprobe, a KEVEX 7000 Series energy dispersive spectrometer and the raw data were processed using full ZAF (i.e. atomic number, mass absorption and secondary fluorescence corrections) with a PIBS style software (Ware, 1981). The following operating conditions were employed: accelerating voltage 15kV, probe current 5nA, beam size 20 μm diameter and counting times 60 seconds life time.

The samples were prepared by attaching a number of flat flakes onto polished blank epoxy resin briquettes and coating them with approximately 25 nm of carbon. A number of point analyses,

ranging from 5 to 15, were carried out on each sample, the averaged results and structural formulae, calculated on the basis of 11 oxygens, are given in the following tables.

Table 2.1: Electron Microprobe Analysis of Sodium Saturated Vermiculites

Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	Total
Llano	37.4	0.21	13.2	0.58	25.8	6.25	83.44
Phalaborwa	37.9		5.4	12.1	23.8	6.5	85.7
Young River	36.4		14.3	5.8	22.2	6.0	84.7

Table 2.2: Electron Microprobe Analysis of Anilinium Intercalated Vermiculites

Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	An ₂ O ⁽¹⁾	Total
Llano	37.2	0.26	12.4	0.42	23.4	12.8	86.48
Phalaborwa	37.5		5.0	11.6	21.6	15.6	91.3
Young River	34.4		13.1	5.2	20.5	17.8	91.0

¹ An₂O = anilinium oxide (C₆H₅NH₃)₂O. The carbon, nitrogen and hydrogen analyses were carried out by Australian Microanalytical Service, Melbourne, Australia and by Canadian Microanalytical Service Ltd., Vancouver, Canada giving the following values:

Llano

C=9.00 N=1.80 H=2.06%

Phalaborwa

C=11.00 N=2.07 H=1.89%

Young River

C=12.58 N=2.37 H=1.98%

The molecular weight percent values of anilinium oxide given in Table 2.2 were calculated from the microanalytical carbon and nitrogen figures received (the values quoted are the average of two molecular weights calculated using carbon and nitrogen figures separately).

Using the results given in Tables 2.1 and 2.2, structural formulae were calculated for the three sodium and the three anilinium intercalated vermiculites. The values obtained are given in Table 2.3.

The number of anilinium cations per structural formula given in Table 2.3 were calculated using the anilinium oxide figures from Tables 2.1 and 2.2. The accuracy of these values was checked by measuring the densities of each vermiculite and their unit cell volumes (obtained during crystal structure determination) and calculating the mass of unit cell ($M=D \times V$). Knowing the weight percent of carbon and nitrogen present in the samples (from the microanalytical results) and the number of carbon and nitrogen atoms in one anilinium cation, the number of anilinium cations per structural formula was calculated. The values obtained were 0.61, 0.75 and 0.85 for the Llano, Phalaborwa and Young River vermiculites respectively, which are almost exactly the same as the ones given in Table 2.3 (0.61, 0.76 and 0.86).

2.3.2.1 Accuracy of microprobe analysis

The unit cells of the vermiculites studied contained two formula units per cell, therefore the interlayer charges in the sodium saturated vermiculites were 1.86, 1.96 and 1.78 respectively. These values agree with the figure given by Norrish (1973) for Llano (1.89) but are too high for the Phalaborwa and Young River vermiculites when compared with the figures given by Norrish (1.58 and 1.46 respectively). The accuracy of the microprobe analyses was therefore suspected and subsequently checked by

Table 2.3: Structural Formulae (O = 11) for Sodium and Anilinium $[\text{C}_6\text{H}_5\text{NH}_3]^+$ Intercalated Llano, Phalaborwa and Young River Vermiculites

Sample	Tetrahedral $\Sigma=4$			Octahedral				Octa- hedral Total	Interlayer	
	Si	Al	Fe^{3+}	Mg	Fe^{3+}	Ti	Al		Na^+	$[\text{C}_6\text{H}_5\text{NH}_3]^+$
Llano Na^+	2.86	1.14	-	2.94	0.03	0.01	0.05	3.03	0.93	-
Llano $[\text{C}_6\text{H}_5\text{NH}_3]^+$	3.01	0.99	-	2.82	0.03	0.02	0.20	3.07	-	0.61
Phalaborwa Na^+	2.96	0.50	0.54	2.77	0.17	-	-	2.94	0.98	-
Phalaborwa $[\text{C}_6\text{H}_5\text{NH}_3]^+$	3.09	0.48	0.43	2.65	0.29	-	-	2.94	-	0.76
Young River Na^+	2.79	1.21	-	2.54	0.32	-	0.09	2.95	0.89	-
Young River $[\text{C}_6\text{H}_5\text{NH}_3]^+$	2.83	1.17	-	2.52	0.32	-	0.10	2.94	-	0.86

analysing a sample of calcium saturated vermiculite from Young River previously analysed by Norrish (1973). The results obtained agreed within experimental errors with those of Norrish, showing that the microprobe analyses were reliable, at least for calcium, and most probably for the anilinium intercalated vermiculites, but that the analyses for the sodium saturated vermiculites were somewhat unreliable as far as the sodium figures were concerned. Sodium is known to be difficult to determine accurately in clay silicates, due to the heating effect of the electron beam and the volatility of the sodium.

Velde (1984) investigated the accuracy of electron microprobe analyses of sodium and potassium in clay silicates and established that it was possible to obtain accurate results provided that the beam current was kept below 2nA, the counting times were kept below 200 seconds and that energy dispersive spectrometers were used, conditions that were not fully realised in the author's analyses, since the beam current was 5nA as required by the computer program used. The program was, therefore, modified by reducing the beam current to 2nA and extending the counting time to 150 seconds. These conditions did not, however, improve the results significantly; but the problem was finally solved when the stationary 20 μ m beam was changed to a scanning mode during the analyses at a magnification of $\times 4000$ times. The values obtained under these conditions were consistent with each other and with the results obtained by Norrish (1973) using X-ray fluorescence analysis.

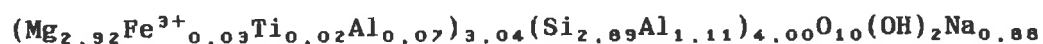
The new results (average of 5 analyses) obtained for the sodium saturated Llano, Phalaborwa and Young River vermiculites are given in Table 2.4.

Table 2.4: Electron Microprobe Analysis of Sodium Saturated Vermiculites

Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	Total
Llano	39.3	0.28	13.6	0.63	26.6	6.2	86.61
Phalaborwa	38.1	0.25	4.8	13.5	22.3	4.9	83.85
Young River	37.2		14.9	6.7	22.1	5.2	86.1

From the above results the following structural formulae were calculated.

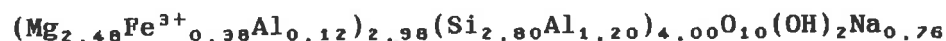
1. Llano vermiculite



2. Phalaborwa vermiculite



3. Young River vermiculite



The small variations in interlayer charge between the results obtained by Norrish (1.89, 1.58 and 1.46) and the results obtained by the author (1.76, 1.52 and 1.52) for the Llano, Phalaborwa and Young River vermiculites respectively, can be attributed to experimental errors present in both analytical techniques and to possible sampling problems, as the X-ray fluorescence analysis requires a much larger sample and gives an average result, while the microprobe analysis consists of point analyses of only several crystal flakes, the compositions of which are not necessarily exactly the same, as shown in Table 2.5, which gives the individual analyses of five different crystal flakes and not just their averaged values as given in the previous tables.

Table 2.5: Sodium Saturated Llano Vermiculite

Flake No.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	Total
1	38.3	0.19	13.3	0.53	26.2	6.6	85.12
2	38.9	0.37	13.7	0.71	26.7	6.5	86.88
3	39.1	0.29	13.2	0.68	26.3	5.9	85.47
4	39.9	0.27	13.7	0.72	26.9	6.5	87.99
5	40.1	0.28	14.0	0.53	27.1	5.7	87.71
Average	39.3	0.28	13.6	0.63	26.6	6.2	86.61

The anilinium intercalated vermiculites were also re-analysed but the new values did not differ significantly from those obtained previously.

2.3.3 Interlayer water content

The number of water molecules present in a unit cell (equal to 2 formula units) can be calculated by assuming that the amounts of water present in the samples are the difference between the oxide weight percent obtained from microprobe and microanalytical results and the total of 100%. Using these differences and the structural formulae, the number of water molecules per unit cell was thus calculated to be 6.46, 5.45 and 5.82 for the sodium saturated Llano, Phalaborwa and Young River vermiculites respectively. For the anilinium intercalated Llano, Phalaborwa and Young River vermiculites the figures were 5.31, 2.14 and 2.82 respectively. The accuracy of the last three figures was checked by measuring the densities and the unit cell volumes ($D_m=2.21$, 2.21 and 2.25 g cm⁻³ and $V=726.0$, 728.7 and 734.2 Å³ respectively) and knowing the weight percent of water (by difference) the numbers of water molecules per unit cell were calculated. These gave 5.24, 2.45 and 2.87 of water molecules per unit cell respectively; results which agree reasonably well with the values

obtained using only the analytical results.

The two different methods used above are, however, not fully independent since they both use the combined microprobe and microanalytical analyses in their calculations. Another approach was, therefore, also used, which relied only on the microanalytical results obtained for hydrogen, plus the measured density (D_m) and the volume (V) of the unit cell. Assigning the appropriate amounts of hydrogen to the anilinium cations and the hydroxyl groups the remainder was assumed to be due to water; this method gave values of 3.0, 1.9 and 0.95 for the anilinium Llano, Phalaborwa and Young River vermiculites respectively. These figures are very much lower than the ones obtained previously but they most probably represent only water coordinated to the inorganic cations as the samples were oven-dried at 100°C prior to the actual microanalyses.

2.4 Discussion

A closer inspection of the structural formulae of the anilinium intercalated vermiculites revealed that the interlayer charges are not exactly satisfied by the anilinium cations present. The interlayer charges for Llano, Phalaborwa and Young River vermiculites are 1.89, 1.58 and 1.46 (Norrish) and 1.76, 1.52 and 1.52 (the author), while the anilinium cation figures are 1.22, 1.52 and 1.72 respectively, which is less than the amount required for Llano, about right for Phalaborwa and too much for the Young River vermiculite. Therefore, to balance the layer charges completely some other inorganic cations must be present in the interlayer of the Llano vermiculite, none in the Phalaborwa, while some of the anilinium cations must be reduced to neutral aniline in the Young River vermiculite.

A further discrepancy is the small but significant increase in silicon in the anilinium intercalated vermiculites, as compared

to the sodium saturated varieties. This increase is at first sight unexpected because the silicon is situated in the tetrahedral sites, which are the most stable units in the silicate structure; however the explanation might be found in the fact that the anilinium intercalation was carried out in an acidic environment (the pH of the 1% aniline hydrochloride solution was 2.3) for prolonged periods and that some vermiculite dissolution would have taken place, especially of the octahedral cations, and thus reducing the number of cations in the silicate layers, with the resulting increase in the layer charge and a net increase in the silicon values. These dissolved octahedral cations would then compete with the anilinium cations in the intercalation process. The presence of magnesium and aluminium ions in the aniline hydrochloride solutions was reported during intercalation by Pisaniello (1984). The dissolution rates of the related mineral phlogopite were studied by Lin and Clemency (1981) in rain water saturated with carbon dioxide at a pH of 5 to 6. They reported the dissolution rates of various cations present and established that silicon was released by the least amount, a result consistent with the microprobe analyses, which show an apparent increase of silicon in the structural formulae of the anilinium, when compared with the sodium intercalated vermiculites. This apparent increase in the number of silicons is in effect a decrease in the number of octahedral cations, which are dissolved first, resulting in an increased number of silicon atoms when the structural formulae are calculated from their oxide weight percent values based on 11 oxygens and normal valencies; i.e. no cation deficiencies being assumed. This discrepancy is most pronounced in the Llano vermiculite, which was intercalated for 10 weeks as opposed to the usual 2 weeks, but is still observable in the other two vermiculites though to a much smaller degree.

Selected crystal flakes of the three anilinium intercalated vermiculites were next X-rayed, using Weissenberg and precession photography, to determine the degree of three-dimensional order,

the presence or otherwise of superlattice reflections and the general suitability of these materials for full X-ray structure determinations.

CHAPTER 3

ANILINIUM INTERCALATED VERMICULITES: X-RAY DATA COLLECTION

CHAPTER 3

ANILINIUM INTERCALATED VERMICULITES: X-RAY DATA COLLECTION

3.1 Introduction

Naturally occurring vermiculites often consist of several polytypes; they also usually contain a number of stacking disorders. Therefore, in addition to the normal crystal selection using light microscopy, the crystal flakes intended for full X-ray structure determination had to be initially examined using X-ray photographic techniques. Weissenberg and Buerger precession methods were used from which a considerable amount of information can be obtained by inspection and by simple measurements and calculations.

The first thing to establish in the crystals photographed was the presence of a superlattice, which would indicate an ordered stacking arrangement of the anilinium cations in the interlayer region. Next the degree of a regular stacking sequence of individual layers, shown by the sharpness of the reflections produced, especially of the $k \cdot 3n$ reflections, reveal the extent of three-dimensional order in the vermiculites photographed. The value of the d-spacings between the layers yields the periodicity of the materials along the c-axis. All these phenomena are immediately apparent on a Weissenberg or a precession photograph: the crystal system and the lattice parameters can also be easily obtained. For each vermiculite a number of crystal flakes had to be thus examined before one suitable for structure analysis was found.

Superlattice reflections, as well as three-dimensional ordering, were indeed found in the three intercalated vermiculites, though

the intensity of the superlattice reflections, and the degree of layer ordering varied somewhat between the three different vermiculites. The superlattice reflections and the residual disorders present, especially for the $k \neq 3n$ reflections showing irregular $\pm b/3$ interlayer shifts, are shown in Figures 3.1 to 3.3. The Young River vermiculite also revealed some splitting of the $0kl$ ($k \neq 3n$) reflections along the c^* direction. This phenomenon indicates a polytype with the c -axis being three times the normal interlayer value of about $15\text{\AA}$, i.e. about $45\text{\AA}$.

3.2 Apparatus and Techniques

3.2.1 The CAD4 diffractometer

The diffractometer used was an Enraf-Nonius computer assisted four-circle diffractometer (CAD4). The diffractometer's movements within the four circles were processed in terms of four angular settings which were linked to the computer. The three angles corresponding to crystal movements were labelled ϕ , κ and ω , where ϕ corresponded to the rotation of the goniometer head about its longitudinal axis. The detector's movement in the horizontal plane was described by the fourth angle θ . The four angles could be set manually or under computer control. The manual control of the first three angles was necessary for centering the crystal with respect to these angular movements.

The computer hardware consisted of a PDP-8/a(DEC) central processor with a hard disk, a Kennedy 9-track 800bpi magnetic tape drive and a Decwriter-II(DEC) hardcopy terminal which acted as the main user interface. The software operating system was OS8 and the program, called CAD4, and its subsidiaries were coded in FORTRAN-IV. The programs allowed for nearly all the necessary manipulations. For example, the systematic searching of reciprocal space for reflections, indexing these reflections and

FIG. 3.1 Zero level precession photograph of anilinium intercalated Llano vermiculite (CoK α radiation) showing $2a \times 2b$ superlattice reflections (faint spots marked S) formed by the anilinium ions.

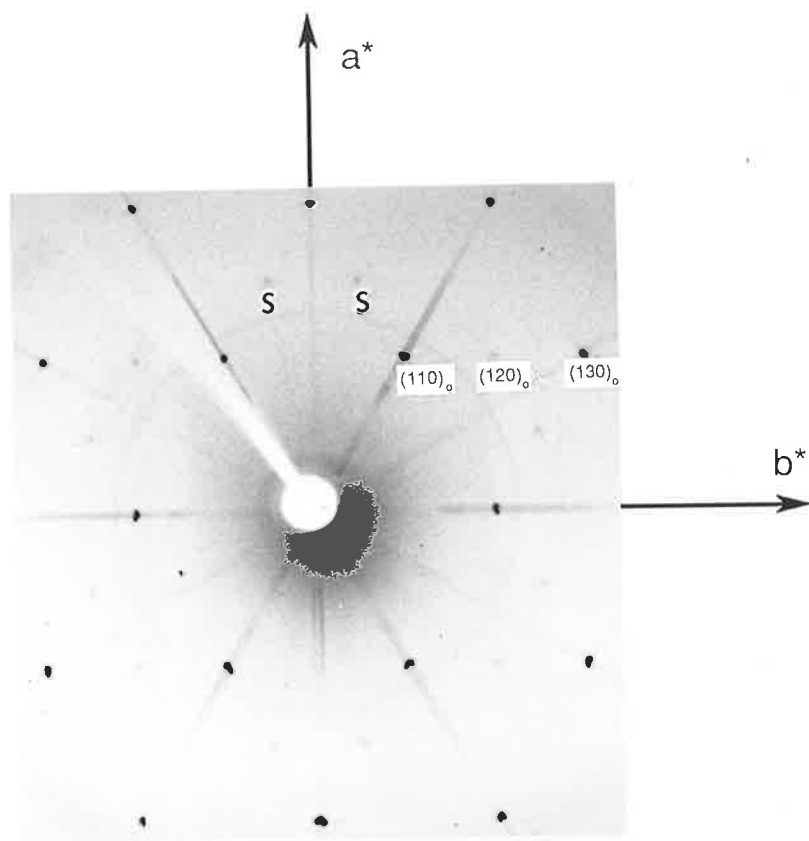


Fig. 3.1

FIG. 3.2 Zero level precession photograph of anilinium intercalated Young River vermiculite (MoK α radiation) showing sharp (hk0) reflections (vermiculite) and fainter $2a \times 2b$ superlattice reflections due to anilinium ions (marked S).

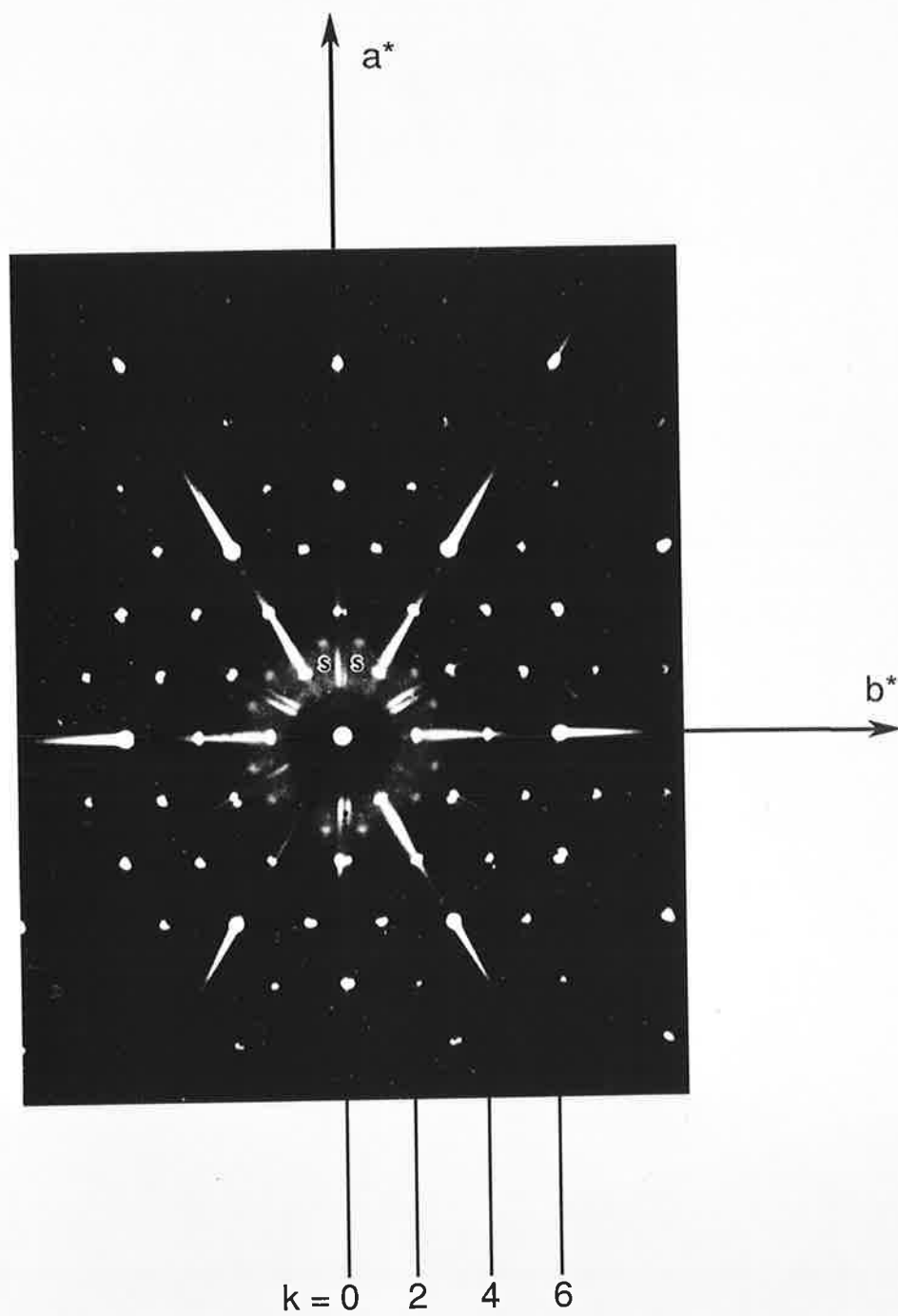


Fig. 3.2

FIG. 3.3 Zero level precession photograph of aninilium intercalated Young River vermiculite (MoK α radiation) showing some layer disorder and splitting of 0kl ($k \neq 3n$) reflections along c^* direction (arrowed).

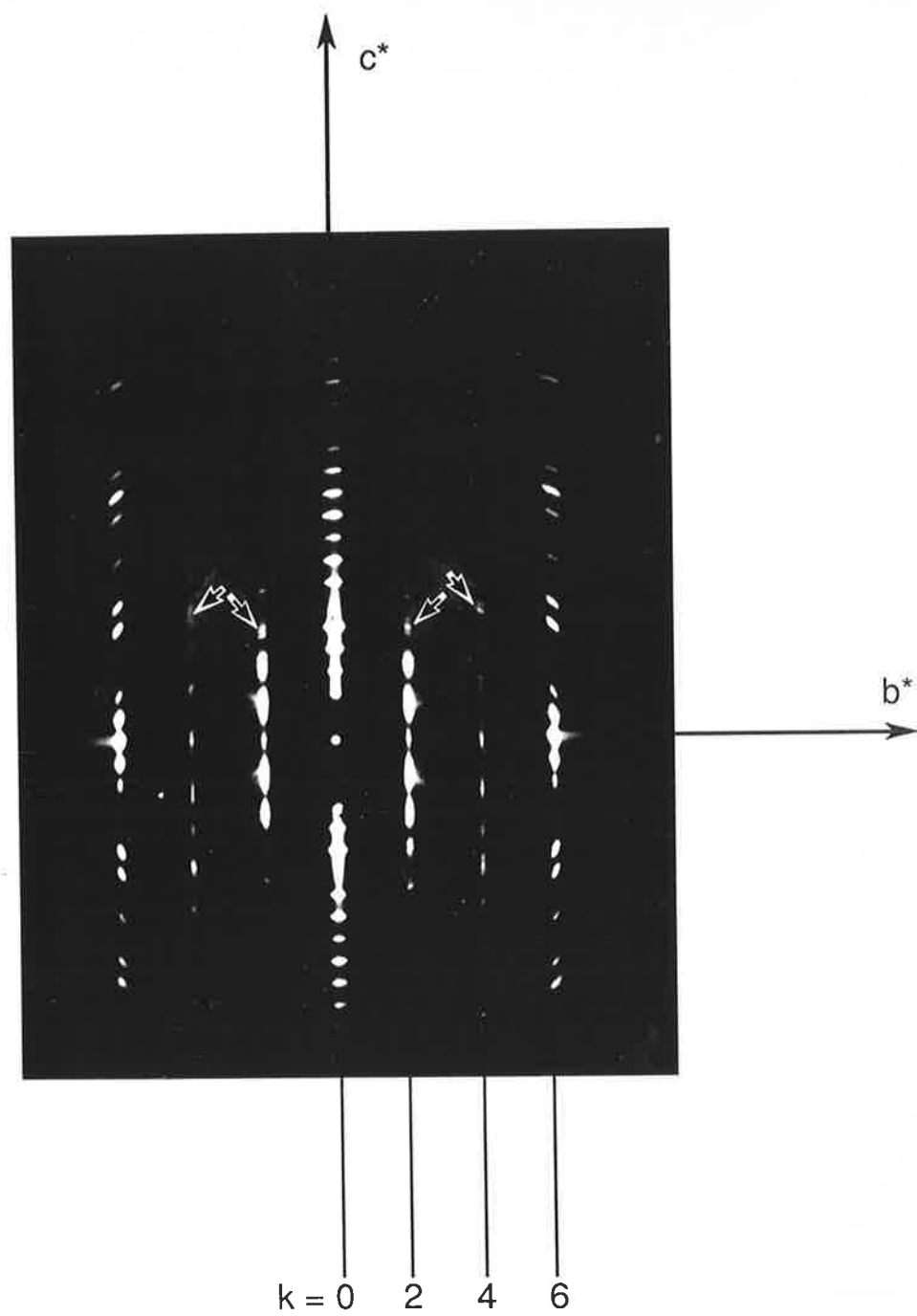


Fig. 3.3

calculating the unit cell, obtaining an intensity distribution of a reflection, various vector and matrix calculations and the collection of reflection intensities. The intensities of up to 9000 reflections could be temporarily stored on disk before being transferred to a VAX computer via magnetic tape.

The X-ray source was a Mo fine-focus tube, running at 50kV and 25mA, and the beam was monochromated by a curved graphite crystal to give MoK α radiation ($\lambda=0.71073$).

3.2.1.1 Unit cell parameters and orientation determination

To find the cell parameters and orientations of the crystals the diffractometer searched systematically through separate areas of reciprocal space to find up to 25 reflections, centre them, and record their setting angles and intensities. The CAD4 program then computed the indices of these reflections and the unit cell parameters and orientations giving a primitive unit cell. If the computed unit cell was not considered suitable, the program provided a choice of other possible cells from a list of 10 alternatives. If the second cell chosen still appeared unsatisfactory then the unsatisfactory reflections, e.g. especially broad ones (with large scan angles) or low intensities could be deleted and more reflections from another region of space collected. A new cell would then be computed and compared with the first cell until a satisfactory unit cell was found.

If the unit cell of the crystal studied was known from previous work, or from photographic studies, and if the setting angles of two reflections were known, or if one reflection and the crystal orientation was known, then an orientation matrix was computed by the CAD4 program and the random search through reciprocal space to find reflections could be omitted. The next step was to refine the orientation matrix by least-squares procedures, which gave more accurate unit cell parameters and their standard

deviations, as well as the intensities of the reflections, their indices, their setting angles and the angular deviations between the computed and measured positions of these reflections.

3.2.1.2 Data collection

The CAD4 data collection program allowed a large number of parameters to be varied to suit the conditions of the particular crystal studied. The measurements of each reflection consisted of a pre-scan and a second final scan if required. The speed of the pre-scan, and the accuracy of the intensity measured for the final scan could be stipulated by stating the intensity (I) required below which reflections would not be recorded. After the pre-scan the speed of the final scan was computed by the CAD4 program to give the required accuracy with an upper time limit of 10 minutes per reflection. A final scan could always be forced on the system if weak reflections were expected which might not be detected in the pre-scan.

The scan angle through which each reflection was measured could be varied by stating the omega (ω) scan angle, and its increase with theta (θ), to account for the crystal mosaic spread, the divergence of the primary X-ray beam and the widening of the reflection due to split-up in theta. The horizontal aperture scan could also be varied in the same manner as the omega scan. The vertical aperture consisted of a number of fixed manually inserted slits. The type of scan available consisted of a pure omega (ω) scan (a moving crystal method - no theta movement), or a variable omega/two theta ($\omega/2\theta$) scan (a moving crystal and a moving detector method) with a maximum two theta speed equal to omega. A facility for analysing the shape of a reflection, which consisted of carrying out omega and theta scans simultaneously and printing the profiles of these reflections, enabled one to choose the most appropriate scan type for the crystal under investigation. The actual range of the reflections to be

measured could be selected stating the minimum and maximum theta limits, or the range of Miller indices. The presence of systematic absences could also be entered to speed up the data collection process. For columnar or platelet crystals the data collection could be set to proceed in such a way as to scan with a different unit cell orientation for each reflection measured, so that absorption effects were minimised. Intensity and orientation checks could be performed at stipulated intervals during the data collection to correct for crystal decomposition and movement respectively. The information, recorded on disk during the data collection, was transferred via magnetic tape to the Cyber or VAX computers for processing.

3.2.2 The CAD4 low temperature device

The CAD4 diffractometer possessed a cooling device, designed by Enraf-Nonius especially for the CAD4 diffractometer. This apparatus allowed the crystals to be cooled to approximately -140°C by a stream of cold dry nitrogen gas. The cold stream was surrounded by a stream of warm dry nitrogen to prevent ice formation on the crystal, and to stabilise the cold stream and hence the temperature of the crystal being cooled. The velocity and temperature of both streams were adjustable by an electronic control box. Both the cold and warm streams were supplied by heating liquid nitrogen in the same 5 litre Dewar, which was automatically refilled from a 75 litre Dewar acting as a reservoir.

The temperature of the crystal X-rayed, which was placed about 5 mm from the tip of the nitrogen gas nozzle, was measured with a copper-constantan thermocouple, the cold junction of which was situated about 2 mm outside the gas nozzle. The temperature was read by a digital temperature reader manufactured by Anritsu Meter Co. Ltd. This low temperature device was calibrated by placing a chromel-alumel thermocouple in the position usually

taken by the crystals and reading the temperature with another digital temperature reader.

To overcome any ice formation on the crystal being cooled it was necessary to seal the box containing the X-ray tube, the four circle diffractometer and drive mechanisms and to keep this box under a positive pressure of dry nitrogen. Some moisture, however, still found its way into the box so that dishes containing P_2O_5 desiccants had to be placed within the box to minimise the amount of water present.

3.3 Experimental

3.3.1 Llano vermiculite - initial study

The crystal of anilinium intercalated Llano vermiculite chosen for X-ray data collection with the CAD4 diffractometer was selected from a number of crystals examined by Weissenberg and precession methods. Zero level photographs showed that this material was monoclinic, containing only a single silicate layer ($c=14.8\text{\AA}$). Upper level Weissenberg photographs about the a -axis, however, revealed not only b^* curving, as expected for a monoclinic unit cell, but also a slight curvature in c^* , making the unit cell triclinic. The crystal finally chosen was the one containing the least streaking along the c^* direction, the smallest number of stacking faults and displaying pronounced superlattice reflections. This crystal was $0.67\times0.57\times0.02$ mm in size. The unit cell parameters were determined by searching the reciprocal space for 25 reflections, from which the lattice cell parameters were calculated, using least-squares refinement. The unit cell parameters and their standard deviations are given in Table 3.1.

Table 3.1: Cell Parameters of Anilinium Intercalated Llano Vermiculite

```
=====
Triclinic C1,  a=5.347(7),  b=9.27(1),  c=14.76(2)Å,
α=89.5(1),  β=96.4(1),  γ=89.9(1)°.  V=726.5Å³,  Z=2,
Dm=2.21,  Dx=2.30 g cm-3,  μ=8.39 cm-1 (MoKα).
=====
```

The X-ray data collection was carried out using the minimum absorption method, a facility available on CAD4 which orients the crystal in such a way as to minimise the loss of reflection intensity due to X-ray absorption effects. As the vermiculite crystals are flat (001) plates, the minimum absorption method requires the (001) plane to be perpendicular to the X-ray beam during a reflection measurement, a condition also required for scanning the crystal perpendicular to c^* , which was also the direction of maximum spread of the reflections. This technique minimised the possibility of neighbouring reflections overlapping each other and interfering with the data collection.

Utilising the CAD4 facility of drawing two-dimensional profiles of omega and two theta scans it was determined that the omega/two theta scans were most appropriate for the crystal studied. The omega scan angle was set to $(1.0 + 2.0\tan\theta)^\circ$ and the horizontal aperture width to $(3.0 + 2.0\tan\theta)\text{mm}$. The space group chosen was P1 with the additional condition of C-centering. Data were collected in the theta range of 1.3 to 37.0°, with the index ranges: $0 \leq h \leq 6$, $-10 \leq k \leq 10$, $-26 \leq l \leq 26$. The crystal orientation was checked after every 100 reflections, and an intensity check was carried out by measuring the same three reflections after every 4000 seconds of X-ray exposure time. Reflections (h+k) odd, absent in C-centered cells, were not collected. The maximum time spent on measuring one reflection was 250 seconds. 2237 unique reflections were measured, out of which 639 reflections were suppressed ($|F| < 2.5\sigma|F|$), leaving 1598 reflections to be used in

the structure refinement process. Data reduction for Lorentz and polarization effects and linear absorption corrections were applied using the programs SUSCAD (Guss, 1979) and ABSORB (Guss, 1980) respectively.

The structure refinement was carried out using the program SHELX (Sheldrick, 1976). The initial positional parameters of the silicate layer atoms were taken from Slade and Stone (1984). The position of one octahedral cation (0, 1/2, 0) was fixed in all refinements. Using unit weights, fixed site occupancies and isotropic temperature factors, and only the silicate layer atoms, the structure refined to $R=23.6\%$ ($R=\sum(|F_o|-|F_c|)/\sum|F_o|$). Using anisotropic temperature factors and a weighting scheme, the R factor fell to 18.7%, but some of the temperature factors became non positive definite.

The structure was not refined any further as at this stage new improved X-ray data became available from P.G. Slade of CSIRO, Division of Soils, Urrbrae, South Australia, which were collected with great care over a period of some months. This superior set of data was used in a new structure refinement and the full silicate structure, plus its interlayer anilinium positions were determined; these results are reported in Chapter 4. Using the atomic coordinates and thermal parameters obtained with the CSIRO data the CAD4 data were refined again, this time giving an R factor of 15.8%, but still some of the thermal parameters were found to be non positive definite, therefore the refinement of the CAD4 data was not pursued any further and no final results are reported in this thesis.

3.3.2 Phalaborwa vermiculite

The crystal of anilinium intercalated Phalaborwa vermiculite chosen for X-ray data collection with the CAD4 diffractometer was again selected using Weissenberg and precession methods. The

crystal was found to be triclinic and to contain superlattice reflections. As the CAD4 diffractometer possessed a cooling device it was decided to cool the crystal to reduce the thermal motions of the anilinium cations and thus make their positions easier to determine. It was known from the microchemical analysis that there were only 1.5 anilinium cations per unit cell, and as there were four available sites, plus two probable orientations for each site (Slade and Stone, 1984), the electron density of a carbon atom could be as low as 1.1 electron and hence difficult to detect at room temperature.

The crystal chosen was glued to a thin glass rod with a silicone rubber sealant (Silastic), as the common glues were found to be too brittle at low temperatures. The crystal size was $0.69 \times 0.66 \times 0.01$ mm. The crystal was oriented on the CAD4 at room temperature (25°C). The orientation and lattice parameters were determined by least-squares refinement, based on the setting angles of 25 unique reflections collected at theta between 18 and 42° . Using the Enraf-Nonius low temperature equipment (section 3.2.2) the crystal was cooled slowly to -97°C : its orientation and lattice parameters were re-measured at 30°C intervals during cooling. The temperature of the crystal was maintained at $-97 \pm 5^\circ\text{C}$ during all the data collection. The unit cell parameters and their standard deviations are given in Table 3.2.

Table 3.2: Cell Parameters of Anilinium Intercalated
Phalaborwa Vermiculite

=====

Triclinic C1, $T=25^\circ\text{C}$, $a=5.360(1)$, $b=9.292(2)$, $c=14.832(6)\text{\AA}$,
 $\alpha=89.81(4)$, $\beta=96.71(4)$, $\gamma=90.03(2)^\circ$, $V=734.2\text{\AA}^3$, $D_m=2.20$,
 $D_x=2.247\text{ g cm}^{-3}$, $\mu=12.39\text{ cm}^{-1}$ (MoK α).

$T=-97^\circ\text{C}$: $a=5.363(2)$, $b=9.291(3)$, $c=14.808(5)\text{\AA}$, $\alpha=89.87(5)$,
 $\beta=96.66(5)$, $\gamma=89.95(3)^\circ$, $V=732.9\text{\AA}^3$.

=====

The X-ray data collection was carried out using the minimum absorption method (see section 3.2.1.2). The omega-theta profiles of three typical reflections indicated that the maximum balanced intensity could be obtained with omega/two theta scans. The omega scan angle was set to $(1.2 + 2.3 \tan \theta)^\circ$ and the horizontal aperture width to $(3.0 + 1.0 \tan \theta) \text{ mm}$. The space group chosen was P1, with the additional condition of C-centering. Data were collected in the theta range of 1.3 to 30.0° , with the index ranges: $0 \leq h \leq 6$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$. The crystal orientation was checked after every 200 reflections and an intensity check was carried out after every 3600 seconds of X-ray exposure time. Reflections $(h+k)$ odd, absent in C-centered cells, were not collected. The maximum time spent on measuring one reflection was 600 seconds. Reflections unique to the supercell ($2a \times 2b$) were not detected. Of the 1911 unique reflections measured, 62 were suppressed ($|F| < 2\sigma|F|$), leaving 1849 reflections for the structure refinement process. Data reduction for Lorentz and polarization effects were applied using the program SUSCAD (Guss, 1979), and for linear absorption corrections the program ABSORB (Guss, 1980) was used.

3.3.3 Young River vermiculite

The crystal of anilinium intercalated vermiculite chosen for X-ray data collection with the CAD4 diffractometer was selected using Weissenberg and precession methods. The crystals were found to contain a single silicate layer, to be triclinic and to contain strong superlattice reflections. The crystal from which the X-ray data were finally collected was $0.60 \times 0.40 \times 0.05 \text{ mm}$ in size. The orientation and lattice parameters were determined by least-squares refinement, based on the setting angles of 25 independent reflections collected at theta angles between 24 and 43° . The unit cell parameters and their standard deviations are given in Table 3.3.

Table 3.3: Cell Parameters of Anilinium Intercalated
Young River Vermiculite

```
=====
Triclinic C1,    a=5.343(1),    b=9.255(5),    c=14.85(6)Å,
α=89.91(5),    β=95.30(5),    γ=90.00(4)°,    V=728.7Å³,    Dm=2.21,
Dx=2.209 g cm-3,    μ=8.84 cm-1 (MoKα).
=====
```

The X-ray data collection was carried out using the minimum absorption method and omega-theta profiles carried out on the three typical reflections again indicated that the maximum balanced intensity would be obtained with omega/two theta scans. The omega scan angle was set to $(1.2 + 2.3\tan\theta)^\circ$ and the horizontal aperture width to $(3.0 + 1.0\tan\theta)\text{mm}$. The space group chosen was P1, with the additional condition of C-centering. Data were collected in the theta range of 1.3 to 30.0° , with the index ranges: $0 \leq h \leq 6$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$. The crystal orientation was checked after every 200 reflections and an intensity check was carried out after every 3600 seconds of X-ray exposure time. Reflections $(h+k)$ odd, absent in C-centered cells, were not collected. The maximum time spent on measuring one reflection was 600 seconds. Reflections unique to the supercell ($2a \times 2b$) were detected but could not be measured with adequate accuracy. Of the 2315 unique reflections measured, 232 were omitted ($|F| < 2.5\sigma|F|$), leaving 2083 for structure refinement. Data reduction for Lorentz and polarization effects were applied using the program SUSCAD (Guss, 1979), and for linear absorption corrections the program ABSORB (Guss, 1980) was used.

3.3.4 Llano vermiculite - CSIRO data

At the time when X-ray data were being collected on the three anilinium intercalated vermiculites with the CAD4 diffractometer, X-ray data were also being collected by P.G. Slade at CSIRO, Division of Soils, Urrbrae, South Australia, on a crystal of

anilinium intercalated Llano vermiculite using a two-circle Supper diffractometer. This CSIRO data collection was carried out with great care over an extended period of time in order to obtain the very best possible results.

The crystal chosen for the data collection with the Supper diffractometer was first examined with the Weissenberg and precession methods. It was found to be triclinic with C-centering. Its size was $0.90 \times 0.53 \times 0.02$ mm. Equi-inclination geometry was used to record data from five reciprocal lattice layers along the [100] rotation axis. The index ranges were: $0 \leq h \leq 4$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$. An omega/two theta step-scan mode and filtered $\text{MoK}\alpha$ radiation were employed. To increase the reliability of the intensity measurements, especially for the weak reflections, which comprised a very significant portion of the total diffraction pattern, counting was prolonged between 30 and 100 seconds at each 0.05° step of the scan range ($\Delta\omega$). $\Delta\omega$ was varied according to the formula of Guss *et al.* (1970). Of the 1928 unique reflections measured, 1825 were above zero intensity. Experimental intensities were corrected for Lorentz and polarization effects and linear absorption. The transmission factors ranged between 0.95 and 0.70. The space group assumed for the data collection was P1, with the additional condition of C-centering. The unit cell parameters and their standard deviations are given in Table 3.4.

Table 3.4: Cell Parameters of Anilinium Intercalated Llano Vermiculite

=====					
Triclinic C1,	$a=5.326(3)$,	$b=9.264(4)$,	$c=14.82(5)\text{\AA}$,		
$\alpha=99.31(7)$,	$\beta=96.70(6)$,	$\gamma=89.55(5)^\circ$,	$V=726.02\text{\AA}^3$,	$Z=2$,	
$D_m=2.21$,	$D_x=2.30 \text{ g cm}^{-3}$,	$\mu=8.39 \text{ cm}^{-1}$	(MoK α).		
=====					

CHAPTER 4**ANILINIUM INTERCALATED VERMICULITES:
STRUCTURE SOLUTION AND REFINEMENT**

CHAPTER 4

ANILINIUM INTERCALATED VERMICULITES:
STRUCTURE SOLUTION AND REFINEMENT

4.1 General Technique

The program SHELX (Sheldrick, 1976) was used for structure solution and refinement. The starting model was that given by Slade and Stone (1984), and initially only the silicate layer atoms were refined, as these are known to represent at least 70% of the total scattering power. Once the structure converged to a reasonable R value, the interlayer material was substituted as it appeared in the electron difference Fourier maps produced by the peak search routine in SHELX. The interlayer region, however, contained a large number of peaks which were often too small or diffuse to be detected by SHELX, peaks due to labile water, remaining inorganic cations, disordered intercalated material, or peaks due to structural defects, so that contoured difference maps had to be plotted to unravel the structure more fully. The program used to obtain the contoured difference maps was written by C. Dean of the Physical and Inorganic Chemistry Department, University of Adelaide.

The program, called SHECON, instructed SHELX to print out maps in numerical format at specified intervals along any of the three axes of the unit cell. These maps were, however, intercepted before they were printed and their contents transcribed for input into a contouring algorithm, using the contouring program CONTOR (Lilly, 1975) converted to FORTRAN-77. The program SHECON thus consisted of an interface between SHELX and CONTOR. The SHECON program contained the feature which allowed one to specify any desired plane in the unit cell and data points up to any desired

distance from that plane could be projected onto it. Contour maps of any plane, specified by three points, could thus be plotted. The contouring package was used on both the CYBER and VAX computers and plotted on the Calcomp and Nicolet-Zeta plotters. For drawing crystal structures the program PLUTO78 (Motherwell, 1978), designed for drawing molecular structures, and the more general program ORTEP-II (Johnson, 1976), designed for drawing any type of structure, were used. The program ORTEP-II was modified by C. Dean to allow drawing of planes, such as faces of silicate tetrahedra, and to allow various shading of the atoms.

During refinement the pseudo-monoclinic symmetry of the structures resulted in large correlations between some of the variables and in order to reduce them it was necessary to apply damping during least-squares refining. A damping factor of 500 was used, which made the reduction in the R factor after about four cycles of refinement comparable to one cycle of undamped refinement. Fully ionised scattering factors were assigned to the metallic elements (International Tables for X-ray Crystallography, 1974); the scattering factor for the oxygen atoms belonging to the silicate layers was O^{2-} (Tokonami, 1965). The scattering factors used for the water and anilinium cations were those for the neutral atoms (program SHELX, Sheldrick, 1976). The site occupancy factors were in accordance with the values obtained for the structure formulae from the chemical analyses.

Atoms of the same element were mostly given a common isotropic temperature factor, with the exception of the atoms found in different coordination environment. For example, the temperature factor for the tetrahedral (surface) oxygens was not tied to that for the octahedral oxygens. All the temperature factors were isotropic; group rather than individual temperature factors were usually assigned because the anisotropic diffuseness of the electron density peaks indicated that the structures possessed a

low degree of crystallinity and therefore did not warrant individual thermal parameters. Also the number of reflections (observations) did not permit the use of additional variables. For some atoms in disordered sites it was also necessary to refine both the site occupancy factors and the thermal parameters.

4.2 Phalaborwa Vermiculite

The initial structure solution consisted of refining only the silicate atoms; their starting positions were the ones given by Slade and Stone (1984). After 25 cycles of least-squares refinement of these positional coordinates, their thermal parameters and the overall scale factor, the R value converged to 24.7%. The largest remaining peaks in the difference list calculated by SHELX were present in the silicate layer and corresponded to irregular layer shifts by approximately $\pm b/3$, with smaller shifts of $\pm na/5$, where $n=1$ to 4, also being evident (see Figure 4.1a). The irregular displacement of silicate layers by $\pm b/3$ commonly occurs in vermiculites to a greater or lesser extent, see for example Shirozu and Bailey (1966). Since in the fully ordered structure the octahedral magnesium atoms are separated by $\pm b/3$, no extra peaks were present due to these irregular $\pm b/3$ layer shifts. Likewise no extra apical oxygen peaks were involved. The strongest additional peaks, due to these irregular $\pm b/3$ displacements, were from the tetrahedral silicon and aluminium atoms because these atoms were separated by approximately $2b/3$ and so the $\pm b/3$ displacements overlapped. The surface oxygens also appeared as extra peaks. The actual displacements in any one direction were not exactly the same for all atoms, and it was therefore not possible to model the displacements by a rigid group translation. Consequently the coordinates of these additional atoms were refined individually. These shifts refined to approximately $\pm 0.31b$ rather than the ideal $\pm b/3$. The refinement of the site occupancy of the atoms in

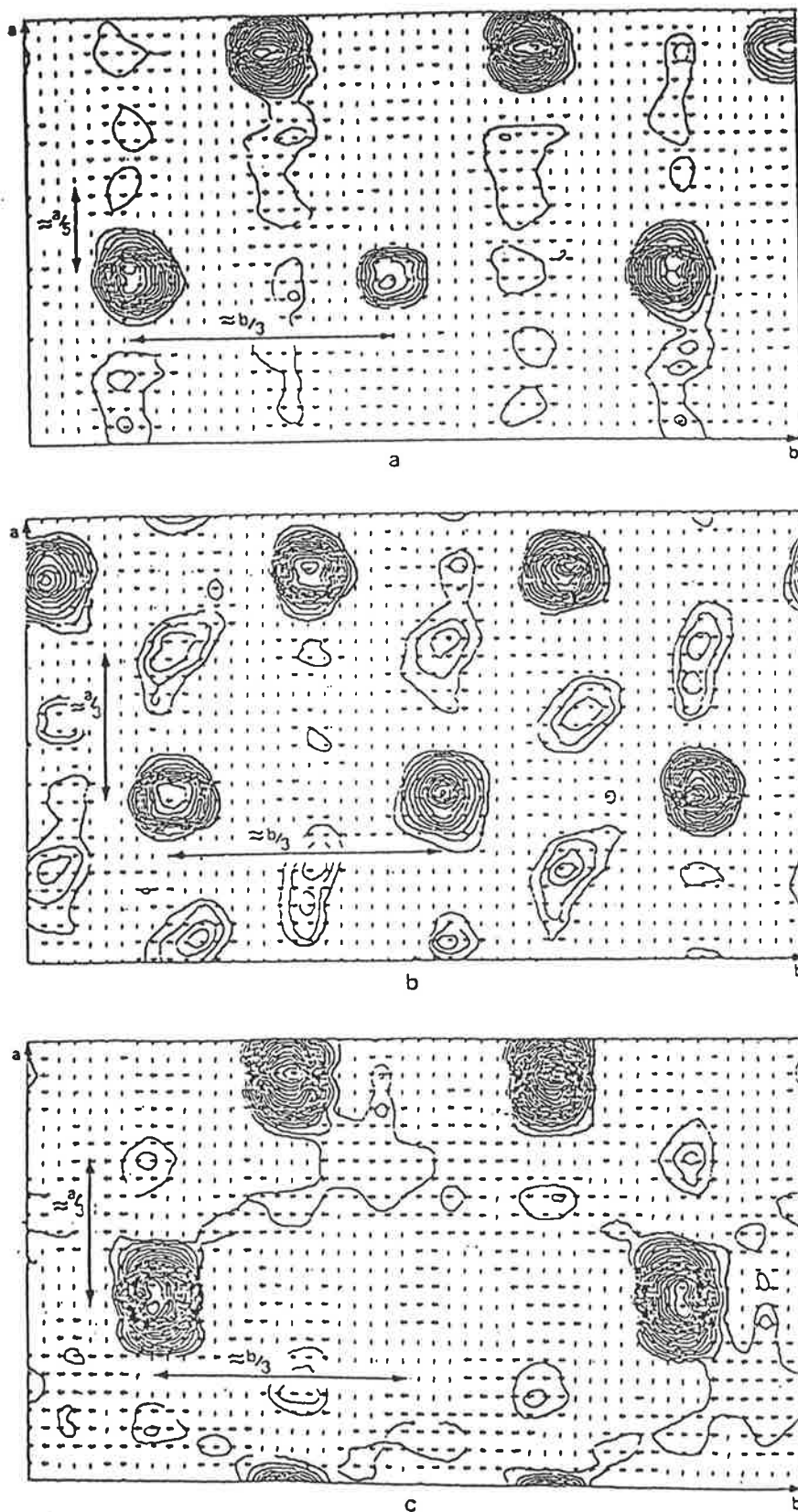


FIG. 4.1

Contoured difference Fourier sections parallel to (001) at the level of the Si (tetrahedral) atoms ($z=0.18$) in anilinium (a) Phalaborwa, (b) Young River and (c) Llano vermiculites. The maps show the amounts of translational disorder of the silicate layer parallel to the a - and b - axes. The contour intervals are (a) $0.50 \text{ e } \text{\AA}^{-3}$, (b) $0.22 \text{ e } \text{\AA}^{-3}$ and (c) $0.96 \text{ e } \text{\AA}^{-3}$. The most intense peaks (4 on each map) correspond to the original, untranslated atoms.

the $\pm b/3$ shifts revealed the proportion of the silicate layer which translated along b to be 0.22. The occupancy for atoms at the $\pm a/5$ positions was 0.03. Due to the large number of atoms involved in the $\pm na/5$ shifts and their small site occupancy only atoms with $n=1$ were refined. After refinement of all the above mentioned atoms in the silicate layer region the R value dropped to 22.8%.

The peaks present in the interlayer region were investigated using contoured difference maps. The interlayer electron density could be divided into peaks due to the intercalated anilinium ions and peaks due to hydrated inorganic cations. The interlayer inorganic cations and their associated waters gave a packing arrangement which was very similar to that given for Mg-Llano vermiculite by Shirozu and Bailey (1966); however, there were some substantial positional deviations from their values. In their Mg-vermiculite the interlayer Mg^{2+} ions were in the middle of the interlayer region ($z = 0.5$) with the water molecules lying in two sheets on either side of the plane at $z = 0.5$. In the anilinium intercalated material investigated here the metallic cations were split into two adjacent sites, on either side of the mid-plane with the associated spreading of their water sites. Water sites were also present in the middle of the interlayer region such that their positions were primarily projections of their positions from either side of the mid-plane.

Due to the large amount of disorder, the inorganic cation-water system could not be properly modelled and refined. However, four magnesium and eight water molecules were placed at the positions of sharp maximum electron density. The interlayer inorganic cations were assigned the scattering curve of Mg^{2+} and their thermal parameters were fixed at $U = 0.02$; the interlayer water sites were assigned the scattering curve of neutral oxygen and their thermal parameters were fixed at $U = 0.05$. The interlayer Mg^{2+} ions were given a common site occupancy factor to be refined and similarly for the water molecules. A weighting scheme was

incorporated in which reflections were given weights (w), where $w=k/(\sigma^2 F_o + |g|F_o^2)$ and k and g were given random values and then refined. The R factors reduced to $R=20.3\%$ and $R_w=21.4\%$. The total site occupancies of the interlayer Mg^{2+} and water were 0.4 and 1.9 respectively per unit cell.

The aminium groups $[NH_3]^+$ of the anilinium cations were known to lodge themselves into the ditrigonal holes formed by the surface oxygens of the silicate layers in the vermiculites (Slade and Stone, 1984). The nitrogen atoms of the anilinium cations were therefore expected to be present above the ditrigonal holes. Since there are four ditrigonal cavities in the unit cell, there are four sites to which the aminium groups can attach themselves. Two are over the ditrigonal cavities near the base of the cell and two are below the cavities near the top of the cell. The ditrigonal cavities are centred over one another and consequently so are the aminium groups. Due to the C-centering of the cell, these four positions reduce to two unique ones; one near the base of the cell and one near the top. The largest remaining peaks in the difference Fourier map calculated by SHELX were possible positions of the nitrogen atoms from the two anilinium ions. These nitrogen atoms were assigned an isotropic thermal parameter of $U=0.05$ and their positions and site occupancies refined. The resulting site occupancies, for the individual lower and upper nitrogen atoms (named N(1) and N(2) respectively) were both 0.27, which implied a total of 1.1 anilinium ions per unit cell. The positions of the ipso carbons (named C(1) and C(12)) of the anilinium ions were in such positions with respect to the nitrogens as to imply that the planes of the aromatic rings were approximately perpendicular to the planes of the silicate layers and therefore placed the para carbon atoms (named C(4) and C(42)) near the nitrogens and ipso carbons of the opposing rings. The para carbon atoms were in fact located in the predicted positions on the contoured difference maps. The closeness of the various carbon and nitrogen atoms meant that the anilinium cations had to be refined as rigid groups in their idealised positions. The

nitrogen to ipso carbon distances chosen were 1.32Å. The ortho and meta carbon atoms (the "wing" carbons) of the anilinium ions could not be clearly located in the contoured difference maps and they were placed in their geometrically correct positions with a C-C distance of 1.395Å using SHELX. The aromatic hydrogens were also included and placed in their ideal positions with C-H=1.08Å. Due to the likelihood of different planar orientations of the anilinium cations, the "wing" carbon and hydrogen atoms were assigned site occupancies of half the occupancy of the nitrogen and the ridge (ipso and para) carbon atoms. The thermal parameters of the atoms in the anilinium ions were set at $U=0.05$. The two geometrically ideal anilinium ions were then refined as rigid groups. The final positions of the "wing" carbon atoms were close to some of the interlayer water sites and consequently no definite set of coordinates could be assigned for them. The final R values for this anilinium intercalated Phalaborwa vermiculite were $R=19.0\%$ and $R_w=20.2\%$. For the weighting scheme k and g refined to 5.53 and 0.0085 respectively. Selected atomic coordinates and bond lengths are given in Tables 4.1-4.2. The list of observed and calculated structure factors is given in Appendix A.1.

Inspection of the nitrogen-oxygen distances in Table 4.2 shows that the anilinium cations are embedded in the ditrigonal holes formed by the surface oxygens. The anilinium cations are in fact hydrogen bonded to one of the triad of the surface oxygens with a N-H-O distance of about 2.90Å. The positional parameters of the nitrogens and the ipso and para carbons show the anilinium cations to be virtually perpendicular to the silicate layers. However, the inability to locate the ortho and meta carbons does not allow one to state the orientation of the plane of aromatic rings due to the large amount of water present in this sample. Contoured difference maps revealed many more diffuse low density peaks in the interlayer region, which are most probably due to labile water present in the sample, in addition to the water coordinated around the inorganic cations.

Table 4.1: Positional and Temperature Parameters for Phalaborwa Vermiculite-anilinium Intercalate

	x	y	z	U
Mg(1)	.000	.5000	.0000	.004(1)
Mg(2)	.001(1)	.8334(6)	.0005(4)	.004(1)
Mg(3)	.001(1)	-.8332(6)	.0003(4)	.004(1)
O(1)	.867(2)	-.014(1)	.072(1)	.003(1)
O(2)	-.842(2)	-.011(1)	-.073(1)	.003(1)
O(3)	.374(2)	.153(1)	.075(1)	.003(1)
O(4)	.377(2)	-.180(1)	.075(1)	.003(1)
O(5)	-.339(2)	.156(1)	-.077(1)	.003(1)
O(6)	-.346(2)	-.178(1)	-.076(1)	.003(1)
T(1)	.416(1)	.1475(7)	.1874(5)	.009(1)
T(2)	.409(1)	.8343(7)	.1879(5)	.009(1)
T(3)	.616(1)	.1725(7)	.8143(5)	.009(1)
T(4)	.622(1)	.822(7)	.8140(5)	.009(1)
O(7)	.147(3)	.222(2)	.226(1)	.012(1)
O(8)	.173(3)	-.242(2)	.228(1)	.012(1)
O(9)	-.120(3)	.227(2)	-.227(1)	.012(1)
O(10)	-.139(3)	-.241(2)	-.227(1)	.012(1)
O(11)	.454(3)	-.008(2)	.226(1)	.012(1)
O(12)	-.426(3)	-.009(2)	-.225(1)	.012(1)
N(1)	.478(4)	.483(4)	.330(3)	.050
C(1)	.520(4)	.492(4)	.419(3)	.050
C(4)	.598(4)	.510(4)	.607(3)	.050
N(2)	.571(4)	.485(4)	.672(3)	.050
C(12)	.568(4)	.483(4)	.584(3)	.050
C(42)	.561(4)	.473(4)	.396(3)	.050
Cat(1)	.506(4)	.165(4)	.495(4)	.050
Cat(2)	.521(4)	.134(4)	.524(4)	.050
Cat(3)	.453(4)	.491(4)	.501(4)	.050
Cat(4)	.514(4)	.830(4)	.474(4)	.050
H ₂ O(1)	.850(4)	.470(4)	.438(3)	.050
H ₂ O(2)	.189(4)	.471(4)	.568(3)	.050
H ₂ O(3)	.864(4)	.486(4)	.522(3)	.050
H ₂ O(4)	.270(4)	.182(4)	.408(3)	.050
H ₂ O(5)	.355(4)	.291(4)	.491(3)	.050
H ₂ O(6)	.662(4)	.420(4)	.518(3)	.050
H ₂ O(7)	.318(4)	.638(4)	.508(3)	.050
H ₂ O(8)	.646(4)	.715(4)	.476(3)	.050

Table 4.2: Bond Distances (Å) for Silicate and Nitrogen and Surface Oxygen Atoms

Atoms	Distance	Atoms	Distance	Atoms	Distance
Mg(1)-O(3)	2.10(2)	T(1)-O(11)	1.55(3)	N(1)-O(8)	2.87(5)
-O(2)	2.02(2)	-O(3)	1.66(3)	-O(7)	2.89(5)
-O(5)	2.08(2)	-O(7)	1.77(3)	-O(11)	3.03(5)
-O(1)	2.13(2)	-O(8)	<u>1.77(3)</u>	-O(11)	3.13(5)
-O(4)	2.14(2)	mean	1.69	-O(8)	3.28(5)
-O(6)	<u>2.23(2)</u>			-O(7)	3.29(5)
mean	2.12				
		T(2)-O(11)	1.59(3)		
		-O(8)	1.62(3)	N(2)-O(10)	2.87(5)
Mg(2)-O(1)	1.97(2)	-O(4)	1.67(3)	-O(12)	2.93(5)
-O(2)	2.04(2)	-O(7)	<u>1.68(3)</u>	-O(9)	2.97(5)
-O(6)	2.06(2)	mean	1.64	-O(9)	3.17(5)
-O(3)	2.15(2)			-O(12)	3.23(5)
-O(4)	2.18(2)			-O(10)	3.27(5)
-O(5)	<u>2.26(2)</u>	T(3)-O(5)	1.61(3)		
mean	2.11	-O(10)	1.63(3)		
		-O(9)	1.68(3)		
		-O(12)	<u>1.80(3)</u>		
Mg(3)-O(4)	1.99(2)	mean	1.68		
-O(5)	2.03(2)				
-O(6)	2.05(2)	T(4)-O(10)	1.60(3)		
-O(1)	2.15(2)	-O(6)	1.63(3)		
-O(3)	2.17(2)	-O(9)	1.63(3)		
-O(2)	<u>2.22(2)</u>	-O(12)	<u>1.67(3)</u>		
mean	2.10	mean	1.63		

The amount of water, and especially of inorganic cations, is surprising since the layer charge per unit cell in the Phalaborwa vermiculite is 1.58 (Norrish, 1973) and the anilinium charge from microanalytical results is 1.52, leaving virtually no charge surplus to accommodate any inorganic cations. An explanation of this phenomenon may be the presence of some anilinium as neutral molecules and the probability of some vermiculite dissolution during the long intercalation process carried out at a low pH of about 2.3. The result of dissolution would be a cation deficient species with the cation loss occurring mainly from the octahedral sites, these cations could then diffuse into the interlayer

region.

The large amount of disorder in the silicate layers and the excessive presence of inorganic cations and water molecules in the interlayer region, made the full elucidation of the anilinium cation positions an impossible task. It was, therefore, decided not to pursue the refinement any further and to collect a new set of X-ray data on an anilinium intercalated vermiculite from a different locality, namely the vermiculite from Young River, Western Australia. This vermiculite was known from microanalytical data to contain a little more anilinium and from precession photographs a more pronounced superlattice, facts which suggested a more amenable material.

4.3 Young River Vermiculite

The structure solution was started by refining the positional coordinates and group thermal parameters of the silicate layers only; their starting positions were again taken from Slade and Stone (1984). After a number of least-squares refinement the structure refined to an R value of 35%. Fourier difference maps printed out by SHELX revealed a large number of additional peaks in the silicate layer region. Contoured difference maps plotted through the various silicate sheets, showed clearly that the additional peaks were due to the silicate layers being disordered by $\pm b/3$, with some additional $\pm a/3$ disorder also being present (Figure 4.1b). This disorder was greater than in the corresponding Phalaborwa vermiculite (see Figure 4.1a). When the atoms corresponding to the most highly occupied disordered sites were included the structure refined to an R value of 27%.

The interlayer region was also found to contain numerous peaks, the strongest of which corresponded to the nitrogen and ipso carbons of the anilinium cations. These atoms were disordered in a pattern which was roughly equivalent to the disorder found in

the silicate layers. The organic atoms were assigned the same thermal parameters as those in the Phalaborwa vermiculite, added to the atoms found in the silicate layers and the structure refined again, giving final R values of $R=23.1\%$ and $R_w=21.8\%$. The site occupancies for the nitrogen and carbon atoms were as high as 0.6 in some sites and as low as 0.2 in others.

After accounting for the nitrogen and carbon atoms, a large number of often diffuse peaks still remained in the interlayer region, which due to the severe disorder of the structure could not be properly accounted for. Further refinement was, therefore, discontinued and future work was concentrated on solving the structure of anilinium intercalated Llano vermiculite, the X-ray data of which became available from P.G. Slade of CSIRO, Division of Soils, Urrbrae, South Australia.

4.4 Llano Vermiculite - CSIRO Data

4.4.1 Initial adjustment of silicate layer parameters

The structure refinement was initially carried out at CSIRO using the program ORFLS (Busing *et al.*, 1962). A trial model for the silicate atoms was taken from the atomic coordinates given by Slade and Stone (1984). Because the present work showed the structure to be triclinic and because superlattice reflections were not included in the data set, the asymmetric unit chosen had the lowest symmetry likely to be shown by the silicate-only portion of the structure, namely C1. (The non-primitive unit cell with C1 symmetry enables the structure to be directly compared with those of other layer silicates). The interlayer structure as determined by X-rays represents an average over many cells, each of which is able to incorporate an organic molecule in one of four equivalent sites. Because the average structure was expected to have a centre of symmetry, the origin of the cell

used for this work was moved by b/6 with respect to the cell origin previously chosen by Slade and Stone (1984).

For the octahedral and tetrahedral cation sites, "mixed-atom" scattering factors were computed from the structural formula based on 2.86 silicons (see Table 2.3), in conjunction with the scattering curves for fully ionised cations. For oxygen, two scattering curves were used - initially only the one for non-ionised atoms, but as refinement proceeded the octahedral anions were found to be more appropriately assigned to the O^{2-} curve of Tokonami (1965). All other scattering factors were taken from the International Tables for X-ray Crystallography (1974).

After the scaling factors for the reciprocal lattice layers were adjusted, the positional parameters for pseudo-symmetrically related atoms were adjusted independently. The position of one octahedral cation was fixed at 0,0.5,0 in all refinements. The isotropic temperature factors for pseudo-symmetry related atoms were independently adjusted. For these initial calculations unit weights were used and reflections for which $|F_o| < 0.5$ and $||F_o| - |F_c|| > 3.0$ were excluded. All positional parameters were then adjusted simultaneously, followed by more cycles of least-squares refinement during which all the temperature factors were released to give an R value of 17.5% on 1685 reflections.

The peak profiles of all reflections with $||F_o| - |F_c|| > 3$ were inspected for any obvious measurement errors. A significant number were found to be affected by overlap with adjacent peaks or counting problems. Where possible, peak profiles were re-determined and new structure amplitudes were calculated.

After these corrections were made, difference Fourier maps were computed. These maps represent the residual electron densities after subtraction of the electron densities described by the model for the silicate portion only. The interlayer atomic

sites, therefore, show up as strong peaks. A difference Fourier map through silicon atoms (Figure 4.1c) shows some silicate layer $\pm b/3$ disorder.

4.4.2 Positioning of the anilinium ions from difference Fourier maps

The sections, shown in Figures 4.2-4.7, were sited according to the positions at which the organic interlayer atoms were expected from the previously published one- and two-dimensional projections. Figure 4.2, the section at $y = 1/2$, shows substantial peaks in pairs on opposite sides of the interlayer. For comparison, two aniline molecules are shown drawn at the same scale. (Note that only the carbon atoms along the line between the upper and lower nitrogen atoms are close to the plane of this Fourier section.) Figure 4.3 is a section through the peak ascribed to nitrogen at $z = 2/3$ and Figures 4.4 and 4.5 are sections through the expected C(1) and C(4) positions. The peaks associated with these positions were well defined and helped to confirm that the principal axes of the anilinium groups, i.e., N-C(1)...C(4) are aligned approximately perpendicular to the silicate layers, as shown by Slade and Stone (1984).

The probable z coordinates for the carbon atoms C(2), C(3), C(5) and C(6), the "wing" carbons, were determined from the known geometry of the aniline molecule (Brown, 1949). This known geometry also determined approximately where, on the appropriate Fourier sections, peaks belonging to the "wing" carbons might be. Figures 4.6 and 4.7 show the difference Fourier sections at $z=0.46$ and $z=0.55$ on which the "wing" carbons should be visible. Although other sections were computed, only those at $z = 1/2$, $x = 1/2$, $y = 1/6$, and $y = 5/6$ revealed significant extra interlayer peaks (Figures 4.8-4.11). The relative positions of the peaks shown in these sections indicated that cations and water molecules also occupied interlayer sites.

FIG. 4.2

Difference Fourier contour map at $y = 1/2$ showing substantial peaks in pairs on opposite sides of the interlayer with two anilinium ions drawn in on the same scale. Contour interval is $0.17 \text{ e } \text{\AA}^{-3}$.

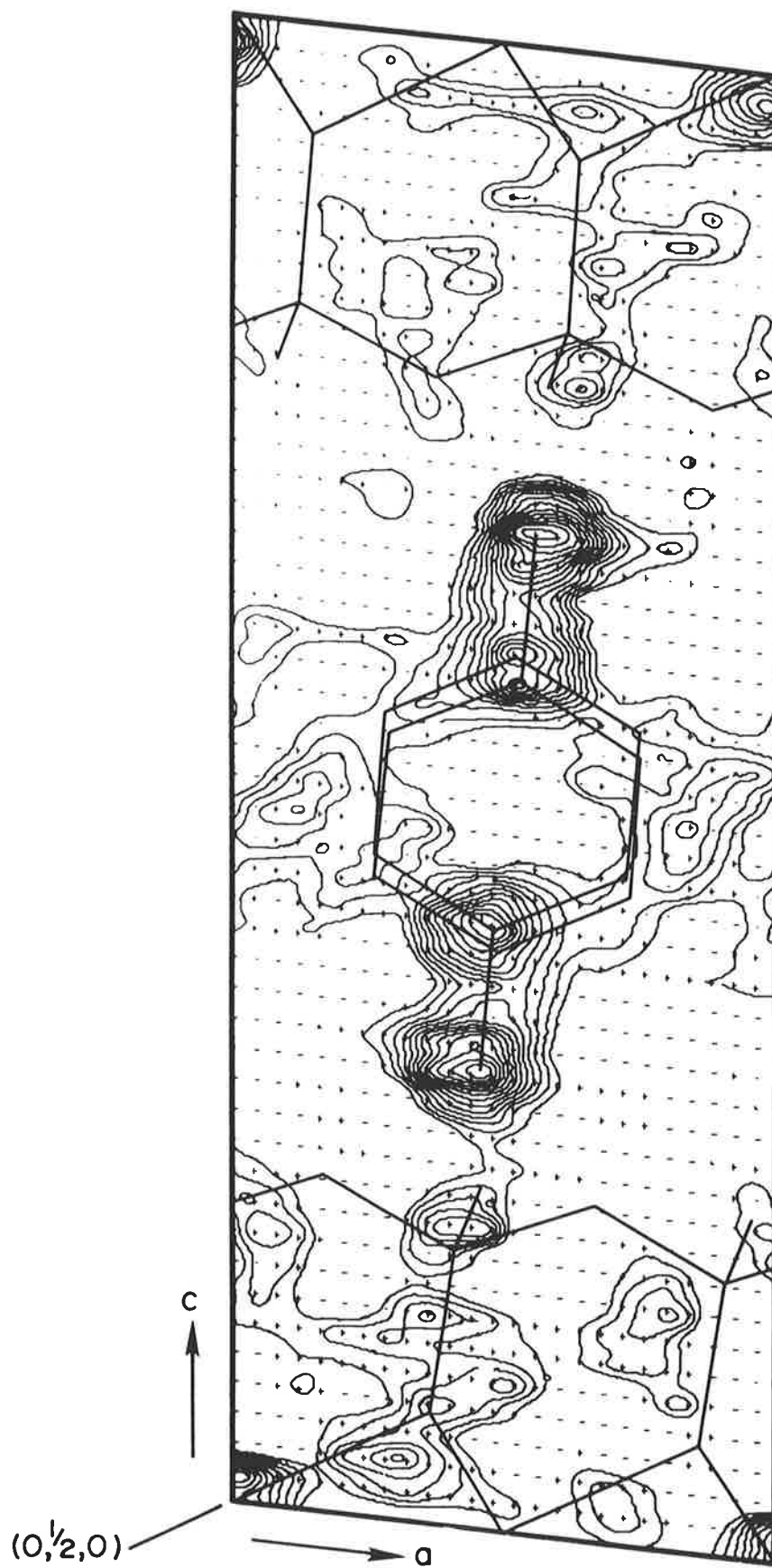


Fig. 4.2

FIG. 4.3 Difference Fourier contour map at $z=0.66$
intersecting the expected nitrogen atoms N(2) and
N(2') of the anilinium ions. Contour interval is
 $0.09 \text{ e } \text{\AA}^{-3}$.

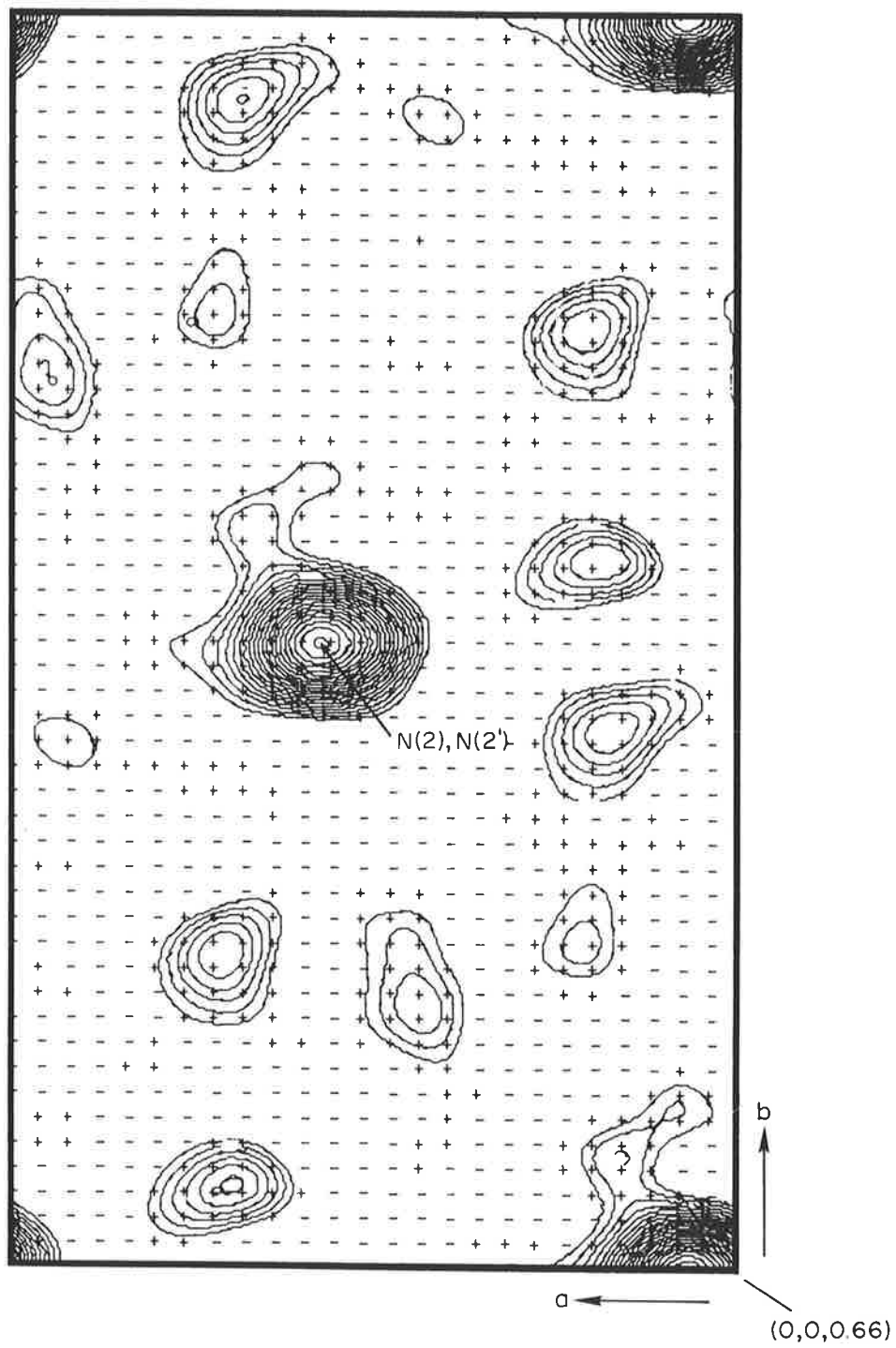


Fig. 4.3

FIG. 4.4 Difference Fourier contour map at $z=0.42$ intersecting the expected ipso carbons C(1) and C(1') of the anilinium ions. Contour interval is $0.09 \text{ e } \text{\AA}^{-3}$.

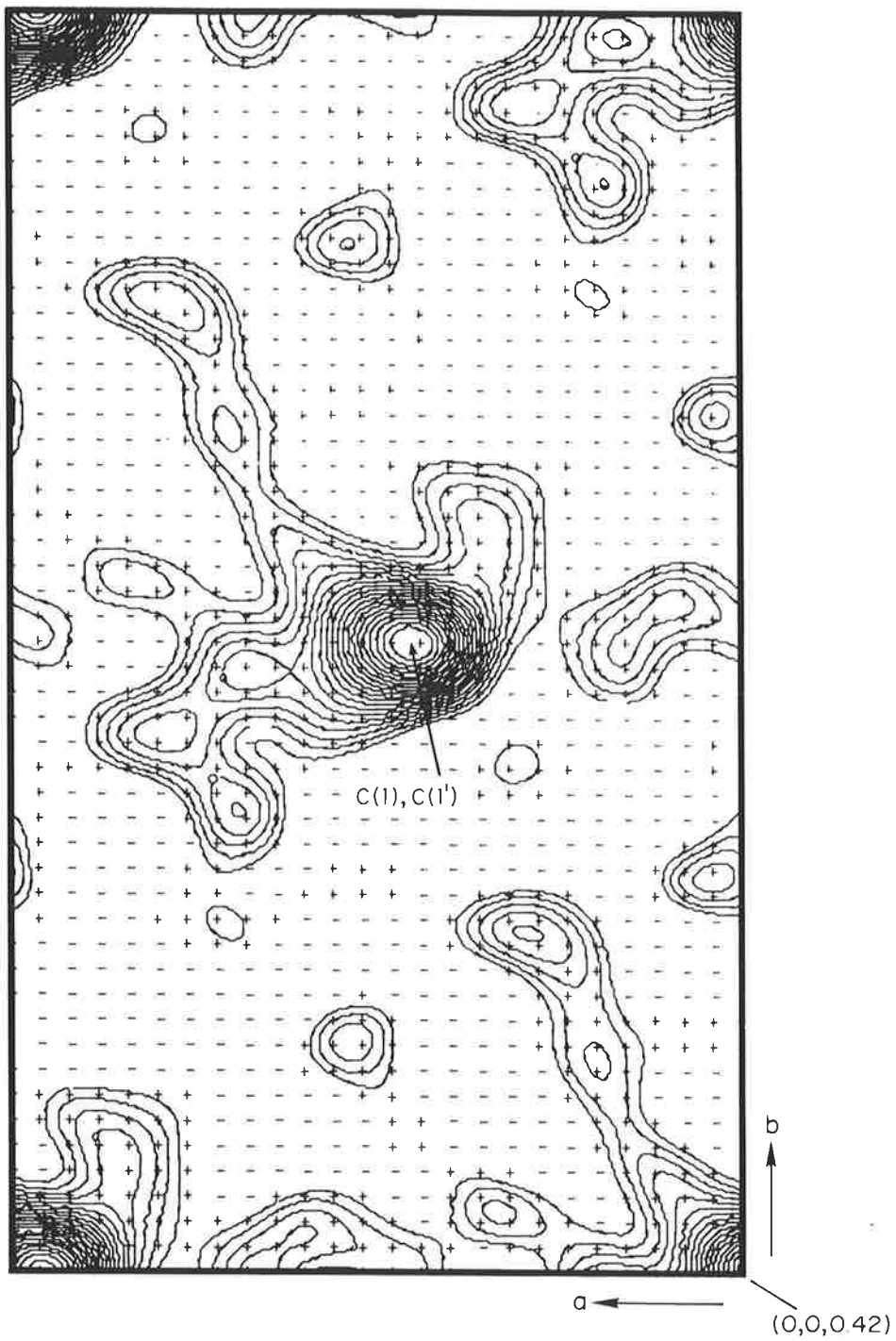


Fig. 4.4

FIG. 4.5 Difference Fourier contour map at $z=0.60$
intersecting the expected para carbons C(4) and
C(4') of the anilinium ions. Contour interval is
 $0.09 \text{ e } \text{\AA}^{-3}$.

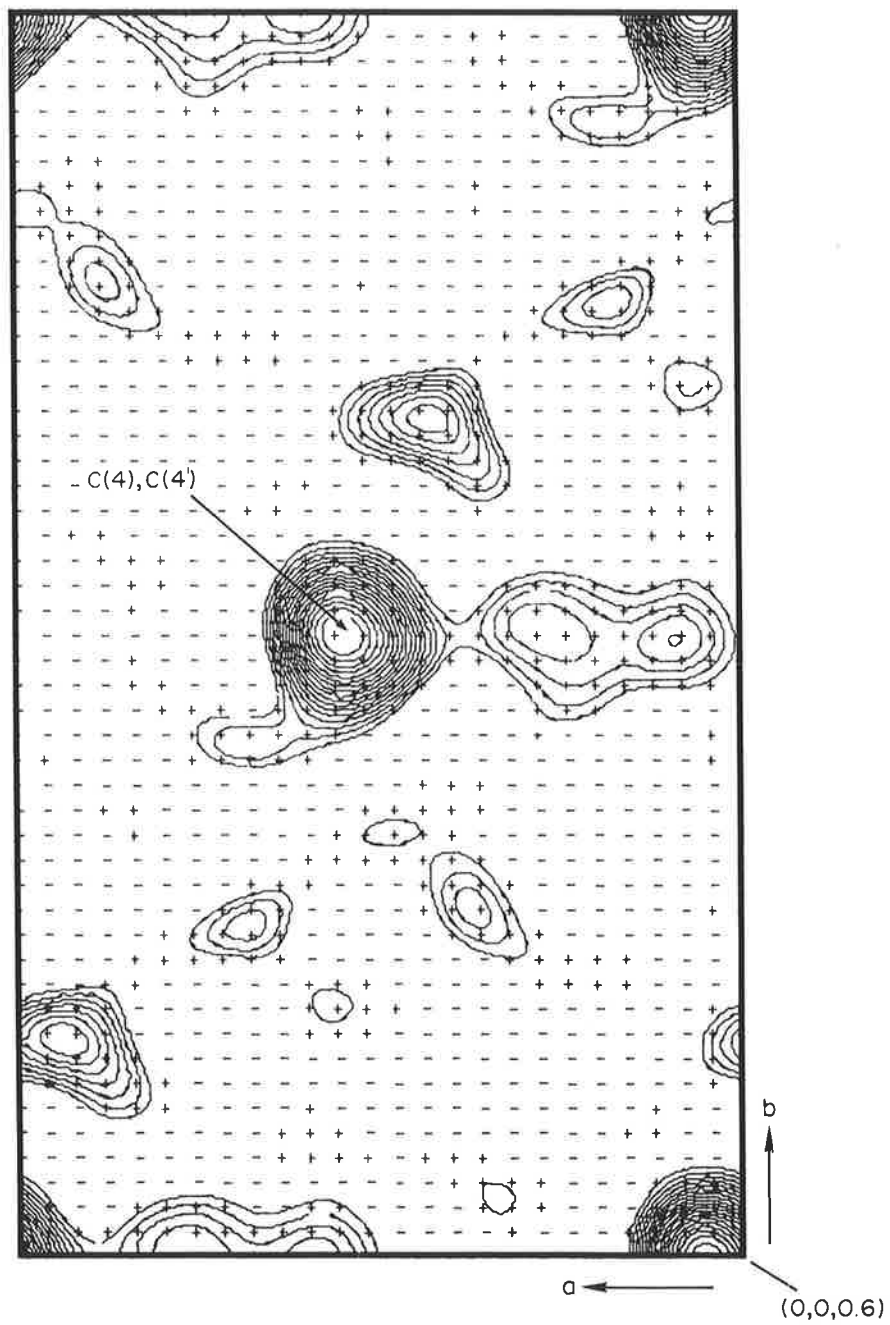


Fig. 4.5

FIG. 4.6 Difference Fourier contour map at $z=0.46$
intersecting the expected "wing" carbons C(2),
C(32'), C(6) and C(52') of the anilinium ions.
Contour interval is $0.09 \text{ e } \text{\AA}^{-3}$.

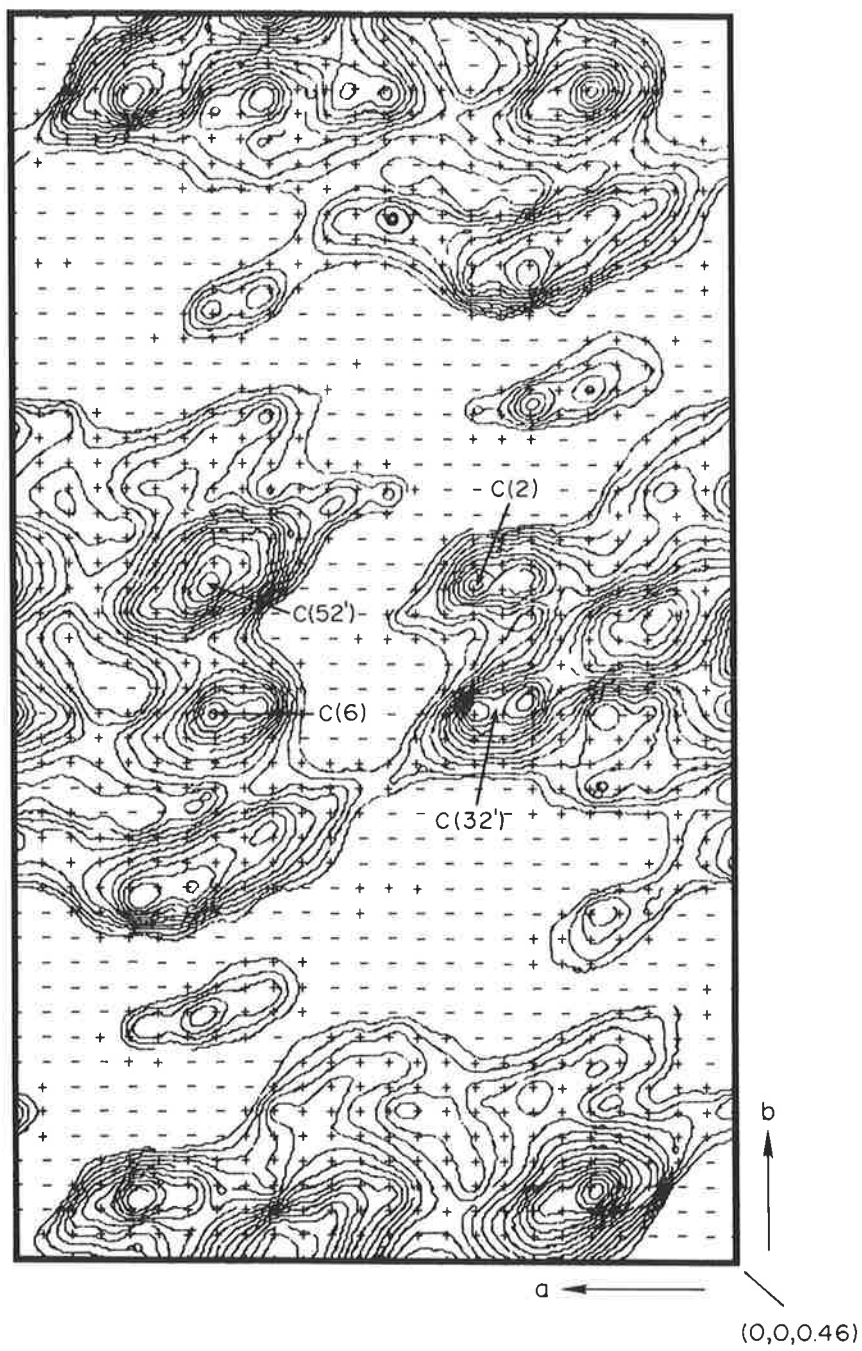


Fig. 4.6

FIG. 4.7 Difference Fourier contour map at $z=0.55$
intersecting the expected "wing" carbons C(5),
C(62'), C(3) and C(22') of the anilinium ions.
Contour interval is $0.09 \text{ e } \text{\AA}^{-3}$.

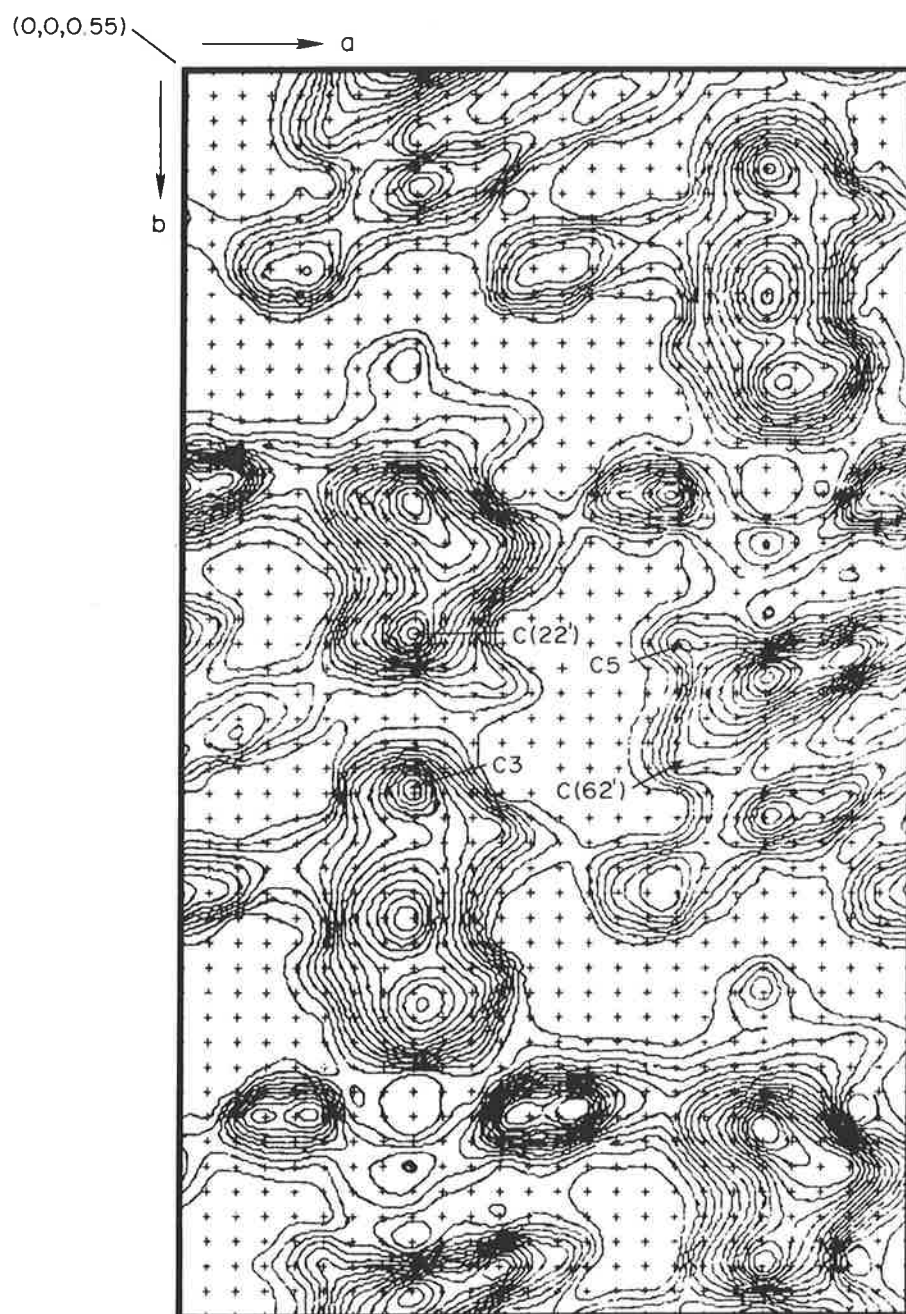


Fig. 4.7

FIG. 4.8 Difference Fourier contour map at $z = 1/2$ showing the presence of inorganic cations and water molecules in the interlayer region. Contour interval is $0.09 \text{ e } \text{\AA}^{-3}$.

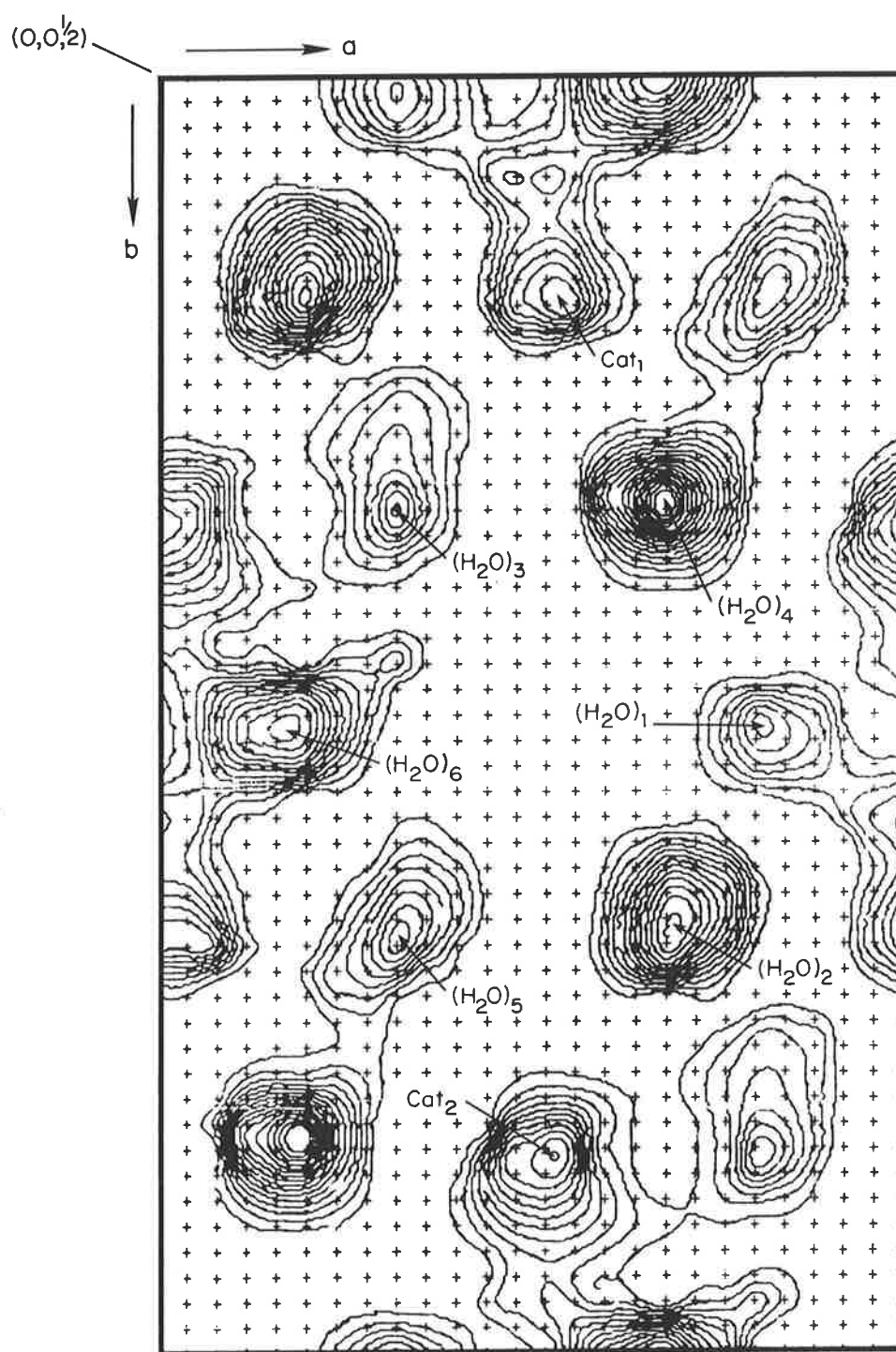


Fig. 4.8

FIG. 4.9 Difference Fourier contour map at $x = 1/2$ showing the presence of inorganic cations and the nitrogens and ridge carbons of the anilinium ions in the interlayer region. Contour interval is $0.09 \text{ e } \text{\AA}^{-3}$.

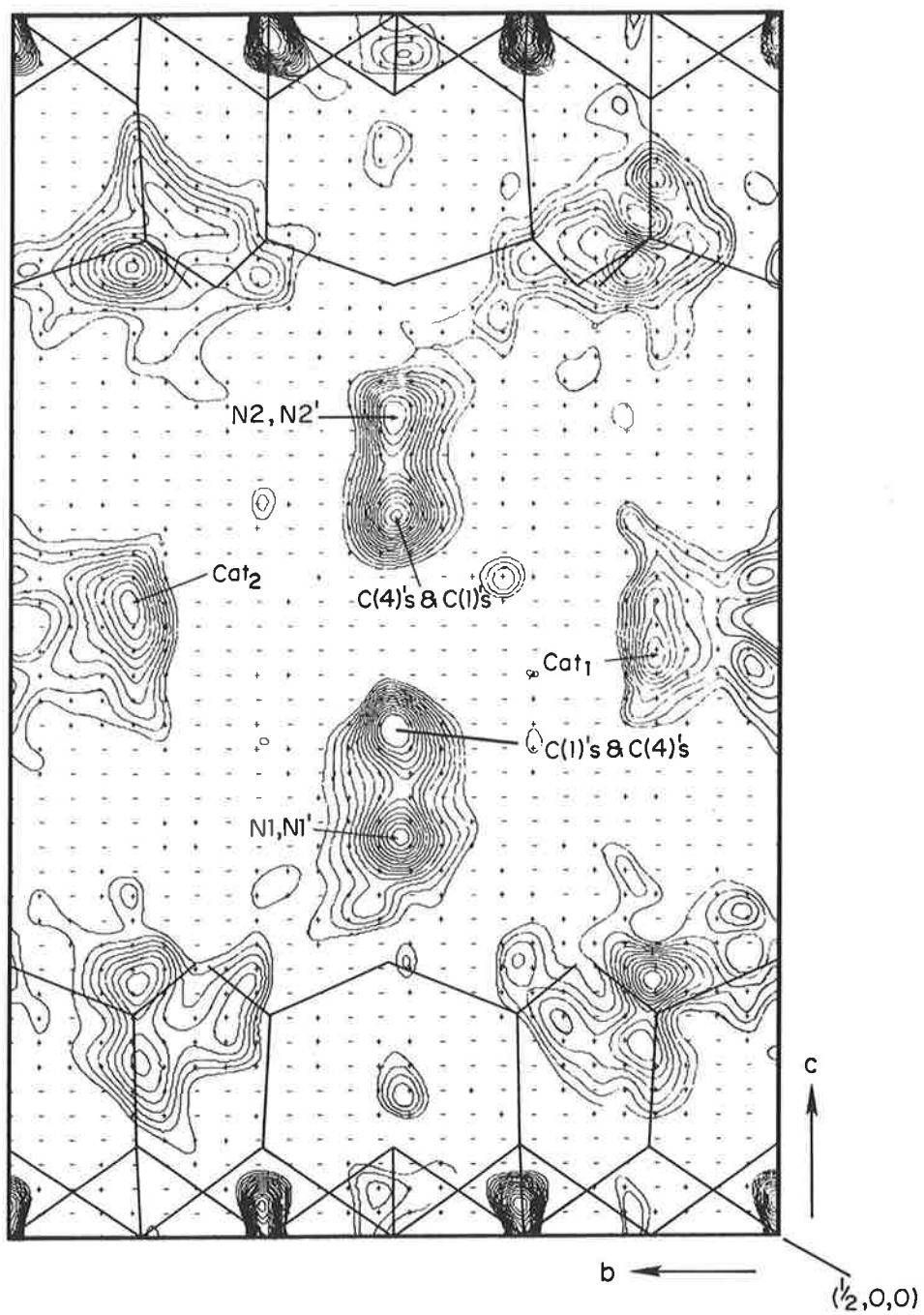


Fig. 4.9

FIG. 4.10 Difference Fourier contour map at $y = 1/6$ showing an inorganic cation and two water molecules in the interlayer region. Contour interval is $0.13 \text{ e } \text{\AA}^{-3}$.

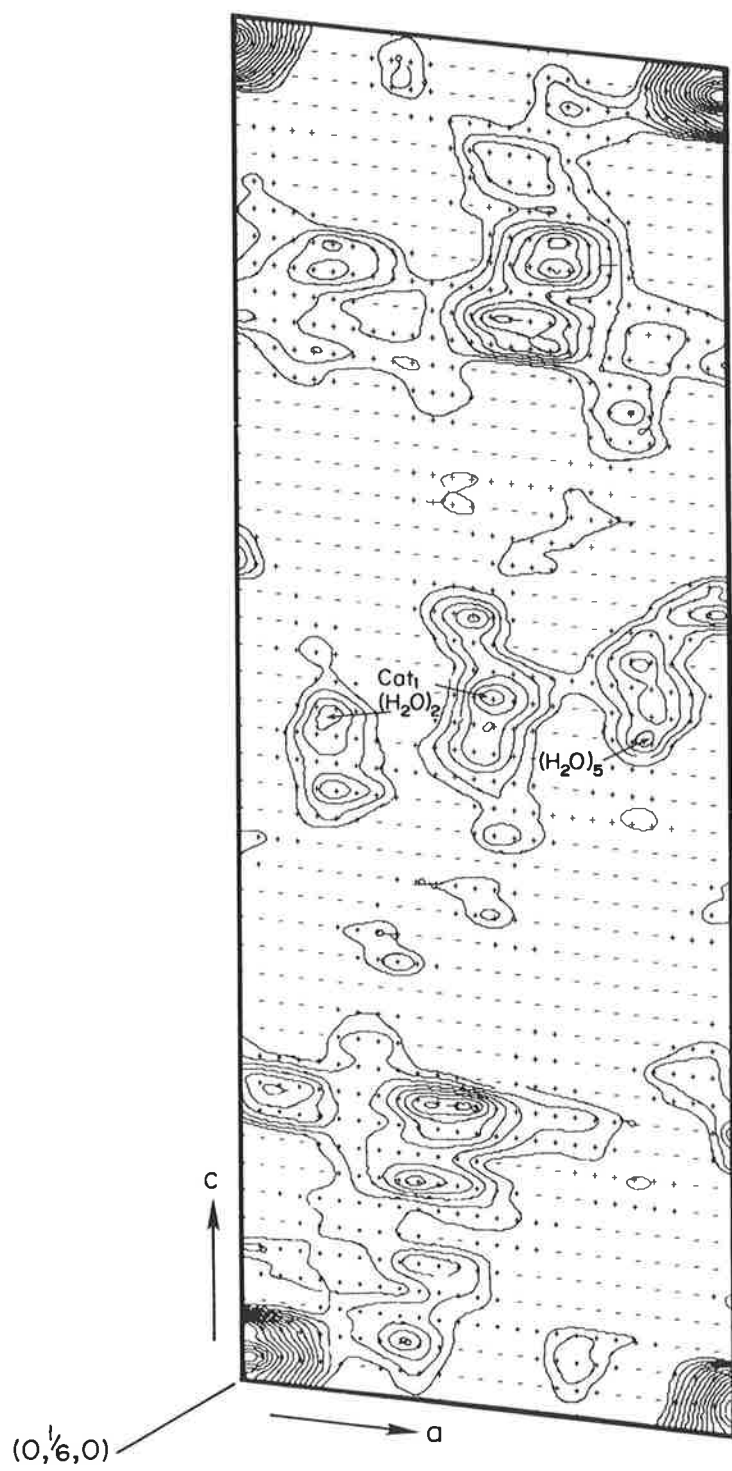


Fig. 4.10

FIG. 4.11 Difference Fourier contour at $y=0.84$ showing an inorganic cation and two water molecules in the interlayer region. Contour interval is $0.17 \text{ e } \text{\AA}^{-3}$.

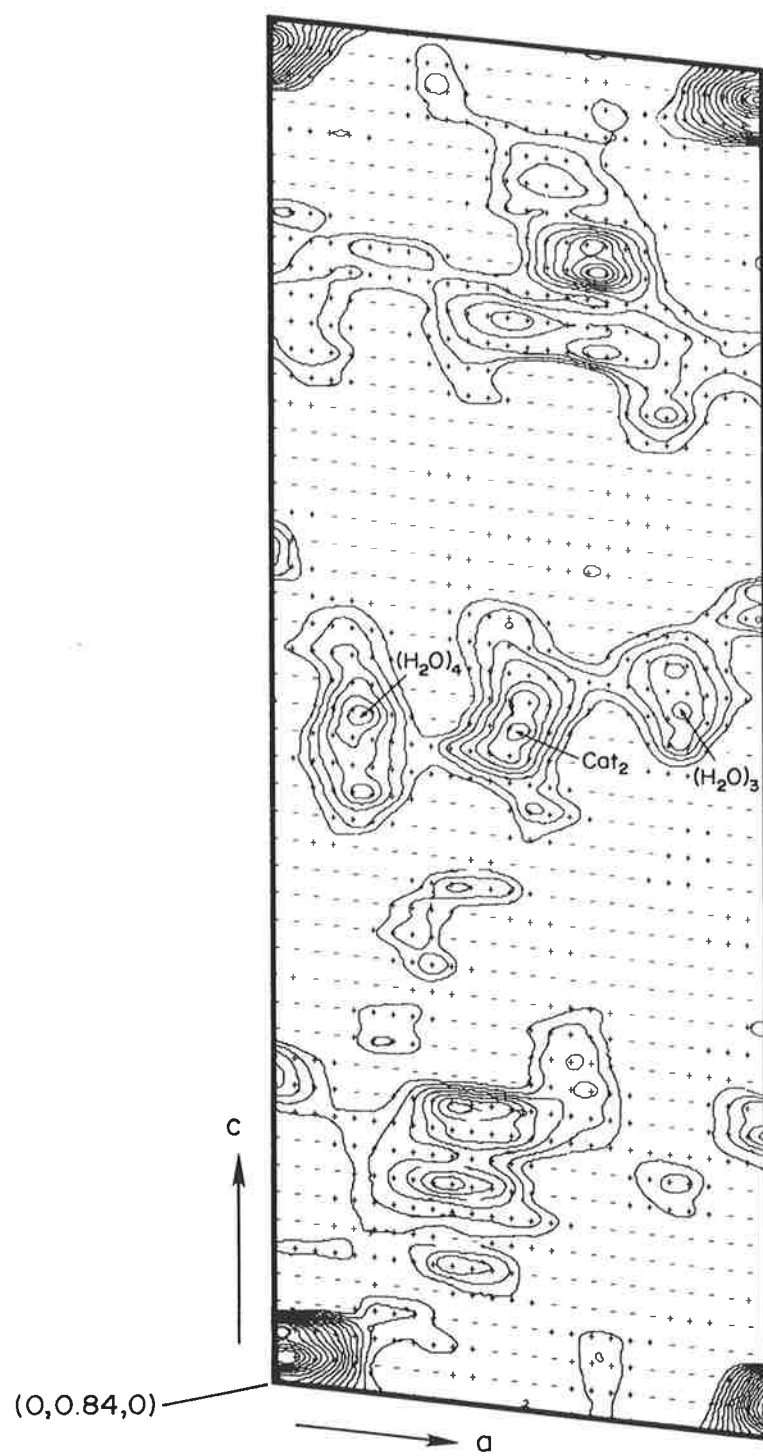


Fig. 4.11

4.4.3 Initial refinement of parameters for interlayer organic atoms

Because four ditrigonal cavities are present in the unit cell under consideration four alternative ditrigonal rings of surface oxygen atoms exist to which the aminium groups of the anilinium ions can be attached. Two rings surround the ditrigonal cavities in the silicate half-layer at the base of the cell, and two surround the cavities in the half-layer at the top of the cell. Due to the C-centering of the cell, however, only two of the ditrigonal rings are crystallographically unique.

For the postulated nitrogen sites a trial set of positional parameters was read from the Fourier maps and then refined by two cycles of least-squares. Subsequently, the trial site-occupancy factors assigned to each site (0.25) were varied during two additional cycles, and values of 0.23 and 0.31 for the lower and upper sites, respectively, were obtained. The temperature factors were arbitrarily maintained at $B=2.5$. These adjustments reduced R by only 0.1%.

The relative insensitivity of the R factor to changes in the parameters for the interlayer atoms, compared with changes in parameters for silicate-layer atoms, prompted a transfer of the data and the partially adjusted model from the program ORFLS (Busing *et al.*, 1962) to the program SHELX (Sheldrick, 1976) for further calculations. The latter program allows a refinement to be made of the parameters for a rigid group of atoms, and thereby produces a greater overall effect upon the least-squares fit. Furthermore, the program allows for the geometric idealization of positional parameters which, on input, may only approximate those of an aromatic ring. Aromatic hydrogens can also be placed in idealized positions. Of the 1928 measured reflections, 577 had $|F| < 0.7$ and were omitted from the structure refinement with SHELX which therefore used the remaining 1351 reflections.

The chemical analysis indicated that an average unit cell contains 1.22 anilinium ions. If the probability of an anilinium ion being attached to the oxygens about one ditrigonal cavity is the same as the probability of its being attached to those about another cavity, the four sites will each have site occupancy factors of about 0.3. The average (0.27) of the experimentally determined site occupancy factors for the nitrogen atoms is therefore close to the expected value.

The peaks ascribed to the "wing" carbons on the difference Fourier sections shown in Figures 4.6 and 4.7 indicated that individual organic cations had the planes of their aromatic rings directed at about $\pm 30^\circ$ to the a-axis of the unit cell. Because the "wing" carbons are not on the central axes of the molecules, these atoms have lower site occupancy factors (0.13).

After obtaining a set of trial positional coordinates for the carbon atoms, the structure analysis was continued as follows. Initially SHELX was used to modify the coordinates to suit the geometry of the hexagonal aromatic ring portion of an anilinium ion. The rigid group refinement option was then used to obtain the best positional coordinates for atoms in the four unique configurations adopted by the organic ions.

4.4.4 Fourier sections in the planes of the organic molecules

To obtain a satisfactory visual representation of the organic molecules, the program to project the difference electron densities calculated by SHELX onto planes at any orientation in a unit cell and to contour the resultant maps was used (see Section 4.1). Each plane was specified by the coordinates of three atoms. Figures 4.12 and 4.13 show the difference electron densities on planes, each of which is defined by three atoms (one nitrogen and two carbon atoms), whose positions were established by the rigid group refinement.

FIG. 4.12 Difference Fourier contour map through a plane defined by the N(1), C(1) and C(2) atoms with the anilinium ion sketched in. Contour interval is $0.14 \text{ e } \text{\AA}^{-3}$.

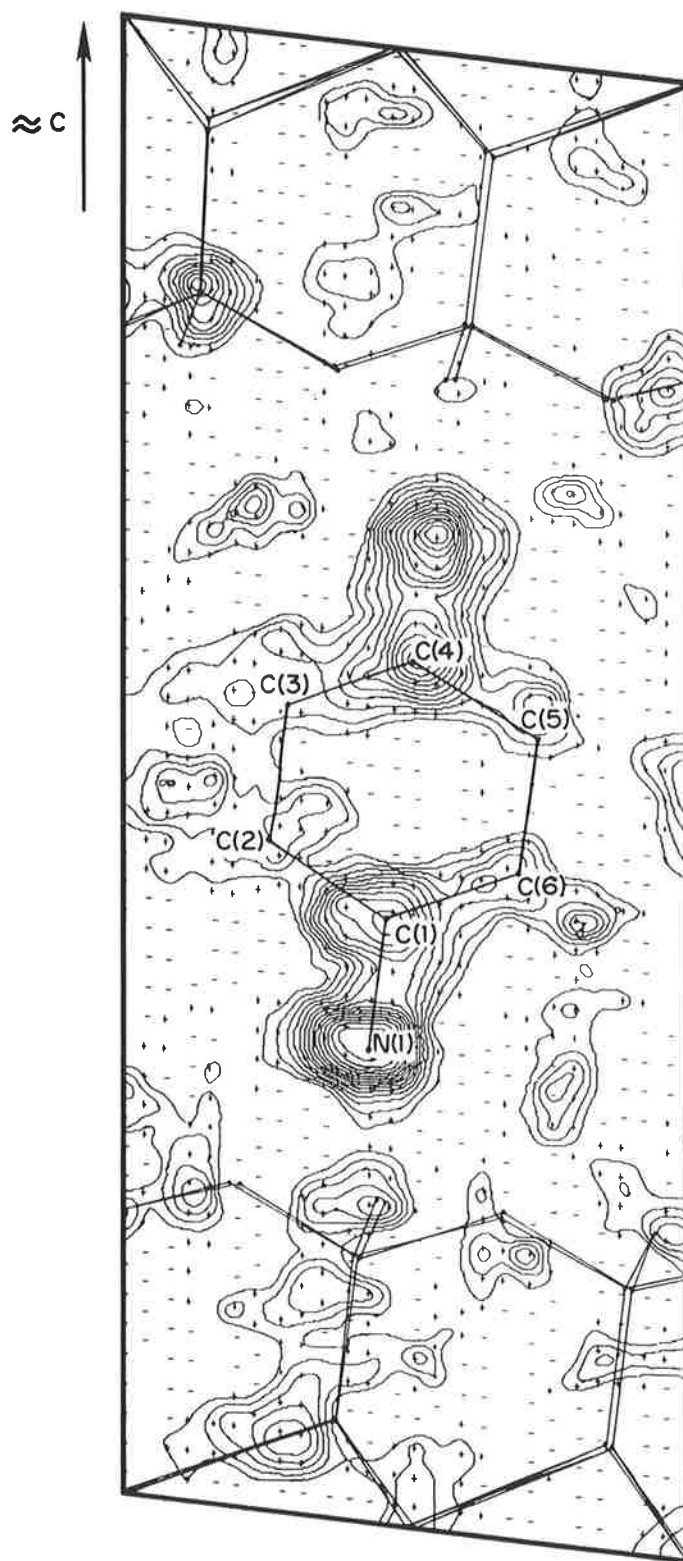


Fig. 4.12

FIG. 4.13 Difference Fourier contour map through a plane defined by the N(2'), C(12') and C(22') atoms with the anilinium ion sketched in. Contour interval is $0.16 \text{ e } \text{\AA}^{-3}$.

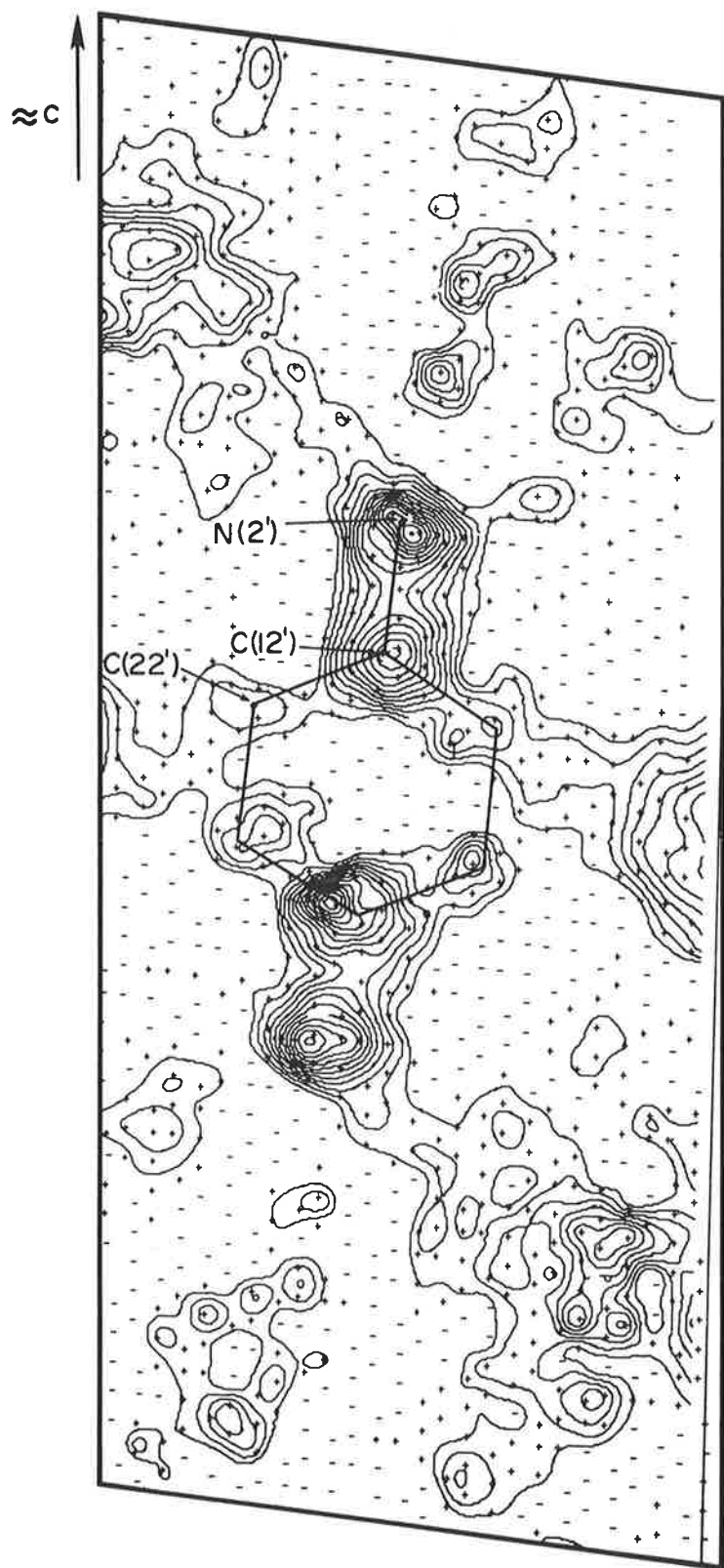


Fig. 4.13

4.4.5 Non-organic interlayer sites

As mentioned above, certain difference sections (e.g., at $x = 1/2$, $y = 1/2$, and $z = 1/2$) show peaks attributable to partially occupied interlayer cation and water sites. From the section at $x = 1/2$, Figure 4.9, the cation sites arrowed at ($y = 1/6$ and $y = 5/6$, $z = 1/2$) show considerable positional variation and low levels of occupancy. The adjacent water sites seen in the other two sections, Figures 4.2 and 4.8, are also diffuse and indicate that the water molecules may have different arrangements throughout the structure.

The principal arrangement adopted is apparent from the section $z = 1/2$ (Figure 4.8), which shows three weak and three stronger peaks about each cation site. To maintain water-water contact distances of about $2.8\text{\AA}$, however, only three of the six sites about any one cation can be occupied. The alternative set of three sites can only be occupied in other cells. Apparently the water molecules form triangular clusters, the planes of which are tilted out of the plane at $z = 1/2$; the sections at $y = 1/2$ (Figure 4.2) and $y = 1/6$ and $y = 0.84$ (Figures 4.10 and 4.11) show the water peaks tail away from the plane at $z = 1/2$. In addition to the relatively well-developed peaks considered above, weaker ones exist at the positions occupied by water in two water-layer hydrates (Slade *et al.*, 1985).

The positional parameters and site occupancy factors for the interlayer cations (assigned to the scattering curve for Mg^{2+}) and the oxygens of the water molecules were refined by initially holding their thermal parameters fixed at 5.0 and 2.5, respectively. All parameters for the whole structure were then released, but for interlayer atoms of a similar kind group isotropic temperature factors and site occupancy factors were adjusted. The final R values were $R = 14.4\%$ and $R_w = 15.8\%$ (Table 4.3). The weighting scheme applied gave reflections weights $w = k/(\sigma^2 F + |g| F^2)$, where k and g were refined.

Table 4.3: Final Positional and Temperature Parameters for the Llano Vermiculite-anilinium Intercalate

=====				
Atom	x	y	z	B
Mg(1)	0.0000	0.5000	0.0000	0.94(1)
Mg(2)	-0.0030(1)	0.8309(1)	0.0013(6)	1.00(1)
Mg(3)	-0.0012(7)	-0.8325(7)	0.0017(6)	0.75(1)
T(1)	0.4079(6)	0.1597(8)	0.1832(6)	0.34(7)
T(2)	0.4049(1)	0.8382(8)	0.1831(6)	0.59(1)
T(3)	0.6176(9)	0.1713(9)	0.8141(6)	0.92(1)
T(4)	0.6209(2)	0.8253(9)	0.8141(6)	1.15(1)
O(1)	0.8604(7)	0.0012(6)	0.0735(9)	1.01(2)
O(2)	-0.8567(5)	0.0019(3)	-0.0673(8)	1.00(2)
O(3)	0.3619(2)	0.1703(1)	0.0725(9)	0.87(2)
O(4)	0.3584(1)	-0.1639(2)	0.0757(4)	0.87(2)
O(5)	-0.3606(3)	0.1700(2)	-0.0704(1)	1.60(2)
O(6)	-0.3521(2)	-0.1630(1)	-0.0743(5)	1.78(2)
O(7)	0.1688(5)	0.2416(3)	0.2240(2)	2.48(2)
O(8)	0.1787(5)	-0.2381(1)	0.2237(1)	1.65(2)
O(9)	-0.1193(6)	0.2350(2)	-0.2252(6)	1.50(2)
O(10)	-0.1236(5)	-0.2340(5)	-0.2244(8)	1.05(2)
O(11)	0.4525(1)	0.0053(4)	0.2256(9)	1.14(2)
O(12)	-0.4196(9)	0.0058(7)	-0.2239(7)	1.48(2)
N(1)	0.425(1)	0.487(5)	0.320(6)	2.2(2)
C(1)	0.443(4)	0.487(3)	0.410(3)	2.2(2)
C(2)	0.236(4)	0.528(3)	0.454(3)	2.2(2)
C(3)	0.255(4)	0.529(3)	0.548(3)	2.2(2)
C(4)	0.482(4)	0.488(3)	0.599(3)	2.2(2)
C(5)	0.589(4)	0.447(3)	0.555(3)	2.2(2)
C(6)	0.669(4)	0.446(3)	0.460(3)	2.2(2)
N(2)	0.565(6)	0.483(2)	0.667(4)	2.2(2)
C(12)	0.543(4)	0.466(3)	0.578(3)	2.2(2)
C(22)	0.350(4)	0.536(3)	0.523(3)	2.2(2)
C(32)	0.328(4)	0.517(3)	0.429(3)	2.2(2)
C(42)	0.499(4)	0.428(3)	0.390(3)	2.2(2)
C(52)	0.692(4)	0.358(3)	0.446(3)	2.2(2)
C(62)	0.714(4)	0.377(3)	0.540(3)	2.2(2)
N(1')	0.459(1)	0.483(6)	0.310(3)	2.2(2)
C(1')	0.529(4)	0.461(3)	0.397(3)	2.2(2)
C(2')	0.371(4)	0.388(3)	0.450(3)	2.2(2)
C(3')	0.448(4)	0.364(3)	0.542(3)	2.2(2)
C(4')	0.682(4)	0.414(3)	0.582(3)	2.2(2)
C(5')	0.840(4)	0.487(3)	0.529(3)	2.2(2)
C(6')	0.764(4)	0.510(3)	0.437(3)	2.2(2)

Table 4.3 (Contd.)

Atom	x	y	z	B
N(2')	0.575(2)	0.495(6)	0.676(7)	2.2(2)
C(12')	0.538(4)	0.500(3)	0.586(3)	2.2(2)
C(22')	0.319(4)	0.444(3)	0.539(3)	2.2(2)
C(32')	0.284(4)	0.450(3)	0.444(3)	2.2(2)
C(42')	0.467(4)	0.513(3)	0.397(3)	2.2(2)
C(52')	0.686(4)	0.569(3)	0.445(3)	2.2(2)
C(62')	0.722(4)	0.563(3)	0.539(3)	2.2(2)
Cat(1)	0.5279(1)	0.1614(6)	0.4671(7)	5.5(4)
Cat(2)	0.5116(8)	0.8424(7)	0.4978(2)	5.5(4)
H ₂ O(1)	0.3217(7)	-0.0036(1)	0.4848(9)	5.0(4)
H ₂ O(2)	0.2599(3)	0.1672(7)	0.4455(1)	5.0(4)
H ₂ O(3)	0.2953(4)	0.3092(6)	0.4916(4)	5.0(4)
H ₂ O(4)	0.7499(1)	0.2981(5)	0.4503(2)	5.0(4)
H ₂ O(5)	0.8342(4)	0.1560(6)	0.4974(1)	5.0(4)
H ₂ O(6)	0.5588(5)	0.0325(6)	0.4721(9)	5.0(4)

The list of observed and calculated structure factors is given in Appendix A.1.

The presence of interlayer inorganic cations was unexpected inasmuch as none of the sodium which had saturated the exchange sites prior to the anilinium intercalation was found by a flame-photometric analysis of the intercalate itself. The identity of the residual, inorganic, interlayer cations is uncertain, but they are probably magnesium ions. These, along with aluminium ions, are released from vermiculite when it takes up anilinium ions from aqueous aniline hydrochloride solutions at a pH of 2.8 (Pisaniello, 1984). A back-reaction was then responsible for the incorporation of the cations into the interlayer sites identified from the difference Fourier maps.

4.4.6 Residual silicate disorder

Although the intercalation of anilinium ions into Llano vermiculite orders the stacking of the silicate layers such that they have relative positions resembling those found in 1M mica-type structures, the process is not fully achieved throughout the crystal. Residual disorder is therefore present and is seen, for example, on the difference section at $z = 0.18$ (the level of the tetrahedral cations) where the positions at the centres of the rings of tetrahedra were found to be slightly occupied. Sections through the surface oxygens, parallel to the basal plane, also showed peaks associated with the residual disorder, but no extra peaks were found on a section through the octahedral cations. The residual disorder appeared to be largely associated with irregular shifts of the whole silicate layer by $\pm b/3$. Because the octahedral cations are already separated by $b/3$, no extra peaks on the section were present through the octahedral cations. Refinement of the site occupancy of the atoms as a group in the alternate $\pm b/3$ shifts showed that the amount of each layer in a $+b/3$ or $-b/3$ position was about 5% of the total number of layers.

4.5 Results and Discussion

4.5.1 General remarks

This study of anilinium-vermiculite illustrates some of the problems that can affect crystallographic work on clay-organic materials. For example, although anilinium ions and some substitute anilinium ions improve the stacking order in vermiculites, some degree of residual disorder remains. Part of the remainder probably results from an incomplete reaction between the organic species and the clay. Transmission electron micrographs of edge-on views of flakes of anilinium intercalated

and magnesium saturated Llano vermiculites showed randomly distributed packets of unopened (mica-like) layers.

Atoms having low site occupancy factors can be difficult to locate. In this study "wing" carbons, having site occupancy factors of only 0.13, were difficult to find. Fortunately, the higher occupancy factors for atoms along the axes of the aniline molecules enabled the ipso, C(1), and the para, C(4), carbons to be readily found. The true unit cell of the intercalate has four times the volume of the cell actually used in this study; therefore, the images of the interlayer structure, shown by the Fourier maps, are averages of the contents of the four different cells that together comprise the supercell. Although this averaging was confusing, the geometrical relationships possible between the organic atoms enabled the weak images of the "wing" carbons to be found. These atoms were more readily located because of the close proximity of the sites of carbon atoms in the upper and lower rings. Therefore, peaks belonging to the "wing" carbons were mutually reinforcing.

Although the earlier studies of Slade and Stone (1983, 1984), based only upon one- and two-dimensional Fourier projections, correctly located the nitrogen atoms, and also the ipso and para carbons, the "wing" carbons were located incorrectly. As a result, the planes containing the aromatic rings were reported to be parallel and perpendicular to [010]. The present study, based upon three-dimensional data, has located the ring planes to be about $\pm 60^\circ$ to [010]. In the vermiculite-anilinium intercalate (Figure 4.14) the planes of the aromatic rings are therefore similarly oriented to those proposed by Slade and Raupach (1982) for a vermiculite-benzidine intercalate. Bond lengths for a selection of interlayer and surface oxygen atoms are given in Table 4.4.

FIG. 4.14 A modified ORTEP-II drawing of the structure of anilinium intercalated Llano vermiculite. For clarity only two out of the four possible anilinium ions are shown.

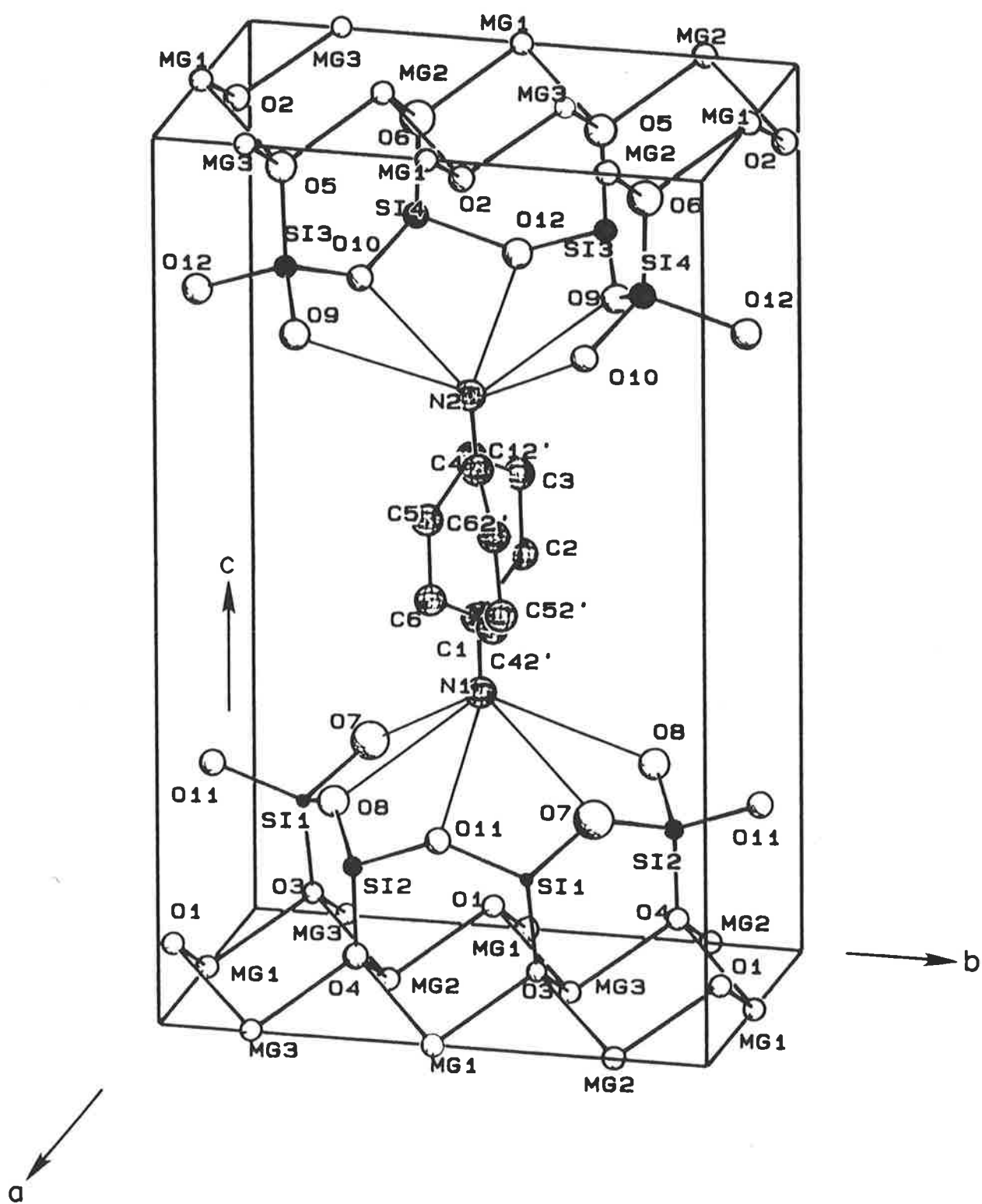


Fig. 4.14

4.5.2 Superstructure

A more serious difficulty, associated with the description of the structure for the vermiculite-anilinium intercalate in a sub-cell, arises because the absolute positions of the inorganic cations, the water molecules, and the organic cations cannot readily be uniquely determined. To investigate how the superstructure might govern the arrangement of water molecules and cations (both organic and inorganic), several possible arrangements were examined with the molecule drawing program PLUTO78 (Motherwell, 1978). For an average sub-cell to contain about one anilinium ion, each sub-cell must contain one organic unit. Alternatively, co-existing anilinium-rich and anilinium-poor domains might co-exist throughout the crystal. No superstructure arrangement could be found in which each sub-cell contained an anilinium ion and also allowed for triangular groups of water molecules about cation positions, as found, between

Table 4.4: Bond Distances ($\text{\AA}$) for a Selection of Interlayer Atoms and Surface Oxygen Atoms

=====			
Atoms	Distance ⁽¹⁾	Atoms	Distance ⁽¹⁾
O(1)-N(1)	2.93	O(9)-C(4)	3.55
O(8)-N(1)	2.93	O(10)-C(4)	3.44
O(11)-N(1)	2.74	O(12)-C(4)	3.58
O(9)-N(2)	3.04	O(7)-C(42)	3.34
O(10)-N(2)	2.84	O(8)-C(42)	3.14
O(12)-N(2)	3.03	O(11)-C(42)	3.64
O(7)-N(1')	2.93	O(9)-C(4')	3.38
O(8)-N(1')	2.74	O(10)-C(4')	3.74
O(11)-N(1')	2.85	O(12)-C(4')	3.48
O(9)-N(2')	2.90	O(7)-C(42')	3.60
O(10)-N(2')	2.87	O(8)-C(42')	3.66
O(12)-N(2')	2.92	O(11)-C(42')	3.51
=====			

¹Standard deviations for all bond lengths are 0.03 $\text{\AA}$

tetrahedral bases. The alternative model, involving domains, was therefore examined.

Sub-cells in anilinium-rich domains can contain a maximum of two anilinium ions arranged as in Figure 4.15. A similar close-packed arrangement exists in aniline hydrochloride (Brown, 1949) and in aniline hydrobromide (Nitta *et al.*, 1948) and has been postulated for benzidine in a vermiculite-benzidine intercalate (Slade and Raupach, 1982). For the arrangement shown in Figure 4.15, the repeat distance along a row perpendicular to the b-axis is $\sim 5.33\text{\AA}$. This distance is also the intermolecular distance and the b-axis length in aniline hydrochloride. In aniline hydrobromide the anilinium groups are displaced alternately up and down in the direction of their N-C(1) ... C(4) axes. The similar packing arrangement in the intercalated vermiculite maintains the interlayer separation.

To accommodate the triangular groups of water molecules expected about the inorganic cations, anilinium-poor domains must exist in the close-packed array shown in Figure 4.15. Figure 4.16, therefore, shows how water molecules can form triangular groups about cations in an anilinium-poor domain. The presence of such domains requires that anilinium ions must also exist in close-packed arrays so that the overall arrangement will consist alternately of more and less densely populated domains. In the overall domain system the arrangement of organic ions, water molecules and metal cations must conform to the superstructure even while the intercalation reaction proceeds, because only one set of superlattice reflections has ever been observed.

Young River and Phalaborwa vermiculites can take up more anilinium ions than the material from Llano, Texas (see Section 2.4). The overall packing density can be expected to reflect the extent of organic uptake. In turn, the organic uptake will be governed by the layer charge and the competition between anilinium ions and those ions, initially from the clay,

FIG. 4.15

A computer drawing (PLUT078) of anilinium ions in a closest packed domain in the interlayer region of the intercalate formed with Llano vermiculite. Anilinium ions, drawn to the same scale as the silicate surface oxygens, are shown with their aminium groups directed alternately up and down. This arrangement is only one of the possible arrangements for these groups.

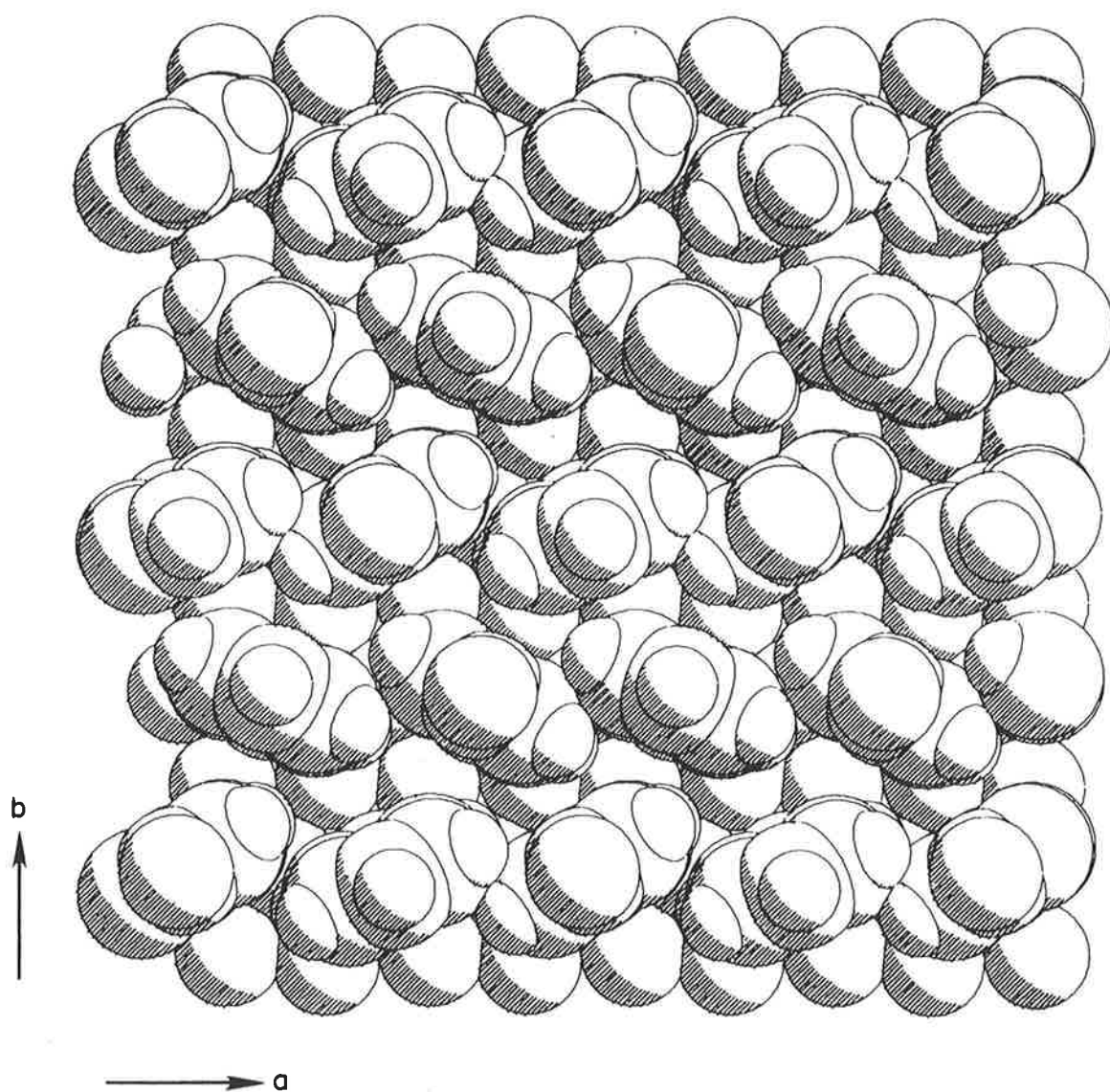


Fig. 4.15

FIG. 4.16 Computer drawing (PLUTO78) of water molecules, anilinium ions and inorganic cations as might be organised in a domain having a low density of organic units. Overall the arrangement conforms to the superstructure.

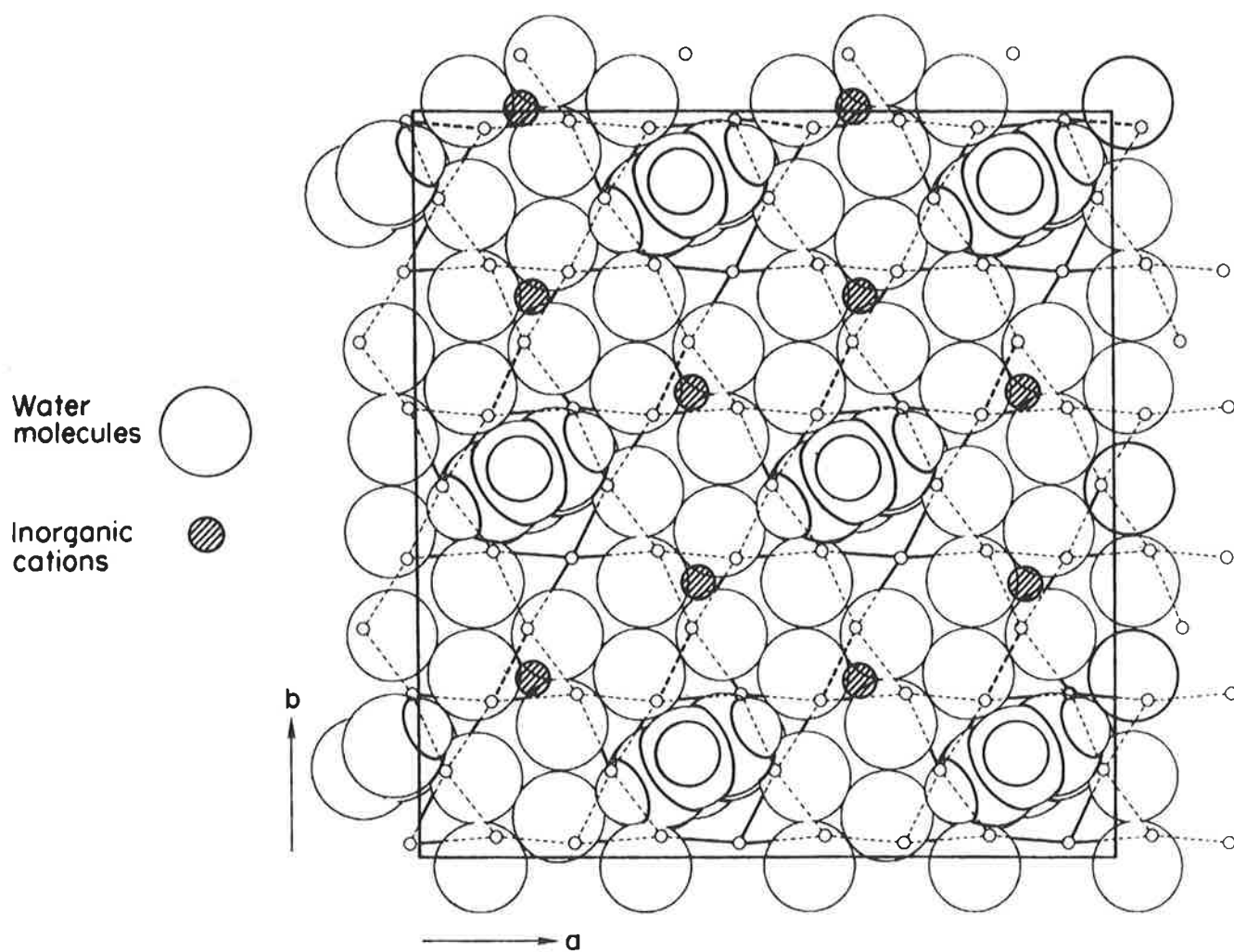


Fig. 4.16

entering the interlayer via a back-reaction.

For large organic molecules to enter interlayer sites, both water molecules and inorganic cations must be removed. Thus, although the high layer charge of Llano vermiculite could have been expected to produce a complete coverage of the silicate layer surfaces by anilinium ions, the back reaction in the acidic medium used for the exchange restricted the coverage to about one half.

4.5.3 Interlayer water molecules

If vermiculites having two sheets of water molecules between their silicate layers are dehydrated, a phase is produced in which single sheets of water molecules are interleaved with the silicate layers (de la Calle *et al.*, 1985). Vermiculites having single interlayer water sheets contain extensive stacking disorder which causes their $0kl$ reflections, where $k \neq 3n$, to be streaked. As a result of their degraded diffraction patterns, the hydrates with single water sheets are not structurally well defined.

This study has shown that the water molecules in the vermiculite-anilinium intercalate are also in a planar network, albeit a slightly puckered network. Although the positions of the water molecules have not been uniquely determined, the comparatively sharp sub-cell reflections used for the work have allowed their probable positions in an average sub-cell to be found. Earlier studies have only been able to determine x and z coordinated from $h0l$ reflections (de la Calle *et al.*, 1985).

The x and y coordinates for the water molecules in the intercalate are essentially the same as those for water molecules forming the upper and lower triangular faces of the octahedrally arranged clusters about cations in vermiculites having two

interlayer water sheets. On dehydration, a phase having a single water sheet forms from a phase having two sheets if three out of every six water molecules are lost. This process can be thought of as a movement of either an upper or lower triad of water molecules from an octahedron to the middle of the interlayer. Apparently the cations may also be partially displaced from their positions at the middle of the interlayer.

4.5.4 Structure of the silicate layers

The structure of a natural two-layer Mg-vermiculite from Llano, Texas, was determined and comprehensively described by Shirozu and Bailey (1966). The material was found to be affected by stacking disorder, as was the Kenya vermiculite studied earlier by Mathieson and Walker (1954). Because the anilinium intercalation reaction substantially reduces the stacking disorder of vermiculites and thereby reduces streaking in their XRD patterns, these are measured more easily. The details of the silicate part of the intercalated structure, although partially damaged by acid attack, are of interest if determined from such an "improved" diffraction pattern.

Table 4.5 gives the structural data for Llano vermiculite as calculated from the positional coordinates in Table 4.3. Except for the averages of the bond lengths about individual tetrahedra, the data in Table 4.5 accord well with those given for Llano vermiculite by Shirozu and Bailey (1966). The present averages for the tetrahedral bond lengths do not show the consistent differences necessary to confirm the long-range Si/Al ordering pattern described by Shirozu and Bailey (1966). The errors associated with the T-O bonds in the intercalate are greater than those claimed by Shirozu and Bailey (1966) and may obscure any differences associated with long-range ordering. That short-range Si/Al ordering occurs in Llano vermiculite is shown by the nuclear magnetic resonance ^{29}Si spectrum of Thompson

(1984). This spectrum showed three peaks; hence, over short distances at least, three non-equivalent sites must exist for Si atoms. For these three sites to exist in an ordered array through the crystal, the symmetry must be lower than $C2/c$ as used by Shirozu and Bailey (1966).

Table 4.5: Interatomic Distances ($\text{\AA}$) and Angles ($^\circ$)
for the Silicate Layer Atoms

=====			
Atoms	Distance	Atoms	Distance
Tetrahedron about T(1)			
T(1)-O(3)*	1.63	O(3)-O(7)	2.66
-O(7)	1.65	-O(8)	2.78
-O(8)	1.78	O(7)-O(8)	2.73
-O(11)	<u>1.57</u>	O(11)-O(3)	2.74
mean	1.66	-O(7)	<u>2.65</u>
		mean	2.70
Tetrahedron about T(2)			
T(2)-O(4)*	1.58	O(4)-O(7)	2.74
-O(7)	1.71	-O(11)	2.71
-O(8)	1.58	O(8)-O(4)	2.59
-O(11)	<u>1.68</u>	-O(7)	2.62
mean	1.64	-O(11)	2.69
		O(11)-O(7)	<u>2.69</u>
		mean	2.67
Tetrahedron about T(3)			
T(3)-O(5)*	1.70	O(9)-O(5)	2.83
-O(9)	1.69	O(10)-O(5)	2.69
-O(10)	1.60	-O(9)	2.70
-O(12)	<u>1.64</u>	-O(12)	2.64
mean	1.66	O(12)-O(5)	2.72
		-O(9)	<u>2.67</u>
		mean	2.71
Tetrahedron about T(4)			
T(4)-O(6)*	1.65	O(6)-O(12)	2.71
-O(9)	1.59	O(9)-O(6)	2.68
-O(10)	1.63	-O(10)	2.66
-O(12)	<u>1.77</u>	-O(12)	2.73
mean	1.66	O(10)-O(6)	2.73
		-O(12)	<u>2.71</u>
		mean	2.71
=====			

Table 4.5 (Contd.)

Atoms	Distance	Atoms	Distance
Octahedron about Mg(1)			
Mg(1)-OH(1)	2.09	O(3)-O(4)	3.10
-O(3)	2.08	-OH(1)	3.07
-O(4)	2.09	O(4)-OH(1)	3.09
-OH(2)	2.04	O(5)-O(6)	3.09
-O(5)	2.08	-OH(2)	3.08
-O(6)	<u>2.07</u>	O(6)-OH(2)	<u>3.09</u>
mean	2.08	mean (unshared)	3.09
Shared edges between Mg(1) and Mg(3)			
		O(3)-OH(2)	2.74
		O(5)-OH(1)	2.79
		O(6)-O(4)	<u>2.85</u>
		mean	2.79
Octahedron about Mg(2)			
Mg(2)-OH(1)	2.08	O(3)-O(4)	3.06
-O(3)	2.01	-OH(1)	3.06
-O(4)	2.10	O(4)-OH(1)	3.05
-OH(2)	2.09	O(5)-O(6)	3.02
-O(5)	2.02	-OH(2)	3.07
-O(6)	<u>2.08</u>	O(6)-OH(2)	<u>3.05</u>
mean	2.06	mean (unshared)	3.05
Shared edges between Mg(2) and Mg(3)			
OH(1)-OH(2)	2.71	O(3)-O(5)	2.72
O(3)-O(6)	2.80	O(4)-OH(2)	2.76
O(4)-O(5)	<u>2.80</u>	O(6)-OH(1)	<u>2.80</u>
mean	2.77	mean	2.76
Octahedron about Mg(3)			
Mg(3)-OH(1)	2.07	O(3)-O(4)	3.09
-O(3)	2.09	-OH(1)	3.11
-O(4)	2.09	O(4)-OH(1)	3.10
-OH(2)	2.03	O(5)-O(6)	3.14
-O(5)	2.08	-OH(2)	3.09
-O(6)	<u>2.15</u>	O(6)-OH(2)	<u>3.11</u>
mean	2.08	mean	3.11

Table 4.5 (Contd.)

=====			
Atoms	Distance	Atoms	Distance
=====			
Angles about T(1)		Angles about T(2)	
O(11)-T(1)-O(3)	117.2	O(8)-T(2)-O(4)	110.0
O(11)-T(1)-O(7)	110.7	O(8)-T(2)-O(11)	111.4
O(11)-T(1)-O(8)	106.1	O(8)-T(2)-O(7)	105.1
O(3)-T(1)-O(7)	107.9	O(4)-T(2)-O(11)	112.2
O(3)-T(1)-O(8)	109.0	O(4)-T(2)-O(7)	112.2
O(7)-T(1)-O(8)	<u>105.4</u>	O(11)-T(2)-O(7)	<u>105.3</u>
mean	109.4	mean	109.4
Angles about T(3)		Angles about T(4)	
O(10)-T(3)-O(12)	109.1	O(9)-T(4)-O(10)	111.6
O(10)-T(3)-O(9)	110.3	O(9)-T(4)-O(6)	111.9
O(10)-T(3)-O(5)	108.8	O(9)-T(4)-O(12)	108.9
O(12)-T(3)-O(9)	106.7	O(10)-T(4)-O(6)	113.2
O(12)-T(3)-O(5)	109.0	O(10)-T(4)-O(12)	106.0
O(9)-T(3)-O(5)	<u>112.9</u>	O(5)-T(4)-O(12)	<u>104.8</u>
mean	109.5	mean	109.4
=====			

* Apical oxygens.

Standard deviation for all bond lengths is 0.02Å.

CHAPTER 5

CRYSTAL STRUCTURE OF TRIETHYLENEDIAMINE DIHYDROCHLORIDE

CHAPTER 5

CRYSTAL STRUCTURE OF TRIETHYLENEDIAMINE DIHYDROCHLORIDE

5.1 Introduction

The compound triethylenediamine dihydrochloride (TEDA.2HCl), also known as 1-4-diazabicyclo[2,2,2]octane dihydrochloride (DABCO.2HCl), was intercalated by Shabtai *et al.* (1977), into the clay silicate montmorillonite to form a swelling resistant molecular sieve which was used successfully in catalysing the esterification of carboxylic acids. The intercalate, called by Shabtai DABCO-M, was reported to have a basal spacing of 14.8Å and a calculated lateral distance of about 6Å between the edges of adjacent organic cations [TEDAH₂]. This uniform interlayer pore size implies that the organic cations must form ordered arrays on the surface of the silicate layers and, therefore, likely to enhance the stacking order of adjacent silicate layers.

Work by Slade *et al.* (1978, 1982, 1983, 1984 and 1987), made use of X-ray superlattice reflections to characterise ordered arrays formed when some organic species were intercalated into vermiculites. For a vermiculite-anilinium intercalate, Slade and Stone (1984) and Slade *et al.* (1987), found sharp discrete 0kl X-ray reflections indicative of a well-ordered structure in which the silicate layers are stacked with their ditrigonal cavities essentially opposite each other as in micas. It was decided, therefore, to intercalate vermiculite with TEDA.2HCl in order to study the X-ray structure of the resulting intercalate in more detail than given by Shabtai *et al.* (1977). A literature search (Cambridge data base) revealed that the structure of TEDA.2HCl was not carried out and, therefore, it was decided that this structure should be solved prior to the anticipated structure

solution of the [TEDAH₂]-vermiculite intercalate itself. The crystal structure of the parent compound triethylenediamine (TEDA), which exists as two phases, has been reported by Weiss *et al.* (1964), and by Nimmo and Lucas (1976a,b), and a preliminary structure report of the [TEDAH][ClO₄] salt has also been reported by Glowiak *et al.* (1975).

5.2 Experimental

The compound TEDA.2HCl was prepared by passing dry HCl gas (generated by dripping H₂SO₄ on NaCl) through an ethanolic solution of TEDA (Shabtai *et al.*, 1977). The TEDA.2HCl thus precipitated was filtered off, washed with ethanol and dried under vacuum. Microchemical analysis, carried out by Canadian Microanalytical Service, Vancouver, gave the following results: C=39.0, H=7.6, Cl=38.3 and N=15.0%; while TEDA.2HCl(C₆H₁₄Cl₂N₂) requires C=38.9, H=7.6, Cl=38.3 and N=15.1%.

Crystals suitable for X-ray diffraction studies were obtained from the vapour diffusion of ethanol into an aqueous solution of the compound under reduced pressure. The cell parameter data are given in Table 5.1.

Table 5.1: Cell Parameters for Triethylenediamine Dihydrochloride

=====

Orthorhombic, Pna2₁, a=11.723(3), b=6.944(2), c=11.003(2)Å,
Z=4, D_m=1.35, D_x=1.373 g cm⁻³

=====

Intensity data were measured on an Enraf-Nonius CAD4 diffractometer using the $\omega:2\theta$ scan technique in the range $1 \leq \theta \leq 30^\circ$ with graphite-monochromatized MoK α radiation. Cell parameters were refined by a least-squares procedure on the setting angles of 25 reflections ($10 \leq \theta \leq 15^\circ$). No detectable decomposition of the

crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects; no correction was applied for absorption due to the low value for μ of 5.97 cm^{-1} . The systematic absences, as determined from the data collection, were consistent with the space groups $\text{Pna}2_1$ and Pnam (non-standard setting of Pnma); the subsequent details pertain to the non-centrosymmetric space group. Of the 2025 reflections measured, 1441 were unique and 1101 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability.

The structure was solved with the aid of the MITHRIL (Gilmore, 1984) direct-methods program for the space group $\text{Pna}2_1$. The structure was refined by a full-matrix least-squares procedure based on F with the use of SHELX76 (Sheldrick, 1976). Non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were refined isotropically. A weighting scheme of the form $k/(\sigma^2 F + |g|F^2)$ was introduced and the refinement continued until convergence; $R=0.028$ ($R=0.044$ for all data), $R_w=0.027$, $k=9.56$, and $g=0.0004$. The absolute conformation of the cations was not determined as there were no significant differences in the Friedel pairs included in the data set. The maximum and minimum residual electron density peaks in the final difference map were 0.21 and $-0.33 \text{ e } \text{\AA}^{-3}$ respectively. The analysis of variance showed no special features and no extinction correction was applied.

The scattering factors for the atoms were those incorporated in the SHELX76 (Sheldrick, 1976) program. Atomic coordinates for all atoms are listed in Table 5.2, the numbering scheme used is shown in Figure 5.1 and selected interatomic parameters are listed in Table 5.3. Thermal parameters, interatomic parameters involving hydrogen atoms and mean plane data, are given in Tables 5.4-5.6. The list of observed and calculated structure factors is given in Appendix A.2.

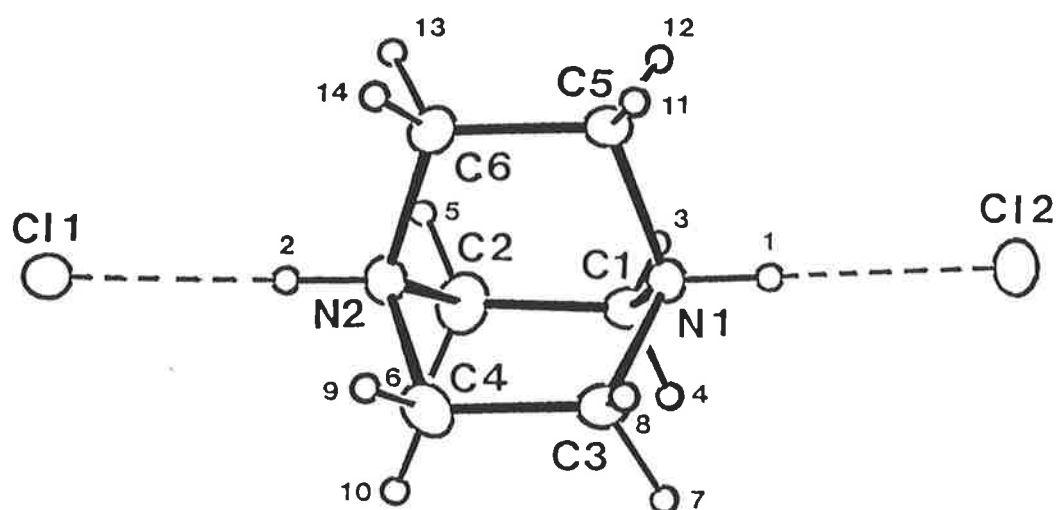


FIG. 5.1

The molecular structure and numbering scheme for TEDA.2HCl; note that atoms otherwise not indicated are hydrogen atoms (Johnson 1976).

5.3 Results and Discussion

The structure determination of TEDA.2HCl confirms the stoichiometry of the compound as $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}][2\text{Cl}]$. The cation geometry is comprised of two +NH units connected by three $-\text{CH}_2\text{CH}_2-$ links as shown in Figure 5.1. An inspection of the bond distances and angles, listed in Table 5.3, shows no special features; the N-C and C-C bonds are equivalent within experimental errors. The intramolecular N(1)...N(2) and H(1)...H(2) separations are 2.475(4) and 4.2(1)Å respectively.

Although the cation does not possess any crystallographic symmetry higher than 1, it is noted that the atoms N(1), C(1), C(2) and N(2) define an approximate mirror plane; deviations from the least-squares plane for N(1): -0.004(2); C(1): 0.012(3); C(2): -0.020(3); N(2): 0.004(2)Å with the Cl(1) and Cl(2) atoms being 0.187(1) and -0.131(1)Å out of the pseudo-m plane respectively. The lack of molecular symmetry in the cations (and associated Cl atoms) therefore precludes the choice of Pnma as the space group (see Experimental).

Associated with each of the cations, within 2.2Å, are the chloride anions Cl(1) and Cl(2). The hydrogen-bonding contacts of 2.14(2)Å for Cl(1)...H(2) and 2.19(2)Å for Cl(2)...H(1) are well within the sum of the van der Waals radii for H and Cl of 3.0Å (Hamilton and Ibers, 1968). The angles subtended at the H(1) and H(2) atoms by the nitrogen and chloride atoms have been calculated to be 174(3) and 151(3)° respectively, consistent with substantial hydrogen bonding of the type N-H...Cl. The next nearest contacts in the crystal lattice involving the chloride anions occur between Cl(1)...H(4') ($-1-x, -y, 1/2+z$) at 2.70(2)Å and at 2.95(2)Å between Cl(2)...H(13') ($1/2-x, -1/2+y, 1/2+z$) and while these contacts are less than the sum of the van der Waals radii for these atoms, they are not indicative of significant hydrogen bonding between the molecules. The closest intermolecular H...H contact in the structure occurs between

Table 5.2: Fractional Atomic Coordinates and B_{eq} values for TEDA.2HCl.

$$B_{eq} = 8\pi^2 (U_{11} + U_{22} + U_{33}) / 3.$$

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
Cl(1)	-0.8333(1)	-0.0057(1)	0.0(-)	3.38
Cl(2)	0.0243(1)	-0.4472(1)	-0.1734(1)	4.09
N(1)	0.1252(2)	-0.1357(3)	-0.3309(2)	3.18
N(2)	0.2167(2)	0.1180(3)	-0.4552(2)	3.34
C(1)	0.1091(2)	-0.1823(4)	-0.4628(3)	3.47
C(2)	0.1674(3)	-0.0310(6)	-0.5371(3)	4.90
C(3)	0.0704(2)	0.0534(4)	-0.3024(3)	3.50
C(4)	0.1227(3)	0.2062(5)	-0.3831(4)	4.93
C(5)	0.2498(2)	-0.1283(4)	-0.3011(3)	3.22
C(6)	0.3041(2)	0.0302(5)	-0.3762(4)	4.59
H(1)	0.0950(29)	-0.2313(54)	-0.2906(24)	5.80
H(2)	0.2501(27)	0.2121(50)	-0.4950(40)	4.84
H(3)	0.1393(24)	-0.2855(52)	-0.4816(34)	3.98
H(4)	0.0312(26)	-0.1896(53)	-0.4735(34)	4.59
H(5)	0.2413(39)	-0.0769(62)	-0.5802(42)	5.82
H(6)	0.1130(43)	0.0403(56)	-0.5954(53)	6.21
H(7)	-0.0135(28)	0.0289(48)	-0.3084(35)	4.02
H(8)	0.0778(26)	0.0904(47)	-0.2226(33)	3.57
H(9)	0.1620(40)	0.3001(95)	-0.3409(56)	9.34
H(10)	0.0763(39)	0.2582(84)	-0.4316(52)	9.51
H(11)	0.2614(28)	-0.1023(47)	-0.2191(31)	3.70
H(12)	0.2759(24)	-0.2512(42)	-0.3120(33)	3.88
H(13)	0.3684(66)	-0.0191(81)	-0.4350(61)	9.22
H(14)	0.3467(34)	0.1111(72)	-0.3394(46)	6.37

Table 5.3: Selected Bond Distances (Å) and Angles (°) for
TEDA.2HCl

=====			
Atoms	Distance	Atoms	Distance
N(1)-C(1)	1.499(3)	N(2)-C(2)	1.489(4)
N(1)-C(3)	1.495(3)	N(2)-C(4)	1.490(4)
N(1)-C(5)	1.498(3)	N(2)-C(6)	1.475(4)
N(1)-H(1)	0.87(4)	N(2)-H(2)	0.88(4)
H(1)...Cl(2)	2.14(2)	H(2)...Cl(1)	2.19(2)
C(1)-C(2)	1.496(5)	C(3)-C(4)	1.513(4)
C(5)-C(6)	1.516(4)		
Atoms	Angle	Atoms	Angle
C(1)-N(1)-C(3)	109.8(2)	C(2)-N(2)-C(4)	108.7(3)
C(1)-N(1)-C(5)	110.0(2)	C(2)-N(2)-C(6)	109.8(3)
C(3)-N(1)-C(5)	110.1(2)	C(4)-N(2)-C(6)	111.7(3)
H(1)-N(1)-C(1)	106(3)	H(2)-N(2)-C(2)	113(3)
H(1)-N(1)-C(3)	113(3)	H(2)-N(2)-C(4)	107(2)
H(1)-N(1)-C(5)	108(2)	H(2)-N(2)-C(6)	107(2)
N(1)-C(1)-C(2)	108.6(2)	N(2)-C(2)-C(1)	109.6(2)
N(1)-C(3)-C(4)	108.6(2)	N(2)-C(4)-C(3)	108.9(2)
N(1)-C(5)-C(6)	108.3(2)	N(2)-C(6)-C(5)	109.3(2)
N(1)-H(1)...Cl(2)	174(3)	N(2)-H(2)...Cl(1)	151(3)
=====			

Table 5.4: Anisotropic Thermal Parameters ($\text{\AA}^2$; $\times 10^4$) for Non-hydrogen Atoms in TEDA.2HCl and Isotropic Thermal Parameters ($\times 10^3$) for Hydrogen Atoms

Atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Cl(1)	408(2)	429(2)	446(3)	43(2)	-3(3)	-40(2)
Cl(2)	591(3)	494(3)	468(3)	-119(3)	1(3)	57(3)
N(1)	364(9)	394(9)	450(11)	4(8)	26(8)	72(9)
N(2)	448(10)	435(9)	387(9)	-55(8)	-26(9)	72(9)
C(1)	377(11)	396(10)	544(13)	22(10)	-64(10)	-91(11)
C(2)	744(22)	778(21)	338(12)	-164(17)	-45(12)	-43(12)
C(3)	403(11)	518(12)	410(12)	80(10)	42(9)	-17(10)
C(4)	752(20)	426(13)	697(19)	154(14)	188(17)	51(14)
C(5)	368(10)	476(12)	379(11)	60(10)	-13(9)	37(9)
C(6)	396(12)	710(18)	636(18)	-94(13)	-97(12)	219(15)
H(1)	74(11)					
H(2)	61(9)					
H(3)	50(8)					
H(4)	58(9)					
H(5)	74(11)					
H(6)	79(13)					
H(7)	51(9)					
H(8)	45(8)					
H(9)	118(20)					
H(10)	121(22)					
H(11)	47(8)					
H(12)	49(8)					
H(13)	117(20)					
H(14)	81(13)					

Where the anisotropic thermal parameter is given by the following expression:

$$T_{\text{aniso}} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

Table 5.5: Interatomic Hydrogen Atom Parameters for TEDA.2HCl

=====			
Atoms	Distance	Atoms	Distance
C(1)-H(3)	0.83(4)	C(2)-H(5)	1.04(5)
C(1)-H(4)	0.92(4)	C(2)-H(6)	1.03(5)
C(3)-H(7)	1.00(3)	C(4)-H(9)	0.92(6)
C(3)-H(8)	0.92(4)	C(4)-H(10)	0.84(5)
C(5)-H(11)	0.93(4)	C(6)-H(13)	1.05(7)
C(5)-H(12)	0.91(3)	C(6)-H(14)	0.85(5)
=====			
Atoms	Angle	Atoms	Angle
H(3)-C(1)-H(4)	110(3)	H(5)-C(2)-H(6)	112(4)
H(3)-C(1)-N(1)	112(3)	H(5)-C(2)-N(2)	100(3)
H(3)-C(1)-C(2)	106(2)	H(5)-C(2)-C(1)	115(2)
H(4)-C(1)-N(1)	105(2)	H(6)-C(2)-N(2)	106(2)
H(4)-C(1)-C(2)	115(2)	H(6)-C(2)-C(1)	113(3)
H(7)-C(3)-H(8)	102(3)	H(9)-C(4)-H(10)	110(5)
H(7)-C(3)-N(1)	105(2)	H(9)-C(4)-N(2)	101(3)
H(7)-C(3)-C(4)	119(2)	H(9)-C(4)-C(3)	114(4)
H(8)-C(3)-N(1)	114(2)	H(10)-C(4)-N(2)	108(4)
H(8)-C(3)-C(4)	109(2)	H(10)-C(4)-C(3)	114(4)
H(11)-C(5)-H(12)	105(3)	H(13)-C(6)-H(14)	95(4)
H(11)-C(5)-N(1)	111(2)	H(13)-C(6)-N(2)	106(4)
H(11)-C(5)-C(6)	109(2)	H(13)-C(6)-C(5)	114(3)
H(12)-C(5)-N(1)	105(2)	H(14)-C(6)-C(5)	114(3)
H(12)-C(5)-C(6)	118(2)	H(14)-C(6)-C(5)	118(3)
=====			

Table 5.6: Mean Plane Data for TEDA.2HCl

Least-squares plane in the form $1X + mY + nZ - d = 0$ and distances ($\text{\AA}$) of the atoms from the plane. The atomic coordinates have been weighted according to the following expression:

$$W_i = (\sigma_i^2)^{-1}.$$

Plane: $-0.857X - 0.515Y - 0.015Z + 1.685 = 0$

=====

Atoms	Distance
N(1)	-0.004(2)
C(1)	0.012(3)
C(2)	-0.020(3)
N(2)	0.004(2)
Cl(1)*	0.187(1)
Cl(2)*	-0.131(1)
C(3)*	1.218(3)
C(4)*	1.253(4)
C(5)*	-1.234(3)
C(6)*	-1.201(3)

=====

* Atom not included in plane.

H(6) and H(7') $(-x, -y, -1/2+z)$ at $2.66\text{\AA}$. The crystal structure of TEDA.2HCl may therefore be considered as being comprised of discrete units of $\text{Cl}\dots\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}\dots\text{Cl}$, the molecules being held together in the lattice by normal van der Waals contacts. The a-, b- and c-axes ^{i.e.} views of the unit cell contents are shown in Figures 5.2-5.4.

The lack of molecular symmetry found for the cation in TEDA.2HCl contrasts with that observed for the parent compound TEDA (Nimmo and Lucas, 1976a) and the $[\text{TEDAH}][\text{ClO}_4]$ compound (Glowiak *et al.*, 1975). In the room-temperature form of TEDA, the molecular symmetry is $\bar{6}m2$ (i.e. the asymmetric unit is defined by $1/3\text{N}$ and

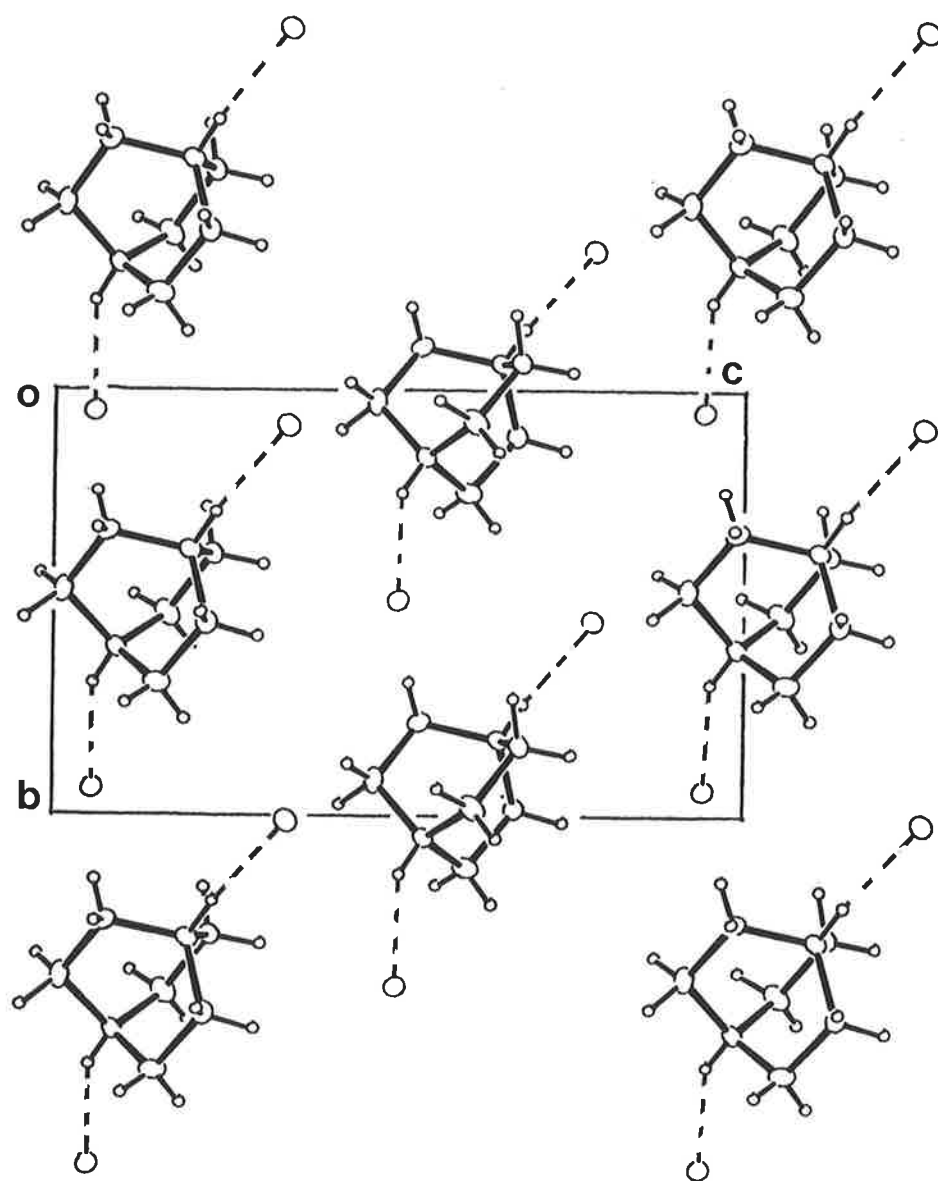


FIG. 5.2 The unit cell contents of TEDA.2HCl as viewed down the a-axis direction highlighting the N-H...Cl hydrogen bonding.

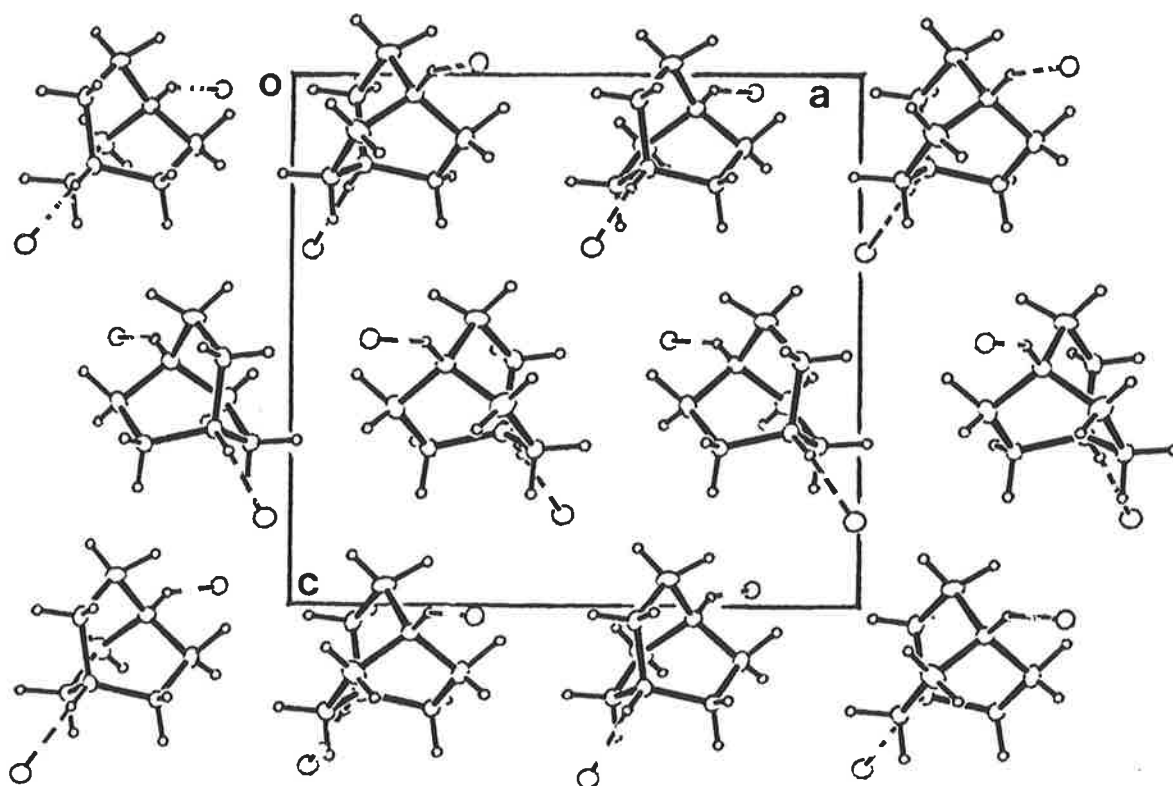


FIG. 5.3 The unit cell contents of TEDA.2HCl as viewed down the b-axis direction highlighting the N-H...Cl hydrogen bonding.

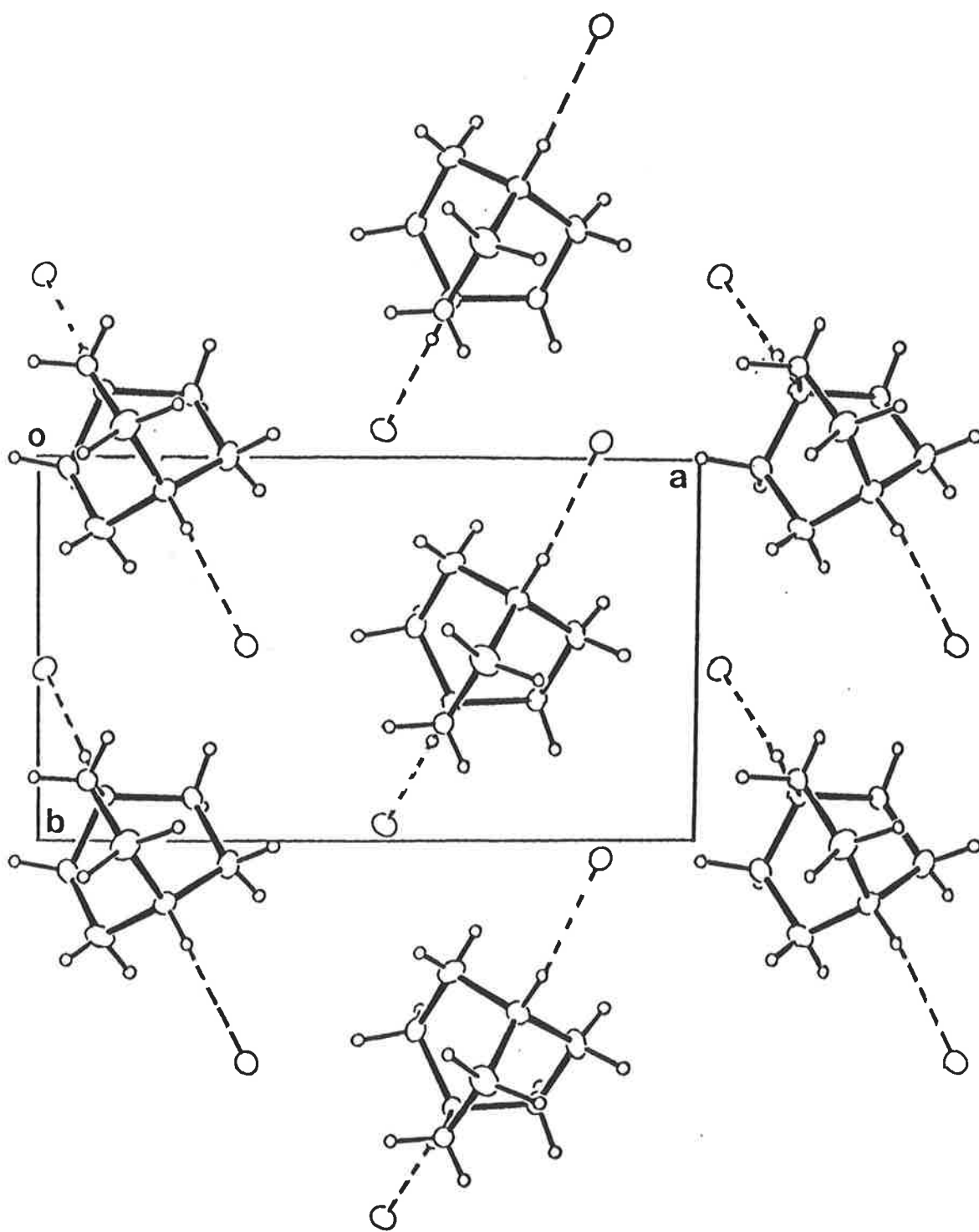


FIG. 5.4

The unit cell contents of TEDA.2HCl as viewed down the c-axis direction highlighting the N-H...Cl hydrogen bonding.

CH₂) which yields a regular structure of non-twisted rigid molecules (Nimmo and Lucas, 1976a). In the protonated compound [TEDAH][ClO₄], the molecular symmetry is *m* and the crystal structure is comprised of polycationic chains which arise as a result of substantial N-H...N interactions such that the angle subtended at the bridging hydrogen atom is 166° (Glowiak *et al.*, 1975). There are no close contacts between the TEDAH cation and the perchlorate anions.

The successful intercalation process between organic amines and sheet silicates requires the N-H group(s) of the organic species to form hydrogen bonds to the silicate oxygen atoms (Slade and Raupach, 1982). However, a successful intercalation also depends on the size of the intercalating species to be of the same magnitude as the hexagonal holes formed by the basal oxygens of the 2:1 sheet silicates (Slade *et al.*, 1987). In the hexagonal array the holes are about 5.3Å apart and therefore organic molecules which pack such that their centres are approximately this distance apart should be successful intercalants. It is noted that in TEDA.2HCl the Cl...Cl separations in the planes perpendicular to the N(1)...N(2) intramolecular vectors (these Cl...Cl separations approximate the [TEDAH₂]²⁺ cation...cation interionic separations) are in the range 5.12-5.69Å, i.e. they are of the correct magnitude for intercalation to take place.

CHAPTER 6

TRIETHYLENEDIAMINIUM INTERCALATED VERMICULITES: PREPARATION AND ANALYSIS

CHAPTER 6

TRIETHYLENEDIAMINIUM INTERCALATED VERMICULITES:
PREPARATION AND ANALYSIS

6.1 Introduction

Three different vermiculites were chosen for this intercalation process: one from Llano County, Texas, U.S.A., and two from Africa: one from Kenya and one from Nyasaland (now Malawi). The vermiculite chosen from Llano County, Texas was from the same mine as the one used for the anilinium intercalation, but it was taken from a different area of the mine, namely Stop 11 and not Stop 12 as used for the anilinium intercalation (see Norrish, 1973). These three vermiculites were chosen because they possessed different cation exchange capacities; their respective charges per unit cell were 1.82, 1.38 and 1.22, as determined by Norrish (1973) using Ca-saturated samples and X-ray fluorescence analysis. The triethylenediaminium dications $[\text{TEDA}\text{H}_2]^{2+}$ were obtained from triethylenediamine dihydrochloride ($\text{TEDA}\cdot 2\text{HCl}$), which is also known as 1-4-diazabicyclo[2,2,2]octane dihydrochloride ($\text{DABCO}\cdot 2\text{HCl}$). The $\text{TEDA}\cdot 2\text{HCl}$ was prepared from commercially available TEDA by passing dry hydrogen chloride gas through an ethanolic solution of TEDA and precipitating $\text{TEDA}\cdot 2\text{HCl}$. The hydrogen chloride gas was obtained by dripping pure sulphuric acid onto sodium chloride and drying the gas by bubbling it through concentrated H_2SO_4 . The $\text{TEDA}\cdot 2\text{HCl}$ produced was finally washed with ethanol and dried under vacuum and kept in a desiccator.

6.2 Preparation

The intercalation process was similar to that used in the anilinium intercalation given in Chapter 2: that is the Mg-vermiculite flakes were first cut to approximately 1-2 mm squares and refluxed with 2M NaCl solution at 80°C for one week. The solution was changed daily and finally the vermiculite crystals were washed with water, to remove any residual NaCl, and then air dried. The Na-saturated vermiculites were then refluxed in one percent TEDA.2HCl solutions, the pH of which was 2.3, for periods up to 10 days at 50°C. The Llano vermiculite was also intercalated with a 10% solution, the pH of which was 1.7. During the intercalation process the solutions were changed daily, at which time a few vermiculite flakes were removed for examination with an X-ray powder diffractometer. The diffractometer technique was the same as given in Chapter 2.1 for the preparation of anilinium intercalated vermiculites; i.e. the progress of the intercalation was monitored by observing the development of a new set of rational 001 reflections. The intercalation was judged to be complete when the new set of 001 reflections was stable even when heated to 80°C. The reaction was then stopped, the flakes removed, washed with hot distilled water and allowed to air dry.

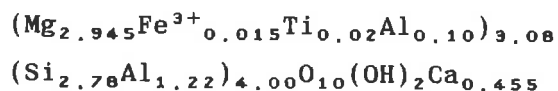
6.3 Chemical Analyses

Chemical analyses were carried out by Norrish (1973) using Ca-saturated vermiculite and X-ray fluorescence technique, and by the author, using Na-saturated and $[\text{TEDAH}_2]^{2+}$ intercalated vermiculites and the electron microprobe. Additional microanalysis was carried out on the $[\text{TEDAH}_2]^{2+}$ intercalated samples for carbon, nitrogen and hydrogen. These combined results enabled structural formulae to be calculated.

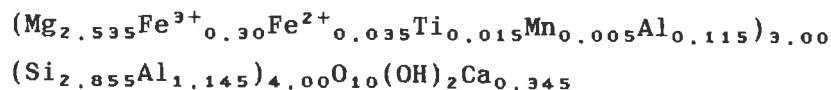
6.3.1 X-ray fluorescence analysis

The above three vermiculites were analysed by Norrish (1973) using X-ray fluorescence technique and calcium intercalated samples. The original magnesium vermiculites were intercalated with calcium cations, as these enter only the interlayer region, so that in addition to the chemical analysis the charges of the three vermiculites could be obtained. From his analyses Norrish obtained the following structural formulae:

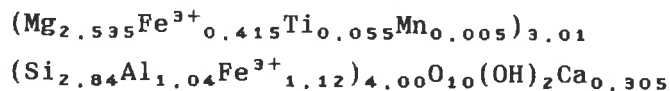
1. Llano vermiculite



2. Kenya vermiculite



3. Nyasaland vermiculite



Since there are two formula units in a unit cell, the interlayer charges per unit cell are 1.82, 1.38 and 1.22 respectively.

6.3.2 Electron microprobe analysis

A number of crystal flakes of sodium and $[\text{TEDAH}_2]^{2+}$ intercalated vermiculites, from the three different localities, were analysed using a JEOL 733 Superprobe, a KEVEX 7000 Series energy dispersive spectrometer and the raw data were processed using full ZAF corrections with a PIBS style software (Ware, 1981). The following operating conditions were employed: accelerating voltage 15kV, probe current 5nA, beam size 20 μm diameter, counting times 60 seconds life time and the samples were scanned

during analyses at a magnification of $\times 4000$ to avoid sample damage.

The samples were prepared by attaching a number of flat crystal flakes onto polished blank epoxy resin briquettes and coating them with approximately 25 nm of carbon. Point analyses, using the above mentioned conditions, were carried out on several flakes of each sample, the results averaged and structural formulae calculated. The results obtained are given in Tables 6.1-6.2.

Table 6.1: Electron Microprobe Analysis of Sodium Saturated Vermiculites

Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	MgO	Na ₂ O	Total
Llano	39.3	0.28	13.6	0.63	-	26.6	6.2	86.61
Kenya	37.8	0.71	14.2	6.7	-	22.8	4.7	86.91
Nyasaland	38.0	0.97	11.5	9.1	0.41	23.1	4.3	87.38

Table 6.2: Electron Microprobe Analysis of (TEDAH₂)²⁺ Saturated Vermiculites

Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	MgO	TO ⁽¹⁾	Total
Llano	38.9	0.29	13.1	0.31	-	23.8	5.9	82.30
Kenya	38.8	0.64	14.8	6.5	-	23.3	7.7	91.74
Nyasaland	37.2	0.96	11.1	8.9	0.40	21.6	7.1	87.26

(1) TO=(C₂H₄)₃(NH)₂O=triethylenediaminium oxide or [TEDAH₂]⁺O. The carbon, nitrogen and hydrogen analyses were carried out by the Canadian Microanalytical Service Ltd., Vancouver, Canada. The following results were obtained for the three vermiculites intercalated:

Llano

C=3.28 N=1.27 H=2.50%

Kenya

C=4.40 N=1.62 H=2.14%

Nyasaland

C=3.80 N=1.60 H=2.09%

The [TEDAH₂] oxide weight percent values given in Table 6.2 were calculated from the microanalytical carbon and nitrogen figures received (the values quoted are the average of two molecular weights calculated using the carbon and nitrogen figures separately).

Using the microprobe and microanalytical results given in Tables 6.1 and 6.2 structural formulae were calculated for the three sodium and three [TEDAH₂]²⁺ vermiculites. The results are given in Table 6.3.

Since the unit cell contains two formula units, the interlayer charges per unit cell in the sodium intercalated Llano, Kenya and Nyasaland vermiculites are 1.76, 1.36 and 1.24 respectively. These values compare very well with the figures of 1.82, 1.38 and 1.22 obtained by Norrish (1973). The interlayer charges obtained for the [TEDAH₂] intercalated Llano, Kenya and Nyasaland vermiculites, using the [TEDAH₂] cations as the only interlayer material present, are 0.96, 1.04 and 1.04. These value are quite different from their sodium counterparts. There are not enough [TEADH₂] cations to replace all the sodium cations in these vermiculites, but since the microprobe analyses did not detect the presence of any sodium, some of the original sodium must have been replaced by other cations, which must have come from the silicate layers themselves - most probably from the octahedral sites, elements such as magnesium, aluminium or iron.

Table 6.3: Structural Formulae (O = 11) for Sodium and [TEDAH₂]²⁺
Intercalated Llano, Kenya and Nyasaland Vermiculites

Sample	Tetrahedral Σ=4			Octahedral					Octa- hedral Total	Interlayer	
	Si	Al	Fe ³⁺	Mg	Fe ³⁺	Ti	Cr	Al		Na ⁺	[TEDAH ₂] ²⁺
Llano Na ⁺	2.89	1.11	—	2.92	0.03	0.02	—	0.07	3.04	0.88	—
Llano [TEDAH ₂] ²⁺	2.94	1.06	—	2.78	0.02	0.02	—	0.15	2.97	—	0.24
Kenya Na ⁺	2.81	1.19	—	2.53	0.38	0.04	—	0.06	3.01	0.68	—
Kenya [TEDAH ₂] ²⁺	2.84	1.16	—	2.54	0.36	0.03	—	0.11	3.04	—	0.26
Nyasaland Na ⁺	2.84	1.01	0.15	2.57	0.36	0.05	0.02	—	3.00	0.62	—
Nysaland [TEDAH ₂] ²⁺	2.89	1.02	0.09	2.50	0.43	0.06	0.03	—	3.02	—	0.26

To check the accuracy of the above [TEDAH₂] figures their values were recalculated by measuring the densities and volumes of the unit cells, obtained by precession and CAD4 methods, these gave the mass of the unit cells ($M=D \times V$). Knowing the weight percent of carbon and nitrogen present in the samples from microanalytical results, and the number of carbon and nitrogen atoms in one [TEDAH₂] dication, the number of [TEDAH₂] dications per structural formula was calculated. The values obtained were 0.23, 0.26 and 0.27 for the Llano, Kenya and Nyasaland vermiculites respectively, which are almost the same as obtained by the use of the microprobe and microanalytical results previously (0.24, 0.26 and 0.26). The interlayer charges per unit cell are four times the above figures, i.e. 0.92, 1.04 and 1.08, and 0.96, 1.04 and 1.04.

The accuracy of the amount of [TEDAH₂] intercalated into the various vermiculites was further checked by intercalating another batch of Nyasaland vermiculite using the same experimental conditions as before. The microanalytical results gave the following values:

C=3.89, N=1.49, H=2.37%

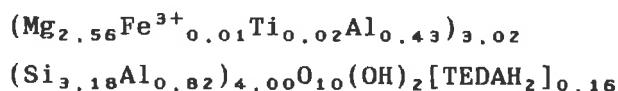
which in conjunction with the density and volume of the unit cell, gave [TEDAH₂] equal to 0.26, a value which is almost exactly equal to the corresponding first value of 0.27 obtained for the first intercalation.

A further check was also carried out using Llano vermiculite, but this time intercalating with a 10% solution of TEDA.2HCl and not the usual 1% solution used in all the previous intercalations. The pH of the 10% solution was measured at 1.7, which is substantially lower than the 2.3 figure obtained for the 1% solution. The microanalytical figures obtained for carbon, nitrogen and hydrogen were:

C=2.53, N=0.95, H=2.58%

figures which are lower than the ones obtained for the 1% solution. Combining the above figures with the density and

volume of the unit cell gave a figure of only 0.16 for the [TEDAH₂] dication, as opposed to 0.24 for the 1% solution. Microprobe analysis of the 10% solution intercalation gave the same [TEDAH₂] value of 0.16, and the following structural formula:



The formula shows an apparent increase in the number of silicon atoms and a decrease in the magnesium value, which can be explained as a partial dissolution of the octahedral sites at the lower pH values, where a subsequent loss of magnesium occurs into the solution followed by a likely partial introduction of the magnesium atoms into the interlayer region to replace some of the sodium cations.

6.4 X-Ray Analysis: Photographic Techniques

The intercalated vermiculite crystal flakes were first examined optically using a binocular microscope. Crystals not containing any apparent defects, such as bending, splitting of layers, or other visible imperfections, were mounted on X-ray goniometer arcs and X-rayed using precession, Weissenberg and powder diffractometer methods, to establish the presence or otherwise of superlattice reflections, the degree of three-dimensional order and other crystal defects, as well as identifying the crystal system and providing data for lattice parameter measurements.

From the photographs obtained it was evident that superlattices were present in all three vermiculites, forming a lattice in which the [TEDAH₂] cations occupied the corners and centres of a cell $3a \times b$ when compared to the standard vermiculite cell (Figure 6.1). The superlattice of the Llano vermiculite was more diffuse than in the other two materials, with the Nyasaland

FIG. 6.1

Stationary crystal-cylindrical film photograph of $[\text{TEDAH}_2]^{2+}$ intercalated Kenya vermiculite ($\text{CoK}\alpha$ radiation) showing $3a \times b$ superlattice reflections (fainter spots - marked S) formed by the $[\text{TEDAH}_2]^{2+}$ ions.

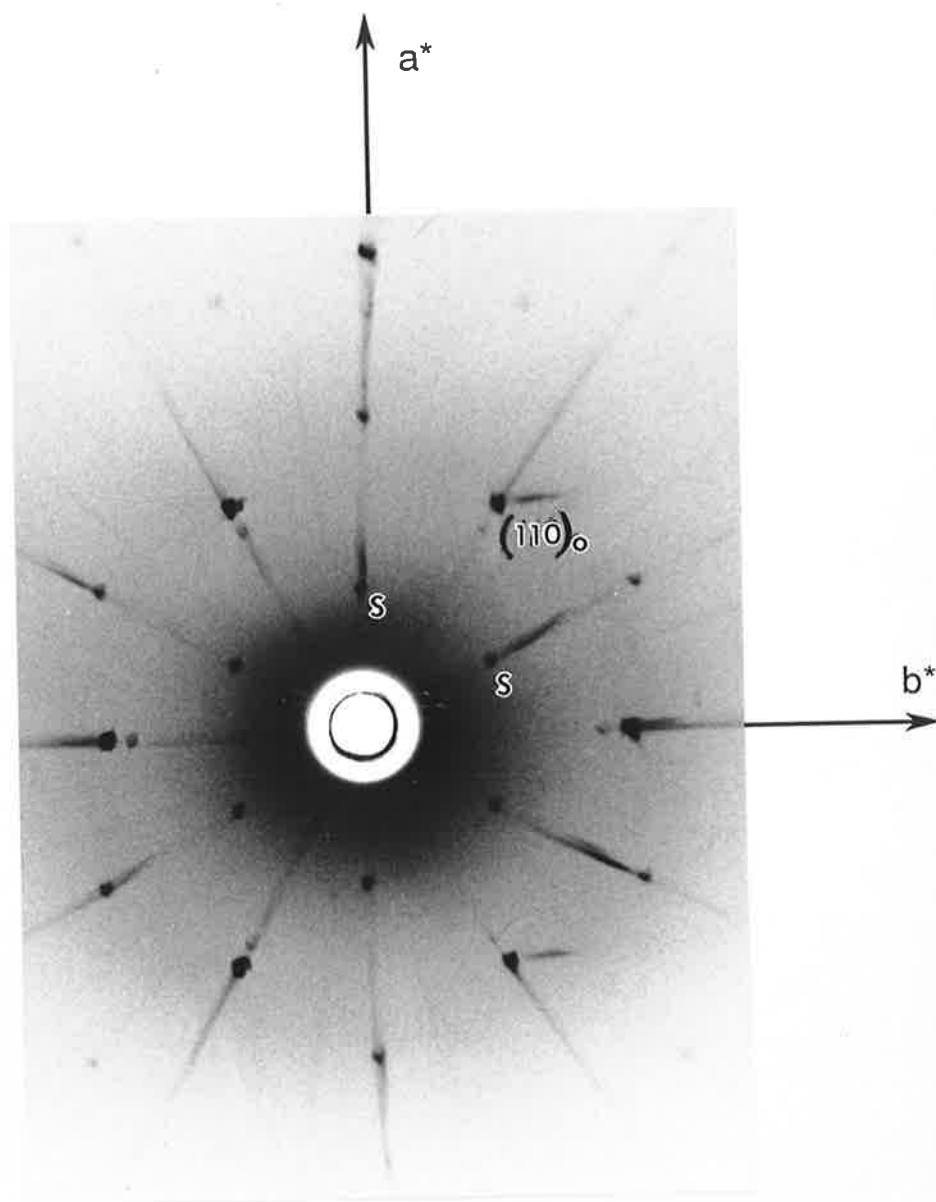


Fig. 6.1

vermiculite giving the sharpest superlattice spots.

Precession methods usually consisted of zero level photographs, with the X-ray beam along the a-or c-axis to yield reflections in the b^*c^* and a^*b^* planes respectively. In these photographs stacking disorders cause streaking of $0kl$ reflections along the c^* direction when $k \neq 3n$. All three vermiculites showed relatively sharp reflections, indicating an ordered layer sequence after intercalation with $[\text{TEDAH}_2]$ cations (Figure 6.2).

Shabtai *et al.* (1977), intercalated montmorillonite with $[\text{TEDAH}_2]$ cations and obtained a product which was stable up to a temperature of 345°C . This intercalate was used by them as a swelling resistant molecular sieve in catalysing the esterification of carboxylic acids. To prove whether our intercalated vermiculites displayed a corresponding thermal stability they were heated to 350°C on the precession camera and zero level photographs taken in the b^*c^* plane, where the $k \neq 3n$ reflection broadening, as well as any collapse of the c-dimension, would be observed.

The heating device used for single crystal high temperature diffractometry, which fitted a standard goniometer head of the Enraf-Nonius type, was purchased from Enraf-Nonius, Holland, minus the temperature controller and the gas supply unit. The heating part of the device consisted of two concentric quartz tubes, through which flowed two gas streams, the central one being heated by means of a Kanthal resistance wire. The crystals to be X-rayed were attached with Araldite to Pyrex fibres and lowered into a stainless steel capillary tube, which was concentric with the inner quartz tube containing the heating wires. The crystals were mounted just protruding above the quartz tubes so that they provided an unobstructed path for the X-ray beam, while being heated with a stream of hot air; this hot gas stream was surrounded by an outer cold stream to maintain temperature stability. A temperature of 1000K was claimed for

FIG. 6.2 Zero level precession photograph of $[\text{TEDAH}_2]^{2+}$ intercalated Nyasaland vermiculite ($\text{MoK}\alpha$ radiation) showing relatively sharp reflections. Room temperature.

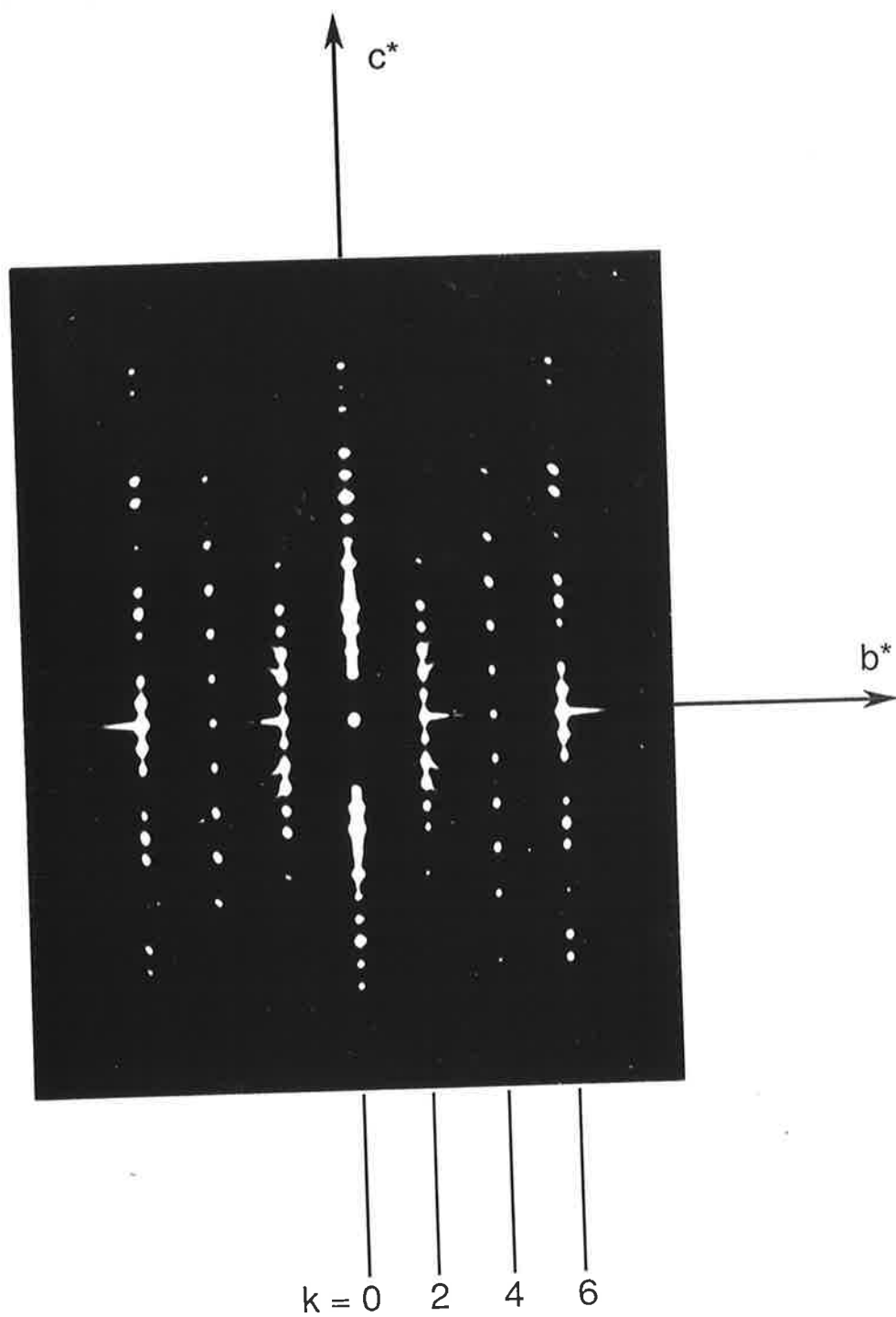


Fig. 6.2

this apparatus with a stated stability of $\pm 1\text{K}$. The heating device outlined above is described fully by Tuinstra and Fraase Storm (1978). The electronic control and gas supply units were manufactured in the University of Adelaide workshops.

As stated before, zero level precession photographs, with the X-ray beam along the a-axis, of the three $[\text{TEDAH}_2]$ intercalated vermiculites show relatively sharp $k\cdot 3n$ reflections at room temperature (Figure 6.2). The actual degree of stacking order, observed as sharper $k\cdot 3n$ reflections, increased from Llano, through Kenya, to Nyasaland vermiculites. The same trend was evident in the sharpness and intensity of superlattice reflections. The structural ordering appeared to follow the amount of $[\text{TEDAH}_2]$ dications intercalated into the interlayer region (0.48, 0.52 and 0.52 per unit cell), and to be inversely proportional to the layer charge (1.76, 1.36 and 1.24). The c-dimensions of Llano, Kenya and Nyasaland vermiculites were 14.1, 14.3 and 14.4 Å respectively, as measured from the precession photographs and the powder diffractometer charts, which corresponded to a slightly increased c-spacings for the more highly $[\text{TEDAH}_2]$ intercalated and lower charged vermiculites.

Heating the vermiculites to about 100°C did not produce any significant change in the structures, although the c-dimensions dropped by about 0.5 Å. Above that temperature the stacking disorders increased, which manifested themselves mainly as more and more diffuse $k\cdot 3n$ reflections; there was also a slow progressive decline in the c-dimensions by a further 0.2 to 0.3 Å at 350°C (Figure 6.3). The structures were still basically stable at that temperature, and when cooled to room temperature and allowed to reach equilibrium with ambient air, regained their original ordered state as well as their original basal spacings.

Transmission electron micrographs of the edge-on view of flakes of the $[\text{TEDAH}_2]$ intercalated vermiculites, taken by Dr. P.G. Self of CSIRO, Division of Soils, Urrbrae, South Australia, revealed

FIG. 6.3 Zero level precession photograph of $[\text{TEDAH}_2]^{2+}$ intercalated Nyasaland vermiculite ($\text{MoK}\alpha$ radiation) showing diffuse reflections but no appreciable c-dimension collapse. Temperature 350°C .

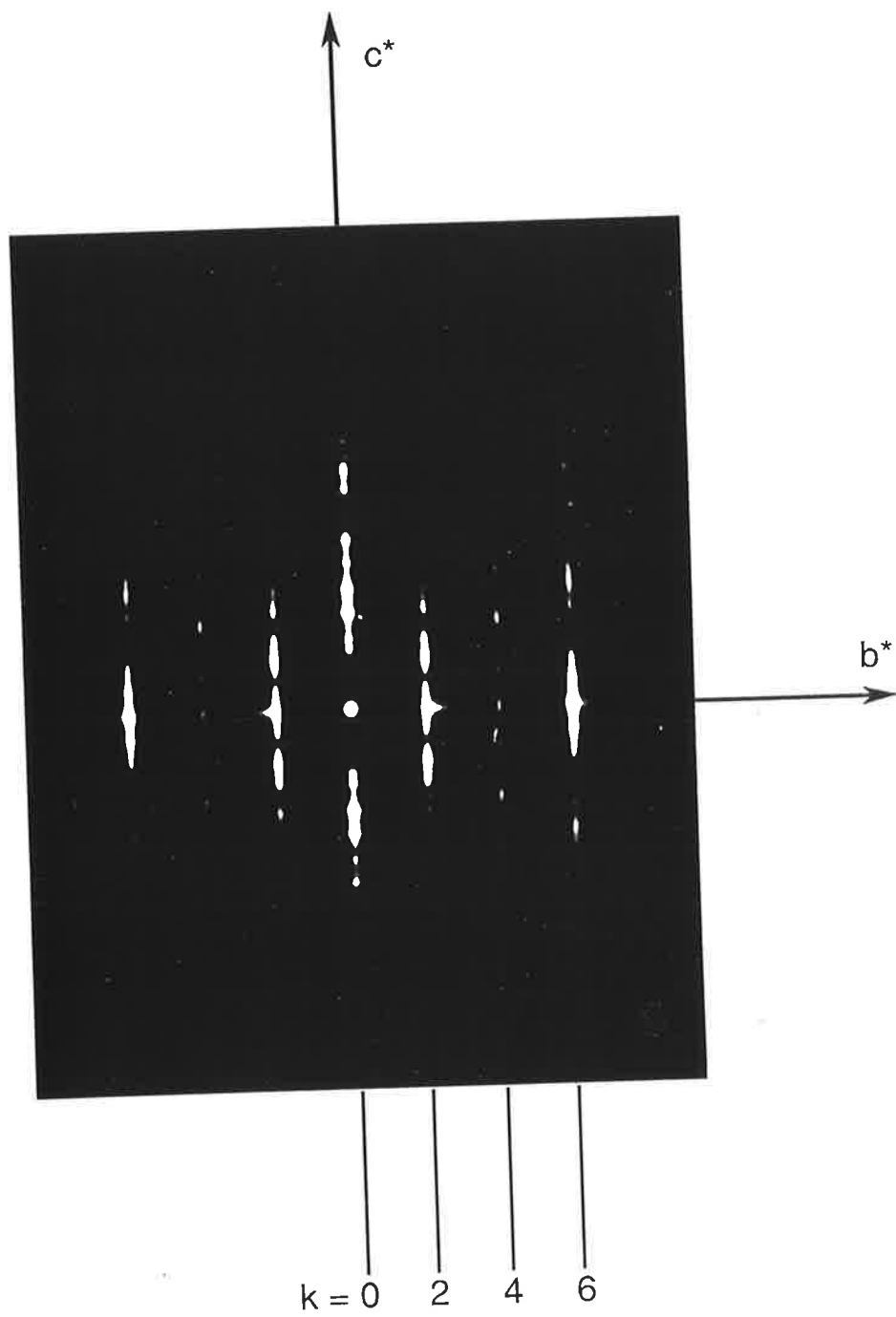


Fig. 6.3

an unexpected repeat distance between the silicate layers of about 12.5Å. This value differed markedly from the value of about 14.4Å determined by X-rays and was surprising because the cross-linking [TEDAH₂] dications in the model of Shabtai *et al.* (1977), were reported to be stable up to 345°C. This unexpected collapse of the spacings to about 12.5Å in the electron microscope seemed incompatible with a model in which rigid, thermally stable, cage-like "pillars" determined the interlayer separations. Therefore it was decided to undertake a full structure analysis of one of the intercalated vermiculites, namely Nyasaland vermiculite, as it possessed the sharpest superlattice, as well as the least diffuse $k \neq 3n$ reflections, using a computer controlled fully automated four-circle single crystal diffractometer (CAD4).

CHAPTER 7

CRYSTAL STRUCTURE OF TRIETHYLENEDIAMINIUM INTERCALATED NYASALAND VERMICULITE

CHAPTER 7

CRYSTAL STRUCTURE OF TRIETHYLENEDIAMINIUM
INTERCALATED NYASALAND VERMICULITE

7.1 Experimental

A crystal flake, measuring 0.06×0.68×0.88 mm, was selected for structure analysis using an ENRAF-NONIUS CAD4 four-circle diffractometer equipped with a graphite monochromator and a molybdenum tube to yield MoK α radiation ($\lambda=0.71073\text{\AA}$). The cell dimensions, given in Table 7.1, were obtained by least-squares refinement of 25 selected low to medium angle reflections.

Table 7.1: Cell Parameters of [TEDAH₂] Intercalated
Nyasaland Vermiculite

=====			
Monoclinic C1,	a=5.341(2),	b=9.249(3),	c=14.50(1) $\text{\AA}$,
$\beta=96.98(5)$:	V=710.95 $\text{\AA}^3$,	Z=2,	$D_m=2.27$, $D_x=2.17 \text{ g cm}^{-3}$,
$\mu=10.93 \text{ cm}^{-1}$.			
=====			

Utilising the CAD4 facility of drawing two-dimensional profiles of omega and theta scans, it was established that the omega/two theta scans were most appropriate for the material studied. The omega scan angle was set to $(1.2 + 2.3 \tan\theta)^\circ$ and the horizontal aperture width to $(3.0 + 1.0 \tan\theta)\text{mm}$. The slit height was set to 6 mm. The space group chosen was P1, with the additional condition of C-centering. Data were collected in the theta range of 1.5 to 30 $^\circ$, with the index ranges of $-6 \leq h \leq 6$, $-12 \leq k \leq 12$, $-18 \leq l \leq 18$. During data collection crystal and instrumental stability was checked by remeasuring the intensities of three selected reflections every 30000 seconds of X-ray exposure time.

Reflections ($h+k$) odd, absent in C-centered cells, were not collected. The maximum time spent on measuring one reflection was 400 seconds. A total of 2570 reflections with $|F_o|/\sigma|F_o| > 5.0$ were observed. The integrated intensities were corrected for Lorentz and polarization effects and for absorption ($\mu = 10.93 \text{ cm}^{-1}$); maximum and minimum transmission factors were 0.943 and 0.558 respectively.

7.2 Structure Solution and Refinement

A trial model for the silicate structure was derived from the atomic coordinates given by Slade *et al.* (1987). The asymmetric unit for the silicate only part of the structure was chosen with the lowest likely symmetry, i.e. C1. Superlattice reflections were not taken into account and therefore the interlayer structure to be described was averaged over sub-cells.

The scattering factors for the octahedral and tetrahedral sites were in accord with the structural formula and fully ionised cations. For oxygen, the O^{2-} value of Tokonami (1965) was used; other values were taken from the International Tables for X-ray Crystallography (1974). The program SHELX76 (Sheldrick, 1976) was used for all the structural refinements.

7.2.1 Initial adjustment of the silicate layer parameters

To start with the positional parameters of all but one octahedral cation (fixed at $0, \frac{1}{2}, 0$) were refined. The isotropic temperature factors were next adjusted in further cycles.

Weighting was not used, but reflections for which $I < 2.5\sigma(I)$ were excluded. The R factor at this stage was 22.8%. The adjusted model for the silicate-only part of the structure enabled the observed structure amplitudes to be converted to observed

structure factors (F_o values). These, along with the F_c values from the silicate-only model, allowed sections through the three-dimensional ($F_o - F_c$) map to be calculated. The difference Fourier sections at the heights of the tetrahedral cations showed that the stacking order of the silicate layers was imperfect; the positions at the centres of the rings of tetrahedra were partially occupied. Residual disorder also showed up on other sections parallel to the basal plane. The disorder, associated with remaining $\pm b/3$ shifts, was modelled as well as possible, after which the R value fell to 16.1%.

7.2.2 Position of $[\text{TEDAH}_2]^{2+}$ ions

Figure 7.1, the difference Fourier section at $y = 1/2$, shows substantial peaks in the interlayer on either side of the middle at $z = 1/2$. The peaks, labelled A, B, C and D in Figure 7.1, were attributed to the organic moieties. They were ascribed as follows: A and C to nitrogens in a lower $[\text{TEDAH}_2]^{2+}$ cation and B and D to nitrogens in an upper cation. This assignment was based on the distances between peaks A and C and B and D being the same as the distance (2.475 Å) between the nitrogen atoms in $\text{TEDA} \cdot 2\text{HCl}$ molecule (Kennedy *et al.*, 1987). The intramolecular N...N vectors were essentially parallel to the c-axis and directed towards the centres of the ditrigonal cavities in opposite silicate layers. The lower cation contacted the lower silicate surface and the upper cation contacted the upper silicate surface. Also implicit in this assignment was the concept that upper and lower cations were not present simultaneously in a single $5 \times 9 \text{ Å}$ unit cell. Both cations appear on the map because the X-ray structure was averaged over many cells, any one of which could only incorporate a single organic cation in one of four equivalent, potentially available, sites.

The section at $y = 1/2$ also showed a series of diffuse interlayer peaks which may have been associated with pairs of ethylene

FIG. 7.1

Difference Fourier contour map at $y = 1/2$ showing substantial peaks in the interlayer region. Peaks A and C are attributed to the two nitrogen atoms in the lower [TEDAH₂] cation and peaks B and D to the nitrogen atoms in the upper cation. Two water molecules are also seen. Contour interval is 0.1 e Å⁻³.

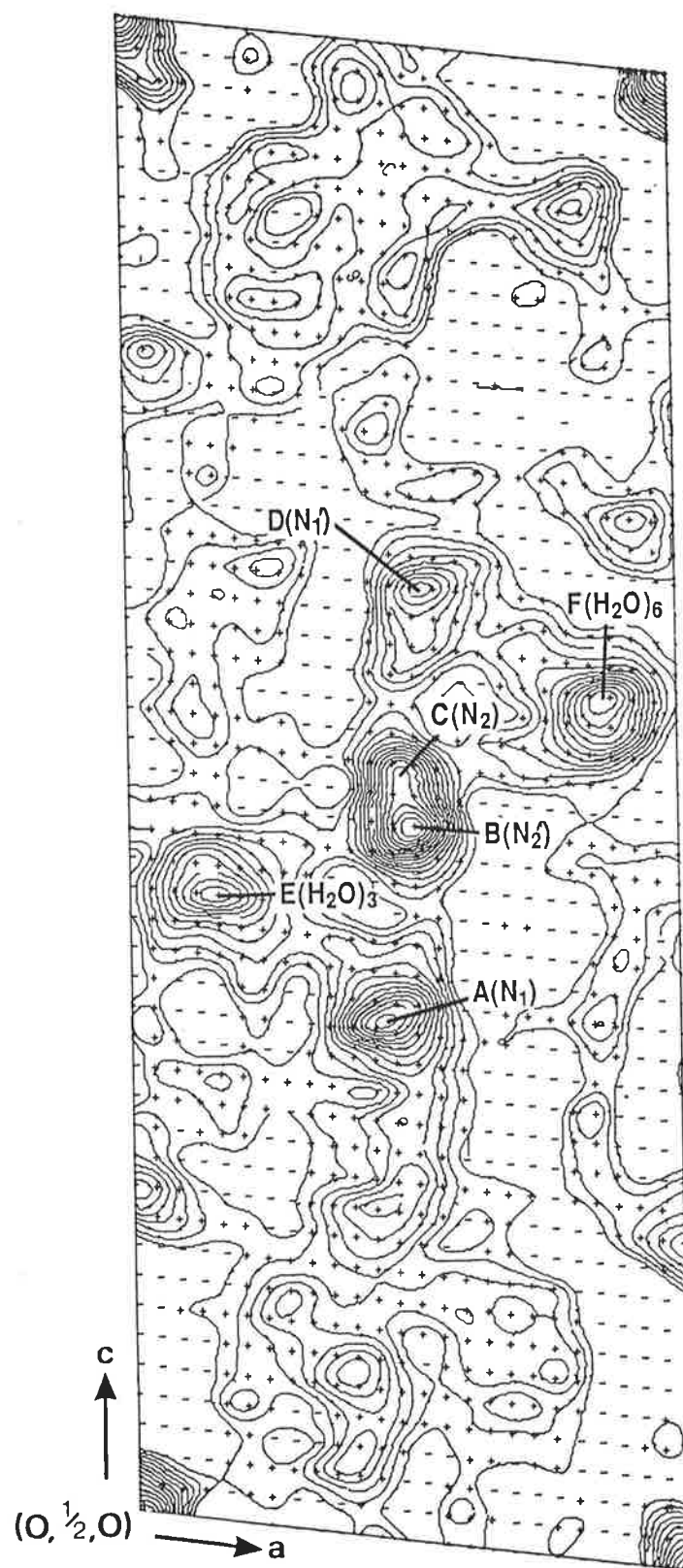


Fig. 7.1



carbons. Their images, however, were not clear, perhaps because of positional disorder, but more certainly because there were other interlayer components (see below) producing overlapping images in the sub-cell used to represent the structure.

7.2.3 Additional interlayer components

The difference Fourier section at $z = 1/2$ (Figure 7.2) shows a series of well-defined peaks which, with the exception of the weaker one at $1/2, 1/2, 1/2$, are of equal strength. The stronger peaks corresponded with sites mid-way between the tetrahedral bases and therefore are associated with inorganic interlayer cations. The peak at $1/2, 1/2, 1/2$ resulted from overlap of the nitrogen peaks B and C referred to above.

Further evidence for the structure of the interlayer appear on sections at $z = 0.43$, $z = 0.57$, and $y = 1/2$. Collectively, these sections show peaks at positions where water molecules, octahedrally coordinated at distances $\sim 2.05\text{\AA}$ from the interlayer inorganic cations, were expected. The interlayer structure therefore included not only [TEDAH₂] cations, but also a network of inorganic cations and water molecules. A full trial-set of positional coordinates for each of the interlayer members was obtained from the difference Fourier sections and then refined. For these calculations the isotropic thermal parameters belonging to similar kinds of atoms were adjusted in groups and the inorganic interlayer cations were, as explained later, assigned to the Fe³⁺ scattering factor.

Refinement of the final model led to an R value = 12.6% for 1814 reflections and 220 parameters; unit weights were used throughout. Table 7.1 shows the resulting positional and thermal parameters. The bond lengths are given in Tables 7.2 and 7.3. The relatively large temperature factor for the surface oxygen atoms was associated with some remaining positional disorder

FIG. 7.2 Difference Fourier contour map at $z = 1/2$ showing
the presence of inorganic cations. Contour
interval is $0.3 \text{ e } \text{\AA}^{-3}$.

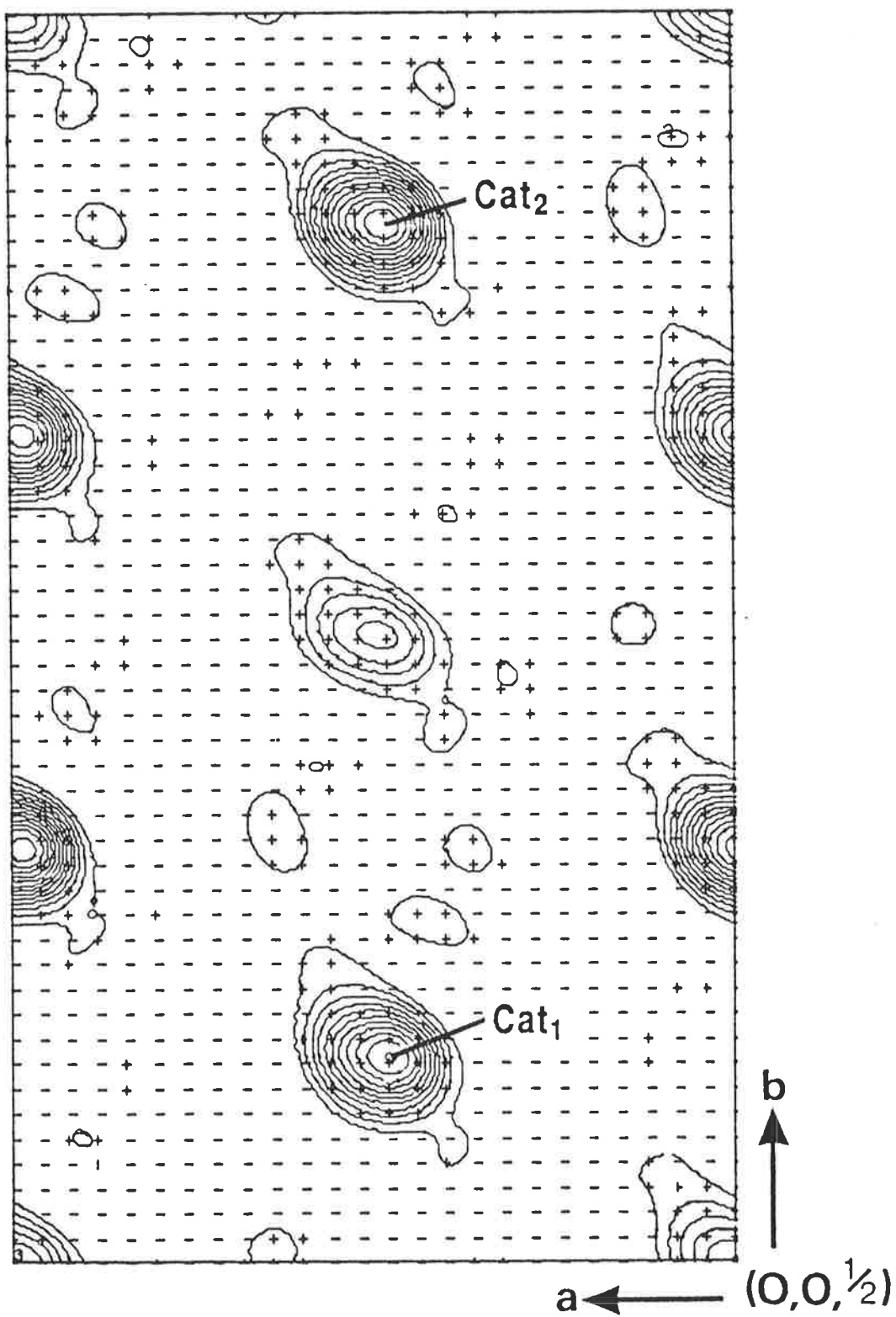


Fig. 7.2

Table 7.1: Positional and Temperature Parameters for
[TEDAH₂]²⁺ Intercalated Nyasaland Vermiculite

Atom	x	y	z	B
Mg(1)	0.0000	0.5000	0.0000	0.16
Mg(2)	0.000(1)	0.8329(8)	0.0012(7)	0.16
Mg(3)	-0.003(1)	-0.8350(8)	0.0008(6)	0.16
T(1)	0.391(1)	0.1628(6)	0.1867(5)	0.26
T(2)	0.392(1)	0.8304(7)	0.1864(5)	0.26
T(3)	0.594(2)	0.161(1)	0.808(1)	1.26
T(4)	0.598(2)	0.830(1)	0.8068(8)	1.26
O(1)	0.360(2)	0.163(1)	0.0740(9)	0.51
O(2)	0.361(2)	-0.170(1)	0.0734(9)	0.51
O(3)	0.859(2)	-0.001(1)	0.072(1)	0.51
O(4)	-0.353(3)	0.165(1)	-0.074(1)	0.51
O(5)	-0.353(3)	-0.168(2)	-0.076(1)	0.51
O(6)	-0.855(3)	-0.001(2)	-0.075(1)	0.51
O(7)	0.145(2)	0.234(1)	0.227(1)	3.2
O(8)	0.144(2)	-0.242(2)	0.226(1)	3.2
O(9)	0.431(3)	-0.005(1)	0.227(1)	3.2
O(10)	-0.143(6)	0.219(4)	-0.234(3)	3.2
O(11)	-0.151(7)	-0.221(6)	-0.241(4)	3.2
O(12)	-0.032(7)	0.505(6)	-0.233(4)	3.2
Cat(1)	0.487(8)	0.160(2)	-0.495(2)	2.3
Cat(2)	0.487(8)	-0.172(2)	-0.498(2)	2.3
H ₂ O(1)	0.115(8)	0.159(6)	-0.575(5)	0.83
H ₂ O(2)	0.113(8)	-0.174(6)	-0.576(5)	0.83
H ₂ O(3)	0.623(8)	-0.005(6)	-0.573(5)	0.83
H ₂ O(4)	0.841(8)	0.159(6)	-0.439(5)	0.83
H ₂ O(5)	0.849(8)	-0.176(6)	-0.437(5)	0.83
H ₂ O(6)	0.337(8)	-0.010(6)	-0.437(5)	0.83
N(1)	0.469(8)	0.491(6)	0.349(5)	0.45
N(2)	0.476(8)	0.497(7)	0.514(6)	0.45
N(1')	0.566(9)	0.489(8)	0.638(7)	0.45
N(2')	0.488(8)	0.497(7)	0.476(6)	0.45

Table 7.2: Bond Distances ($\text{\AA}$) Involving a Selection of Interlayer Atoms in $[\text{TEDAH}_2]^{2+}$ Intercalated Nyasaland Vermiculite

=====	
Atoms	Distance
N(1)-O(7)	3.08(5)
N(1)-O(8)	3.04(5)
N(1)-O(9)	3.21(5)
N(1')-O(10)-N(2)	3.12(6)
N(1')-O(11)-N(2)	2.95(6)
N(1')-O(12)	2.97(6)
Cat(1)-H ₂ O(1)	2.17(5)
Cat(1)-H ₂ O(2)	2.09(6)
Cat(1)-H ₂ O(3)	2.08(7)
Cat(1)-H ₂ O(4)	1.97(5)
Cat(1)-H ₂ O(5)	1.93(7)
Cat(1)-H ₂ O(6)	<u>1.99(6)</u>
Mean	2.04
Cat(2)-H ₂ O(1)	2.08(5)
Cat(2)-H ₂ O(2)	2.17(5)
Cat(2)-H ₂ O(3)	2.07(7)
Cat(2)-H ₂ O(4)	1.99(6)
Cat(2)-H ₂ O(5)	2.03(5)
Cat(2)-H ₂ O(6)	<u>1.96(6)</u>
Mean	2.05
=====	

Table 7.3: Interatomic Distances (Å) for Silicate Layer Atoms in [TEDAH₂]²⁺ Intercalated Nyasaland Vermiculite

=====

Tetrahedron about T(1)		Tetrahedron about T(2)	
T(1)-O(1)*	1.62(1)	T(2)-O(2)*	1.63(1)
-O(7)	1.64(1)	-O(7)	1.67(1)
-O(8)	1.65(1)	-O(8)	1.65(1)
-O(9)	<u>1.66(1)</u>	-O(9)	<u>1.64(1)</u>
mean	1.64	mean	1.65
Tetrahedron about T(3)		Tetrahedron about T(4)	
T(3)-O(4)*	1.70(2)	T(4)-O(5)*	1.69(2)
-O(10)	1.68(4)	-O(10)	1.70(2)
-O(11)	1.79(5)	-O(11)	1.65(5)
-O(12)	<u>1.58(5)</u>	-O(12)	<u>1.64(1)</u>
mean	1.69	mean	1.69
Octahedron about Mg(1)		Octahedron about Mg(2)	
Mg(1)-O(1)	2.04(1)	Mg(2)-O(1)	2.08(1)
-O(2)	2.08(1)	-O(2)	2.08(1)
-(OH) ₁	2.07(1)	-(OH) ₁	2.04(1)
-O(4)	2.08(2)	-O(4)	2.11(2)
-O(5)	2.11(2)	-O(5)	2.07(2)
-(OH) ₂	<u>2.07(2)</u>	-(OH) ₂	<u>2.09(2)</u>
mean	2.08	mean	2.08
Octahedron about Mg(3)			
Mg(3)-O(1)	2.09(1)		
-O(2)	2.04(1)		
-(OH) ₁	2.04(1)		
-O(4)	2.05(2)		
-O(5)	2.12(2)		
-(OH) ₂	<u>2.10(2)</u>		
mean	2.07		

=====

* Apical oxygens.

caused by $\pm b/3$ translations. The list of observed and calculated structure factors is given in Appendix A.3.

7.3 Results and Discussion

The X-ray diffraction analysis reported here unambiguously located the positions of the pivotal nitrogen atoms, as well as those of the inorganic cations and water molecules. The ethylene

carbon atoms, however, were not clearly seen, even in the Fourier images calculated after the final refinement. The $[\text{TEDAH}_2]^{2+}$ cation has three vertical mirror planes at 120° to each other. In the intercalate, therefore, despite any rotational disorder which may be present, one of these mirror planes is always likely to be coplanar with the plane through the unit cell at $y = 1/2$. With the ethylene bridges so positioned, Figure 7.3 shows that a $[\text{TEDAH}_2]^{2+}$ cation keys into a ditrigonal cavity in the surface of a silicate layer. The ethylene carbon atoms then make van der Waals contact with the surface oxygens.

7.3.1 Superstructure

In the C-centered super-cell $[\text{TEDAH}_2]$ cations are in sites over the ditrigonal cavities, with the adjacent equivalent surrounding sites unoccupied. This arrangement apparently prevents steric hinderances, but it may also better satisfy the charge distribution in local domains. Alcover *et al.* (1973) suggested that the exchangeable inorganic cations and water molecules in a Kenya vermiculite were also distributed over the lattice points in a C-centered cell with dimensions $3a \times b$, which, by inference, represents the charge distribution in the silicate layers. For the vermiculite from Llano County, Texas, de la Calle *et al.* (1976), Thompson (1984), and Slade *et al.* (1987) showed that only short-range ordering of tetrahedral cations exists in local domains. Consequently, if local charge balance operates in Llano vermiculite its interlayer cations should also be ordered only in local domains; however, for the Nyasaland and Kenya vermiculites, the local domains of short-range order may well be larger. The superlattice spots for $[\text{TEDAH}_2]^{2+}$ Nyasaland vermiculite were indeed sharper than for $[\text{TEDAH}_2]^{2+}$ Llano vermiculite, which is consistent with the local domains being larger in $[\text{TEDAH}_2]^{2+}$ Nyasaland vermiculite.

Full occupancy of the all available sites in a $3a \times b$ supercell

FIG. 7.3

A molecular model showing the [TEDHA₂] cation keyed into a ditrigonal cavity on the surface of a silicate layer with the ethylene carbon atoms making van der Waals contacts with the surface oxygens.

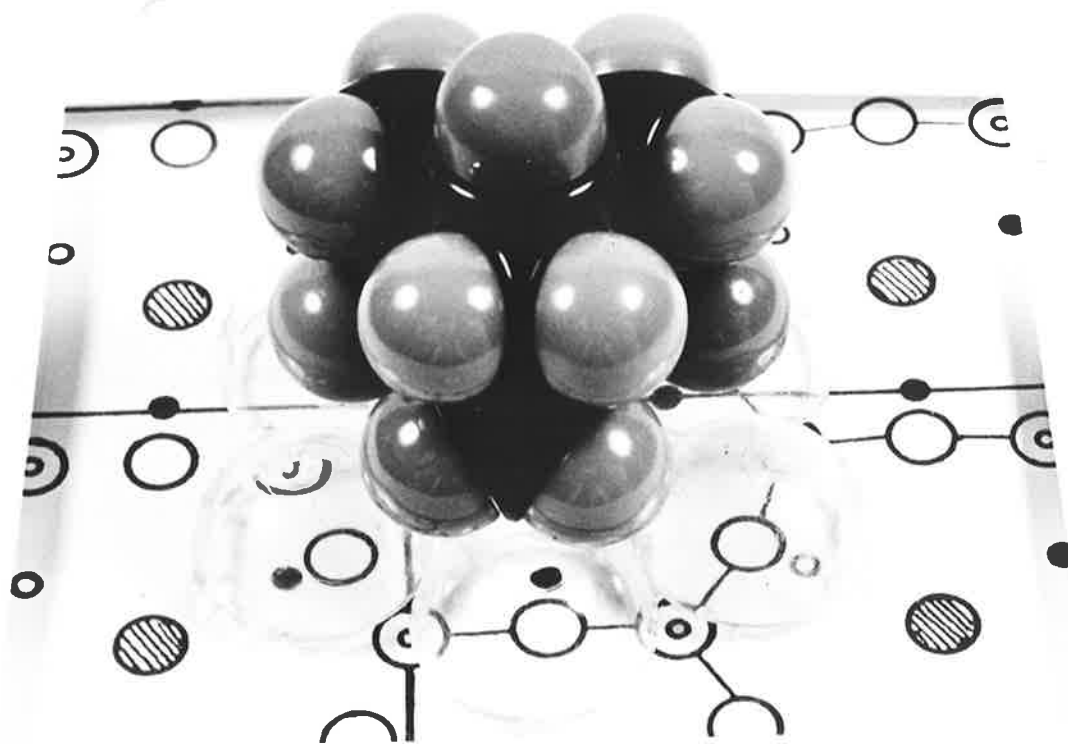


Fig. 7.3

requires a total of two $[\text{TEDAH}_2]^{2+}$ units, or on average $2/3$ of a unit in each sub-cell. At this theoretical maximum level of occupancy, the layer charge (1.24 electrons per sub-cell) of Nyasaland vermiculite should be satisfied by divalent cations; however chemical analysis showed that on average, a sub-cell contained only 0.5 of a $[\text{TEDAH}_2]^{2+}$ cation. The difference between the actual level of occupancy and the theoretical maximum should lead to a charge imbalance if inorganic cations were not present. In $[\text{TEDAH}_2]^{2+}$ Llano vermiculite, the organic cations were only imperfectly ordered, which may reflect the natural layer charge distribution of the material over only short distances or, its more limited uptake of $[\text{TEDAH}_2]^{2+}$ ions. The high layer charge for Llano vermiculite may have inhibited a free exchange between the inorganic cations and the more bulky organic cations.

The X-ray diffraction data collected for $[\text{TEDAH}_2]^{2+}$ intercalated Nyasaland vermiculite were only indexed for a sub-cell; hence, the Fourier images obtained were the average of those for the sub-cells comprising the super-cell. The structure of the larger cell, however, was inferred as shown in Figure 7.4 where, for improved clarity, $[\text{TEDAH}_2]^{2+}$ ions have been omitted. The packing of the water molecules about the organic cations is more clearly demonstrated by the scale model shown in Figure 7.5. Here, the water molecules, whose images appear as peaks E and F on Figure 7.1, are marked for reference.

7.3.2 Relative positions of the silicate layers

The spacings between adjacent silicate layers of the $[\text{TEDAH}_2]^{2+}$ vermiculite intercalate were apparently governed by the presence of water molecules and cations. The differences between the basal spacings of $[\text{TEDAH}_2]^{2+}$ montmorillonite, Nyasaland, Kenya and Llano vermiculites under ambient conditions were attributed to charge differences between the parent silicate layers. At a

FIG. 7.4

Computer drawing (PLUT078) showing water molecules and inorganic cations forming a superstructure in the interlayer region.

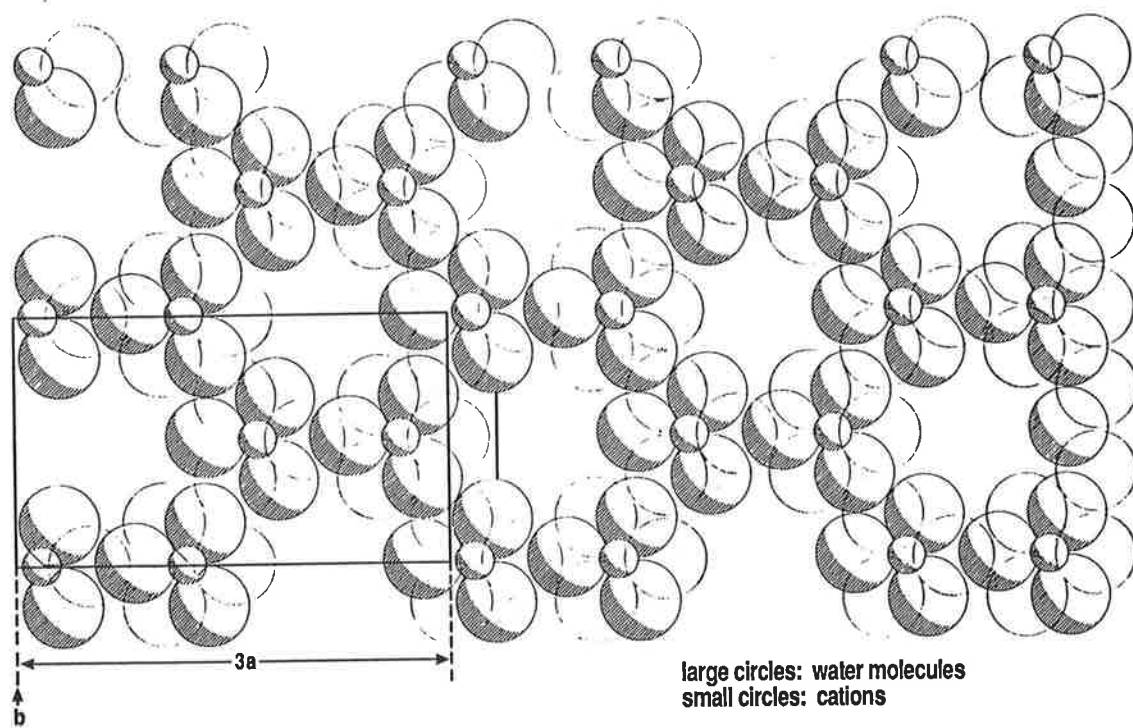


Fig. 7.4

FIG. 7.5 Scale model of [TEDAH₂] cation embedded in the
water network illustrated in FIG. 7.4.

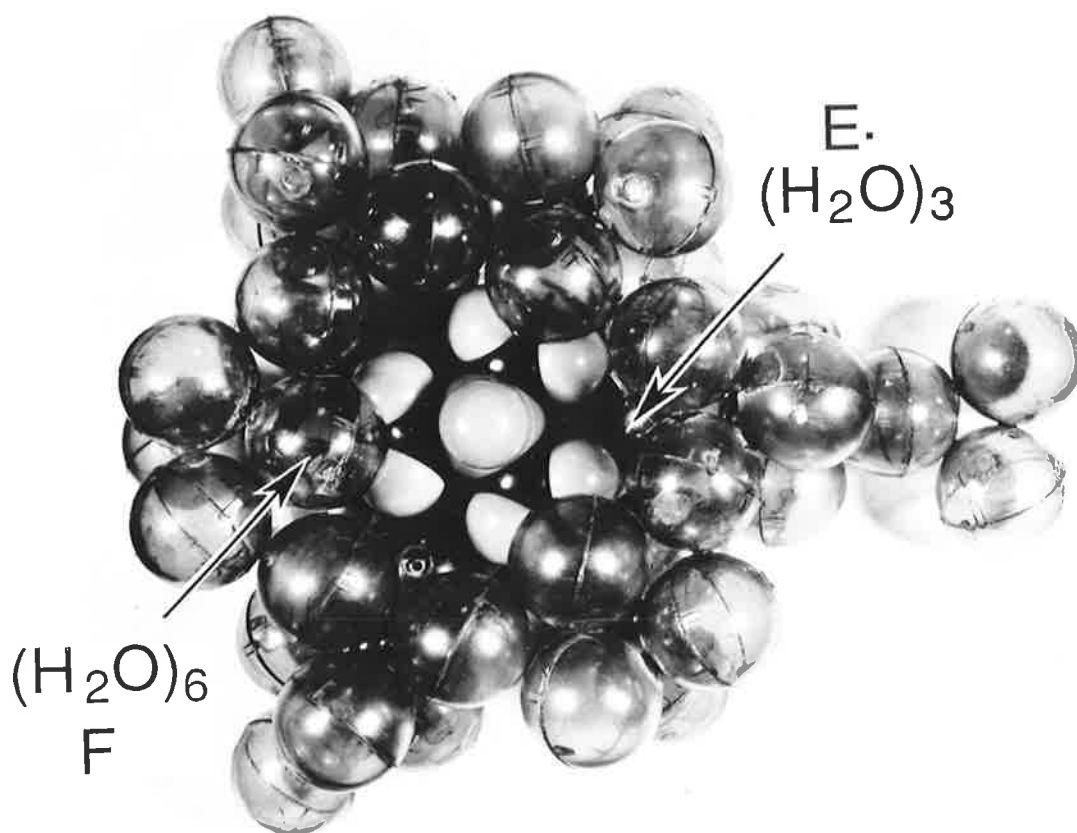


Fig. 7.5

given relative humidity an increase in the attraction between more highly charged silicate layers and a specific interlayer cation can be reflected by smaller basal spacings (MacEwan and Wilson, 1980).

Samples in the electron microscope showed layer separations of only $\sim 12.5\text{\AA}$. Apparently a high vacuum and the heating caused by the beam destroyed the interlayer water structure so that the silicate layers were separated only by organic units. Scale models (Figure 7.3) show that $[\text{TEDAH}_2]^{2+}$ cations, by keying into opposed silicate surfaces, can produce an interlayer spacing of $12.5\text{\AA}$, a value considerably less than that suggested by Shabtai *et al.* (1977). Samples heated with warm air for X-ray diffraction examination at 250°C had a higher spacing ($13.7\text{\AA}$), a value retained even at 350°C . These relatively moderate conditions apparently removed enough interlayer water to weaken substantially the linkages holding the ditrigonal cavities in adjacent silicate layers opposite each other. With reference to Figures 7.4 and 7.5, for a silicate layer having an attached single sheet of water molecules, to move by either $\pm b/3$ requires that some water be lost. The disordering produced by this dehydration will bring the bases of tetrahedra opposite ditrigonal cavities. With such stacking, only one aminium group per $[\text{TEDAH}_2]^{2+}$ ion can key into a silicate surface; the second group will ride upon the oxygen atoms forming a tetrahedral base. The average N.....O (basal) distances will then be about $2.9\text{\AA}$. Scale models show that such an arrangement will produce a spacing of $\sim 13.7\text{\AA}$. Water molecules therefore have an important structural role in $[\text{TEDAH}_2]$ vermiculite and, by inference, also in $[\text{TEDAH}_2]$ montmorillonite.

7.3.3 Cationic charge

Each organic cation in $[\text{TEDAH}_2]$ vermiculite has one of its nitrogen atoms linked directly to a silicate surface; however,

the second nitrogen atom is near the interlayer mid-plane so that the latter atom's attachment to a silicate surface is less direct. These different situations imply that the nitrogen atoms may carry different charges. The total number of charges carried by an intercalated [TEDAH₂] unit is difficult to determine, but the site multiplicities (0.35) found for the inorganic interlayer cations, when assigned to the Mg²⁺ scattering factor, exceed the result expected (0.11) if the organic cations were divalent. The argument is not conclusive, however, because the interlayer inorganic cations were not identified beyond the fact that they were not Na (electron microprobe examination of the intercalates showed them to contain no Na (detection limit = 0.1% Na)). Previously Slade *et al.* (1987) reported that Al, Mg and Fe can be lost from layer silicates if they are intercalated in acidic media. These ions may then be co-adsorbed with the organic cations onto the exchange sites. In the present study, the Mg²⁺ scattering factor was arbitrarily used initially, but subsequently, in order to obtain more meaningful temperature factors, the sites were assigned to the Fe³⁺ scattering factor. Although the crystallographic evidence for the charge status of the organic cations was not conclusive, the asymmetry of the structural environment about their nitrogen atoms may indicate that these ions were not divalent.

The dissociation constants for TEDA (pK₁=8.19, pK₂=4.18; Terrin, 1965), however, indicate that the dication was favoured by ~10⁴:1. Hence, a mechanism to neutralize the cationic charges furthest from the silicate surfaces must be considered.

The model illustrated in Figure 7.5 allowed three extra water molecules to be accommodated in a trigonal close-packed formation above the [TEDAH₂] unit. Such water molecules, being polar, will diffuse any adjacent positive charge upon the organic dications. Of necessity, the water molecules involved will be slightly displaced out of the planes of the main water sheets. Diffuse peaks on difference Fourier sections as $z = 0.37$ and $z = 0.63$

provide evidence for appropriate displacements of the water network.

7.4 Conclusions

Na-saturated vermiculites are easily intercalated with $[\text{TEDA}\text{H}_2]^{2+}$ cations. The intercalate was found to have nearly the same *c*-dimensions as the original Mg-vermiculite found in nature (about 14.3Å). The product also showed improved crystallinity and a superlattice of $3a \times b$.

The amount of divalent $[\text{TEDA}\text{H}_2]$ cations adsorbed by the Nyasaland vermiculite was just over one half per unit cell (0.52), which is nearly enough to neutralise its layer charge of 1.24 (no Na was found to remain in the intercalant). Structure refinement of the interlayer region, however, showed the presence of inorganic cations at $z=0.5$, which when assigned to Mg^{2+} gave a site occupancy of about 35%. The accompanying octahedrally coordinated water was also clearly seen on difference Fourier maps printed by the SHELX program, as well as on the two-dimensional difference Fourier maps plotted through $z = 0.47$ and $z = 0.53$. The presence of the inorganic cations in the interlayer region could only have come from the octahedral sites of the vermiculite which dissolve to a small degree when vermiculites are placed in acid solutions (Slade *et al.*, 1987). The pH of the 1% $\text{TEDA} \cdot 2\text{HCl}$ solution used in the intercalation process was 2.3. This small loss of octahedral cations would increase the layer charge on the surface oxygens, thus requiring more cations in the interlayer to form a neutral intercalate.

The *c*-dimension of the $[\text{TEDA}\text{H}_2]$ intercalated Nyasaland vermiculite is about 14.4Å, which leaves an interlayer space of just under 5Å (assuming 9.5Å for the silicate layer). This space appears to be about right for the $[\text{TEDA}\text{H}_2]$ cation, which has a H-H intramolecular distance of 4.2Å (Kennedy *et al.*, 1987).

Shabtai *et al.* (1977) assumed that this was indeed the case in their [TEDAH₂] intercalated montmorillonite, with the [TEDAH₂] forming pillars between the silicate layers. Their assertion, however, assumed that the [TEDAH₂] ions form straight line hydrogen bonding to the surface oxygens, as indeed is the case in TEDA.2HCl (Kennedy *et al.* 1987) where the Cl--H-N(C₂H₄)₃N-H--Cl distance is 8.5Å and where the chloride ions form hydrogen bonding to the [TEDAH₂] cations in a straight line. In the Nyasaland vermiculite the distance between the centres of the surface oxygens across the interlayer is 7.8Å, or slightly smaller, but allowing for the smaller radius of the oxygen ion compared to the chloride ions is of the right magnitude. In reality, however, the [TEDAH₂] cations lodge themselves into the ditrigonal holes formed by the surface oxygens, and it is the ethylene carbon atoms which form van der Waals bonds to the surface oxygens, while the aminium group is lodged deeper into the ditrigonal hole. Assuming the latter case, then the 5Å distance between layers is too large for the [TEDAH₂] cations to form pillars between the silicate layers; the distance then required is about 3Å (the C-C distance in the TEDA molecule is 1.5Å, requiring a space of just over 3Å to fit in) which gives a total c-dimension of about 12.5Å, a distance obtained when the [TEDAH₂] vermiculite is examined with a transmission electron microscope, where the heating effect of the electron beam and the high vacuum will combine to dehydrate completely the interlayer region, leaving the [TEDAH₂] cation to form the only remaining pillars. It is assumed here that at the temperature attained with the electron microscope the intercalant [TEDAH₂] is not decomposed (the melting point of TEDA.2HCl is 315°C).

The room temperature [TEDAH₂] vermiculite having the c-dimension of about 14.4Å therefore, cannot form direct pillars bridging the interlayer space and being recessed into the two opposite ditrigonal holes. The [TEDAH₂] cation can only attach itself either to the lower or the upper ditrigonal hole, but not to both at the same time.

Refinement of the Nyasaland vermiculite located peaks in the ditrigonal holes at $z = 0.35$ and $z = 0.52$ and at $z = 0.64$ and $z = 0.47$ distances $2.47\text{\AA}$ apart, which is exactly the distance between the nitrogens in the $[\text{TEDAH}_2]$ cation (Kennedy *et al.*, 1987). The corresponding distances for these atoms found in the ditrigonal holes at $z = 0.35$ and $z = 0.64$ to their respective surface oxygens is just over $3\text{\AA}$, a distance compatible with N-H-O bonding (see Table 7.2).

The site occupancy of the $[\text{TEDAH}_2]$ cations from microanalytical results is just over half (0.52), but as there are 4 ditrigonal holes per unit cell, the electron density for each nitrogen is just under 2 electrons, making the nitrogen peaks weak but yet clearly discernable. The carbon peaks were, however, not detected clearly as one would expect since the TEDA molecule has a trigonal symmetry along the N-N line and therefore can exist in 2 different orientations when recessed between the six oxygen atoms in the ditrigonal hole (see Figures 7.3 and 7.4). The electron density for carbon is, therefore, not nearly 2 as for the nitrogen atoms but less than 1, a value which is too low to observe with X-ray diffraction techniques. This simple model also assumes rigid spheres for the atoms and saddle point between the surface oxygens, in reality there is probably a good deal of $[\text{TEDAH}_2]$ rotation which would smear out the already very weak electron density of the carbon atoms.

The positions of the carbon atoms were, therefore, not detected but the nitrogen atoms are well defined and the dimensions of the $[\text{TEDAH}_2]$ cation, the N-H-surface oxygen distances, the interlayer distances and the 3-dimensional ordering clearly point to a structure where the c-dimension is governed basically by the inorganic cations with their octahedrally coordinated waters; this structure is stabilised by the presence of $[\text{TEDAH}_2]$ cations, which attach themselves to either the upper or the lower ditrigonal hole, but not to both, while at the same time the water molecules key themselves between the carbon atoms of the

[TEDAH₂]²⁺ cation, thus making the coordinated water molecules more stable. All this results in a structure that is essentially stable up to about 350°C as described by Shabtai *et al.*, (1977) and in this thesis. Some water loss and disorder is, however, apparent at high temperatures, as seen on the two precession photographs (see Figure 6.3), where the c-dimension drops from 14.4Å at room temperature to 13.7Å at 350°C. The harsher conditions of the electron microscope finally manage to expel all the water and the structure collapses to $c = 12.5\text{\AA}$, forming true [TEDAH₂] pillars between the silicate layers. The charge on the unattached end of the [TEDAH₂]²⁺ cation in the room temperature intercalated vermiculite seems to be neutralised by triads of water molecules above the unattached ends, which in turn form hydrogen bonds to the surface oxygens. Weak peaks corresponding to these water triads were detected on difference Fourier maps.

Finally the site occupancy of the ditrigonal holes by the [TEDAH₂] cations, and the inorganic atoms, still leaves well over half the ditrigonal holes unoccupied, or free interlayer space through which other, e.g. organic molecules can diffuse so that the intercalated vermiculite can act as an effective molecular sieve in heterogeneous catalysis as described by Shabtai *et al.* (1977) for the [TEDAH₂] intercalated montmorillonite for example. However, this crystallographic study shows that the structural details for a pillared clay must be known if its properties as a molecular sieve are to be understood. It also highlights how water molecules and different kinds of cations interact to determine the interlayer structure.

CHAPTER 8**P-PHENYLENEDIAMINIUM INTERCALATED VERMICULITES**

CHAPTER 8

P-PHENYLENEDIAMINIUM INTERCALATED VERMICULITES

8.1 Introduction

The organic compound p-phenylenediamine dihydrochloride ($\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2 \cdot 2\text{HCl}$), hereafter referred to as PHEDA.2HCl, was next considered as a suitable substance for intercalation into vermiculites. This compound dissociates in aqueous solutions into p-phenylenediaminium dications, hereafter called $[\text{PHEDAH}_2]^{2+}$, and chloride anions. The structure of p-phenylenediamine dihydrochloride, and the geometry of the p-phenylenediaminium dication, was determined first by Chandrasekaran (1969) and in greater detail by Domenicano *et al.* (1977). The p-phenylenediaminium dication was found to be planar, except for the amino hydrogens, which were oriented almost tetrahedrally towards the three chloride ions, to which they were connected via hydrogen bonding.

The p-phenylenediaminium dication is almost identical to the anilinium cation, except that it possesses two aminium groups rather than one present in the anilinium cation, and since the anilinium cation was successfully intercalated into vermiculites, where it forms superlattices and reduced stacking disorders, it was therefore expected that p-phenylenediaminium dication could be successfully intercalated as well. It was also expected that it might bridge the interlayer space and form direct bonds to both surface layers as it possessed protonated amino groups at both ends; the positions of the anilinium cations in the Llano, Phalaborwa and Young River vermiculites and the dimensions of the two cations indicated that it might do so. However, the intercalant triethylenediaminium $[\text{TEDHA}_2]$ dication, which also

possesses two aminium groups did not bond directly to the surface oxygens of both layers at room temperature and, as described in Chapter 7, the c-dimensions were determined by the inorganic cations and their coordinated water molecules and not by the organic intercalant. But since the [PHEDAH₂] dication is larger than the [TEDAH₂] dication it was thought that [PHEDAH₂] might form direct pillars between the layers resulting in stable and ordered intercalates.

On the strength of the above arguments it was decided to undertake the intercalation of three vermiculites with the p-phenylenediaminium dications, even though it was realised that as the cation was divalent only roughly half the number of cations would be intercalated relative to the number of anilinium cations, it was anticipated however that bonding to both surfaces would decrease the stacking disorders to such an extent as to make a full three-dimensional structure determination possible.

8.2 Preparation

The three vermiculites chosen were the same as used in the [TEADH₂] intercalation in Chapter 6, namely one from Llano County, Texas, U.S.A. (Stop 11), and two from Africa: one from Kenya and one from Nyasaland (now Malawi). These three vermiculites were again chosen because they possessed different cation exchange capacities; their respective charges per unit cell were 1.82, 1.38 and 1.22, as determined by Norrish (1973) using Ca-saturated samples and X-ray fluorescence analysis, and 1.76, 1.36 and 1.24 using the author's microprobe analyses of the Na-saturated samples (see Table 6.3). The intercalant p-phenylenediaminium dication was obtained from a solution of p-phenylenediamine dihydrochloride (NH₂C₆H₄NH₂·2HCl), or PHEDA·2HCl, which was obtained from Tokyo Kasei Chemical Company, Tokyo, Japan.

The intercalation process was similar to that used in the [TEDAH₂] intercalation given in Chapter 6; i.e. the Mg-vermiculite flakes were first cut to approximately 1-2 mm squares and refluxed with 2M NaCl solution at 80°C for one week. The solution was changed daily and finally the vermiculite crystals were washed with water to remove any residual NaCl, and then air dried. The Na-saturated vermiculites were then refluxed in one percent PHEDA.2HCl solutions, the pH of which was 2.3, for periods up to 10 days at 50°C. Due to the reactivity of the PHEDA.2HCl with oxygen, these intercalations had to be carried out under nitrogen in an oxygen free environment by bubbling oxygen-free nitrogen gas through the solutions. The high purity nitrogen gas used (nominally containing only 10 ppm oxygen) was further purified by passing it through a 0.1M vanadyl sulphate (VOSO₄) solution, acidified with H₂SO₄ and containing pieces of zinc metal amalgamated with mercury. This procedure is recommended by Meites and Meites (1948) for removing the last traces of oxygen from nitrogen gas. The open end of the reflux condenser was attached to a flask containing concentrated H₂SO₄ so as to prevent any oxygen backstreaming into the reaction vessel. The 1% PHEDA.2HCl solution was made using doubly distilled water, which was boiled and allowed to cool without being disturbed, so as to minimise the presence of any oxygen in the solution.

During the intercalation process the solutions were changed daily, at which time a few vermiculite flakes were removed for examination with an X-ray powder diffractometer. The diffractometer technique was the same as given in Chapter 2 for the preparation of anilinium intercalated vermiculites; i.e. the progress of the intercalation was monitored by observing the development of a new set of rational 001 reflections. The intercalation was judged to be complete when the new set of 001 reflections was stable even when heated to 80°C. The reaction was then stopped, the flakes removed, washed with hot distilled water and allowed to air dry.

8.3 Electron Microprobe Analysis

A number of crystal flakes of $[\text{PHEDAH}_2]^{2+}$ intercalated vermiculites, from the three different localities, were analysed using a JEOL 733 Superprobe, a KEVEX 7000 Series energy dispersive spectrometer and the raw data were processed using full ZAF corrections with a PIBS style software (WARE, 1981). The same operating conditions were used as for the $[\text{TEDAH}_2]$ intercalated samples, namely the accelerating voltage was 15KV, probe current 5nA, beam size 20 μm diameter, counting times 60 seconds life time and the samples were scanned during analyses at a magnification of $\times 4000$ to avoid sample damage. The sodium saturated samples were not analysed as they were the same as those for the $[\text{TEDAH}_2]$ intercalation: their analyses are given in Chapter 6, and repeated here in Table 8.2 for easy comparison with the intercalated values.

Prior to the analyses the $[\text{PHEDAH}_2]^{2+}$ intercalated crystal flakes were attached to polished blank epoxy resin briquettes and coated with approximately 25 nm of carbon. Point analyses, using the above mentioned conditions, were carried out on several flakes of each sample, the results averaged and structural formulae calculated. The results obtained are given in Table 8.1.

Table 8.1: Electron Microprobe Analysis of $[\text{PHEDAH}_2]^{2+}$ Intercalated Vermiculites

Locality	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	MgO	PHO ⁽¹⁾	Total
Llano	39.6	0.15	16.0	0.25	—	25.0	3.1	84.10
Kenya	35.8	0.62	13.6	6.2	—	21.7	8.4	86.32
Nyasaland	37.0	0.92	11.5	6.4	0.57	21.4	7.8	85.59

(¹) PHO = $[\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2 \cdot 2\text{H}]^+\text{O}^-$.

The analyses for carbon, nitrogen and hydrogen were carried out by Canadian Microanalytical Service Ltd., Vancouver, Canada. The

following results were obtained for the three vermiculites intercalated:

Llano

C=1.89 N=0.75 H=2.41%

Kenya

C=4.98 N=1.78 H=1.98%

Nyasaland

C=4.61 N=1.68 H=2.02%

The [PHEDAH₂]O weight percent values given in Table 8.1 were calculated from the microanalytical carbon and nitrogen figures received (the values quoted are the average of two molecular weights calculated using the carbon and nitrogen figures separately).

Using the microprobe and microanalytical results given in Table 8.1 structural formulae were calculated for the three [PHEDAH₂]²⁺ vermiculites and are given in Table 8.2. The structural formulae for the three Na-saturated vermiculites, given in Chapter 6, are also given for comparison with the intercalated values.

Since a unit cell contains two formula units, the interlayer charges per unit cell in the sodium intercalated Llano, Kenya and Nyasaland vermiculites are 1.76, 1.36 and 1.24 respectively. These values compare very well with the figures of 1.82, 1.38 and 1.22 obtained by Norrish (1973). The interlayer charges obtained for the [PHEDAH₂]²⁺ intercalated Llano, Kenya and Nyasaland vermiculites, using the [PHEDAH₂] cations as the only interlayer material present, are 0.44, 1.24 and 1.16. These values are quite different from their sodium counterparts. There are not

Table 8.2: Structural Formulae (O = 11) for Sodium and [PHEDAH₂]²⁺
Intercalated Llano, Kenya and Nyasaland Vermiculites

Sample	Tetrahedral $\Sigma=4$			Octahedral					Octa- hedral Total	Interlayer	
	Si	Al	Fe ³⁺	Mg	Fe ³⁺	Ti	Cr	Al		Na ⁺	[PHEDAH ₂] ²⁺
Llano Na ⁺	2.89	1.11	-	2.92	0.03	0.02	-	0.07	3.04	0.88	-
Llano [PHEDAH ₂] ²⁺	2.97	1.03	-	2.79	0.02	0.01	-	0.38	3.20	-	0.11
Kenya Na ⁺	2.81	1.19	-	2.53	0.38	0.04	-	0.06	3.01	0.68	-
Kenya [PHEDAH ₂] ²⁺	2.81	1.19	-	2.54	0.37	0.04	-	0.07	3.02	-	0.31
Nyasaland Na ⁺	2.84	1.01	0.15	2.57	0.36	0.05	0.02	-	3.00	0.62	-
Nysaland [PHEDAH ₂] ²⁺	2.92	1.07	0.01	2.52	0.37	0.05	0.04	-	2.98	-	0.29

enough [PHEADH₂] cations to replace all the sodium cations in these vermiculites, but since the microprobe analyses did not detect the presence of any sodium, some of the original sodium must have been replaced by other cations, which must have come from the silicate layers themselves - most probably from the octahedral sites, elements such as magnesium, aluminium or iron.

To check the accuracy of the above [PHEDAH₂] figures their values were recalculated by measuring the densities and volumes of the unit cells, obtained by precession method, which gave the mass of the unit cells ($M=D \times V$). Knowing the weight percent of carbon and nitrogen present in the samples from microanalytical results, and the number of carbon and nitrogen atoms in one [PHEDAH₂] cation, the number of [PHEDAH₂] cations per structural formula was calculated. The values obtained were 0.12, 0.31 and 0.29 for the Llano, Kenya and Nyasaland vermiculites respectively, which are almost the same as obtained by the use of the microprobe and microanalytical results previously, namely 0.11, 0.31 and 0.29. The interlayer charges per unit cell are four times the above figures, i.e. 0.44, 1.24 and 1.16, and 0.48, 1.24 and 1.16 respectively.

8.4 X-Ray Analysis

The intercalated vermiculite crystal flakes were first examined under a binocular microscope. Crystals which were free from apparent defects, such as bending, splitting of layers, or any other visible imperfections, were mounted on X-ray goniometer arcs and X-rayed using precession and sometimes Weissenberg techniques in order to establish the presence or otherwise of superlattice reflections, the degree of three-dimensional order and other crystal defects. The photographs were also used to identify the crystal system and to obtain data for lattice parameter measurements.

Precession methods usually consisted of zero level photographs, with the X-ray beam along the a - or c -axis to yield reflections in the b^*c^* and a^*b^* planes respectively. In these photographs stacking disorders can clearly be seen as elongations of the b^* reflections along the c^* direction (diffuse $k \neq 3n$ reflections).

The thermal stability of these intercalated vermiculites was checked by heating the Nyasaland vermiculite to 350°C on the precession camera employing the same Enraf-Nonius heating device as used for heating the [TEADH₂] intercalated vermiculites described in Chapter 6. Photographs were taken at 25° intervals during a heating run.

8.5 Results and Discussion

All three vermiculites showed relatively diffuse reflections, indicating a disordered layer sequence, as seen in Figure 8.1. The precession photographs also did not reveal the presence of any superlattice reflections, showing that intercalating with [PHEDAH₂] did not result in either an ordered intercalant, or a significantly improved stacking sequence of the silicate layers themselves.

The precession photographs obtained on heating showed that the already diffuse reflections became gradually more diffuse as the temperature increased, but that there was no decrease in the c -dimension; on the contrary the c -spacing increased somewhat (e.g. from the original 14.4 to 15.0 Å in the Nyasaland case). The c -dimensions of these [PHEDAH₂] intercalated Llano, Kenya and Nyasaland vermiculites, at room temperature, were 14.1, 14.3 and 14.4 Å respectively, which shows that the more highly charged vermiculites have a slightly smaller c -dimension as would be expected from the increased attraction between the same cations and the more highly charged silicate layers (MacEwan and Wilson, 1980).

FIG. 8.1

Zero level precession photograph of $[\text{PHEDAH}_2]^{2+}$ intercalated Kenya vermiculite ($\text{MoK}\alpha$ radiation) showing diffuse $k \neq 3n$ reflections indicating severe layer disorder.

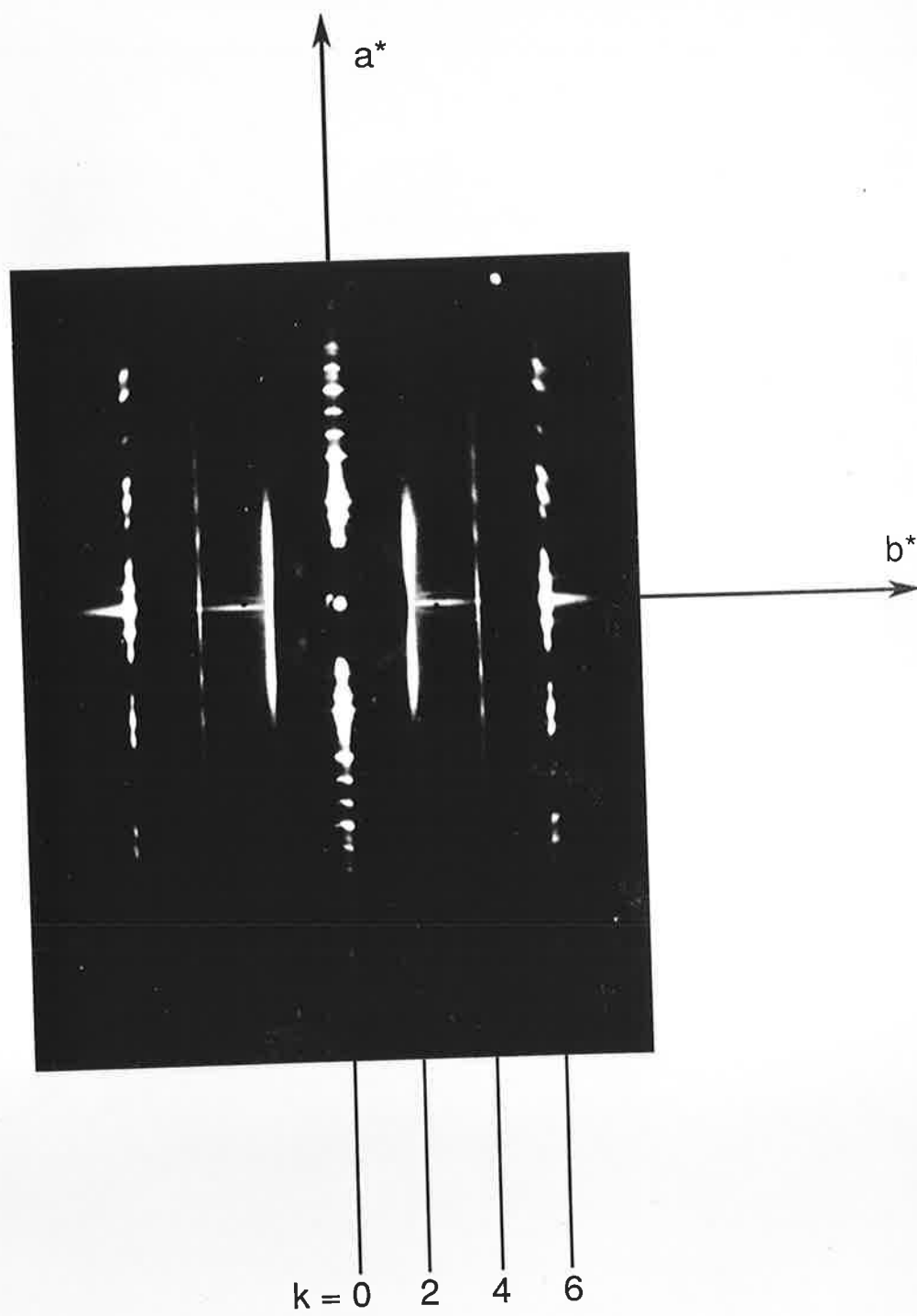


Fig. 8.1

The thermal stability of these intercalated vermiculites supports the hypothesis of Shabtai *et al.* (1977), which assumes that the organic cations form stable pillars, but seems at odds with our findings in the case of [TEDAH₂] intercalated vermiculites, in which the c-spacing diminishes a little (14.4 to 13.7 Å in the case of [TEDAH₂] intercalated Nyasaland vermiculite for example).

The postulate in the [TEDAH₂] intercalated vermiculites was that the [TEDAH₂] dication is not large enough to span the interlayer distance between the two silicate layers and that the presence of inorganic cations, with their coordinated water molecules, determines the interlayer spacing at room temperature. One aminium group of the [TEDAH₂] dication then fits into the ditrigonal cavity of one layer and the other is bonded, via water molecules, to the other ditrigonal cavity, thus ordering the stacking sequence of the layer silicates. On heating the loss of some water collapses the interlayer space and the [TEDHA₂] dication is now hydrogen bonded to a ditrigonal cavity in one layer but to basal oxygens of the tetrahedral sheet in the other layer since there is not enough water present to form direct hydrogen bonds to the ditrigonal cavity in the other layer. A $\frac{1}{3}$ disorder puts a triad of basal oxygens of one layer opposite a ditrigonal hole of the other layer thus making a direct bond between them possible and favouring a disordered state. In the electron microscope, where all the water is lost, including the water coordinated around the inorganic cations, the [TEDAH₂] dication now bonds to opposite ditrigonal cavities and the c-spacing collapses to 12.5 Å and an ordered structure again results.

The same situation is stipulated here for the [PHEDAH₂]²⁺ intercalated vermiculites where due to the disorder present in the structure, as seen in the precession photographs, the ditrigonal cavities are not found present opposite other ditrigonal cavities but opposite basal oxygens of the tetrahedral

sheet. The somewhat larger [PHEDAH₂] dication, where the intramolecular N-N distance is 4.8Å (Domenicano *et al.*, 1977), as compared to [TEDAH₂] dication, where the N-N distance is 2.8Å (Kennedy *et al.*, 1987), means that at room temperature the [PHEDAH₂] cation already fits neatly into the interlayer space, i.e. space provided by the original largely disordered vermiculites where the ditrigonal cavities are found opposite the tetrahedral basal oxygens. Which means that on heating no further collapse of the c-dimension is possible; on the contrary thermal expansion means that a small increase in the c-spacing will take place as indeed is found experimentally to be the case.

In view of the lack of sufficient three-dimensional order in the [PHEDAH₂]²⁺ intercalated vermiculites a full crystal structure analysis of these compounds could not be undertaken.

CHAPTER 9

CRYSTAL STRUCTURE OF EPHESITE

CHAPTER 9

CRYSTAL STRUCTURE OF EPHESITE

9.1 Preliminary Remarks

X-ray examination of various intercalated vermiculites (Slade and Stone, 1984; Slade *et al.*, 1987) have shown that the symmetry usually assumed for the vermiculites (monoclinic Cc or C2/c) was in general too high and that the true symmetry was lower (triclinic plus C-centering). It was also noted (Slade and Radoslovich, 1985) that the related layer silicates, such as the brittle micas margarite and ephesite (soda-margarite) likewise possessed a lower symmetry than the Cc or C2/c previously assumed for them. Slade and Radoslovich (1985), using heavily overexposed Weissenberg photographs, found 70 additional weak reflections in the Postmasburg ephesite, which implied that the ephesite did not possess a true c-glide plane and that the structure was really triclinic, C1. It was, therefore, decided to redetermine the crystal structure of ephesite in the lower space group assuming only C-centering.

9.2 Introduction

The average structure of ephesite- $2M_1$, $\text{Na}(\text{LiAl}_2)(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$, has been described in space-group Cc by Slade and Radoslovich (1985). Sokolova *et al.* (1979) have reported the structure of ephesite-1M in space group C2. Broadly both structures are similar to that of margarite- $2M_1$. However, Slade and Radoslovich (1985) found that crystals of ephesite- $2M_1$ gave weak h0l reflections with $l=2n+1$; these are forbidden in space group Cc so the true internal symmetry of the material must be triclinic.

Specifically, the c-glide operator is absent. Similar forbidden reflections have also been found in the a^*c^* planes of some margarites (Slade and Radoslovich, 1985) so these may also have lower symmetry than that of space group Cc as used by Guggenheim and Bailey (1975, 1978), and also by Joswig *et al.* (1983), to describe the specimens they studied.

Both ephesite and margarite have ordered alternations of Si and Al in tetrahedra about the ditrigonal cavities in each tetrahedral sheet. Space group Cc requires adjacent tetrahedral sheets across the interlayer to have the Si/Al ordering pattern rotated by 60° so that two adjacent tetrahedra (across the interlayer) are not occupied by the same kind of cations. The absence of a c-glide operator still allows complete Si/Al ordering about ditrigonal rings, but it also allows Si^{4+} cations to face each other across the interlayer as reported for ephesite-1M by Sokolova *et al.* (1979).

The octahedral cations in ephesite are ordered so that the M(1) sites are occupied by lithium plus small residual amounts of aluminium and probably minor amounts of other cations including iron and magnesium. The crystallographically independent M(2) and M(3) sites are fully occupied by aluminium. A similar distribution of cations in the octahedral sites was reported by Sokolova *et al.*, (1979) for ephesite-1M. In both structures the M(1) sites are incompletely filled and so any ordering of vacancies would lower the symmetry from Cc (Slade and Radoslovich, 1985).

The interlayer sodium cations in ephesite-2M₁ and -1M conform to a C-centred distribution and further ordering is unlikely.

The data set used by Slade and Radoslovich (1985) comprised reflections from only a quadrant of reciprocal space and necessarily did not allow refinement in the true, lower symmetry. Nevertheless, a refinement in the expected C1 symmetry was

predicted to be difficult because the deviations from the average symmetry were apparently small. In spite of the known crystallographic problems associated with refining non-centrosymmetric structures with marked pseudosymmetry, further work on ephesite was warranted because of its implications for the margarite structure and possibly also for the lepidolite-2M₁ structure. The c-glide operator in the latter was reported by Swanson and Bailey (1981) to be violated by the presence of weak h0l, l odd, reflections.

Important constraints on a refinement of the ephesite structure in low symmetry are given by the optical second harmonic study of Bish *et al.*, (1979) and also by the ²⁹Si NMR study reported by Slade and Radoslovich (1985). These studies respectively, confirmed the absence of a centre of symmetry and the presence of complete Si/Al ordering. With these important constraints established, the present study was undertaken to determine the structure of ephesite in its true symmetry.

9.3 Experimental

The flake of the Postmasburg ephesite used for this work was the same as the one previously described by Slade and Radoslovich (1985). Its size was 0.91×0.82×0.703 mm. An Enraf-Nonius CAD4 four-circle diffractometer, using graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$), was employed to re-measure the crystal data. The cell dimensions of $a=5.123(2)$, $b=8.872(3)$, $c=19.307(3)\text{\AA}$ and $\alpha=89.97(2)$, $\beta=95.15(2)$, $\gamma=89.96(2)^\circ$, which differ slightly from those previously reported, were obtained by least-squares refinement of 25 low to medium-angle reflections. Reflection intensities were measured in just over four octants of the limiting sphere in the theta range of 1.8 to 32°. The data were collected in the omega/two-theta variable scan mode, with the omega scan angle set to $(1.55 + 1.5 \tan\theta)^\circ$. The slit height was 4 mm and the aperture width $(3.00 + 1.0 \tan\theta)\text{mm}$. The indices

ranged between $-6 \leq h \leq 6$, $-1 \leq k \leq 10$ and $-20 \leq l \leq 20$. Crystal orientation was checked after every 350 reflections and an intensity check was carried out after every 4000 seconds of exposure time. Reflections $(h+k)$ odd, absent in C-centred cells, were not collected. The maximum time spent on measuring one reflection was 600 seconds. The data were collected in the minimum absorption method (see 3.1.3) in order to minimise the loss of reflection intensity due to X-ray absorption effects. A total of 2655 reflections were recorded with $|F_o|/\sigma|F_o| > 2.5$. The integrated intensities were corrected for Lorentz and polarization effects and linear absorption using the programs SUSCAD (Guss, 1979) and ABSORB (Guss, 1980) respectively.

The chemical composition of the ephesite was checked by carrying out electron microprobe analyses, using the same experimental conditions as described in Chapter 2 (2.3.2). Fifteen point analyses were carried out on three crystal flakes. The averaged weight percent values and the structural formula, based on 11 oxygens, are given in Table 9.1.

Table 9.1: Electron Microprobe Analysis of Ephesite

Weight Percent		Cations per 11 Oxygens		
SiO ₂	28.9	Si	1.92	} 4.00
Al ₂ O ₃	52.4	Al	2.08	
Fe ₂ O ₃	0.27	Al	2.02	} 2.95
MnO	0.06	Fe ³⁺	0.015	
MgO	0.28	Mn	0.05	
Li ₂ O ⁽¹⁾	3.4	Mg	0.03	
Na ₂ O	7.6	Li	0.905	} 0.995
CaO	0.23	Na	0.975	
K ₂ O	0.06	Ca	0.015	
		K	0.005	
Total	93.20			

⁽¹⁾ Atomic absorption analysis.

The above results agree very closely with those given by Slade and Radoslovich (1985) using X-ray fluorescence analysis except that in the microprobe results the silicon value is a little lower and the aluminium value a little higher compared with the XRF results. A possible silica impurity in the bulk XRF analysis could explain this slight discrepancy.

9.4 Refinement

The model for the refinement was developed from the coordinates of Slade and Radoslovich (1985) and since there was no photographic evidence to the contrary, the structure was maintained as C-centred. To isolate and overcome difficulties caused by closely correlated pseudosymmetrically-related variables, the refinement was tested by independently using the programs ORFLS (Busing *et al.*, 1962) and SHELX (Sheldrick, 1976).

With ORFLS, the parameters of pseudosymmetrically related atoms were adjusted in blocks both before and after they had been slightly offset from the values obtained by expansion of the set given by Slade and Radoslovich (1985). An unblocked refinement of positional parameters which had not been offset was also carried out with ORFLS.

SHELX provides damping to assist in the refinement of structures in which severe correlations are expected. In the present work this facility was used in a series of unblocked refinements of the parameters obtained from the expansion of the set given by Slade and Radoslovich (1985).

Scattering factors for fully ionized cations were taken from Tables 2.2A and 2.2B of Vol. IV, International Tables for X-ray Crystallography (1974). For SHELX calculations the scattering factors were used in their analytical form and anomalous dispersion corrections (International Tables for X-ray

Crystallography, Vol. IV, 1974) were incorporated. The scattering factor for O^{2-} was that of Tokonami (1965).

9.4.1 Refinement with ORFLS

This refinement commenced by adjusting the overall scale factor followed by the positional parameters, either in blocked or unblocked mode. One sodium atom was always held fixed. In subsequent cycles, the temperature factors and positional parameters were adjusted simultaneously. ORTEP (Johnson, 1976) was used to calculate bond lengths from the final positional parameters. The bond lengths for the model to which the ORFLS refinements converged corresponded to a disordered distribution of silicon and aluminium in tetrahedral sites. The mean tetrahedral bond length was $1.688 \pm 0.025 \text{ \AA}$. The difference between the greatest and the least bond lengths in any one tetrahedron was $0.066 \text{ \AA}$. The minimum R value on 2320 unique reflections was 6.1%, this fell to 4.3% on 2099 reflections when those with $||F_o| - |F_c|| > 5.5$ were rejected. Both unit and σ weights were tried for various refinements with ORFLS, but at convergence a disordered Si/Al distribution was always found. By contrast, the ordering of cations in the octahedral sites followed the scheme described by Slade and Radoslovich (1985).

9.4.2 Refinement with SHELX

With this program refinements converged to either of two models for the tetrahedral sites depending on whether damping was applied to the parameter shifts during the initial refinement cycles. Sheldrick (1976) suggested that a damping factor of 1000 be used when refining highly correlated parameters with SHELX. In the present case this factor (1000), applied from the outset, resulted in one model (A) but a second model (B) was produced on one occasion when the same damping factor was introduced after

running 10 undamped cycles. In each of the models A and B the average bond lengths in individual tetrahedra (1.742 or 1.637Å) were close to those expected for purely aluminous or purely siliceous tetrahedra (1.752 or 1.623Å respectively, according to Baur, 1981). The tetrahedra were occupied so that Si^{4+} opposed Si^{4+} and Al^{3+} opposed Al^{3+} cations across the interlayer as seen in Figure 9.1. In this way the c-glide operator was violated in both models. However, the models differed in that the T(1) site in A was occupied by silicon but in B this site was occupied by aluminium. Hamilton's (1975) residual ratio test indicated that the models are indistinguishable at the 50% significance level.

To test for the absolute configuration of the structure the signs of the positional coordinates for all atoms in the initial trial model were reversed and this set was also refined. The R values were compared at equivalent stages to the R values given by the refinement of the unchanged coordinates from the initial set. The R values (R_g and R_w) for the model produced by changing the sign of the coordinates were significantly lower (even at the 0.5% significance level) at every stage of the refinement. The atomic positional coordinates reported in Table 9.1 are those found for the model which consistently gave the lower R factors and therefore represent the absolute configuration of the structure.

The distribution of tetrahedral cations described here as model A, resulted from the refinements of both the absolute and the non-absolute configurations. However, although model B, which turned up once when refining a non-absolute configuration, was not produced by refining the absolute configuration this appears to be only change as the experimental data do not favour either A or B. For convenience only the positional coordinates for Model A are given in Table 9.1. The scattering factors to which the tetrahedral cations were assigned during the later stages of refinement were consistent with model A. The list of observed and calculated structure factors is given in Appendix A.4.

FIG. 9.1 An ORTEP-II drawing of ephesite - projected on to the bc plane - showing silicon opposing silicon and aluminium opposing aluminium ions across the interlayer.

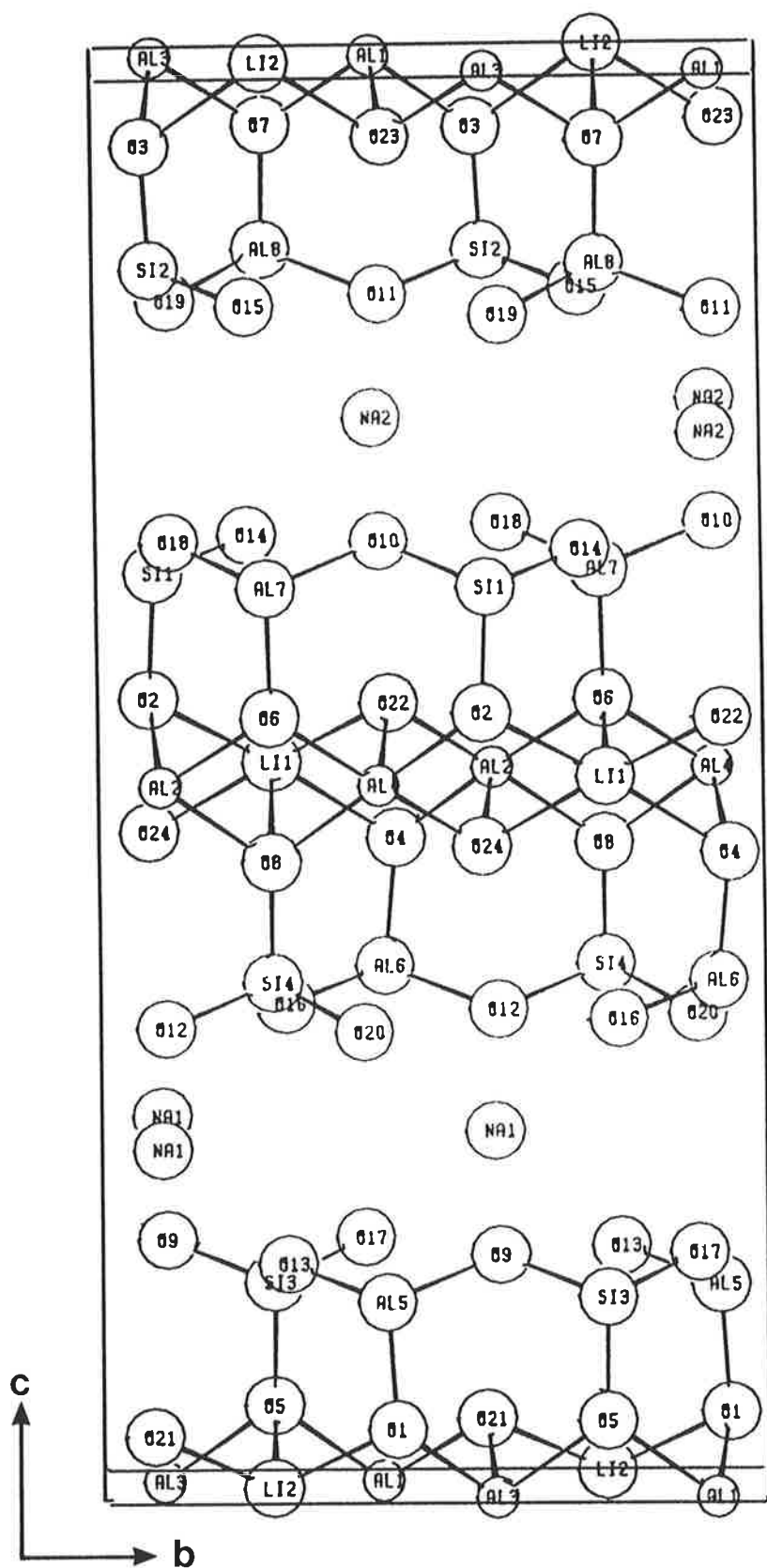


Fig. 9.1

Inspection of an $(F_o - F_c)$ map during the refinement revealed a set of minor peaks caused by a small amount of structural disorder produced by irregular $\pm b/3$ layer translations. From the average refined site occupancy (0.028) for the scatterers producing these peaks, approximately 3% of the silicate layers were found to be disordered.

Refinement of temperature factors in their anisotropic mode was attempted by releasing them simultaneously. However, some values became non-positive definite while others seemed dubious so only those for sodium were retained and adjusted in anisotropic form. For all other atoms of a similar kind group isotropic temperature factors were assigned and adjusted.

An $(F_o - F_c)$ map, calculated after adjusting the isotropic temperature factors, however, showed weak anisotropic peaks associated with the cation sites. This thermal motion or positional disorder remains uncorrected in the present refinement. The $(F_o - F_c)$ map also clearly showed peaks corresponding to about 0.8 electrons above background. The positions of these peaks approximately corresponded to those expected for the hydrogen atoms of the OH groups. The coordinates for the peak positions were entered into the model and held constant while a common isotropic temperature factor was refined. The value for this factor was held constant during a subsequent, unsuccessful, attempt to refine the positional coordinates for the individual hydrogen atoms. After re-entering the original coordinates they, and the common isotropic temperature factor, were successfully adjusted by restraining the O-H bond length to 0.90Å. This was the average of the four O-H bond lengths initially found.

In the final cycle $R^{(1)} = 4.69\%$, $R_w^{(2)} = 6.18\%$, $w = 19.8896[\sigma^2|F| + 0.000041|F|^2]^{-1}$ for 2657 reflections and 219 parameters. The

$$^{(1)}R = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|).$$

$$^{(2)}R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}.$$

maximum and minimum residual electron densities were 1.02 and 1.22 e Å⁻³ respectively.

9.5 Results and Discussion

The structure of ephesite determined in the present study is basically very similar to that reported by Slade and Radoslovich (1985), but the ordering scheme has produced a lower symmetry. Tables 9.2 and 9.3 show the important structural details computed from the data in Table 9.1.

The total numbers of tetrahedral aluminium cations calculated from a linear relationship between the Si-O and the Al-O bond lengths given by Baur (1981) and from the regression equation of Hazen and Burnham (1973) are 4.141 and 4.000 Al respectively. Each of these values is in close agreement with the electron microprobe value (4.16) and closer to that obtained from the XRF analysis (3.977) than calculated previously by Slade and Radoslovich (1985) from the data based upon the space group Cc refinement (3.632).

The ordering in the T(1)', T(11)', T(2)' and T(22)' sites is more complete than in the T(1), T(11), T(2) and T(22) sites. This causes small differences in the compositions of the tetrahedral sheets in the 2:1 layers (1.025 and 0.963, 1.037 and 0.975) but the effect is smaller than previously reported by Slade and Radoslovich (1985).

During the present study, the distribution of cations over the tetrahedral sites in ephesite has been found to conform to either of two models (A or B). Each of these places like cations opposite each other across the interlayer and therefore contrasts with the arrangement in margarite where Si⁴⁺ ions are opposite Al³⁺ ions. The latter trans-interlayer distribution of cations reduces the electrostatic repulsion that would operate if like

ions were opposed across the interlayer distance of $2.87\text{\AA}$. The greater interlayer separation in ephesite ($3.06\text{\AA}$ from Sokolova *et al.* (1979) or $3.08\text{\AA}$ from the present work) resulting from the smaller charge of the monovalent Na^+ ions, permits the potentially unstable arrangement of opposing Si^{4+} and opposing Al^{3+} ions.

This study of ephesite leads to the suggestion that the forbidden h0l reflections found by Slade and Radoslovich (1985), in X-ray photographs of margarite from Chester, Massachusetts; Woodside, South Australia; and Greiner, Austria may result from their ephesitic components. Reliable analytical data are not available for the Woodside margarite, but the results of Langer *et al.* (1983) and Joswig *et al.* (1983) respectively show that the Chester material can contain between 18.5–36 mole% ephesite and the Greiner specimens 21%. A comparison of the intensities of the extra reflections in the three margarites shows that those for the Greiner material are relatively much weaker than might be expected from its substantial ephesitic component. Apparently then, the manner of incorporation of the ephesite component into the margarite structure determines the intensity of the extra reflections.

If the trioctahedral component is present in extended domains, which have the ephesite structure, coherent diffraction effects will be produced and are likely to be observable. However, if the sodic component is uniformly dispersed through the margarite lattice the weak additional reflections associated with ephesite are unlikely to be seen. Any lattice strain associated with a domain structure may account for the poor quality of the diffraction patterns given by the Chester and Woodside margarites. The Greiner material produces a sharp, good quality diffraction pattern consistent with a homogeneous, unstrained structure.

In their study of the Biskupice lepidolite- 2M_1 , Swanson and

Bailey (1981) found weak $h0l$ reflections which violated the c -glide operator of space group $C2/c$ used for their refinement. Although deviations of the data set from $C2/c$ symmetry were very small Swanson and Bailey (1981) concluded that the true symmetry was most likely $C1$. No tetrahedral Si/Al ordering was detected, but with the reported low concentration of tetrahedrally coordinated aluminium ($\approx 10\%$), the tendency towards such ordering would also be small. However, given the relatively large interlayer separation ($3.365\text{\AA}$) any ordering present, and concentrated in domains, may locally violate the c -glide operator.

Giese (1979) has defined an angle (ρ) between the O-H bond and (001) measured with respect to the M(1) site. For ephesite, the ρ values from the hydrogen coordinates given in Table 9.1 are 76.5° for O-H(1), 88.6° for O-H(1)', 82.9° for O-H(11) and 75.7° for O-H(11)'. While two of these values are very close to the angle calculated from Giese's regression equation for trioctahedral micas (76.2°) the other two are a little higher. These differences, and the different B values for the M(1) and M(1)' sites, may be taken to indicate that this pair of octahedral sites have slightly different cation occupancies. This is compatible with the reduced symmetry.

The overall veracity of this refinement of the structure of ephesite is supported by the close correspondence between the F_{obs} and F_{calc} values for the weak $h0l$, l odd reflections.

Table 9.1: Atomic Coordinates and Isotropic Thermal Parameters for Ephesite.

For Sodium Cations $B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} \alpha_i^* \alpha_j^* a_i \cdot a_j$.

	X	Y	Z	B_{eq} or $B(\text{\AA}^2)$
Na	0.0000	-0.0914	-0.2500	0.86
Na'(1)	-0.0009(4)	0.0833(3)	-0.7508(1)	0.94(3)
M(1)	-0.252(1)	0.250(1)	-0.0049(6)	0.70(7)
M(1)'	-0.258(1)	-0.247(1)	-0.5037(7)	1.05(8)

Table 9.1 (Contd.)

	X	Y	Z	B _{eq} or B(Å ²)
M(2)	-0.7514(4)	-0.9199(3)	-0.0003(2)	0.17(1)
M(2)'	-0.7444(4)	0.9107(3)	-0.5005(2)	0.17(1)
M(3)	-0.2625(4)	-0.0905(3)	-0.0001(2)	0.17(1)
M(3)'	-0.2552(4)	0.0812(3)	-0.5005(2)	0.17(1)
T(1)	-0.4695(3)	-0.9262(3)	-0.1435(2)	0.21(1)
T(1)'	-0.4634(4)	0.9177(3)	-0.6426(2)	0.21(1)
T(11) ⁽²⁾	-0.5396(4)	-0.0837(3)	-0.8581(2)	0.21(1)
T(11)'	-0.5340(3)	0.0748(3)	-0.3570(2)	0.21(1)
T(2)	-0.4619(4)	-0.2552(3)	-0.1431(2)	0.21(1)
T(2)'	-0.4558(3)	0.2494(3)	-0.6442(2)	0.21(1)
T(22)	-0.5467(3)	-0.7513(3)	-0.8576(2)	0.21(1)
T(22)'	-0.5421(4)	0.7450(3)	-0.3587(2)	0.21(1)
O(1)	-0.9546(6)	-0.4335(5)	-0.0554(3)	0.27(2)
O(1)'	-0.9464(6)	0.4304(5)	-0.5520(3)	0.27(2)
O(11)	-0.0512(6)	-0.5659(5)	-0.9474(3)	0.27(2)
O(11)'	-0.0444(6)	0.5611(5)	-0.4437(3)	0.27(2)
O(2)	-0.4099(6)	-0.2583(5)	-0.0524(2)	0.27(2)
O(2)'	-0.4097(6)	0.2441(5)	-0.5574(2)	0.27(2)
O(22)'	-0.6067(6)	-0.7571(5)	-0.9435(2)	0.27(2)
O(22)'	-0.6112(6)	0.7441(5)	-0.4491(2)	0.27(2)
O(3)	-0.3605(6)	-0.0829(5)	-0.1726(3)	0.46(2)
O(3)'	-0.3569(6)	0.0889(5)	-0.6728(3)	0.46(2)
O(33)	-0.6538(6)	-0.9122(5)	-0.8283(3)	0.46(2)
O(33)'	-0.6476(6)	0.9177(5)	-0.3284(3)	0.46(2)
O(4)	-0.2908(7)	-0.7836(5)	-0.1661(3)	0.46(2)
O(4)'	-0.2647(6)	0.7659(5)	-0.6655(3)	0.46(2)
O(44)	-0.7321(6)	-0.2333(5)	-0.8355(3)	0.46(2)
O(44)'	-0.7075(6)	0.2144(5)	-0.3361(3)	0.46(2)
O(5)	-0.2779(6)	-0.4010(5)	-0.1743(3)	0.46(2)
O(5)'	-0.2890(6)	0.3826(5)	-0.6741(3)	0.46(2)
O(55)	-0.7164(6)	-0.6147(5)	-0.8292(3)	0.46(2)
O(55)'	-0.7262(6)	0.5971(5)	-0.3286(3)	0.46(2)
OH(1)	-0.4491(7)	-0.5758(5)	-0.0499(3)	0.28(2)
OH(1)'	-0.4398(6)	0.5685(5)	-0.5473(3)	0.28(2)
OH(11)	-0.5550(6)	-0.4366(5)	-0.9511(3)	0.28(2)
OH(11)'	-0.5476(6)	0.4297(5)	-0.4490(3)	0.28(2)
H(1)	-0.429(1)	-0.590(1)	-0.095(1)	1.52(9)
H(1)'	-0.465(1)	0.575(1)	-0.594(1)	1.52(9)
H(11)	-0.546(1)	-0.424(1)	-0.904(1)	1.52(9)
H(11)'	-0.574(1)	0.416(1)	-0.405(1)	1.52(9)

⁽¹⁾c-glide related atoms in one layer are indicated by a prime symbol (') applied to the corresponding atom in the other layer.

⁽²⁾Pseudo-centre related atoms in one tetrahedral sheet indicated by doubling the last digit of the symbol for the corresponding atom in the other sheet.

Table 9.2: Interatomic Distances (Å) and Angles (°)

Atoms	Distance	Atoms	Distance	Angle
Tetrahedron about T(1)				
T(1)-O(1)*	1.699(5)	O(1)-O(3)	2.705(5)	109.2(2)
-O(3)	1.618(5)	-O(4)	2.714(5)	108.6(2)
-O(4)	1.643(4)	-O(5)	2.723(6)	108.7(2)
-O(5)	<u>1.652(5)</u>	O(3)-O(4)	2.682(6)	110.7(2)
mean	1.653(5)	-O(5)	2.676(5)	109.9(3)
		O(4)-O(5)	<u>2.695(5)</u>	<u>109.8(3)</u>
		mean	2.699(5)	109.5(2)
Tetrahedron about T(1)'				
T(1)'-O(1)'	1.748(5)	O(1)'-O(3)'	2.796(6)	106.9(2)
-O(3)'	1.733(5)	-O(4)'	2.858(6)	108.8(3)
-O(4)'	1.768(4)	-O(5)'	2.841(6)	108.6(2)
-O(5)	<u>1.751(4)</u>	O(3)'-O(4)'	2.907(6)	112.3(2)
mean	1.750(5)	-O(5)'	2.871(6)	111.0(3)
		O(4)'-O(5)'	<u>2.868(6)</u>	<u>109.2(3)</u>
		mean	2.857(6)	109.5(3)
Tetrahedron about T(11)				
T(11)-O(11)*	1.727(5)	O(11)-O(33)	2.766(6)	105.6(3)
-O(33)	1.747(5)	-O(44)	2.847(6)	110.6(3)
-O(44)	1.734(4)	-O(55)	2.764(6)	106.5(3)
-O(55)	<u>1.721(5)</u>	O(33)-O(44)	2.880(6)	111.7(2)
mean	1.732(5)	-O(55)	2.873(6)	111.9(3)
		O(44)-O(55)	<u>2.836(6)</u>	<u>110.4(2)</u>
		mean	2.828(6)	109.4(3)
Tetrahedron about T(11)'				
T(11)'-O(11)'	1.675(5)	O(11)'-O(33)'	2.658(6)	107.3(3)
-O(33)'	1.626(5)	-O(44)'	2.680(6)	109.9(3)
-O(44)'	1.597(4)	-O(55)'	2.654(6)	106.7(3)
-O(55)'	<u>1.634(5)</u>	O(33)'-O(44)'	2.654(6)	110.8(2)
mean	1.633(5)	-O(55)'	2.683(6)	110.7(3)
		O(44)'-O(55)'	<u>2.667(6)</u>	<u>111.3(3)</u>
		mean	2.666(6)	109.5(3)
Tetrahedron about T(2)				
T(2)-O(2)*	1.747(5)	O(2)-O(3)	2.823(6)	108.7(2)
-O(3)	1.728(5)	-O(4)	2.812(6)	108.3(2)
-O(4)	1.722(5)	-O(5)	2.809(6)	107.3(2)
-O(5)	<u>1.750(4)</u>	O(3)-O(4)	2.846(6)	111.2(2)
mean	1.734(5)	-O(5)	2.855(6)	110.9(2)
		O(4)-O(5)	<u>2.843(6)</u>	<u>110.4(3)</u>
		mean	2.831(6)	109.5(2)

Table 9.2: (Contd.)

Atoms	Distance	Atoms	Distance	Angle
Tetrahedron about T(2)'				
T(2)'-O(2)'	1.672(4)	O(2)'-O(3)'	2.654(6)	107.3(2)
-O(3)'	1.625(5)	-O(4)'	2.648(6)	107.8(2)
-O(4)'	1.605(5)	-O(5)'	2.686(6)	110.5(2)
-O(5)'	<u>1.597(4)</u>	O(3)'-O(4)'	2.627(6)	108.8(2)
mean	1.625(5)	-O(5)'	2.631(6)	109.5(2)
		O(4)'-O(5)'	<u>2.667(6)</u>	<u>112.8(2)</u>
		mean	2.652(6)	109.5(2)
Tetrahedron about T(22)				
T(22)-O(22)*	1.662(4)	O(22)-O(33)	2.646(6)	106.1(2)
-O(33)	1.648(5)	-O(44)	2.713(6)	110.7(2)
-O(44)	1.637(5)	-O(55)	2.649(6)	107.8(2)
-O(55)	<u>1.616(4)</u>	O(33)-O(44)	2.695(6)	110.2(2)
mean	1.641(5)	-O(55)	2.660(6)	109.2(2)
		O(44)-O(55)	<u>2.707(6)</u>	<u>112.6(2)</u>
		mean	2.678(6)	109.4(2)
Tetrahedron about T(22)'				
T(22)'-O(22)'	1.750(4)	O(22)'-O(33)'	2.816(6)	107.4(2)
-O(33)'	1.745(5)	-O(44)'	2.879(6)	110.7(2)
-O(44)'	1.751(5)	-O(55)'	2.775(6)	105.1(2)
-O(55)'	<u>1.745(4)</u>	O(33)'-O(44)'	2.901(6)	112.1(2)
mean	1.748(5)	-O(55)'	2.874(6)	110.9(2)
		O(44)'-O(55)'	<u>2.869(6)</u>	<u>110.3(2)</u>
		mean	2.852(6)	109.4(2)
Octahedron about M(1)				
M(1)-OH(1)	2.001(10)	O(1) -O(2)	3.190(5)	
-O(11)	2.180(10)	-OH(1)	3.177(5)	
-O(2)	2.050(10)	O(2) -OH(1)	3.206(5)	
-OH(11)	2.156(10)	O(11)-O(22)	3.320(5)	
-O(22)	2.258(10)	-OH(11)	3.291(5)	
-O(1)	<u>2.123(10)</u>	O(22)-OH(11)	<u>3.258(5)</u>	
mean	2.128(10)	mean (unshared)	3.240(5)	
H(1) -OH(1)	0.891(23)			
H(11)-OH(11)	0.908(23)			
		shared edges between M(1) and M(3)		
		O(22)-OH(1)	2.784(6)	
		O(2) -O(11)	2.796(6)	
		O(1) -OH(11)	<u>2.734(6)</u>	
		mean	2.773(6)	

Table 9.2: (Contd.)

Atoms	Distance	Atoms	Distance
Octahedron about M(1)'			
M(1)-OH(1)'	2.029(10)	O(1)' -O(2)'	3.217(5)
-O(11)'	2.280(10)	-OH(1)'	3.213(5)
-O(2)'	2.142(10)	O(2)' -OH(1)'	3.152(5)
-OH(11)'	2.131(10)	O(11)'-O(22)'	3.319(5)
-O(22)'	2.177(10)	-OH(11)'	3.272(5)
-O(1)'	<u>2.030(10)</u>	O(22)'-OH(11)'	<u>3.324(5)</u>
mean	2.132(10)	mean (unshared)	3.250(5)
H(1)' -OH(1)'	0.904(23)	shared edges between	
H(11)'-OH(11)'	0.887(23)	M(1)' and M(3)'	
		O(22)'-OH(1)'	2.664(6)
		O(2)' -O(11)'	2.864(6)
		O(1)' -OH(11)'	<u>2.720(6)</u>
		mean	2.749(6)
Octahedron about M(2)			
M(2)-OH(1)	1.920(5)	O(1) -O(2)	2.807(5)
-O(11)	1.892(5)	-OH(1)	2.841(5)
-O(2)	1.891(5)	O(2) -OH(1)	2.825(5)
-OH(11)	1.899(5)	O(11)-O(22)	2.757(5)
-O(22)	1.922(5)	-OH(11)	2.819(5)
-O(1)	<u>1.936(5)</u>	O(22)-OH(11)	<u>2.788(5)</u>
mean	1.910(5)	mean (unshared)	2.806(5)
shared edges between			
M(2) and M(3) octahedra			
O(1) -O(11)	2.479(5)	shared edges between	
O(2) -O(22)	2.498(5)	M(1) and M(2)' octahedra	
OH(1)-OH(11)	<u>2.377(5)</u>	OH(1)'-O(11)'	2.716(6)
mean	2.451(5)	O(2)' -OH(11)'	2.805(6)
		O(22)'-O(1)'	<u>2.773(6)</u>
		mean	2.765(6)
Octahedron about M(2)'			
M(2)'-OH(1)'	1.901(5)	O(1)' -O(2)'	2.887(5)
-O(11)'	1.959(5)	-OH(1)'	2.817(5)
-O(2)'	1.986(5)	O(2)' -OH(1)'	2.891(5)
-OH(11)'	1.926(5)	O(11)'-O(22)'	2.836(5)
-O(22)'	1.874(5)	-OH(11)'	2.823(5)
-O(1)'	<u>1.903(5)</u>	O(22)'-OH(11)'	<u>2.776(5)</u>
mean	1.925(5)	mean (unshared)	2.838(5)
shared edges between			
M(2)' and M(3)' octahedra			
O(1)' -O(11)'	2.482(5)	shared edges between	
O(2)' -O(22)'	2.477(5)	M(1)' and M(2) octahedra	
OH(1)'-OH(11)'	<u>2.370(5)</u>	OH(1)-O(11)	2.711(6)
mean	2.443(5)	O(2) -OH(11)	2.671(6)
		O(22)-O(1)	<u>2.833(6)</u>
		mean	2.738(6)

Table 9.2: (Contd.)

Atoms	Distance	Atoms	Distance
Octahedra about M(3)			
M(3)-OH(1)	1.948(5)	O(1) -O(2)	2.893(6)
-O(11)	1.881(5)	-OH(1)	2.874(6)
-O(2)	1.917(5)	O(2) -OH(1)	2.860(6)
-OH(11)	1.927(5)	O(11)-O(22)	2.835(6)
-O(22)	1.964(5)	-OH(11)	2.796(6)
-O(1)	<u>1.963(5)</u>	O(22)-OH(11)	<u>2.863(6)</u>
mean	1.933(5)	mean (unshared)	2.854(6)
Octahedra about M(3)'			
M(3)'-OH(1)'	1.925(5)	O(1)' -O(2)'	2.794(6)
-O(11)'	1.928(5)	-OH(1)'	2.864(6)
-O(2)'	1.941(5)	O(2)' -OH(1)'	2.859(6)
-OH(11)'	1.932(5)	O(11)'-O(22)'	2.759(6)
-O(22)'	1.867(5)	-OH(11)'	2.809(6)
-O(1)'	<u>1.889(5)</u>	O(22)'-OH(11)'	<u>2.809(6)</u>
mean	1.914(5)	mean (unshared)	2.816(6)
Polyhedra about Na			
Na-O(3)	2.479(4)		3.477(5)
-O(4)	2.523(4)		3.570(5)
-O(5)	2.448(4)		3.476(5)
-O(33)'	2.459(4)		3.520(5)
-O(44)'	2.560(4)		3.581(4)
-O(55)'	<u>2.475(4)</u>		<u>3.507(4)</u>
mean (inner)	2.491(4)	(outer)	3.522(5)
Polyhedra about Na'			
Na'-O(3)'	2.468(5)		3.501(5)
-O(4)'	2.540(5)		3.588(5)
-O(5)'	2.500(5)		3.439(5)
-O(33)	2.424(5)		3.538(5)
-O(44)	2.523(5)		3.588(5)
-O(55)	<u>2.510(5)</u>		<u>3.463(5)</u>
mean (inner)	2.494(5)	(outer)	3.520(5)

Table 9.3: Important Structural Details

=====	
Tetrahedral rot, α°	22.09, 21.84, 22.55, 22.51
O-T-O angle, r° Si	108.84, 107.95, 108.52, 108.20, (108.38)
Al	108.08, 107.58, 108.06, 107.73 (107.87)
Octahedral angle, ν°	59.37, 59.43
Sheet thickness ($\text{\AA}$)	
tetrahedral	2.224, 2.180 (2.202) 2.143, 2.270 (2.207)
octahedral	2.023 2.019
Interlayer separation ($\text{\AA}$)	3.08 3.08
Basal oxygen ΔZ_{ave} ($\text{\AA}$)	0.141, 0.147, 0.153, 0.130
T-O	T(1) =1.653, T(11) =1.732 (1.693) T(1)' =1.750, T(11)' =1.633 (1.692) T(2) =1.734, T(22) =1.641 (1.688) T(2)' =1.625, T(22)' =1.748 (1.687)
M(1,2,3)...O, OH	2.218, 1.910, 1.933
M(1,2,3)'...O', OH'	2.132, 1.925, 1.914
Mean bond lengths ($\text{\AA}$)	
(Na, Ca)...O	
inner	2.491
outer	3.522
(Na, Ca)'...O	
inner	2.494
outer	3.520
=====	

CHAPTER 10**CONCLUSIONS**

CHAPTER 10

CONCLUSIONS

The clay minerals smectites and vermiculites are important natural layer silicates which readily undergo cation exchange reactions with a variety of inorganic and organic species. These minerals are of great economic importance as they can act as heterogeneous catalysts in a wide range of chemical reactions (Thomas, 1982). Their presence and reactivity in the soil also makes them important on environmental grounds. Therefore the knowledge of the compositions and the crystal structures of these clay minerals and their intercalates is essential if one is to understand the chemical reactions involved.

To that end vermiculites from Llano County, Texas, Phalaborwa, Transvaal and Young River, Western Australia were intercalated with anilinium cations, their compositions determined and full three-dimensional X-ray structure analyses carried out. The structure analyses revealed that the anilinium cations form a $2a \times 2b$ superlattice and produce bonding between the silicate layers which improves their stacking order, placing the ditrigonal cavities in adjacent silicate layers opposite each other. The principal axes of the anilinium ions i.e. N-C(1)-C(4) directions were found to be nearly perpendicular to the silicate layers. The planes of the aromatic rings were about $+30^\circ$ to the a -axis. It was found however that the anilinium ions do not bridge the interlayer space but that some of them lodge themselves into the lower and some into the upper ditrigonal cavities and are hydrogen bonded, via the aminium $(\text{NH}_3)^+$ group, to the surface oxygens of one layer only. The interlayer spacings are in the main governed by the inorganic cations and their coordinated water molecules, which are also present in the

interlayer space. The amount of anilinium intercalated was found not to be directly proportional to the interlayer charge density in the three vermiculites studied.

The intercalation of Llano County, Texas, Kenya and Nyasaland (now Malawi) vermiculites with triethylenediaminium $[\text{TEDAH}_2]^{2+}$ cations produced similar results to the anilinium intercalations. But this time the intercalants were found to possess a $3a \times b$ superlattice; they were positioned vertically to the silicate layers and again not fully bridging the interlayer space. The $[\text{TEDAH}_2]^{2+}$ ions keyed into ditrigonal cavities of one silicate layer only, where one of the aminium groups of the $[\text{TEDAH}_2]$ ion is hydrogen bonded to the surface oxygens, while the other aminium group is only indirectly bonded, via water molecules, to the other silicate layer. The presence of inorganic cations and octahedrally coordinated water molecules was again detected. These intercalates were found to be thermally stable up to 350°C , as stated by Shabtai *et al.* (1977) for the $[\text{TEDAH}_2]$ montmorillonite. The stacking sequence, however, deteriorated with increasing temperature but reverted to its original ordered state on cooling. Again the amount of intercalant adsorbed was not proportional to the charge density of the vermiculites intercalated. The intercalation of the last three vermiculites with p-phenylenediaminium $[\text{PHEDAH}_2]^{2+}$ cations did not produce an intercalate with sufficiently ordered layers to make a three-dimensional structure determination possible.

The microanalytical and three-dimensional X-ray structure determinations carried out on the intercalated vermiculites have shown that the intercalation processes are very complex, with the end results depending on the size, shape and charge of the intercalant, the surface charge of the layer silicates and the pH under which the reactions are carried out. It became also evident that substantial amounts of inorganic cations and water molecules were also present, at least under the conditions used in this study. These inorganic cations and water molecules were

largely responsible for the c-dimensions of the intercalates.

The symmetry of the intercalated vermiculites was found to be lower than previously assumed; the only symmetry present was C-centering and no evidence for the long-range Si/Al ordering in the tetrahedral sites was detected.

The symmetry of the brittle mica ephesite from Postmasburg district, South Africa, was found by Slade and Radoslovich (1985) to be C1 although these authors only used Cc in their structure refinement. The lower symmetry was found in this study to be due to aluminium ions facing aluminium ions and silicon ions facing silicon ions across the interlayer region. The c-glide operator of space group Cc positioned silicon ions opposite aluminium ions.

The important result obtained from this study of anilinium and $[\text{TEDAH}_2]^{2+}$ intercalated vermiculites is that these intercalants are not positioned symmetrically between the silicate layers. These findings differ from the model proposed by Shabtai *et al.* (1977), who suggested that the silicate layers in montmorillonite were cross-linked by $[\text{TEDAH}_2]$ cations, whose opposite aminium groups were in direct contact with adjacent silicate layers.

APPENDIX**OBSERVED (F_o) AND CALCULATED (F_c) STRUCTURE
FACTOR TABLES**

A.1 Anilinium - vermiculites

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Observed and calculated structure factors for anilinium-Phalaborwa vermiculite

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h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
2	-2	-20	9	16	3	-3	-17	64	61	1	5	-16	12	13	0	8	-15	10	13
2	0	-20	28	47	2	-2	-17	18	21	3	5	-16	7	6	2	8	-15	13	11
1	1	-20	14	7	4	-2	-17	17	15	0	6	-16	69	65	1	-9	-14	30	25
2	2	-20	11	16	3	-1	-17	6	9	2	6	-16	14	17	0	-8	-14	18	17
1	-5	-19	13	10	2	0	-17	21	26	0	-8	-15	19	17	2	-8	-14	11	14
0	-4	-19	7	10	3	1	-17	9	10	2	-8	-15	10	12	3	-7	-14	13	12
2	-4	-19	12	7	2	2	-17	20	24	3	-7	-15	10	12	2	-6	-14	30	21
0	-2	-19	12	13	4	2	-17	11	13	0	-6	-15	53	50	4	-6	-14	48	39
0	0	-19	16	30	3	3	-17	66	64	2	-6	-15	41	34	1	-5	-14	12	14
3	1	-19	9	9	0	4	-17	7	7	4	-6	-15	28	25	5	-5	-14	14	14
2	2	-19	9	14	2	4	-17	9	10	1	-5	-15	9	13	0	-4	-14	18	21
0	4	-19	8	10	4	4	-17	15	15	3	-5	-15	6	7	2	-4	-14	10	8
2	4	-19	9	5	1	5	-17	9	7	0	-4	-15	15	20	4	-4	-14	24	28
2	-6	-18	19	22	0	6	-17	14	26	2	-4	-15	12	15	2	-2	-14	19	20
1	-5	-18	8	14	2	6	-17	10	10	4	-4	-15	13	12	4	-2	-14	10	14
0	-4	-18	18	22	1	7	-17	10	9	5	-3	-15	27	24	3	-1	-14	11	14
2	-4	-18	8	15	0	-8	-16	12	15	2	-2	-15	28	26	5	-1	-14	14	10
1	-3	-18	62	86	3	-7	-16	9	10	4	-2	-15	8	11	2	0	-14	41	51
3	-3	-18	37	33	0	-6	-16	66	68	3	-1	-15	7	8	4	0	-14	40	36
4	-2	-18	24	9	2	-6	-16	22	30	5	-1	-15	13	7	5	1	-14	12	12
3	-1	-18	7	4	1	-5	-16	8	12	2	0	-15	59	62	0	2	-14	17	17
2	0	-18	6	15	0	-4	-16	15	21	4	0	-15	22	33	2	2	-14	10	15
4	0	-18	18	26	4	-4	-16	19	19	1	1	-15	9	9	4	2	-14	10	15
1	1	-18	9	12	3	-3	-16	45	44	5	1	-15	13	9	5	3	-14	11	10
2	2	-18	17	13	5	-3	-16	41	43	2	2	-15	28	27	0	4	-14	22	23
4	2	-18	11	5	0	-2	-16	7	10	3	3	-15	7	16	2	4	-14	9	9
1	3	-18	59	87	4	-2	-16	11	12	5	3	-15	35	24	4	4	-14	24	25
3	3	-18	18	31	1	-1	-16	7	10	0	4	-15	8	13	1	5	-14	10	10
0	4	-18	14	18	5	-1	-16	9	10	4	-1	-15	17	5	3	5	-14	8	10
2	4	-18	10	14	1	1	-16	7	10	1	5	-15	6	7	5	5	-14	10	11
1	5	-18	11	13	0	2	-16	9	10	3	5	-15	9	6	2	6	-14	27	27
0	-6	-17	36	42	4	2	-16	8	7	0	6	-15	55	64	4	6	-14	41	42
1	-5	-17	11	11	3	3	-16	55	52	2	6	-15	39	34	3	7	-14	14	13
0	-4	-17	6	11	0	4	-16	18	23	4	6	-15	14	13	0	8	-14	18	18
2	-4	-17	9	13	2	4	-16	10	10	1	7	-15	18	8	2	8	-14	11	7
4	-4	-17	15	15	4	4	-16	20	19	3	7	-15	12	11	0	-10	-13	15	12

Observed and calculated structure factors for anilinium-Phalaborwa vermiculite

page 2

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	4	-13	24	28	1	-1	-12	12	17	1	-7	-11	20	14	4	4	-11	29	25
2	4	-13	12	13	3	-1	-12	19	21	3	-7	-11	12	14	6	4	-11	12	3
4	4	-13	21	13	5	-1	-12	16	6	5	-7	-11	17	12	1	5	-11	16	14
1	5	-13	15	13	6	0	-12	66	55	0	-6	-11	90	94	3	5	-11	23	21
3	5	-13	10	11	1	1	-12	11	17	2	-6	-11	53	48	5	5	-11	12	18
5	5	-13	12	14	3	1	-12	21	20	4	-6	-11	32	38	0	6	-11	86	94
2	6	-13	11	15	5	1	-12	13	9	1	-5	-11	13	14	2	6	-11	33	37
4	6	-13	36	34	2	2	-12	47	38	3	-5	-11	25	25	4	6	-11	35	34
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Observed and calculated structure factors for anilinium-Phalaborwa vermiculite

page 3

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Observed and calculated structure factors for anilinium-Phalaborwa vermiculite

page 4

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0	-2	-1	24	26	2	8	-1	18	16	4	-2	0	43	36	0	10	0	18	15	4	0	1	54	48
2	-2	-1	21	10	4	8	-1	10	11	6	-2	0	15	10	2	10	0	11	16	6	0	1	19	20
4	-2	-1	32	25	1	9	-1	59	47	3	-1	0	23	16	4	10	0	21	20	1	1	1	44	51
6	-2	-1	13	10	3	9	-1	110	83	5	-1	0	25	25	0	-10	1	21	22	3	1	1	34	31
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3	-1	-1	37	37	0	10	-1	22	22	4	0	0	72	63	1	-9	1	22	21	0	2	1	25	26
5	-1	-1	18	10	2	10	-1	15	15	6	0	0	34	24	3	-9	1	34	19	2	2	1	15	15
0	0	-1	189	68	4	10	-1	20	31	3	1	0	22	13	5	-9	1	51	33	4	2	1	32	14
2	0	-1	33	18	0	-10	0	13	15	5	1	0	27	25	0	-8	1	15	13	6	2	1	16	15

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
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3	3	1	44	39	5	-7	2	20	18	2	4	2	32	26	6	-6	3	41	38	1	5	3	47	39
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2	4	1	41	42	4	-6	2	53	46	1	5	2	27	19	5	-5	3	17	18	0	6	3	10	10
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4	-8	2	16	8	3	3	2	11	10	2	-6	3	22	13	4	4	3	19	23	1	-5	4	31	33
1	-7	2	24	25	5	3	2	55	41	2	-6	3	22	13	4	4	3	19	23	1	-5	4	31	33

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
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5	-5	4	15	18	0	6	4	25	28	3	-3	5	50	52	0	8	5	18	19	5	-1	6	13	11
0	-4	4	28	29	2	6	4	19	11	5	-3	5	91	85	2	8	5	18	18	2	0	6	111	116
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4	-4	4	23	13	6	6	4	40	23	2	-2	5	38	39	1	9	5	24	24	6	0	6	25	24
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3	-3	4	66	66	5	7	4	12	4	1	-1	5	24	24	2	10	5	17	20	5	1	6	12	13
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0	-2	4	27	17	2	8	4	25	22	5	-1	5	12	15	0	-10	6	12	18	2	2	6	26	16
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4	-2	4	30	22	1	9	4	48	46	2	0	5	60	60	1	-9	6	14	14	6	2	6	18	18
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1	1	4	28	24	0	-8	5	14	12	6	2	5	11	6	2	-6	6	93	105	3	5	6	11	12
3	1	4	25	22	2	-8	5	19	19	1	3	5	34	44	4	-6	6	50	39	5	5	6	15	12
5	1	4	14	2	4	-8	5	16	16	3	3	5	68	62	1	-5	6	28	27	0	6	6	56	75
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4	2	4	32	15	5	-7	5	15	8	2	4	5	24	16	2	-4	6	26	27	1	7	6	12	12
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1	3	4	103	107	2	-6	5	81	82	6	4	5	21	13	6	-4	6	21	17	0	8	6	22	20
3	3	4	92	64	4	-6	5	9	16	1	5	5	33	23	1	-3	6	21	22	2	8	6	24	18
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2	4	4	39	34	5	-5	5	15	16	0	-2	6	67	73	0	-2	6	19	14	0	10	6	14	16
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3	5	4	24	20	6	-4	5	18	15	1	7	5	22	18	1	-1	6	28	25	1	-9	7	41	44

Observed and calculated structure factors for anilinium-Phalaborwa vermiculite

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h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
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2	-8	7	15	18	2	4	7	21	21	5	-3	8	25	35	1	9	8	69	61	2	2	9	39	33
4	-8	7	16	14	4	4	7	20	15	0	-2	8	15	16	3	9	8	24	12	4	2	9	18	10
1	-7	7	8	14	6	4	7	16	4	2	-2	8	27	19	0	10	8	15	16	6	2	9	19	20
3	-7	7	14	20	1	5	7	21	13	4	-2	8	21	16	2	10	8	18	19	1	3	9	161	156
0	-6	7	21	15	5	5	7	10	8	6	-2	8	18	14	0	-10	9	17	17	3	3	9	73	66
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4	-6	7	78	72	2	6	7	85	68	3	-1	8	13	11	1	-9	9	91	69	0	4	9	33	31
1	-5	7	19	21	4	6	7	86	69	5	-1	8	9	17	3	-9	9	62	48	2	4	9	23	20
5	-5	7	15	16	1	7	7	11	13	0	0	8	15	24	0	-8	9	26	26	4	4	9	19	6
0	-4	7	27	26	3	7	7	20	20	4	0	8	82	77	2	-8	9	18	16	1	5	9	19	16
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3	-1	7	11	15	1	-9	8	62	70	0	4	8	37	37	4	-4	9	24	13	1	9	9	85	82
5	-1	7	8	6	3	-9	8	32	20	2	4	8	23	20	1	-3	9	126	142	3	9	9	51	45
0	0	7	49	79	0	-8	8	21	21	4	4	8	31	29	3	-3	9	61	72	0	10	9	11	16
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4	2	7	23	23	3	-5	8	7	7	1	7	8	6	6	2	0	9	38	55	1	-7	10	9	14
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3	3	7	55	47	2	-4	8	18	14	0	8	8	22	22	1	1	9	17	20	1	-5	10	16	13

Observed and calculated structure factors for anilinium-Phalaborwa vermiculite

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h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
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5	-5	10	10	13	4	8	10	20	19	1	5	11	21	21	2	2	12	31	33	0	4	13	32	31
0	-4	10	25	22	1	9	10	62	53	3	5	11	10	12	4	2	12	8	8	4	4	13	21	18
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3	-3	10	82	86	2	10	10	21	18	2	6	11	22	23	2	4	12	14	14	1	7	13	8	10
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2	-2	10	36	36	2	-8	11	14	14	0	8	11	27	25	3	5	12	6	8	1	9	13	27	23
4	-2	10	89	21	1	-7	11	6	9	2	8	11	15	13	0	6	12	60	68	0	-8	14	17	18
3	-1	10	16	19	3	-7	11	9	11	1	9	11	22	9	2	6	12	38	39	2	-8	14	8	8
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0	2	10	20	20	3	-3	11	36	44	3	-7	12	10	14	0	-8	13	19	19	2	-2	14	23	23
2	2	10	39	33	5	-3	11	36	41	0	-6	12	41	49	2	-8	13	9	12	4	-2	14	10	7
4	2	10	20	17	0	-2	11	14	17	2	-6	12	31	34	1	-7	13	9	12	4	0	14	13	20
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Observed and calculated structure factors For anilinium-young river vermiculite

page 3

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-2	2	-2	11	10	-5	-1	-1	15	15	4	-4	0	12	13	4	-6	1	31	17	1	-9	2	39	23

Observed and calculated structure factors For anilinium-young river vermiculite

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h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
-2	-8	2	22	15	0	0	2	34	52	-2	-2	3	19	20	-4	-4	4	17	19	3	-7	5	21	14
0	-8	2	9	20	-5	1	2	21	24	0	-2	3	18	21	-2	-4	4	32	29	-4	-6	5	30	23
2	-8	2	15	14	-3	1	2	14	16	2	-2	3	26	25	0	-4	4	11	11	-2	-6	5	18	21
-3	-7	2	28	10	-1	1	2	21	21	-5	-1	3	23	21	2	-4	4	33	28	0	-6	5	30	56
-1	-7	2	18	18	-4	2	2	40	28	-3	-1	3	34	39	4	-4	4	14	12	2	-6	5	51	48
1	-7	2	25	23	-2	2	2	25	26	-1	-1	3	48	27	-5	-3	4	14	8	-3	-5	5	15	12
3	-7	2	15	11	-3	3	2	13	18	1	-1	3	19	13	-3	-3	4	42	57	-1	-5	5	28	34
-4	-6	2	15	13	-1	-9	3	20	17	-4	0	3	79	57	-1	-3	4	21	28	1	-5	5	19	15
-2	-6	2	115	69	1	-9	3	87	50	-2	0	3	32	41	1	-3	4	52	65	3	-5	5	26	24
0	-6	2	118	117	-2	-8	3	63	24	0	0	3	89	70	3	-3	4	12	13	-4	-4	5	14	12
2	-6	2	33	21	0	-8	3	41	32	-5	1	3	15	11	-4	-2	4	27	30	-2	-4	5	35	31
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-3	-5	2	32	29	-3	-7	3	18	17	-1	1	3	45	47	0	-2	4	36	36	2	-4	5	18	17
-1	-5	2	37	35	-1	-7	3	29	26	-4	2	3	24	23	2	-2	4	12	14	4	-4	5	12	12
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-4	-4	2	6	9	-4	-6	3	20	29	-3	3	3	25	25	-1	-1	4	24	16	-1	-3	5	35	45
-2	-4	2	36	35	-2	-6	3	86	69	-4	4	3	17	17	-1	-1	4	40	49	1	-3	5	35	30
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-4	-2	2	18	22	-2	-4	3	31	47	3	-7	4	16	17	-5	3	4	17	19	1	-1	5	30	31
-2	-2	2	29	32	0	-4	3	24	17	-4	-6	4	35	38	-3	3	4	68	83	-4	0	5	16	12
0	-2	2	43	52	2	-4	3	28	42	-2	-6	4	29	34	-4	4	4	12	12	-2	0	5	34	42
2	-2	2	10	12	4	-4	3	7	9	0	-6	4	13	11	-1	-9	5	38	46	0	0	5	208	283
-5	-1	2	13	9	-5	-3	3	37	27	2	-6	4	36	46	-2	-8	5	16	14	-5	1	5	10	16
-3	-1	2	20	24	-3	-3	3	13	25	4	-6	4	104	60	0	-8	5	12	16	-3	1	5	14	16
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-2	0	2	22	29	-4	-2	3	44	29	3	-5	4	36	19										

Observed and calculated structure factors For anilinium-young river vermiculite

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h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
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-4	4	5	25	21	-5	1	6	14	22	1	-1	7	42	39	1	-1	8	9	10	-2	0	9	28	32
-2	-8	6	22	13	-3	1	6	17	14	-4	0	7	77	38	-4	0	8	122	74	-1	1	9	19	24
0	-8	6	17	22	-1	1	6	32	29	-2	0	7	62	40	-2	0	8	43	52	-4	2	9	25	6
2	-8	6	17	13	-4	2	6	29	25	0	0	7	89	73	0	0	8	41	35	-2	2	9	44	43
-3	-7	6	15	17	-2	2	6	22	32	-5	1	7	15	10	-5	1	8	11	17	-3	3	9	61	50
-1	-7	6	21	-20	-5	3	6	69	61	-3	1	7	7	11	-3	1	8	11	12	-4	4	9	22	20
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-4	-6	6	14	12	-2	-8	7	23	19	-2	2	7	42	40	-2	2	8	22	24	-2	-6	10	18	25
-2	-6	6	62	42	0	-8	7	21	16	-3	3	7	45	45	-3	3	8	16	15	0	-6	10	14	16
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-3	-5	6	12	17	1	-7	7	22	20	-1	-7	8	12	12	1	-7	9	22	18	-1	-5	10	24	28
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3	-5	6	37	14	2	-6	7	12	15	0	-6	8	9	16	2	-6	9	74	26	0	-4	10	43	21
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-4	-2	6	34	26	-1	-3	7	23	21	-1	-3	8	43	61	1	-3	9	46	29	-1	-1	10	20	26
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-5	-1	6	16	22	-2	-2	7	26	19	-2	-2	8	38	31	0	-2	9	16	20	0	0	10	60	91
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Observed and calculated structure factors For anilinium-young river vermiculite

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h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
-3	3	10	81	67	-2	-2	11	59	28	-1	-5	12	26	27	-3	1	12	14	24	-2	0	13	52	37
-2	-6	11	10	22	0	-2	11	6	15	1	-5	12	19	14	-1	1	12	8	17	-3	1	13	8	8
0	-6	11	88	56	2	-2	11	36	32	-2	-4	12	19	15	-2	2	12	43	35	-1	1	13	7	12
-3	-5	11	10	12	-3	-1	11	18	17	0	-4	12	50	12	-3	3	12	19	18	-2	2	13	13	14
-1	-5	11	15	14	-1	-1	11	19	32	2	-4	12	19	16	-1	-5	13	13	10	0	-4	14	20	12
1	-5	11	52	15	1	-1	11	5	5	-3	-3	12	76	44	-2	-4	13	13	21	-1	-3	14	42	46
-2	-4	11	16	20	-4	0	11	23	17	-1	-3	12	6	8	0	-4	13	43	29	1	-3	14	57	25
0	-4	11	37	30	-2	0	11	18	17	1	-3	12	18	19	1	-3	13	79	40	-2	-2	14	23	22
2	-4	11	8	13	-3	1	11	16	16	-2	-2	12	19	23	-2	-2	13	33	19	-1	-1	14	6	5
-3	-3	11	111	67	-1	1	11	25	22	0	-2	12	16	18	0	-2	13	15	15	-2	0	14	25	10
-1	-3	11	56	43	-4	2	11	14	15	2	-2	12	44	25	2	-2	13	40	21	-1	1	14	9	9
1	-3	11	37	35	-2	2	11	38	31	-3	-1	12	11	11	-3	-1	13	8	5	-2	2	14	31	27
3	-3	11	65	47	-3	3	11	57	51	1	-1	12	21	20	-1	-1	13	11	13	-2	0	15	14	15
-4	-2	11	21	24	0	-6	12	83	53	-2	0	12	49	26	1	-1	13	16	15					

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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4	2	-18	7	4	4	8	-12	21	18	4	-2	-7	7	7	4	-8	-3	110	7	-1	5	0	24	28
4	-4	-17	13	16	4	-8	-11	18	15	4	0	-7	76	62	4	-6	-3	62	65	1	5	0	31	30
4	-2	-17	15	15	4	-6	-11	25	30	4	-4	-7	25	23	4	-2	-3	20	32	3	5	0	13	13
4	0	-17	8	9	4	-4	-11	27	26	4	6	-7	34	27	4	2	-3	22	30	-2	6	0	67	55
4	2	-17	17	14	4	2	-11	9	12	4	8	-7	14	18	4	6	-3	66	63	0	6	0	156	136
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4	-6	1	15	11	3	5	1	28	30	2	-6	2	94	76	2	4	2	31	31	4	-8	3	18	17
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4	-4	1	18	16	-2	8	1	22	19	0	-4	2	34	34	0	6	2	43	38	4	-6	3	35	31
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1	3	1	78	70	0	-8	2	9	14	0	2	2	62	63	0	-10	3	21	22	3	-1	3	75	68
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-2	4	1	37	41	4	-8	2	14	9	4	2	2	32	42	4	-10	3	16	13	2	0	3	61	67
0	4	1	12	13	-3	-7	2	13	14	-3	3	2	78	87	-3	-9	3	24	13	-3	1	3	92	98

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ANILINE LLANO VERMICULITE

PAGE 3

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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1	1	3	76	68	2	10	3	16	16	4	-2	4	20	22	-3	9	4	15	9	1	-3	5	33	20
3	1	3	20	19	4	10	3	17	15	-3	-1	4	51	51	-1	9	4	38	30	3	-3	5	57	58
-2	2	3	34	37	-2	-10	4	15	8	-1	-1	4	65	57	1	9	4	37	32	-2	-2	5	41	34
0	2	3	62	51	0	-10	4	13	12	3	-1	4	29	24	3	9	4	43	36	0	-2	5	46	43
2	2	3	28	29	2	-10	4	17	14	-2	0	4	42	35	-2	10	4	16	10	2	-2	5	52	50
4	2	3	19	23	4	-10	4	12	12	0	0	4	122	109	0	10	4	11	13	4	-2	5	33	33
-3	3	3	35	34	-3	-9	4	15	4	2	0	4	44	48	2	10	4	19	16	-3	-1	5	6	6
-1	3	3	118	112	1	-9	4	40	35	-3	1	4	48	52	4	10	4	14	10	-1	-1	5	40	34
1	3	3	41	36	3	-9	4	48	36	-1	1	4	62	59	-2	-10	5	15	15	1	-1	5	30	32
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3	7	3	14	8	-2	-4	4	44	41	-2	6	4	78	77	2	-6	5	70	63	4	4	5	28	25
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2	8	3	22	17	4	-4	4	17	15	-3	7	4	23	23	-1	-5	5	22	18	1	5	5	19	24
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-1	9	3	73	63	1	-3	4	82	83	3	7	4	20	23	-2	-4	5	16	10	0	6	5	61	53
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ANILINE LLANO VERMICULITE

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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	7	5	37	36	3	-5	6	10	11	0	6	6	54	54	0	-4	7	24	24	0	6	7	3	5
1	7	5	18	18	-2	-4	6	23	24	2	6	6	97	92	2	-4	7	19	18	2	6	7	62	57
3	7	5	18	17	0	-4	6	49	50	-3	7	6	16	17	4	-4	7	20	14	4	6	7	56	54
-2	8	5	9	13	2	-4	6	32	32	-1	7	6	21	9	-3	-3	7	56	53	-3	7	7	15	16
0	8	5	16	9	4	-4	6	31	25	1	7	6	14	16	-1	-3	7	102	104	-1	7	7	28	29
2	8	5	12	7	-3	-3	6	63	55	3	7	6	11	12	1	-3	7	34	25	3	7	7	20	20
4	8	5	17	15	-1	-3	6	61	60	-2	8	6	15	10	3	-3	7	50	44	-2	8	7	15	14
-3	9	5	22	15	1	-3	6	18	16	0	8	6	30	26	-2	-2	7	30	31	0	8	7	14	12
-1	9	5	9	11	-2	-2	6	38	37	2	8	6	23	21	0	-2	7	31	30	2	8	7	15	15
1	9	5	18	12	0	-2	6	19	21	4	8	6	17	13	2	-2	7	48	48	4	8	7	16	9
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2	10	5	22	21	1	-1	6	34	32	0	10	6	15	16	1	-1	7	6	9	0	10	7	12	14
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-1	-3	8	95	103	1	9	8	64	52	3	-1	9	9	10	3	9	9	36	35	3	-1	10	19	20
1	-3	8	105	117	-2	10	8	11	20	-2	0	9	101	110	-2	10	9	17	11	-2	0	10	126	131
-2	-2	8	52	42	0	10	8	15	15	0	0	9	34	30	0	10	9	13	12	0	0	10	56	65
0	-2	8	18	20	0	-10	9	13	12	4	0	9	33	35	2	10	9	25	20	2	0	10	35	31
4	-2	8	15	19	-2	-10	9	23	20	-3	1	9	24	28	-2	-10	10	26	20	-1	1	10	24	27
-3	-1	8	15	20	-3	-9	9	24	21	-1	1	9	14	12	0	-10	10	18	12	1	1	10	6	5
1	-1	8	19	23	1	-9	9	72	65	1	1	9	18	19	2	-10	10	27	17	3	1	10	20	21
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ANILINE LLANO VERMICULITE

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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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0	-10	11	19	14	4	0	11	3	4	-3	-9	12	54	44	-2	2	12	39	39	4	-6	13	33	34
2	-10	11	7	12	-3	1	11	18	19	-1	-9	12	12	10	0	2	12	4	5	-3	-5	13	5	4
-1	-9	11	24	17	-1	1	11	9	11	1	-9	12	11	10	2	2	12	39	40	-1	-5	13	14	13
-2	-8	11	8	3	1	1	11	24	21	-2	-8	12	16	12	4	2	12	10	8	1	-5	13	9	10
0	-8	11	38	32	-2	2	11	17	19	2	-8	12	22	14	-3	3	12	55	69	-2	-4	13	15	17
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-2	-6	11	35	35	3	3	11	35	48	0	-6	12	51	50	-1	5	12	6	10	1	-3	13	36	38
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3	-5	11	9	9	1	5	11	21	19	2	-4	12	15	15	-1	7	12	13	15	-1	-1	13	18	16
-2	-4	11	7	6	3	5	11	6	10	4	-4	12	10	10	1	7	12	16	17	3	-1	13	14	15
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-1	-1	11	10	13	-2	10	11	14	13	4	0	12	9	16	-3	-7	13	5	9	-2	4	13	14	18
1	-1	11	24	22	0	10	11	20	15	-3	1	12	18	20	-1	-7	13	11	11	0	4	13	29	34
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PAGE 2																								
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-1	-3	17	25	27	4	4	17	6	7	-3	-1	18	10	8	-2	6	18	22	18	0	2	19	15	16
1	-3	17	25	23	0	4	17	4	6	-1	-1	18	15	13	0	6	18	8	7	2	2	19	21	11
3	-3	17	5	5	2	4	17	6	8	1	-1	18	8	6	-1	-5	19	13	13	-1	3	19	39	46
-2	-2	17	25	23	-3	5	17	9	8	-2	0	18	22	25	-2	-4	19	11	5	1	3	19	23	32
0	-2	17	14	10	-2	6	17	9	5	0	0	18	10	15	0	-4	19	15	15	-2	4	19	11	6
2	-2	17	26	21	0	6	17	29	32	2	0	18	32	47	-1	-3	19	36	46	0	4	19	14	15
-3	-1	17	12	10	0	-6	18	20	8	-3	1	18	13	9	-3	-1	19	38	34	-1	-3	20	6	13
1	-1	17	9	16	-1	-5	18	16	12	-2	1	18	8	13	-2	-2	19	14	9	6	15			
-2	0	17	20	21	1	-5	18	8	5	-2	2	18	15	18	0	-2	19	18	16	0	-2	20	15	8
0	0	17	46	48	-2	-4	18	19	16	0	2	18	5	3	2	-2	19	16	12	1	-1	20	15	17
2	0	17	49	63	0	-4	18	23	18	-3	3	18	33	32	-3	-1	19	10	4	-2	0	20	24	31
3	1	17	9	8	2	-4	18	10	10	-1	3	18	47	59	-1	-1	19	16	14	0	0	20	16	16
-1	2	17	15	15	-3	-3	18	27	31	-2	4	18	21	16	-1	-1	19	12	11	-1	1	20	8	5
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0	2	17	11	11	-2	-2	18	10	7	2	4	18	10	11	2	0	19	20	15	-2	2	20	19	16
2	2	17	22	21	-2	-2	18	10	17	-3	5	18	11	6	-1	1	19	19	13	0	2	20	6	7
-3	3	17	46	54	0	-2	18	6	5	-1	5	18	13	14	1	1	19	12	11	-1	3	20	8	17
1	3	17	19	22																				

A.2 Triethylenediamine dihydrochloride

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [HN(CH2CH2)3NH] (2CL)																PAGE 1			
H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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4	0-15	9	8	1	5-13	4	4	11	1-11	6	5	6	0-10	7	7	6	4-10	9	9
1	1-15	6	5	0	0-12	8	7	1	2-11	4	4	8	0-10	5	5	7	4-10	5	6
3	1-15	2	2	2	0-12	9	9	2	2-11	11	11	10	0-10	8	8	8	4-10	5	5
1	2-15	5	4	6	0-12	14	14	3	2-11	6	7	12	0-10	9	9	9	4-10	3	3
0	0-14	9	9	1	1-12	8	8	4	2-11	7	7	1	1-10	19	19	1	5-10	3	3
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5	1-13	8	7	2	4-12	5	5	2	4-11	9	10	5	2-10	5	5	6	0-9	10	10
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3	2-13	5	5	5	5-12	6	6	8	4-11	8	8	9	2-10	5	5	1	1-9	22	22
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8	2-13	6	5	4	0-11	9	9	1	5-11	7	7	1	3-10	12	12	4	1-9	14	14
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [HN(CH2CH2)3NH] (2CL)																PAGE 2			
H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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7	2-9	8	9	5	7-9	7	7	5	3-8	10	11	0	8-8	6	6	3	3-7	8	8
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10	2-9	11	11	2	0-8	26	26	7	3-8	8	8	2	0-7	34	32	5	3-7	18	19
12	2-9	2	2	4	0-8	28	27	8	3-8	7	7	4	0-7	22	22	6	3-7	8	8
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1	6-9	8	9	12	2-8	6	7	8	6-8	4	4	10	2-7	10	10	4	6-7	10	10
2	6-9	9	9	1	3-8	14	14	9	6-8	5	6	14	2-7	4	3	5	6-7	5	5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [HN(CH₂CH₂)₃NH] (2CL)

PAGE 3

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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8	6	-7	5	5	5	2	-6	14	14	2	5	-6	6	6	12	0	-5	6	6	7	3	-5	6	6
10	6	-7	5	5	6	2	-6	26	27	3	5	-6	12	13	14	0	-5	11	10	8	3	-5	6	7
0	7	-7	6	6	7	2	-6	14	13	4	5	-6	6	5	0	1	-5	19	19	9	3	-5	9	9
1	7	-7	9	9	8	2	-6	7	7	5	5	-6	11	11	1	1	-5	18	18	11	3	-5	10	9
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5	7	-7	4	4	10	2	-6	7	7	7	5	-6	6	6	3	1	-5	15	15	1	4	-5	9	8
6	7	-7	3	3	12	2	-6	7	7	8	5	-6	10	10	4	1	-5	19	18	2	4	-5	22	22
7	7	-7	6	6	13	2	-6	5	5	9	5	-6	8	8	5	1	-5	46	46	3	4	-5	25	25
1	8	-7	3	3	14	2	-6	5	5	10	5	-6	3	3	6	1	-5	8	8	4	4	-5	12	13
4	8	-7	7	7	1	3	-6	3	3	11	5	-6	5	5	7	1	-5	15	15	5	4	-5	13	14
0	0	-6	78	80	2	3	-6	17	18	0	6	-6	8	8	8	1	-5	8	8	6	4	-5	8	8
2	0	-6	14	13	3	3	-6	28	29	1	6	-6	5	4	9	1	-5	14	14	7	4	-5	8	8
4	0	-6	6	6	4	3	-6	4	4	2	6	-6	10	10	11	1	-5	12	12	8	4	-5	12	13
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8	0	-6	5	5	6	3	-6	8	9	4	6	-6	10	10	13	1	-5	5	5	0	5	-5	22	22
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12	0	-6	7	6	9	3	-6	14	14	6	6	-6	6	6	1	2	-5	18	19	2	5	-5	16	17
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4	1	-6	7	7	14	3	-6	2	2	1	7	-6	11	12	6	2	-5	8	8	7	5	-5	8	8
5	1	-6	10	9	0	4	-6	24	25	2	7	-6	4	4	7	2	-5	13	13	8	5	-5	4	4
6	1	-6	14	14	1	4	-6	7	7	3	7	-6	6	6	8	2	-5	24	25	11	5	-5	5	5
7	1	-6	11	11	2	4	-6	12	12	5	7	-6	6	6	9	2	-5	6	7	13	5	-5	5	5
8	1	-6	4	4	3	4	-6	11	11	6	7	-6	4	4	10	2	-5	5	5	1	6	-5	12	12
9	1	-6	17	17	4	4	-6	5	5	7	7	-6	7	7	11	2	-5	3	3	2	6	-5	10	9
10	1	-6	7	7	5	4	-6	11	12	8	7	-6	6	6	12	2	-5	5	5	3	6	-5	9	9
11	1	-6	5	5	6	4	-6	15	15	0	8	-6	3	3	14	2	-5	9	9	4	6	-5	9	9
12	1	-6	3	3	7	4	-6	9	9	2	8	-6	8	8	0	3	-5	36	38	5	6	-5	3	4
13	1	-6	5	5	8	4	-6	11	11	4	8	-6	9	8	1	3	-5	30	31	8	6	-5	5	6
0	2	-6	48	49	9	4	-6	7	7	2	0	-5	22	21	2	3	-5	22	22	9	6	-5	6	6
1	2	-6	9	9	10	4	-6	6	6	4	0	-5	21	20	3	3	-5	16	16	10	6	-5	7	8
2	2	-6	9	10	11	4	-6	7	7	6	0	-5	8	8	4	3	-5	8	8	11	6	-5	3	3
3	2	-6	6	5	12	4	-6	6	6	8	0	-5	36	37	5	3	-5	22	23	0	7	-5	7	7

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [HN(CH₂CH₂)₃NH] (2CL)

PAGE 4

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	7	-5	6	6	2	2	-4	27	27	11	4	-4	9	9	2	8	-4	5	6	0	3	-3	21	21
2	7	-5	6	6	12	4	-4	12	12	12	4	-4	9	9	6	8	-4	7	7	1	3	-3	28	28
3	7	-5	4	4	4	2	-4	35	37	13	4	-4	5	5	8	8	-4	6	6	2	3	-3	36	36
4	7	-5	4	4	5	2	-4	11	11	14	4	-4	4	4	1	9	-4	4	4	3	3	-3	13	12
5	7	-5	4	4	6	2	-4	24	24	1	5	-4	9	8	3	9	-4	6	7	4	3	-3	26	26
6	7	-5	4	4	7	2	-4	4	4	2	5	-4	11	11	2	0	-3	30	30	5	3	-3	6	6
7	7	-5	10	11	8	2	-4	9	9	3	5	-4	19	19	4	0	-3	28	29	6	3	-3	12	12
10	7	-5	4	5	9	2	-4	15	15	4	5	-4	12	12	6	0	-3	42	41	7	3	-3	31	31
2	8	-5	4	4	10	2	-4	11	11	5	5	-4	10	10	8	0	-3	11	11	8	3	-3	6	6
3	8	-5	5	5	11	2	-4	6	6	6	5	-4	13	12	10	0	-3	27	27	13	3	-3	8	8
4	8	-5	5	6	12	2	-4	12	12	7	5	-4	7	7	12	0	-3	12	12	1	4	-3	26	26
6	8	-5	5	5	13	2	-4	4	4	8	5	-4	7	6	16	0	-3	6	5	2	4	-3	14	14
0	9	-5	4	4	14	2	-4	2	3	9	5	-4	12	13	0	1	-3	28	29	3	4	-3	14	14
1	9	-5	5	5	1	3	-4	35	36	10	5	-4	7	7	1	1	-3	58	59	4	4	-3	23	23
3	9	-5	4	4	2	3	-4	13	12	11	5	-4	6	6	2	1	-3	39	40	5	4	-3	14	14
0	0	-4	37	36	3	3	-4	35	34	0	6	-4	16	16	3	1	-3	28	28	6	4	-3	8	8
2	0	-4	52	53	4	3	-4	24	22	1	6	-4	12	12	4	1	-3	11	11	7	4	-3	10	10
4	0	-4	33	33	5	3	-4	10	10	2	6	-4	4	4	5	1	-3	4	4	8	4	-3	6	7
6	0	-4	21	21	6	3	-4	12	12	3	6	-4	7	6	6	1	-3	12	11	9	4	-3	6	6
8	0	-4	14	13	7	3	-4	12	12	4	6	-4	8	8	7	1	-3	34	35	10	4	-3	12	12
10	0	-4	15	15	8	3	-4	11	12	5	6	-4	6	5	8	1	-3	4	4	12	4	-3	2	2
12	0	-4	17	17	9	3	-4	16	16	6	6	-4	14	14	9	1	-3	15	15	13	4	-3	3	3
1	1	-4	67	70	10	3	-4	7	7	7	6	-4	12	12	10	1	-3	5	5	14	4	-3	6	6
2	1	-4	12	12	11	3	-4	5	5	8	6	-4	5	4	11	1	-3	10	10	0	5	-3	32	32
3	1	-4	45	46	15	3	-4	4	4	9	6	-4	4	5	13	1	-3	12	12	1	5	-3	17	17
4	1	-4	16	15	0	4	-4	10	10	11	6	-4	5	4	1	2	-3	27	27	2	5	-3	13	14
5	1	-4	34	35	1	4	-4	5	5	12	6	-4	5	5	2	2	-3	36	36	3	5	-3	7	7
6	1	-4	12	12	2	4	-4	8	8	1	7	-4	5	5	3	2	-3	12	12	4	5	-3	15	14
7	1	-4	15	15	3	4	-4	6	7	2	7	-4	7	8	4	2	-3	24	26	5	5	-3	13	13
8	1	-4	16	16	4	4	-4	15	15	3	7	-4	15	15	5	2	-3	22	22	6	5	-3	7	7
9	1	-4	19	19	5	4	-4	8	8	4	7	-4	6	6	6	2	-3	15	16	7	5	-3	16	16
11	1	-4	8	8	6	4	-4	19	19	5	7	-4	7	7	7	2	-3	9	9	8	5	-3	4	4
12	1	-4	4	4	7	4	-4	14	15	6	7	-4	6	6	9	2	-3	7	7	11	5	-3	6	7
15	1	-4	6	6	8	4	-4	9	9	7	7	-4	3	3	10	2	-3	23	23	1	6	-3	7	7
0	2	-4	29	30	9	4	-4	10	10	9	7	-4	6	6	11	2	-3	5	5	2	6	-3	12	12
1	2	-4	30	30	10	4	-4	7	7	0	8	-4	12	12	12	2	-3	7	7	3	6	-3	13	12

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [HN(CH ₂ CH ₂) ₃ NH][2CL]										PAGE 5									
H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	6	-3	13	12	8	1	-2	4	4	1	4	-2	10	10	2	7	-2	7	7
5	6	-3	12	12	9	1	-2	17	16	2	4	-2	20	20	3	7	-2	15	15
6	6	-3	4	4	10	1	-2	6	7	3	4	-2	12	12	4	7	-2	8	8
7	6	-3	6	6	11	1	-2	8	8	4	4	-2	20	19	5	7	-2	4	4
8	6	-3	10	10	15	1	-2	10	11	5	4	-2	9	9	6	7	-2	4	4
9	6	-3	4	4	0	2	-2	45	46	6	4	-2	21	20	8	7	-2	6	6
0	7	-3	14	15	1	2	-2	16	16	7	4	-2	16	16	9	7	-2	9	9
1	7	-3	10	10	2	2	-2	60	63	8	4	-2	6	6	11	7	-2	3	3
2	7	-3	5	5	3	2	-2	38	38	9	4	-2	13	13	0	8	-2	11	12
4	7	-3	5	5	4	2	-2	29	29	10	4	-2	9	10	1	8	-2	5	4
5	7	-3	12	11	5	2	-2	6	6	11	4	-2	6	6	3	8	-2	4	4
6	7	-3	5	5	6	2	-2	33	33	12	4	-2	12	12	4	8	-2	6	6
11	7	-3	6	6	7	2	-2	15	15	1	5	-2	15	15	6	8	-2	10	10
1	8	-3	5	5	8	2	-2	19	19	2	5	-2	14	13	8	8	-2	6	6
2	8	-3	9	10	9	2	-2	16	16	3	5	-2	22	22	3	9	-2	8	8
4	8	-3	4	4	10	2	-2	9	10	4	5	-2	17	16	2	0	-1	59	64
8	8	-3	8	8	11	2	-2	5	5	5	5	-2	9	9	4	0	-1	58	58
0	9	-3	5	5	12	2	-2	13	13	6	5	-2	5	5	6	0	-1	25	24
1	9	-3	4	4	13	2	-2	7	6	7	5	-2	10	10	8	0	-1	19	39
4	9	-3	3	3	14	2	-2	4	4	8	5	-2	10	10	10	0	-1	24	24
5	9	-3	8	8	1	3	-2	23	23	9	5	-2	12	12	12	0	-1	6	6
0	0	-2	64	72	2	3	-2	3	3	10	5	-2	9	9	14	0	-1	10	9
2	0	-2	88	97	3	3	-2	45	45	11	5	-2	5	5	0	1	-1	28	28
4	0	-2	63	67	4	3	-2	15	15	12	5	-2	6	6	1	1	-1	47	51
6	0	-2	44	43	5	3	-2	22	22	0	6	-2	24	24	2	1	-1	7	7
8	0	-2	19	18	6	3	-2	21	20	1	6	-2	16	16	3	1	-1	15	14
10	0	-2	4	4	7	3	-2	20	20	2	6	-2	6	6	4	1	-1	23	23
12	0	-2	10	10	8	3	-2	8	8	3	6	-2	4	4	5	1	-1	40	40
16	0	-2	7	7	9	3	-2	21	22	4	6	-2	8	8	6	1	-1	5	5
1	1	-2	71	76	10	3	-2	13	13	5	6	-2	10	9	7	1	-1	31	31
2	1	-2	6	6	11	3	-2	4	4	6	6	-2	14	14	8	1	-1	14	14
3	1	-2	59	62	12	3	-2	6	5	7	6	-2	10	9	9	1	-1	16	15
4	1	-2	5	5	13	3	-2	5	4	8	6	-2	5	5	10	1	-1	2	2
5	1	-2	47	47	14	3	-2	5	5	9	6	-2	6	6	11	1	-1	23	22
6	1	-2	16	15	15	3	-2	7	6	12	6	-2	7	6	13	1	-1	10	10
7	1	-2	21	21	0	4	-2	34	33	1	7	-2	7	7	14	1	-1	5	5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [HN(CH ₂ CH ₂) ₃ NH][2CL]										PAGE 6									
H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
8	4	-1	10	10	4	8	-1	8	7	1	3	0	19	18	13	5	0	3	3
10	4	-1	6	6	6	8	-1	5	5	2	3	0	19	18	0	6	0	16	15
14	4	-1	4	4	1	9	-1	4	5	3	3	0	31	30	1	6	0	5	5
0	5	-1	19	19	5	9	-1	4	4	5	3	0	13	12	2	6	0	15	14
1	5	-1	18	18	2	0	0	30	30	6	3	0	3	3	3	6	0	11	10
2	5	-1	22	21	4	0	0	11	11	7	3	0	8	8	4	6	0	19	18
3	5	-1	11	11	6	0	0	36	34	8	3	0	22	22	5	6	0	12	12
4	5	-1	16	16	8	0	0	7	6	9	3	0	32	31	6	6	0	10	9
5	5	-1	10	10	12	0	0	7	7	10	3	0	11	10	7	6	0	2	2
6	5	-1	12	12	14	0	0	8	8	11	3	0	10	10	8	6	0	6	6
7	5	-1	14	14	1	1	0	26	26	12	3	0	8	8	9	6	0	9	9
8	5	-1	5	5	2	1	0	18	18	13	3	0	12	12	10	6	0	4	4
11	5	-1	9	9	3	1	0	99	108	15	3	0	5	5	1	7	0	12	12
13	5	-1	4	4	4	1	0	11	11	0	4	0	25	26	2	7	0	9	9
1	6	-1	18	19	5	1	0	22	22	1	4	0	7	7	3	7	0	7	6
2	6	-1	9	9	6	1	0	10	10	2	4	0	4	4	5	7	0	13	12
3	6	-1	10	10	8	1	0	11	11	3	4	0	20	19	6	7	0	7	7
4	6	-1	16	16	9	1	0	21	20	4	4	0	16	16	7	7	0	8	9
5	6	-1	9	9	10	1	0	6	6	5	4	0	25	23	9	7	0	3	3
6	6	-1	5	5	11	1	0	5	5	6	4	0	31	32	0	8	0	3	3
7	6	-1	8	8	12	1	0	7	7	7	4	0	8	8	1	8	0	4	4
8	6	-1	8	8	13	1	0	10	10	8	4	0	21	20	2	8	0	15	16
10	6	-1	9	9	15	1	0	5	4	9	4	0	5	5	4	8	0	5	5
0	7	-1	4	4	0	2	0	97	102	10	4	0	7	7	5	8	0	7	7
1	7	-1	10	10	1	2	0	8	8	11	4	0	11	11	6	8	0	4	4
2	7	-1	8	8	3	2	0	4	4	12	4	0	9	8	7	8	0	4	4
3	7	-1	4	4	4	2	0	17	18	1	5	0	17	17	1	9	0	7	7
4	7	-1	5	4	5	2	0	25	23	3	5	0	18	18	2	9	0	5	4
5	7	-1	7	8	6	2	0	50	49	4	5	0	4	4	5	9	0	7	7
6	7	-1	5	5	7	2	0	25	24	5	5	0	3	3	8	1	1	15	14
7	7	-1	9	9	8	2	0	25	23	6	5	0	20	20	9	1	1	15	15
9	7	-1	5	5	9	2	0	5	5	7	5	0	16	15	7	2	1	13	12
11	7	-1	4	4	10	2	0	9	9	8	5	0	13	13	8	2	1	25	24
1	8	-1	3	3	11	2	0	8	8	9	5	0	7	7	9	2	1	2	2
2	8	-1	8	8	12	2	0	13	12	11	5	0	7	7	6	3	1	12	12
3	8	-1	5	5	15	2	0	8	7	12	5	0	5	5	7	3	1	3	3

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[illegible]

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA, VERMICULITE

PAGE 1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	-5-18	15	17		1	3-17	81	116		3	3-16	97	97		-2	2-15	38	39		-2	-4-14	14	17	
1	-5-18	19	23		3	3-17	117	124		5	3-16	75	69		0	2-15	20	23		0	-4-14	27	33	
0	-4-18	23	32		-2	4-17	17	22		0	4-16	53	49		2	2-15	17	36		2	-4-14	24	23	
-2	-2-18	27	26		4	4-17	35	36		2	4-16	21	24		4	2-15	14	11		4	-4-14	32	33	
2	-2-18	31	33		1	5-17	22	26		4	4-16	27	31		-3	3-15	126	133		-3	-3-14	105	95	
4	-2-18	18	17		2	6-17	19	34		-1	5-16	14	20		1	3-15	22	29		-1	-3-14	54	86	
-1	-1-18	26	30		-1	-7-16	24	28		1	5-16	17	16		3	3-15	59	50		5	-3-14	19	22	
4	0-18	54	71		3	-7-16	24	28		-2	6-16	61	85		5	3-15	74	65		-2	-2-14	37	38	
-1	1-18	18	28		-2	-6-16	73	72		0	6-16	124	129		-2	4-15	18	27		0	-2-14	18	19	
3	1-18	15	12		0	-6-16	118	128		2	6-16	20	25		0	4-15	25	34		2	-2-14	23	40	
-2	2-18	39	39		2	-6-16	18	34		-1	7-16	14	24		2	4-15	15	18		4	-2-14	15	22	
0	2-18	24	26		1	-5-16	26	27		0	-8-15	31	26		4	4-15	22	29		-3	-1-14	21	24	
2	2-18	25	30		-2	-4-16	18	18		2	-8-15	18	20		-3	5-15	21	26		-1	-1-14	13	24	
4	2-18	23	21		0	-4-16	19	36		3	-7-15	17	12		-1	5-15	14	22		3	-1-14	17	22	
0	4-18	27	28		2	-4-16	17	24		0	-6-15	94	95		1	5-15	26	29		5	-1-14	17	17	
2	4-18	27	23		4	-4-16	35	35		2	-6-15	59	63		0	6-15	93	101		-4	0-14	18	26	
-1	5-18	22	20		-1	-3-16	56	64		-3	-5-15	16	22		2	6-15	58	57		-2	0-14	19	32	
1	5-18	20	21		3	-3-16	99	103		1	-5-15	16	21		4	6-15	14	18		0	0-14	46	74	
2	-6-17	20	44		5	-3-16	75	71		3	-5-15	17	17		-1	7-15	27	28		2	0-14	111	106	
-1	-5-17	16	15		-2	-2-16	19	33		0	-4-15	53	55		1	7-15	13	12		4	0-14	62	59	
0	-4-17	41	46		0	-2-16	19	28		2	-4-15	20	22		3	7-15	21	17		6	0-14	47	50	
2	-4-17	24	31		2	-2-16	33	43		4	-4-15	36	38		0	8-15	38	35		-3	1-14	19	21	
4	-4-17	34	32		4	-2-16	16	19		-3	-3-15	116	120		2	8-15	14	13		-1	1-14	12	24	
3	-3-17	121	129		-3	-1-16	14	18		3	-3-15	63	55		-1	-9-14	75	63		1	1-14	13	20	
0	-2-17	36	35		-1	-1-16	18	31		5	-3-15	75	64		1	-9-14	22	25		3	1-14	16	20	
2	-2-17	14	21		3	-1-16	19	22		-2	-2-15	47	44		0	-8-14	36	34		5	1-14	24	23	
2	-2-17	40	43		5	-1-16	16	8		2	-2-15	51	50		-3	-7-14	16	19		-4	2-14	15	14	
4	-2-17	23	27		-2	0-16	92	117		4	-2-15	22	17		-1	-7-14	20	21		-2	2-14	47	47	
-3	-1-17	27	27		-3	1-16	25	22		-3	-1-15	15	23		0	-6-14	67	51		4	2-14	17	16	
1	-1-17	21	24		1	1-16	22	31		1	-1-15	20	22		4	-6-14	87	78		-3	3-14	102	101	
2	0-17	57	65		5	1-16	19	14		5	-1-15	17	17		0	-6-14	18	19		5	3-14	16	19	
-3	1-17	17	22		-2	2-16	44	47		-4	0-15	23	37		-3	-5-14	22	17		-4	4-14	35	30	
-1	1-17	23	23		0	2-16	14	22		-3	1-15	22	29		3	-5-14	18	22		0	4-14	49	45	
3	1-17	17	20		2	2-16	46	47		-1	1-15	18	28		5	-5-14	28	23		2	4-14	14	10	
2	2-17	31	39		4	2-16	22	23		3	1-15	16	10		-4	-4-14	36	36		-3	5-14	27	27	
4	2-17	15	14		-1	3-16	59	64																

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA, VERMICULITE

PAGE 2

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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3	5-14	13	15		-1	-3-13	114	108		-4	6-13	82	78		1	-5-12	19	17		1	3-12	74	84	
5	5-14	17	13		1	-3-13	109	123		-2	6-13	33	35		3	-5-12	34	30		3	3-12	149	146	
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1	-9-13	84	75		-3	1-13	22	21		0	-10-12	25	18		-5	-1-12	13	16		2	6-12	40	30	
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA, VERMICULITE

PAGE 3

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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3	-9	-11	104	90	6	-2	-11	40	35	-2	6	-11	61	63	5	-7	-10	30	32
-2	-8	-11	15	11	-5	-1	-11	17	16	0	6	-11	162	148	-2	-6	-10	18	3
0	-8	-11	42	35	-3	-1	-11	18	24	2	6	-11	56	53	0	-6	-10	156	133
2	-8	-11	22	13	-1	-1	-11	25	26	4	6	-11	65	67	2	-6	-10	182	181
4	-8	-11	38	34	3	-1	-11	30	32	-3	7	-11	25	27	4	-6	-10	35	42
-3	-7	-11	21	21	5	-1	-11	20	17	-1	7	-11	14	15	-5	-5	-10	13	12
-1	-7	-11	18	15	-4	0	-11	32	20	1	7	-11	23	17	-3	-5	-10	16	12
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5	-7	-11	26	26	4	0	-11	15	51	-2	8	-11	30	29	3	-5	-10	42	33
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3	-5	-11	37	32	4	2	-11	11	17	-2	10	-11	25	19	-4	-2	-10	20	23
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2	-4	-11	30	31	5	3	-11	157	157	-1	9	-11	71	66	6	-2	-10	20	28
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0	-2	-11	25	25	3	5	-11	25	31	-1	-7	-10	15	15	4	0	-10	15	16
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA, VERMICULITE

PAGE 4

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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0	8	-10	47	44	-3	-5	-9	11	14	-3	1	-9	17	18	5	7	-9	16	20
2	8	-10	18	15	-1	-5	-9	38	36	-1	1	-9	38	45	-4	8	-9	45	39
4	8	-10	32	32	1	-5	-9	21	19	3	1	-9	35	37	-2	8	-9	26	29
-3	9	-10	133	115	3	-5	-9	51	41	5	1	-9	21	18	0	8	-9	41	35
-1	9	-10	75	61	5	-5	-9	22	20	-6	2	-9	28	24	2	8	-9	21	21
1	9	-10	69	66	-4	-4	-9	34	39	-4	2	-9	40	34	4	8	-9	21	18
3	9	-10	22	25	-2	-4	-9	21	19	-2	2	-9	81	66	-3	9	-9	147	124
-2	10	-10	44	39	0	-4	-9	44	48	0	2	-9	32	38	-1	9	-9	182	167
0	10	-10	18	18	2	-4	-9	31	30	2	2	-9	63	55	1	9	-9	31	31
2	10	-10	39	42	4	-4	-9	34	30	4	2	-9	9	10	3	9	-9	41	41
-1	11	-10	16	11	6	-4	-9	15	10	6	2	-9	22	26	-2	10	-9	40	36
1	11	-10	20	23	-5	-3	-9	24	26	-5	3	-9	18	23	2	10	-9	21	22
-2	10	-9	34	37	-3	-3	-9	152	132	-3	3	-9	164	148	1	11	-9	33	31
0	10	-9	20	14	1	-3	-9	75	84	-1	3	-9	301	286	1	-11	-8	26	72
2	10	-9	37	37	3	-3	-9	88	79	1	3	-9	43	46	-2	-10	-8	33	34
-3	9	-9	111	106	-6	-2	-9	30	29	3	3	-9	66	72	0	-10	-8	20	15
-1	9	-9	156	156	-4	-2	-9	22	23	5	3	-9	85	79	2	-10	-8	17	15
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3	9	-9	43	50	0	-2	-9	24	30	-2	4	-9	51	47	-3	-9	-8	29	30
-4	8	-9	29	27	2	-2	-9	52	52	0	4	-9	94	71	-1	-9	-8	122	120
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4	8	-9	37	33	-3	-1	-9	25	26	-3	5	-9	24	23	-2	-8	-8	21	20
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3	7	-9	25	22	3	-1	-9	23	20	4	6	-9	82	74	4	-8	-8	20	29
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2	6	-9	194	182	2	0	-9	230	241	-3	7	-9	28	28	5	-7	-8	27	26
4	6	-9	141	117	4	0	-9	88	88	-1	7	-9	25	30	-4	-6	-8	157	159

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA. VERMICULITE

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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-5	1	-8	20	23	-3	7	-8	39	35	-5	-7	-7	15	19	-5	-1	-7	25	21	6	4	-7	21	16
-3	1	-8	26	25	-1	7	-8	14	15	-3	-7	-7	19	22	-3	-1	-7	12	13	-5	5	-7	32	28
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA. VERMICULITE

PAGE 6

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PASS																														
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3	-5	-2	38	60	0	2	-2	46	58	1	9	-2	137	143	-3	-7	-1	35	37	-1	-1	-1	18	48						
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PAGE 10																			
H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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3	1	-1	33	44	-2	8	-1	24	26	-5	-7	0	24	24	-3	-1	0	27	32
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-6	2	-1	13	15	-3	9	-1	30	35	-1	-7	0	43	40	1	-1	0	18	40
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0	2	-1	23	31	3	9	-1	181	179	5	-7	0	36	28	-6	0	0	51	48
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4	2	-1	26	27	-4	10	-1	43	37	-4	-6	0	33	40	-2	0	0	136	154
-5	3	-1	172	164	0	10	-1	23	29	-2	-6	0	133	124	2	0	0	138	152
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1	7	-1	29	35	5	-9	0	159	113	0	-2	0	20	40	0	4	0	17	23
3	7	-1	30	29	-2	-8	0	19	26	2	-2	0	19	21	2	4	0	32	37

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TEDA NYASA. VERMICULITE

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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

PAGE 1

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1	-1	-20	9	7	3	7	-20	25	26	5	5	-19	16	17	6	2	-18	9	10	4	0	-17	9	9
3	-1	-20	15	16	-2	8	-20	7	6	-2	6	-19	9	7	-5	3	-18	8	3	6	0	-17	5	6
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

PAGE 2

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-1	7	-17	40	41	-5	3	-16	8	6	3	-1	-15	31	31	-4	6	-15	6	5	-1	1	-14	71	67
1	7	-17	29	28	3	3	-16	7	9	5	-1	-15	47	48	-2	6	-15	9	8	1	1	-14	63	66
3	7	-17	23	22	-4	4	-16	23	24	-4	0	-15	5	4	0	6	-15	14	15	3	1	-14	46	46
5	7	-17	6	9	-2	4	-16	33	33	-2	0	-15	6	5	4	6	-15	16	17	5	1	-14	43	46
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2	8	-17	11	11	4	4	-16	46	49	6	0	-15	12	13	-1	7	-15	14	13	-4	2	-14	8	9
4	8	-17	27	29	6	4	-16	15	17	-5	1	-15	20	21	1	7	-15	26	26	-2	2	-14	50	47
-1	9	-17	68	68	-5	5	-16	39	37	-3	1	-15	48	48	3	7	-15	29	30	0	2	-14	30	25
1	9	-17	26	25	-3	5	-16	19	20	-1	1	-15	10	10	5	7	-15	40	42	2	2	-14	57	55
3	9	-17	23	27	-1	5	-16	12	12	1	1	-15	58	61	-4	8	-15	12	12	4	2	-14	18	18
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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5	7-14	20	20	-3	3-13	99	98	-3	3-13	114	109	0	4-12	54	55	3	-1-11	32	33					
-4	8-14	5	4	-1	3-13	71	72	3	9-13	32	29	2	4-12	47	48	5	-1-11	24	23					
-2	8-14	37	35	3	3-13	61	60	-2	10-13	18	17	4	4-12	12	12	-6	0-11	12	13					
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

PAGE 4

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

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2	2	-3	38	37	-2	8	-3	42	43	-2	2	-2	35	34	-2	8	-2	17	15	0	2	-1	44	41
4	2	-3	14	14	0	8	-3	31	31	0	2	-2	40	42	0	8	-2	33	33	2	2	-1	20	22
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3	3	-3	30	30	-1	9	-3	95	91	1	3	-2	5	4	-1	9	-2	8	4	1	3	-1	90	88
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

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5	7	-1	29	30	5	1	0	6	6	-1	7	0	45	47	-1	1	1	77	81	6	6	1	8	6
-6	8	-1	30	30	-6	2	0	10	12	1	7	0	43	45	1	1	1	29	31	-5	7	1	30	30
-4	8	-1	20	16	-4	2	0	30	29	3	7	0	5	3	3	1	1	22	23	-3	7	1	6	5
-2	8	-1	14	15	-2	2	0	19	23	5	7	0	20	21	5	1	1	30	31	-1	7	1	88	87
0	8	-1	34	33	0	2	0	18	21	-6	8	0	10	11	-6	2	1	10	10	1	7	1	23	23
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-3	-1	5	73	78	-5	5	5	7	6	-3	-1	6	45	46	6	4	6	11	11	-3	-1	7	13	9	-3	-1	7	13	9
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESEITE

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-6	0	7	7	6	1	5	7	23	26	-6	0	8	81	83	5	5	8	21	18	-4	0	9	4	3
-4	0	7	10	11	5	5	7	51	51	-4	0	8	46	46	-6	6	8	65	63	-2	0	9	4	4
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3	1	7	17	17	-3	7	7	17	18	3	1	8	37	38	-1	7	8	22	22	-6	2	9	29	30
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESEITE

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

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PAGE 14																								
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-4	0	15	5	1	-5	7	15	43	43	-2	2	16	12	7	-2	10	16	10	8	-5	5	17	15	15
2	0	15	5	5	-3	7	15	30	29	0	2	16	46	44	0	10	16	15	14	-3	5	17	12	13
-5	1	15	48	48	-1	7	15	26	24	2	2	16	29	30	2	10	16	20	21	-1	5	17	26	24
-3	1	15	30	30	1	7	15	16	11	4	2	16	9	9	-5	-1	17	10	10	1	5	17	7	3
-1	1	15	61	59	3	7	15	23	24	-3	3	16	8	9	-3	-1	17	25	25	3	5	17	27	28
1	1	15	9	9	-4	8	15	38	37	3	3	16	4	2	-1	-1	17	36	36	5	5	17	27	26
3	1	15	48	48	-2	8	15	43	41	5	3	16	7	6	1	-1	17	26	25	-4	6	17	7	6
5	1	15	20	21	0	8	15	42	38	-6	4	16	15	17	3	-1	17	31	32	-2	6	17	12	9
-6	2	15	14	12	2	8	15	24	23	-4	4	16	48	48	5	-1	17	20	20	2	6	17	15	16
-4	2	15	47	49	4	8	15	12	13	-2	4	16	12	6	-6	0	17	5	6	4	6	17	7	4
-2	2	15	76	72	-3	9	15	83	80	0	4	16	39	36	-4	0	17	9	9	-5	7	17	7	7
0	2	15	56	52	-1	9	15	14	12	2	4	16	33	34	4	0	17	6	5	-3	7	17	24	19
2	2	15	32	31	1	9	15	33	31	4	4	16	23	23	-5	1	17	10	8	-1	7	17	30	29
4	2	15	16	16	3	9	15	41	43	-5	5	16	48	46	-3	1	17	26	25	1	7	17	42	39
6	2	15	18	16	-2	10	15	42	41	-3	5	16	22	21	-1	1	17	36	36	3	7	17	27	26
-5	3	15	33	37	0	10	15	35	33	-1	5	16	40	37	1	1	17	26	25	-4	8	17	30	30
-3	3	15	93	95	-5	-1	16	52	53	1	5	16	13	15	3	1	17	31	32	-2	8	17	11	12
-1	3	15	32	31	-3	-1	16	29	29	3	5	16	21	19	5	1	17	19	18	0	8	17	6	4
1	3	15	7	8	-1	-1	16	28	26	5	5	16	38	41	-6	2	17	8	9	2	8	17	33	33
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5	3	15	12	15	3	-1	16	9	6	-2	6	16	25	25	-2	2	17	10	9	-1	9	17	24	23
-6	4	15	24	25	5	-1	16	32	35	0	6	16	56	57	0	2	17	10	5	1	9	17	69	69
-4	4	15	36	36	-6	0	16	65	68	2	6	16	32	32	2	2	17	34	37	-2	10	17	23	20
-2	4	15	72	72	-4	0	16	23	26	4	6	16	64	68	4	2	17	12	9	0	10	17	26	25
0	4	15	52	50	-2	0	16	8	11	-5	7	16	36	36	-5	3	17	35	36	-5	-1	18	12	11
2	4	15	19	16	0	0	16	67	73	-3	7	16	33	32	-3	3	17	45	48	-3	-1	18	27	29
4	4	15	40	40	2	0	16	43	43	-1	7	16	5	4	-1	3	17	53	50	-1	-1	18	10	10
-5	5	15	17	18	4	0	16	83	86	1	7	16	21	19	1	3	17	118	119	1	-1	18	13	15
-3	5	15	65	64	-5	1	16	52	54	3	7	16	16	16	3	3	17	12	13	3	-1	18	14	16
1	5	15	9	6	-3	1	16	30	30	-4	8	16	48	50	5	3	17	92	93	5	-1	18	16	16

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR EPHESITE

PAGE 15

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-6	0	10	22	25	3	5	10	12	13	-3	1	19	20	21	2	6	19	15	10	4	2	20	44	46
-4	0	10	40	42	-4	6	18	24	26	-1	1	19	7	6	4	6	19	6	1	-5	3	20	8	7
-2	0	10	117	122	-2	6	18	91	90	1	1	19	12	14	-3	7	19	20	20	-3	3	20	6	9
0	0	18	39	43	0	6	18	18	17	3	1	19	6	6	-1	7	19	10	10	-1	3	20	10	9
2	0	18	141	147	2	6	18	114	112	5	1	19	6	3	1	7	19	25	24	3	3	20	8	8
4	0	18	48	49	4	6	18	43	44	-6	2	19	22	21	3	7	19	19	17	-4	4	20	13	14
-5	1	18	12	13	-3	7	18	28	29	-4	2	19	10	8	-2	8	19	27	28	-2	4	20	18	19
-3	1	18	29	29	-1	7	18	12	11	-2	2	19	30	33	0	8	19	15	15	0	4	20	18	15
-1	1	18	9	8	1	7	18	12	8	2	2	19	23	25	2	8	19	23	23	2	4	20	11	10
3	1	18	12	16	3	7	18	22	22	4	2	19	12	12	-1	9	19	94	91	4	4	20	32	32
3	1	18	13	14	-4	8	18	17	15	-5	3	19	65	68	1	9	19	48	46	-5	5	20	35	36
5	1	18	15	17	-2	8	18	13	14	-3	3	19	19	21	-5	-1	20	27	31	-3	5	20	8	7
-6	2	18	9	9	0	8	18	24	24	-1	3	19	151	148	-3	-1	20	16	15	-1	5	20	17	20
-4	2	18	21	21	2	8	18	15	12	1	3	19	74	72	-1	-1	20	9	7	1	5	20	10	9
-2	2	18	6	6	-3	9	18	3	3	3	3	19	101	103	3	-1	20	13	13	3	5	20	10	11
0	2	18	26	27	-1	9	18	18	18	5	3	19	12	12	-4	0	20	116	117	-4	6	20	96	95
2	2	18	19	19	1	9	18	7	4	-4	4	19	5	3	-2	0	20	72	74	-2	6	20	53	53
4	2	18	14	14	0	10	18	23	21	-2	4	19	18	18	0	0	20	122	123	0	6	20	103	101
-5	3	18	10	10	-5	-1	19	7	7	0	4	19	30	28	2	0	20	49	50	2	6	20	28	29
3	3	18	4	10	-3	-1	19	19	20	2	4	19	5	4	4	0	20	12	14	-3	7	20	26	26
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2	4	18	6	6	5	-1	19	7	7	-1	5	19	8	7	3	1	20	13	13	-2	8	20	8	7
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-3	5	18	17	17	-4	0	19	9	7	3	5	19	12	15	-2	2	20	10	10	2	8	20	9	12
-1	5	18	14	13	4	0	19	6	3	-4	6	19	14	12	2	2	20	7	8	-1	9	20	15	16
1	5	18	17	17	-5	1	19	6	4															

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