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MONOGRAPH NO. 5

CRYSTAL STRUCTURES OF CLAY MINERALS
AND THEIR X-RAY IDENTIFICATION

EDITED BY
G. W. BRINDLEY

*Department of Geosciences, and Materials Research Laboratory,
The Pennsylvania State University, University Park,
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and

G. BROWN
*Soils and Plant Nutrition Department,
Rothamsted Experimental Station, Harpenden,
Hertfordshire AL5 2JQ, England*

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PREFACE

THE study of clay minerals has changed greatly since the first edition of this monograph appeared in 1951 and to a lesser extent since the second edition was published in 1961. When we, as editors of these two editions, met in 1971 to consider what might be the best form of a new edition it was apparent that the subject had grown so much that merely to update the earlier editions was not the best policy. The previous editions dealt chapter by chapter with the various mineral groups and this led to much repetition of concepts common to clay mineral structures. In this edition we have separated to a considerable extent the two functions that the X-ray monographs have served—to provide an authoritative account of the fundamentals of the structures of clay minerals and also to be a laboratory handbook. The first four chapters deal with the former aspect while the remainder of the book covers the practical aspects of the X-ray identification of clays. The change in format has allowed more comprehensive treatment of the crystal structures of layer silicates on which our understanding of clay mineral structures is largely based, and is indicated by the new title “Crystal Structures of Clay Minerals and their X-ray Identification”.

In the years 1930–1950 clay mineral identification involved mainly a combination of X-ray powder diffraction and chemical analysis, with some assistance from other techniques, notably differential thermal analysis. In the period 1950–1970 additional procedures have emerged including infrared analysis, electron optical methods and a variety of thermal methods. These procedures are now treated in other monographs sponsored by the Mineralogical Society and in many other publications. Despite the availability of other techniques, X-ray diffraction remains a basic tool for studying minerals and we hope that this monograph will continue to serve, as did the previous editions, both those concerned with the more academic aspects of clay mineralogy and also those, such as geologists, civil engineers and soil scientists for whom identification and quantitative estimation of the minerals in natural clayey materials is a practical requirement.

G. W. BRINDLEY
G. BROWN

April 1980

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The Editors thank all authors for their cooperation and forbearance when the whole work could not be published as quickly as they themselves finished their chapters. We regret that a final chapter on the geology of clays could not be completed in time for this publication; however it might well have added considerably to the size of the book. We are grateful to the Mineralogical Society for sponsoring its production, to the printers for the excellence of their work, and particularly to our secretarial assistants for their patient labour in the cause of science.

G. Brown is grateful to Dr L. Fowden, Director of Rothamsted Experimental Station, for permission to undertake the duties of co-editor. He also acknowledges the help of his colleagues, especially Dr J. H. Rayner and Miss L. Parry, Soils and Plant Nutrition Department, Rothamsted Experimental Station, the former for frequent consultation and advice, the latter for preparing the tables from which the Appendix was reproduced directly from the computer output.

Dr A. R. Woolley, as Publications Officer of the Mineralogical Society for the period 1974–1979, and Mr J. F. Pettitt of Spottiswoode Ballantyne, greatly assisted in the production of the book.

The considerable computer costs involved in preparing Chapter 4 were provided by the Kiewit Computational Center at Dartmouth College. Dr E. J. W. Whittaker supplied Figure 2.7; Dr A. Plançon, Figure 2.9; and Dr A. Plançon and Dr C. Tchoubar, Figure 2.10. The Joint Committee on Powder Diffraction Standards gave permission to quote diffraction patterns from the Powder Data File.

The Mineralogical Society also acknowledges the cooperation of authors and publishers for permission to reproduce figures. These include the Mineralogical Society of America for Figures 1.28, 1.31, 2.14, 2.15, 2.20, 3.9, 3.10 and 3.11; the U.S. Government Printing Office for Figures 1.16, 1.20, 1.21 and 1.25; the Clay Minerals Society for Figure 1.32; the Mineralogical Journal and Dr H. Takeda for Figure 1.22; Professor J. Konta for Figure 2.8; Professor P. G. Owston and Oxford University Press for Figure 3.1; Dr R. Glaeser and Académie des Sciences for Figures 3.3 and 3.4; Professor G. Lagaly for Figures 3.12, 3.13, 3.14, 3.15 and 3.16; Consejo Superior de Investigaciones Científicas for Figures 3.17 and 3.18; and the New Zealand Journal of Science for Figure 3.20.

LIST OF CONTRIBUTORS

- S. W. BAILEY, Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.
- G. W. BRINDLEY, Department of Geosciences, and Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.
- G. BROWN, Soils and Plant Nutrition Department, Rothamsted Experimental Station, Harpenden, Hertfordshire AL5 2JQ, England.
- D. M. C. MACEWAN, 52 Ormonde Road, Hythe, Kent CT21 6DW, England.
- R. C. REYNOLDS, Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755, U.S.A.
- M. J. WILSON, Department of Pedology, Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen AB9 2QJ, Scotland.

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S. W. BAILEY

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1. INTRODUCTION

THE hydrous layer silicates commonly known as clay minerals are part of the larger family of phyllosilicates. The layer silicates considered here contain continuous two-dimensional *tetrahedral sheets* of composition T_2O_3 (T = tetrahedral cation, normally Si, Al, or Fe^{3+}), in which individual tetrahedra are linked with neighboring tetrahedra by sharing three corners each (the basal oxygens) to form an hexagonal mesh pattern (Fig. 1.1*a*). The fourth tetrahedral corner (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 (Fig. 1.1*b*). The common plane of junction between the tetrahedral and octahedral sheets consists of the shared apical oxygens plus unshared OH groups that lie at the center of each tetrahedral six-fold ring at the same z -level as the apical oxygens. F may substitute for OH in some species. The octahedral cations normally are Mg, Al, Fe^{2+} , and Fe^{3+} , but other medium-sized cations such as Li, Ti, V, Cr, Mn, Co, Ni, Cu, and Zn also occur in some species. The smallest structural unit contains three octahedra. If all three octahedra are occupied, *i.e.* have octahedral cations at their centers, 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 assemblage formed by linking one tetrahedral sheet with one octahedral sheet is known as a *1:1 layer*. In such layers the uppermost, unshared plane of anions in the octahedral sheet consists entirely of OH groups. A *2:1 layer* links two tetrahedral sheets with one octahedral sheet. In order 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 (Fig. 1.1*c*). Both octahedral anion planes then are of the same O,OH composition. If the 1:1 or 2:1 layers are not electrostatically neutral, the excess layer charge is neutralized by various *interlayer* materials, including individual cations, hydrated cations, and hydroxide octahedral groups and sheets. The

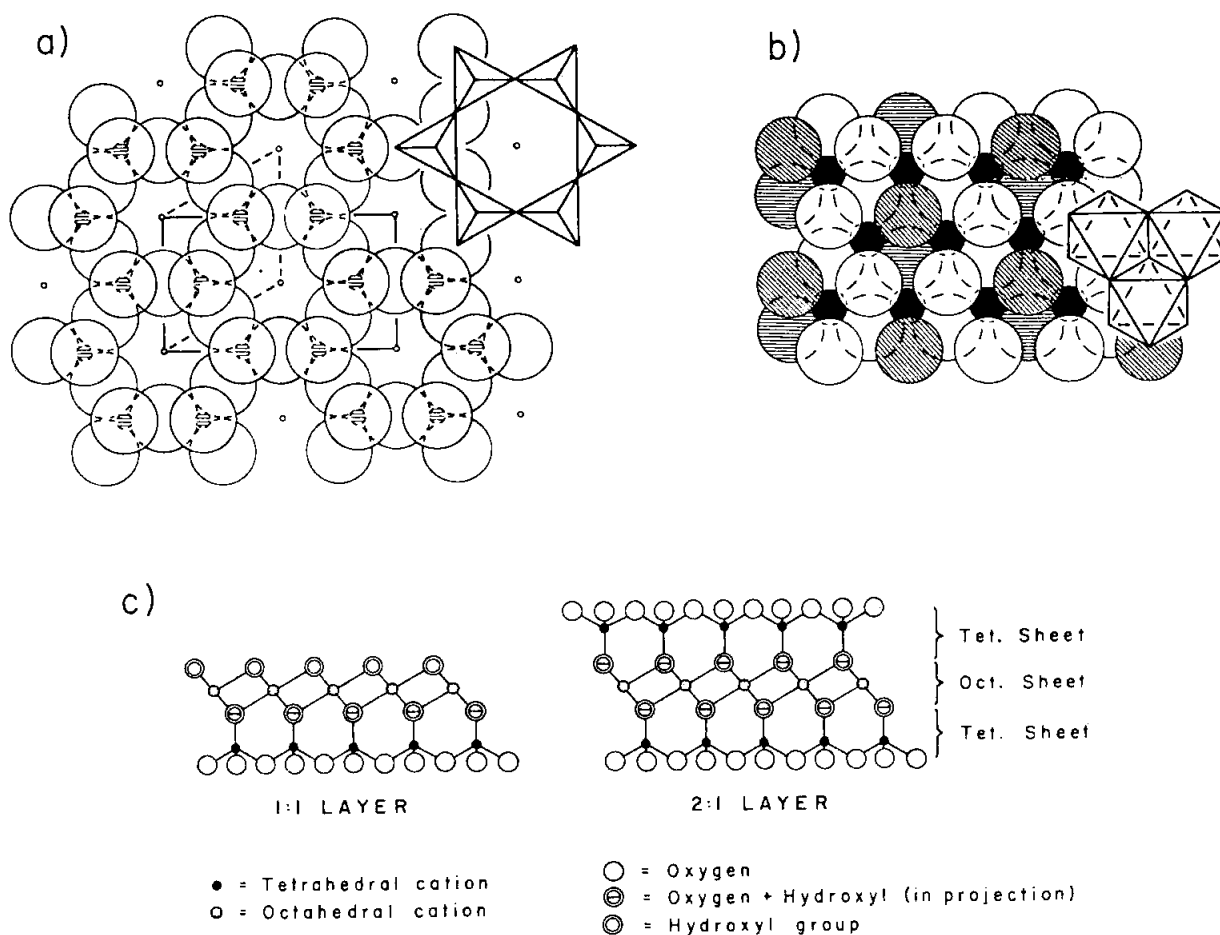


FIG. 1.1. (a) Plan view of ideally hexagonal tetrahedral sheet. Alternative hexagonal *P*- (dashed) and orthogonal *C*-cells (full lines) are shown connecting lattice points. (b) Octahedral sheet with inner hydroxyl groups of 2:1 layer shown as shaded. (c) Junction of sheets to form 1:1 and 2:1 layers.

total assemblage of a layer plus interlayer is referred to as a *structure unit*. It contains one or more chemical formula units (*Z*). It should be noted that the terms plane, sheet, layer, and unit structure as used here have precise meanings and are not interchangeable. They refer to increasingly thicker parts of the layered arrangement.

In order to fit together in a common layer the tetrahedral and octahedral sheets must have similar lateral dimensions. Sheets that fit together only with difficulty tend to have strained planes of junction that influence greatly the resultant crystal size, morphology, and structure. An idea of the relative degree of fit between the tetrahedral and octahedral sheets can be obtained by estimating the lateral dimensions such sheets would have in the free state. Free octahedral sheets occur in the structures of some of the hydroxide minerals, which thus can be used as analogues to estimate the ideal lateral dimensions for the octahedral sheets in layer silicates of similar composition. Thus, gibbsite and bayerite have $b = 8.64 \text{ \AA}$ and $8.67 \text{ \AA}$, respectively, for the dioctahedral $\text{Al}(\text{OH})_3$ composition and brucite has $b = 9.36 \text{ \AA}$ for the trioctahedral $\text{Mg}(\text{OH})_2$ composition. Although tetrahedral sheets do not exist in an unconstrained state in minerals, it is possible to estimate their ideal lateral dimensions in the free state by assuming an average T—O bond length and ideal tetrahedral angles [$a = (4\sqrt{6}/3)(\text{T—O})$; $b = a\sqrt{3} = (4\sqrt{2})(\text{T—O})$]. Thus, for hexagonal geometry and $\text{Si—O} = 1.618 \pm 0.01 \text{ \AA}$ the resulting lateral dimensions are $a = 5.28 \pm 0.03 \text{ \AA}$ and $b = 9.15 \pm 0.06 \text{ \AA}$. Substitution of the larger Al for Si in the tetrahedral sites increases these values. Assuming $\text{Al}^{\text{IV}}\text{—O} = 1.748 \pm 0.01 \text{ \AA}$, then $b = 9.89 \pm 0.06 \text{ \AA}$ or $b(\text{Si}_{1-x}\text{Al}_x) \cong 9.15 \text{ \AA} + 0.74x$. This relationship should be considered as only approximate, not

only because of the uncertainties in the assumed bond lengths but also because the tetrahedral angles are known to vary somewhat from structure to structure.

Despite these uncertainties it is evident that a tetrahedral sheet containing only Si has an ideal lateral b dimension that is intermediate between those of the ideal octahedral sheets containing only Mg or only Al. The magnitude of the misfit is approximately 3–5% for these compositions. Structural adjustments of some type are necessary in order to eliminate this misfit and to articulate the tetrahedral and octahedral sheets into a layer with common planes of junction.

In the great majority of 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. Zvyagin (1957) and Radoslovich (1961) have 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 expression, which is only an approximation 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 13.4% for a maximum possible rotation of 30° that would bring basal oxygens into contact at the center of each hexagonal ring. The effective maximum rotation undoubtedly is less than 30° due to increasing repulsion between tetrahedral cations as they approach more closely. Because adjacent tetrahedra rotate in opposite directions the symmetry of the network changes from hexagonal to approximately ditrigonal (e.g. compare Fig. 1.1a with Fig. 1.23). Because the sheets are semi-elastic some adjustment can be accomplished also by thickening the tetrahedral sheet and thinning the octahedral sheet, thereby decreasing and increasing, respectively, their lateral dimensions. These adjustments can be expressed either in terms of the measured sheet thicknesses or of the τ_{tet} and ψ_{oct} angles. An ideal tetrahedron has an angle $\tau = (\text{O}_{\text{apical}}-\text{T}-\text{O}_{\text{basal}}) = 109^\circ 28'$, 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 will be calculated here as $\cos \psi = \text{oct. thickness}/2(\overline{\text{M}-\text{O}, \text{OH}})$, where $\overline{\text{M}-\text{O}, \text{OH}}$ is the mean of all octahedral cation–anion distances, including vacancies. The ideal ψ angle is $54^\circ 44'$, which increases with octahedral thinning.

It is more difficult to stretch the lateral dimensions of a tetrahedral sheet in order to fit with a larger octahedral sheet, and the structural adjustments may be more drastic as a result. Mechanisms observed in layer silicates include adjustment of sheet thicknesses, tetrahedral tilting that may lead to curling in the case of 1:1 layers, and inversion of tetrahedral apical directions in some periodic pattern. Examples are restricted to species with little or no tetrahedral substitution and with trioctahedral sheets populated with relatively large cations of the size of Mg, Ni, Co, Zn, Fe^{2+} , and Mn^{2+} .

The individual sheets making up a layer have hexagonal symmetry when undistorted (Figs. 1.1a,b). In an actual crystal, however, the resultant three-dimensional symmetry may be lowered either because of the geometry of stacking of successive layers along the Z direction or because of layer distortions due to tetrahedral–octahedral sheet misfit, cation ordering, or ionic interactions. If the resultant symmetry remains hexagonal or trigonal, the smallest unit cell is primitive and has an 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 $a = b \cong 5.1\text{--}5.4 \text{ \AA}$ and $c \cong n \times \text{unit structure thickness}$, where n = number of 1:1 or 2:1 layers in the unit cell. A 1-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, alternatively, can 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 (Fig. 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 of the greater ease of indexing X-ray powder patterns on an orthogonal rather than hexagonal cell, the larger C-cell often is used for indexing until the true symmetry of the mineral is known. C-cells normally 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.

Layer silicate minerals can be classified conveniently on the basis of layer type (1:1 or 2:1), layer charge, and type of interlayer into eight major groups. Further subdivision into sub-groups and species is made on the basis of the octahedral sheet type (dioctahedral or trioctahedral), chemical composition, and the geometry of superposition of individual layers and interlayers. Such a classification scheme is given in Table 1.1. The structures of these major groups are shown diagrammatically in Fig. 1.2. The names used for groups, sub-groups, and species are those approved by the AIPEA Nomenclature Committee or by the IMA Commission on New Minerals and Mineral Names.

The structures of the major groups of layer silicates and of selected species are discussed in more detail in the following sections of this chapter, although the structures of smectites and of certain species with irregular or disordered structures are treated separately in other chapters. Emphasis in this chapter will be placed on the regular structures and on those structural results that include some degree of refinement of the atomic positions. Although in many cases these structural studies necessarily have been made on macroscopic crystals, the results are believed to hold true for clay-sized particles of the same species. In order to give a complete crystal chemical account, some species will be described that either occur rarely in clays or, if they do occur, are difficult to identify precisely. DTA curves, IR spectra, chemical analyses, and electron micrographic data will not be presented here because these are available in other monographs. Identification procedures will be discussed in Chapter 5 but X-ray powder patterns for well crystallized

TABLE 1.1. Classification of phyllosilicates related to clay minerals

Layer type	Group (x = charge per formula unit)†	Sub-group	Species*
1:1	Serpentine-kaolin ($x \sim 0$)	Serpentines Kaolins	Chrysotile, antigorite, lizardite, amesite Kaolinite, dickite, nacrite
2:1	Talc-pyrophyllite ($x \sim 0$)	Talcs Pyrophyllites	Talc, willemseite Pyrophyllite
	Smectite ($x \sim 0.2-0.6$)	Saponites Montmorillonites	Saponite, hectorite, sauconite Montmorillonite, beidellite, nontronite
	Vermiculite ($x \sim 0.6-0.9$)	Trioctahedral vermiculites Dioctahedral vermiculites	Trioctahedral vermiculite Dioctahedral vermiculite
	Mica ($x \sim 1.0$)	Trioctahedral micas Dioctahedral micas	Phlogopite, biotite, lepidolite Muscovite, paragonite
	Brittle mica ($x \sim 2.0$)	Trioctahedral brittle micas Dioctahedral brittle micas	Clintonite, anandite Margarite
	Chlorite (x variable)	Trioctahedral chlorites Dioctahedral chlorites Di, trioctahedral chlorites	Clinochlore, chamosite, nimite Donbassite Cookeite, sudoite
2:1 inverted ribbons	Sepiolite-palygorskite (x variable)	Sepiolites Palygorskites	Sepiolite, loughlinitite Palygorskite

* Only a few examples are given.

† x refers to an $\text{O}_{10}(\text{OH})_2$ formula unit for smectite, vermiculite, mica and brittle mica.

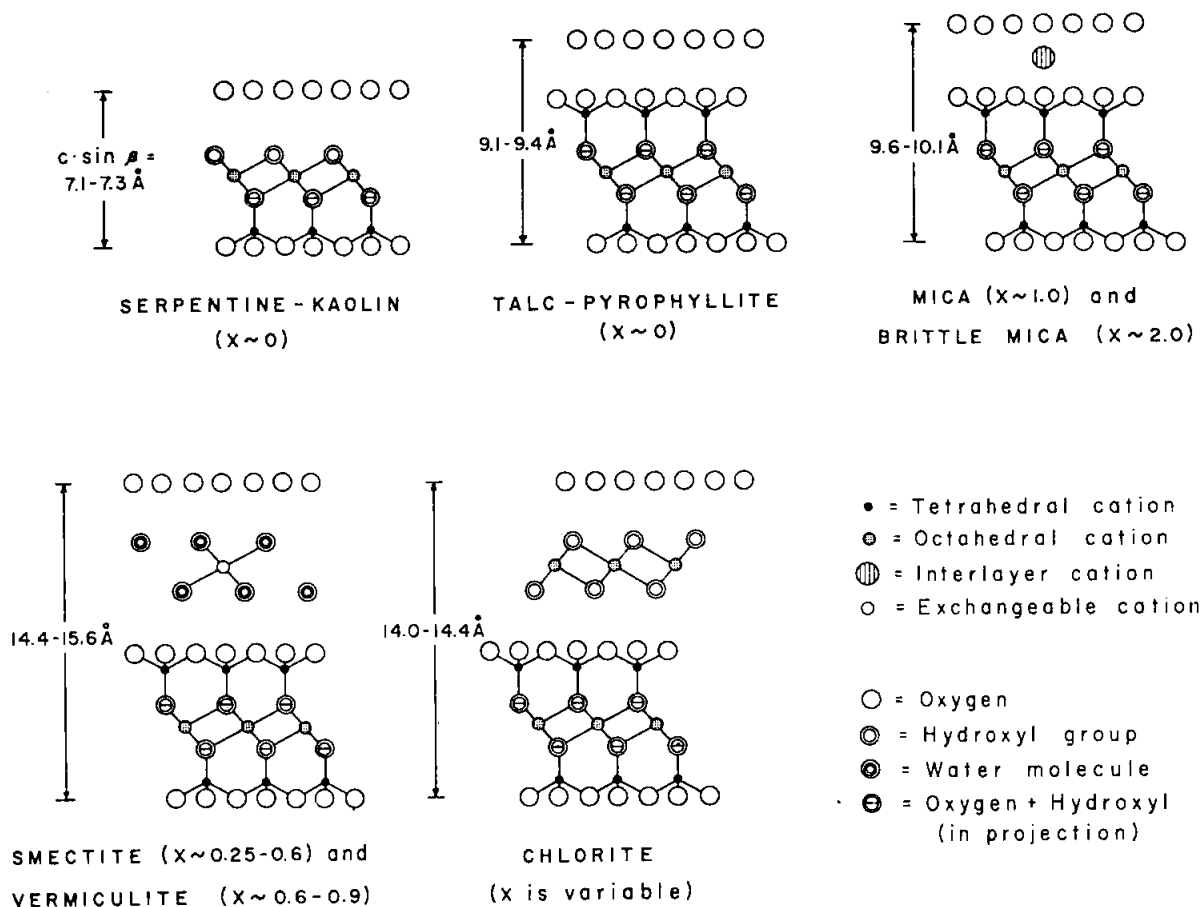


FIG. 1.2. [010] view of structures of major clay mineral groups. See Figs. 1.34, 1.35 for sepiolite-palygorskite. Layer charge per formula unit = X .

species will be tabulated in this chapter and a few representative X-ray photographs of polytypes will be illustrated also.

2. SERPENTINE-KAOLIN GROUP

2.1 General

All regular structures of the 1:1 layer type will be included in this category. A single name for the group is desirable, but no name proposed to date has proved universally acceptable. The suggested names *septechlorite* and *kandite* have not received approval from the AIPEA Nomenclature Committee and should be avoided.

In all planar 1:1 layer structures studied in detail, the positions of adjacent layers are governed by the requirement for the pairing of each oxygen on the basal tetrahedral surface of one layer with an OH group on the upper octahedral surface of the layer below (Fig. 1.3) (Hendricks, 1939b). This O—OH pairing results in the formation of long and relatively weak hydrogen bonds, approximately $3.0 \text{ \AA}$ between the anion centers, that help bond the layers together. Curling of the layers into tubes, as in chrysotile, prevents ideal hydrogen bonds of this sort (Wicks and Whittaker, 1975). And energy calculations for some 1:1 species suggest that not all O—OH pairs participate in the interlayer bonding even for planar structures (Giese, 1973a, Giese and Datta, 1973). The interpretation of infrared absorption spectra relating to hydrogen bonding in kaolinite is controversial. Cruz, Jacobs, and Fripiat (1973) consider three of the observed spectra to be due to coupling between three nearly equivalent OH groups and calculate that the bonding between layers is primarily electrostatic in nature, due to attraction

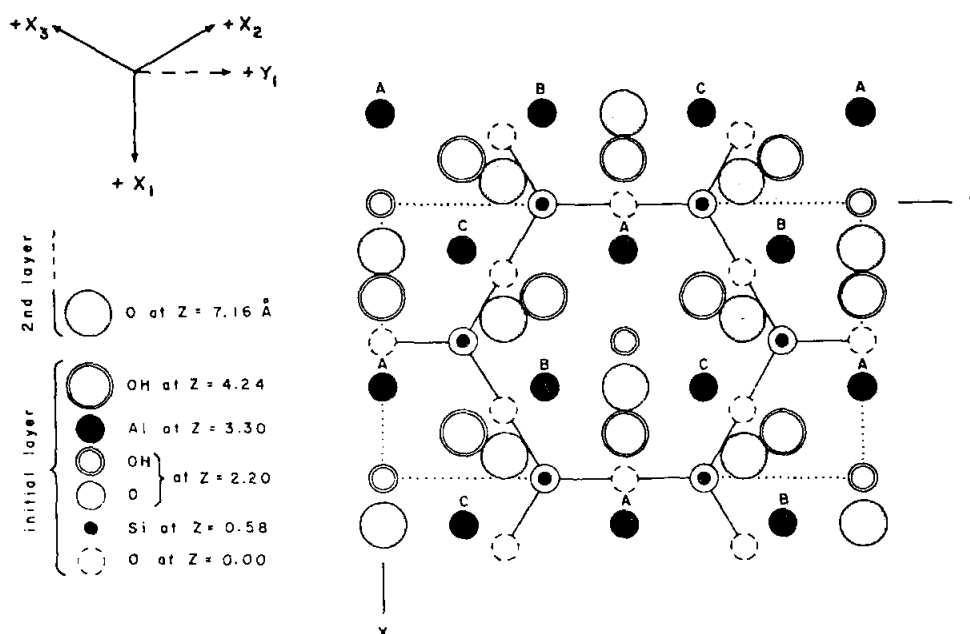


FIG. 1.3. Pairing of basal tetrahedral oxygens (stippled) of upper 1:1 layer with surface octahedral hydroxyls (large double circles) of layer below (modified from Bailey, 1969).

between the negative and positive charges of the oxygen and hydroxyl oxygen of adjacent layers. On the other hand, Wieckowski and Wiewióra (1976) have used a model of bent hydrogen bonds to calculate that the cohesion between layers is due mainly to hydrogen bonding with a smaller contribution from van der Waals forces. Additional ionic bonds between layer surfaces may exist as a result of tetrahedral and octahedral substitutions within each layer. Rouxhet *et al.* (1977), on the basis of infrared study of synthetic kaolinites with differing degrees of deuteration, attribute two of the observed OH stretching bands to coupled vibrations between two surface OH groups in similar structural environments with O—H axes nearly normal to (001) and a third band to a surface OH group oriented with its O—H axis close to the plane of (001). These conclusions are in accord with O—H orientations calculated by Giese and Datta (1973) from electrostatic considerations.

2.2 Derivation of standard trioctahedral structures

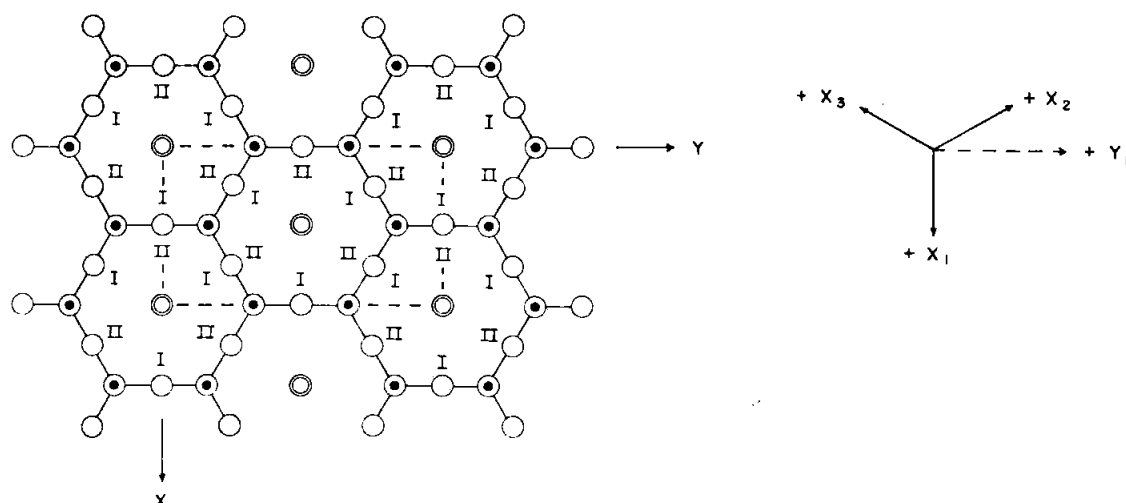
Within each 1:1 layer, octahedral cations can occupy either set I or set II positions above the tetrahedral sheet, as defined in Fig. 1.4a relative to fixed hexagonal axes. The uppermost plane of hydroxyls then must fit above the occupied I or II sites to form octahedra that slant in opposite directions for the two cases (Fig. 1.4b). It is evident that set I transforms to set II by rotation of the layer by $\pm 60^\circ$ or 180° . The important part in what follows is not which set is occupied but whether the same set of three octahedral positions is occupied in each successive layer or whether there is an alternation between the I and II sets in successive layers. The latter is equivalent to relative layer rotations.

Bailey (1963, 1969) has shown that for planar structures interlayer hydrogen bonds can be formed from the following three relative positions of adjacent 1:1 layers.

(1) No shift of the second layer. The hexagonal rings in the tetrahedral sheets of adjacent layers are exactly superimposed (aside from possible rotations of $\pm 60^\circ$ or 180°).

(2) Shift of the second layer by $a/3$ along the fixed axes X_1 , X_2 , or X_3 of the initial layer, with or without rotation of the second layer. Because of the different slant of the I and II octahedra,

a)



b)

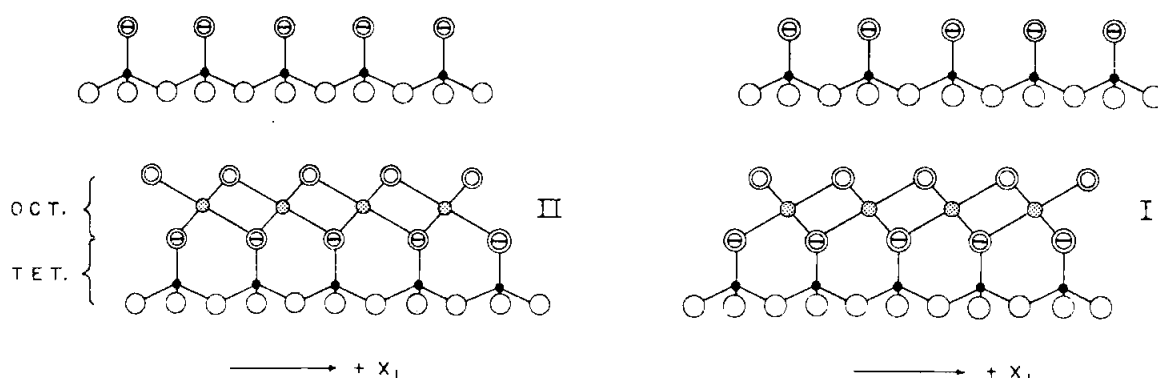


FIG. 1.4. (a) Definition of I and II sets of octahedral cation positions above a tetrahedral net for a 1:1 layer, relative to a fixed set of hexagonal axes. (b) Octahedral sheets slant in opposite directions relative to a fixed X_1 axis due to occupancy of I or II octahedral cation sets (from Bailey, 1969).

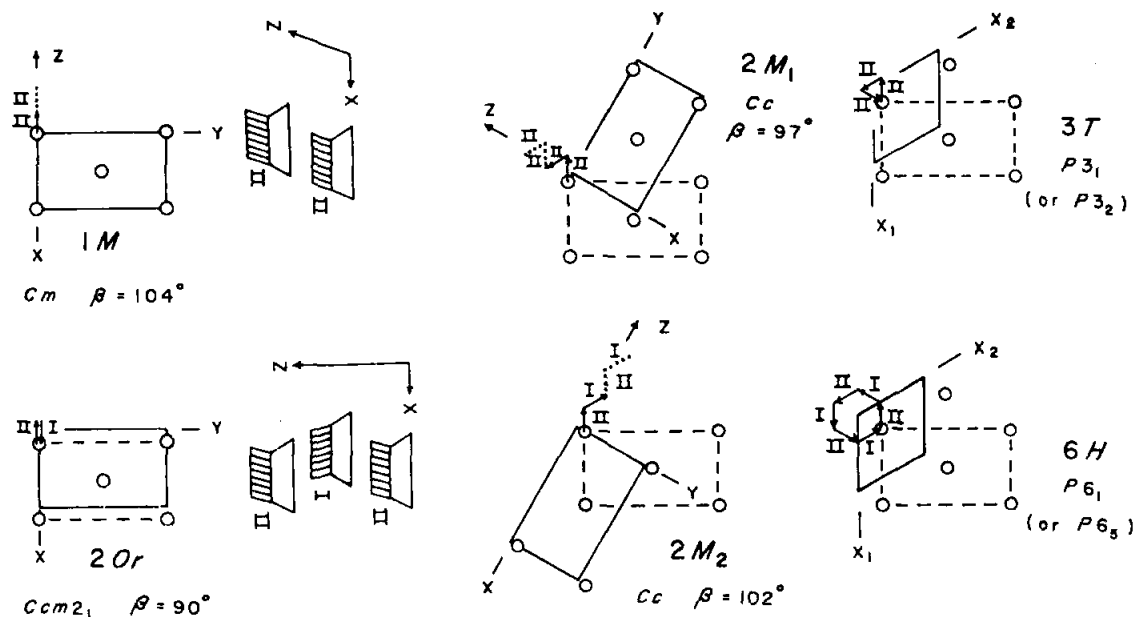
the interlayer shift must be in the negative direction if the II octahedral set is occupied in the initial layer, as shown in Fig. 1.3, or in the positive direction if the I octahedral set is occupied.

(3) Shift of the second layer by $\pm b/3$ along any of the three hexagonal Y axes of the initial layer (normal to the three X axes), with or without rotation of the second layer. If the layers are assumed to be undistorted, shifts along the three Y axes give identical results so that the particular Y axis used is immaterial. Interlayer shifts along the positive or negative directions of Y are both possible, regardless of the octahedral set occupied in the initial layer.

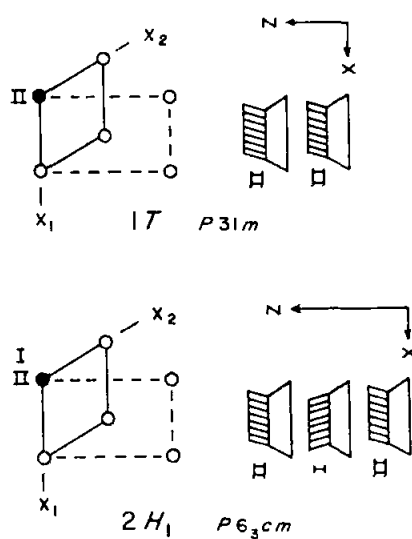
Variability both in the positioning of adjacent layers and in the occupancy of octahedral sets within each layer (equivalent to layer rotations) lead to different permissible stacking sequences of layers. Structures resulting from different stacking sequences of layers are termed *polytypes*, provided the layer compositions are similar. If the three types of relative layer positioning listed above are not intermixed in the same crystal, Bailey (1969) has shown that there are 12 different trioctahedral 1:1 type polytypes, plus four enantiomorphs, with periodicities between one and six layers.

The stacking sequences for the 12 ideal trioctahedral polytypes are shown diagrammatically in Fig. 1.5. In all cases it is assumed that the II set of octahedral cation positions is occupied in the initial layer. The interlayer shifts are shown as vectors directed from the center of an hexagonal ring in the tetrahedral sheet of a lower layer to the center of an hexagonal ring in the layer above,

a) INTERLAYER SHIFT ALONG X-AXIS



b) NO SHIFT



c) INTERLAYER SHIFT ALONG Y-AXIS

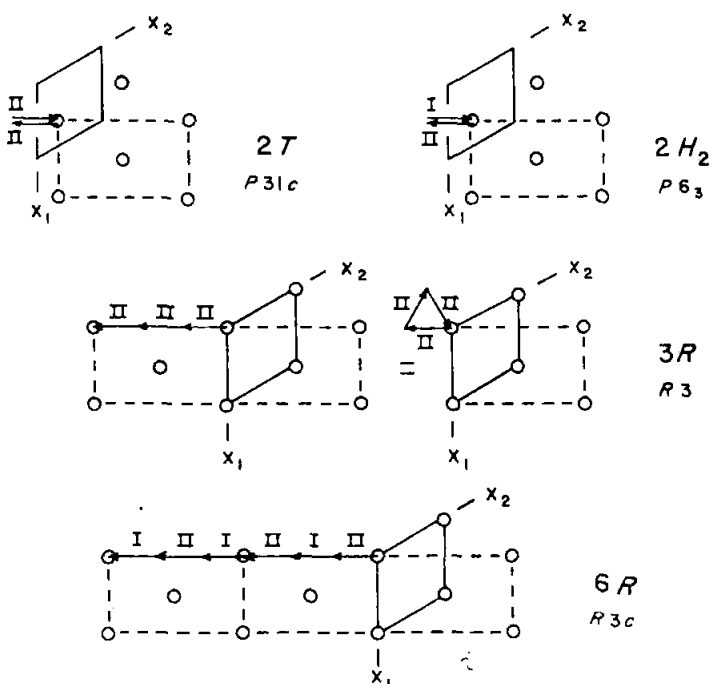


FIG. 1.5. Derivation of 12 ideal 1:1 polytypes (modified from Bailey, 1969). The orientation of Fig. 1.3 is assumed for the first layer of each polytype with the II set of octahedral cation positions occupied. The base of the resultant unit cell (solid lines) may or may not coincide with the fixed cell (dashed lines) used for the first layer. The origin of each resultant unit cell has been placed as close to the center (circles) of an hexagonal ring in the first layer as the symmetry permits. Two equivalent interlayer sequences are illustrated for the 3R polytype.

and having projected lengths on (001) of $a/3$ in Fig. 1.5a, zero in Fig. 1.5b, and $b/3$ in Fig. 1.5c. The interlayer stacking angle will be defined as the angle between two adjacent vectors, as measured in a counterclockwise direction in projection on (001). The six possible interlayer

stacking angles are 0° , 60° , 120° , 180° , 240° , and 300° . Because of the plane of symmetry that is parallel to the interlayer shift vector, angles 60° and 300° are equivalent, as are angles 120° and 240° .

Each ideal polytype in Fig. 1.5 is designated by a structural symbol consisting of a number to indicate the number of layers in the repeating unit along Z and letters to indicate the resulting lattice symmetry (M = monoclinic, T = trigonal, H = hexagonal, R = rhombohedral, Or = orthorhombic, and Tc = triclinic). Subscripts 1 and 2 are used to differentiate structures that have the same periodicity and symmetry.

Other derivations for planar 1:1 type polytypes have been given by Newnham (1961), Zvyagin (1962, 1967), Steadman (1964), and Dornberger-Schiff and Āurovič (1975a,b). The original references should be consulted for details. Wicks and Whittaker (1975) give a notation for cylindrical structures.

2.3 Identification of planar structures

For identification purposes the 12 planar polytypes can be divided into four groups ($A-D$), for which the strongest reflections ($k = 3n$ for monoclinic- and orthorhombic-shaped C -cells or hhl and equivalents for hexagonal-shaped P -cells) have identical calculated intensities within each group but quite different values between groups (Table 1.2). Thus, classification of a good X-ray diffraction pattern of an unknown planar 1:1 layer silicate into one of four groups can be accomplished by means of the most intense reflections. This immediately defines the direction of interlayer shift and the occupancy pattern of octahedral cation sets in the structure. Further differentiation between the three structures within each group must be made on the basis of the weaker reflections, some of which are sensitive to the precise layer stacking sequence. If these reflections are very weak or are streaked out due to stacking disorder, the three structures within each group are indistinguishable but the four groups are still evident from the stronger non-streaked reflections. Bailey (1969) gives calculated powder patterns for all 12 ideal polytypes.

Examination of natural specimens has shown that examples of all four major groups exist in

TABLE 1.2. Structure amplitudes and intensities for strong reflections of four groups of standard 1:1 polytypes

Group A 1M-2M ₁ -3T			Group B 2Or-2M ₂ -6H			Group C 1T-2T-3R		Group D 2H ₁ -2H ₂ -6R	
d (Å)	$ F_c $	I	d (Å)	$ F_c $	I	$ F_c $	I	$ F_c $	I
2.649	25	26	2.670	11	6	12	5	8	3
2.590	17	12	2.624	17	27	0	0	11	12
2.387	54	100	2.499	24	51	18 + 51	100	34	98
2.262	13	6	2.326	32	78	0	0	22	35
2.007	33	25	2.134	17	18	19 + 39	45	17	17
1.886	18	6	1.945	15	10	0	0	27	35
1.665	47	32	1.771	25	24	9 + 45	32	18	12
1.568	31	14	1.615	33	34	0	0	25	20
1.396	16	3	1.478	8	2	44 + 30	28	29	21
1.322	44	16	1.358	28	16	0	0	20	8
1.191	14	32	1.254	21	7	32 + 10	8	19	6
1.134	6	7	1.162	3	<1	0	0	12	2

Calculations made with $B = 1.2$, 0.8 , and 2.0 for Mg, Si, and O, OH respectively, and normalized to one formula unit. Indices are of type $20l$ for monoclinic and orthorhombic C -cells (except $2M_2$) and $11l$ for hexagonal P -cells. In group C, $|F_c(11l)| \neq |F_c(11\bar{l})|$ (modified from Bailey, 1969).

TABLE 1.3. Natural examples of 1:1 structures

	Trioctahedral		Diocahedral
lizardite	1T, 2H ₁ , 1M-3T (+2Or rare)	kaolinite	1Tc = [1M _{ord}]
amesite	2H ₂ (+2H ₁ , 6R rare)	dickite	2M = [1M _{ord}]
kellyite	2H ₂	nacrite	2M = [6R _{ord}]
berthierine	1T, 1M-3T		
brindleyite	group C + group A		
caryopillite	group A + group C		
cronstedtite	1T, 3T, 2H ₁ , 2H ₂ , 2T, 1M, 2M ₁		
greenalite	group C + group A		
baumite	group C		
garnierite	groups C & D		
nepouite	2Or		

nature, including at least nine of the 12 individual structures. Correlations of natural species with the ideal structures are listed in Table 1.3. There is a strong tendency for certain compositions to prefer specific stacking sequences so that most natural specimens are neither polytypic nor polymorphic with one another. They may be described instead as *polytypoids*. There is moderately good agreement of the relative abundances in nature of examples of the four major groups of structures with their relative structural stabilities ($C > D > A > B$) as estimated qualitatively by Bailey (1969) from the relative amounts of attraction and repulsion between the ions.

Although the ideal structures were derived assuming trioctahedral compositions, the dioctahedral kaolin minerals adopt similar stacking sequences. In each of the three kaolins, however, the ordered location of the vacant octahedral site in successive layers is such that it changes the resultant space group from that of the ideal structure and changes the layer periodicity in two of the three examples (Bailey, 1963).

2.4 Serpentine minerals

2.4.1 General

The crystal morphologies and structures of the serpentines range from planar (lizardite, amesite, and several unnamed aluminian species) to alternating waves (antigorite) to cylindrical rolls (chrysotile). These differences have been attributed (Bates, 1951, 1959; Roy and Roy, 1954) to the degree of fit between the lateral dimensions of the tetrahedral and octahedral sheets.

In chrysotile and antigorite there is little or no tetrahedral substitution so that the lateral dimensions of the Si-rich tetrahedral sheet are smaller than those of the Mg-rich octahedral sheet. Articulation is accomplished in the case of chrysotile by tetrahedral tilting in which the 1:1 layers curl into cylindrical rolls with the larger octahedral sheet on the outer convex size. End-on electron micrograph views (Yada, 1967, 1971) of the fibers in the chrysotile form of asbestos show beyond dispute that the fibers actually are curled layers in the form of concentric cylinders, spirals and multi-spirals, and cone-in-cone structures. Pundsack (1956) pointed out that the density of chrysotile is too high for a model of closely packed hollow cylindrical tubes. Electron micrographs show that many tubes indeed are hollow, but that others are filled in part by extraneous material. Electron diffraction of this material, after removal by ultrasonic treatment, shows it to be amorphous (Martinez and Comer, 1964).

Yada (1971) has shown that the diameters of individual fibers are variable from sample to sample, but that the most frequently occurring values of the outer diameters are in the range 220–270 Å and of the inner diameters 70–80 Å. Fibrils thicker than 350 Å seem to have formed

by a discontinuous-step growth process due to a change in growth conditions. Jagodzinski and Kunze (1954) have postulated two growth mechanisms involving radial and axial dislocations in the fibers.

In antigorite a similar curling tendency is interrupted periodically by inversion of the tetrahedra so that the curvature changes direction by 180° . Although this periodic inversion creates a macroscopically platy crystal, the structure actually is that of an alternating wave with a superstructure periodicity between waves of about 40 Å along the X direction (Fig. 1.6). Certain Mg and OH ions have to be omitted from the structure in the region of tetrahedral inversion, so that antigorite ideally is Mg- and OH-deficient relative to chrysotile. Although the differences are small, the most careful chemical studies consistently have shown such deficiencies in antigorite (Faust and Fahey, 1962; Page, 1968; Whittaker and Wicks, 1970). Chrysotile, on the other hand, is close to its ideal composition, although some specimens show excess H_2O on analysis that may represent substitution of OH for O (Kalousek and Muttart, 1957).

Some, but apparently not all, antigorites show an additional small substitution of Al or Fe^{3+} for Si in the tetrahedral sites and for Mg in the octahedral sites. It has been pointed out that these substitutions both go in the direction of minimizing the tetrahedral–octahedral misfit. But it has not yet been proven beyond dispute that such substitutions are essential for formation of the antigorite alternating wave structure. Kunze (1961) suggests that although such cation substitutions should have the effect of changing the degree of sheet misfit and thus the radius of sheet curvature, the stopping of the rolling process by sheet inversion in antigorite actually is due to a higher pressure during crystallization than for chrysotile. The slopes of the stability fields in the synthesis data of Evans *et al.* (1976), however, suggest that temperature is more important than pressure in determining the species that will crystallize. Oxygen isotope studies by Wenner and Taylor (1971) indicate that antigorite is a higher temperature, metamorphic variant of lizardite and chrysotile and is not a stress mineral. Lizardite–clinochrysotile assemblages from several localities were found to have equilibrated at 85° – $115^\circ C$, whereas antigorites consistently gave an isotopic fractionation suggestive of regional metamorphism in the range 220° – $460^\circ C$.

With still greater tetrahedral and octahedral substitution of R^{3+} , as in most lizardites, in amesite, and in other aluminian serpentines, the tetrahedral lateral dimensions are either equal to or larger than the corresponding octahedral dimensions. Such sheets can accommodate each other by adjustment of their thicknesses or by tetrahedral rotation so that the resultant structures and morphologies are planar. The validity of the importance of tetrahedral–octahedral misfit in influencing morphology and structure (excluding the sheet inversion in antigorite) has been demonstrated convincingly by the synthesis of serpentines with different size cations in both sheets (Roy and Roy, 1954). Natural platy serpentines apparently can tolerate a complete range of R^{3+} substitutions from high Fe^{3+} (but low Fe^{2+}) to high Al, and often show excess H_2O similar to chrysotile.

Analyses presently available suggest that a few platy serpentines with the smallest substitutions overlap in composition those chrysotiles that have the larger amounts of substitution. Synthesis data by Gillery (1959) were interpreted to indicate that the general formula $(Mg_{3-x}Al_x)(Si_{2-x}Al_x)O_5(OH)_4$ must have $x = 0.125$ or greater in order to form platy rather than fibrous crystals. Olsen (1961) has suggested that $x \geq 0.05$ fits natural specimens better, but Radoslovich (1963*b*) favors the larger x value on the basis of calculated values of tetrahedral distortions. The most recent study by Chernosky (1975) indicates that although the X-ray powder pattern of the synthetic product with $x = 0$ is that of clinochrysotile and for $x = 0.125$ is that of lizardite, electron micrographs show that both fibrous and platy morphologies are present over the entire range from $x = 0$ to $x = 0.125$. The compositions of the

individual phases are not known in this two-phase region, but the chrysotile fibers are observed to become shorter, thicker, and less abundant as x increases. These observations suggest that (1) a small amount of Al may enter the chrysotile structure, and (2) platy serpentine can exist at $x = 0$ with no Al present. Chernosky was able to recrystallize the mixture of tubes and plates to a complete assemblage of clinochrysotile tubes at 431°C and 2 kbar and to obtain a complete assemblage of lizardite plates for $x = 0$ at 413°C and 2 kbar.

2.4.2 Clinochrysotile $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

Chrysotile- $2M_{c1}$ $a \cong 5.34, b \cong 9.25, c \cong 14.65 \text{ \AA}, \beta \cong 93.3^\circ$

Chrysotile- $1M_{c1}$ $a \cong 5.35, b \cong 9.25, c \cong 7.33 \text{ \AA}, \beta \cong 94.2^\circ$

Clinochrysotile is the major component of the chrysotile form of silky asbestos and occurs also as smaller fibers in more massive or splintery specimens. The fibers consist of 1:1 layers that are curled into cylindrical rolls. As a result of the rolling, the X-ray diffraction pattern of a stationary single fiber resembles that of a crystal that has been rotated through 360° about the fiber axis. The pattern consists of sharp $h0l$ and diffuse $hk0$ reflections. From the displacement of the $60\bar{1}$ reflections of a specimen from Thetford, Quebec, it is concluded that the ends of the cylindrical rolls do not match, but form a helix with an overlap of one unit cell parallel to the fiber (Whittaker, 1956a). This overlap predicts a mean value of the inner and outer radii of the fibers of 84 Å.

From the width of the $00l$ reflections and the shift in position of $hk0$ reflections it can be concluded further that the wall thickness for fibers of many specimens is remarkably constant at about 10 layers of 7.3 Å thickness and that the mean of the internal and external diameters is 180–250 Å (Whittaker, 1957; Toman and Frueh, 1968a,b). These calculated values are in good agreement with observation. Different specimens show different degrees of axial disorder parallel to the fiber axis but nearly complete azimuthal disorder around the roll of the fiber. The fiber direction is always along the 5.3 Å repeat axis, which is normally the a repeat for a layer silicate but has been labeled the c repeat in much of the chrysotile literature. In this chapter, however, the normal layer silicate directions will be used.

In this structure the octahedral cations occupy the same set of positions in each layer. As a result of the curling there is a continuously changing register between successive layers so that normal hydrogen bonding between layers is inhibited (Wicks and Whittaker, 1975). Instead, adjacent layers are anchored in the X direction parallel to the fibers by a corrugated basal oxygen surface in which projecting O(1) atoms fit between parallel rows of OH groups on the surface of the lower layer and retracted O(2) atoms fit approximately over the OH groups. The rows of OH groups extend parallel to the Y direction around the roll of the fibers and are spaced at intervals of $a/2$ along the fiber axis. There is disorder in the placement of adjacent layers in the Y direction, probably both because of the changing cylindrical register along Y and the possibility of adoption of layer positions that differ by $a/2$ along the cylinder (equivalent to lateral Y shifts). Wicks and Whittaker (1975) consider the buckled oxygen surface to be a direct result of the misfit of the lateral dimensions of the tetrahedral and octahedral sheets. In addition to the rolling effect already mentioned, there also is believed to be a compressional buckling of the plane of octahedral Mg cations, which in turn causes a buckling of the basal oxygens in the radial Z direction.

The stacking of adjacent layers in chrysotiles is governed by steric packing considerations involving the buckled basal oxygen surface rather than by hydrogen bond positions, so that the theoretical polytypes developed for planar structures are inapplicable. Whittaker (1953, 1956a)

has shown by analysis of the strong $h0l$ reflections of clinochrysotile that, in order to adopt the steric keying together of opposing O and OH surfaces, the upper layer is shifted parallel to the cylinder axis along $+X_1$, as defined in Fig. 1.4, by a regular small amount ($0.078a = 0.417 \text{ \AA}$) to give $\beta = 93^\circ 16'$. There is an additional smaller distortional shift along X of $\delta = 0.019a = 0.101 \text{ \AA}$ that changes direction in adjacent layers so that there is no resultant effect on the β -angle. But the δ shift does create a 2-layer repeat along Z that is documented only by a few l odd reflections that are quite weak relative to the l even reflections. Wicks and Whittaker (1975) use the symbol $2M_{c1}$ to describe this cylindrical structure, where the subscript c stands for cylindrical. A second theoretical monoclinic 2-layer structure is postulated with β about 90.4° in which the octahedral cation sets I and II alternate in adjacent layers, as do the directions of the δ shifts.

Shitov and Zvyagin (1966) have described three 1-layer clinochrysotile specimens with β angles near 106.5° . The structure has not been determined in detail, but probably corresponds to Wicks and Whittaker's $1M_{c1}$ model with shifts of $0.417 \text{ \AA} + \delta$ between every layer (ideal $\beta = 94.1^\circ$ or 106.4°). This $1M_{c1}$ structure would differ from the $2M_{c1}$ structure only in that the small distortional δ shifts do not change direction in successive layers and, therefore, every layer is identical. Wicks and Whittaker (1975) point out that a second 1-layer cylindrical structure, designated $1M_{c2}$, with shifts of $0.417 \text{ \AA} - \delta$ between each layer is theoretically possible also. This structure would have β near 92.5° . The reasons governing the direction of the small δ shifts are not understood.

Faust, Fahey, Mason, and Dwornik (1969) have described a natural nickel analogue of clinochrysotile to which they have given the name *pecoraite*. Co^{2+} - and Fe^{2+} -analogues of chrysotile have been synthesized by Noll, Kircher, and Sybertz (1960) and Jasmund and Sylla (1970).

2.4.3 *Orthochrysotile* $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_5$

$$\text{Chrysotile-}2Or_{c1} \quad a \cong 5.34, b \cong 9.25, c \cong 14.63 \text{ \AA}, \beta \cong 90^\circ$$

Orthochrysotile is an orthorhombic form of chrysotile, based on a cylindrical lattice that is non-helical (*i.e.* the ends of the rolls match) for the specimen studied. It is normally present only in small amounts in fibrous or splintery serpentines, but occasionally occurs as the major component. As in clinochrysotile, the fiber axis coincides with the X crystallographic axis in orthochrysotile and there is a similar keying of extended and retracted basal oxygens relative to rows of OH groups on opposing layer surfaces. Alternating layers now are rotated 180° (equivalent to alternating I and II octahedral cation sets), however, and the small shifts necessary to key them together cancel one another as a result to give $\beta = 90^\circ$. The 2-layer character of orthochrysotile is more pronounced (and the $h0l$, l odd reflections more intense) than in clinochrysotile, however, because of the alternation of the I and II octahedral cation sets in adjacent layers (Whittaker, 1956*b*). Wicks and Whittaker (1975) designate this observed structure, in which the δ distortional shifts are "undershifts" (opposite in direction to the $0.4 \text{ \AA}$ displacements), as $2Or_{c1}$. A second structure designated $2Or_{c2}$, similar to $2Or_{c1}$ except with δ "overshifts", is theoretically possible and should be recognizable by different $20l$ intensities.

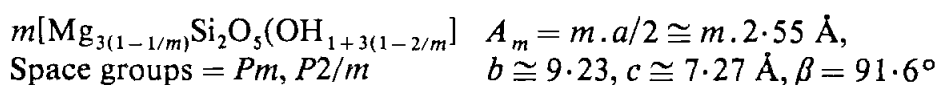
2.4.4 *Parachrysotile* $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

$$a \cong 5.3, b \cong 9.24, c \cong 14.7 \text{ \AA}, \beta \cong 90^\circ$$

Parachrysotile is a minor component of chrysotile samples. The name is used to designate fibers elongated along the Y-axis, instead of along the X-axis (Whittaker and Zussman, 1956). Whittaker (1956*c*) has shown that such fibers are in the form of a cylindrical helix with a mean

radius of about 97 Å. The structure is that of a 2-layer orthorhombic form. As in the other chrysotile structures the layers are displaced randomly around the cylinder walls, but this direction is now X instead of Y. The anchoring layer corrugations occur at intervals of $nb/6$ along the fiber axis Y and the layers probably are randomly displaced by these intervals also. This means that the normally strong $h0l$ reflections of a layer silicate are absent, and that the normally weak $0kl$ reflections are present only for $k = 6n$. Whittaker suggests alternate layers may be displaced by relative shifts of $b/12$, but the structure has not been determined in detail because of the few reflections available.

2.4.5 Antigorite



The name *antigorite* as used here corresponds to a morphologically platy or splintery serpentine, which may be of clay size, in which there is a superlattice with a large repeat distance along the X direction. Zussman (1954) followed up an earlier oral suggestion by L. Onsager to show by X-ray and optical diffraction that the superlattice must be due to a repeating wave structure, either of the rectified or alternating type. Kunze (1956, 1958, 1961) verified by more detailed structural analysis that the correct model has an alternating wave form in which the 1:1 layer reverses sides at each wave null point (Fig. 1.6). To a first approximation each half-wave can be considered as bent to a radius of 70 Å similar to that found in chrysotile cylinders. Examination in more detail shows the waves are slightly asymmetric, and that adjacent half-waves have slightly different radii of curvature. In the specimen examined by Kunze the superlattice repeat A was 43.3 Å in a horizontal plane or 8.5 times the normal a repeat of the subcell as measured along the wave form at the z -level of the basal oxygens of the tetrahedral sheet. Adjacent half-waves are of different widths due to inclusion of nine tetrahedra in one half-wave and only eight tetrahedra in the other. This leads to an average of 8.5 tetrahedra per half-wave or to 17 tetrahedra in the full wave and, because one tetrahedral edge is of width $a/2$, to the observed superlattice of $A = 17 \times a/2 = 43.3$ Å. The repeat distance as measured along the wave surface varies with the z height of measurement, and corresponds to only $8a$ at the octahedral Mg level. Thus each full wave contains 16 octahedra.

The tetrahedral sheet requires structural modification at the point of inversion within each full wave (*i.e.* at line QQ' in Fig. 1.6) in order to articulate the 17 tetrahedra with the 16 octahedra. Kunze (1958) has shown, as predicted by Onsager, that along this inversion line the six-fold

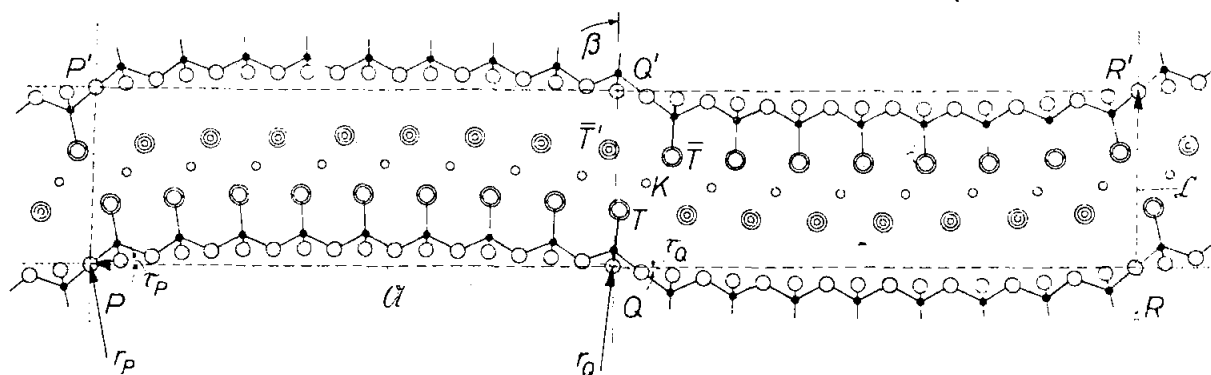


FIG. 1.6. Antigorite alternating wave structure, in which tetrahedra of adjacent half waves point in different directions. Superstructure of $A = 43.3$ Å along X between lines PP' and RR' includes 17 tetrahedra and 16 octahedra in this specimen (from Kunze, 1961).

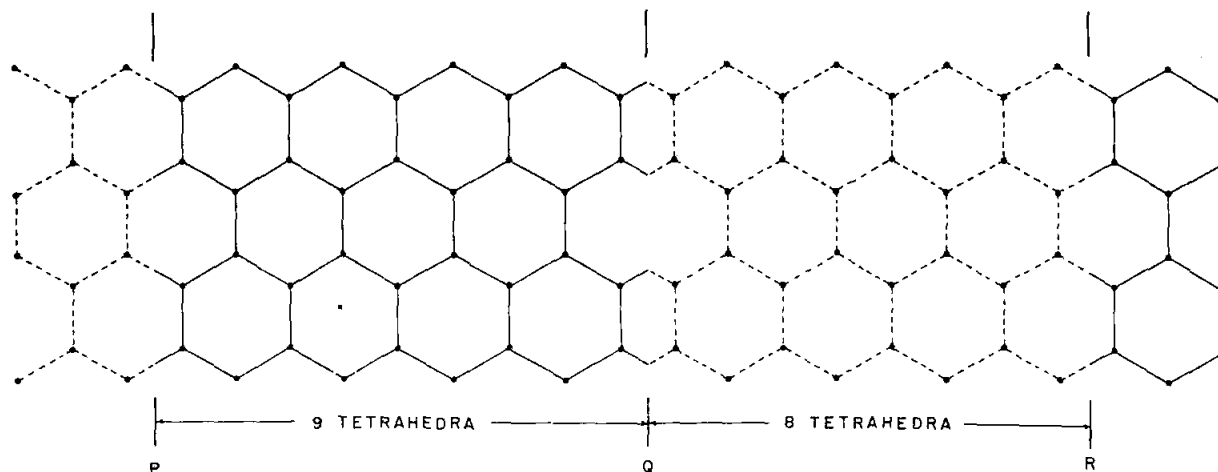


FIG. 1.7. Change of 6-fold rings to 4-fold and 8-fold rings in antigorite along inversion line QQ' of Fig. 1.6. Tetrahedra alternately point up (solid lines) and down (dashed lines) in adjacent half waves (modified from Kunze, 1961).

tetrahedral rings change to an alternation in the Y direction of eight-fold and four-fold rings with half of the tetrahedra in these rings pointing in opposite directions, as shown in Fig. 1.7. This introduces an extra $a/2$ into the full wave repeat at the z level of the tetrahedra. The 16 octahedral Mg atoms extend in a continuous sinusoidal wave along X throughout the structure, and one Mg serves as a linking bridge between adjacent half-waves at the inflection line QQ' (see point K in Fig. 1.6). Although the Mg coordination remains octahedral despite the layer reversals, $1/3$ of the Mg at QQ' change nearest neighbors from the customary $4OH + 2Ox$ to $2OH + 4Ox$. At the z level of the uppermost octahedral OH surface there are only $15 a/2$ repeats, as measured along the full wave, and the change in nearest neighbors of these bridging Mg atoms is due to some of the OH groups being eliminated at QQ' in order to fit the wave form in the inversion region. The inflection points at PP' and RR' are not equivalent to QQ' , and the structural modifications of the tetrahedral and octahedral sheets observed at QQ' are not repeated here because of the presence of two bridging Mg atoms, rather than just one.

The antigorite structure cannot be discussed in terms of planar polytypes because the curvature inhibits normal hydrogen bonding and because the layers are interconnected at the two inversion points. The inversion waves create a slight layer displacement and a resultant monoclinic β angle of 91.6° . Although the subcell ($5 \times 9 \text{ \AA}$) remains C-centered, closely spaced superlattice reflections with $h + k = 2n + 1$ violate this extinction. Kunze (1958) determined the superlattice space group as Pm for the $43.3 \text{ \AA}$ specimen, but suggests (1961) that specimens with an even number of tetrahedra in the repeating superlattice may belong to space group $P2/m$. Streaks along Z^* in X-ray photographs of many antigorites suggest some randomness in the stacking of adjacent layers. A triclinic antigorite with a doubled c -repeat is postulated as theoretically possible but not yet identified in nature.

The superlattice alternating wave always is observed along the X direction, although the reason for this has not been explained. The macroscopic morphology is platy, but often elongate as laths or splinters parallel to the elongate crests and troughs of the wave form (the Y direction). Kunze (1958) has suggested that small differences in composition will change the curvature radius of the waves and the magnitude of the superlattice A repeat. Although the structure was determined for a specimen with $A = 43.3 \text{ \AA}$ and 17 tetrahedra (of width $a/2$) in the full wave, similar waves corresponding to different numbers (m) of tetrahedra are possible with superlattice repeats $A_m = m \cdot a/2$. Zussman, Brindley, and Comer (1957), Chapman and Zussman (1959), Kunze (1961), and Shitov and Zvyagin (1966) have recorded a number of different

superlattice repeats for different specimens by electron diffraction and electron optical fringe measurements. The values range from 18 Å to over 110 Å, but with most values between 25.5 Å and 51.0 Å (*i.e.* $m = 10$ to 20). Kunze (1961) has predicted that when adjacent half waves have equal numbers of tetrahedra ($m = 2n$) the layer inversion will require four-fold and eight-fold tetrahedral rings at all three inversion points P, Q, and R and, because of the odd number ($m - 1$) of Mg present in the full wave, also will require the creation at P and R of new 10-fold coordination groups around a pair of Mg atoms.

The ideal structure with $A = 43.3$ Å contains 17 Si tetrahedra, 16 Mg, and 15 upper OH groups. This corresponds to an ideal composition of $17(\text{O}_3 + \text{Si}_2 + \text{O}_2\text{OH}) + 16\text{Mg}_3 + 15(\text{OH})_3 = 17(\text{O}_3 + \text{Si}_2 + \text{O}_2\text{OH} + \text{Mg}_{48/17} + (\text{OH})_{45/17}) = \text{Mg}_{2.8235}\text{Si}_2\text{O}_5(\text{OH})_{3.647}$. Antigorites with different values of the superlattice repeat and thus with different numbers (m) of tetrahedra in the full wave will have different ideal compositions of the form $m[\text{Mg}_{3(1-1/m)}\text{Si}_2\text{O}_5(\text{OH})_{1+3(1-2/m)}]$. For any value of m , these compositions correspond to removal of $\text{Mg}_3(\text{OH})_6$ from an ideal formula of $m[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$. For $m = 10$ and $m = 20$ the respective compositions would be $\text{Mg}_{2.70}\text{Si}_2\text{O}_5(\text{OH})_{3.40}$ and $\text{Mg}_{2.85}\text{Si}_2\text{O}_5(\text{OH})_{3.70}$.

2.4.6 Magnesian lizardite $\sim \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

Lizardite-1*T* Space group = $P31m$ $a = b = 5.31, c = 7.31$ Å, $\gamma = 120^\circ$

Lizardite-2*H*₁ Space group = $P6_3cm$ $a = b = 5.31, c = 14.62$ Å, $\gamma = 120^\circ$

Magnesian lizardite, often with a small amount of substitution of Al or Fe^{3+} for both Si and Mg, is the most abundant serpentine variety in massive, fine-grained specimens. Whittaker and Zussman (1956) defined lizardite as a platy serpentine having a 1-layer orthogonal unit cell. Wicks and Whittaker (1975) later recommended that the name lizardite be broadened to cover all planar serpentine structures. The latter recommendation will be followed here for species in the Mg-Al system, but excluding the well-established mineral amesite.

Rucklidge and Zussman (1965) examined small crystals of lizardite-1*T* from the type locality in the Lizard area, Kennack Cove, Cornwall, and found a number of deviations from the ideal 1*T* structure (Fig. 1.5*b*). The crystals are distorted macroscopically to the shape of spherical caps, perhaps due to the small amount of tetrahedral and octahedral substitution in this specimen. Individual layers have a 40% probability of being randomly displaced by $\pm b/3$, thus leading to streaking of $k \neq 3n$ reflections (indexed on an orthohexagonal cell) parallel to Z^* . Some crystals show extra reflections, which may be sharp or diffuse, at positions intermediate to those given by the ideal 1*T* structure. These extra spots, plus the observation that the intensities of $h0l$ and $h0\bar{l}$ reflections are not equal, are interpreted to indicate the existence of small domains in the crystals. Some domains contain layers with the octahedral sheet oriented only in the set I positions, other domains are oriented only in set II positions, and a third type of domain has a fairly regular alternation of I and II octahedral sets (2*H*₁ sequence). Variations from crystal to crystal in the proportions of the three types of domains and in the regularity of alternation of the I and II octahedral sets in the third type of domain account for the observed variations in the degree of diffuseness and the positions of the extra spots as well as the inequality of the $h0l$ and $h0\bar{l}$ intensities.

Krstanović (1968, pers. comm.) has examined disordered lizardites from Avala Mtn., Yugoslavia, that are characterized by streaked $k \neq 3n$ reflections (as indexed on an orthohexagonal cell) and extreme 40° elongation of all reflections. A partial two-dimensional refinement of the structure using only $h0l$ reflections indicated that the octahedral Mg cations are located in a plane closer to the upper plane of OH anions than to the apical oxygen plus inner

TABLE 1.4. X-ray powder data for serpentine minerals; spacings in Å

A. Chrysotile					B. Antigorite					C. Lizardite-1T				
I		2		3	I		I		I		I		I	
hkl	d(calc.)	d(obs.)	I	d(obs.)	I	hkl	d(calc.)	d(obs.)	I	hkl	d(calc.)	d(obs.)	I	
002	7.32	7.36	10	7.36	10	001	7.26	7.30	400	001	7.31	7.4	VS	
020	4.60	4.58	6	4.56	6	201	6.93	6.95	24	020	4.60	4.6	s	
022	3.89					301	6.56	6.52	16	021	3.89	3.9	m	
						401	5.96	5.80	8	002	3.66	3.67	s	
004	3.66	3.66	10	3.66	8	710	5.15	5.11	3	022	2.862	2.875	VW	
024	2.86					810	4.68	4.67	6	200	2.655	2.663	mw	
130	2.66	2.66	4	2.66	2	020	4.63	4.64	7	201	2.496	2.505	VS	
201†	2.614					910	4.28	4.27	4	003	2.437	2.410	VVW	
201*	2.590	2.594	4	2.604	4	811	3.95	3.95	6	040	2.300	2.307	VVW	
202*	2.548	2.549	6	2.547	1	102; 102̄; 002	3.63	3.63	300	202	2.148	2.156	s	
						302; 202	3.50	3.52	24	042	1.947	1.945	VVW	
202†	2.497					14,0,1̄	2.88	2.88	2	004	1.828	1.835	VW	
202*	2.454	2.456	8	2.451	7	15,0,1	2.66	2.66	3	203	1.795	1.799	m	
006	2.438					930	2.60	2.60	4	310	1.738	1.743	mw	
						17,0,0; 16,0,1̄	2.55	2.57	8	311	1.691	1.692	VW	
203†	2.332					16,0,1	2.52	2.53	70	312	1.570	1.572	VVW	
040	2.301					931	2.46	2.46	9	060	1.533	1.538	s	
203*	2.280	2.282	2	2.285	1	003; 18,0,0	2.42	2.42	38	061,204	1.503	1.505	s	
204*	2.214	2.215	2	2.212	1	17,0,1; 303̄; 10,3,1̄	2.39	2.39	9	005	1.462	1.462	VW	
204†	2.148					403?	2.35	2.35	5	062	1.414	1.416	m	
204*	2.094	2.096	6	2.093	4	15,0,2	2.24	2.24	6	400	1.328	1.332	w	
						16,0,2̄	2.20	2.21	7	401	1.306	1.310	ms	
205†	1.966					832	2.169	2.169	22	205	1.281	1.281	m	
008	1.829	1.829	2	1.828	2	16,0,2	2.150	2.153	20	402	1.248	1.253	w	
206†	1.796					932	2.126	2.127	4	006	1.218	1.219	VW	
206*	1.748	1.748	6	1.746	4	17,0,2̄	2.113	2.113	4	403	1.166	1.169	m	
						11,3,2̄	2.033	2.035	4	206	1.107	1.110	VVW	

310	1.739	1.536	8	1.531	7	15.0,3̄	1.879	1.879	3	404	1.074	1.078	w
028	1.698					15.0,3̄	1.836	1.832	12	510,065	1.055	1.058	w
207†	1.643					004; 104̄; 833	1.815	1.813	23	007	1.044	1.045	vw
060	1.534	1.536				933	1.782	1.782	14	530	1.004	1.002	vw
						10.3,3̄	1.756	1.755	4	531	0.994	0.993	m
208†	1.506					17.0,3̄	1.737	1.738	10	405	0.983	0.981	vw
0.0,10	1.463	1.465	2	1.464	2	21.3,1̄	1.680	1.680	2	532	0.968	0.968	w
064	1.414					22.3,1̄	1.636	1.638	2	066	0.954	0.952	w
400	1.328					14.0,4̄	1.583	1.587	3	533	0.928	0.923	w
402*	1.322	1.317	4	1.319	4	24.3,0̄	1.561	1.563	12	008	0.914	0.912	vw
402†	1.307			1.310	4	060	1.541	1.541	9	600	0.885	0.885	m
						24.3,1̄	1.531	1.534	9	601,504	0.879	0.880	vw
						15.0,4; 16.0,4̄; 22.3,2̄	1.522	1.523	13	067,208,602	0.862	0.861	m
						061	1.508	1.509	8	603	0.832	0.834	vw
						17.0,4̄; 934̄	1.495	1.497	10	407	0.821	0.828	vw
						934	1.479	1.480	7	068	0.785	0.786	vw
						18.0,4̄	1.467	1.468	6				
						10.3,4̄	1.462	1.462	6				
						205	1.451	1.452	10				
						205	1.446	1.448	9				

- A. 1 Indices and spacings based on $a = 5.32 \text{ \AA}$, $b = 9.20 \text{ \AA}$, $c = 14.64 \text{ \AA}$, $\beta = 93.33^\circ$ or 90° ; * signifies $\beta = 90^\circ$; † signifies $\beta = 93.33^\circ$; no symbol signifies d independent of β -angle.
2 Clino-chrysotiles from Zermatt, Switzerland, and Reichenstein, Silesia.
3 Mixture 85% clino-, 15% ortho-chrysotile, from serpentine in dolomite, Transvaal.
(Whittaker and Zussman, 1956.)
B. $d(\text{obs.}) = \text{values in } \text{\AA}$ obtained by combining data for specimens from New York, Caracas (Venezuela), Mikonui (New Zealand), Glen Urquhart (Scotland), Val Antigorio (Switzerland).
 $d(\text{calc.})$ based on $a = 43.5$, $b = 9.25$, $c = 7.26 \text{ \AA}$, $\beta = 91.38^\circ$.
(Whittaker and Zussman, 1956.)
C. Indices on basis of cell with $a = 5.31$, $b = 9.20$, $c = 7.31 \text{ \AA}$, $\beta = 90^\circ$.
Specimen from Kenack Cove, Cornwall, England.
(Rucklidge and Zussman, 1965.)

OH anions. The disorder noted is attributed to random adoption of the I and II sets of octahedral cation positions throughout the crystal plus random interlayer shifts of $\pm b/3$. The $h0l$ and $h0\bar{l}$ reflections are of equal intensities, as a result of equal numbers of I and II type layers, and no diffuse maxima were noted that would indicate a 2-layer Z axis periodicity similar to that of the Kennack Cove lizardite.

Other disordered lizardite crystals from the Radusa Chromite mine, Yugoslavia, were noted to have unequal $h0l$ and $h0\bar{l}$ intensities as a result of adoption of unequal numbers of I and II type octahedral orientations (Krstanović, 1968). Crystals showing the greatest deviations between $h0l$ and $h0\bar{l}$ intensities, however, were shown to contain only one type of layer and to come closest to the $1T$ structure. Partial structural analysis of two such crystals of near end-member composition indicated non-trigonal symmetry, however, and considerable distortion of the structure. In particular, the 1:1 layer is buckled in such a manner that the octahedral Mg cations are not coplanar and the basal oxygens are separated by 0.4 Å in the Z direction. The extended O(1) atoms lie over grooves between surface OH groups of the layer below and the retracted O(2) atoms lie approximately over the OH groups, similar to the steric packing of layers observed in chrysotile.

X-ray powder patterns for chrysotile, antigorite, and lizardite are listed in Table 1.4.

2.4.7 Amesite $[(\text{Mg}, \text{Fe}^{2+})_{2.0}\text{Al}_{1.0}](\text{Si}_{1.0}\text{Al}_{1.0})\text{O}_5(\text{OH})_4$

$$\begin{aligned}\text{Space group} &= C1 \quad a = 5.319, b = 9.208, c = 14.060 \text{ Å}, \\ &\quad \alpha = 90.01^\circ, \beta = 90.27^\circ, \gamma = 89.96^\circ\end{aligned}$$

Amesite is a rare, platy serpentine, usually in the form of hexagonal prisms elongated parallel to Z, that has a maximum amount of tetrahedral and octahedral Al-substitution. For many years this mineral was classified as an end member within the chlorite series, but Gruner (1944a) showed that it is based on a 1:1 type layer. Gruner (1944a) and Brindley, Oughton, and Youell (1951) observed that amesite crystals often show streaking of $k \neq 3n$ reflections, indicative of random layer displacements of $\pm b/3$. Most crystals of amesite that show more regular layer stacking are based on a distortion of the $2H_2$ layer sequence (Fig. 1.5c). Steinfink and Brunton (1956) refined the structure of a crystal from the Saranovskoye chromite deposit, U.S.S.R., on the basis of the ideal $2H_2$ space group ($P6_3$) and found no ordering of the tetrahedral or octahedral cations. They mentioned the observation of six-fold biaxial twin sections on (001), but attributed the biaxial nature to strain. Hall (1974), however, showed that biaxial twins are commonplace in amesite crystals from Antarctica and cannot be attributed to strain. Although the twinned crystals produce an average diffraction symmetry that is hexagonal, individual twin sectors cut from the larger aggregate have 2V optical angles consistently near 20° , slightly triclinic unit cell geometry, and triclinic diffraction symmetry. Although the structure has not been refined completely, Hall attributes the triclinic symmetry to both octahedral and tetrahedral cation ordering. Of the six independent octahedra in the 2-layer structure, two are observed to be smaller in size than the other four. The smaller octahedra are interpreted as Al-rich and the larger octahedra as Mg-rich. The pattern of tetrahedral cation ordering is such that tetrahedra of adjacent layers that should be equivalent to each other in the ideal $2H_2$ structure actually have different Si,Al contents, as judged by the differences in mean T—O bond lengths.

A few crystals of amesite have been found that are based on regular layer stacking sequences different from that of the $2H_2$ structure. Steinfink (in Oughton, 1957) has discovered a $2H_1$ amesite crystal of ideal space group $P6_3cm$. Hall and Bailey (1976) describe crystals of amesite from Antarctica that have layer sequences like that of the ideal $6R$ polytype, but whose optical

TABLE 1.5. X-ray powder data for amesite and kellyite; spacings in Å

A. Amesite (Brindley <i>et al.</i> 1951)				B. Kellyite (Peacor <i>et al.</i> , 1974)			
<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i>
002	7.00	7.06	10	002	7.0	7.0	90
021*	4.59	4.54	2	004	3.51	3.51	100
004	3.502	3.517	10	111	2.67	2.67	40
200	2.652			112	2.54	2.53	60
201	2.605	2.609	2	113	2.35}	2.34	40
202	2.480	2.478	6	006	2.34}		
006	2.335}	2.325	5	114	2.15	2.15	10
203	2.306}			115	1.954	1.954	30
204	2.114	2.110	3	116	1.774}	1.768	10
205	1.926	1.925	7	008	1.755}		
206	1.752}	1.749	5	117	1.614	1.612	10
008	1.750}			300	1.570	1.570	30
207	1.597	1.596	6	302	1.532	1.533	5
060	1.531	1.531	6	118	1.475	1.477	10
062	1.496	1.495	2	304	1.433	1.434	5
208	1.461	1.461	6	0,0,10	1.404	1.403	10
004	1.403}	1.401	6	308	1.170}	1.169	5
0,0,10	1.401}			0,0,12	1.170}		
209	1.342	1.342	5	0,0,14	1.003	1.003	5
262	1.303	1.304	1				
263	1.276	1.276	1				
2,0,10	1.239	1.238	3				
265	1.198	1.198	1				
0,0,12	1.167	1.167	2				
2,0,11	1.148	1.149	2				
267	1.105	1.106	1				
2,0,12	1.068	1.069	1				
268	1.057	1.056	1				
0,6,10	1.034	1.034	2				
0,0,14	1.001	1.000	3				

A. Indexed as $2H_2$ polytype on orthohexagonal axes, $a = 5.31$, $b = 9.19$, $c = 14.01$ Å.

Specimen from Chester, Mass.

* Edge of 021 diffraction band.

B. Indexed as $2H_2$ polytype on hexagonal axes, $a = 5.438$, $c = 14.04$ Å, $\gamma = 120^\circ$.

Specimen from Bald Knob, North Carolina.

extinction patterns suggest the true symmetry is lower than rhombohedral. Steadman and Nuttall (1962) have reported a different 6-layer structure that is triclinic but distorted only slightly from rhombohedral symmetry $R3$. This latter structure can be described as resulting from the operation of a three-fold screw axis on the ideal $2H_1$ structure. This creates a layer stacking sequence in which interlayer shifts of $b/3$ along Y alternate regularly with zero interlayer shifts. Mixing of these different types of layer superposition was not considered by Bailey (1969) and, as a result, this stacking sequence (termed $6R_2$ by Hall *et al.*, 1976) is not included among his ideal structures. All of these less abundant polytypes of amesite share in common with the $2H_2$ structure the characteristic of regular alternation of I and II octahedral cation sets in adjacent layers. The X-ray powder patterns of all would be identical except for the $k \neq 3n$ reflections that indicate the exact stacking sequence. The latter are so weak that they may not be visible on powder photographs (Table 1.5).

The Mn^{2+} -analogue of amesite has been named *kellyite* (Peacor *et al.*, 1974). In addition to crystals showing stacking disorder, 2-layer and 6-layer forms with considerable regularity of

stacking have been recognized. The 2-layer form of space group $P6_3$ is the same $2H_2$ polytype that also is most abundant in amesite, and the 6-layer form is similar to that found in amesite by Steadman and Nuttall (1962) and described above. A Zn analogue of amesite has been named *zinalsite* (Chukhrov and Petrovskaja, 1971).

2.4.8 *Aluminian lizardite* $[\text{Mg}_{3-x}(\text{Al}, \text{Fe}^{3+})_x][\text{Si}_{2-x}(\text{Al}, \text{Fe}^{3+})_x]\text{O}_5(\text{OH})_4$

Gillery (1959) investigated the substitution of Al for Mg and Si in serpentine by hydrothermal synthesis. Below 500°C aluminian lizardite formed, perhaps as a metastable crystallization product, but above 500°C a chlorite of similar composition was the stable form. Gillery found that lizardite-1T was the predominant polytype at the magnesian end of the system, but that a 6-layer form increased in amount as the Al substitution increased from about $x = 0.25$ to $x = 1.00$ in the composition $(\text{Mg}_{3-x}\text{Al}_x)(\text{Si}_{2-x}\text{Al}_x)\text{O}_5(\text{OH})_4$. Radoslovich (1963b) has pointed out that for the larger values of Al-substitution the lateral dimensions of the tetrahedral sheet become larger than those of the octahedral sheet, so that articulation is accomplished by reducing the former by tetrahedral rotation. This changes the hexagonal rings to a ditrigonal shape, which should favor formation of a multi-layer structure of periodicity $3n$. The 1-layer structure should be favoured at low Al-substitution where the tetrahedral rings will be essentially hexagonal. Gillery has termed the 6-layer structure as the 6(3) type because its strong reflections resemble those of a 3-layer orthogonal (or 1-layer monoclinic) structure (Table 1.6).

Bailey and Tyler (1960) have described a natural occurrence of an aluminian serpentine (their type F) that gives a powder pattern similar to that of Gillery's synthetic 6-layer material, as have Jahanbagloo and Zoltai (1968), but there are differences in the weak reflections. The type F powder pattern lacks the weak reflections indicative of a 6-layer repeat and is identified by Bailey (1969) as either the 1M or 3T polytype. Single crystals of the Jahanbagloo and Zoltai lizardite show weak extra reflections indicating a 9-layer or 18-layer repeat. In all of these specimens, the strong reflections of index 20l and 13l for an orthohexagonal cell indicate that the same set of octahedral positions is occupied in every layer.

The most abundant multi-layer lizardite in nature is a 6-layer orthohexagonal structure first described from Unst in the Shetland Islands by Brindley and von Knorring (1954). The same structure has been described since then from several other localities with a wide range of R^{3+} -substitutions, and also has been made synthetically by Roy and Roy (1954) with the composition $\text{Mg}_3\text{Ge}_2\text{O}_5(\text{OH})_4$ and by Jasmund and Sylla (1971, 1972) with the probable compositions $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. In the latter study, tubes of Ni-chrysotile and Mg-chrysotile were found to convert to hexagonal platelets of the 6-layer form after holding at $320^\circ\text{--}350^\circ$ and 200–250 atm for several weeks. Shirozu and Momoi (1972) also have synthesized this structure in the Mg–Al–Si system. They confirmed Gillery's results in which the amount of 6-layer lizardite increased at the expense of the 1-layer form with increasing Al substitution. They also found that different structures formed at different temperatures and pressures for the high Al compositions. At $300^\circ\text{--}400^\circ\text{C}$ and 18,000 psi the same 6(3) form crystallized that Gillery found in his study. At 590°C and 35,000 psi, however, Shirozu and Momoi found that a 6(2)-layer structure formed, similar to the Unst serpentine, whose strong reflections resemble those of a 2-layer structure. A series of weaker reflections of index 02l and 11l for an orthogonal cell indicate the 6-layer periodicity.

Hall, Guggenheim, Moore, and Bailey (1976) have determined the structure of the 6(2) or Unst-type serpentine, which they designate as lizardite-6T₁ (Table 1.6). The first four layers in the 6-layer cell are identical to the layer sequence in amesite-2H₂, in which the interlayer shifts are alternately $+b/3$ and $-b/3$. The next two layers have the same sequence as in the 2H₁

TABLE 1.6. X-ray powder data for 6-layer serpentines; spacings in Å

A. 6(2)-structure = lizardite-6T ₁ (Hall <i>et al.</i> , 1976)										B. 6(3) structure (Gillery, 1959)				
hk.l	d(obs.)	I(obs.)	I(calc.)	d(calc.)	hk.l	d(obs.)	I(obs.)	I(calc.)	d(calc.)	hk.l	d	Camera	d	I(obs.)
00.6	7.270	100	100.0	7.268	12.3	1.728	w	2.8	1.730	006	7.09	7.08	7.10	100
01.0	4.585	34	15.8	4.609	11.21	1.638	12	20.2	1.637	020,021	4.59	4.59	4.597, 4.570	35
01.1			30.8	4.584	12.9	1.536	35	28.3	1.639	022	4.493	4.493	4.493	5
01.2			7.4	4.509	03.0	1.536		13.0	1.536	024	4.212	4.212	4.221	5
01.3	4.402	7.3	27.6	4.393	11.24	1.502	20	32.3	1.501	026	3.842	3.842	3.859	5
01.4	4.251	3.9	6.2	4.245	03.6	1.462	ww	0.3	1.503	027	3.658	3.658	3.669	5
01.5	4.074	5.0	5.4	4.075	02.23	1.462	ww	0.3	1.464	00.12	3.551	3.551	3.552	100
01.6	3.890	6.1	19.8	3.892	00.30	1.453	2.2	1.8	1.454	028	3.474	3.474	3.480	5
01.7	3.637	84	73.1	3.705	03.12	1.415	3.9	7.0	1.415	029	3.289	3.289	3.299	5
00.12			69.1	3.634	12.18	1.381	5.6	0.7	1.414	02.10	3.127	3.127	3.125	5
01.8	3.521	3.9	3.3	3.520	11.27	1.327	1.7	4.3	1.381	02.12	2.816	2.816	2.811	5
01.9	3.340	3.4	11.1	3.340	22.0	1.276	6.1	0.6	1.331	200	2.635	2.635	2.634	15
01.10	3.170	2.8	2.3	3.168	02.27	1.250	ww	0.9	1.323	202	2.613	2.613	2.609	55
01.11	3.004	2.2	1.9	3.006	22.3	1.210	3.4	1.4	1.325	203	2.571	2.571	2.576	25
01.12	2.859	1.7	6.2	2.854	11.30	1.183	w	2.1	1.276	204	2.531	2.531	2.534	40
01.13	2.710	2.2	1.3	2.712	22.12	1.168	mw	4.1	1.249	205	2.486	2.486	2.486	15
11.0	2.659	w	3.1	2.661	00.36	1.121		4.8	1.211	206	2.429	2.429	2.433	35
11.3	2.617	14	10.1	2.618	22.15	1.074		3.8	1.210	207	2.379	2.379	2.375	15
01.14	2.585	w	1.0	2.585	11.33	1.056	mw	0.4	1.184	208	2.351	2.351	2.351	80
11.6	2.502	72	90.4	2.499	12.27	1.028	w	1.8	1.184	209	2.250	2.250	2.253	10
01.15	2.457	2.8	3.2	2.459	03.24	1.006		3.7	1.173	20.10	2.126	2.126	2.126	15
00.18	2.424	1.1	5.3	2.423	13.15	0.965	m	1.7	1.170	20.12	2.001	2.001	2.001	5
11.9	2.333	26	30.7	2.332	22.18	0.965	w	2.7	1.166	20.14	1.937	1.937	1.940	30
02.3	2.274	w	1.0	2.276	22.21	0.965	m	0.2	1.120	20.15	1.881	1.881	1.880	10
01.17	2.200	w	0.5	2.197	02.36	0.965	w	1.2	1.072	20.16	1.769	1.769	1.767	5
02.6			1.8	2.197	22.24	0.965	w	1.8	1.073	20.18	1.735	1.735	1.737, 1.736, 1.731	5
01.18	2.148	17	19.4	2.144	03.30	0.965	m	1.7	1.027	310,311,312	1.662	1.662	1.662	15
11.12			17.7	2.147	22.27	0.965	w	1.7	0.963	20.20	1.608	1.608	1.611	5
02.9	2.090	w	1.6	2.081	14.6	0.965	m	1.7	0.963	20.21	1.561	1.561	1.561, 1.565	10
01.19			0.4	2.084	14.9	0.965	w	1.7	0.963	31,12,20,22	1.534	1.534	1.532	65
02.10	2.020	w	1.2	2.038	11.42	0.965	w	1.7	0.963	060	1.499	1.499	1.498	10
02.11			0.4	1.992	23.18	0.965	w	1.7	0.963	066	1.470	1.470	1.472, 1.476	5
11.15	1.962	27	31.8	1.963	14.12	0.965	w	1.7	0.963	068,20,24	1.422	1.422	1.421	5
02.13	1.895	w	0.4	1.899						00.12	1.407	1.407	1.407	5
01.21			1.3	1.893						06.12	1.392	1.392	1.395	10
00.24	1.817	3.4	1.5	1.817						20.26	1.352	1.352	1.352	5
11.18	1.792	4.5	10.7	1.791						400	1.321	1.321	1.327	10
12.0	1.742		1.4	1.742						06.18	1.287	1.287	1.286	10
12.1			2.2	1.741							1.269	1.269		5

A. Specimen from Unst, Shetland Islands, as described by Brindley and von Knorring (1954).

 $a = 5.322$, $c = 43.61$ Å.B. Specimen of composition $9 \text{ MgO} \cdot 3 \text{ Al}_2\text{O}_3 \cdot 5 \text{ SiO}_2$ treated hydrothermally for 41 days at 450°C and 15,000 psi. $a = 5.308$, $b = 9.193$, $c = 42.62$ Å.

polytype, with zero interlayer shifts. Octahedral cation sets I and II alternate regularly in successive layers.

2.4.9 *Nickelian lizardite–nepouite series* $\sim(\text{Mg}_{3-x}\text{Ni}_x)\text{Si}_2\text{O}_5(\text{OH})_4$

Maksimović (1973) has shown that Ni^{2+} can substitute isomorphously for Mg in any amount in the planar lizardite structure. When Ni constitutes more than half of the octahedral cation total, the name *nepouite* has been proposed. Brindley and Wan (1975) have studied a large number of Ni-bearing serpentines in which there is considerable variation in the regularity of layer stacking. The nepouite specimens studied showed less structural regularity than the nickelian lizardites in general. Even the latter could not be correlated in detail with specific polytypes, except for two specimens that gave X-ray powder patterns close to that of the *2Or* form. Some specimens also gave reflections suggestive of a monoclinic component.

2.4.10 *Berthierine* $\sim(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_{3-x}(\text{Fe}^{3+}, \text{Al})_x(\text{Si}_{2-x}\text{Al}_x)\text{O}_5(\text{OH})_4$

$$a \cong 5.40, b \cong 9.36, c \sin \beta \cong 7.10 \text{ \AA}, \beta \cong 104.5^\circ \text{ and } 90^\circ$$

Berthierine is the preferred term for the fine grained iron-rich 1:1 layer silicate commonly present in unmetamorphosed sedimentary iron formations. In the past this mineral often has been called *chamosite*, but the same name has been used also for a 14 Å Fe-rich chlorite. The material from the type locality in Chamoson, France, is known now to be a true chlorite so that the term “*chamosite*” should no longer be used for the 1:1 layer type material.

Berthierine is known in two structural forms, often intimately intermixed in nature. One is of apparent trigonal symmetry and the other of apparent monoclinic symmetry. The true symmetries are unknown because single crystals have not been found and the powder patterns are not definitive. The trigonal *berthierine* has the *1T* structure according to the work of Brindley (1951). Each layer is identical and there is no interlayer shift. Despite the apparent trigonal symmetry it is convenient to index the powder pattern on a C-centered orthogonal cell. For this reason the compound sometimes is termed the orthohexagonal variety in the literature. The less abundant monoclinic *berthierine* can be described as the *1M* structure, in which each layer is displaced by $a/3$ along $-X_1$. The smallest unit cell for this structure is an inclined 1-layer cell with $\cos \beta = -a/3c$. The possibility of this mineral being the *3T* structure cannot be dismissed, however, because the calculated powder patterns of the ideal *1M* and *3T* layer sequences are identical for trioctahedral compositions. This illustrates the point that any monoclinic n -layer unit cell with an interlayer shift of exactly $a/3$ can be described also by a larger orthogonal cell containing $3n$ -layers, as in Fig. 1.8. Because *berthierine* often shows some randomness in the layer stacking, it is preferable to use the *1M* description in the absence of definitive evidence of a larger cell.

A natural Ni analogue of *berthierine* has been named *brindleyite*. Although originally believed to be an analogue of *amesite*, further study has shown that it is more like *berthierine* in that the tetrahedral substitution is only about $\text{Si}_{1.5}\text{Al}_{0.5}$ and that the natural samples are mixtures of both hexagonal and monoclinic polytypes (Maksimović and Bish, 1978).

Esquevin (1957) has synthesized a Zn-analogue of *berthierine* at low temperature.

2.4.11 *Baumite*

$$a = 5.37, b = 9.22, c = 7.09 \text{ \AA}$$

The name *baumite* has been given to a black serpentine occurring at Franklin, New Jersey, U.S.A., which is unique in containing large amounts of ZnO and MnO in addition to MgO and

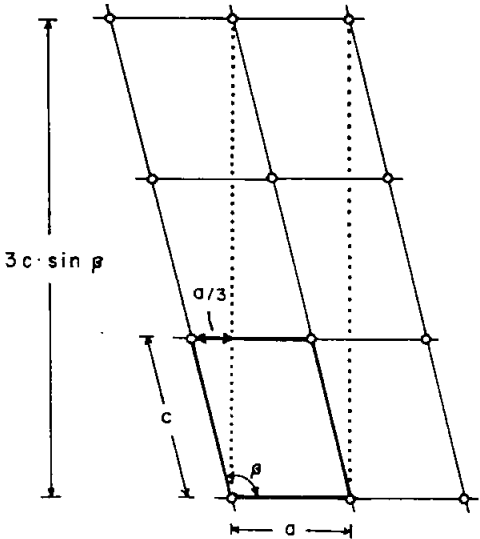


FIG. 1.8. Monoclinic 1-layer cell with interlayer shift of $a/3$ (heavy outline) also can be described by a larger orthohexagonal 3-layer cell (dotted lines).

TABLE 1.7. X-ray powder data for Fe- and Mn-rich minerals having 1 : 1 type layers; spacings in Å

A. Berthierine (Brindley, 1961)						B. Greenalite (Bailey, unpublished)					
Monoclinic (calc.)		Observed		Orthogonal (calc.)		1T (calc.)		Observed		1M (calc.)	
<i>d</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>d</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>hkl</i>
7.04	001	7.05	10	7.04	001	7.213	001	7.20	100	7.213	001
4.666	020	4.67	2	4.666	020	3.607	002	3.61	50	3.607	002
4.568	110	4.58	2			2.800	200	2.78	30	2.780	201̄, 130
4.282	111̄	4.28	1			2.609	201	2.605	60		
3.887	021	3.90	1	3.887	021			2.486	30	2.488	202̄, 131
3.520	002	3.520	10	3.520	002	2.404	003	2.408	10	2.404	003
2.810	022	2.801	?	2.807	022			2.355	10	2.353	201, 132̄
2.684	201̄					2.211	202	2.210	40		
2.674	130	2.678	4	2.693	200			2.078	15	2.077	203̄, 132
		2.519	9	2.516	201			1.944	5	1.947	202, 133̄
2.410	202̄	2.404	4			1.824	203	1.823	15		
2.401								1.715	10	1.713	204̄, 133
		2.337	1			1.616	060	1.616	60	1.616	060, 331̄
2.275	201	2.273	1			1.577	061	1.577	45	1.577	061, 330, 332̄
2.274	132̄					1.516	204	1.519	10		
		2.141	6	2.139	202	1.475	062	1.474	15	1.475	062, 331, 333̄
2.016	203̄	2.011	1			1.443	005	1.442	5	1.443	005
2.009	132̄					1.399	400	1.397	10		
1.902	133̄					1.374	401	1.373	10		
1.888	202̄	1.894	1					1.358	5	1.354	204, 135̄
		1.768	4	1.769	203	1.341	063	1.340	10	1.341	063, 332, 334̄
		1.693	?	1.710	241	1.305	402	1.302	5		
1.667	204̄	1.665	1			1.202	006	1.202	5	1.202	006
1.661	133̄										
1.565	134̄										
1.555	331̄: 060	1.555	7	1.555	060						
1.523		1.521	3	1.519	061						
1.519	061	1.473	1	1.473	204						
		1.425	1	1.423	062						
1.425	331	1.407	1	1.408	005						
1.423	062	1.261	1								
1.408	005	1.347	1	1.347	400						
		1.326	1	1.323	401						

A. Specimen from Ayrshire (Scotland) contains about 1 : 2 ratio of monoclinic and orthogonal forms.
d(calc.) based on the following cells:
Monoclinic, $a = 5.39$, $b = 9.33$, $c \sin \beta = 7.04$ Å, $\beta = 104.5^\circ$.
Orthogonal, $a = 5.39$, $b = 9.33$, $c = 7.04$ Å.
B. Specimen from Bluebell mine, Riondel, British Columbia.
1T $a = 5.598$, $b = 9.696$, $c = 7.213$ Å, $\beta = 90^\circ$.
1M $a = 5.598$, $b = 9.696$, $c = 7.439$ Å, $\beta = 104.2^\circ$.

TABLE 1.7.—*continued*

C. Caryopilite (Bailey, unpublished)						D. Baumite (Fron del and Ito, 1975)		
1T (calc.)		Observed		1M (calc.)		1T structure		
<i>d</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>
7.275	001	7.30	80	7.275	001	7.23	10	001
3.638	002	3.639	50	3.638	002	4.614	1	020
		2.825	60	2.822	201, 130	3.590	6	002
2.650	201	2.648	5			2.68	?	200
		2.521	100	2.523	202, 131	2.510	3	201
2.425	003	2.427	7	2.425	003	2.104	1	202
		2.382	20	2.384	201, 132	1.537	2	060
2.241	202	2.239	4					
		2.101	35	2.101	203, 132			
		1.968	20	1.970	202, 133			
1.846	203	1.850	2					
1.819	004	1.820		1.819	004			
		1.731	25	1.732	204, 133			
1.643	060	1.643	35	1.643	060, 331			
		1.626	20	1.628	203, 134			
1.603	061	1.603	25	1.603	061, 330, 332			
1.533	204	1.540	3					
1.497	062	1.497	10	1.497	062, 331, 333			
1.455	005	1.453	10	1.455	005			
		1.445		1.446	205, 134			
		1.420	10	1.420	401, 261			
		1.377	15	1.377	400, 262			
		1.367	20	1.367	204, 135			
1.295	205	1.295	10	1.295	401, 263			
		1.260	2	1.261	404, 262			
1.219	064	1.215	2	1.219	064, 333, 335			
1.212	006			1.212	006			
		1.192	10	1.192	402, 264			
		1.154	5	1.156	405, 263			
1.089	065	1.087	5	1.089	065, 334, 336			
				1.086	403, 265			

C. Specimen from Hurricane Claim, Olympic Peninsula, Washington, U.S.A.
1T $a \approx 5.692, b = 9.858, c = 7.275 \text{ \AA}, \beta = 90^\circ$.
1M $a \approx 5.692, b = 9.858, c = 7.518 \text{ \AA}, \beta = 104.6^\circ$.
D. Specimen from Franklin, New Jersey.
 $a \approx 5.37, b \approx 9.22, c \approx 7.09 \text{ \AA}$.

FeO (Fron del and Ito, 1975). The powder pattern (Table 1.7) is that of a group C polytype, but no diagnostic $k \neq 3n$ reflections are present to identify a specific stacking sequence.

2.4.12 Greenalite $\sim(\text{Fe}^{2+}, \text{Mg}, \text{Mn})_3\text{Si}_2\text{O}_5(\text{OH})_4$

For 1T: Space group = $P31m$
 $a = b \approx 5.60, c \approx 7.21 \text{ \AA}, \alpha \approx \beta = 90^\circ, \gamma = 120^\circ$
For 1M: Space group = Cc
 $a \approx 5.60, b \approx 9.70, c \approx 7.44 \text{ \AA}, \beta \approx 104.2^\circ$

Early attempts by a number of workers at indirect chemical analyses of type greenalite from the Biwabik iron-formation of Minnesota suggested a purely siliceous tetrahedral sheet and a primarily ferrous octahedral sheet with smaller amounts of Mg, Mn, Al, and Fe^{3+} . Later electron microprobe analysis of greenalite from the Gunflint iron-formation of Canada by Floran and Papike (1975) gave average values of only 3.8% MgO, 0.1% MnO, and 0.2% Al_2O_3 as possible substituting elements for Fe.

Gruner (1936) was the first to point out the similarity of the greenalite X-ray powder pattern to those of the platy serpentines. Steadman and Youell (1958) confirmed that the structure is that of a 1:1 layer silicate and suggested that it is based on a 1-layer orthogonal cell. This would correspond to the 1T structure, so that greenalite would differ from lizardite-1T and berthierine-1T primarily in its higher Fe-content and larger cell dimensions according to this analysis.

Guggenheim, Wilkes, and Bailey (in preparation) have examined pure samples of greenalite from several localities, however, which they show to be coherent intergrowths of a trigonal structure belonging to group C of Table 1.2 with minor amounts of a monoclinic structure belonging to group A. No $k \neq 3n$ reflections were observed that would indicate the precise polytypes involved. The simplest polytypes in groups C and A, namely $1T$ and $1M$ respectively, have been assumed for the heading of this section and in Table 1.7. The monoclinic layers are believed to exist as small isolated islands within the trigonal host and to have tetrahedral sheets that are inverted in order to fit better with the lateral dimensions of the Fe-rich octahedral sheets. In electron diffraction photographs this intergrowth leads to groups of six satellite spots around each central diffraction spot due to a 20 Å domain structure. The authors find no evidence from the electron diffraction photographs or from dark field photographs to support the suggestion of Floran and Papike (1975) that greenalite may have a sinusoidal wave structure similar to that of antigorite.

2.4.13 *Caryopilite* $\sim (\text{Mn}_{3-x}^{2+}\text{R}_x^{3+})(\text{Si}_{2-x}\text{R}_x^{3+})\text{O}_5(\text{OH})_4$

$$a \cong 5.65, b \cong 9.78, c \cong 7.50 \text{ Å}, \beta \cong 104.5^\circ$$

Caryopilite often has been called bementite in the past. Kato (1963), however, has shown that two different Mn-rich materials have been called bementite in the literature. One mineral from Franklin, New Jersey, U.S.A., apparently belongs to the friedelite group of minerals. The name bementite is reserved now for this mineral. The other bementite-like mineral was described by Kato as of the chamosite-type, and was believed to have a structure similar to that of chamosite (now called berthierine). Materials called caryopilite and ektropite are of this type also, and the former name has priority for this serpentine-like mineral. Shirozu and Hirowatari (1955) have described the structure as the $1M$ structural type. Kato (1963), however, has detected satellite spots on electron diffraction photographs that are similar to the satellites observed for greenalite and thus indicate a more complex structure. Guggenheim, Wilkes, and Bailey (in preparation) interpret both electron and X-ray data for caryopilite as due to a coherent intergrowth of a small amount of a trigonal phase (group C) with a monoclinic phase (group A).

Tosalite is believed to be an intermediate member of the greenalite-caryopilite series (Yoshimura, 1967). *Grovesite*, originally stated by Bannister *et al.* (1955) to be a Mn-serpentine, has been shown by Peacor *et al.* (1974) to be a 1-layer Mn-chlorite instead of a serpentine.

2.4.14 *Cronstedtite* $(\text{R}_{3-x}^{2+}\text{Fe}_x^{3+})(\text{Si}_{2-x}\text{Fe}_x^{3+})\text{O}_5(\text{OH})_4$ with $x \sim 0.5$ to 1.0

$$a \cong 5.49, b \cong 9.51, c \sin \beta \cong n \times 7.08 \text{ Å}$$

Cronstedtite occurs as jet black crystals of brilliant vitreous luster in low temperature hydrothermal sulfide veins. It is distinguished chemically by the unusual tetrahedral composition $\text{Si}:\text{Fe}^{3+} \cong 1:1$ and by nearly complete occupation of octahedral sites by Fe. There still is some question as to the ideal ratio of $\text{Fe}^{2+}:\text{Fe}^{3+}$ in the octahedral sites (or whether this ratio is variable), and as to the manner of cation-anion charge balance. Hendricks (1939a) proposed a structural formula based on an analysis of Kisbanya, Roumania, cronstedtite by Gossner (1935) in which the octahedral Fe is primarily ferrous and the tetrahedral substitution of Fe^{3+} is compensated by replacing the apical oxygen by (OH) for each Fe^{3+} -tetrahedron. Brindley (1961) prefers to balance the tetrahedral Fe^{3+} with an equivalent amount of octahedral Fe^{3+} and to maintain the normal anion composition of a 1:1 layer silicate of $\text{O}_5(\text{OH})_4$.

Both Gossner (1935) and Hendricks (1939a) have confirmed that cronstedtite is based on a 1:1 type layer. More detailed studies by Frondel (1962) and Steadman and Nuttall (1963, 1964)

have shown an extraordinary amount of variation in the layer stacking sequences. Frondel (1962) recognized crystals with periodicities of 1, 2, 3, and 9 layers as well as those with considerable stacking disorder. Steadman and Nuttall (1963, 1964) found eight different stacking sequences in an examination of about 200 crystals from nine localities. These can be correlated with the ideal polytypes $1T$, $1M$, $2T$, $2H_1$, $2H_2$, $2M_1$, and $3T$ of Fig. 1.5, plus the same hybrid $6R_2$ structure found in amesite in which interlayer shifts of $b/3$ along Y alternate regularly with zero interlayer shifts.

Steadman and Nuttall (1963) refined the atomic positions of the $1T$, $3T$, and 6-layer structures to a slight extent by electron density maps plus trial-and-error adjustment of individual atomic parameters. They found that the large lateral dimensions of the tetrahedral sheet due to the presence of 50% Fe^{3+} are reduced by tetrahedral rotations between 2° and 8° to fit the slightly smaller dimensions of the Fe-rich octahedral sheet. The direction of rotation was found to be governed by the attraction of the basal tetrahedral oxygens of one layer to the octahedral cations of the layer below rather than to the cations in the same layer or to the OH groups in the layer immediately below. This direction of rotation was observed to increase the O—OH interlayer bond distance in the 1-layer and 6-layer structures, but to decrease it in the 3-layer structure. For the partly refined structures the symmetry of the ideal space groups permits octahedral and tetrahedral cation ordering only in the 3-layer and 6-layer structures, and no evidence for such ordering was observed for these two crystals.

Henry (1974) has presented evidence for ordering of tetrahedral Si and Fe^{3+} in cronstedtite- $2H_2$ by the observation of $06l$, l odd reflections (as indexed on an orthogonal cell). Radoslovich and Norrish (1962) have shown that these reflections should have zero intensities in a truly hexagonal structure in which the tetrahedral cations have y coordinates that are exact multiples of $b/12$ and are disordered. In hexagonal cronstedtite, calculations show that the observed intensities must be due to the differences in X-ray scattering powers of ordered tetrahedral Si and Fe^{3+} plus the differences in positions of their coordinating oxygens as a consequence of ordering. Henry and Bailey (in preparation) have confirmed tetrahedral ordering for cronstedtite- $2H_2$ by determination of two quite different tetrahedral mean bond lengths in the refined structure. In this structure the direction of tetrahedral rotation is such as to move the basal oxygens away from the octahedral cations of the adjacent layer and towards both the octahedral cations in the same layer and the surface OH groups of the adjacent layer.

2.5 Kaolin minerals

2.5.1 General

The kaolin minerals include all of the dioctahedral 1:1 layer silicates. As in all natural dioctahedral minerals, the vacant and occupied octahedral sites form a distorted hexagonal pattern in which each large vacancy is surrounded by six smaller occupied sites (Fig. 1.9). Newnham (1961), Radoslovich (1963a), and Takeuchi (1965) have pointed out that enlargement of the vacant site is due to mutual repulsion between adjacent Al^{3+} cations and concomitant movement of coordinating anions toward one another along the shared octahedral edges. Shortening of the shared edges automatically enlarges the unshared lateral edges around the vacancy, twists other unshared lateral edges, and thins the entire octahedral sheet. Another way of viewing the enlargement of the vacant site is simply that there is no central cation present to pull in the neighboring anions by tight bonds.

The coordinating oxygen anions in the plane immediately below the octahedral cations are also the apices of tetrahedra. Tetrahedra linked in this manner to the smaller, twisted octahedral edges can adjust their orientations by the mechanism of tetrahedral rotation. The enlarged edges

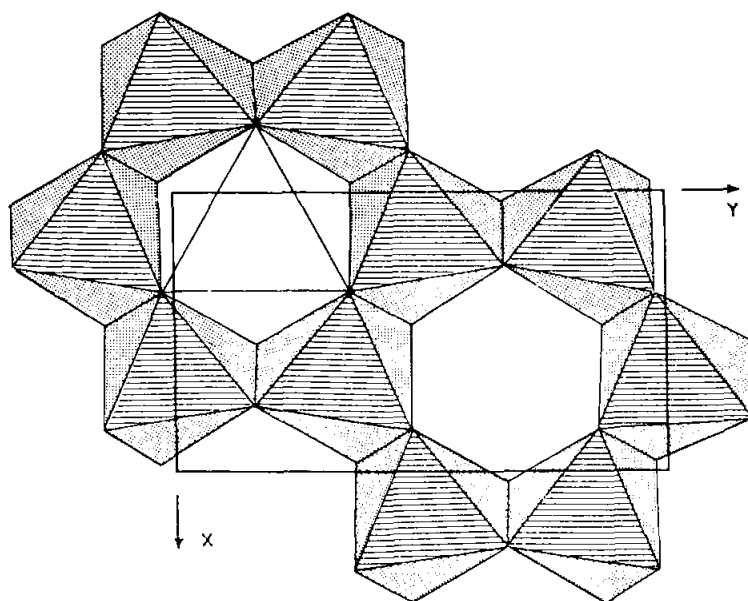


FIG. 1.9. Pattern of occupied octahedra (shaded) surrounding larger vacant site in dickite structure.

around the vacant octahedral site, however, are larger than the corresponding distances between tetrahedral apices. Articulation is possible here only by tilting the tetrahedra so that the apices of adjacent tetrahedra point slightly away from one another along each elongate octahedral edge. The tilting plus compression of the basal oxygen surface due to tetrahedral rotation have the effect of elevating the bridging oxygen between each pair of tilted tetrahedra by 0.1 to 0.2 Å above the other two basal oxygens in a direction toward the vacant octahedral site. The non-elevated basal oxygens form zigzag ridges that run parallel to $[110]$ if the vacant site is at position C in Fig. 1.3, or parallel to $[1\bar{1}0]$ if the vacant site is at position B. In order that the O—OH interlayer bond involving the elevated oxygen should not be significantly longer than the other two such bonds, its bonding OH also should be elevated above the surface of the layer below. This is most easily possible if that OH lies on a shared octahedral edge that is not anchored by an apical tetrahedral oxygen but instead by the inner OH, *i.e.* the entire OH—OH shared edge can be elevated. Giese and Datta (1973) have shown by lattice energy calculations for all three kaolin minerals that the H^+ proton associated with the inner OH is positioned *inside* the octahedral sheet so that the O—H bond is $12\text{--}19^\circ$ from horizontal and points toward the vacant octahedral site. This orientation appears to be a characteristic of a 1:1 layer, as similar calculations for dioctahedral 2:1 micas show that the O—H bonds point *away* from the octahedral sheet (Giese, 1971). Adams *et al.* (1976) have used powder neutron diffraction data to show for a kaolinite-formamide intercalate complex that the inner O—H bond is oriented about 25° from the horizontal.

Newnham (1961) showed that six 1-layer and 108 2-layer dioctahedral structures are possible theoretically for the kaolin minerals. He justified nature's preference for kaolinite as the only observed 1-layer form and dickite and nacrite as the only 2-layer forms on the basis of three structural features: (1) the highly charged Si and Al cations tend to avoid superposition in adjacent layers, (2) the basal oxygens rotate toward the hydroxyls in the adjacent layer to strengthen the interlayer O—OH bond, and (3) the elevated oxygen in the tetrahedral surface should match with an elevated hydroxyl on the surface of the layer below.

The dickite and nacrite structures are the only 2-layer forms that satisfy all three criteria and are considered by Newnham to be the most stable configurations. The kaolinite structure does not satisfy the criterion of matching of the elevated oxygen and hydroxyl, but is the only 1-layer

Kaolin minerals—diagnostic X-ray diffraction lines (cf. Fig. 1.10)

Kaolinite				Dickite			
	d (Å)	I	hkl		d (Å)	I	hkl
1.	3.842	$4\frac{1}{2}$	$02\bar{1}$	1.	3.262	1	023
2.	3.143	$2\frac{1}{2}$	$11\bar{2}$	2.	3.097	1	$11\bar{4}$
	3.096	3	$1\bar{1}2$	3.	2.937	1	113
3.	2.750	$3\frac{1}{2}$	022	4.	2.795	1	024
4.	2.340	9	$20\bar{2}, 1\bar{3}1$	5.	2.324	$9\frac{1}{2}$	$132, 20\bar{4}$
5.	2.290	8	131	6.	2.211	$1\frac{1}{2}$	$13\bar{4}, 202$
6.	2.184	3	201	7.	1.974	4	$134, 20\bar{6}$
7.	1.992	5B	$20\bar{3}$	8.	1.860	$1\frac{1}{2}$	$13\bar{6}, 204, 22\bar{3}$
	1.986		$1\bar{3}2$	9.	1.457	$1\frac{1}{2}$	$330, 062, 33\bar{4}$
8.	1.839	4	$1\bar{3}\bar{3}, 202$	10.	1.375	$1\frac{1}{2}$	$33\bar{6}, 064, 332$
9.	1.619	6	$133, 1\bar{5}1$	11.	1.318	$3\frac{1}{2}$	$1, 3, 10; 208$
10.	1.545	5B	$22\bar{4}, 1\bar{3}4$				
	1.538		$203, 31\bar{3}$				
11.	1.339	4	$13\bar{5}$				
12.	1.307	3	$1\bar{3}\bar{5}$				
	1.302	3	204				

$a = 5.139 \text{ Å}$
 $b = 8.932$
 $c = 7.371$
 $\alpha = 91.6^\circ$
 $\beta = 104.8$
 $\gamma = 89.9$

$a = 5.150 \text{ Å}$
 $b = 8.940$
 $c = 14.736$
 $\beta = 103.6^\circ$

Nacrite				Metahalloysite			
	d (Å)	I	hkl		d	I	hkl
1.	3.476	2	$20\bar{4}$	1.	4.45	10	02.11
	3.413	2	112	2.	2.57	4	20.13
2.	3.118	1	$11\bar{4}$	3.	2.22	$\frac{1}{2}$	04.22
	3.060	2	202	4.	1.685	2	$24, 15, 31$
3.	2.927	1	113	5.	1.285	$1\frac{1}{2}$	40.26
4.	2.432	10B	$31\bar{4}, 022$	6.	1.235	$1\frac{1}{2}$	$42, 17, 35$
	2.404		310				
	2.395		006				
5.	2.280	$\frac{1}{2}$	$31\bar{5}, 023, 204$				
	2.246	$\frac{1}{2}$	311				
6.	2.111	$\frac{1}{2}$	$31\bar{6}$				
	2.092	$\frac{1}{2}$	024				
	2.070	1	$312, 22\bar{4}$				
7.	1.937	$1\frac{1}{2}$	$31\bar{7}, 22\bar{5}, 116$				
	1.917	$1\frac{1}{2}$	025				
	1.897	$1\frac{1}{2}$	313				
8.	1.682	2B	$42\bar{2}, 130, 22\bar{7}+$				
	1.655		$42\bar{4}, 51\bar{2}, 515+$				
9.	1.627	$1\frac{1}{2}$ B	$13\bar{3}$				
	1.619		$51\bar{6}, 31\bar{9}, 51\bar{1}$				
	1.605		027, 132				
10.	1.270	2B	$62\bar{6}, 338$				
	1.263		$042: 62\bar{2}; 3, 1, 1\bar{2}$				

$a = 8.909 \text{ Å}$
 $b = 5.146$
 $c = 15.697$
 $\beta = 113.7^\circ$

$a = 5.15 \text{ Å}$
 $b = 8.92$
 $c \sin \beta = 7.214$

form to satisfy both of the other two criteria. Some of Newnham's theoretical structures are equivalent to one another, and Zvyagin (1962) later showed that there are only 52 theoretical dioctahedral structures with periodicities between one and six layers. Radoslovich (1963a) has extended Newnham's stability analysis by pointing out that the O—OH interlayer bond extending out from each surface OH ideally should be nearly coplanar with the bonds from the OH to its two coordinating Al cations. The favored stacking sequences that position the basal oxygens so as to minimize the angular strain in such directed interlayer O—OH bonds are those of kaolinite, dickite, and nacrite. Wolfe and Giese (1973) have made quantitative calculations that show that the three 1-layer stacking sequences that lead to the lowest overall electrostatic energy potential for the entire crystal are those of the two enantiomorphic forms of kaolinite plus an as yet unobserved monoclinic 1-layer structure with a vacant octahedral site at position A of Fig. 1.3.

Bailey (1963) has analyzed the structural differences between the three kaolin minerals, as follows. Kaolinite and dickite both are based on the $1M$ stacking sequence of layers, and would be identical if trioctahedral. In kaolinite the vacant octahedral site is in the same place in each layer, and can be located either at site B or site C in Fig. 1.3. Kaolinite with site B vacant is a mirror image of, and cannot be distinguished easily from, kaolinite with site C vacant. Location of the vacant site at either B or C imposes triclinic symmetry on the structure due to loss of the mirror plane that normally relates B to C in a trioctahedral structure. Ionic interactions also distort the structure to triclinic geometry as a separate anorthic effect. In dickite the vacant octahedral site alternates between B and C in successive layers to create a 2-layer structure. The alternation of vacant sites creates monoclinic glide planes parallel to (010) and balances the stress distribution in the two layers so that the cell shape remains monoclinic also. Thus, dickite can be considered as a regular alternation of right- and left-handed kaolinite layers, in one sense, or as a superstructure of the ideal $1M$ polytype due to a particular ordering pattern of octahedral cations and vacancies. Nacrite, on the other hand, is based on an entirely different stacking sequence of layers—that of the ideal trioctahedral $6R$ structure. The vacant octahedral site varies regularly in successive layers so that the resultant symmetry is reduced from rhombohedral to monoclinic, and an inclined Z-axis can be selected along which there is true 2-layer periodicity. The similarity in the structures of kaolinite and dickite and the contrast with that of nacrite can be seen by comparison of their X-ray powder patterns (Fig. 1.10, Table 1.8). Diagnostic reflections for the kaolin minerals are numbered on Fig. 1.10 and listed on the opposite page. The species *halloysite* with water between the layers and its dehydrated counterpart both incorporate considerable interlayer randomness and are considered in Chapter 2.

2.5.2 Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

$$\begin{aligned}\text{Space group} &= C1 \quad a = 5.139, b = 8.932, c = 7.371 \text{ \AA}, \\ &\quad \alpha = 91.6^\circ, \beta = 104.8^\circ, \gamma = 89.9^\circ\end{aligned}$$

The triclinic nature of *kaolinite* was recognized first by Brindley and Robinson (1945, 1946), who found that the indexing of X-ray powder patterns required a unit cell shape slightly distorted from the monoclinic geometry reported originally by Ross and Kerr (1931) from microscopic evidence and by Gruner (1932a) from X-ray evidence. Gruner (1932a) had postulated two alternative 2-layer monoclinic structures for kaolinite that appeared to satisfy the powder diffraction data equally well. Both structures incorporated a resultant interlayer shift of $-a/2$ per two layers. Brindley and Robinson on the basis of better powder data determined correctly that kaolinite instead must have a 1-layer structure in which adjacent layers are shifted by $-a/3$, i.e. a dioctahedral modification of the $1M$ structure. Although the structure was not refined further at

that time, Brindley and Nakahira (1968) later were able by comparison with the better-refined structure of dickite to explain the triclinic cell shape as a result of the optimum mode of superposition of dioctahedral layers that have been distorted to ditrigonal symmetry by tetrahedral rotation.

Although vermicular, macroscopic crystals of kaolinite exist, Mansfield and Bailey (1972) have shown that these always are complexly intergrown by $\pm 120^\circ$ pseudotwin rotations about the layer normal and sometimes, in addition, by 180° twin rotation about the X-axis. Drits and Kashaev (1960) reported a single crystal structure determination of kaolinite. Their description of certain of the X-ray reflections obtained as being doubled and requiring a different scale factor relative to single spots suggests that the crystal used was twinned in a similar manner, and that details of the refinement accordingly should be used with caution. This problem does not apply to a refinement of the structure by Zvyagin (1960) using texture electron diffraction photographs of a powder. Zvyagin used about 100 reflections to refine the structure by a series of electron density projections and difference maps on (100) and (010). The individual structural amplitudes F_{obs} , obtained by applying various geometric corrections to the observed intensities, can be compared to the F values calculated from the final structure to yield a residual value (or reliability factor) R of 21%.

In the structure determined by Zvyagin adjacent tetrahedra are rotated in opposite directions

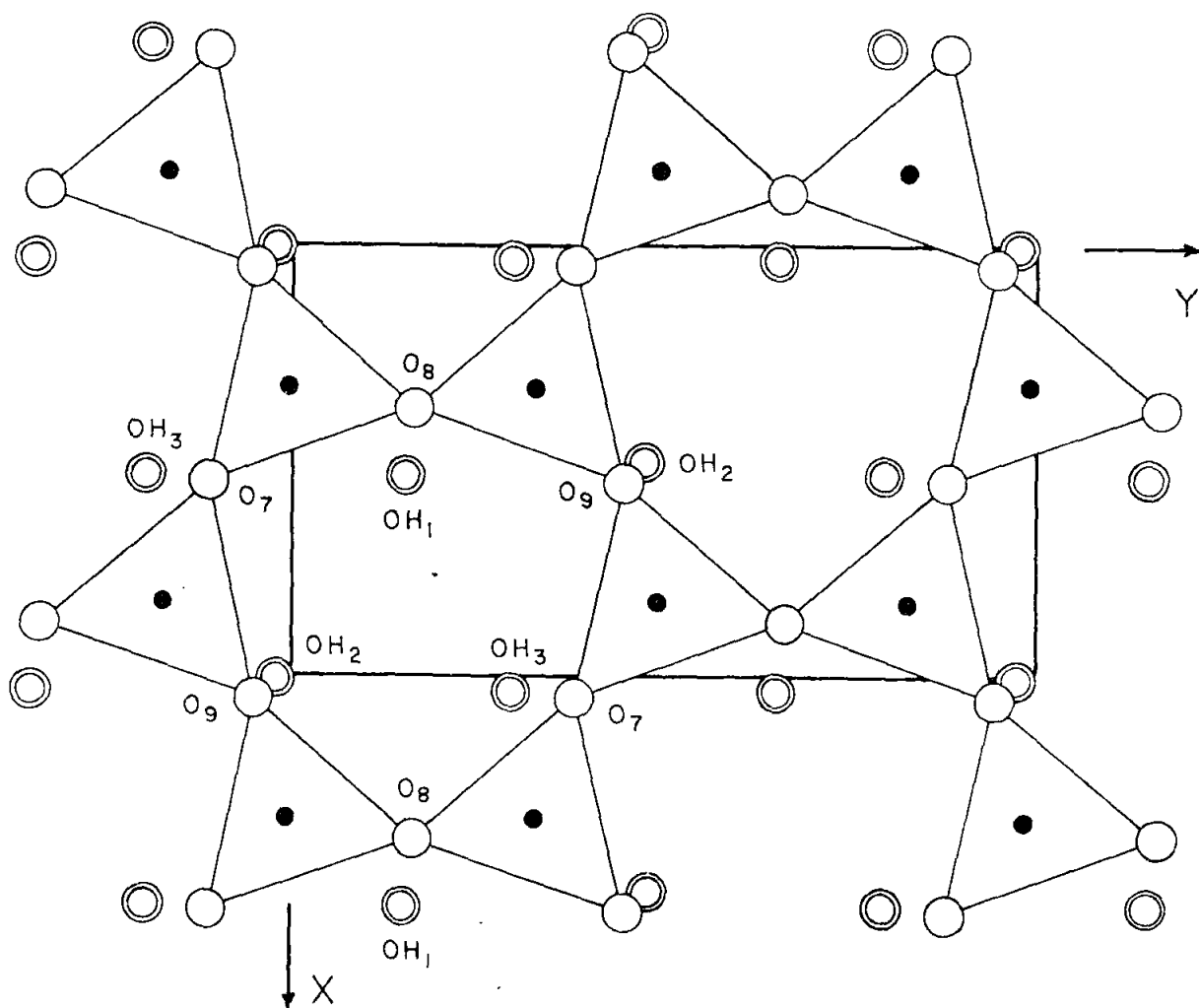


FIG. 1.11. Orthogonal projection of kaolinite structure on XY plane to show pairing of surface O and OH of adjacent layers. Structure modified from that of Zvyagin (1960) to show tetrahedra pointing up.

by 11.4° to form a ditrigonal motif. The Al and Si atoms are not situated at the centers of their coordination groups, but are displaced slightly away from one another—Si toward the basal oxygens and Al toward the upper hydroxyls. The vacant site is located at position B. The basal oxygen surface does not have the ideal corrugation shape found in other dioctahedral layer silicates, probably because the ideal geometry of matching such corrugated surfaces across the interlayer space is possible in a 1-layer structure only if the vacant site is at position A. In kaolinite, two basal oxygens are elevated into the layer, instead of just one, to create a series of grooves and ridges running parallel to [100]. The elevation of one of the oxygens O(9) can be explained by the expected tetrahedral tilt around the vacant site. Unexpectedly, O(9) is found to be paired with a similarly elevated OH(2) from the adjacent layer (Fig. 1.11), even though OH(2) lies on a shared octahedral edge that is anchored by an apical oxygen rather than by an inner OH. The reason for the elevation of a second basal oxygen O(7) has not been explained on structural grounds. It is paired with OH(3), which lies on an OH—OH shared octahedral edge within its layer but is not elevated. The O(7)—OH(3) distance is the largest ($3.024 \text{ \AA}$) of the three O—OH interlayer contacts. Giese and Datta (1973) have used Zvyagin's atomic coordinates to calculate that the minimum electrostatic energy is given if the O—H bond from OH(3) is oriented only 14° from the horizontal and effectively does not participate in the interlayer hydrogen bonding. This is in accord with energy calculations from infrared absorption spectra by Wieckowski and Wiewióra (1976). The latter authors use a model of bent, rather than linear, hydrogen bonds to explain the interlayer cohesion in kaolinite, and they classify the bond from OH(3) as a declining hydrogen bond of very low energy.

In addition to well-crystallized varieties, kaolinite occurs with varying degrees of stacking disorder, as discussed in Chapter 2. The species *anauxite*, originally believed to have a higher ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ than kaolinite, has been discredited and shown to be a mixture of kaolinite and amorphous silica (Langston and Pask, 1968; Allen, Fahey, and Ross, 1969; Bailey and Langston, 1969). A multi-layer monoclinic kaolinite described by Krstanović and Radošević (1961) has been shown by Mansfield and Bailey (1972) to be normal triclinic kaolinite that appears monoclinic because of two types of twinning or pseudotwinning that are present.

2.5.3 *Dickite* $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Space group = Cc $a = 5.15$, $b = 8.94$, $c = 14.736 \text{ \AA}$, $\beta = 103.58^\circ$

The first structures proposed for *dickite* were by Gruner (1932b) on the basis of X-ray powder data. Gruner postulated two 2-layer monoclinic structures for *dickite*, both being dioctahedral modifications of the $2M_1$ stacking sequence. Because of discrepancies between some of Gruner's observed and calculated intensities, Newnham and Brindley (1956) reinvestigated the structure with single crystal data. They showed that, instead of the zigzag $2M_1$ sequence of layers, each *dickite* layer must be shifted in the same direction, and the vacant octahedral site must alternate in adjacent layers between the B and C sites of Fig. 1.3. The structure was refined in more detail by Newnham (1961) by a series of electron density and difference maps projected on (100) and (110). A total of 420 single crystal X-ray reflections were used in the latter study to attain a final reliability factor R of 7.5%.

In the refined structure each layer was found to be distorted by rotation of the upper and lower octahedral triads by 8.2° as a result of shortening of shared edges (Fig. 1.9) and by tetrahedral rotation of 7.3° . The direction of tetrahedral rotation is to move the basal oxygens toward the Al cations in the same layer, which also is in a direction that would shorten the interlayer O—OH bond distances. The Al cations are closer to the uppermost plane of OH anions than to the lower

O,OH plane. Newnham explained this as due to repulsion of Al by Si, but Radoslovich (1963*a*) prefers an explanation involving differences in bond strengths due to polarization of the surface OH groups by the H^+ protons and the adjacent Al^{3+} cations. Calculations of minimum electrostatic energies by Giese and Datta (1973) and of lattice energy by Giese (1973*a*) indicate all three surface O—H bonds are oriented $66\text{--}76^\circ$ from the horizontal and participate in the interlayer hydrogen bonding.

Each dickite layer is shifted by $a/3$, as in kaolinite. The original axes were selected to give a β angle of 96.73° to be in accord with earlier optical goniometric measurement. This inclines the Z axis in a direction opposite to the actual layer shift, however, so that a different and more appropriate cell orientation has been assumed at the front of this section. This gives a β angle of 103.58° and a cell shape directly comparable to that of the closely related kaolinite structure (Bailey, 1963). Partial randomness in stacking is observed in dickite (Schroeder and Hayes, 1968), but less frequently than in kaolinite.

2.5.4 Nacrite $Al_2Si_2O_5(OH)_4$

Space group = Cc $a = 8.909$, $b = 5.146$, $c = 15.697$ Å, $\beta = 113.70^\circ$

The correct structure of *nacrite*, first reported by Hendricks (1939*b*), has the layer stacking sequence of the ideal trioctahedral $6R$ structure. Each successive layer is shifted by $-1/3$ of the 8.9 Å lateral repeat distance, and alternate layers are rotated by 180° , *i.e.* octahedral sets of positions I and II are occupied in alternate layers. The vacant octahedral site alternates between B and C (allowing for 180° rotation) in successive layers so that the symmetry is reduced from

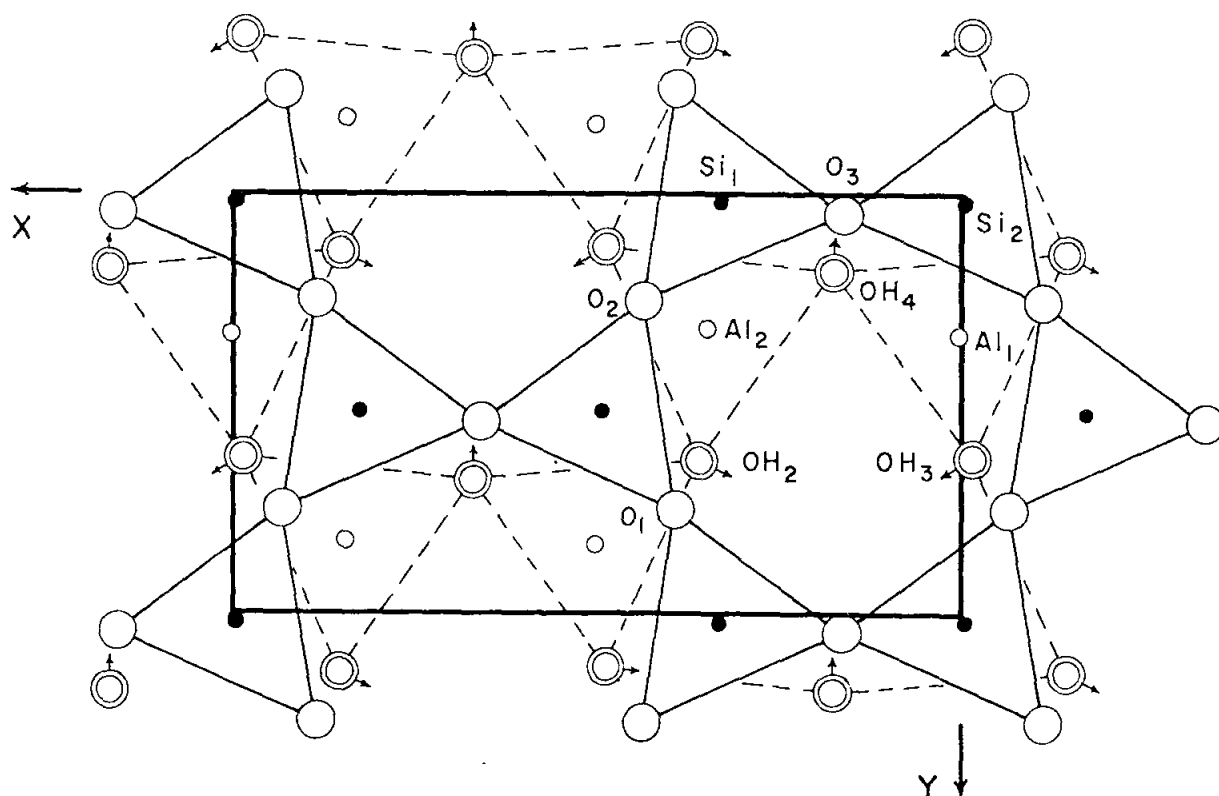


FIG. 1.12. Orthogonal projection of nacrite structure on XY plane to show interlayer pairing of basal oxygens of second layer (full lines) with surface hydroxyls of first layer (double circles). Arrows attached to OH groups show ideal directions of interlayer long hydrogen bonds on the assumption that each is coplanar with two Al—OH bonds below (modified from Blount *et al.*, 1969).

TABLE 1.8. X-ray powder data for kaolinite, dickite and nacrite; spacings in Å

A. Kaolinite (Indexing modified from Brindley, 1961)							
<i>d</i> (obs.)	<i>I</i>	<i>d</i> (calc.)	<i>hkl</i>	<i>d</i> (obs.)	<i>I</i>	<i>d</i> (calc.)	<i>hkl</i>
7.16	10+	7.14	001			1.472	24 $\bar{3}$
4.46	4	4.47	020	1.467	2	1.469	06 $\bar{1}$
4.36	5	4.36	1 $\bar{1}$ 0			1.467	33 $\bar{2}$
		4.34	110			1.455	33 $\bar{2}$
4.18	5	4.172	11 $\bar{1}$			1.453	15 $\bar{3}$
4.13	3	4.120	1 $\bar{1}$ $\bar{1}$	1.452	4B	1.452	330
3.845	4	3.842	02 $\bar{1}$			1.450	061
3.741	2	3.739	021	1.429	4	1.428	005
3.573	10+	3.571	002			1.405	242
		3.417	1 $\bar{1}$ $\bar{1}$	1.403	2	1.402	20 $\bar{5}$
3.372	4	3.372	111			1.391	33 $\bar{3}$
3.144	3	3.147	11 $\bar{2}$	1.390	2	1.390	06 $\bar{2}$
3.097	3	3.096	1 $\bar{1}$ $\bar{2}$			1.375	044
		2.832	02 $\bar{2}$	1.371	2	1.373	33 $\bar{3}$
2.753	3	2.750	022			1.369	33 $\bar{1}$
2.558	6	2.562	1 $\bar{3}$ 0	1.338	4	1.339	13 $\bar{5}$
		2.561	20 $\bar{1}$	1.305	6B	1.307	13 $\bar{5}$
2.526	4	2.531	13 $\bar{1}$			1.302	204
2.491	8	2.497	13 $\bar{1}$	1.292	2	1.291	26 $\bar{1}$
		2.488	200	1.282	5	1.285	26 $\bar{1}$
2.379	6	2.381	003			1.282	40 $\bar{1}$
2.338	9	2.340	20 $\bar{2}$	1.264	3	1.266	26 $\bar{2}$
		2.335	13 $\bar{1}$	1.246	3	1.248	26 $\bar{2}$
2.288	8	2.292	13 $\bar{1}$			1.244	400
2.247	2	2.249	13 $\bar{2}$			1.237	17 $\bar{1}$
2.186	3	2.183	201	1.235	3	1.236	170
2.131	3	2.128	02 $\bar{3}$			1.233	42 $\bar{2}$
2.061	2	2.060	22 $\bar{2}$			1.220	045
1.989	6	1.992	20 $\bar{3}$			1.219	350
		1.985	13 $\bar{2}$	1.217	1	1.217	35 $\bar{2}$
1.939	4	1.938	132			1.215	31 $\bar{3}$
1.896	3	1.895	13 $\bar{3}$			1.214	11 $\bar{6}$
1.869	2	1.870	04 $\bar{2}$	1.200	3	1.200	420
1.839	4	1.843	13 $\bar{3}$	1.190	3	1.191	42 $\bar{3}$
		1.834	202			1.190	006
1.809	2	1.809	11 $\bar{4}$	1.168	2	1.170	404
		1.805	22 $\bar{3}$			1.167	35 $\bar{3}$
1.781	4	1.785	004	1.124	1	1.125	264
1.707	2	1.708	22 $\bar{2}$	1.094	3	1.097	264
1.685	2	1.689	24 $\bar{1}$			1.092	402
		1.665	204	1.082	2	1.085	405
1.662	7	1.662	13 $\bar{3}$			1.082	263
		1.662	15 $\bar{1}$	1.057	1	1.058	263
1.619	6	1.620	15 $\bar{1}$	1.049	2	1.049	336
		1.619	133			1.047	06 $\bar{5}$
1.584	4	1.587	134	1.039	2	1.042	207
		1.548	224			1.039	136
1.542	5B	1.543	134			1.038	046
		1.541	31 $\bar{3}$	1.021	2	1.020	007
		1.536	203			1.019	136
		1.490	060	1.013	2	1.013	334
1.489	8	1.488	33 $\bar{1}$				
		1.485	33 $\bar{1}$				

A. $a = 5.146$, $b = 8.946$, $c = 7.388$ Å, $\alpha = 91.7^\circ$, $\beta = 104.7^\circ$, $\gamma = 89.8^\circ$.

TABLE 1.8.—*continued*

B. Dickite (Bailey, 1963)

<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)		
7.152	100	002	7.162	100	1.626	3	241	1.627	2		
4.442	30	{020 111}	4.470 4.439	{4 34}	38	1.611	10	{152 244}	{1.611 1.611}	{2 3}	5
4.362	30	110	4.368	38	1.589	10	{315 225}	{1.591 1.587}	{3 2}	5	
4.264	20	021	4.267	28	1.573	3	154	1.572	2		
4.119	65	112	4.124	60	1.557	20	{138 206}	{1.558 1.555}	{11 4}	15	
3.954	10	111	3.958	13	1.552	3	{153 228}	{1.550 1.549}	{1 2}	3	
3.790	55	022	3.792	45	1.526	3	312	1.524	2		
3.578	90	{113 004}	3.612 3.581	{9 77}	86	1.507	3	047	1.509	2	
3.428	20	112	3.430	19	1.489	40	{060 332}	{1.490 1.488}	{10 21}	31	
3.261	8	023	3.263	5	1.469	5	226	1.468	5		
3.095	10	114	3.098	6	1.457	15	{062 334}	{1.459 1.457}	{3 2}	10	
2.936	8	113	2.937	6	1.432	10	{330 229}	{1.456 1.434}	{5 3}	5	
2.794	10	024	2.795	8	1.428	3	{0,0,10 156}	{1.432 1.430}	{2 1}	2	
2.657	2	115	2.658	1	1.398	10	244	1.428	1		
2.558	35	{130 202}	2.561 2.557	{16 11}	27	1.392	10	{155 048}	{1.404 1.397}	{1 4}	9
2.505	50	{114 132 200}	2.527 2.509 2.503	{8 28 14}	50	1.375	15	{2,0,10 138}	{1.392 1.391}	{1 3}	
2.412	2	025	2.412	2	1.362	3	{064 314}	{1.376 1.376}	{3 1}	10	
2.386	15	006	2.387	9	1.329	3	{336 332}	{1.375 1.373}	{4 2}		
2.324	95	{132 204}	2.324 2.324	{60 26}	86	1.318	35	227	1.361	1	
2.211	15	{134 202}	2.212 2.207	{7 5}	12	1.296	2	{2,2,10 1,3,10}	{1.329 1.319}	{2 17}	26
2.183	2	220	2.184	2	1.296	2	208	1.317	9		
2.132	2	042	2.134	1	1.288	10	049	1.296	1		
2.104	5	026	2.106	3	1.279	4	{261 262}	{1.289 1.287}	{1 6}	10	
2.062	2	224	2.062	1	1.279	4	{402 260}	{1.285 1.280}	{3 2}	4	
2.026	3	043	2.024	1	1.263	6	404	1.279	2		
1.974	40	{206 134}	1.975 1.974	{11 20}	31	1.253	15	{066 338}	{1.264 1.263}	{1 1}	4
1.937	5	{225 116}	1.939 1.935	{2 1}	3	1.236	15	{334 264}	{1.262 1.254}	{2 6}	11
1.896	10	044	1.896	6	1.236	15	400	1.252	5		
1.860	15	{136 204}	1.861 1.857	{7 4}	14	1.223	5	{171 170}	{1.239 1.238}	{2 1}	
1.852	8	223	1.848	3	1.223	5	{262 353}	{1.235 1.234}	{3 2}	10	
1.805	10	226	1.806	5	1.223	5	406	1.234	2		
1.790	10	{008 118}	1.790 1.790	{6 1}	7	1.223	5	{316 421}	{1.226 1.224}	{1 2}	6
1.764	3	045	1.762	2	1.223	5	354	1.221	2		
1.717	3	224	1.715	2	1.223	5	350	1.220	1		
1.685	10	{241 312}	1.687 1.686	{2 1}	7	1.223	5				
1.668	10	{150 242}	1.683 1.683	{1 3}	7	1.223	5				
1.650	50	{152 240}	1.669 1.667	{2 5}	7	1.223	5				
1.643	5	{151 208 136}	1.657 1.651 1.650	{4 12 24}	40	1.223	5				
		{314 310}	1.642 1.640	{5 3}	8	1.223	5				

TABLE 1.8.—*continued*

B. Dickite (Bailey, 1963)											
<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)		
1.206	5	$\left\{ \begin{array}{l} 172 \\ 0,4,10 \\ 159 \\ 420 \\ 35\bar{5} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.208 \\ 1.206 \\ 1.205 \\ 1.205 \\ 1.199 \end{array} \right\}$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{array} \right\}$	5	1.191	10	$\left\{ \begin{array}{l} 0,0,12 \\ 2,0,\bar{1}\bar{2} \\ 1,3,10 \\ 26\bar{6} \\ 42\bar{6} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.194 \\ 1.192 \\ 1.191 \\ 1.189 \\ 1.189 \end{array} \right\}$	$\left\{ \begin{array}{l} 2 \\ 1 \\ 3 \\ 2 \\ 1 \end{array} \right\}$	9
						1.182	2	$\left\{ \begin{array}{l} 2,4,\bar{1}0 \\ 421 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.182 \\ 1.179 \end{array} \right\}$	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right\}$	2

B. $a = 5.150$, $b = 8.940$, $c = 14.736$ Å, $\beta = 103.58^\circ$. Specimen from Geneva mine, Michigan.

C. Nacrite (Bailey, 1963)									
<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)
7.178	100	002	7.186	100	2.039	2	{ 400	2.039	2
4.441	30	111	4.438	34			{ 117	2.033	1
4.361	80	{ 202	4.383	46	1.996	2	406	1.999	2
		{ 110	4.352	33			{ 222	1.969	4
4.130	70	{ 112	4.137	64	1.970	5	{ 208	1.960	3
		{ 200	4.079	6			{ 225	1.948	3
3.943	20	111	3.938	10	1.937	15	{ 317	1.938	14
3.629	5	113	3.633	8			{ 116	1.931	1
3.588	80	004	3.593	76	1.917	15	025	1.917	15
3.476	20	204	3.477	20	1.898	15	313	1.896	11
3.413	20	112	3.413	19	1.842	2	223	1.838	3
3.117	7	114	3.119	6	1.818	5	226	1.816	5
3.061	20	202	3.059	18	1.797	5	008	1.797	6
2.929	10	113	2.924	5			{ 402	1.783	1
2.675	2	115	2.677	2	1.774	5	{ 206	1.777	1
		{ 020	2.573	3			{ 318	1.773	7
2.571	10	{ 312	2.571	6	1.755	2	026	1.753	4
		{ 206	2.564	2			{ 408	1.739	4
		{ 313	2.541	3	1.736	5	{ 314	1.734	4
2.533	B 20	{ 021	2.533	8	1.710	2	224	1.706	2
2.518		{ 311	2.522	4			{ 227	1.685	2
		114	2.518	7			{ 423	1.684	1
					1.682		{ 131	1.683	1
2.432	60	{ 022	2.438	34			{ 514	1.681	1
		{ 314	2.422	38			{ 513	1.680	1
2.404	40	{ 310	2.404	38			{ 130	1.679	3
		{ 006	2.395	8			{ 422	1.676	4
2.321	15	116	2.319	5			{ 424	1.668	5
2.287	B 5	{ 315	2.287	4			{ 132	1.665	1
		{ 204	2.280	1			{ 515	1.660	2
2.273		{ 023	2.267	3	1.655		{ 512	1.657	3
2.247	5	311	2.245	6			{ 131	1.652	1
2.213	2	{ 222	2.219	1	1.627		{ 133	1.627	3
		{ 402	2.209	1			{ 319	1.622	5
2.179	2	220	2.176	2	1.619	10	{ 516	1.618	5
2.111	5	316	2.114	6			{ 511	1.614	1
2.092	5	024	2.092	7			{ 027	1.605	5
2.071	7	{ 312	2.069	8	1.605	5	{ 132	1.605	3
		{ 224	2.068	1	1.589	5	315	1.587	6

TABLE 1.8.—*continued*

C. Nacrite (Bailey, 1963)									
<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i> (calc.)
1.574	5	{ 225 426 134	1.580 1.579 1.572	2 2 3	1.287	B 5	{ 040 624 625 4,0,12 138 041 623 6,0,10	1.287	1
1.558	5	{ 228 510 118	1.559 1.555 1.548	2 1 1				1.286	2
1.531	5	{ 421 404	1.536 1.529	1 4				1.283	1
1.514	2	{ 427 518 4,0,10	1.513 1.492 1.490	1 1 1	1.282	B 20	{ 138 041 623 6,0,10	1.282	2
1.486	40	{ 3,1,10 332 604	1.488 1.485 1.484	10 20 10				1.281	1
1.473	5	{ 028 422	1.473 1.465	8 3				1.281	1
1.460	20	{ 226 606 316 334 330	1.462 1.461 1.458 1.458 1.451	4 1 9 2 4	1.270	B 20	{ 626 338 3,1,12 042 622	1.278	1
1.441 B	2	{ 602 229 428 0,0,10	1.446 1.444 1.441 1.437	2 3 1 2				1.277	1
1.415	4	{ 519 512	1.419 1.412	1 2				1.271	6
1.381	5	{ 608 336	1.385 1.379	2 3	1.263	B 5	{ 626 338 3,1,12 042 622	1.270	1
1.369	5	{ 3,1,11 332	1.370 1.366	5 2				1.270	1
1.357	5	{ 600 029 137 227	1.360 1.357 1.356 1.355	1 3 1 2				1.267	4
1.342 B	3	{ 317 2,2,10	1.343 1.339	3 2	1.254	3	{ 228 0,2,10 334	1.266	6
1.317 B	3	{ 136 406	1.324 1.314	1 2				1.261	6
								1.259	1
					1.244	3	{ 0,2,10 334	1.255	4
								1.255	2
								1.247	1
					1.235	B 5	{ 602 318 043	1.243	4
								1.242	2
								1.235	1
					1.231	3	{ 715 534 241 716 714 240	1.235	2
								1.235	1
								1.231	2
					1.208	5	{ 714 240 535 243	1.231	2
								1.227	2
								1.226	1
					1.197	3	{ 535 243	1.225	1
								1.209	1
								1.207	2
					1.184	5	{ 244 531	1.207	1
								1.198	2
								1.195	1
					1.166	3	{ 718 242 629 530 3,1,13	1.186	1
								1.184	1
								1.182	1
					1.160	6	{ 426 719 0,2,11 621 2,2,12 6,0,12	1.176	1
								1.170	1
								1.167	1
								1.165	1
								1.164	1
								1.160	1
								1.159	1

C. $a = 8.909, b = 5.146, c = 15.697 \text{ \AA}, \beta = 113.60^\circ$. Specimen from Tracy mine, Michigan.

rhombohedral to monoclinic. Because of this pattern of vacant sites, an inclined Z axis can be selected along which there is 2-layer rather than 6-layer periodicity (Newnham, 1961; Bailey, 1963). A second consequence of the pattern of vacant sites is that the monoclinic (010) symmetry plane is normal to the 5.15 Å repeat direction. This requires interchange of the X and Y axes in nacrite from their usual designations in layer silicates ($a = 5.1, b = 8.9 \text{ \AA}$).

The structure has been refined by Blount, Threadgold, and Bailey (1969) by electron density and least squares methods using 814 single crystal reflections. The 1:1 layer is found to be

distorted in a manner very similar to dickite. Al–Al repulsion shortens the octahedral shared edges, rotates the octahedral triads by an average angle of 6.2° , and enlarges the vacant octahedral site. The SiO_4 tetrahedra are rotated by 7.3° in a direction that is both toward the Al in the same layer and toward the nearest OH in the layer below. The corrugations in the basal surfaces run parallel to $[110]$ and $[1\bar{1}0]$ in successive layers and mesh ideally across the interlayer space. The O–OH interlayer bonds average $3.00 \text{ \AA}$ in length and, as in dickite, the elevated O(1)–OH(2) distance is longer ($3.06 \text{ \AA}$) than those of the other two (2.97 – $2.98 \text{ \AA}$). In this case, however, Giese and Datta (1973) have calculated that the elevated interlayer contact is not a true interlayer hydrogen bond. The O–H bond coming from OH(2) is inclined only 38° from the (001) plane. The stacking arrangement in nacrite imposes more strain on the directed O–OH bonds (Fig. 1.12) than in dickite and kaolinite, as only one of the three basal oxygens O(3) is located so it can pair up ideally with a directed hydrogen bond [from OH(4)].

Zvyagin, Soboleva, and Fedotov (1972) also have refined the nacrite structure using high voltage electron diffraction data from a powder. Their results are similar to those of Blount *et al.* cited above, except for a smaller tetrahedral rotation angle of 3.3° , which they attribute to the inhibiting influence of the octahedral cations in the adjacent layer. They prefer to use a smaller β angle of 100° rather than the 114° angle selected by Blount *et al.* as giving a cell shape directly related to the amount of interlayer shift.

3. TALC-PYROPHYLLITE GROUP

3.1 Introduction

Talc and pyrophyllite are the trioctahedral and dioctahedral members, respectively, of the simplest form of 2:1 layer. These 2:1 layers are electrostatically neutral, in the ideal case, with no interlayer material present. Giese (1975) has calculated that even for neutral layers the interlayer van der Waals bonding is supplemented by a small ionic attraction between adjacent layers. Natural specimens commonly exhibit small amounts of tetrahedral and octahedral substitution, however, so that the interlayer forces then are supplemented by additional ionic attractions.

Structural variability between different talc specimens and between different pyrophyllite specimens theoretically can arise because of the possibility of (1) intralayer tetrahedral shifts of $a/3$ along different X-axes in adjacent layers, (2) shifting adjacent neutral layers in different directions, and (3) for dioctahedral pyrophyllite the location of the vacant octahedral site at different positions in adjacent layers. But in actuality only the second factor is needed to explain differences observed to date. The reader is referred to the section on micas and Fig. 1.14 for a more detailed discussion of the possible tetrahedral shifts within a 2:1 layer.

The stacking of adjacent 2:1 layers is restricted neither by the need for the superposition of hexagonal rings around interlayer cations, as in micas, nor by the need for optimum hydrogen bond positions with interlayer materials, as in all other 2:1 layer types. Structural studies have shown that the oxygen surfaces in adjacent layers in both talc and pyrophyllite do not adopt the closest packing possible. Instead, four of the six basal oxygens within an hexagonal ring of an upper layer superimpose approximately at the midpoint of a tetrahedral edge (*i.e.* between two oxygens) of an hexagonal ring of the layer below (Fig. 1.13). This arrangement, which gives an interlayer shift of about $0.3a$ along one of the three pseudohexagonal X-axes, provides a minimum amount of Si–Si repulsion between adjacent layers (Zvyagin, Mishchenko, and Soboleva, 1969).

Gruner (1934a) described both talc and pyrophyllite as 2-layer monoclinic structures, and

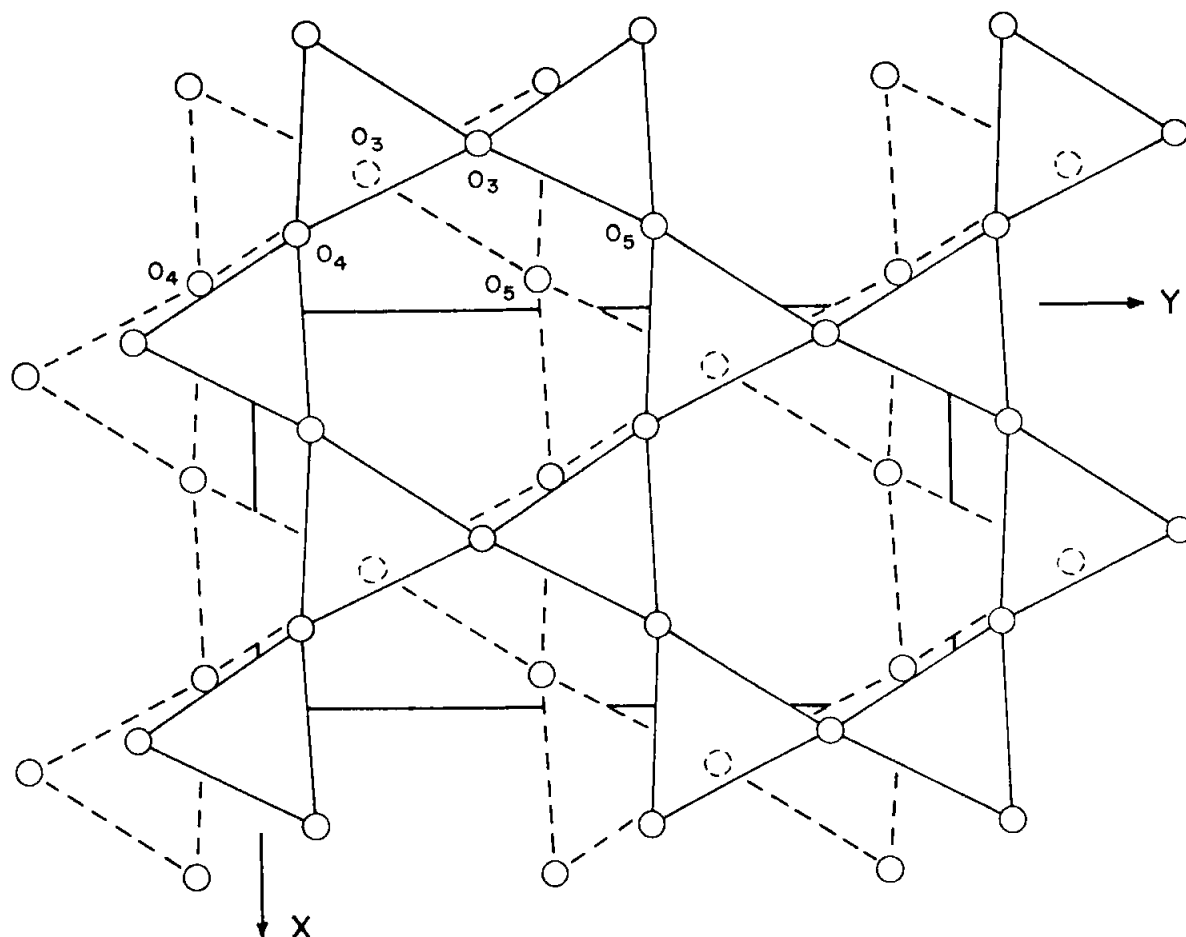


FIG. 1.13. Juxtaposition of oxygen surfaces of adjacent 2:1 layers in talc-1Tc structure. Minimal Si-Si repulsion results from superposition of four of six basal oxygens of an hexagonal ring in upper layer (full lines) approximately at the midpoint of tetrahedral edges of layer below (dashed lines) (modified from Rayner and Brown, 1973).

suggested a specific arrangement of layers on the basis of X-ray powder data. Zvyagin, Mishchenko, and Soboleva (1969) showed by texture electron diffraction of powders that (a) talc has a 1-layer triclinic structure (1Tc), and (b) natural pyrophyllite usually adopts the 2M structure but a 1Tc structure can be made synthetically. They showed further that Gruner's structure for the 2M form is not correct, and worked out what are considered now to be the correct stacking sequences for both the 1Tc and 2M structures. The 1Tc layer sequence of space group $C1$ can be described either as $\sigma_2\tau_4\sigma_2$ or its enantiomorph $\sigma_4\tau_2\sigma_4$ by use of the stacking vector symbols of Zvyagin (1967). In these symbols σ_i refers to the relative displacement of tetrahedral and octahedral sheets within a layer, and τ_k refers to the relative displacement of adjacent layers. The subscripts define the azimuthal orientation of the displacements. The 2M structure of space group Cc has the symbol $\sigma_3\tau_3\sigma_3\tau_1\sigma_3$, and consists of a combination of the two enantiomorphic 1-layer forms. In both the 1Tc and 2M forms of pyrophyllite the vacant octahedral sites lie on the mirror plane of each individual 2:1 layer. Brindley and Wardle (1970) have recognized both the 1Tc and 2M structures in natural pyrophyllites plus mixtures of the two forms in some samples.

3.2 Talc $\sim \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$

$$\begin{aligned} \text{Space group} &= C\bar{1} \quad a = 5.293, b = 9.179, c = 9.496 \text{ \AA}, \\ &\quad \alpha = 90.57^\circ, \beta = 98.91^\circ, \gamma = 90.03^\circ \end{aligned}$$

Although talc was reported first as a 2-layer monoclinic form (Gruner, 1934a; Hendricks, 1938; Stemple and Brindley, 1960), reexamination of the original specimens has failed to verify

TABLE 1.9. X-ray powder data for talc, willemseite, and minnesotaite; spacings in Å

A. Talc-1Tc (Ross <i>et al.</i> , 1968)				B. Willemseite (de Waal, 1970b)				C. Minnesotaite (Blake, 1965)	
C-setting <i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i>	<i>d</i>	<i>I</i>
001	9.333	9.34	vs	002	9.36	9.40	100	9.6	100
002	4.667	4.68	w	004	4.68	4.68	<1	4.78	20
020	4.568	4.56	s	020	4.57	4.57	16	4.58	10
$\bar{1}10$	4.531			$11\bar{4}$	3.53	3.55	3	3.33	25
$\bar{1}10$	4.523			006	3.12	3.12	28	3.17	50
$\bar{1}\bar{1}1$	4.316			130	2.635	2.636	3	2.75	22
$\bar{1}11$	4.298			$13\bar{2}$	2.596	2.599	3	2.65	22
$0\bar{2}1$	4.125	4.14	vw	$13\bar{3}$	2.507	2.503	23	2.52	70
021	4.082			008	2.339	2.338	1	2.399	20
$\bar{1}\bar{1}1$	3.885	3.85	vw	$13\bar{5}$	2.249	2.245	8	2.310	5
$\bar{1}11$	3.862			117	2.166	2.165	2	2.240	5
$\bar{1}\bar{1}2$	3.504	3.43	w	028	2.082	2.085	3	2.204	20
$\bar{1}12$	3.481			$137(?)$	—	1.957	1	2.105	10
022	3.287			0,0,10	1.871	1.873	<1	2.003	5
022	3.243			$24\bar{2}$	1.729	1.729	1	1.952	5
003	3.111	3.115	s					1.907	10
$\bar{1}\bar{1}2$	3.061			241	1.698	1.700	2	1.818	10
$\bar{1}12$	3.040			208	1.611	1.609	2	1.692	5
$\bar{1}\bar{1}3$	2.751			0,0,12	1.559	1.560	2B	1.651	10
$\bar{1}13$	2.733			060	1.525	1.524	7	1.606	20
$\bar{1}30$	2.632			$1,3,11$	1.489	1.488	1	1.592	15
$\bar{1}30$	2.627	2.632	wm	247	1.378	1.379	3	1.563	20
201	2.617			0,0,14	1.336	1.336	2	1.541	10
200	2.606	2.598	m	260	1.318	1.318	3	1.524	5
$\bar{1}31$	2.590			262	1.290	1.289	2	1.508	10
$0\bar{2}3$	2.588			$42\bar{4}$	1.269	1.270	1	1.450	10
$\bar{1}31$	2.578			$42\bar{5}$	1.258	1.257	2	1.362	15
023	2.555			0,0,16	1.169	1.170	2B	1.351	15
$\bar{1}31$	2.490	2.48	s-d	281	1.051	1.051	1	1.325	15
$\bar{1}31$	2.472			0,0,18	1.039	1.039	1	1.307	10
202	2.442					0.9938	3	1.176	20
$\bar{1}\bar{1}3$	2.424							1.102	15
201	2.415							1.051	15
$\bar{1}\bar{1}3$	2.409								
$\bar{1}32$	2.382							1.018	15
$\bar{1}32$	2.361							0.989	10
004	2.333	2.336	vw						
040	2.284	2.284	vw						
		2.219	m-d						
		2.103	m-d						
		1.994	wm						
		1.871	m						
		1.731	w						
		1.688	vw-d						
		1.558	w						
		1.527	ms						
		1.515	w						
		1.320	w						
		1.296	w						
		1.271	vw						

A. Specimen from Arnold Pit, Gouverneur, New York.

 $a = 5.275, b = 9.137, c = 9.448 \text{ Å}, \alpha = 90.77^\circ, \beta = 98.92^\circ, \gamma = 90.0^\circ.$

B. Specimen from Barberton, South Africa.

 $a = 5.316, b = 9.149, c = 18.994 \text{ Å}, \beta = 99.96^\circ.$

C. Specimen from Sagamore pit, Cuyuna district, Minnesota.

an authentic 2-layer structure (Rayner and Brown, 1973). Instead, all talcs examined in detail to date are based on a 1-layer triclinic structure (Ross, Smith, and Ashton, 1968; Zvyagin *et al.*, 1969). Observations also suggest that most talcs have at least partial randomness in the interlayer stacking.

Zvyagin, Mishchenko, and Soboleva (1969) determined the stacking arrangement of layers that is necessary in order to generate calculated intensities in agreement with observed intensities for talc-1Tc. This structure (or more precisely the $\sigma_2\tau_4\sigma_2$ sequence) was refined in more detail by Rayner and Brown (1973) for a specimen from Harford County, Maryland, U.S.A. They used 669 non-equivalent X-ray reflections in several cycles of least squares refinement to achieve a reliability factor of 13.5%. In the structure each layer has the same *intralayer* shift of $+0.334a$ along X_3 . *Adjacent layers* then are shifted by $+0.293a$ along X_2 to give a *resultant* shift of $-0.278a$ along X_1 and a β angle of 98.91° . The triclinic geometry arises from a small displacement ($0.010b$) of adjacent layers along $-Y_1$ ($\gamma = 90.57^\circ$). The juxtaposition of oxygen surfaces of adjacent layers is shown in Fig. 1.13. Rayner and Brown differ from Zvyagin *et al.* in assigning space group $C\bar{1}$ to talc-1Tc, rather than $C1$. The X-ray powder patterns of talc and related minerals are listed in Table 1.9.

Although the lateral dimensions of the Si-rich tetrahedral sheet might be expected to be smaller than those of the Mg-rich octahedral sheet, as in chrysotile, this apparently is not the case. Adjacent tetrahedra are found to be rotated by a small angle (3.4°), which implies that the tetrahedral sheet has slightly larger lateral dimensions than those of the octahedral sheet. Analysis of the component sheet thicknesses suggests that the tetrahedral sheet lateral dimensions have been increased by the mechanism of sheet thinning ($\tau = 109.0^\circ$). The observed tetrahedral sheet thickness of $2.162 \text{ \AA}$ is less than that of any other trioctahedral layer silicate studied to date, for which the range is $2.17 \text{ \AA}$ (phlogopite) to $2.41 \text{ \AA}$ (cronstedtite). At the same time the octahedral sheet has been thinned less ($2.201 \text{ \AA}$, $\psi = 58.1^\circ$) than in most other trioctahedral layer silicates (range 2.02 – $2.23 \text{ \AA}$, $\psi = 57.2$ – 59.6°).

Talc can incorporate about 4.0% Al_2O_3 in its structure (Fawcett, 1963). Ni-rich talc can be synthesized readily in the laboratory (Stubican and Roy, 1961). A natural example close to the Ni end member composition has been named *willemseite*, and has been indexed as a $2M$ form (de Waal, 1970b).

Minnesotaite has been suggested by Gruner (1944b) as an iron analogue of talc, with 75% or more of the Mg replaced by Fe^{2+} . Examination of analyses of natural talcs, however, suggests that Fe^{2+} replaces Mg only up to about 33%. The occurrence of Fe^{3+} in natural talcs is not well documented, but Forbes (1969) has found that Fe^{2+} in synthetic talc is accompanied by a small substitution of Fe^{3+} for Si^{4+} and an increase in the basal spacing due to the compensating hydroxylation of basal oxygens. Guggenheim, Wilkes, and Bailey (in preparation) have determined that the structure of minnesotaite is much more complex than that of talc, because of long-period superlattices along all three directions X, Y, and Z.

3.3 Pyrophyllite $\sim \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$

1Tc Space group = $C\bar{1}$

$a = 5.161, b = 8.958, c = 9.351 \text{ \AA}$,

$\alpha = 91.03^\circ, \beta = 100.37^\circ, \gamma = 89.75^\circ$

2M Space group = Cc

$a = 5.172, b = 8.958, c = 18.67 \text{ \AA}, \beta = 100^\circ$

Wardle and Brindley (1972) have confirmed the correctness of the Zvyagin *et al.* (1969) model for *pyrophyllite*-1Tc by calculation of intensities for all possible models. They also have partially refined the structure from X-ray powder diffractometer data for a specimen from

Coromandel, New Zealand, by use of trial-and-error methods. The published atomic coordinates correspond to the sequence $\sigma_4\tau_2\sigma_4$ of Zvyagin *et al.* (but of space group $C\bar{1}$), and thus are similar to those of the talc-17c specimen refined by Rayner and Brown (1973).

In the structure the vacant octahedral site located at the origin on a center of symmetry is enlarged relative to the occupied sites, and the tetrahedra are tilted by 4° to form corrugations in

TABLE 1.10. X-ray powder data for triclinic and monoclinic forms of pyrophyllite (Brindley and Wardle, 1970); spacings in Å

Triclinic (New Zealand)				Monoclinic (Honami, Japan)			
<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)
001	9.204	9.20	80	002	9.204	9.21	100
002	4.602	4.60	30	004	4.602	4.61	40
020	4.479			020	4.479		
110	4.417	4.42	100	110	4.428	4.42 ^b	60
111	4.265	4.26	80	021	4.352		
111	4.239			112	4.248		
021	4.061	4.06	60	111	4.164	4.18 ^b	90
021	3.995			022	4.027		
111	3.785						
111	3.749	3.764	5				
112	3.486	3.492*	5				
112	3.451	3.454*	5				
022	3.177	3.178	20				
003	3.068	3.068	100	006	3.068	3.069	100
112	2.953	2.953	20				
113	2.740	2.741*	3				
113	2.712	2.710*	4				
130	2.580			130	2.576		
201	2.572			202	2.572	2.571	15
130	2.571	2.569	30				
131	2.548						
200	2.544	2.547	30				
131	2.532	2.532	40	200	2.547	2.550*	15
023	2.507			132	2.539		
202	2.416			026	2.531	2.534	20
131	2.410	2.416	80	132	2.426		
132	2.355			204	2.413	2.419 ^b	45
201	2.347			202	2.352	2.352*	1
113	2.346	2.341 ^b	10	134	2.337	2.334	3
004	2.301	2.300	5				
220	2.216			008	2.301	2.303	4
220	2.209	2.215 ^b	4				
114	2.174			220	2.214	2.216 ^b	1
041	2.166	2.170*	15				
203	2.155						
132	2.148	2.152	15	134	2.168	2.166*	9
222	2.133	2.135*	2	206	2.152	2.151*	9
222	2.120	2.116*	2				
221	2.087						
133	2.084	2.083	20				
221	2.072						
024	2.064			222	2.082	2.086	10
133	2.048	2.059*	25				
042	2.031						
024	2.030	2.026 ^b	3	136	2.064		
042	1.997	1.998	2	028	2.047	2.059	15

TABLE 1.10.—*continued*

Triclinic (New Zealand)				Monoclinic (Honami, Japan)			
<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)
22 $\bar{3}$	1.951	1.952 ^b	<1				
2 $\bar{2}2$	1.893	1.887 ^{vb}	12				
20 $\bar{4}$	1.881			136	1.893	1.892	6
133	1.874			20 $\bar{8}$	1.877	1.876*	1
005	1.841	1.841	10	0,0,10	1.841	1.842	10
04 $\bar{3}$	1.827	1.823*	2				
13 $\bar{4}$	1.815	1.812*	3				
11 $\bar{5}$	1.808						
203	1.807			206	1.811	1.814 ^b	1
22 $\bar{4}$	1.7430	1.7439	1				
2 $\bar{2}4$	1.7252	1.7223	1				
24 $\bar{1}$	1.6907	1.6894	12	31 $\bar{2}$	1.6928	1.6879*	14
025	1.6902			150	1.6901		
150	1.6879			24 $\bar{2}$	1.6889		
24 $\bar{1}$	1.6873			240	1.6817		
2 $\bar{2}3$	1.6846						
240	1.6841						
15 $\bar{1}$	1.6839						
240	1.6778	1.6674*	12				
15 $\bar{1}$	1.6758			310	1.6681	1.6662*	15
310	1.6653			31 $\bar{4}$	1.6617		
31 $\bar{2}$	1.6636	1.6529*	30				
13 $\bar{4}$	1.6589			134	1.6458	1.6469*	20
15 $\bar{1}$	1.6525			152	1.6455		
24 $\bar{2}$	1.6483	1.6327*	20				
15 $\bar{1}$	1.6375			2,0, $\bar{1}0$	1.6325	1.6313*	15
24 $\bar{2}$	1.6362						
20 $\bar{5}$	1.6356						
134	1.6296						
24 $\bar{1}$	1.6276						
15 $\bar{2}$	1.6266						
044	1.6219	1.6213*	3				
11 $\bar{5}$	1.6192						
15 $\bar{2}$	1.6086	1.6068	<1				
115	1.6076			1,1,10	1.6155	1.6104 ^b	2
311	1.5898	1.5851	4	048	1.6049		
044	1.5883						
31 $\bar{3}$	1.5869	1.5653	3	31 $\bar{6}$	1.5832	1.5789 ^b	4
31 $\bar{3}$	1.5829			208	1.5766		
15 $\bar{2}$	1.5682						
24 $\bar{3}$	1.5620	1.5443*	2				
152	1.5459						
22 $\bar{5}$	1.5445						
24 $\bar{3}$	1.5441	1.5318*	3				
006	1.5340			0,0,12	1.5340	1.5348	4
24 $\bar{2}$	1.5320			22 $\bar{5}$	1.5338		
15 $\bar{3}$	1.5306	1.5218*	<1				
11 $\bar{6}$	1.5189						
242	1.5130	1.5142*	<1				
15 $\bar{3}$	1.5068	1.5053*	1				
060	1.4930	1.4929	30	060	1.4930	1.4935	20
33 $\bar{1}$	1.4927			33 $\bar{2}$	1.4929		
33 $\bar{1}$	1.4926						
224	1.4921	1.4894*	10				
31 $\bar{2}$	1.4885			314	1.4890	1.4898*	5

TABLE 1.10.—*continued*

Triclinic (New Zealand)				Monoclinic (Honami, Japan)			
<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)
330	1.4723	1.4716	8	334	1.4715	1.4708	7
332	1.4695						
061	1.4689						
244	1.4505						
135	1.4499	1.4513*	<1	156	1.4456	1.4407 ^{*b}	3
026	1.4420						
153	1.4321						
206	1.4308						
244	1.4302	1.4291*	6	248	1.4386	1.4260 ^{*b}	4
062	1.4289						
331	1.4266						
135	1.4258						
336	1.4130	1.4118	4	0,4,10	1.4221	1.4154 ^{*b}	2
062	1.4115						
136	1.3846						
116	1.3811						
313	1.3703	1.3703 ^{*b}	30	1,1,12	1.3862	1.3858	15
226	1.3699						
332	1.3509						
334	1.3446						
332	1.3398	1.3462 ^{*b}	10	1,3,12	1.3720	1.3697	29
154	1.3382						
334	1.3336						
063	1.3316						
245	1.3311	1.3347*	2	316	1.3706	1.3491*	4
007	1.3149						
154	1.3127						
225	1.3119						
				334	1.3475		
				066	1.3425	1.3432*	1
				338	1.3374	1.3365*	2
				0,0,14	1.3146	1.3159	1.5

1Tc $a = 5.173$, $b = 8.960$, $c = 9.360$ Å, $\alpha = 91.2^\circ$, $\beta = 100.4^\circ$, $\gamma = 90.0^\circ$.

2M $a = 5.172$, $b = 8.958$, $c = 18.676$ Å, $\alpha = 90.0^\circ$, $\beta = 100.0^\circ$, $\gamma = 90.0^\circ$.

vb = very broad; b = broad; * not completely resolved.

the basal oxygen surface that run parallel to [110]. The angle of tetrahedral rotation is 10° . The sheet thicknesses are similar to those of other dioctahedral layer silicates, and the interlayer region is similar to that shown in Fig. 1.13 for talc.

Giese (1973b) has used the 1Tc atomic coordinates to calculate the orientation of the inner hydroxyl O—H bond in pyrophyllite. The minimum electrostatic energy is obtained when the O—H bond points away from the octahedral sheet at an angle of 26° toward the adjacent tetrahedral sheet and makes an angle of 31.5° with the Y axis in projection on (001). The 26° angle is larger than the 12° angle found experimentally for muscovite-2M₁ by Rothbauer (1971) using neutron diffraction data, and is due to the absence in pyrophyllite of repulsion by the interlayer cation. On the other hand, it is not as large as the 53° angle found by Giese (1971) by similar electrostatic calculations for muscovite if the interlayer cation is assumed absent. The smaller angle is attributed to repulsion of H⁺ by the higher charge on the tetrahedral cations (all Si) in pyrophyllite.

Stacking irregularities that lead to diffuse $k \neq 3n$ reflections are common in natural pyrophyllites. Rayner and Brown (1965) examined one specimen of this type from Graves



Mountain, Georgia, U.S.A. Although the specimen is of the $2M$ type, the authors were only able to determine the average structure of an individual layer by using 125 of the sharp $k = 3n$ reflections from a single crystal. This means that the vacant octahedral site cannot be distinguished from the occupied sites, but that other structural details that do not have a $b/3$ indeterminacy can be worked out. The tetrahedral rotation angle is 10° , and each tetrahedron is tilted 4.1° to form a corrugated basal oxygen surface. In particular, this structural determination gave the first indication of the possible modes of packing of adjacent layers in pyrophyllite and talc, although the precise juxtaposition was indeterminate for this specimen because of the average nature of the results.

Both natural and synthetic pyrophyllites commonly show a small substitution of Al for Si in tetrahedral sites. Because substituted specimens also have larger H_2O+ contents and larger basal spacings than end member compositions, the tetrahedral substitution is believed to be compensated by hydroxylation of basal oxygens (Rosenberg, 1974). This may lead to formation of a few interlayer hydrogen bonds and increased thermal stability.

X-ray powder patterns for the triclinic and monoclinic forms of pyrophyllite are listed in Table 1.10.

4. TRUE MICA GROUP

4.1 Introduction

Because of their abundance in nature and excellence of crystalline perfection, the micas have been studied more than other layer silicate minerals. The general outlines of the structure were determined by Pauling (1930a) and, at about the same time and in more detail, by Jackson and West (1930, 1933). Since these early studies, many detailed structural refinements of particular species have been published.

The mica structure consists of negatively charged 2:1 layers that are "keyed" together by large interlayer cations. In the true micas considered here the interlayer cation is univalent, whereas in the brittle micas it is divalent. The layer charge in true mica ideally is -1.0 per formula unit and arises by some combination of three mechanisms: (1) substitution of R^{3+} (primarily Al, Fe, or Cr) for Si^{4+} in tetrahedral positions, (2) substitution of R^{1+} or R^{2+} for R^{2+} or R^{3+} in octahedral positions, or (3) vacancies in octahedral positions. The resultant layer charge may originate entirely within the tetrahedral sheet or entirely within the octahedral sheet in some species, or may come partly from both sheets. It also is possible for the octahedral sheet to have an excess positive charge, which is always the case when the tetrahedral charge exceeds -1.0 .

Many different medium-sized cations are known to occur in the octahedral sheet, primarily Al, Mg, and Fe, but with appreciable amounts of Li, Cr, Ni, Mn, Ti, Zn, Co, Cu, and V in certain species. The interlayer cation normally is K, occasionally Na, and rarely Rb or Cs. The 2:1 layers must superimpose so that the hexagonal rings of adjacent basal surfaces line up and enclose the interlayer cations. In most species adjacent layers are propped slightly apart by the interlayer cation. This is because tetrahedral rotation moves every other basal oxygen towards the center of each ring and thereby reduces the size of the opening. The interlayer cation then has only six nearest oxygen neighbors, rather than twelve for the case of ideal hexagonal geometry. The resultant basal spacing of $10 \text{ \AA}$ is slightly larger than the thickness of the layer itself (approximately $9.3\text{--}9.5 \text{ \AA}$). The interlayer separations (average distance between centers of basal oxygens in adjacent layers) found in various micas are documented in Tables 1.14, 1.18, 1.20. These values are to be compared with values of 2.77 and $2.86 \text{ \AA}$ for pyrophyllite and talc

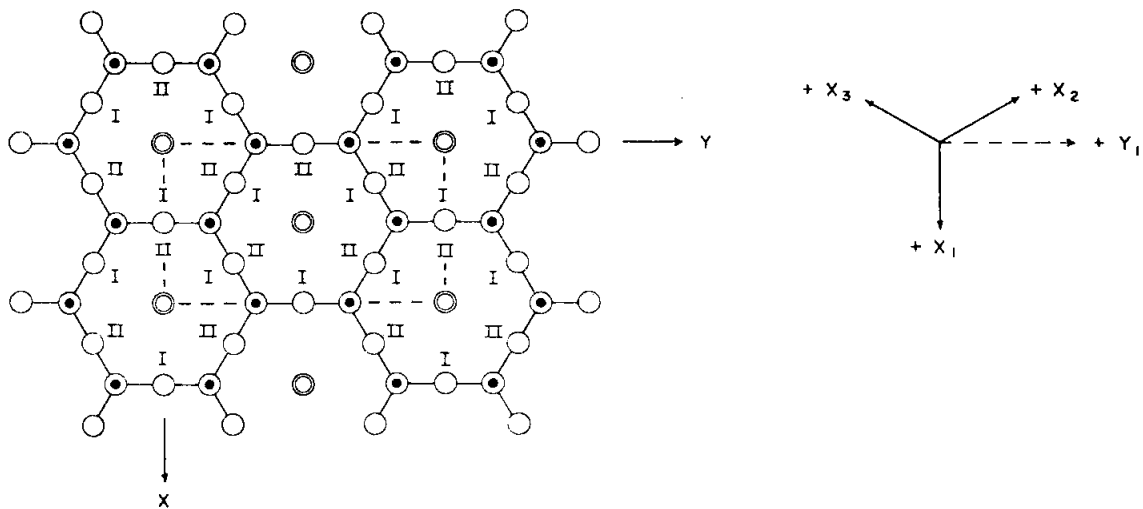
where the basal oxygen surfaces are known to be in contact. The interlocking of adjacent layers by the interlayer cation limits the structural diversity of micas to the variations possible at the octahedral interface, and is believed to account for the observed elasticity of mica laminae.

4.2 Derivation of standard trioctahedral polytypes

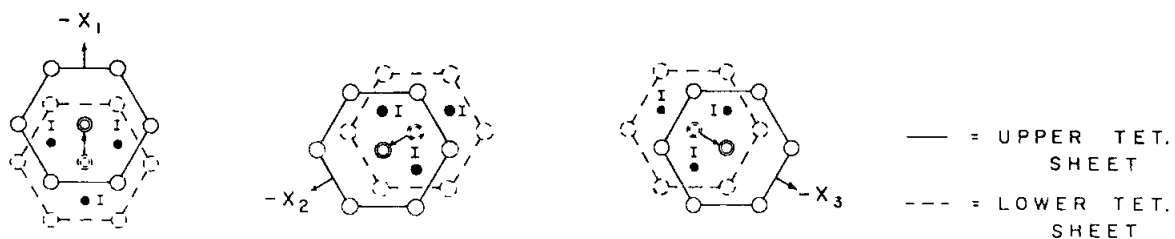
Mauguin (1928) and Hendricks and Jefferson (1939) were the first to demonstrate the existence of polytypism in micas by X-ray study. Smith and Yoder (1956) derived the six simplest polytypes that are theoretically possible, and correlated these polytypes with a variety of natural specimens. They assumed in their study that the hexagonal rings are undistorted, the octahedral positions are all occupied, no cation ordering takes place, and in a given crystal the same interlayer stacking angle is found between all the layers.

Because adjacent 2:1 layers must line up so the hexagonal rings superimpose around the interlayer cation, the only degree of freedom comes at the octahedral interface within each layer. The upper tetrahedral sheet must be staggered by $a/3$ relative to the lower tetrahedral sheet in

a)



b)



c)

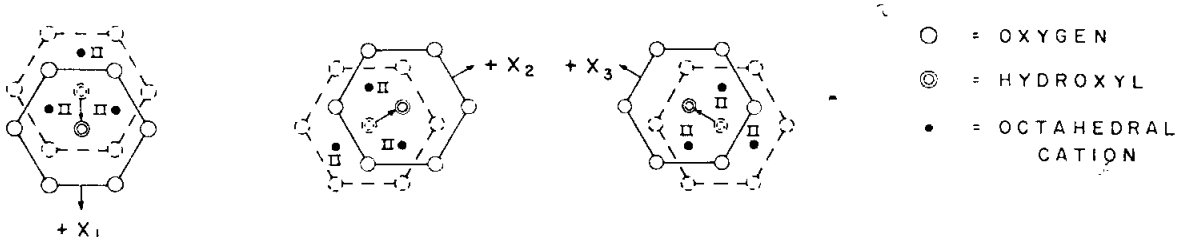


FIG. 1.14. (a) Definition of I and II sets of octahedral cation positions above a tetrahedral net relative to a fixed set of hexagonal axes for a 2:1 layer. (b) Three possible directions of intralayer shift when octahedral cation set I is occupied. (c) Three possible directions of intralayer shift when octahedral cation set II is occupied.

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 pseudohexagonal axes X_1 , X_2 , or X_3 . Relative to a fixed set of initial axes, as defined in Fig. 1.14a, the three octahedral cations can occupy either the three sites labeled I in each hexagonal ring or the three sites labeled II. If the I sites are occupied, then octahedral coordination about them can be provided by fitting the upper tetrahedral sheet on in any of the three positions shown in Fig. 1.14b. 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, then the upper tetrahedral sheet can fit on as shown in Fig. 1.14c, in which the $a/3$ shifts are along the positive directions 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 distinction 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.

It will be assumed here that the I set of octahedral positions is occupied in the first layer of every polytype and that the tetrahedral stagger of $a/3$ is directed along $-X_1$ (relative to a fixed set of axes oriented as in Fig. 1.14a). One then must consider the six possible directions of shift within the succeeding layers relative to that in the first layer. In order to depict the possible layer sequences graphically, it is convenient to show the shift within each layer as a vector directed from the center of an hexagonal ring in the lower tetrahedral sheet to the center of a ring in the upper tetrahedral sheet, as viewed in projection on (001). The interlayer stacking angle will be defined as the angle between two such projected vectors in adjacent layers, as measured in a counterclockwise direction. The six possible interlayer angles are 0° , 60° , 120° , 180° , 240° , and 300° . Because of the plane of symmetry that is parallel to the intralayer vector, angles 60° and 300° are equivalent, as are angles 120° and 240° .

Smith and Yoder (1956) have shown that there are only six mica polytypes that can be formed with periodicities between one and six layers if only one interlayer stacking angle, positive or negative, is permitted in a given crystal. These possibilities are illustrated graphically in Fig. 1.15. The structure with 0° stacking angle, corresponding to successive $-X_1$ shifts, is the $1M$ polytype. The $2Or$ polytype 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 gives rise to the $2M_1$ polytype and a continuous alternation of $\pm 60^\circ$ angles to the $2M_2$ polytype. Note that the fixed axes and unit cell (dashed lines) used to derive these theoretical structures are not the best axes to use for the resultant structure (solid lines). Also, 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. Although only the X_1 and X_2 axes were used here, any two X axes could be used. The same two structures would be derived, differing only in the orientation of the resultant unit cells 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.

In summary, two polytypes can be derived using shifts along just one X axis. A second group of two polytypes involves shifts along two axes, and a third group involves shifts along all three axes. One member of each group involves 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 rotations).

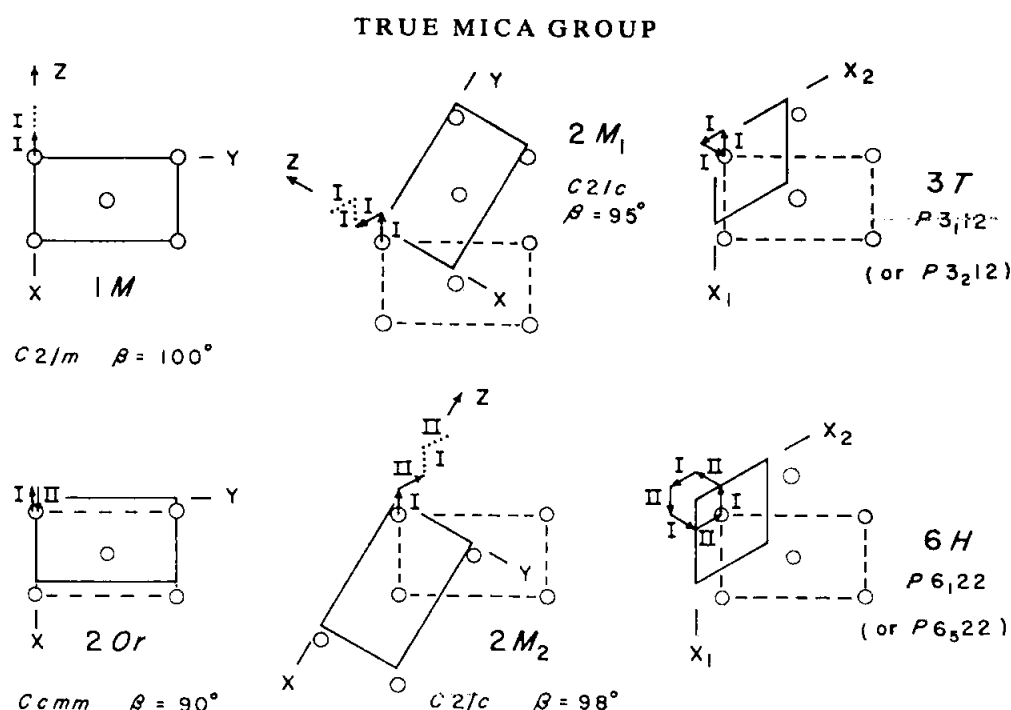


FIG. 1.15. Derivation of six ideal mica polytypes (modified from Smith and Yoder, 1956). The orientation of Fig. 1.14a is assumed for the first layer of each polytype with the I set of octahedral cation positions occupied and the intralayer shift $-a_1/3$. The base of the resultant unit cell (solid lines) 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 center (circles) of an hexagonal ring in the first layer as the symmetry permits.

More complex layer sequences can be derived if mixtures of different interlayer stacking angles are allowed in a crystal. The reader should consult Ross, Takeda, and Wones (1966), Takeda and Sadanaga (1969), and Takeda (1971) for a derivation of these complex sequences and for suggested nomenclature systems. Smith and Yoder used Ramsdell structural symbols to designate their theoretical polytypes. These are the symbols used in this chapter. Zvyagin (1967) has used another system, in which a Greek symbol σ_i designates the relative displacement of tetrahedral and octahedral sheets within each layer, where the subscript i defines the azimuthal orientation of the displacements in 60° clockwise increments about the cleavage normal.

4.3 Identification of structures

The six simple mica structures can be identified in part by X-ray powder patterns and in part by single crystal patterns. Powder patterns are distinctive for the $2M_1$ and $2Or$ structures, but are identical for the trioctahedral $1M$ and $3T$ structures and for the trioctahedral $2M_2$ and $6H$ structures. Single crystal study is necessary to distinguish the members of the latter pairs. The dioctahedral $1M$ and $3T$ structures are distorted sufficiently that their powder patterns are slightly different (see Fig. 1.17). The $2M_1$ structure has its optic axial plane normal to (010), whereas for the $1M$ structure the optic plane is parallel to (010). Twinning, however, may affect the position of the optic plane as well as the magnitude of the optic angle.

Table 1.11 lists the identifications that have been made for different mica species. Four of the six theoretical structures have been reported from natural true mica specimens, and a fifth structure ($2Or$) has been identified in a brittle mica. Only the $6H$ example has not yet been found. There is a noticeable tendency for compositional control of the layer sequences actually adopted by natural micas. For example, the $2M_1$ structure is predominant for dioctahedral muscovite, with $1M$ and $3T$ structures less abundant. Although only two of the three octahedral positions are occupied in dioctahedral micas, there is no change from the theoretical space group

TABLE 1.11. Observed natural mica structures

Trioctahedral				Diocahedral			
Species	Abundance			Species	Abundance		
	High	Medium	Low		High	Medium	Low
phlogopite	1M, 1Md	3T	2M ₁	muscovite	2M ₁	1M, 1Md	3T
biotite	1M, 1Md	3T	2M ₁	paragonite	2M ₁	1M	
annite	1M			lithian muscovite	2M ₁		
siderophyllite	1M			Ba-muscovite	1M		
lepidomelane	1M			manganoan	1M		
lepidolite	1M, 2M ₂	3T	2M ₁	muscovite			
zinnwaldite	1M, 1Md	2M ₁ , 3T		roscoelite	1M		
taeniolite	1M, 3T	2M ₁		chernykhite	2M ₁		
ephesite	2M ₁			illite	2M ₁ , 1Md, 1M		3T
hendricksite	1M	2M ₁	3T	phengite	1M, 1Md, 3T	2M ₁	2M ₂
manganoan	1M	2M ₁		alurgite	2M ₁ , 3T		
phlogopite				mariposite	2M ₁ , 1M		
				glauconite	1M, 1Md		
				celadonite	1M, 1Md		

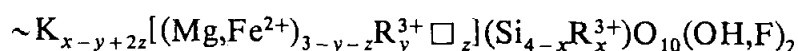
or periodicity as derived on the assumption of trioctahedral compositions. The 1M structure is most abundant for trioctahedral micas, with 3T and 2M₁ less abundant. Disordered stacking sequences, termed 1Md, are observed in addition to the regular sequences for both dioctahedral and trioctahedral compositions, but are most abundant for trioctahedral species. Because of the compositional control of the stacking it is evident that many of the natural mica structures are neither polytypic nor polymorphic with one another. They may be described instead as *polytypoids*.

Another point to be noted in Table 1.11 is that stacking sequences based on 0°, 120°, and 240° stacking angles (occupation of the same set of octahedral positions in every layer) occur more frequently than those based on 60°, 180°, and 300° angles (involving alternation between I and II octahedral sets in successive layers). That is, the 1M, 2M₁, and 3T structures occur more abundantly than the 2M₂, 2Or, and 6H structures. Radoslovich (1959) notes that the opposing basal oxygen surfaces in most micas are distorted from hexagonal to trigonal or ditrigonal symmetry as a result of tetrahedral rotation. He suggests that this distortion favors structures in which the relation of interlayer stacking angles is also trigonal, *i.e.* differ by 0°, 120°, or 240°. Under this view, interlayer stacking angles differing by ±60° or 180° would occur only when tetrahedral rotation is small and the basal oxygen surfaces nearly hexagonal. Although this hypothesis has some validity for layer silicates in which opposing layer surfaces are in contact and can influence one another, it has been pointed out above that in most micas adjacent layers are propped apart by the interlayer cation and are not in contact. Detailed refinement of the 2M₂ and 2Or structures has shown also that the oxygen surfaces in these cases are not necessarily hexagonal, with α up to 11.2°. The important feature appears to be that interlayer stacking angles of 0° or ±120° cause the six nearest oxygen neighbors to form an energetically stable octahedral coordination group around the interlayer cation. Stacking angles of ±60° or 180°, on the other hand, create a trigonal prism coordination in which three basal oxygens from one layer directly superimpose on three basal oxygens from the layer below. The latter coordination is energetically unstable in most cases because tetrahedral substitution leads to unsatisfied negative charges on these basal oxygens so they will tend to repel one another. This

condition is minimized to the extent that $\pm 60^\circ$ or 180° stacking angles may be adopted if tetrahedral substitution is small. See the brittle mica anandite-2*Or*, however, for an exception.

Although X-ray powder patterns can be used to identify in part the structures adopted by micas, it is much more difficult to identify a particular trioctahedral or dioctahedral species. Species identification from a powder pattern alone requires knowledge of the relatively small changes in line spacings and intensities that result from differences in the sizes and scattering powers of the ions involved. The reader should note in Table 1.11 and in the sections that follow on individual structures that species identification here usually has been based on a combination of chemical analysis, optical study, and X-ray single crystal study.

4.4 Trioctahedral phlogopite–biotite–annite



4.4.1 General

X-ray examination of about 250 single crystals of natural Mg, Fe trioctahedral micas has shown that the great majority crystallize as the 1*M* structural form, and only a few as the 3*T* or 2*M*₁ structures (Levinson and Heinrich, 1954). A disordered stacking sequence 1*Md* also is of common occurrence. Several more complex stacking sequences have been identified in biotites (Ross, Takeda, and Wones, 1966). Representative phlogopite X-ray powder patterns are listed in Table 1.12.

From the chemical analyses of more than 200 trioctahedral micas, Foster (1960*a*) found that for small amounts of substitution of R^{3+} for octahedral Mg (less than 0.3–0.4 atoms per 3.0 octahedral sites) charge compensation is achieved by an equivalent amount of substitution of R^{3+} for Si in the tetrahedral positions. For larger amounts of octahedral substitution, however, octahedral vacancies become increasingly important as an additional method of charge compensation. For most biotites, therefore, tetrahedral R^{3+} is greater than the 1.00 total needed to balance the interlayer cation and the octahedral cation total is less than 3.00. The maximum amount of substitution of R^{3+} for octahedral Mg appears limited to one atom per three octahedral sites.

Coincident with replacement of Mg by R^{3+} is replacement of Mg by Fe^{2+} on an ion for ion basis. On the basis of gaps in the observed compositional distribution of these micas (Fig. 1.16), Foster (1960*a*) defined *phlogopite* as having more than 70% Mg in the octahedral sites, *biotite* between 60% and 20% Mg, and *siderophyllite* and *lepidomelane* less than 10% Mg. In *siderophyllite* the octahedral R^{3+} cation ideally is Al and in *lepidomelane* it is Fe^{3+} . The theoretical Fe^{2+} end member *annite* was not encountered in this study, and Foster suggested 2.20 atoms as the limit of Fe^{2+} octahedral substitution.

Foster (1964) found that a large percentage of trioctahedral micas have low (OH, F) values. In some cases this can be explained by internal oxidation of Fe and a compensating dehydroxylation of OH to O. But oxidation of Fe will not explain all such examples of low (OH, F) values for Fe-rich micas, nor the significant number of Fe-poor samples that have low (OH, F) values. Forbes (1972) has documented by synthesis of an OH-deficient mica of composition $KMg_3Si_4O_{10}(OH)O$ that it is possible for anion charges to vary in response to cation charge variations not connected with oxidation. He also showed by regression analysis with data for 100 natural phlogopites and biotites that 91% of the variation of (OH + F + Cl) from its ideal value of 2.0 can be explained by variation of the octahedral and tetrahedral cation charges from their ideal values of +6 and +15, respectively, and only 5% by variation of interlayer cation charge. The range in OH content for muscovites is less than for trioctahedral

TABLE 1.12. X-ray powder data for polytypic forms of phlogopite; spacings in Å

A. 1M			B. 3T			C. 2M ₁		
hkl	I	d	hkl	I	d	hkl	I	d
001	>100	9.97	0003	>100	10.129	002	>100	10.129
002	6	5.02	0006	23	5.022	004	18	5.056
020	7	4.588	10 $\bar{1}$ 0	8	4.596	110	19	4.612
110	5	4.553	10 $\bar{1}$ 1	8	4.546	020		
111	3	3.923	10 $\bar{1}$ 4	3	3.941	021	7	4.515
112	7	3.654	10 $\bar{1}$ 5	7	3.663	112	5	4.079
022	20	3.389	10 $\bar{1}$ 6	45	3.393	023	18	3.814
003	>100	3.348	0009	>100	3.354	114	33	3.540
112	10	3.144	10 $\bar{1}$ 7	25	3.148	006	>100	3.362
113	7	2.916	10 $\bar{1}$ 8	21	2.917	114	38	3.283
023	3	2.708	10 $\bar{1}$ 9	12	2.710	115	9	3.156
130	7	2.642	1121	10	2.643	025	40	3.040
201			1122	30	2.618	115	8	2.926
200	30	2.614	0,0,0,12	52	2.513	116	22	2.818
131			1,0,1,10			131	22	2.651
004	15	2.515	1124	17	2.431	116	>100	2.624
113			1125			008	28	2.522
131			2021			133	40	2.439
202			1127			117	16	2.361
			2023	2	2.243			
132	15	2.430	1128	21	2.171	220	9	2.304
201			0,0,0,15	>100	2.011	040		
221	3	2.292	1,1,2,10	12	1.996	135	9	2.270
220	?	2.26	1,1,2,11	4	1.908	135	45	2.180
132			1,1,2,13	3	1.748	224	21	2.039
203	?	2.24	1,1,2,14	35	1.675	0,0,10	66	2.017
041			3030	25	1.536	137	20	2.000
133	15	2.170	3033	2?	1.516	137	5	1.914
202	30	2.012				139	3	1.751
005	7	1.995				227	5	1.737
204						153	47	1.677
133	2	1.910				060	50	1.538
134						330		
203	?	1.748				062	10	1.521
205								
134	15	1.674						
135								
204	15	1.535						
060	15	1.535						
061	2?	1.517						
330								

A. 1M $a = 5.312$, $b = 9.20$, $c = 10.204$ Å, $\beta = 99.82^\circ$.

B. 3T $a = 5.317$, $c = 30.168$ Å.

For similar composition specimens, it is likely that the 1M and 3T patterns would be indistinguishable. (Modified from Smith and Yoder, 1956.)

C. $a = 5.347$, $b = 9.227$, $c = 20.252$ Å, $\beta = 95.02^\circ$.

Specimen from Burgess, Ontario (U.S.N.M. 106758). (Yoder and Eugster, 1954.)

micas and the correlation with cation charge variation is not as large (67%), but the trend is similar.

Hazen and Wones (1972) synthesized trioctahedral analogues of phlogopite with Co, Ni, Cu, and Fe²⁺ substituting for octahedral Mg, with B³⁺, Ga³⁺, and Fe³⁺ substituting for tetrahedral

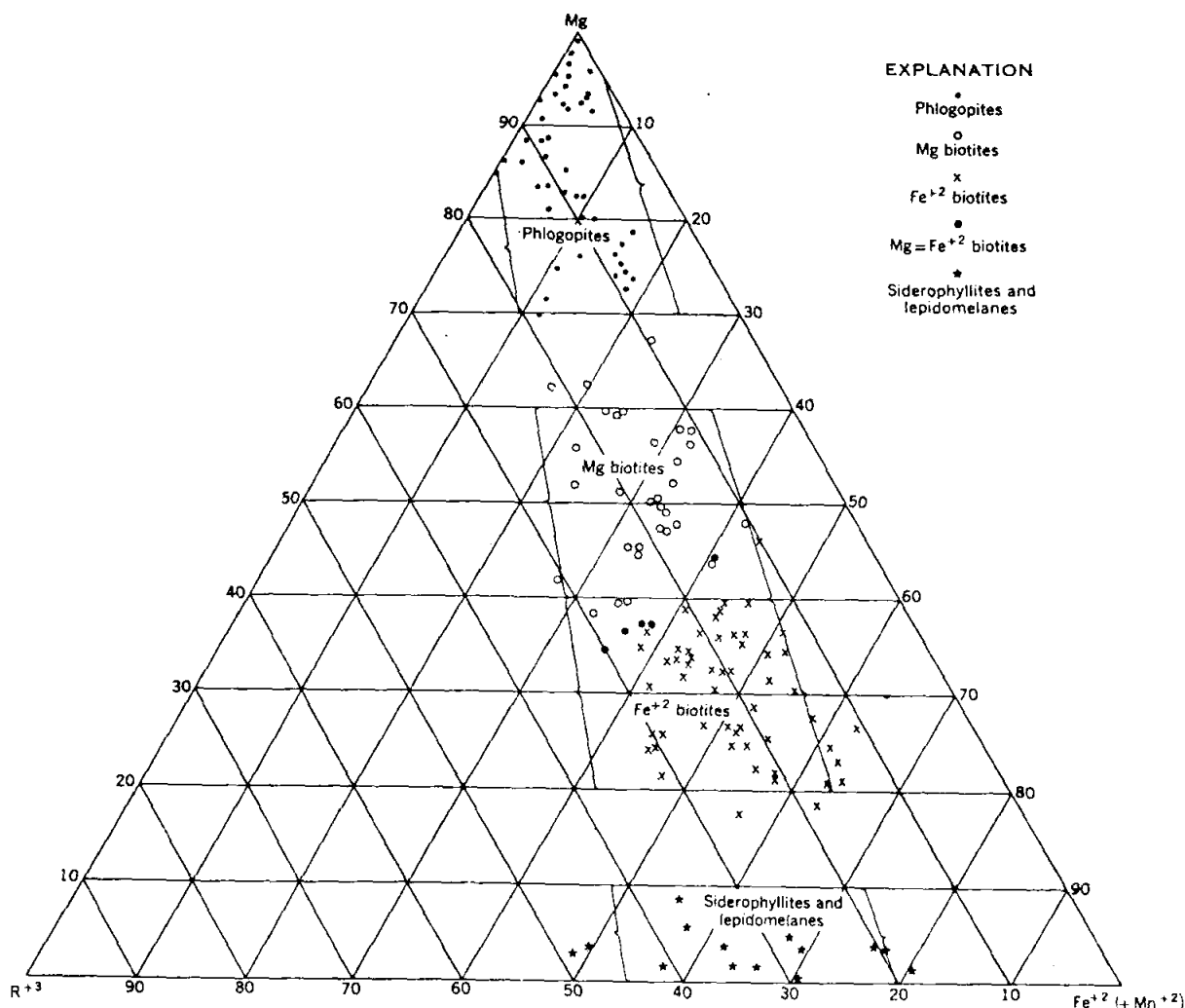


FIG. 1.16. Distribution of natural trioctahedral micas on triangular Mg-Fe²⁺-R³⁺ diagram, according to Foster (1960a).

Al, with Ge⁴⁺ substituting for tetrahedral Si, and with Cs substituting for interlayer K. They calculated that the tetrahedral rotation angle α should decrease regularly with increasing radius of the octahedral cation, and should reach 0° at $r = 0.76 \text{ \AA}$ for a tetrahedral composition of Si₃Al. Octahedral cations larger than this should not form stable mica structures. This apparently is why a pure Fe²⁺ annite end member ($r = 0.77 \text{ \AA}$) does not form. Mössbauer and chemical analyses demonstrate that even the synthetic annites are not of ideal composition, but have both octahedral and tetrahedral Fe³⁺ present. Tateyama (1975) also has synthesized trioctahedral 1M micas with a variety of partial octahedral and tetrahedral R²⁺ substitutions (Be, Mg, Mn, Ni).

Whittaker (1969) has pointed out that tetrahedral rotation angles tend to be smaller in trioctahedral micas than in the dioctahedral micas because of the larger sizes of the octahedral cations and consequent better lateral fit of the octahedral and tetrahedral sheets. One consequence of a smaller rotation angle is a larger hole for the interlayer cation. In order for a smaller cation, such as Na, to fit in the interlayer position the lateral misfit must be accentuated enough to cause appreciable tetrahedral rotation and consequent decrease of the interlayer opening. This is accomplished in the trioctahedral Na-mica *ephesite* Na(LiAl₂)(Si₂Al₂)O₁₀(OH)₂ by substitution of two atoms of Al for Si in the tetrahedral sheet (increasing its lateral size) and by a small trioctahedral sheet that actually has the dimensions and configuration of a

dioctahedral sheet because of the presence of two Al atoms plus a Li atom that is the same size as a vacancy.

In K-biotites Hewitt and Wones (1975) have shown by calculation that the α rotation angle should increase with increasing Al substitution in the series $K(Mg_xFe_yAl_z)(Al_{1+z}Si_{3-z})O_{10}(OH)_2$ up to the point at which the K—O bond length decreases to a minimum stable value believed to be near 2.80 Å. This is calculated to occur near $z = 3 - x - y = 0.75$ for Fe-rich compositions or near $z = 0.65$ for Mg-rich compositions, in reasonable agreement with the maximum limits of Al substitution observed in synthetic biotites and phlogopites by Rutherford (1973), Hewitt and Wones (1975), and Robert (1975). The reason for these limits is that the interlayer cation blocks further tetrahedral rotation and, as a consequence, limits any additional substitutions, such as Al, that would increase the need for rotation.

Seifert and Schreyer (1971) have synthesized a magnesian mica that is intermediate between trioctahedral and dioctahedral with the composition $[K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2]$. Kwak (1971) has confirmed this synthesis and, in addition, has synthesized the $Fe_{2.5}^{2+}$ and $Fe_{1.25}^{2+}Mg_{1.25}$ analogues as well as micas with partial tetrahedral substitutions of Mg and Fe^{2+} in Al-free systems. Rimsaite (1967) has pointed out that weathered biotites of high Fe content may approach a total of 2.5 octahedral cations as a result of oxidation during the process of alteration to chlorite or vermiculite.

Manganooan phlogopite (or *manganophyllite*) with $MnO + Mn_2O_3$ up to 12.2% has been identified by Levinson and Heinrich (1954) as primarily the 1M form. The name *hendricksite*

TABLE 1.13. X-ray powder data for annite and hendricksite; spacings in Å

A. Synthetic annite (Eugster and Wones, 1962)				B. Hendricksite (Fron del and Ito, 1966)		
<i>d</i> (obs.)	<i>I</i>	1M setting <i>hkl</i>	3T setting <i>hkl</i>	<i>d</i> (obs.)	<i>I</i>	<i>hkl</i>
10.264	100	001	003	10.20	100	001
5.070	3	002	006	5.094	36	002
4.644	5	020	100	3.398	60	003
3.975	3	111	104	2.682	7	130, 20 $\bar{1}$
3.711	5	11 $\bar{2}$	105	2.652	13	13 $\bar{1}$, 200
3.380	80	003	009	2.546	35	004
3.179	15	112	107	2.462	9	201, 13 $\bar{2}$
3.106	10	?	?	2.202	8	202, 13 $\bar{3}$
2.734	5	023	109	2.034	9	005
2.654	70	200, 13 $\bar{1}$	112	2.016	5	204, 133
2.532	15	004, 20 $\bar{2}$, 131	0, 0, 12; 114	1.696	17	006
2.465	40	201, 13 $\bar{2}$	115	1.554	10	060
2.199	20	202, 13 $\bar{3}$	118	1.495	3	205
2.018	10	204, 133	1, 1, 10	1.454	6	007
1.932	5	203, 134	1, 1, 11	1.378	6	027, 136
1.692	20	006, 204, 13 $\bar{5}$	0, 0, 18; 1, 1, 14	1.327	3	117, 206
1.635	1	152, 24 $\bar{3}$	217	1.272	5	008
1.556	40	060, 33 $\bar{1}$, 206, 135	300; 1, 1, 16	1.002	5	
1.538	10	061, 33 $\bar{2}$	303	0.974	5	
1.485	5	062, 331	306			

A. 1M $a = 5.39$, $b = 9.30$, $c = 10.30$ Å, $\beta = 100.1^\circ$.

3T $a = b = 5.39$, $c = 30.43$ Å, $\gamma = 120^\circ$.

Indexing modified from Eugster and Wones (1962).

B. 1M $a = 5.37$, $b = 9.32$, $c = 10.30$ Å, $\beta = 99^\circ$.

Specimen from Franklin, New Jersey.

has been given to a trioctahedral mica rich in both Zn^{2+} and Mn^{2+} , but with $\text{Zn} > \text{Mn}$ (Fron del and Ito, 1966). Most specimens are of the 1M polytype (Tables 1.11,13).

4.4.2. Details of trioctahedral 1M structure

Space group = $C2/m$ $a \cong 5.33$, $b \cong 9.24$, $c \cong 10.22$ Å, $\beta \cong 100^\circ$

A large number of structural refinements have been conducted on trioctahedral 1M micas of varying tetrahedral and octahedral compositions. These include texture electron diffraction refinement of a powder (Zvyagin and Mishchenko, 1962), neutron diffraction study of a single crystal (Joswig, 1972; Rayner, 1974) plus single crystal X-ray diffraction studies of several specimens. The results of these refinements are summarized in Table 1.14.

The ideal space group $C2/m$ for the 1M structure has only one independent tetrahedron. All tetrahedra must have the same average composition, as a result, and tetrahedral cation order is not possible. Space group $C2/m$ has two independent types of octahedra, M(1) on the mirror plane and a pair of equivalent M(2) octahedra related to each other by the mirror plane. The two OH groups of each octahedron lie on the mirror plane, but in different orientations. The OH of M(1) are in the *trans* orientation, whereas those of M(2) are in the *cis* orientation and form a shared edge between adjacent symmetry-related M(2) octahedra. Although octahedral cation ordering theoretically is possible, Table 1.14 shows that most of the 1M micas selected for crystallographic refinement do not have octahedral compositions conducive to ordering. The only specimens that have any appreciable octahedral substitution (biotite and annite) did not show significant ordering. Mössbauer spectra of several biotites have been interpreted by Annersten (1974) and by Bancroft and Brown (1975) to indicate a high degree of octahedral disorder, but with a small preference of Fe^{2+} for M(2) and of Fe^{3+} for M(1). A strong preference of Fe^{2+} for M(2), and of Al for M(1) by inference, was found by Annersten (1975) from Mössbauer data for a synthetic Al-biotite of maximum octahedral Al substitution ($\text{Fe}_{2.25}^{2+}\text{Al}_{0.75}$). Krzanowski and Newman (1972) have shown by computer calculations that, if Pauling's local charge balance rule is obeyed, octahedral R^{3+} cations should form either trigonal groups around vacancies or chains of alternating R^{3+} cations and vacancies. This implies that at least short-range octahedral order should be present for such compositions, if not long-range order.

The angles of tetrahedral rotation (α) found in different specimens range from 1° to 11° . In all micas the direction of rotation is a movement of the basal oxygens toward the positions of the octahedral cations in the same layer. McCauley and Newnham (1971) by analysis of all refined mica structures have determined a linear relationship between α and the difference between the inner and outer K—O distances, as listed in Table 1.14. They further showed by multiple regression analysis that for micas the magnitude of α depends, on the average, 90% on the misfit of the lateral dimensions of the tetrahedral and octahedral sheets and 10% on the effect of the interlayer cation, as measured by its field strength (ratio of valence to ionic radius). These average values do not apply necessarily to specific cases, and the interlayer cation may have a large influence on α in some micas. The authors consider that their derived equations can be used to predict α and the nature of the interlayer region from chemical composition alone. Donnay, Donnay, and Takeda (1964) have given equations to predict the detailed shapes and sizes of the octahedral and tetrahedral sheets from the composition and cell dimensions. These relations have been modified by Drits (1969) to take into account additional data on observed distortions of the polyhedra.

TABLE 1.14. Structural details

Reference	Species	Composition	# Refl.	Final R	α_{tet}	τ_{tet}	ψ_{OCT}
Zvyagin and Mishchenko (1962)	phlogopite	$\sim(\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	109	18.8%	5.9°	108.9°	58.1°
Steinfink (1962)	ferriphlogopite	$(\text{K}_{0.9}\text{Mn}_{0.1})\text{Mg}_3[\text{Si}_3(\text{Fe}^{3+}, \text{Mn})]\text{O}_{10}(\text{OH})_2$	392	13.1	11.0	110.0	58.2
Donnay, Morimoto, Takeda and Donnay (1964)	synthetic ferriannite	$\text{KFe}_3^{2+}(\text{Si}_3\text{Fe}^{3+})\text{O}_{10}(\text{OH})_2$	433	9.3	6.4	110.3	59.1
Takeda & Donnay (1966)	synthetic lithian fluorophlogopite	$\text{K}_{0.95}(\text{Mg}_{2.8}\text{Li}_{0.2})(\text{Si}_{3.25}\text{Al}_{0.75})\text{O}_{10}\text{F}_2$	472	7.3	6.2	110.6	59.3
Tepikin, Drits and Alexandrova (1969)	biotite	$(\text{K}_{0.88}\text{Ca}_{0.02}\text{Na}_{0.07}\text{H}_3\text{O}_{0.04})(\text{Si}_{2.71}\text{Al}_{1.29})$ $(\text{Fe}_{2.31}^{2+}\text{Mg}_{0.28}\text{Al}_{0.18}\text{Ti}_{0.1}\text{Li}_{0.04}\text{Fe}_{0.01}^{3+})$ $\text{O}_{10}\text{OH}_{1.86}\text{F}_{0.14}$	420	13.5	1.4	110.3	59.6
Joswig (1972)	(F,OH)-phlogopite	$(\text{K}_{0.90}\text{Na}_{0.02})(\text{Mg}_{2.7}\text{Fe}_{0.16}^{2+}\text{Al}_{0.07}\text{Ti}_{0.03})$ $(\text{Si}_{2.91}\text{Al}_{1.09})\text{O}_{9.9}\text{F}_{1.13}(\text{OH})_{0.97}$	468	2.0	7.7	110.6	59.2
McCauley, Newnham and Gibbs (1973)	synthetic fluoro-phlogopite	$(\text{K}_{0.98}\text{Na}_{0.04})(\text{Mg}_{2.97}\text{Si}_{2.98}\text{Al}_{1.02})$ $\text{O}_{9.9}\text{F}_{1.94}(\text{OH})_{0.16}$	535	6.1	5.9	110.1	59.0
Takeda and Morosin (1975)	synthetic fluoro-phlogopite	(as above)	458	4.3	6.5	110.7	59.4
Hazen and Burnham (1973)	(F,OH)-phlogopite	$(\text{K}_{0.77}\text{Na}_{0.16}\text{Ba}_{0.02})\text{Mg}_3(\text{Si}_{2.95}\text{Al}_{1.05})$ $\text{O}_{10}\text{F}_{1.3}(\text{OH})_{0.7}$	1691	4.1	7.5	110.5	59.0
Hazen and Burnham (1973)	annite	$(\text{K}_{0.88}\text{Na}_{0.07}\text{Ca}_{0.03})(\text{Si}_{2.81}\text{Al}_{1.19})$ $(\text{Fe}_{2.22}^{2+}\text{Mg}_{0.12}\text{Mn}_{0.05}\text{Fe}_{0.19}^{3+}\text{Al}_{0.09}\text{Ti}_{0.22})$ $\text{O}_{10.35}(\text{OH})_{1.38}\text{F}_{0.22}\text{Cl}_{0.05}$	1517	4.5	1.6	110.3	58.4
Rayner (1974)	phlogopite	$(\text{K}_{0.93}\text{Na}_{0.04}\text{Ca}_{0.03})(\text{Mg}_{2.77}\text{Fe}_{0.10}\text{Ti}_{0.11})$ $(\text{Si}_{2.88}\text{Al}_{1.12})\text{O}_{10}(\text{OH})_{1.49}\text{F}_{0.51}$	293	6.6	8.7	110.4	59.1
Tateyama, Shimoda and Sudo (1974)	synthetic Mg ^{IV} phlogopite	$(\text{K}_{0.96}\text{Na}_{0.04})\text{Mg}_{2.84}(\text{Si}_{3.63}\text{Mg}_{0.31}\text{Fe}_{0.03})$ $\text{Al}_{0.03}\text{O}_{10}(\text{OH})_2$	385	10.4	7.4	110.9	58.2
Takeda and Ross (1975)	biotite	$(\text{K}_{0.78}\text{Na}_{0.16}\text{Ba}_{0.02})(\text{Mg}_{1.68}\text{Fe}_{0.71}^{2+}\text{Fe}_{0.19}^{3+})$ $\text{Ti}_{0.34}\text{Al}_{0.19}\text{Mn}_{0.01}(\text{Si}_{2.86}\text{Al}_{1.14})$ $\text{O}_{11.12}(\text{OH})_{0.71}\text{F}_{0.17}$	649	4.4	7.6	110.4	59.0
Toraya <i>et al.</i> (1976)	synthetic fluor mica 1M	$\sim\text{K}_{0.88}\text{Mg}_{2.56}\text{Si}_4\text{O}_{10}\text{F}_2$	1.057	3.8	1.4	111.8	58.0

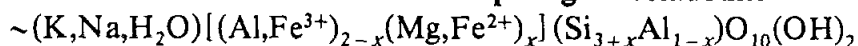
indicates number of independent reflections used in structure determination.

4.4.3 Biotite- $2M_1$ structure

Space group = $C2/c$ $a \cong 5.33$, $b \cong 9.23$, $c \cong 20.10$ Å, $\beta \cong 95.1^\circ$

Takeda and Ross (1975) have refined the structures of coexisting $1M$ and $2M_1$ forms of biotite from a lava flow in New Mexico, U.S.A. The original specimens, which were oxybiotites, were reduced by hydrogenation prior to structural analysis. Aside from the layer stacking sequences, the major structural difference in the two forms is a shift of the upper and lower octahedral anion triads in opposite directions along the Y axis for the $2M_1$ form. This twists the shared octahedral edges and lowers the symmetry of the 2:1 layer from approximately $C2/m$ to $C\bar{1}$, but most other structural features of the two polytypes are nearly identical. Because the compositions of the two crystals are the same, the differences in layer distortions are attributed to the constraints imposed by adjacent layers in the two different stacking sequences.

4.5 Dioctahedral muscovite–phengite–celadonite



4.5.1 General

The dioctahedral micas in most cases possess the structural features that have been discussed previously as inherent in dioctahedral layer silicates. As a result of cation repulsion, shared octahedral edges are shortened and twisted. The vacant octahedral site is enlarged relative to the occupied sites. The angle of tetrahedral rotation is relatively large, and the basal oxygen surface is corrugated in a direction parallel to the direction of intralayer shift (see Fig. 1.24 for an example).

In the kaolin minerals it was noted that the position of the vacant octahedral site in adjacent layers is such that the resultant symmetry and Z-axis periodicity no longer accord with those of

of trioctahedral 1M micas

Sheet thickness		Interlayer separation	Basal oxygen Δz	Mean bond lengths				Intralayer shift	Layer offset	Resultant shift
				T—O	M—O	R^{1+} —O				
Tet.	Oct.					Inner	Outer			
2.168 Å	2.192 Å	3.620 Å	0.10 Å	1.627 × 2 Å	2.075, 2.075 × 2 Å	3.075 Å	3.334 Å	−0.319 a_1	−0.014 a_1	−0.333 a_1
2.280	2.218	3.475	0.01	1.681 × 2	2.101, 2.105 × 2	2.945	3.452	−0.338	+0.001	−0.337
2.317	2.152	3.395	0.01	1.687 × 2	2.107, 2.106 × 2	3.055	3.351	−0.327	−0.006	−0.333
2.273	2.101	3.328	0.01	1.651 × 2	2.061, 2.060 × 2	2.995	3.278	−0.332	0	−0.332
2.274	2.100	3.353	0.06	1.667 × 2	2.078, 2.076 × 2	3.134	3.197	−0.330	−0.004	−0.334
2.268	2.116	3.356	0.01	1.654 × 2	2.066, 2.063 × 2	2.970	3.319	−0.334	0	−0.334
2.251	2.124	3.356	0.00	1.642 × 2	2.063, 2.064 × 2	3.006	3.273	−0.334	0	−0.334
2.277	2.095	3.329	0.01	1.650 × 2	2.056, 2.058 × 2	2.987	3.282	−0.334	0	−0.334
2.261	2.125	3.352	0.00	1.649 × 2	2.063, 2.065 × 2	2.969	3.312	−0.334	−0.001	−0.335
2.252	2.208	3.380	0.01	1.659 × 2	2.121, 2.101 × 2	3.143	3.215	−0.334	−0.018	−0.352
2.270	2.126	3.418	0.01	1.659 × 2	2.076, 2.064 × 2	2.967	3.360	−0.332	−0.003	−0.335
2.231	2.205	3.461	0.03	1.650 × 2	2.083, 2.094 × 2	3.010	3.347	−0.335	−0.003	−0.338
2.271	2.138	3.334	0.01	1.659 × 2	2.086, 2.068 × 2	2.972	3.318	−0.335	−0.002	−0.337
2.243	2.186	3.337	0.00	1.625 × 2	2.062, 2.064 × 2	3.079	3.142	−0.333	+0.001	−0.332

the theoretical trioctahedral polytypes. This is not the case for the dioctahedral micas because the vacant octahedral site always is located in M(1) in its unique position on the symmetry plane of each layer. As a result, the dioctahedral micas show no deviation in layer periodicity or space group from the theoretical values. They show, however, a more decided preference for different polytypes than the trioctahedral micas. The stable polytype for *muscovite* $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ is the $2M_1$ structure, and the $1M$, $1Md$, and $3T$ structures are metastable and less abundant in nature (Velde, 1965a). Dioctahedral micas that deviate from the ideal muscovite composition toward the *phengite* variety $\text{K}(\text{Al}_{1.5}\text{R}_{0.5}^{2+})(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}(\text{OH})_2$, or beyond to *celadonite* $\text{K}(\text{R}^{2+}\text{R}^{3+})\text{Si}_4\text{O}_{10}(\text{OH})_2$, or that are K-deficient show more preference for the $1M$, $1Md$, and $3T$ structures, although $2M_1$ is still encountered and $2M_2$ is very rare (Table 1.11). Most of these correlations of structure with composition have been made by Levinson (1955) for illites and hydrous micas, by Heinrich and Levinson (1955a) for high-silica “sericites” [*phengite*, *alurgite* (Mn-rich), and *mariposite* (Cr-rich)], by Heinrich and Levinson (1955b) for the V-mica *roscoelite* ($\text{V}_2\text{O}_3 \sim 17\%$) and for Ba-muscovite ($\text{BaO} \sim 10\%$), by Ankinovich *et al.* (1972) for *chernykhite*, the Ba-analogue of *roscoelite*, and by Heinrich and Levinson (1955c) for manganoan muscovite ($\text{MnO} \sim 2\%$). Characteristic powder patterns for muscovite are illustrated in Fig. 1.17. Powder data for muscovite and the Na-analogue *paragonite* are listed in Tables 1.15 and 1.16.

Schaller (1950) was the first to suggest a compositional trisilicic–tetrasilic series from muscovite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ to Mg–Al celadonite $\text{K}(\text{MgAl})\text{Si}_4\text{O}_{10}(\text{OH})_2$. Foster (1956) examined the chemical analyses of a large number of natural dioctahedral micas and found that all of the well-crystallized specimens would fit this series. For a constant layer charge of -1.0 and full interlayer cation occupancy, increase of tetrahedral Si requires concomitant replacement of Al by R^{2+} (usually Mg). The seat of the layer charge changes from entirely tetrahedral at the

Muscovite micas—diagnostic X-ray diffraction lines (cf. Fig. 1.17)

$2M_1$				$1M$			
	d (Å)	I	hkl		d (Å)	I	hkl
1.	4.29	1	111	1.	4.35	$1\frac{1}{2}$	$11\bar{1}$
2.	4.09	1	022	2.	4.12	1	021
3.	3.88	3	$11\bar{3}$	3.	3.66	5	$11\bar{2}$
4.	3.72	3	023	4.	3.07	5	112
5.	3.49	3	$11\bar{4}$	5.	2.93	1	$11\bar{3}$
6.	3.20	3	114	6.	2.69	2	023
7.	2.98	$3\frac{1}{2}$	025				
8.	2.86	3	115				
9.	2.79	$2\frac{1}{2}$	$11\bar{6}$				
10.	2.15	1	206,222				
	2.12	3	135,043				
$a = 5.201 \text{ \AA}$				$a = 5.208 \text{ \AA}$			
$b = 8.967$				$b = 8.995$			
$c = 20.058$				$c = 10.275$			
$\beta = 95.8^\circ$				$\beta = 101.6^\circ$			

$3T$				$2M_2$			
	d (Å)	I	$hkil$		d (Å)	I	hkl
1.	3.87	$3\frac{1}{2}$	$10\bar{1}4$	1.	4.34	2	$20\bar{2}, 111$
2.	3.60	3	$10\bar{1}5$	2.	3.90	3	$11\bar{3}$
3.	3.11	3	$10\bar{1}7$	3.	3.68	4	$20\bar{4}$
4.	2.88	4	$10\bar{1}8$	4.	3.52	4	$11\bar{4}$
5.	2.68	1	$10\bar{1}9$	5.	3.21	4	114
				6.	3.07	4	204
				7.	2.87	2	$11\bar{5}$
				8.	2.81	2	$11\bar{6}$
$a = 5.196 \text{ \AA}$				$a = 9.017 \text{ \AA}$			
$b = 5.196$				$b = 5.210$			
$c = 29.970$				$c = 20.437$			
$\beta = 90^\circ$				$\beta = 100.4^\circ$			
$\gamma = 120^\circ$							

trisilicic end to entirely octahedral at the tetrasilicic end. The charge is 50% tetrahedral and 50% octahedral in origin at the ideal phengite composition $K(Al_{1.5}R_{0.5}^{2+})(Si_{3.5}Al_{0.5})O_{10}(OH)_2$. Foster noted that from ideal muscovite to ideal phengite the octahedral R^{3+} cation is primarily Al, but is Fe at the celadonite end. Later work indicates the series probably is discontinuous from phengite to celadonite (Velde, 1965*b*).

4.5.2 Illite

The term *illite* was proposed by Grim, Bray, and Bradley (1937) as a group name for the clay-size micaceous components in argillaceous sediments. Illite is predominantly dioctahedral, but differs from ideal muscovite in having on the average more Si, Mg, and H₂O, but less interlayer K. Although many clays termed illite in the literature are known to contain expandible layers in addition to micaceous layers, illite should be used to designate only non-expandible 10 Å mica.

The most recent survey of illite compositions by Weaver and Pollard (1973) indicates the average 10 Å illite has about half as much tetrahedral Al as ideal muscovite, has about 1/8 of its

octahedral cations in the form of Mg or Fe^{2+} , and has a total layer charge of about -0.75 per formula unit.

Levinson (1955) found by X-ray powder study that fine grained illites and hydrous micas crystallize in the same structural forms as the coarser crystals of muscovite. He recognized $1Md$, $1M$, $2M_1$, and $3T$ illites. Since then, a few examples of fine-grained $2M_2$ illites have been reported also (Drits, Zvyagin, and Tokmakov, 1966; Shimoda, 1970).

Brown and Norrish (1952) proposed that the excess H_2O in chemical analyses of illite is present in the interlayer sites in the form of oxonium H_3O^+ (= hydronium). Although this concept can be used to allocate chemical analyses to reasonable structural formulas, no successful synthesis of an oxonian mica has been reported. Sclar, Carrison, and Schwartz (1965), however, have reported synthesis at high pressures (32–90 kbar) of a cation-deficient talc with oxonium in the interlayers. Rosenqvist (1963) concluded from a study of deuterium-treated natural illites that neutral water molecules (instead of H_3O^+) must be present in the interlayer sites not occupied by K and, in addition, that some H must be added to the apical oxygens of Al-tetrahedra. White and Burns (1963), however, have interpreted infrared absorption spectra of H-saturated micas as indicating the presence of H_3O^+ .

4.5.3 *Glaucinite–celadonite*

Natural glauconites and celadonites are iron-rich dioctahedral micas that, like illite, are K-deficient and have small tetrahedral substitutions. Interstratification with expansible layers is present in varying degrees. *Glaucinite* is used to designate the Fe-rich, green, pelletal micas of marine origin, whereas *celadonite* is used to designate the non-marine occurrences such as vesicle-fillings and veins in basalts or alteration products of volcanic rocks. Because a genetic classification of this sort is not entirely satisfactory, increasing usage is being made of celadonite to refer to the ideal end member composition $\text{K}(\text{R}^{3+}\text{R}^{2+})\text{Si}_4\text{O}_{10}(\text{OH})_2$. Glaucinite and celadonite have been recognized only in the $1M$ and $1Md$ structural forms (Table 1.17).

Compilations of chemical analyses by Hendricks and Ross (1941), Foster (1969), and Weaver and Pollard (1973) agree in assigning slightly different average compositions to these two minerals, listed by Weaver and Pollard as $\text{R}_{0.78}^{1+}(\text{Fe}_{1.01}^{3+}\text{Al}_{0.45}\text{Mg}_{0.39}\text{Fe}_{0.20}^{2+})_{2.05}(\text{Si}_{3.65}\text{Al}_{0.35})\text{O}_{10}(\text{OH})_2$ for marine glauconite and $\text{R}_{0.83}^{1+}(\text{Fe}_{0.72}^{3+}\text{Al}_{0.49}\text{Mg}_{0.63}\text{Fe}_{0.21}^{2+})_{2.05}(\text{Si}_{3.81}\text{Al}_{0.19})\text{O}_{10}(\text{OH})_2$ for non-marine celadonite. The main differences are a smaller tetrahedral Al content and a lower Fe/Mg ratio in celadonite. The average source of layer charge changes from almost 50:50 tetrahedral:octahedral in glauconite to largely octahedral in celadonite. Weaver and Pollard emphasize structural control of the octahedral composition of both glauconite and celadonite. They cite the lack of any strong dominance of total octahedral R^{3+} relative to R^{2+} in celadonite as a possible reason why all three octahedra, including the vacant site, were found to be about the same size in the structure determination by Zvyagin (1957) and as a possible criterion for distinction of celadonite from glauconite. Nevertheless, they conclude from the overlap of compositions that a continuous series is likely between glauconite and celadonite, but with two well developed nodes of slightly different average compositions. Porrenga (1968) has summarized several occurrences of non-pelletal green clay lenses and layers in non-marine sediments in which the dioctahedral micas have compositions intermediate between illite and glauconite.

Buckley, Bevan, Brown, Johnson, and Farmer (1978), on the other hand, found little overlap in the compositions of 16 glauconites and 10 celadonites that were carefully purified prior to analysis. They propose that each is a distinct species, but with considerable isomorphous substitutions. Celadonite is characterized by less than 0.17 atoms of tetrahedral Al

TABLE 1.15. X-ray powder data for polytypic forms of muscovite; spacings in Å

A. 1M			B. 2M ₁			C. 2M ₂			D. 3T		
hkl	I	d	hkl	I	d	hkl	I	d	hkl	I	d
001	>100	10.077	002	>100	10.014	002	55	10.25	0003	>100	9.969
002	37	5.036	004	55	5.021	004	42	5.06	0006	53	4.991
020	90	4.488	110	55	4.478	110:111	60	4.49	1010	19	4.492
111	27	4.349	111	65	4.458	202	15	4.37	1011	19	4.460
021	16	4.115	021	14	4.391	111	5	4.31	1014	10	3.873
112	60	3.660	111	21	4.296	112	5	3.966	1015	8	3.596
003	>100	3.356	022	14	4.109	113	21	3.921	0009	>100	3.331
022			112	12	3.973	204	43	3.681	1017	10	3.110
112	50	3.073	113	37	3.889	114	33	3.520	1018	16	2.884
113	6	2.929	023	32	3.735	006	58	3.348	1121	15	2.589
023	16	2.689	114	44	3.500	114	28	3.211	1122	27	2.564
130	50	2.582	006 } 024 }	>100	3.351	204	40	3.066	0,0,0,12	11	2.499
131	90	2.565				206	15	2.946	1124	7	2.457
200	22	2.550	114	47	3.208	115	22	2.869	1125	8	2.384
131	11	2.450	025	47	2.999	116	18	2.812	2020	5	2.254
132	4	2.405	115	35	2.871	021	90	2.583	1127	4	2.222
114	12	2.380	116	22	2.803	008	10	2.513	2023	4	2.197
040	8	2.246	131	50	2.589	314	16	2.450	1128	12	2.136
220	7	2.219	116	45	2.580	023	15	2.426	2026	3	2.056
041	4	2.191	202	90	2.562	312	14	2.402	0,0,0,15	47	1.999
133	20	2.156	008	20	2.514	313	4	2.285	1,1,2,10	7	1.966
202	6	2.109	133	19	2.458	221:402	8	2.252	1,1,2,11	2	1.885
005	32	2.013	202	12	2.446	221:400	7	2.210	1,1,2,14	10	1.654
133	7	1.957	204	10	2.396	025:223	7	2.186	2,1,3,5	3	1.638
134	4	1.900	133	24	2.380	317:402	20	2.082	2,1,3,6	3	1.614

116	18	1-668	221	12	2-247	026	15	2-055	2,1,3,8	2	1-551
151	12	1-653	040			0,0,10	30	2-006	1,1,2,16	6	1-521
204	12	1-635	041	5	2-236	228;1,1,11	3	1-750	3,0,3,0	11	1-502
135	4	1-514	221	5	2-201	1,3,10	10	1-717			
060	33	1-499	223	7	2-184	029;131;227	15	1-694			
			222	10	2-149	318;2,0,12	15	1-668			
			043	23	2-132	133;425	8	1-633			
			135			3,1,11,516	8	1-614			
			044	6	2-051	135;0,2,10;423	8	1-585			
			0,0,10	75	2-010	319	5	1-569			
			137	14	1-975	602;331;428	30	1-500			
			139	6	1-736	2,0,12;331;600	4	1-481			
			150	6	1-699						
			241								
			2,0,10	12	1-670						
			314	17	1-653						
			313	7	1-602						
			331	40	1-499						
			060								

- A. 1M $a = 5.208$, $b = 8.995$, $c = 10.275$ Å, $\beta = 101.58^\circ$.
 Synthetic specimen (Yoder and Eugster, 1955).
 B. 2M₁ $a = 5.189$, $b = 8.995$, $c = 20.097$ Å, $\beta = 95.18^\circ$.
 Synthetic specimen (Yoder and Eugster, 1955).
 C. 2M₂ $a = 9.017$, $b = 5.210$, $c = 20.437$ Å, $\beta = 100.4^\circ$.
 Hydromuscovite specimen from Shakanai mine, Japan.
 (Indexing modified from Shimoda, 1970.)
 D. 3T $a = 5.203$, $c = 29.988$ Å, $\gamma = 120^\circ$.
 Specimen from Sultan Basin, Washington, U.S.A.
 (Yoder and Eugster, 1955.)

TABLE 1.16. X-ray powder data for polytypic forms of synthetic paragonite, spacings in Å (Chatterjee, 1970)

A. 1M				B. 2M ₁			
hkl	I(obs.)	d(obs.)	d(calc.)	hkl	I(obs.)	d(obs.)	d(calc.)
001	80	9.665	9.6334	002	31	9.633	9.6226
002	50	4.822	4.8167	004	21	4.814	4.8113
020	35	4.442	4.4423	110	37	4.437	4.4416
111	20	4.236	4.2283	111	42	4.392	4.3925
021	3	4.029	4.0340	111	7	4.270	4.2660
112	18	3.497	3.4930	112	4	4.140	4.1391
003	100	3.212	3.2111	022	7	4.040	4.0352
112	31	3.058	3.0547	113	7	3.763	3.7713
113	6	2.778	2.7785	023	6	3.654	3.6536
023	8	2.602	2.6024	114	10	3.368	3.3777
130	12	2.557	2.5581	024	21	3.267	3.2649
131	19	2.523	2.5215	006	100	3.207	3.2075
131	9	2.426	2.4262	114	19	3.163	3.1603
201	3	2.364	2.3666	115	3	3.020	3.0097
132	3	2.336	2.3357	025	16	2.910	2.9097
041	3	2.164	2.1643	115	16	2.822	2.8174
024	4	2.116	2.1172	116	10	2.680	2.6867
133	6	2.083	2.0812	131	22	2.557	2.5561
005	25	1.9279	1.9267	131	48	2.528	2.5304
115	3	1.6851	1.6846	202			2.5261
151	3	1.6653	1.6667	202	19	2.427	2.4312
204	3	1.6268	1.6265	133	20	2.416	2.4145
006	5	1.6045	1.6056	133	11	2.350	2.3512
060	10	1.4816	1.4808	027	6	2.335	2.3382
206	4	1.4623	1.4626	135	10	2.172	2.1738
				222	2	2.133	2.1330
				043	12	2.100	2.1000
				224	6	2.073	2.0695
				044	3	2.018	2.0176
				0,0,10	31	1.9248	1.9245
				137	2	1.8413	1.8408
				046	4	1.8275	1.8268
				151	7	1.6771	1.6772
				244	8	1.6114	1.6110
				060	31	1.4814	1.4816
				331	17	1.4685	1.4687

A. 1M $a = 5.139$, $b = 8.885$, $c = 9.750$ Å, $\beta = 98.87^\circ$.B. 2M₁ $a = 5.143$, $b = 8.890$, $c = 19.302$ Å, $\beta = 94.41^\circ$.

per formula unit whereas Al^{IV} for glauconites is in the range 0.17–0.43. Total octahedral R³⁺ is quite constant at 1.04 ± 0.15 atoms for celadonite and 1.34 ± 0.15 for glauconite, although the amounts of Al and Fe³⁺ may be variable. Celadonite is believed to give sharper infrared spectra and X-ray patterns than glauconite due to its smaller tetrahedral substitution and to the smaller deviation of its octahedral R³⁺/R²⁺ ratio from the optimum 1:1 value (see also Chapter 5, Section 5.1.2).

4.5.4 Details of muscovite-2M₁ structure

Space group = C2/c $a \cong 5.19$, $b \cong 9.00$, $c \cong 20.00$ Å, $\beta \cong 95.7^\circ$

The structure of the 2M₁ form of muscovite has been investigated by Radoslovich (1960), Burnham and Radoslovich (1964), and Güven (1971a) using single crystal X-ray methods, by

TABLE 1.17. X-ray powder data for glauconite, celadonite, and roscoelite; spacings in Å

A. Glauconite-1M (Warshaw, 1957)			B. Celadonite-1M (Wise and Eugster, 1964)				C. Roscoelite-1M (Heinrich and Levinson, 1955b)	
<i>d</i> (obs.)	<i>I</i>	<i>hkl</i>	<i>hkl</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>I</i>	<i>d</i> (obs.)	<i>I</i>
10.1	100	001	001	9.97	9.94	47	10.0	100
4.98	*	002	020	4.53	4.53	85	5.01	30
4.53	80	020	111	4.35	4.36	42	4.54	80
4.35	20	111	021	4.14	4.123	37	4.39	10
4.12	10	021	112	3.635	3.638	80	4.13	10
3.63	40	112	022	3.35 ¹	3.349	60	3.91	30
3.33	60	003,022	003	3.318 ¹	3.314	70	3.66	50
3.09	40	112	112	3.087	3.081	80	3.35	80
2.89	5	113	113	2.90 B	2.901	10	3.11	50
2.67	10	023	023	2.678	2.675	75	2.90	40
2.587	100	{ 130,131 200	130	2.604	2.605	70	2.70	30
2.396	60	132,201	131	2.580	2.581	100	2.60	80
2.263	20	040,221	132	2.402	2.404	75	2.42	50
2.213	10	220,041	040	2.264	2.265	18	2.28	30
2.154	20	133,202	041	2.209	2.208	25	2.21	30
1.994	20 B	005	133 }	2.148	{ 2.150 2.125 }	31	2.16	50 B
1.817	5	224	202 }	2.092	1.988	10	2.00	50 B
1.715	10	311,241	005	1.65 B	1.665	15	1.72	10
1.66	30 B	{ 240,312 310,241	151	1.509	1.510	60	1.67	40 B
1.511	60	060,331	060				1.52	60
1.495	10	330					1.44	10 B
1.307	30	260,400					1.38	30
1.258	10	{ 170,350 420					1.35	30
							1.31	30 B
							1.26	30

A. * Obtained only with oriented sample.

$a = 5.234$, $b = 9.066$, $c = 10.16$ Å, $\beta = 100.5^\circ$.

Specimen from Vidono Fm., Anzoategui, Venezuela.

B. ¹ The exact location of these two peaks is difficult to obtain. B = broad peak.

$a = 5.23$, $b = 9.06$, $c = 10.13$ Å, $\beta = 100^\circ 55'$.

Specimen from Wind River area, Washington.

C. Specimen from Paradox Valley, California.

Zvyagin and Mishchenko (1960) using texture electron diffraction of a powder, and by Rothbauer (1971) using single crystal neutron diffraction. In addition, the $2M_1$ form of a potassian paragonite has been studied by Burnham and Radoslovich (1964) and of a phengite by Güven (1971a). Some of the structural results of these studies are tabulated in Table 1.18. Fig. 1.18 from Güven (1971a) is representative of the structures.

The angle of tetrahedral rotation α ranges from 11° to 13° in different muscovite specimens. The phengite- $2M_1$ studied by Güven differs from muscovite- $2M_1$ primarily in the increased size of the octahedral cations ($\text{Al}_{1.43}\text{Fe}_{0.05}^{3+}\text{Fe}_{0.09}^{2+}\text{Mg}_{0.50}$ versus Al_2) and the decreased size of the tetrahedral cations ($\text{Si}_{3.39}\text{Al}_{0.61}$ versus Si_3Al). The tetrahedral-octahedral lateral misfit is much smaller for phengite, therefore, with the result that the angle of tetrahedral rotation ($\alpha = 6.0^\circ$) and the amount of basal oxygen corrugation ($\Delta z = 0.16$ Å) are both considerably smaller than the values for true muscovite ($\alpha = 11\text{--}13^\circ$, $\Delta z = 0.21\text{--}0.23$ Å).

Radoslovich and Norrish (1962) have presented evidence that in dioctahedral micas the interlayer K atom is too large for its six-coordinated hole after tetrahedral rotation. This has the

TABLE 1.18. Structural

Reference	Species	Composition	# Refl.	Final R	α_{tet}	τ_{tet}
Radoslovich (1960)	muscovite-2M ₁	(K _{0.94} Na _{0.06})(Al _{1.83} Fe ³⁺ _{0.12} Mg _{0.06})(Si _{3.11} Al _{0.89})O ₁₀ (OH) ₂	550	17.0%	13.1°	110.6°
Gatineau (1963)	muscovite-2M ₁	same	same	8.0	11.7	110.8
Birle and Tettenhorst (1968)	muscovite-2M ₁	same	same	12.0	12.0	110.9
Zvyagin and Mishchenko (1960)	muscovite-2M ₁	not given	134	23.0	9.8	110.7
Burnham and Radoslovich (1964)	sodian muscovite-2M ₁	~(K _{0.65} Na _{0.35})Al ₂ (Si ₃ Al)O ₁₀ (OH) ₂	619	3.8	12.8	110.9
Burnham and Radoslovich (1964)	potassian paragonite-2M ₁	~(Na _{0.85} K _{0.15})Al ₂ (Si ₃ Al)O ₁₀ (OH) ₂	557	3.4	15.9	110.5
Rothbauer (1971)	muscovite-2M ₁	(K _{0.85} Na _{0.09})(Al _{1.81} Fe ³⁺ _{0.14} Mg _{0.12})(Si _{3.09} Al _{0.91})O _{9.81} (OH) ₂ F _{0.19}	625	2.7	11.3	110.9
Güven (1971a)	muscovite-2M ₁	(K _{0.86} Na _{0.10} H ₃ O _{0.01})(Al _{1.9} Mg _{0.06} Fe ²⁺ _{0.05} Fe ³⁺ _{0.02} Ti _{0.01})(Si _{3.02} Al _{0.98})O ₁₀ (OH) _{1.99} F _{0.01}	567	3.5	11.4	111.0
Güven (1971a)	phengite-2M ₁	(K _{0.87} Na _{0.07} R _{0.03})(Al _{1.43} Fe ³⁺ _{0.05} Mg _{0.50} Fe ²⁺ _{0.09} Ti _{0.01})(Si _{3.39} Al _{0.61})O _{10.08} (OH) _{1.92}	557	4.5	6.0	111.4
Zvyagin (1957, 1967)	celadonite-1M	~(K _{0.73} Ca _{0.03})(Fe ³⁺ _{0.01} Fe ²⁺ _{0.28} Mg _{0.57} Al _{0.20} Ti _{0.01})O _{10.14} (OH) _{1.79} F _{0.07}	400	?	7.5	108.1
Sidorenko, Zvyagin and Soboleva (1975)	phengite-1M	(K _{0.66} Na _{0.03})(Al _{1.83} Fe ³⁺ _{0.03} Fe ²⁺ _{0.04} Mg _{0.10})(Si _{3.51} Al _{0.49})O _{10.14} (OH) _{1.79} F _{0.07}	588	10.9	9.3	110.6
Zhoukhlistov, Zvyagin, Soboleva and Fedotov (1973)	phengite-2M ₂	~(K _{0.68} Na _{0.09})Al _{1.93} (Si _{3.3} Al _{0.7})O _{10.06} (OH) _{1.94}	504	11.7	11.2	111.5
Güven and Burnham (1967)	muscovite-3T	(K _{0.9} Na _{0.06} R _{0.02})(Al _{1.83} Fe ³⁺ _{0.04} Ti _{0.01} Fe ²⁺ _{0.04} Mg _{0.09})(Si _{3.11} Al _{0.89})O ₁₀ (OH) _{1.98} F _{0.03}	280	2.4	11.8	110.6
Rozhdestvenskaya and Frank-Kamenetskii (1974)	chernykhite-2M ₁	[Ba _{0.29} Na _{0.20} K _{0.07} (NH ₄) _{0.1}][V ⁴⁺ _{0.30} V ³⁺ _{0.13} Al _{0.65} (Mg,Fe) _{0.20}](Si _{2.30} Al _{1.70})O ₁₀ (OH) ₂	984	12.0	7.0	111.7

indicates number of independent reflections used in structure determination.

result of reducing the amount of tetrahedral rotation that actually occurs, of propping apart the basal oxygen surfaces, and of stretching the octahedral sheet laterally. For a smaller interlayer cation, and the same composition otherwise, one would expect a larger tetrahedral rotation, less

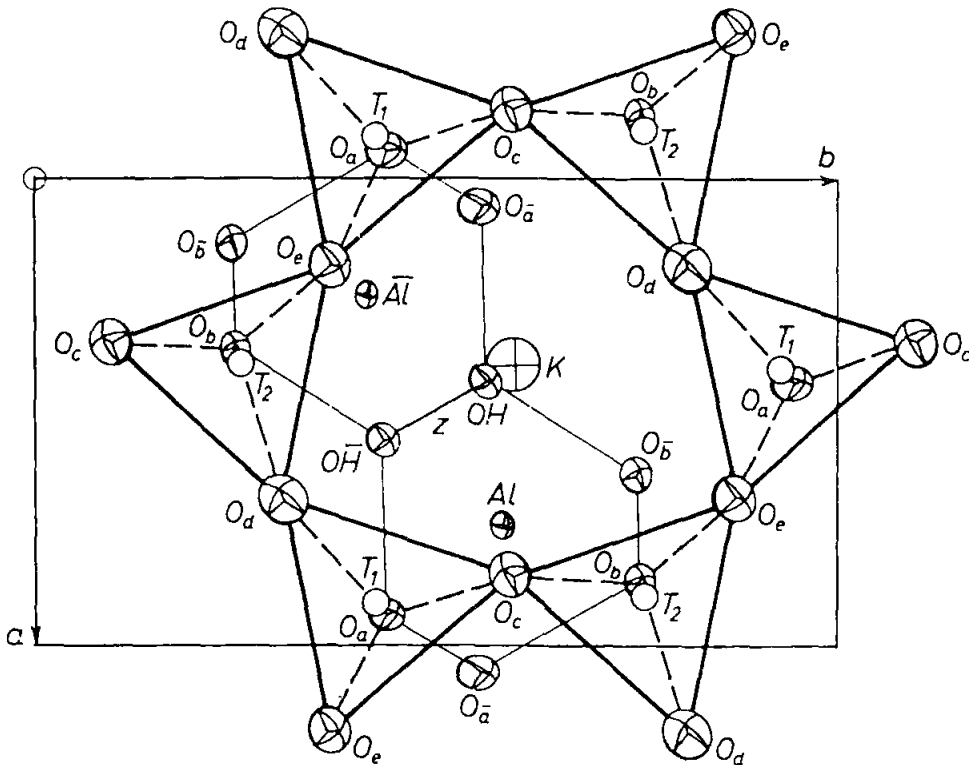


FIG. 1.18. Upper portion of first layer of muscovite-2M₁ structure with ellipsoids of anisotropic thermal vibration for each atom (from Güven, 1971a). Upper tetrahedral sheet is related to lower tetrahedral sheet within 2:1 layer by inversion centers (z) at lattice points. Tetrahedral rotation angle α is 11.4°.

details of dioctahedral micas

ψ_{Oct}	Sheet thickness		Interlayer separation	Basal oxygen Δz	Mean bond lengths		$R^{1+}-O$		Intralayer shift	Layer offset	Resultant shift
	Tet.	Oct.			T-O	M-O	Inner	Outer			
58.7°	2.258 Å	2.120 Å	3.370 Å	0.11 Å	1.695, 1.612 Å	1.956 × 2 Å	2.812 Å	3.389 Å	+0.356 $a_{2,3}$	-0.002 $a_{1,1}$	-0.350 a_1
59.1	2.244	2.092	3.428	0.23	1.653, 1.639	1.924 × 2	2.857	3.378	+0.367 $a_{2,3}$	+0.003 $a_{1,1}$	-0.350 a_1
59.0	2.242	2.096	3.426	0.23	1.660, 1.636	1.924 × 2	2.851	3.382	+0.368 $a_{2,3}$	+0.004 $a_{1,1}$	-0.350 a_1
59.0	2.252	2.080	3.416	0.16	1.648, 1.628	1.972 × 2	2.889	3.323	+0.339 $a_{2,3}$	-0.024 $a_{1,1}$	-0.383 a_1
59.0	2.243	2.091	3.312	0.23	1.645, 1.646	1.923 × 2	2.793	3.369	+0.376 $a_{2,3}$	+0.002 $a_{1,1}$	-0.374 a_1
58.8	2.244	2.092	3.078	0.24	1.654, 1.650	1.913 × 2	2.640	3.371	+0.373 $a_{2,3}$	+0.035 $a_{1,1}$	-0.304 a_1
59.1	2.202	2.089	3.480	0.21	1.645, 1.644	1.930 × 2	2.857	3.362	+0.376 $a_{2,3}$	-0.009 $a_{1,1}$	-0.386 a_1
58.9	2.239	2.103	3.392	0.22	1.643, 1.642	1.933 × 2	2.855	3.362	+0.377 $a_{2,3}$	-0.009 $a_{1,1}$	-0.387 a_1
58.7	2.219	2.126	3.359	0.16	1.621, 1.633	1.956 × 2	2.971	3.236	+0.376 $a_{2,3}$	-0.008 $a_{1,1}$	-0.385 a_1
57.2	2.258	2.238	3.357	0.09	1.643 × 2	2.044 × 2	2.933	3.268	-0.333 a_1	-0.013 a_1	-0.346 a_1
58.7	2.196	2.113	3.399	0.18	1.614, 1.633	1.920, 1.957	2.897	3.306	-0.376 a_1	-0.024 a_1	-0.400 a_1
58.4	2.216	2.133	3.414	0.22	1.619, 1.653	1.956 × 2	2.860	3.354	-0.380 b_3 +0.380 b_2	-0.018 a_1 -0.018 a_1	-0.419 a_1
58.8	2.207	2.112	3.465	0.14	1.670, 1.603	1.973, 1.913	2.868	3.388	+0.379 $a_{2,3,1}$	-0.008 $a_{1,2,3}$	0
58.0	2.269	2.217	3.207	0.15	1.657, 1.660	2.013 × 2	2.937	3.258	-0.361 $a_{2,3}$	-0.11 a_1	-0.375 a_1

interlayer separation, and a smaller b repeat distance. These are all observed in the structure of paragonite relative to muscovite by Burnham and Radoslovich (1964). Burns and White (1963) also have shown that the b value decreases as K is leached from muscovite. The interlayer separation of 3.08 Å for paragonite indicates that adjacent oxygen surfaces are quite close, but not in contact.

Radoslovich (1960) has pointed out that in muscovite- $2M_1$ the interlayer K is not in the exact center of the hexagonal ring, but is displaced along the two-fold axis toward the vacant octahedral site. Other refinements, however, have shown a displacement in the opposite sense. These displacements all lead to small offsets of adjacent layers (as measured between tetrahedral cations) that are larger, on the average, than found for trioctahedral micas. Another distortional effect, observed in dioctahedral but not in trioctahedral micas to date, is the intralayer "overshift" of 0.36 a to 0.38 a instead of the ideal 0.33 a . Bailey (1975a) has shown that the overshift is due to the M(1) vacant octahedron being larger than the M(2) occupied octahedra. The overshifts plus adjacent layer offsets combine to create β angles larger than the ideal values (Table 1.18). Because the intralayer shifts in the $2M_1$ structure are oriented at 120° to each other in adjacent layers, the displacements partly cancel one another so the resultant β angle is only 0.6–0.8° larger than the ideal value. Similar deviations of the observed and ideal β angles are observed in the $1M$ and $2M_2$ forms of phengite. Celadonite- $1M$ is an exception because it does not have typical dioctahedral distortions.

As a result of these structural distortions, single crystal X-ray patterns of muscovite- $2M_1$ exhibit weak reflections of type 06 l with l odd, which would be absent in the undistorted structure. Hendricks and Jefferson (1939), who first noted these 06 l reflections, postulated that the forces responsible for this structural distortion also cause adoption of a unique stacking sequence of layers for muscovite, in which little stacking irregularity is permitted. Other 2-layer dioctahedral structures exhibit similar 06 l , l odd, reflections (e.g. dickite, pyrophyllite- $2M$,

paragonite- $2M_1$, margarite- $2M_1$, and cookeite). The effect is not restricted to dioctahedral structures, however, as it has been observed also in certain polytypes of zinnwaldite, amesite, cronstedtite, and chlorite. Radoslovich and Norrish (1962) have shown for equal tetrahedral sizes and scattering powers (*i.e.* tetrahedral cation disorder) that the effect can be caused by altering the positions of the tetrahedral cations from the ideal model so they no longer have y coordinates that are exact multiples of $b/12$. Henry (1974) also has shown that tetrahedral cation order can cause the effect if the differences in tetrahedral sizes and scattering powers are great enough.

The vacant site in all dioctahedral micas is located in M(1) on a center of symmetry. Hogg and Meads (1970) have interpreted Mössbauer spectra to indicate that small amounts of Fe^{2+} are present in the vacant site of some muscovites, and Güven (1971a) has confirmed small electron densities at this position for muscovite- $2M_1$ and phengite- $2M_1$. The two occupied octahedral sites in muscovite- $2M_1$ are equivalent to each other by the space group symmetry, so that octahedral cation order is not possible. The space group ($C2/c$) does permit tetrahedral cation order, but no proof of such order has been found to date. The results of the study by Radoslovich (1960) did suggest partial tetrahedral cation order, but this later was shown to be due to incomplete refinement. Further refinement of the same data by Gatineau (1963) and by Birle and Tettenhorst (1968) showed that the T—O bond lengths for the two non-equivalent tetrahedra differ by only 0.01 to 0.02 Å, instead of the 0.08 Å found by Radoslovich, so that any long-range tetrahedral ordering must be very small. Similar or identical T(1)—O and T(2)—O bond lengths were found in the structures of the other $2M_1$ specimens that have been studied.

Despite the lack of long-range tetrahedral cation order, Gatineau (1964) has reported the presence of an unusual type of short-range order from study of diffuse scattering in the regions between the normal Bragg reflections on single crystal X-ray photographs. The distribution and intensity of these diffuse streaks have been interpreted as due to concentration in local small domains of Al in zigzag chains within the tetrahedral sheets. In a given domain the direction of chain alignment may be along any one of the three pseudo-hexagonal X axes of the crystal. Chains of pure Al are said to alternate along the Y direction in partly ordered fashion with chains of pure Si.

The type of short-range order deduced in muscovite- $2M_1$ is unusual in that it grossly violates the principle of avoidance of Al—Al neighbors postulated by Loewenstein (1954) and found to be obeyed in a large number of cases of long-range ordering in aluminosilicates. The analysis of diffuse scattering is admittedly complex, and in micas the interpretation is complicated by the finding of Kodama *et al.* (1971) that in the local domains the tetrahedral network is distorted in linear waves characterized by alternating rows of tetrahedra of slightly differing dimensions even in the absence of tetrahedral substitution (as in pyrophyllite and talc). Further study appears required in order to establish the contributions to the diffuse scattering that may be given by local Si,Al ordering, oxygen network distortion, thermal motion, or other phenomena. Güven (1976, personal communication) has suggested that dislocation arrays also may cause a similar diffuse scattering.

The orientation of the O—H transition moment for the OH in the center of each hexagonal ring has been calculated for muscovite- $2M_1$ from infrared measurements by a number of authors. The transition moment need not be identical with the O—H bond direction, but should be within a few degrees of it. There is general agreement in these studies that the H^+ is inclined away from the two coordinating octahedral Al cations so that the transition moment makes an angle of 30° – 39° with the Y axis in projection on the (001) cleavage, and is inclined by 16° – 20° to this cleavage. There is some uncertainty in these measurements because of thermal vibration,

and there is disagreement as to whether the H^+ is located inside or outside the octahedral sheet (*i.e.* pointing into the sheet and toward the vacant octahedral site, as in the kaolin minerals, or pointing out of the octahedral sheet and into the tetrahedral sheet). Giese (1971) used Gattineau's (1963) atomic coordinates to calculate that the minimum electrostatic energy is achieved if the O—H bond points away from the octahedral sheet. This has been confirmed experimentally by Rothbauer (1971), who located the nuclear position of the H^+ precisely by neutron diffraction. The nucleus of H is located 0.93 Å from the nucleus of the associated oxygen and the O—H bond direction lies in the (110) plane, where it makes an angle of 30° with the Y axis. The bond is inclined 12° from the (001) cleavage (78° from the vertical). In this location the hydrogen proton is at a distance of 2.47 Å from a basal oxygen O(2) and is equidistant from two apical oxygens O(4) and O(5) at 2.68 Å.

Giese (1974, personal communication) has calculated the position of the H proton by minimizing the electrostatic energy for three structural forms of muscovite and for the $2M_1$ forms of phengite, paragonite, and margarite. The O—H bond was found to vary in orientation from nearly horizontal in muscovite- $1M$ and phengite- $2M_1$ to 40° from horizontal in margarite- $2M_1$. The angle made by the O—H bond with the (001) plane increases in direct relation to the magnitude of the tetrahedral rotation angle α . This suggests some attraction of H^+ by the nearest basal oxygen that tends to counterbalance partly the repulsion of H^+ by the interlayer cation. The calculations suggest further that the effect of the interlayer cation repulsion is to depress the O—H bond orientation by approximately 30° .

4.5.5. *Muscovite-3T structure*

Space group = $P3_112$ $a = b = 5.196$ Å, $c = 29.970$ Å, $\gamma = 120^\circ$

Güven and Burnham (1967) used single crystal X-ray methods to determine the crystal structure of muscovite- $3T$ from Sultan Basin, Washington, U.S.A. The composition of this specimen is nearly identical to that of the muscovite- $2M_1$ studied by Radoslovich (1960), but there are major structural differences. In addition to the obvious difference in layer stacking sequence (Fig. 1.15), the $3T$ structure differs from the $2M_1$ structure in showing both tetrahedral and octahedral cation ordering. The mean bond length T(1)—O = 1.603 Å indicates occupancy only by Si whereas the mean bond length T(2)—O = 1.671 Å indicates all of the tetrahedral Al and the remainder of the Si are concentrated in T(2) (occupancy $Si_{0.55}Al_{0.45}$). A more complete ordering of Si, Al would require a lower symmetry than is observed. The mean bond lengths to the two independent octahedral cations (1.971 Å and 1.913 Å) indicate site M(1) contains $Al_{0.83}Mg_{0.09}Fe_{0.04}^{2+}Fe_{0.04}^{3+}$ whereas site M(2) contains only Al. There is no occupancy of the third octahedral site.

In discussing the relationship between the $2M_1$ and $3T$ forms of muscovite, Güven (1971b) has pointed out that the two tetrahedral sheets within a single mica layer are related to each other by a center of symmetry in the $2M_1$ structure (Fig. 1.18) but by a lateral two-fold rotation axis in the $3T$ structure. If tetrahedral cation ordering were present in the $2M_1$ structure, there would be two apical oxygens with unbalanced electrostatic charges arrayed along the same octahedral shared edge as a consequence of the inversion center. This potentially unstable arrangement is avoided in the $3T$ structure. In the same way, adjacent layers theoretically can be related to each other in the interlayer region either by an inversion center or by a lateral two-fold axis. Layers related by an inversion center appear to be most stable both from packing and electrostatic charge considerations, and are observed in $1M$ micas of space group $C2/m$. In dioctahedral micas, however, Güven (1971b) believes that anion repulsion between adjacent, non-meshed

corrugated oxygen surfaces, even though not in actual contact, makes the centrosymmetric interlayer region less stable. Adjacent layers in both the $2M_1$ and $3T$ structures of muscovite are related, instead, by a two-fold rotation axis parallel to $[010]$ and differ primarily in their intralayer symmetry ($C\bar{1}$ versus $C2$, respectively).

The angle of tetrahedral rotation in muscovite- $3T$ ($\alpha = 11.8^\circ$) is similar to that in muscovite- $2M_1$, but the amount of corrugation of the basal oxygen surface due to tetrahedral tilt is smaller ($\Delta z = 0.14 \text{ \AA}$). Although the β angle must be 90° as a result of the closed triangle of three intralayer shifts at 120° to each other, each individual layer shows the same intralayer "overshift" ($0.378a$) and adjacent layer offset as found in other muscovites (Table 1.18).

4.5.6 Phengite- $2M_2$ structure

Space group = $C2/c$ $a \cong 8.965$, $b \cong 5.175$, $c \cong 20.31 \text{ \AA}$, $\beta \cong 100.67^\circ$

Diocahedral $2M_2$ structures have been reported by Drits, Zvyagin, and Tokmakov (1966) and by Shimoda (1970) for several hydromicas. It is necessary to use great care in distinguishing the $2M_2$ form from a mixture of $1M + 2M_1$ structures by the X-ray powder method, but texture electron diffraction is more definitive. The structure of a $2M_2$ diocahedral mica from N. Armenia, U.S.S.R., has been studied by high voltage texture electron diffraction by Zhoukhlistov, Zvyagin, Soboleva, and Fedotov (1973). The sample is impure, and the composition had to be derived from tetrahedral bond lengths and least squares iteration of multiplicities. The resulting tetrahedral composition is phengitic ($\text{Si}_{3.5}\text{Al}_{0.5}$), but the usual amount of octahedral R^{2+} cations expected in a phengite is believed by the authors to be absent. The structural evidence on this latter point is not definitive. The mean $\text{M}-\text{O}, \text{OH}$ bond length of $1.956 \text{ \AA}$ is identical to that determined for phengite- $2M_1$ having 0.59 R^{2+} cations present (Güven, 1971a), but the tetrahedral rotation angle of 11.2° is larger than would be expected for this composition. The specimen will be considered here to be a phengite, but may lie along the composition line from muscovite to pyrophyllite instead of from muscovite to $\text{Mg}-\text{Al}$ celadonite. The authors believe the water content to be close to normal. The interlayer $\text{K} + \text{Na}$ totals only 0.77 atoms.

Zhoukhlistov *et al.* (1973) determined the stacking sequence in the Armenian phengite to be of the $2M_2$ type with interlayer stacking vectors of $\pm 60^\circ$ ($\sigma_3\sigma_4$ sequence in the terminology of Zvyagin, 1967), and with the basal oxygens coordinating the interlayer K in the form of a trigonal prism. The octahedral cations alternate regularly in adjacent layers between the I and II octahedral sets of positions. The authors specifically eliminated the possibility of octahedral coordination around the interlayer cation that might result if layers of both type A and B were present (Franzini, 1969), in which the direction of tetrahedral rotation is toward the octahedral cations in type A layers but away from these cations in type B layers. In fact, only type A layers are present. This also will be the case for the lepidolite- $2M_2$ and anandite- $2Or$ structures to be considered later. The octahedral bases are rotated by an average angle of 5.8° . The tetrahedral rotation angle of 11.2° distorts the layers considerably, and is in opposition to Radoslovich's (1959) hypothesis that $\pm 60^\circ$ or 180° interlayer stacking angles should be found only where the layers are relatively undistorted. The scarcity of $\pm 60^\circ$ or 180° interlayer stacking angles instead seems to be related to the anion repulsion inherent in the trigonal prism interlayer coordination. This is minimized in the present case and in lepidolite- $2M_2$ by the small amount of substitution of tetrahedral Al .

The location of the (010) symmetry plane normal to the $5.2 \text{ \AA}$ repeat direction, instead of the more usual location normal to the $9.0 \text{ \AA}$ repeat direction, requires reversal of the X and Y axes.

The observed β angle of $100^\circ 40'$ indicates considerable distortion from the ideal value of 98° . This is due to two larger than ideal intralayer shifts of $0.380b$ at $\pm 60^\circ$ to each other, plus appreciable offsets of adjacent layers by $-0.018a$. This gives a resultant shift for the crystal of $-0.419a$, instead of $-0.333a$, along the $9.0 \text{ \AA}$ repeat direction.

The phengite- $2M_2$ structure is distinctive also in being the second example of a dioctahedral mica with appreciable long-range tetrahedral cation order. The T(1)—O and T(2)—O mean bond lengths of $1.619 \text{ \AA}$ and $1.653 \text{ \AA}$, respectively, are interpreted to indicate tetrahedral occupancies of T(1) = $\text{Si}_{1.0}$ and T(2) = $\text{Si}_{0.75}\text{Al}_{0.25}$. The Al-rich T(2) cation is closer to its apical oxygen than is the Si-rich T(1) cation. This effect, also noted in muscovite- $2M_1$ by Gatineau and Méring (1958), has been interpreted by Aleksandrova, Drits, and Sokolova (1972) as a result of balance of charges. The more highly charged Si can compensate the unsatisfied charges on the basal oxygens by moving closer to them, whereas the weaker Al gives more of its charge to its apical oxygen and moves closer to the latter as a result.

4.5.7 Phengite- $1M$ structure

Space group = $C2/m$ $a \cong 5.17$, $b \cong 8.96$, $c \cong 10.25 \text{ \AA}$, $\beta \cong 101.33^\circ$

Because suitable crystals of $1M$ dioctahedral mica have not been found, the structure is known only from texture electron diffraction study of a powder from Transbaikal, U.S.S.R. This specimen has a composition somewhat similar to that of phengite- $2M_2$ from Armenia in that the tetrahedral substitution is small ($\text{Al}^{\text{IV}} = 0.49$) and the layer charge is enhanced by only a small amount of octahedral R^{2+} substitution ($\text{R}^{2+} = 0.14$). The water content is close to normal, and the interlayer cation total is low ($\text{K} + \text{Na} = 0.69$). In contrast to $1M$ hydromicas, the texture electron diffraction patterns of this phengite- $1M$ are of very high quality.

The structure of this specimen first was refined in the ideal space group $C2/m$ by Soboleva and Zvyagin (1969) using 356 reflections obtained from electron diffraction study at 40 kV. Because the ideal space group does not permit any distinction between different tetrahedral sites or between different occupied octahedral sites, Sidorenko *et al.* (1975) refined the structure again in space group $C2$ by use of 588 reflections obtained by high voltage electron diffraction at 350 kV. The resultant mean T—O bond lengths of 1.614 and $1.633 \text{ \AA}$ and M—O bond lengths of 1.920 and $1.957 \text{ \AA}$ suggest that the small substitutions of tetrahedral Al and of octahedral R^{2+} are ordered in specific sites. The authors note that phengitic micas of $1M$, $2M_2$, and $3T$ types all have been shown to be ordered, and that there appears to be a correlation of order with composition for these structures.

The phengite- $1M$ has an observed β angle of 101.33° that is 1.3° larger than ideal as a result of a large intralayer shift of $-0.376a_1$ plus an offset of adjacent layers by $-0.024a_1$. The observed angle of tetrahedral rotation ($\alpha = 9.3^\circ$) is smaller than in true muscovite, and is in accord with the phengitic composition of the specimen. The octahedral triads are rotated by an average angle of 6.9° . The basal surface of the layer is corrugated by an amount ($\Delta z = 0.18 \text{ \AA}$) comparable to that in other muscovites and phengites, but the tetrahedral sheet average thickness ($2.196 \text{ \AA}$) is smaller than in the others (Table 1.18).

4.5.8 Chernykhite- $2M_1$ structure

Space group = $C2/c$ $a \cong 5.29$, $b \cong 9.182$, $c \cong 20.023 \text{ \AA}$, $\beta \cong 95.68^\circ$

Rozhdestvenskaya and Frank-Kamenetskii (1974) have refined the structure of a chernykhite- $2M_1$ specimen from N. W. Karatau, U.S.S.R., that was first described by Ankinovich *et al.*

(1972). Chernykhite is similar to roscoelite in that both are dioctahedral and have vanadium as the principal octahedral cation. Chernykhite differs from roscoelite in having Ba and Na as major interlayer cations in place of K. Despite a large Al^{IV} content of 1.70 for this specimen, the layer charge is reduced to that of a true mica by a deficiency of octahedral charge (Table 1.18). The 0.28 atoms of interlayer Ba^{2+} are compensated by 0.35 interlayer vacancies or neutral water molecules. A small amount of interlayer $(\text{NH}_4)^{1+}$ is indicated by both chemical and spectrographic analyses.

The structural details are similar in most respects to those of other dioctahedral micas. A small electron density present in the "vacant" M(1) octahedral site is interpreted as due to 0.2 atoms of Mg,Fe. No tetrahedral ordering was detected. The tetrahedral rotation angle of 7.0° appears small in view of the misfit anticipated from the large amount of tetrahedral Al. The misfit is believed to be reduced by thickening of the tetrahedral sheet and by the size of octahedral vanadium, and to be inhibited further by the size of the interlayer Ba and NH_4 . The X-ray refinement in space group $C2/c$ did not permit distinction between the occupied M(2) octahedral sites, but proton magnetic resonance data have been interpreted by Kalinichenko *et al.* (1974) to indicate possible ordering of octahedral V and Al in separate zigzag chains.

4.5.9 Celadonite-1M structure

Space group = $C2/m$ $a \cong 5.20$, $b \cong 9.00$, $c \cong 10.25$ Å, $\beta \cong 100.1^\circ$

Zvyagin (1957) has applied the methods of texture electron diffraction analysis and electron density maps to determine the structure of clay-size celadonite from the Bug River district, U.S.S.R. The occurrence is as veins in metamorphic rocks.

The original description of the structure showed an unusually thick octahedral sheet and a thin tetrahedral sheet. Revised atomic coordinates published by Zvyagin (1967) indicate that while the octahedral sheet is still quite thick (2.238 Å) it is now only slightly thicker than for other micas and that the tetrahedral sheet is of normal thickness. The most unusual feature of this structure is that the occupied octahedra are nearly as large ($\text{M}-\text{O}, \text{OH} = 2.044$ Å) as the vacant site ($\square-\text{O}, \text{OH} = 2.112$ Å) because of the Fe-rich composition.

This celadonite has most of its layer charge originating in the octahedral sheet (Table 1.18) so that the octahedral anions have excess negative charges. Repulsion between these anions along shared octahedral edges probably contributes substantially to the observed thickness of the octahedral sheet (Radoslovich, 1963a). Because the thick octahedral sheet in celadonite necessarily has reduced lateral dimensions, a tetrahedral rotation of 7.5° is necessary in order to articulate the two sheets in spite of the small tetrahedral substitution and the large sizes of the octahedral cations.

The similar sizes of the three octahedra in celadonite lead to intralayer shifts and a β angle of ideal magnitudes. The basal oxygen surface has only a small corrugation ($\Delta z = 0.09$ Å). Thus, although celadonite is compositionally dioctahedral, it does not show the usual dioctahedral distortions.

4.6 Lithian muscovite-lepidolite

4.6.1 General

Hendricks and Jefferson (1939) and Levinson (1953) together studied over 50 Li-bearing muscovites and lepidolites by single crystal and powder X-ray methods. Levinson found that, although all intermediate compositions between dioctahedral muscovite and trioctahedral lepidolite can be found in nature, the sequence is not structurally continuous. Instead, the

dioctahedral muscovite- $2M_1$ structure is found for Li_2O contents up to approximately 3.3% and one of several trioctahedral lepidolite structures for Li_2O contents greater than about 4.0%. Specimens with intermediate compositions are usually fine-grained and are mixtures of muscovite and lepidolite.

Hendricks and Jefferson (1939) and Levinson (1953) recognized lepidolite structures that are known now as $1M$, $2M_2$, and $3T$. The chemical correlations were uncertain, but the $2M_2$ structure (called $6M$ by them) was recognized by Levinson for specimens with Li_2O contents

TABLE 1.19. X-ray powder data for trioctahedral Li-rich micas; spacings in Å

Lepidolites (Bailey, unpublished)							
A. $1M$							
hkl	I	$d(\text{obs.})$	$d(\text{calc.})$	hkl	I	$d(\text{obs.})$	$d(\text{calc.})$
001	40	9.97	9.959	33 $\bar{1}$	50	1.501	{1.504
002	35	4.981	4.979	060			{1.501
020	50	4.498	4.502	061	10	1.480	{1.484
11 $\bar{1}$	20	4.329	4.430	116			{1.480
021	20	4.107	4.103	13 $\bar{6}$	3	1.461	1.460
111	20	3.847	3.845	15 $\bar{4}$	3	1.444	{1.445
11 $\bar{2}$	70	3.615	3.617	22 $\bar{6}$			{1.445
022	70	3.329	{3.340	007	3	1.421	{1.423
003			{3.320	117			{1.422
11 $\bar{2}$	70	3.086	3.085	225	10	1.378	1.380
11 $\bar{3}$	35	2.895	2.890	207	10	1.353	1.353
023	30	2.669	2.672	136	20	1.339	{1.342
20 $\bar{1}$	80	2.594	{2.599	046			{1.336
130			{2.590	26 $\bar{1}$	35B	1.297	{1.300
13 $\bar{1}$	100	2.565	2.565	402			{1.299
113	20	2.479	{2.480	137			{1.299
202			{2.469	227			{1.296
131	30	2.452	2.452	260			{1.295
13 $\bar{2}$	40	2.389	2.390	403	2	1.276	1.276
040	25	2.247	{2.251	261	5	1.267	1.269
22 $\bar{1}$			{2.251				
132	7	2.217	2.216	263	15	1.246	{1.246
041	10	2.193	2.196	008			{1.245
133	30	2.141	2.140	401	3	1.242	1.242
202	20	2.125	2.126	065	10	1.197	{1.199
221	10	2.102	2.103	172			{1.198
042	2	2.051	2.051	421			{1.198
005	40	1.994	1.992	334			{1.195
133	20	1.955	1.956				
224	10	1.809	1.809				
205	5	1.734	1.733				
134	12	1.715	1.717				
135	30	1.657	1.654				
152	25	1.637	{1.639				
241			{1.635				
313	10	1.619	1.619				
243	20B	1.582	{1.586				
152			{1.579				
242	10	1.546	1.546				
206	2	1.524	{1.526				
314			{1.524				

A. $a = 5.212$, $b = 9.005$, $c = 10.129$ Å, $\beta = 100.5^\circ$.
Specimen from Auburn, Maine.

between 4.0 and 5.1% and the $1M$ structure for more Li-rich compositions. Christie (1961) has described the $2Or$ structure for lepidolites from three localities in Sweden and Norway, but further study has shown that these specimens have complex 3-layer stacking sequences (Bailey and Christie, in preparation). Levinson defined *lithian muscovite* as a name for specimens with between about 3.3 and 4.3% Li_2O that have the $2M_1$ structure, but have refractive indices in the lepidolite range and certain intensity differences in X-ray reflections relative to normal muscovite.

TABLE 1.19.—*continued*

Lepidolites (Bailey, unpublished)— <i>continued</i>							
B. $2M_2$							
<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)
002	70	10.01	10.000	133	10	1.633	{ 1.637
004	40	5.002	5.000	425			{ 1.634
111	70	4.464	4.465	516	5	1.611	{ 1.609
202	10	4.338	4.342	3,1,11			{ 1.600
113	20	3.883	3.882	423	8	1.584	{ 1.590
204	40	3.638	3.641	135			{ 1.586
114	40	3.495	3.493	513	5	1.572	{ 1.572
006	60	3.338	3.333	319			{ 1.572
114	40	3.205	3.208	135	3	1.545	{ 1.549
115	5	3.119	3.123	427			{ 1.544
204	40	3.075	3.073	424	2	1.521	{ 1.542
206	25	2.910	2.913	514			{ 1.522
115	30	2.872	2.868	1,1,12	60	1.502	{ 1.521
116	30	2.794	2.793	331			{ 1.503
021	100B	2.578	{ 2.581	602	2	1.478	{ 1.502
310			{ 2.575	600			{ 1.481
116			{ 2.574	2,0,12			{ 1.480
008	8	2.502	2.500	2,2,11	5	1.432	{ 1.476
314	40B	2.429	{ 2.439	2,2,10			{ 1.434
023			{ 2.425	2,0,14			{ 1.432
312			{ 2.409	0,0,14	5	1.417	{ 1.429
315	3	2.317	{ 2.326	1,1,13			{ 1.419
024			{ 2.309	3,1,13			{ 1.415
313	3	2.293	2.291	0,2,12	6	1.397	{ 1.404
221	10	2.253	{ 2.253	1,1,14			{ 1.396
402			{ 2.251	3,1,11	2	1.375	{ 1.392
221	4	2.211	2.211	4,0,10			{ 1.375
025	6	2.182	2.182	2,2,11	4	1.355	1.357
317	10	2.070	2.070	0,2,13	2B	1.324	{ 1.324
026	10	2.041	{ 2.052	2,2,13			{ 1.323
315			{ 2.033	623			{ 1.300
0,0,10	40	2.001	2.000	6,0,10	30B	1.298	{ 1.300
408	5	1.821	1.820	041			{ 1.299
3,1,10	10	1.701	{ 1.705	621			{ 1.297
512			{ 1.704	339			{ 1.294
422			{ 1.703				
421			{ 1.702				
227			{ 1.697				
131	5	1.689	{ 1.692		5	1.674	{ 1.675
029			{ 1.690				{ 1.667
318	5	1.674	{ 1.675				
424			{ 1.667				

B. $a = 9.016$, $b = 5.206$, $c = 20.292$ Å, $\beta = 99.7^\circ$.
Specimen from Hebron, Maine.

Weaker 06*l* reflections with *l* odd were taken to indicate lesser structural distortion than for true muscovite. In this chapter, however, the earlier usage of Schaller (1930) will be followed, in which lithian muscovite merely denotes a Li-bearing muscovite and has no structural connotation. *Lepidolite* will be used as a collective term for all trioctahedral Li-rich micas.

TABLE 1.19.—*continued*

Lepidolites (Bailey, unpublished)— <i>continued</i>								Taeniolite (LaLonde, 1963)		
C. 3T								D. 1M		
<i>hk.l</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hk.l</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)
00.3	30	9.93	9.924	21.8	10	1.548	{1.549	001	74	10.04
00.6	20	4.967	4.962	20.14			{1.546	002	44	5.01
10.1	50	4.449	4.455	21.9	5	1.513	{1.514	020	7	4.48*
10.2	3	4.308	4.313	11.16			{1.513	111	7	3.87
10.3	3	4.095	4.103	30.0	30	1.502	1.502	112	17	3.60*
10.4	30	3.854	3.854	30.3			{1.485	003	100	3.34
10.5	30	3.592	3.593	10.19	5B	1.482	{1.480	112	26	3.12
10.6	100B	{3.331	3.336	11.17			{1.453	113	25	2.88
00.9		{3.310	3.308	20.16	2	1.436	1.435	023	12	2.68
10.7	30	3.093	3.093	00.21	2	1.415	{1.418	131	12	2.60
10.8	30	2.871	2.869	10.20	1	1.382	{1.413	200	13	2.575
10.9	10	2.664	2.666	20.17			1.383	004	9	2.50*
11.1	80	2.591	2.592	10.21	1	1.352	1.352	201,132	17	2.398
11.2	80	2.562	2.563	11.19	10	1.341	1.342	221	2	2.25
10.10	5	2.481	{2.484	20.18	5	1.332	{1.333	220	2	2.23
00.12			{2.481	21.14			{1.329	202,133	11	2.145
11.4	20	2.456	2.456	22.1	15B	1.298	{1.300	005	35	1.999
11.5	25	2.386	2.384	10.22			{1.296	134	4	1.977*
20.0	10	2.248	{2.253	22.2	10	1.285	{1.296	135,006	17	1.655*
20.1			{2.246	20.19			{1.287	331	7	1.521
20.2	5	2.229	2.228	30.12	8	1.271	{1.285	060	5	1.507
20.3	10	2.197	2.197	22.5			{1.271	116	3	1.491*
20.4	5	2.157	2.156	31.2	12B	1.243	{1.245	007	4	1.423
11.8	20	2.133	2.132	22.7			{1.244	136,207	11	1.350
20.5	2	2.106	2.107	20.20	3	1.221	{1.242	117,206	6	1.30
20.6	8	2.051	2.051	31.5			{1.223			
00.15	20	1.985	1.985	21.17	10	1.199	{1.221			
11.10	15	1.959	1.959	11.22			{1.201			
11.11	2	1.875	1.876	20.21	10	1.199	{1.200			
2.0,9	5	1.860	1.862	30.15			{1.198			
11.12	2	1.796	1.795							
20.11	3	1.731	1.731							
11.13	8	1.720	1.719							
21.1	5	1.699	1.700							
21.3	2	1.678	1.678							
21.4	2	1.660	1.660							
11.14	20B	{1.645	1.646							
21.5			1.637							
21.6	15	1.611	1.611							
21.7	8	1.580	1.581							

C. $a = b = 5.203$, $c = 29.771$ Å, $\gamma = 120^\circ$.

Specimen from Kalgoorlie, Australia.

D. * Intensity may be influenced by the presence of dickite.

$a = 5.27$, $b = 9.13$, $c = 10.25$ Å, $\beta = 100^\circ$.

Specimen from Magnet Cove, Ark. Single crystal study of a different specimen from this locality indicates the 3T structure.

Characteristic X-ray powder patterns for lepidolites are shown in Fig. 1.19 and listed in Table 1.19.

Chaudhry and Howie (1973) in a study of lepidolites from Devonshire have recognized a number of deviations from Levinson's empirical relation between structural type and Li_2O content. They suggest instead a genetic relationship for their specimens in which the $2M_2$ structure formed in a volatile-rich, low temperature environment whereas the $1M$ structure formed in a relatively volatile-poor, higher temperature environment.

Foster (1960*b*) converted Levinson's Li_2O contents to structural formulas to show that lithian muscovite can contain a total octahedral occupancy of up to 2.5 atoms, 0.85 of which may be

Lepidolite micas—diagnostic X-ray diffraction lines (cf. Fig. 1.19)

1M				3T			
	<i>d</i> (Å)	<i>I</i>	<i>hkl</i>		<i>d</i> (Å)	<i>I</i>	<i>hkil</i>
1.	4.32	2	11 $\bar{1}$	1.	3.86	3	10 $\bar{1}$ 4
2.	4.11	2	021	2.	3.60	3	10 $\bar{1}$ 5
3.	3.83	2	111	3.	3.09	3	10 $\bar{1}$ 7
4.	3.62	7	11 $\bar{2}$	4.	2.87	3	10 $\bar{1}$ 8
5.	3.08	7	112	5.	2.67	1	10 $\bar{1}$ 9
6.	2.89	3½	11 $\bar{3}$	6.	1.61	1½	21 $\bar{3}$ 6
7.	2.67	3	023	7.	1.55	1	21 $\bar{3}$ 8
							{ 2,0,2,14
	<i>a</i> = 5.206 Å <i>b</i> = 9.018 <i>c</i> = 10.161 β = 100.5°				<i>a</i> = 5.203 Å <i>b</i> = 5.203 <i>c</i> = 29.77 β = 90° γ = 120°		

2M ₂			
	<i>d</i> (Å)	<i>I</i>	<i>hkl</i>
1.	4.34	1	20 $\bar{2}$
2.	3.88	2	11 $\bar{3}$
3.	3.64	4	204
4.	3.50	4	114
5.	3.21	4	114
6.	3.07	4	204
7.	{ 2.91	2½	206
	{ 2.87	3	115
8.	2.79	3	116
9.	2.42	4B	023,314,312
	{ 2.25	1	402,221
10.	{ 2.21	½	221
	{ 2.18	½	025
11.	{ 2.07	2B	317
	{ 2.04		315,026
	{ 1.70		3,1,10+
12.	{ 1.69	2B	029
	{ 1.67		318+
	<i>a</i> = 9.010 Å <i>b</i> = 5.215 <i>c</i> = 20.312 β = 99.7°		

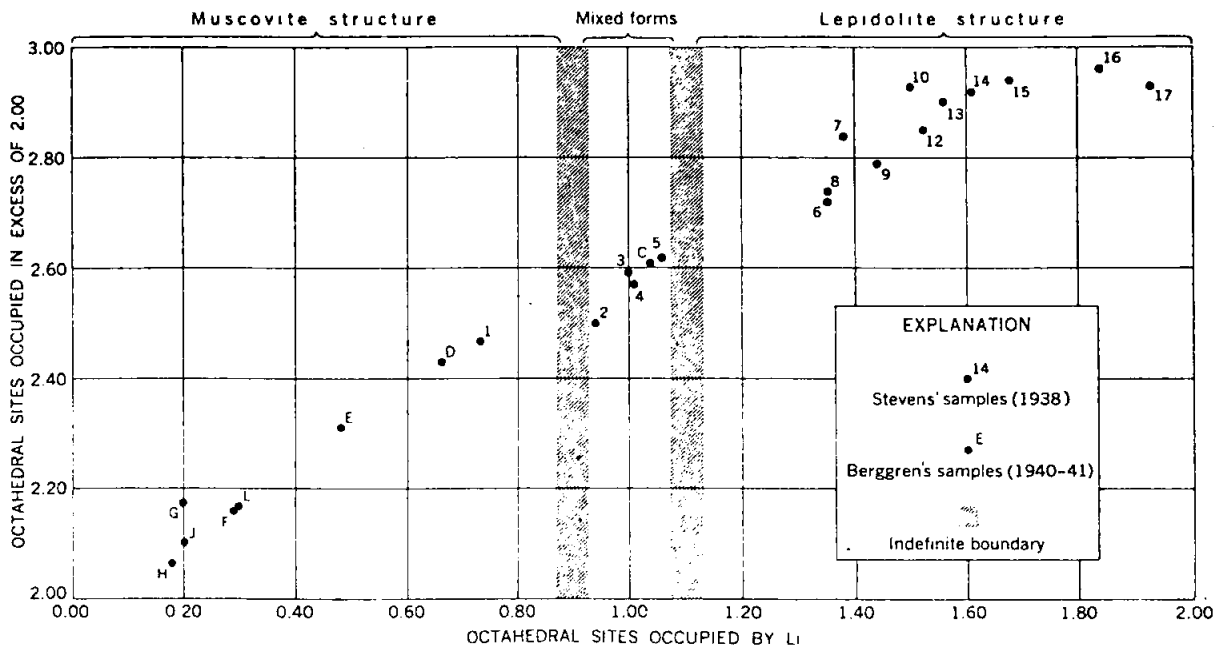


FIG. 1.20. Relationship of structure type to Li content for lithian muscovites and lepidolites, according to Foster (1960b).

Li. Samples with mixed dioctahedral muscovite and trioctahedral lepidolite structures present have bulk compositions with octahedral occupancies between 2.50 and 2.62 sites, of which Li constitutes 0.94 to 1.06 sites (Fig. 1.20). Single phase trioctahedral lepidolites contain more than 2.65 total octahedral cations and more than 1.10 Li. She also showed from a survey of over 100 chemical analyses that lepidolite can be derived from muscovite by progressive replacement of octahedral Al by Li in ratios between 2 and 3 Li per 1 octahedral Al (Fig. 1.21). The 2:1 replacement ratio leads to the end member *polyolithionite* $K(Li_2Al)Si_4O_{10}F_2$, in which the excess negative charge created by substitution of Li is balanced by a decrease in tetrahedral Al. The 3:1 replacement ratio leads to the end member *trilithionite* $K(Li_{1.5}Al_{1.5})(Si_3Al)O_{10}(OH,F)_2$, in which there is no change in tetrahedral composition with Li substitution. A 1:1 relationship was found

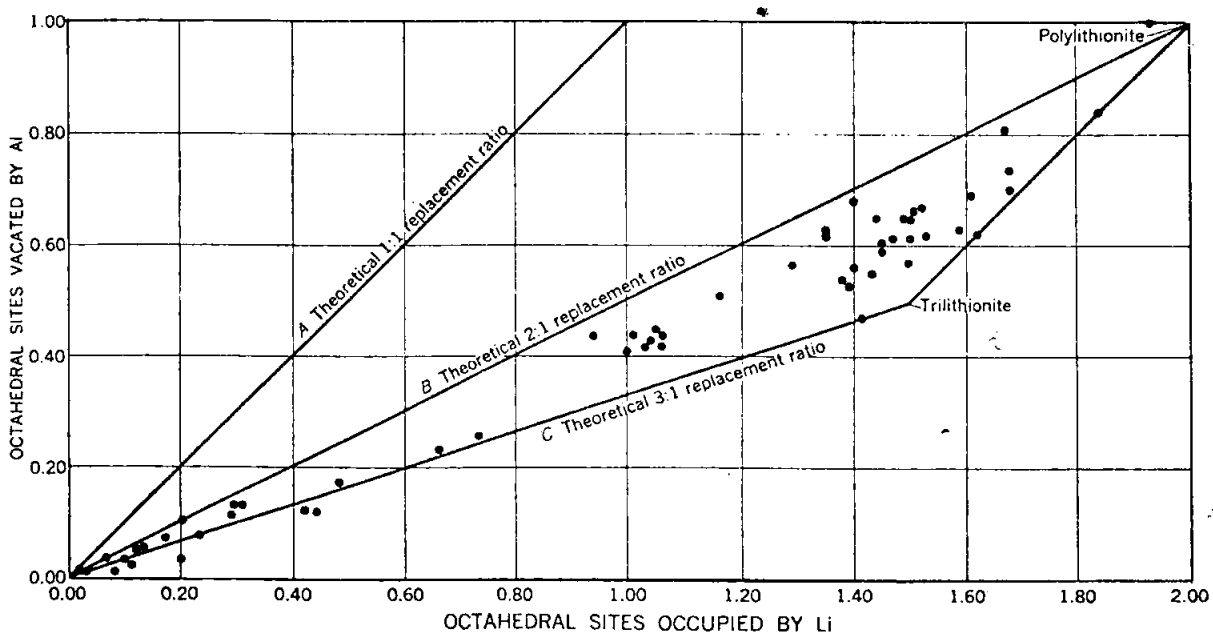


FIG. 1.21. Derivation of lepidolite from muscovite by replacement of octahedral Al by Li in ratios between 2:1 and 1:1, according to Foster (1960b).

between Li_2O and F in these samples. *Taeniolite* is a rare Al-free lepidolite of ideal composition $\text{K}(\text{Mg}_2\text{Li})\text{Si}_4\text{O}_{10}\text{F}_2$. It occurs primarily as the $1M$ and $3T$ polytypes.

Munoz (1968) synthesized micas along the binary joins forming the edges of the muscovite–polyolithionite–trilithionite triangle. Synthetic polyolithionite was found to be strictly a fluoromica, whereas synthetic trilithionite would accept variable amounts of OH and F into its structure, depending on concentration. Sharp discontinuities were found in the $2.0 \text{ \AA}$ basal spacing value between dioctahedral muscovite- $2M_1$ and trioctahedral polyolithionite- $1M$ around $\text{Ms}_{45}\text{Pl}_{55}$ and in the a and c cell dimensions between trioctahedral polyolithionite- $1M$ and trioctahedral $1M + 2M_1$ forms of trilithionite around $\text{Pl}_{30}\text{Tl}_{70}$. The $2M_1$ structure is believed to be the stable structure for trilithionite. It is apparently rare in nature, and has been described only by Černý, Rieder, and Povondra (1970) for a composition halfway between trilithionite and polyolithionite. Only a suggestion of a break in the $2.0 \text{ \AA}$ basal spacing values was found by Munoz along the third join from dioctahedral muscovite- $2M_1$ to trioctahedral trilithionite- $2M_1$. No certain evidence of $2M_2$ or $3T$ structures was found in this study. Munoz suggests that samples found to be mixtures of dioctahedral muscovite and trioctahedral lepidolite should be plotted relative to the discontinuities found in the Ms–Pl–Tl triangle, rather than just as a function of Li_2O content.

Foster (1960b) also showed in her review of chemical analyses that lepidolite can be derived by isomorphous substitution of Li for Fe^{2+} in the structure of *siderophyllite* [$\sim(\text{R}_{1.05}^{3+}\text{R}_{1.50}^{2+})\text{-(Si}_{2.85}\text{Al}_{1.15})\text{O}_{10}(\text{OH},\text{F})_2$ with R^{3+} largely Al]. Li is found to replace Fe^{2+} in this series at an average ratio of 2:1.5, but with individual specimens showing a range in replacement ratios from 2:1 to 1:1. She defines *protolithionite* as having a Li content of 0.50 ± 0.25 Li per formula unit ($\sim 0.75\text{--}2.50\%$ Li_2O), *zinnwaldite* 1.00 ± 0.25 Li ($\sim 2.50\text{--}4.50\%$ Li_2O), and *lepidolite* >1.25 Li ($>4.50\%$ Li_2O). The name *masutomilite* has been proposed for the Mn analogue of zinnwaldite, with $\text{Mn}^{2+} > \text{Fe}^{2+}$ (Harada *et al.*, 1976).

4.6.2 Lepidolite- $1M$ structure

$$\text{Space group} = C2/m \quad a \cong 5.20, b \cong 9.00, c \cong 10.06 \text{ \AA}, \beta \cong 100^\circ$$

The structure of a fluorine end member polyolithionite- $1M$ synthesized by Munoz (1968) has been refined by Takeda and Burnham (1969). The octahedral cations Li_2Al are partially ordered with $\text{Li}_{0.89}\text{Al}_{0.11}$ in site M(1) on the mirror plane and with $\text{Li}_{0.55}\text{Al}_{0.45}$ in each of the two M(2) sites (Fig. 1.22). This distribution was determined by least squares refinement of scattering factors and confirmed further by observed mean bond lengths that are appropriate to these compositions [$\text{M}(1)\text{--O},\text{F} = 2.106 \text{ \AA}$, $\text{M}(2)\text{--O},\text{F} = 1.981 \text{ \AA}$].

The octahedral sheet is thinned to about the same extent as in other trioctahedral $1M$ structures (Table 1.20), but this may be because anion repulsion along shared octahedral edges as a consequence of the octahedral seat of charge (as observed in celadonite- $1M$) is compensated here by the presence of the smaller F. The tetrahedral sheet is unusually thickened ($\tau = 113.8^\circ$), so that the tetrahedral rotation angle of 3.0° is smaller than might be expected from the compositions of the two sheets. The difference between the inner and outer K–O distances is only $0.132 \text{ \AA}$ because of the small value of α . Thus, the coordination approaches 12 around K. The intralayer shift of $-0.351a$ produces a β angle slightly larger than ideal. This brings out the point that the deviation of the intralayer shift from $-a/3$ in micas is not restricted to dioctahedral species and must be related to octahedral ordering, including vacancies (see Tables 1.14, 1.18, 1.20). Depending on the amount of layer offset and the geometry of successive interlayer stacking vectors, such deviations may or may not lead to deviations from the ideal β angles (Bailey, 1975a).

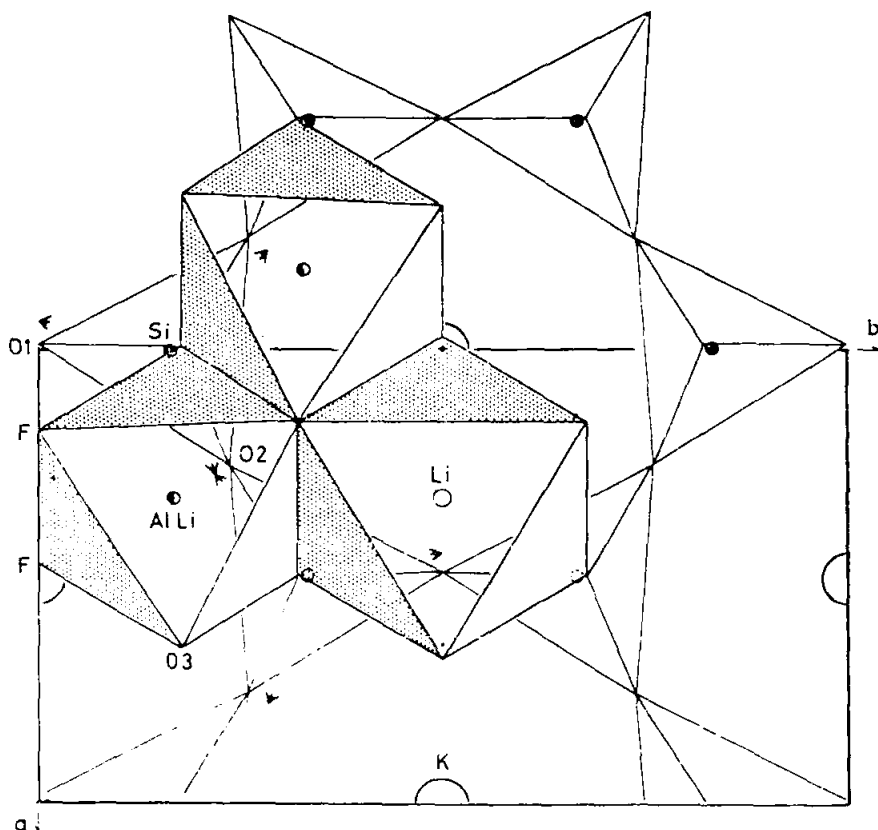


FIG. 1.22. Octahedral ordering pattern in fluoropolythionite-1M (from Takeda and Burnham, 1969).

The structure of a natural lepidolite-1M from the Island of Elba, Italy, has been refined by Sartori (1976). This specimen lies on the Pl-Tl join at $\text{Pl}_{50}\text{Tl}_{50}$, so is more Al-rich than the polythionite-1M specimen studied by Takeda and Burnham (1969). This leads to a larger tetrahedral-octahedral sheet misfit and a larger tetrahedral rotation angle (7.4°) for the Elba specimen (Table 1.20). The octahedral ordering pattern has primarily Li at the large M(1) site on the mirror plane and $\text{Li}_{0.30}\text{Al}_{0.70}$ at the two M(2) sites. Because the structural details and the composition of this crystal are quite similar to those of lepidolite-2M₂ crystals found in the same sample (see below), the author believes neither temperature, pressure, nor composition can be the major factors in determining polytypic stacking sequences.

Gatineau and Méring (1966) have studied the diffuse X-ray scattering for a lepidolite of unstated structural type. The composition is not given, but by implication is that of polythionite. Diffuse spots are observed at positions that are satellitic ($\pm a^*/3$) to the positions of certain of the $h + k = \text{odd}$ Bragg reflections that are forbidden by C-centering. The spots are interpreted to indicate short-range octahedral ordering of 1Al + 2Li in local domains. The ordering takes the form of rows of pure Al and pure Li aligned along one or the other of the three pseudohexagonal Y axes [01], [31], or $[3\bar{1}]$, such that each domain is characterized by only one ordering direction. The ordering is two-dimensional in that the Al rows are spaced regularly within a layer at intervals of $3a/2$ (every third row), but only irregularly between layers. The extent of each domain is small, perhaps due to antiphase relations.

4.6.3 Lepidolite-2M₂ structure

Space group = $C2/c$ $a \cong 9.04$, $b \cong 5.21$, $c \cong 20.18 \text{ \AA}$, $\beta \cong 99.67^\circ$

The structures of two different 2M₂ specimens of natural lepidolite have been refined by

TABLE 1.20. Structural details

Reference	Species	Composition	# Refl.	Final R	α_{tet}	τ_{tet}
Takeda and Burnham (1969)	synthetic fluoro-polyolithionite-1M	$\text{K}(\text{Li}_2\text{Al})\text{Si}_4\text{O}_{10}\text{F}_2$	328	5.1 ¹⁰	3.0°	113.8°
Takeda, Haga and Sadanaga (1971)	lepidolite-2M ₂	$(\text{K}_{0.87}\text{Na}_{0.12}\text{Rb}_{0.06}\text{Ca}_{0.02})(\text{Li}_{1.05}\text{Al}_{1.4}\text{R}_{0.5}^{2+})$ $(\text{Si}_{1.39}\text{Al}_{0.61})\text{O}_{10}(\text{OH})_{0.8}\text{F}_{1.2}$	471	7.2	5.4	112.2
Sartori, Franzini and Merlino (1973)	lepidolite-2M ₂	$(\text{K}_{0.87}\text{Na}_{0.12}\text{Rb}_{0.06}\text{Ca}_{0.02})(\text{Al}_{1.4}\text{Li}_{1.05}\text{R}_{0.5}^{2+})$ $(\text{Si}_{1.39}\text{Al}_{0.61})\text{O}_{10}(\text{OH})_{0.8}\text{F}_{1.2}$	525	9.6	6.5	112.0
Sartori (1976)	lepidolite-1M	$(\text{K}_{0.88}\text{Na}_{0.06}\text{Rb}_{0.05}\text{Ca}_{0.01})(\text{Li}_{1.69}\text{Al}_{1.31})$ $(\text{Si}_{1.37}\text{Al}_{0.63})\text{O}_{10}(\text{OH})_{0.47}\text{F}_{1.53}$	400	6.7	7.4	112.2
Brown (in preparation)	lepidolite-3T	$(\text{K}_{0.85}\text{Na}_{0.11}\text{Rb}_{0.01})(\text{Al}_{1.25}\text{Li}_{1.65}\text{Mn}_{0.09})$ $\text{Fe}_{0.02}\text{Mg}_{0.01})(\text{Si}_{1.48}\text{Al}_{0.52})\text{O}_{10}(\text{OH})_{0.44}\text{F}_{1.54}$	705	4.7	7.6	112.2
Guggenheim and Bailey (in preparation)	zinnwaldite-1M	$(\text{K}_{0.90}\text{Na}_{0.05})(\text{Al}_{1.05}\text{Fe}_{0.16}^{3+}\text{Ti}_{0.01}\text{Fe}_{0.77}^{2+}\text{Mg}_{0.01})$ $\text{Mn}_{0.02}^{2+}\text{Li}_{0.67})(\text{Si}_{1.09}\text{Al}_{0.91})\text{O}_{10}(\text{OH})_{0.79}\text{F}_{1.21}$	1,493	5.7	5.8	111.1
Takeuchi and Sadanaga (1966)	clintonite-1M	$\text{Ca}_{1.1}(\text{Mg}_{2.18}\text{Al}_{0.72})(\text{Si}_{1.05}\text{Al}_{2.95})\text{O}_{10}(\text{OH})_2$	384	10.4	23.0	110.2
Akhundov, Mamedov and Belov (1961)	clintonite-2M ₁	$\text{Ca}(\text{Mg}_{1.7}\text{Al}_{1.1}\text{Ca}_{0.2})(\text{Si}_{1.2}\text{Al}_{2.8})\text{O}_{10}(\text{OH})_2$	?	~19.5	8.6	112.1
Giuseppetti and Tadini (1972)	anandite-2Or	$(\text{Ba}_{0.8}\text{Mn}_{0.04}\text{K}_{0.04}\text{Na}_{0.04})(\text{Fe}_{2.46}^{2+}\text{Mg}_{0.48}\text{Mn}_{0.06})$ $(\text{Si}_{2.84}\text{Fe}_{0.1}^{3+}\text{Fe}_{0.58}^{2+}\text{Al}_{0.08})\text{O}_{10}(\text{OH})(\text{S}_{0.85}\text{Cl}_{0.15})$	853	6.1	3.4	113.4
McCauley and Newnham (1973)	synthetic Ba-Li fluoromica-1M	$\text{Ba}_{0.97}(\text{Mg}_{2.23}\text{Li}_{0.77})(\text{Si}_{2.84}\text{Al}_{1.16})\text{O}_{10}\text{F}_{2.08}$	479	7.1	4.7	112.6
Takeuchi (1965)	margarite-2M ₁	$(\text{Ca}_{0.87}\text{Na}_{0.13})\text{Al}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$	632	16.5	20.4	111.5
Guggenheim and Bailey (1975 and in preparation)	margarite-2M ₁	$(\text{Ca}_{0.81}\text{Na}_{0.19}\text{K}_{0.01})(\text{Al}_{1.99}\text{Fe}_{0.01}\text{Mg}_{0.01})$ $(\text{Si}_{2.11}\text{Al}_{1.89})\text{O}_{10}(\text{OH})_2$	1,071	4.0	20.8	110.6

indicates number of independent reflections used in structure determination.

Takeda, Haga, and Sadanaga (1971) and by Sartori, Franzini, and Merlino (1973). The Takeda *et al.* specimen from Rozna, Czechoslovakia, lies just on the lepidolite side of the mixed phase region in Munoz's (1968) diagram with a composition $\text{Ms}_{40}\text{Pl}_{30}\text{Ti}_{30}$. The Sartori *et al.* specimen from the Island of Elba, on the other hand, lies on the Pl-Ti join at $\text{Pl}_{50}\text{Ti}_{50}$. Despite the differences in octahedral compositions (Table 1.20), the structural details of the two specimens are very similar to one another and to lepidolite-1M.

The same octahedral ordering pattern is found as in lepidolite-1M, namely one large and two small octahedra. The larger octahedron contains $\text{Li}_{0.95}\text{Al}_{0.05}$ in the Sartori *et al.* specimen and $\text{Li}_{0.35}\text{Al}_{0.10}\square_{0.55}$ in the Takeda *et al.* specimen. The two smaller octahedra have nearly identical compositions in the two specimens ($\text{Al}_{0.63}\text{Li}_{0.37}$ and $\text{Al}_{0.65}\text{Li}_{0.35}$). The octahedral and tetrahedral sheets have similar thicknesses and, as in lepidolite-1M, the tetrahedra are elongate ($\tau = 112.0$ and 112.2°). Because of approximately 0.6 atoms of tetrahedral Al, the tetrahedral rotation angle is slightly larger than in polyolithionite-1M ($\alpha = 6.5^\circ$ and 5.4° relative to 3.0°).

In contrast to muscovite-2M₂, bond length calculations for these two lepidolites give no indication of tetrahedral cation ordering.

Because the 2M₂ stacking sequence involves alternation of I and II sets of octahedral positions in adjacent layers and $\pm 60^\circ$ interlayer stacking vectors, the K coordination polyhedron is a slightly distorted hexagonal prism rather than an antiprism (octahedron). The hexagonal prism polyhedron normally would be unstable due to close mutual approach of negatively charged basal oxygens from adjacent layers. This repulsion is minimized in these specimens, as in muscovite-2M₂, by the small amount of tetrahedral substitution. The interlayer separation is greater (3.409 and 3.360 Å) than for polyolithionite (3.274 Å) both because of the anion repulsion inherent in the prismatic coordination and of the cation repulsion of K by the H proton. The latter is minimized by the appreciable substitution of F for OH. The observed β angles (99.58° and 99.77°) are greater than ideal (98.58°) because of larger than ideal intralayer shifts of $0.36b$ due to octahedral ordering.

of lepidolites and brittle micas

M_{tot}	Sheet thickness		Interlayer separation	Basal oxygen Δz	Mean bond lengths						Intralayer shift	Layer offset	Resultant shift
	Tet.	Oct.			T—O	M—O	$R^{1+,2+}-O$						
							Inner	Outer					
58.8	2.247 Å	2.095 Å	3.274 Å	0.04 Å	1.619 × 2 Å	2.106, 1.981 × 2 Å	3.000 Å	3.132 Å (K)	-0.351 a_1	0	-0.351 a_1		
59.2	2.247	2.076	3.360	0.09	1.620, 1.632	2.144, 1.967 × 2	2.980	3.220 (K)	+0.364 b_2 -0.364 b_1	-0.007 a_1 -0.007 a_1	-0.379 a_1		
59.3	2.241	2.074	3.409	0.09	1.630, 1.627	2.123, 1.980 × 2	2.976	3.261 (K)	-0.361 b_1 +0.361 b_2	-0.005 a_1 -0.005 a_1	-0.372 a_1		
59.3	2.255	2.060	3.387	0.06	1.630 × 2	2.113, 1.972 × 2	2.942	3.269 (K)	-0.330 a_1	+0.017 a_1	-0.313 a_1		
59.4	2.257	2.059	3.347	0.13	1.652, 1.617	2.036, 2.113 1.920	2.925	3.265 (K)	-0.354 $a_{2,1,1}$	-0.012 $a_{1,2,3}$	0		
59.6	2.252	2.078	3.333	0.12	1.646, 1.639	2.132, 1.882, 2.131	2.990	3.251 (K)	-0.354 a_1	-0.004 a_1	-0.358 a_1		
58.2	2.342	2.148	2.818	0.06	1.725 × 2	2.019, 2.050 × 2	2.414	3.529 (Ca)	-0.321 a_1	-0.010 a_1	-0.331 a_1		
60.6	2.391	1.958	2.674	0.23	1.695, 1.663	1.995, 1.995 × 2	2.730	3.137 (Ca)	+0.330 $a_{3,2}$	-0.006 $a_{1,1}$	-0.318 a_1		
57.5	2.301	2.338	3.041	0.19	1.675, 1.766	2.105, 2.250 × 2 2.268, 2.096 × 2	3.026	3.241 (Ba)	±0.336 a_1	0	0		
58.6	2.277	2.155	3.172	0.01	1.645 × 2	2.074, 2.062 × 2	2.975	3.192 (Ba)	-0.333 a_1	-0.001 a_1	-0.334 a_1		
58.9	2.330	2.074	2.832	0.19	1.692, 1.702	1.912 × 2	2.458	3.427 (Ca)	+0.372 $a_{2,3}$	+0.013 $a_{1,1}$	-0.360 $a_{1,1}$		
58.7	2.288	2.080	2.875	0.19	1.747, 1.633, 1.623, 1.736	1.915, 1.903	2.454	3.432 (Ca)	+0.366 $a_{2,3}$	+0.012 $a_{3,2}$	-0.357 a_1		

Although in most trioctahedral micas the O—H bond of the hydroxyl group is oriented nearly normal to the layer because of repulsion by three octahedral cations 120° apart, Giese (1974, pers. comm.) has shown by electrostatic minimum energy calculations that this is not true for these two $2M_2$ specimens in which the octahedral cations are of unequal charge. The calculations indicate that the O—H bond is tilted appreciably away from the interlayer cation toward the lowest charge octahedron, by 23.3° toward the Li-rich octahedron for the Sartori *et al.* specimen and by 66° toward the vacancy-rich octahedron for the Takeda *et al.* specimen.

4.6.4 Lepidolite-3T structure

Space group = $P3_112$ $a = 5.200$, $b = 5.200$, $c = 29.76$ Å, $\gamma = 120^\circ$

Brown (in preparation) has refined the structure of a lepidolite-3T from Kalgoorlie, Australia (Table 1.20). Cation multiplicities and mean octahedral bond lengths indicate that all three octahedra are different. M(2) is Li-rich, M(3) is Al-rich, and M(1) is intermediate. The tetrahedral composition is $\text{Si}_{3.48}\text{Al}_{0.52}$, and significant differences in mean T—O bond lengths (1.652, 1.617 Å) indicate that the small amount of tetrahedral Al present is ordered into T(1). The tetrahedra are rotated by 7.6°, and the basal oxygen surfaces are slightly corrugated so that they mesh across the interlayer space. Other structural details are similar to those of other lepidolite polytypes.

4.6.5 Zinnwaldite-1M structure

Space group = $C2$ $a = 5.296$, $b = 9.140$, $c = 10.096$ Å, $\beta = 100.8^\circ$

Rieder (1968) has studied natural zinnwaldites that lie close to the siderophyllite–poly-lithionite join. He agrees with Foster (1960b) that there is always close to 1.0 small, trivalent octahedral cation (Al, Fe³⁺) per formula unit. Although the larger octahedral cations (Li, Fe²⁺,

Mg, Mn) are somewhat variable in number, they never exceed 2.0. This ideal ratio of 1:2 led Rieder to postulate octahedral ordering of the type found in clintonite-1*M* (= xanthophyllite), wherein each small M(1) octahedron is surrounded symmetrically by six larger M(2) octahedra in a 1:2 ratio. This ordering was believed to account for the observation that $d(00N)$ values for natural zinnwaldites are about 0.1 Å smaller than for synthetic specimens. Although such ordering may occur, the observation of smaller $d(00N)$ values for natural specimens is not conclusive evidence because the natural micas are more F-rich than the buffered synthetic specimens. Yoder and Eugster (1954) showed a decrease in basal spacing of 0.18 Å for fluorophlogopite relative to hydroxyphlogopite. Also, the clintonite-1*M* that is the model for the ordering has an octahedral sheet that is not appreciably different in thickness (2.15 Å) than for disordered micas (range 2.09–2.19 Å).

Guggenheim and Bailey (in preparation) have made a crystallographic study of one of Rieder's specimens (#40 from the Sadisdorf mine, D.D.R.), and have found a different octahedral ordering pattern than predicted. The space group is *C2*, rather than *C2/m*, and there are appreciable differences in the electron densities and average bond lengths for the two M(2) octahedra that would be equivalent in the higher symmetry. The composition of the smallest M(2) octahedron is interpreted as essentially Al. Octahedron M(3)[=M(2')] and octahedron M(1) are similar in size and scattering power, so that the remaining Fe, Li, and vacancies are assumed to be distributed nearly equally over these two sites. This ordering pattern is rotated 120° from that predicted by Rieder and would not be possible in the ideal *C2/m* symmetry. A small amount of tetrahedral ordering was detected in the lower symmetry.

5. BRITTLE MICAS

5.1 General

Brittle micas are distinguished from true micas in having a layer charge of -2.0 per formula unit, instead of -1.0 , and in compensation by divalent interlayer cations, instead of univalent. The layer charge may arise entirely within the tetrahedral sheet or partly within the tetrahedral sheet and partly within the octahedral sheet. The tetrahedral composition is known to vary from SiAl_3 to nearly Si_3Al , and to be supplemented by octahedral sheet charges that range from $+1.0$ through 0.0 to nearly -1.0 .

The name *clintonite* has priority for the trioctahedral species of ideal composition $\text{Ca}(\text{Mg}_2\text{Al})(\text{SiAl}_3)\text{O}_{10}(\text{OH})_2$, and supersedes other variety names (based primarily on different colors) of seybertite, xanthophyllite, brandisite, and valuevite (Forman, Kodama, and Maxwell, 1967). The tetrahedral Si:Al ratio varies from about 1.2:2.8 to at least 1.4:2.6 in different specimens of clintonite, and moderate amounts of Fe^{2+} and Fe^{3+} may substitute in the octahedral sheet. The reported structural types are 1*M*, 3*T*, and 2*M*₁. Olesch (1975) could synthesize only the 1*M* form of clintonite, but could vary tetrahedral Si in the trioctahedral system from the maximum value of 1.4 atoms found in natural specimens all the way down to 0.6. Much less substitution was possible toward the dioctahedral composition. The layer stacking sequences become more regular as tetrahedral and octahedral Al increase, as judged by intensities of the *hkl* reflections.

Anandite is a Ba-Fe trioctahedral brittle mica of structural types 2*Or* and 2*M*₁ that is known so far from only one locality in Ceylon (Pattiaratchi, Saari, and Sahama, 1967). The Mg-analogue of anandite is *kinoshitalite*. The latter has been identified as the 2*M*₁ polytype by Yoshii *et al.* (1973) and as the 1*M* polytype by Matsubara *et al.* (1974) from two different localities in Japan. Other trioctahedral Ba brittle micas with Mg as the octahedral cation or with Li and F

substitutions can be made synthetically, but are not known in nature (Hatch, Humphrey, Eitel, and Comeforo, 1957; Frondel and Ito, 1968).

The dioctahedral brittle mica *margarite* of ideal composition $\text{CaAl}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$ is known only in the $2M_1$ structural form (Table 1.21). Na may substitute for Ca in margarite up to about 50%. One method of compensating for the charge difference thus created is addition of Li in the vacant site, thereby trending toward the trioctahedral Na-mica *ephesite* (Schaller, Carron, and Fleischer, 1967).

A second method of compensation is to decrease the amount of tetrahedral Al, thus trending toward the dioctahedral Na-mica paragonite. Velde (1971) suggests an unmixing solvus exists between margarite and paragonite, and that intermediate bulk compositions are two-phase mixtures. Deer, Howie, and Zussman (1962) indicate that some sodian margarites are H_2O -rich, and that replacement of O^{2-} by $(\text{OH})^-$ may be involved in the charge balance also. Apparently K can substitute for Ca in margarite only to about 10%. Tetrahedral Be^{2+} has been found in a few specimens, and appears to be compensated by Li or by replacement of O by OH (Beus, 1956). *Bityite* is a rare Be-rich brittle mica. The ideal composition has been given as $\text{Ca}(\text{Al}_2\text{Li})(\text{Si}_2\text{AlBe})\text{O}_{10}(\text{OH})_2$, but available analyses show octahedral occupancies between 2.3 and 2.6 atoms (Strunz, 1956). Further study is needed to determine the dioctahedral or trioctahedral nature of bityite and its structural type.

5.2 Detailed crystal structures

5.2.1 Clintonite-1M structure $\sim \text{Ca}(\text{Mg}_2\text{Al})(\text{SiAl}_3)\text{O}_{10}(\text{OH})_2$

Space group = $C2/m$ $a \cong 5.19$, $b \cong 9.00$, $c \cong 9.80$ Å, $\beta \cong 100.1^\circ$

The structure of a specimen of clintonite-1M from Japan (called xanthophyllite) has been refined by Takéuchi and Sadanaga (1959, 1966). Ca is much smaller than K, and the interlayer separation of 2.818 Å (Table 1.20) indicates that adjacent layer surfaces are in contact. Because of the unusually large tetrahedral Al content of 2.95 atoms, a tetrahedral rotation of 23° is required to match the lateral dimensions of the octahedral sheet (Fig. 1.23). This is the largest

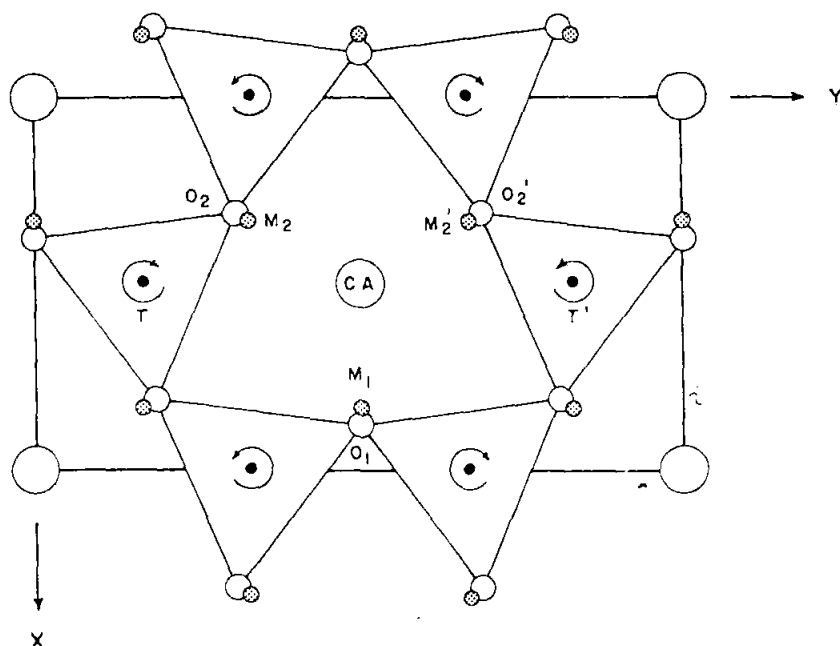


FIG. 1.23. Tetrahedral rotations of 23° to form ditrigonal net in lower tetrahedral sheet of clintonite-1M. Rotation direction brings basal tetrahedral oxygens closer to octahedral cations (M) of same 2:1 layer.

rotation angle recorded in a layer silicate, and amounts to a lateral tetrahedral sheet shrinkage of about 10%. Mean octahedral bond lengths of $M(1)-O, OH = 2.019 \text{ \AA}$ and $M(2)-O, OH = 2.050 \text{ \AA}$ indicate octahedral ordering into a pattern of two large octahedra and one smaller octahedron. Thus, the $Mg_{2.18}Al_{0.72}$ octahedral composition probably is distributed with only Mg in the two M(2) sites and with all of the Al plus a small amount of Mg in the smaller M(1) site. Tables 1.14, 1.18 and 1.20 show for other micas that octahedral ordering with a large M(1) cation or vacancy leads to a larger than ideal intralayer shift. In clintonite-1M the converse is true, as a small M(1) cation leads to a smaller than ideal intralayer shift ($-0.321a$). This is a necessary consequence of the linking of tetrahedral and octahedral sheets. The intralayer shift is supplemented in clintonite-1M by a layer offset in the same direction so that the β angle is close to ideal. Tetrahedral ordering is not possible in space group $C2/m$, because there is only one independent tetrahedron, and infrared evidence (see section on margarite) suggests such ordering does not occur in clintonite.

5.2.2 Clintonite- $2M_1$ structure

Space group $C2/c$ $a \cong 5.18, b \cong 9.09, c \cong 18.90 \text{ \AA}, \beta \cong 95^\circ$

Akhundov, Mamedov, and Belov (1961) have studied the structure of a reported $2M_1$ form of clintonite (called brandisite) from Azerbaidjan, U.S.S.R. The $0kl$ reflections with $k \neq 3n$ are not well-defined, so the structure could not be refined appreciably. The results listed in Table 1.20 refer to the average structure of an individual layer. Because of the lack of refinement, little weight should be given to the finding of a relatively small rotation angle with movement in a direction away from the octahedral cations or to the differences found in the T(1)-O and T(2)-O mean bond lengths.

5.2.3 Anandite- $2Or$ structure $\sim Ba(Fe.Mg)_3(Si_3Fe^{3+})O_{10}(OH)S$

Space group = $Pnmm$ $a = 5.47, b = 9.49, c = 19.96 \text{ \AA}, \beta = 90^\circ$

Anandite is an unusual trioctahedral brittle mica, both compositionally and structurally. It was identified first as the $2M_1$ polytype (Table 1.21). Later some crystals were shown to have the rare $2Or$ structure, in which the layer shifts are $\pm a/3$ with alternation of the I and II sets of octahedral positions within adjacent layers. The ideal space group for this latter structure is $Ccmm$ (Fig. 1.15), but the symmetry of anandite was found to be lowered by ordering of tetrahedral Si and Fe to $Pnmm$ (Giuseppetti and Tadini, 1972). A large number of weak reflections are observed that violate the C-cell centering. The mean bond lengths of T(1)-O = $1.676 \text{ \AA}$ and T(2)-O = $1.766 \text{ \AA}$ were interpreted by the authors to indicate tetrahedral populations of $Si_{0.96}Al_{0.04}$ for T(1) and $Si_{0.36}Fe_{0.35}^{3+}Fe_{0.29}^{2+}$ for T(2). The expected bond length for nearly pure Si should be in the range of $1.61-1.62 \text{ \AA}$, however, so it is likely that T(1) contains some tetrahedral Fe also. The ratio of $Fe^{3+}:Fe^{2+}$ present in the crystal is uncertain.

The octahedral cations are predominantly Fe^{2+} . Mean bond lengths were interpreted by the authors to indicate that the small amount of Mg present is located mainly in octahedral site M(1). The unusual compositional feature of the octahedral sheet is that one of the OH anion groups has been replaced by $(S_{0.85}Cl_{0.15})$. It is not certain whether the S is present as S^{2-} or as SH^- , but the authors favor the former because of the observed tetrahedral coordination provided around S by three octahedral Fe^{2+} cations and the interlayer Ba. The octahedral coordination groups involving S are quite irregular.

The hexagonal rings in anandite appear relatively undistorted according to the average

tetrahedral rotation angle of 3.4° , but the actual distortion shows up in the range of individual rotation angles from 0.4° to 6.9° and in the irregular shapes of the tetrahedra. The authors calculate that α should be around 14° in view of the lateral misfit anticipated from the large tetrahedral Fe content. They attribute the smaller observed angle to the large size and charge of the interlayer Ba, and its tendency to surround itself by as many anions as possible. The coordination around the interlayer Ba includes 12 basal oxygens plus one S (Ba—S = 3.196 Å). Because of the 180° interlayer stacking angle the interlayer polyhedron is an irregular hexagonal prism that is centered on one base by S. The OH is considerably farther away on the other base (Ba—OH = 4.157 Å) because of the repulsive effect of the H^+ proton. Takeda and Burnham (1969) have suggested that there may be a similar attraction by the interlayer cation in polyolithionite-1M, where F substituting for OH is located 3.94 Å from the interlayer K. Some shorter distances involving OH, however, are K—OH = 3.81 Å in celadonite-1M, Ca—OH = 3.83 Å in margarite-2M₁ and 3.86 Å in clintonite-1M.

In anandite the interlayer separation of 3.041 Å suggests that adjacent basal oxygen surfaces are not in contact, contrary to the situation in clintonite and margarite. This undoubtedly is due to the larger size of Ba relative to Ca. The same effect is noted in the structure of a synthetic Ba—Li brittle mica determined by McCauley and Newnham (1973). Other details of the latter structure are summarized in Table 1.20.

5.2.4 Margarite-2M₁ structure $\sim CaAl_2(Si_2Al_2)O_{10}(OH)_2$

Space group = *Cc* $a \cong 5.12$, $b \cong 8.89$, $c \cong 19.22$ Å, $\beta \cong 95.5^\circ$

The structure of margarite-2M₁ from Chester, Mass., U.S.A., has been refined by Takéuchi (1965) in the ideal space group *C2/c*. Although the 50% tetrahedral substitution of Al for Si is not as large as in clintonite, the tetrahedral rotation angle of 20.4° is nearly as large because of the smaller octahedral cations. The interlayer separation of 2.832 Å indicates adjacent basal oxygen surfaces are in contact around the interlayer Ca. The basal surfaces are corrugated to about the same extent as muscovite-2M₁ (Fig. 1.24).

Similar T—O bond lengths indicated tetrahedral cation disorder in Takéuchi's study. Gatineau and Méring (1966) did not observe any diffuse X-ray scattering from a different margarite specimen. They interpret this as indicating perfect long-range Si, Al ordering. Farmer and Velde (1973) have provided additional evidence for tetrahedral ordering by citing the sharp infrared spectra and the lack of Al—O—Al vibrations in both natural and synthetic margarites. They suggest that the symmetry may be lower than the *C2/c* space group assumed by Takéuchi in his structural study, because a noncentrosymmetric space group would permit a more favorable charge distribution in an ordered structure.

Guggenheim and Bailey (1975 and in preparation) have confirmed that margarite from Chester County, Pa., U.S.A., is fully ordered in space group *Cc*. The lower symmetry renders the two tetrahedral sheets within a 2:1 layer non-equivalent so that an ordering pattern over the two sheets becomes possible that would average out to disorder if refined in the higher symmetry of the ideal space group *C2/c*. The observed T—O distances in space group *Cc* are 1.623, 1.633, 1.736, and 1.747 Å. Compositionally similar tetrahedra in adjacent sheets of the same 2:1 layer are not related by an inversion center, as required in the ideal space group, but instead by a lateral two-fold axis that does not hold for the structure as a whole. Güven (1971b) has pointed out that the latter arrangement is energetically more stable because it avoids having two electrostatically unbalanced apical oxygens (of Al-rich tetrahedra) on the same octahedral shared edge. A similar ordering pattern is theoretically possible for muscovite-2M₁ also, but was not found to

TABLE 1.21 X-ray powder data for brittle micas; spacings in Å

A. Clintonite-1M				B. Margarite-2M ₁			C. Anandite-2M ₁			
hkl	I	d(obs.)	d(calc.)	hkl	I	d(obs.)	hkl	I	d(obs.)	d(calc.)
001	5	9.68	9.67	002	10	9.56	002	60	9.92	9.97
020	3	4.50	4.52	004	8	4.77	004	85	4.995	4.98
111	$\frac{1}{2}$	3.82	3.82	110	10	4.42	022	10	4.27	4.27
112	2	3.55	3.56	111	10	4.37	113	20	3.700	3.696
022	$\frac{1}{2}$	3.30	3.30	021	4	4.28	024	40	3.430	3.430
003	7	3.21	3.22	111	4	4.23	006	100	3.320	3.322
112	1	3.05	3.04	022	6	4.01	115	25	3.165	3.160
113	2	2.83	2.83	113	8	3.771	115	25	2.929	2.926
201	$\frac{1}{2}$	2.59	{2.59	023	6	3.636	130	50	2.716	{2.722
130			{2.59	114	8	3.381	026			{2.718
200			{2.56	024	8	3.224	131			{2.713
131	10	2.56	{2.57	006	100	3.180	131	45	2.681	2.681
202	5	2.45	{2.45	114	14	3.123	117	15	2.521	2.522
131			{2.45	115	4	3.001	008	80	2.490	2.492
201			{2.37	025	8	2.883	222	20	2.240	2.242
132	4	2.37	{2.38	115	10	2.775	0,0,10	35	1.991	{1.993
203	4	2.20	{2.20	116	6	2.687	226			{1.989
041			{2.20	200	10	2.549	0,0,12; 245	35	1.660	1.661
132			{2.20	131	10	2.540				
202	7	2.11	{2.11	202	25	2.517				
133			{2.12	131, 116	18	2.508				
221			{2.10	202	12	2.407				
005	4	1.931	1.931	133	8	2.399				
043	2	1.851	1.849	008	6	2.386				
150	2	1.705	{1.704	204, 133+	6	2.343				
311			{1.702	040	4	2.199				
151	*	1.661	{1.661	041, 221	6	2.187				
242			{1.661	204	8	2.168				
135	*	1.622	1.621	135, 223	6	2.161				
006	$\frac{1}{2}$	1.609	1.609	222, 206	8	2.118				
152	*	1.578	{1.577	043, 135+	12	2.077				
243			{1.577	136	6	1.947				
242	*	1.539	1.541	0,0,10; 206	35	1.908				
060	6	1.505	{1.506	137, 241	18	1.903				
314			{1.506	139, 150+	6	1.665				
330			{1.484	2,0,10	10	1.596				
135	5	1.485	{1.486	139	10	1.593				
332			{1.485	331	12	1.475				
063			{1.364	060	16	1.466				
334	3	1.363	{1.362							
	3	1.316								
	3	1.296								
	$\frac{1}{2}$	1.261								
	$\frac{1}{2}$	1.244								
	*	1.225								
	*	1.208								
	3	1.186								
	*	1.124								
	3	1.101								
	3	1.056								
	$\frac{1}{2}$	1.025								
	*	1.015								
	*	0.990								
	3	0.981								

TABLE 1.21.—*continued*

D. Anandite-2Or							
<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)
002	20	9.91	9.926	155	10	1.633	{1.635
004	20	4.960	4.963	245			{1.633
022	5	4.279	4.283	1,3,10	40	1.607	{1.607
113	20	3.847	3.851	2,0,10			{1.606
024	40	3.431	{3.431	060	25	1.582	{1.582
114			{3.426	330			{1.579
006	35	3.309	3.309	316	20	1.573	1.574
115	40	3.039	3.043	062		15	{1.563
026	100	2.710	{2.714	0,2,12	15	1.562	{1.562
131			{2.713	332			{1.559
116			{2.712				
201			{2.707	064	20B	1.507	{1.508
				1,3,11			{1.507
132	40	2.635	{2.640	2,0,11			{1.506
202			{2.634	334	20	1.453	{1.504
133	2	2.527	{2.530	1,1,13		15	{1.453
203			{2.526	0,0,14	15	1.418	{1.418
008	30	2.481	2.482	1,3,12		5	{1.416
117	20	2.432	2.433	2,0,12	5	1.365	{1.415
134	10	2.395	{2.398	261			{1.366
204			{2.394	401	35B	1.357	{1.363
040	5	2.372	2.374				
221	5	2.348	2.351				
				0,2,14	20B	1.332	{1.359
042	5B	2.307	{2.308	0,4,12			{1.357
222			{2.304	262	25	1.282	{1.356
135	5	2.254	{2.254	2,2,12			{1.356
205			{2.251	402	20B	1.332	{1.353
223	2	2.228	2.230	068			{1.334
028	5	2.197	{2.199	1,3,13		15	{1.334
118			{2.198	2,0,13	25	1.242	{1.333
044	7	2.140	{2.141	338			{1.332
224			{2.137	2,2,13	40	2.108	1.283
136	40	2.108	{2.110	0,0,16			1.241
206			{2.107				
225	2	2.030	2.034				
0,0,10	20	1.984	1.985				
137	5	1.969	{1.970				
207			{1.968				
139	30	1.717	{1.718				
209			{1.716				
154	5B	1.685	{1.687				
1,1,11			{1.687				
244			{1.685				
314			{1.683				
0,0,12	25	1.654	1.654				

A. * line is barely visible.

 $a = 5.20_4$; $b = 9.02_6$; $c = 9.81_2$ Å; $\beta = 100.33^\circ$.

Specimen from Zlatoust, S. Urals, Russia.

(Forman *et al.*, 1967.)B. $a = 5.118$, $b = 8.799$, $c = 19.159$ Å, $\beta = 95.15^\circ$.

Specimen from Shin-kiura mine, Oita Pref., Japan.

(Aoki and Shimoda, 1965.)

C. $a = 5.415$, $b = 9.458$, $c = 20.013$ Å, $\beta = 95.1^\circ$.(Indexing modified from Pattiaratchi *et al.*, 1967.)D. $a = 5.465$, $b = 9.494$, $c = 19.853$ Å.

Specimen from Wilagadera, Ceylon.

(Bailey, unpublished).

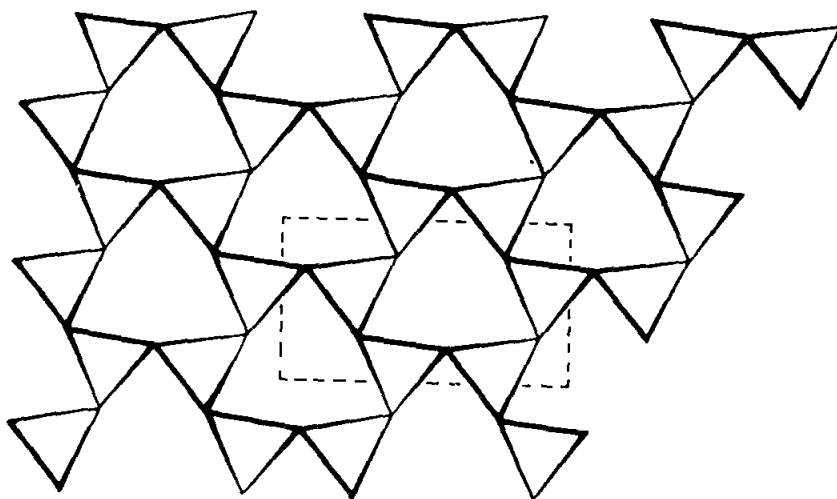
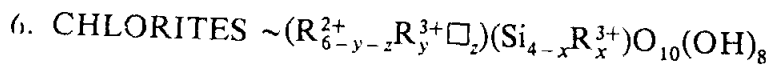


FIG. 1.24. Corrugation of basal oxygen surface in dioctahedral margarite (modified from Takéuchi, 1965). Heavy lines represent elevated tetrahedral edges (apices down) within upper tetrahedral sheet of 2:1 layer. Corrugations alternate parallel to $[110]$ and $[1\bar{1}0]$ in successive layers.

be adopted by muscovite from the Diamond mine, South Dakota, U.S.A. An additional feature of interest in the margarite structure is the finding that the two tetrahedral sheets within the 2:1 layer are not compositionally identical. The tetrahedral Al contents of 1.006 and 0.877 for the two sheets are significantly different according to statistical analysis of the probable errors involved.



$$a \cong 5.3, b \cong 9.2, c \sin \beta \cong n \times 14.2 \text{ \AA}, \beta \cong 97^\circ \text{ or } 90^\circ$$

Space groups: primarily $C2/m$, Cm , $C\bar{1}$, $C1$, or subgroups

6.1 General

The trioctahedral chlorite structure consists of negatively charged 2:1 layers of ideal composition $(R^{2+}, R^{3+})_3(Si_{4-x} R_x^{3+})O_{10}(OH)_2$ that alternate regularly with positively charged interlayer sheets of ideal composition $(R^{2+}, R^{3+})_3(OH)_6$. In addition to this electrostatic interaction, the hydroxyl planes of each interlayer sheet have been found to maintain long hydrogen bond contacts with the basal oxygens of the 2:1 layers above and below. Tetrahedral substitution of R^{3+} for Si^{4+} is primarily by Al, occasionally by Fe^{3+} or B^{3+} . The main constituents of the 2:1 octahedral sheet and of the octahedral interlayer sheet are Mg, Fe^{2+} , Al, and Fe^{3+} , but with important substitutions of Cr, Ni, Mn, V, Cu, or Li in certain species.

Foster (1962) in a study of 150 chlorite analyses found a complete substitutional series between Mg and Fe^{2+} . In most cases octahedral Al is low and other trivalent cations, such as Fe^{3+} or Cr^{3+} , are present to proxy for Al in balancing the negative charges on the tetrahedral sheets. If the total number of trivalent octahedral cations is approximately equal to tetrahedral R^{3+} , the octahedral occupancy is close to 6.00 atoms. If the total number of trivalent octahedral cations is greater than tetrahedral R^{3+} , Foster showed that total octahedral occupancy then is less than 6.00 atoms by an amount equal to one-half the excess of octahedral trivalent cations over tetrahedral R^{3+} . Thus, the excess octahedral trivalent cations replace divalent cations in the ideal formula in the ratio 2:3. The range of tetrahedral substitution found in Foster's study was 0.55 to 1.66 R^{3+} atoms per four tetrahedral sites. The resulting negative charge on the tetrahedral sheets may be compensated partly by a positive charge on the 2:1 octahedral sheet,

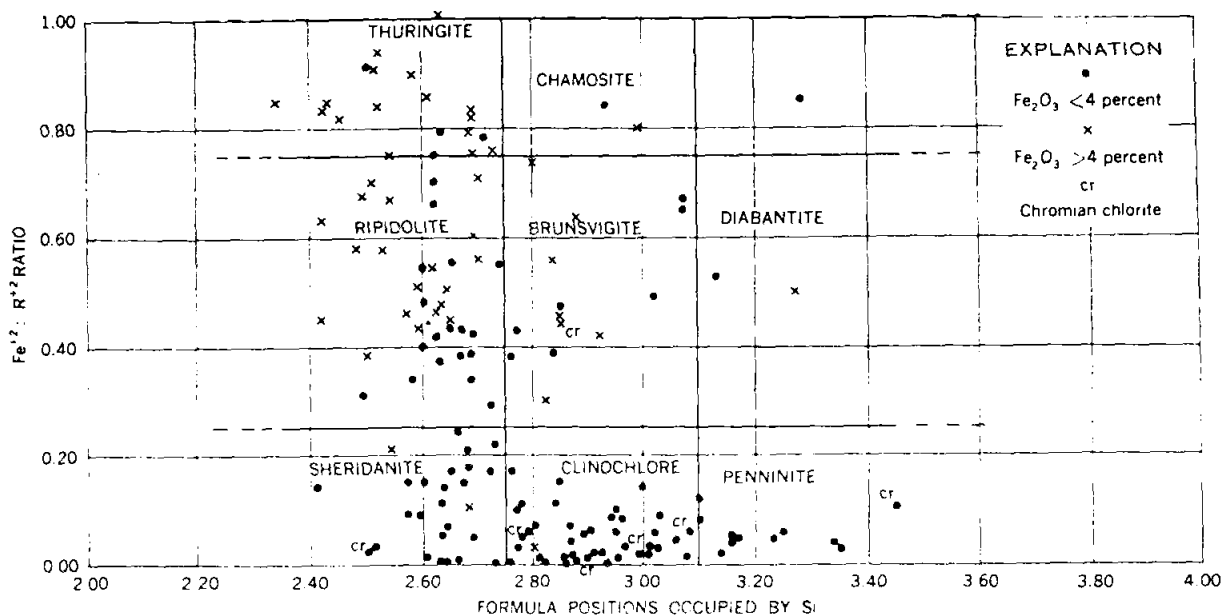


FIG. 1.25. Chlorite classification scheme according to octahedral $\text{Fe}^{2+}:\text{R}^{2+}$ ratio and tetrahedral Si:Al content (from Foster, 1962).

but with the major compensation by a positively charged interlayer sheet. Foster's classification scheme is shown in Fig. 1.25.

The amount of Fe^{3+} present bears no necessary relation to the amount of Fe^{2+} in a particular specimen, but there is a general trend for Fe^{2+} -rich chlorites to contain more Fe^{3+} than do the Fe^{2+} -poor chlorites. In most cases this Fe^{3+} must be considered primary unless there are definite indications of oxidation. Foster (1964) found many Fe-rich chlorites to be (OH)-deficient according to analysis. There is little correlation between ferric iron and excess oxygen in these analyses, however, and internal oxidation and dehydration will explain (OH)-deficiency in only some of the Fe-chlorites.

6.2 Structural types

The general outlines of the chlorite structure were determined by Pauling (1930*b*), with further details supplied by McMurchy (1934), Garrido (1949), Robinson and Brindley (1949), Brindley, Oughton, and Robinson (1950), and Steinfink (1958*a,b*). Bailey and Brown (1962) showed that these earlier workers had studied the same structural type of chlorite but that other structural arrangements, which differ in the orientation of the interlayer sheet relative to the 2:1 layer within a 14 Å unit, also occur in nature in lesser abundance.

Single crystal studies have shown that most chlorites have either regular 1-layer structures or irregular layer sequences characterized by sharp $k = 3n$ reflections and continuous or partial streaking of $k \neq 3n$ reflections. As a result, the structural variations permissible within a 2:1 layer, as outlined for the micas and applicable only to regular multi-layer chlorite structures, may be neglected in an introductory treatment. The reader is referred to Lister and Bailey (1967) and Drits and Karavan (1969) for more detailed descriptions of multi-layer chlorites.

By restricting the discussion to regular 1-layer structures or to irregular layer sequences, only one orientation of the initial 2:1 layer need be considered. This layer will be oriented here as in the micas (Figs. 1.14*a*, 1.15) so that the $a/3$ stagger between the two tetrahedral sheets at the octahedral close packing junction is directed along the $-X_1$ axis. The interlayer sheet will be designated I or II, depending on which set of octahedral cation positions (Fig. 1.26*a*) is occupied in the interlayer. A given interlayer, I or II, may be placed on the initial 2:1 layer in six ways

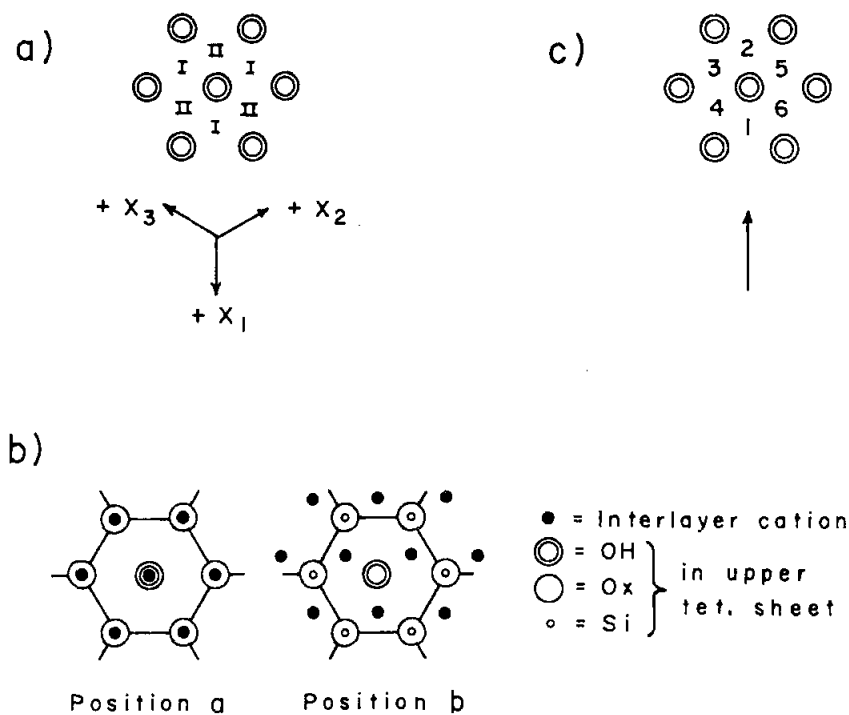


FIG. 1.26. (a) Definition of I and II sets of octahedral cation positions, relative to a fixed set of hexagonal axes, above lower hydroxyl plane of a chlorite interlayer sheet. (b) Two different superposition patterns (*a* and *b*) of interlayer cations onto upper tetrahedral sheet of 2:1 layer below. (c) Six positions for center of an hexagonal ring in upper 2:1 layer in projection onto upper hydroxyl plane of interlayer sheet. Central OH lies on mirror plane of 2:1 layer below, and arrow shows direction of intralayer shift in the first 2:1 layer.

that will provide the necessary hydrogen bond contacts between the adjacent oxygen and hydroxyl surfaces. These six positions can be divided into two sets with three positions in each set. Because the interlayer sheet by itself has trigonal symmetry and all atoms in it repeat at intervals of $b/3$, it suffices to select one position from each set and to label the sets differently, say *a* and *b*. The three *a* positions are equivalent to one another, as are the three *b* positions. In the *a* positions one of the three interlayer cations projects down onto the center of the hexagonal ring of oxygens in the uppermost anion plane of the 2:1 layer and the other two cations project onto tetrahedral cations of this ring (Fig. 1.26*b*). In the three *b* positions the interlayer sheet is shifted by $a/3$ so that the interlayer cations form triads symmetrically disposed in projection to the hexagonal ring below. It is convenient to designate these four structural arrangements Ia, Ib, IIa, and IIb. They represent four different 2:1 layer-interlayer assemblages.

The regular 1-layer polytypes result from different regular ways of positioning the repeating 2:1 layer upon the interlayer sheet to obtain long hydrogen bonds between the adjacent oxygen and hydroxyl surfaces. As with the superposition of the interlayer sheet on the 2:1 layer below, there are six ways to position the upper 2:1 layer on the interlayer to provide hydrogen bonds. These also can be grouped into two sets of positions, which will be distinguished here by "even" or "odd" numbers. The numbered positions, as shown in Fig. 1.26*c*, represent the position of the center of an hexagonal ring in the upper 2:1 layer as superimposed on the uppermost OH surface of the interlayer.

Bailey and Brown (1962) have shown that theoretically there can be 12 different regular 1-layer chlorite polytypes, designated according to the type of interlayer sheet (I or II), the position (*a* or *b*) of the interlayer sheet on the initial 2:1 layer, and the position (1 through 6) of the repeating 2:1 layer on the interlayer sheet. See Zvyagin (1963) and Zvyagin and Mishchenko (1966) for an alternative terminology. Two of the 12 unique polytypes are based on a triclinic-

shaped unit cell with $\alpha \cong 102^\circ$, and have triclinic symmetry. Two are based on an orthorhombic shaped unit cell with $\alpha = \beta = \gamma = 90^\circ$, and have monoclinic symmetry. The remaining eight polytypes are based on a monoclinic-shaped unit cell with $\beta \cong 97^\circ$, and include one monoclinic symmetry and one triclinic symmetry representative of each of the four structural unit types (Ia, Ib, IIa, IIb).

The observation that many chlorites have X-ray reflections that are sharp for index $k = 3n$ but are streaked for index $k \neq 3n$ indicates that the layers and interlayers, although irregular as to relative positions in adjacent 14 Å units, still maintain hydrogen bond contacts and only adopt those positions that are related to one another by shifts of $\pm b/3$ along the three pseudo-hexagonal Y axes. This has been termed semi-random stacking. In the terminology of Bailey and Brown, semi-random stacking permits irregular sequences along Z^* of either the three a positions or the three b positions of the interlayer sheet on the initial 2:1 layer and of the three "even" or the three "odd" positions of the repeating 2:1 layer on the interlayer sheet. In each of these four sets of irregular sequences the three individual positions are related to one another by $\pm b/3$ along the three pseudo-hexagonal Y axes. It is not permissible to mix the a with the b sets or the "even" with the "odd" sets, because this would involve relative shifts of $\pm a/3$ for which there is no diffraction evidence. Shirozu and Bailey (1965) suggest that it is likely that the stacking randomness involves articulation of the interlayer sheet with the 2:1 layers on both sides and not just on one side, although there would be little resultant difference in diffraction intensities because of the trigonal symmetry of the interlayer sheet.

Each of the four structural types of chlorite units can be involved in two different semirandom stacking sequences, which could be termed the "even" and "odd" possibilities (equivalent to the a and b possibilities). The eight resultant structures are reduced to six different structures because of equivalence relationships. Four of the six structures are based on a monoclinic-shaped unit cell with $\beta \cong 97^\circ$, one for each different structural unit type, and the other two structures are based on an orthorhombic-shaped unit cell and Ib or IIa units. The symmetry of all the semi-random stacking sequences is probably triclinic, being a statistical average of one monoclinic and two triclinic arrangements if the three stacking positions in the set are adopted equally.

6.3 Identification of natural examples

The six semi-random stacking structures give different $k = 3n$ X-ray intensities and can be identified by powder patterns (Fig. 1.27, Tables 1.22, 1.23). Bailey and Brown examined some 303 different chlorite specimens with the following results:

<i>Structure</i>	<i>Specimens observed</i>
IIb-even, $\beta = 97^\circ$	243
Ib-odd, $\beta = 90^\circ$	37
Ib-even, $\beta = 97^\circ$	13
Ia-even, $\beta = 97^\circ$	10
IIa-even, $\beta = 90^\circ$	0
IIa-odd, $\beta = 97^\circ$	0

The IIb structural unit accounts for 80% of the specimens examined. This is the structural type present in the specimens previously examined by Pauling, McMurchy, Garrido, and Brindley *et al.*, and appears to be the most stable structural arrangement. The Ia and Ib structures appear to crystallize at lower temperatures, and may be metastable forms. The studies of Bailey and Brown

Chlorite minerals—diagnostic X-ray diffraction lines (cf. Fig. 1.27)

IIb				Ia			
	<i>d</i>	<i>I</i>	<i>hkl</i>		<i>d</i>	<i>I</i>	<i>hkl</i>
1.	2.66	1½	20 $\bar{1}$	1.	2.65	3	200
2.	2.59	6	20 $\bar{2}$	2.	2.59	1½	20 $\bar{2}$
3.	2.55	5	20 $\bar{1}$	3.	2.39	6	20 $\bar{2}$
4.	2.45	5	20 $\bar{3}$	4.	2.27	1	20 $\bar{4}$
5.	2.39	5	20 $\bar{2}$	5.	2.07	½	20 $\bar{5}$
6.	2.26	4	20 $\bar{4}$	6.	2.01	3	204
7.	2.07	1	20 $\bar{5}$				
8.	2.01	6	204				
	<i>a</i> = 5.37 Å <i>b</i> = 9.30 <i>c</i> = 14.19 β = 97.0°				<i>a</i> = 5.34 Å <i>b</i> = 9.25 <i>c</i> = 14.43 β = 97.1°		

Ib (97°)				Ib (90°)			
	<i>d</i>	<i>I</i>	<i>hkl</i>		<i>d</i>	<i>I</i>	<i>hkl</i>
1.	2.68	2½	20 $\bar{1}$	1.	2.69	2	200
2.	2.60	1½	20 $\bar{2}$	2.	2.65	1½	20 $\bar{1}$
3.	2.55	½	20 $\bar{1}$	3.	2.51	10	20 $\bar{2}$
4.	2.47	7B	20 $\bar{3}$	4.	2.34	1	20 $\bar{3}$
5.	2.40	½	20 $\bar{2}$	5.	2.15	4	204
6.	2.30	½	20 $\bar{4}$	6.	1.96	½	20 $\bar{5}$
7.	2.11	2B	20 $\bar{5}$	7.	1.78	3	206.008
8.	2.01	1	204				
	<i>a</i> = 5.36 Å <i>b</i> = 9.29 <i>c</i> = 14.45 β = 97.8°				<i>a</i> = 5.39 Å <i>b</i> = 9.34 <i>c</i> = 14.14 β = 90°		

(1962) and of Hayes (1970) suggest that the chlorite structural types cut across the arbitrary compositional boundaries that have been established for individual species (Fig. 1.25), and that there is no clear cut compositional preference by any structural type. For this reason, Bayliss (1975) has suggested that only four species names be retained—*clinochlore* (Mg-rich), *chamosite* (Fe-rich), *nimite* (Ni-rich), and *pennantite* (Mn-rich). Adjectival modifiers should be used to indicate compositional variations within each of these four species.

X-ray powder patterns normally do not distinguish between semi-random and regular stacking variants within each structural type because of the weak intensities of the diagnostic $k \neq 3n$ reflections. Single crystal studies are necessary both to determine the presence of regular stacking in a given specimen and to identify the exact layer sequence.

6.4 Detailed crystal structures

6.4.1 IIb Structural Type

Steinfink (1958*a,b*, 1961) has refined the crystal structures of both a monoclinic and a triclinic example of the IIb structural type. The monoclinic IIb-2 structure was determined for a prochlorite specimen (or ferrian sheridanite in Foster's 1962 classification), in which the original ferrous iron had changed almost completely to ferric iron between the time of the original analysis in 1891 and the second analysis in 1958. The triclinic IIb-4 structure was that of a Mg-

rich corundophilite (or sheridanite in Foster's classification). Both specimens have regular 1-layer structures and give unstreaked $k \neq 3n$ X-ray reflections.

The monoclinic prochlorite was observed to belong to space group $C2$, rather than the ideal $C2/m$, as a consequence of tetrahedral and octahedral ordering. Based on differences in T—O bond lengths [T(1)—O = 1.73 Å and T(2)—O = 1.63 Å], nearly all of the tetrahedral Al present is concentrated in the T(1) tetrahedron. From the heights of the electron density peaks and the M—O,OH bond lengths it could be determined also that most of the iron is concentrated in the octahedral sheet within the 2:1 layer and that the octahedral Al is in the interlayer sheet. There is a preferential ordering of Mg, Fe, and Al over the six cation sites of the 2:1 octahedral sheet and the interlayer. A tetrahedral rotation of 9.4° was found in a direction that would shorten the O—OH hydrogen bond contacts with the interlayer.

The triclinic corundophilite also was observed to have a reduced symmetry, $C1$ rather than the ideal $C\bar{1}$, but in this case there was no indication of tetrahedral ordering. Smaller M—O,OH bond lengths indicate the octahedral Al is concentrated in the interlayer, however, and that there may be preferential ordering of cations over the three octahedral interlayer sites [M(4)—OH = 2.05, M(5)—OH = 2.02, M(6)—OH = 1.99 Å]. Adjacent tetrahedra have rotated 7.7° toward the nearest interlayer OH.

TABLE 1.22. X-ray powder data for chlorites; spacings in Å (Bailey, 1975b)

A			B		C		D		
<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>
001	14.15	8	14.4	6	14.2	6	001	14.1	8
002	7.05	10	7.15	10	7.10	10	002	7.05	7
003	4.72	6	4.79	4	4.73	4	003	4.70	9
02;11	4.60	2	4.63	4	4.63	1	02;11	4.47	4
004	3.54	10	3.59	7	3.55	8	004	3.52	9
005	2.83	4	2.87	2½	2.84	3	005	2.815	3
201	2.66	1½	2.68	4	—	—	200	2.56	4
200	—	—	—	—	2.66	4	202	2.505	7
202	2.59	5	2.61	1½	2.59	½	201	2.465	½
201	2.54	8	2.55	½	2.55	1	203	2.37	½
203	2.44	7	2.475	6	—	—	006	2.35	½
202	2.38	4	2.39	1	2.395	6	202	2.315	10
204	2.255	4	2.29	1	2.27	1	204	2.205	1
203	—	—	2.20	½	—	—	203	2.14	½
205	2.06	1½	2.105	2	2.07	½	205	—	—
007	—	—	2.045	½	—	—	007	2.015	3
204	2.00	6	2.01	1	2.01	3	204	1.96	5
206	1.88	2½	1.91	½	1.89	½	206	1.845	½
205	1.82	2½	—	—	—	—	008	1.76	1
15;24;31	1.74	1	1.758	2	1.76	½	15;24;31	—	—
207	1.715	½	1.74	1	—	—	207	1.685	3
206	1.66	1½	—	—	1.67	2½	206	1.635	4½
208	1.565	3	—	—	1.57	1	208	1.54	2½
060	1.538	7	1.548	6	1.549	6	060	1.489	7
062	1.503	2½	1.515	3	1.515	3	062	1.458	1½
063	1.462	½	1.478	1	1.472	1	209	—	—
209	—	—	—	—	1.439	½	063	1.420	1½
0,0,10	—	—	1.434	½	—	—	0,0,10	1.410	1½
064	1.414	1	1.420	1	1.420	3	064	—	—
208	1.392	2½	—	—	—	—	208	1.372	1½

TABLE 1.22.—*continued*

E			F			G		
<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>
001	14.2	6	001	14.23	8	002	14.46	9
002	7.10	9	002	7.13	7	004	7.206	10
003	4.75	2½	003	4.735	8	006	4.809	8
02;11	4.62	3½	020,110	4.517	8½	110,020,111,021	4.619	8
004	3.56	7	021	4.314	½	112,022	4.412	2
005	2.85	2	111	4.180	½	113,023	4.175	3
200	2.685	2	112	4.017	½	114,024	3.899	2
201	2.64	1½	022	3.840	¼	115,025,008	3.600	9
202	2.505	10	004	3.552	6½	116,026	3.334	1
203	2.33	1	023	3.272	¼	117,027	3.076	½
204	2.14	4	113	3.084	½	0,0,10;118;028	2.878	4
007	2.03	½	114	2.923	¼	200,130,201,131	2.664	3
205	1.955	½	005	2.839	2	119,029,202,132	2.626	8
206 }	1.78	3	200,201	2.606	1	203,133	2.575	4
008 }			202	2.544	2½	204,134	2.504	8
15;24;31	1.75	1	201	2.501	10	205;135;0,0,12	2.424	10
207	1.62	½	203	2.409	5	206,136	2.340	7
060	1.548	6	202	2.348	2½	223,043,207,137	2.249	1
062	1.515	2½	204	2.230	2½	225,045	2.143	1
208	1.482	2	042	2.160	¼	0,0,14;209;139	2.050	6
064 }	1.422	2	007	2.024	½	2,0,10;1,3,10	1.958	5
0,0,10 }			204	1.984	5 B	2,0,12;1,3,12	1.786	4
065 }	1.360	1	206	1.868	1½	310,240,150	1.749	1½
209 }			205	1.812	2½ B	312;242;152	1.738	1½
			207	1.710	1½ B	2,0,13;1,3,13	1.704	3
			206	1.643	½ B	2,0,14;1,3,14	1.629	4½
			208	1.556	4 B	2,0,15;1,3,15	1.558	3
			060,207	1.511	6	330,060	1.541	9
			062	1.478	1	1,1,18;0,2,18;334;064	1.507	4½
			063	1.439	½	2,2,15;0,4,15;336;066	1.468	2
			0,0,10	1.418	¼	0,0,20	1.437	1
			208,064	1.389	4 B	2,0,17;1,3,17	1.429	1
						068,338	1.416	2

The indices in Col. A apply to the patterns in Cols. A, B and C.
A. 11b chlorite, Buck Creek, North Carolina.
B. 1b chlorite (monoclinic cell), New Britain, Connecticut.
C. 1a chlorite, Vicar mine, Michigan.
D. 1a cookeite, Londonderry, Western Australia.
E. 1b chlorite (orthohexagonal cell), Florence mine, Wisconsin.
F. 11b chlorite (di,triocahedral sheets). Tracy mine, Michigan.
G. 1a chlorite (two-layer orthohexagonal cell), Erzincan, Turkey.

6.4.2 1a Structural Type

Brown and Bailey (1963) have refined the structure of a triclinic 1-layer 1a-4 k  mmererite crystal of space group $C\bar{1}$. The tetrahedral rotation angle is 6.2° (Fig. 1.28). Although the ideal symmetry is retained, there is partial tetrahedral ordering of Si,Al [T(1)–O = 1.69, T(2)–O = 1.64  ] as well as concentration of all the Cr^{3+} in one octahedral interlayer site. This interlayer site is positioned on a vertical line midway between Al-rich T(1) tetrahedra in the 2 : 1 layers above and below. In this way the excess negative charges associated with the ordered Al-tetrahedra are balanced locally by the excess positive charge on the interlayer. This is the same sort of local charge balance found by Shirozu and Bailey (1966) for vermiculite, and is only possible in an α -type of layer–interlayer superposition. This local charge balance may

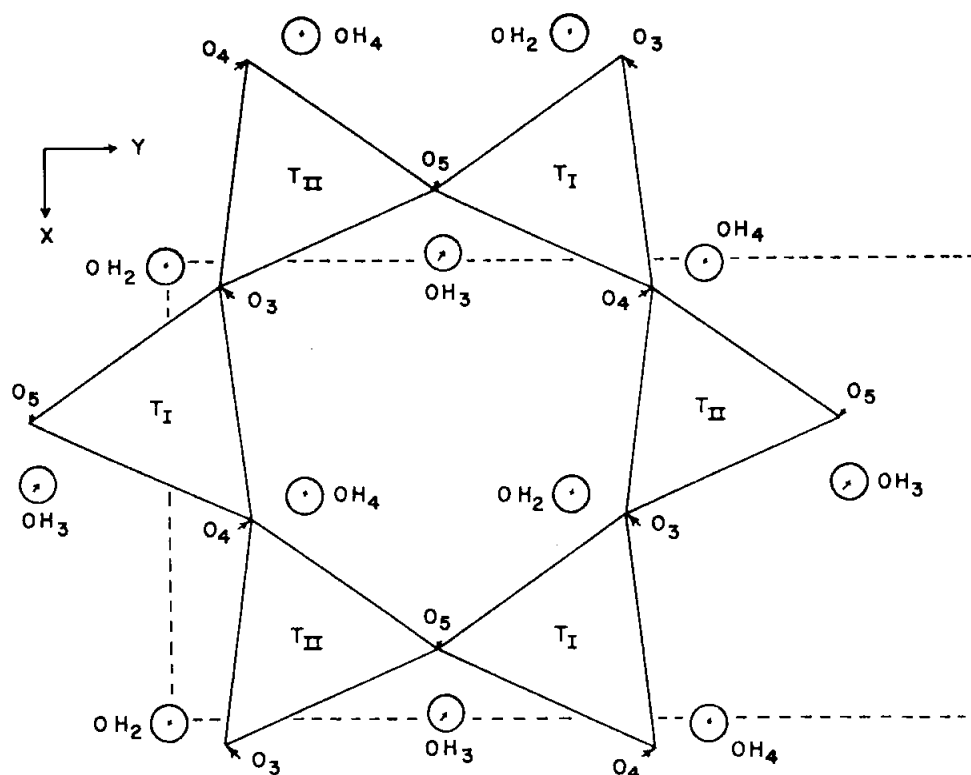


FIG. 1.28. Layer-interlayer relationship in 1a Cr-chlorite (from Brown and Bailey, 1963). Rotation of tetrahedra by 6.2° and interlayer octahedra by 1.5° moves anions towards one another (see arrows) to shorten hydrogen bond contacts. Interlayer Cr lies between Al-rich T(1) tetrahedra above and below to create local charge balance.

compensate partly for the cation repulsion inherent in a 1a unit because of the vertical superposition of interlayer and tetrahedral cations. See Shirozu and Bailey (1965) for further discussion of chlorite structural stabilities.

6.4.3 Orthohexagonal Ib Structural Type

Orthohexagonal chlorites with $\beta = 90^\circ$ were recognized first by von Engelhardt (1942). Although no regular stacking specimens have been found to date, Bailey and Brown (1962) were able to identify the structural type as Ib. Shirozu and Bailey (1965) interpreted the intensities of the observed continuous streaking of $k \neq 3n$ reflections along Z^* as requiring not only random linear displacements of layers by $\pm b/3$ along the three pseudo-hexagonal Y axes, but also random $\pm 120^\circ$ rotations about the cleavage normal. Random linear displacements are equivalent to random adoption of superposition sites 1, 3, and 5 of Fig. 1.24c for this structure, and random 120° rotations are equivalent to random shifts of $a/3$ within the 2:1 layers at the octahedral junction. Refinement of an Fe-rich ripidolite specimen (brunsvigite in Foster's classification) by means of only the sharp $k = 3n$ reflections gave the details of an average layer of symmetry $C2/m$. The average structure does not permit determination of any Si,Al ordering that may be present. A 5.0° tetrahedral rotation of basal oxygens toward the nearest interlayer OH positions was observed. Contrary to the chlorite structures described previously, this direction of rotation is away from the positions of the nearest octahedral cations in the 2:1 layer and in the interlayer. This indicates the primary importance of the hydrogen bonds in determining the rotation direction in chlorites. Electron density peak heights indicated that 60% of the iron is concentrated in the octahedral sheet of the 2:1 layer. Smaller octahedral M—OH distances in the interlayer (2.05 Å versus 2.10 Å) and a thinner octahedral sheet in the interlayer

TABLE 1.23. X-ray powder data for Ni- and Mn-chlorites; spacings in Å

A. Nimite-IIb				B. Nimite-Ia				C. Grovesite			
<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)
001	25	14.2	14.2	002	1	14.20	14.213	1,3,14	5	1.569	1.569
002	100	7.10	7.10	004	100	7.111	7.107	2,0,16	5	1.569	1.569
003	16	4.74	4.73	006	55	4.740	4.738	060	50	1.543	1.545
020	1	4.60	4.61	02,1	10	4.605	4.634	332	30	1.508	1.543
004	45	3.55	3.55	11,1	60	3.556	4.604	064	15	1.469	1.509
005	7	2.841	2.838	008	6	2.845	3.553	336	20	2.43	1.508
200	1	2.644	2.639	0,0,10	40	2.652	2.843	332	40	2.70	1.508
202	3	2.582	2.580	132	15	2.593	2.654	066	10	2.60	1.469
201	2	2.540	2.539	200	30	2.552	2.652	338	80	2.43	1.468
203	2	2.438	2.436	132	10	2.593	2.594	334	20	2.30	1.468
202	2	2.379	2.380	204	1	14.20	2.593	0,0,20	5	2.10	1.421
204	2	2.258	2.255	134	50	2.390	2.552	068	40	2.03	1.417
205	<1	2.062	2.064	202	20	2.264	2.550	3,3,10	15	1.908	1.416
007	1	2.028	2.027	136	2	2.201	2.391	336	30	1.683	1.416
204	3	2.003	2.003	204	10	2.027	2.389	1,3,18	20	1.585	1.398
206	1	1.8827	1.8812	136	50	2.390	2.266	2,0,16	2	1.574	1.398
205	<1	1.8253	1.8239	208	20	2.264	2.265	260	20B	1.537	1.335
206	1	1.6620	1.6625	138	2	2.201	2.202	404	5	1.440	1.334
208	2	1.5661	1.5647	206	10	2.027	2.200	1,3,18	5	1.428	1.323
060	2	1.5349	1.5359	0,0,14	1	1.5012	2.030	2,0,20	5	1.361	1.323
062	1	1.5012	1.5007								

0,0,10	1B	1-4188	1-4192	1,3,10	30	B	2-009	2-010	264			1-297		
064	1B	1-4101	1-4093	208				2-009	408			1-296	1-335	10
208	1	1-3948	1-3948						0,6,12	25	1-295	1-294	1-322	5
400	1B	1-3190	1-3200	1,3,10	5		1-887	1-888	3,3,14			1-293	1-300	5
401	<1	1-3001	1-2995	2,0,12				1-887	3,3,10			1-293	1-246	5
404	1	1-2901	1-2904	1,3,12	2		1-830	1-830					1-150	10
406	1B	1-2179	1-2184	2,0,10				1-829	268	2	1-275	1-276	1-117	10
0,0,12	1B	1-1821	1-1826	1,5,1				1-750	404			1-275	1-059	15
				2,4,1	5		1-745	1-745	0,6,14			1-229		
				3,1,1				1-737	3,3,16			1-229		
				1,3,12	2		1-718	1-719	3,3,12	10B	1-226	1-229		
				2,0,14				1-719	268			1-225		
				1,3,14	15		1-669	1-667	4,0,12			1-224		
				2,0,12				1-667	0,0,24	10	1-184	1-185		
									1,3,22			1-136		
									2,0,24			1-135		
									2,6,12	10B	1-132	1-133		
									4,0,16			1-132		

A. $a = 5.320$, $b = 9.214$, $c = 14.302 \text{ \AA}$, $\beta = 97.10^\circ$.

Specimen from Barberton, South Africa.

(de Waal, 1970a.)

B. $a = 5.346$, $b = 9.268$, $c = 28.649 \text{ \AA}$, $\beta = 97.1^\circ$.

Specimen from Woodline Well, Western Australia, has 2-layer s type structure.

(Bailey, unpublished.)

Indices such as 11.1 indicate edges of two-dimensional bands.

C. * = Impurity line.

$a = 5.44$, $b = 9.40$, $c = 14.27 \text{ \AA}$, $\beta = 97.20^\circ$.

Specimen from Benallt mine, Rhiw, Carnarvonshire, North Wales.

(Peacor *et al.*, 1974.)

(1.98 Å versus 2.18 Å) indicate that most of the octahedral Al is in the interlayer, as it must be in order to have a positively charged interlayer.

6.5 Dioctahedral chlorites

6.5.1 General

Specimens that have been called dioctahedral chlorites fall into three categories (Eggleton and Bailey, 1967).

(1) Chlorites with one dioctahedral sheet and one trioctahedral sheet. Specimens with a trioctahedral 2:1 layer and a dioctahedral interlayer would be termed tri,dioctahedral chlorites, although no well crystallized examples are known to date. If the 2:1 layer is dioctahedral and the interlayer is trioctahedral, these are described as di,trioctahedral chlorites. Examples are *cookeite* and *sudoite*. The octahedral cation total is near 5.0 per formula unit, and $d(060)$ measures between 1.49 and 1.51 Å. X-ray powder patterns for cookeite and sudoite are listed in Table 1.22 (col. 4 and 6).

(2) Chlorites with two dioctahedral sheets, described as di,dioctahedral chlorites. An example is *donbassite*. The octahedral cation total is slightly greater than 4.0 per formula unit, primarily Al, and $d(060)$ measures between 1.49 and 1.50 Å.

(3) Less well-crystallized layer silicates comparable to (a) and (b) above, but with incompletely developed interlayer material. These specimens will not be discussed in this chapter.

6.5.2 Cookeite

Brammall, Leech, and Bannister (1937) give an ideal composition $(\text{LiAl}_4)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ for cookeite, a common alteration product of Li-rich minerals in pegmatite and hydrothermal veins. Černý (1970) in a study of the most reliable cookeite analyses has shown that Si tends to remain nearly constant at 3.0 Si per four tetrahedral positions. Tetrahedral Al occasionally may be substituted for by B or Be. The exact nature of *manandonite*, listed by Frank-Kamenetskii (1960) as a dioctahedral Li-Al chlorite with substantial tetrahedral boron, is uncertain. The total octahedral occupancy in cookeite is close to 5.0, but may be as high as 5.35. The main octahedral substitution is $3(\text{Li,alk.})^{1+}/\text{Al}^{3+}$. Total Li was found to vary from 1.5 to 0.75 atoms per six octahedral positions, with some suggestion that the series may extend to even lower Li-contents. There may be a small octahedral substitution of divalent cations in some specimens. Fluorine substitutes frequently for OH.

Bailey and Brown (1962) and Lister (1966) have shown that cookeite usually adopts one of two layer stacking sequences based on the 1a structural unit. Černý, Povondra, and Staněk (1971), however, have described a I**b** dioctahedral chlorite from Czechoslovakia that will be an exception to this rule if its Li-content can be documented to insure that it is truly cookeite.

Vrublevskaja, Delitsin, Zvyagin, and Soboleva (1975) have described a triclinic 1-layer cookeite in metamorphosed bauxite from Djalair in Middle Asia, which was identified by the authors by means of high voltage electron diffraction (oblique texture) as the 1a-6 polytype of Bailey and Brown (1962) or $|\sigma'_2|\tau_+\tau_+|\sigma'_2|$ in the terminology of Zvyagin (1967). This cookeite with regular-stacking of layers appears to be an especially well crystallized specimen that bears some structural similarity to the more abundant but less regular form of cookeite. Lister (1966) examined single crystals of seven less well crystallized cookeites of the latter type and concluded that they are composed of 1a layers that simulate a 1-layer stacking sequence. Diffuse $0kl$ reflections of the $k \neq 3n$ type, however, suggest that these are really imperfect 2-layer structures similar to the "s" structure of Mathieson and Walker (1954). Lister (1966) also identified a 2-layer cookeite from two localities that is well crystallized and that can be correlated with the

monoclinic enantiomorphic "r" or "q" structures of Mathieson and Walker. The 2-layer "s", "q", and "r" structures are described in more detail in the vermiculite section of this chapter. Bailey (1975a) has summarized results of an incomplete structural analysis of one of the "r" or "q" cookeite crystals from Little Rock, Arkansas, U.S.A. The data suggest ordering of tetrahedral Si,Al and an asymmetry of distribution of Si and Al between the two tetrahedral sheets of the 2:1 layer similar to that found in margarite- $2M_1$.

6.5.3 Sudoite

Di,triocahedral chlorites that are essentially Li-free are termed sudoite. To date these Al-Mg chlorites have been recognized only as fine grained clays associated with ore deposits. Examples described by Bailey and Tyler (1960) and Hayashi and Oinuma (1964) can be interpreted as of the IIb structural type with an overall composition near $(Al_{2.7}Mg_{2.3})(Si_{3.3}Al_{0.7})O_{10}(OH)_8$.

Eggleton and Bailey (1967) have refined the structure of an average IIb layer of the former specimen by using only the $k = 3n$ X-ray powder reflections. The 2:1 layer was found to be dioctahedral and to contain 2.0 Al. The interlayer was found to be triocahedral with a composition $Mg_{2.3}Al_{0.7}(OH)_6$. Tetrahedral and octahedral ordering, if present, cannot be detected by the method used. They report a rather thick interlayer sheet (2.15 Å) compared to the octahedral sheet within the 2:1 layer (2.05 Å), and suggest that this thickening may be a method of compensating for the potential discrepancy in the lateral dimensions between a triocahedral interlayer and a dioctahedral 2:1 layer. Despite the thickened interlayer, the observed $d(001)$ value of 14.177 Å is smaller than would be expected for a triocahedral chlorite of similar net layer charge, and appears due primarily to a closer approach of the basal oxygens to the interlayer hydroxyls in this specimen.

Shirozu and Higashi (1976) have used 00l powder reflections to refine the z atomic coordinates for two sudoites from the Matsumine deposit of the Hanaoka mine and the Uchinotai deposit of the Kosaka mine in northeastern Japan. The interlayer sheets in both specimens were found to be thinner than the octahedral sheets within the 2:1 layer (2.04 and 1.97 Å versus 2.09 and 2.09 Å), in contrast to the Tracy mine specimen above. They suggest that substitutions to give a composition near $(Mg_{0.3}Al_{1.7})$ in the dioctahedral sheet of the 2:1 layer and of $(Mg_{1.3}Al_{1.5}\square_{0.2})$ in the triocahedral interlayer sheet may have alleviated the misfit problems for these specimens. They attribute the smaller $d(001)$ values observed for dioctahedral chlorites to thinner 2:1 layers than for triocahedral chlorites, rather than to a closer approach of the layer and interlayer.

6.5.4 Donbassite

Chlorites with two dioctahedral sheets (donbassite) have an octahedral cation total ranging from 4.27 to 4.49 in specimens recognized to date. This suggests that the positive charge on the interlayer sheet arises primarily from the presence of Al cations in excess of 2.0 in this sheet, in accord with the theoretical formula of $Al_{4+x/3}Si_{4-x}Al_xO_{10}(OH)_8$ given by Brindley and Gillery (1956). In some specimens small amounts of Li may be present also. A fine grained sedimentary specimen described by Müller (1961, 1963) gives the formula $Al_{4.27}(Si_{3.2}Al_{0.8})O_{10}(OH)_8$ after purification. A similar but impure sedimentary specimen (Müller, 1967) can be identified from its powder pattern as having the Ia structural type. Drits and Lazarenko (1967) have identified two different 2-layer donbassites. One has Ia type layers arranged in the enantiomorphic "r" or "q" stacking sequence, and the other has IIb type layers in a sequence that would be designated by $\sigma_6\tau_4\sigma_6\tau_2\sigma_6$ in the terminology of Zvyagin (1967) or by $\bar{x}_1$ -IIb-6: $\bar{x}_1$ -IIb-4 in the terminology of Lister and Bailey (1967).

Aleksandrova, Drits, and Sokolova (1972) have refined the crystal structure of a low-Li donbassite from Novaya Zemlya, U.S.S.R. They used 380 single crystal X-ray reflections in several cycles of least squares refinement to attain a final R value of 9.9%. The structure is that of a regular 1-layer monoclinic form of space group $C2$. It can be described as a distorted $1a-2$ ($|\sigma'_6| \tau_- \tau_+ |\sigma'_6|$) structure in which the vacant octahedral site in the 2:1 layer lies on the symmetry plane of the layer, but the partially vacant octahedral site in the interlayer lies off the projection of the mirror plane (thereby eliminating the mirror for the crystal as a whole). The octahedra in the 2:1 layer are twisted by 9.3° but those in the interlayer by only 6.5° because of the counter attraction of the partly filled third octahedral site in the interlayer. A tetrahedral rotation of 13.7° was found in a direction that tends to shorten the hydrogen bonds from the basal oxygens to the adjacent OH of the interlayer. The mean T—O distances of 1.68 Å and 1.62 Å suggest that all of the tetrahedral Al is ordered in one tetrahedron. The authors postulate that the charge differences resulting from the ordering are responsible for the observed flattening of the larger (Si,Al) tetrahedron and extension of the smaller Si tetrahedron, although both cations lie at the center of gravity of their individual tetrahedra. Local charge balance between the interlayer and adjacent 2:1 layers of the sort found in the $1a$ Cr-chlorite and vermiculite structures is not realized in this donbassite, however, because it is the partly vacant interlayer site that lies on the vertical line between the ordered (Si,Al) tetrahedra in the layers above and below. The basal oxygen surface of each layer is corrugated, as are the two OH surfaces of the interlayer, but the corrugations do not match one another. Thus, one O—OH distance is considerably longer (3.11 Å) than the other two (2.68 and 2.78 Å).

7. VERMICULITES $\sim \text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot \text{Mg}_{0.5}(\text{H}_2\text{O})_{4.0}$

Space groups: Cc and $C2/c$ $a \cong 5.35$, $b \cong 9.25$, $c \cong n \times 14.45$ Å,
 $\beta \cong 97.12^\circ$

7.1 General

Vermiculite is separated here from smectite on the basis of a higher layer charge, tentatively set as greater than 0.6 per formula unit. The higher layer charge leads to its diagnostic physical properties of spontaneous rehydration in the atmosphere after gentle dehydration ($<300^\circ\text{C}$) and acceptance of only one plane of glycerol molecules in the interlayer space upon solvation after Mg-saturation (*i.e.* $d(001) \cong 14.5$ Å after solvation compared with about 18 Å for smectite).

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 the alteration to vermiculite by oxidation of octahedral ferrous iron or by hydroxylation of O to OH. The cell parameters and ideal composition listed above are for trioctahedral vermiculite. Fine grained vermiculite in soils and sediments may be either trioctahedral or dioctahedral. Dioctahedral vermiculite presumably forms primarily by alteration of dioctahedral illite. It can be identified by a smaller $d(060)$ value between 1.49 Å and 1.50 Å, whereas $d(060)$ for trioctahedral vermiculite normally measures between 1.51 Å and 1.53 Å.

The structure of vermiculite was first studied by Gruner (1934*b*), who chose a monoclinic unit cell with $c = 28.57\text{--}28.77$ Å, $\beta = 97.15^\circ$, and space group Cc or $C2/c$. Gruner showed from consideration of powder pattern intensities that the structure must consist of trioctahedral 2:1 layers, between which lie double planes of water molecules occupying a space nearly equal to that of a complete interlayer sheet in the chlorite structure. Hendricks and Jefferson (1938*a*) confirmed Gruner's general conclusions by single crystal study, and suggested that vermiculites

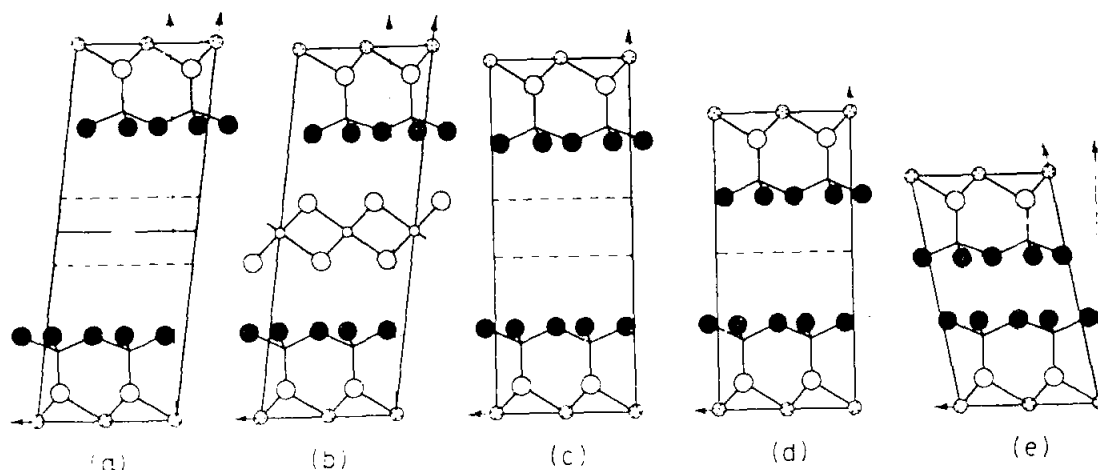


FIG. 1.29. [010] projections of Mg-vermiculite layer-interlayer assemblages in various stages of hydration (from Walker, 1961). (a) 14.81 Å phase, (b) 14.36 Å phase, (c) 13.82 Å phase, (d) 11.59 Å phase, (e) 9.02 Å phase.

have partially random displacements of structural layers parallel to the Y axis. Hendricks and Jefferson (1938*b*) further proposed a hypothetical arrangement of the interlayer water molecules in planar hexagonal rings with the oxygen of each water being tetrahedrally bonded to four neighboring oxygens through hydrogen atoms. Alternate water molecules in each of the two interlayer planes bond to the adjacent 2:1 layer surfaces. No provisions for exchangeable cations were made in any of these earliest studies, but these cations must be present in order to balance the negative charge on the 2:1 layer.

Walker (1956) showed that a Mg-saturated vermiculite in equilibrium with a humid atmosphere gives a basal spacing of 14.36 Å, in which state it contains two slightly incomplete interlayer planes of water molecules as hydration shells around the exchangeable cations. Immersion in water increases that basal spacing to 14.81 Å, and is presumed to complete the two interlayer planes of water molecules. Dehydration of the 14.36 Å phase by gentle heating leads first to a 13.82 Å spacing believed to correspond to a structure containing two slightly incomplete planes of water with a different arrangement than those of the 14.36 Å phase. Continued dehydration leads progressively to a 11.59 Å phase with a single plane of water molecules, a 20.6 Å phase consisting of approximately regular alternation of 11.59 Å and 9.02 Å components, and a 9.02 Å 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 for these phases are shown in Fig. 1.29. Russell and Farmer (1964) have questioned the interpretation of the 20.6 Å phase.

7.2 Structure of 14.36 Å trioctahedral vermiculite

Single crystal studies by Mathieson and Walker (1954), Grudemo (1954), and Mathieson (1958) have demonstrated that the water molecules and exchangeable cations occupy definite sites in the interlayer space. Mathieson and Walker (1954) and Mathieson (1958), who studied a 14.36 Å phase Mg-saturated vermiculite from Kenya by two-dimensional electron density and difference electron density maps, showed that the 2:1 layer tetrahedral networks are distorted from regular hexagons by 5.5° planar rotations of the tetrahedra. The exchangeable Mg^{2+} cations lie in a plane midway between adjacent 2:1 layers and have a plane of water molecules on each side. Thus, 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 specimen studied. The available diffraction data do not specify which of these

fixed sites actually are occupied in adjacent unit cells. Mathieson and Walker favor a dynamic system allowing cation and water migration between the available positions. They further suggested 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 clustering around the occupied cation sites as octahedral hydration shells. Every water molecule is linked by a hydrogen 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 surfaces. This postulated interlamellar structure is quite different from that of Hendricks and Jefferson.

Bradley and Serratosa (1960) have suggested another modification of the interlamellar region. This model retains the tetrahedrally bonded planar water nets of Hendricks and Jefferson but disposes them differently to form an incomplete octahedral sheet in which only certain water molecules furnish hydrogen bonds to the 2:1 layer surfaces. The pattern of occupancy postulated would create a base centered superstructure extending laterally over three unit cells for the lower observed levels of exchangeable cations and a regular array over one cell for the highest level of exchange. The orderly arrays were not believed to extend throughout the entire crystal.

Although theoretically all of the geometric layer–interlayer assemblages derived for chlorite should be possible for the 14.36 Å phase of vermiculite, only the 1a structure has been recognized. Although adjacent 2:1 layers often are stacked in semi-random sequences, indicated

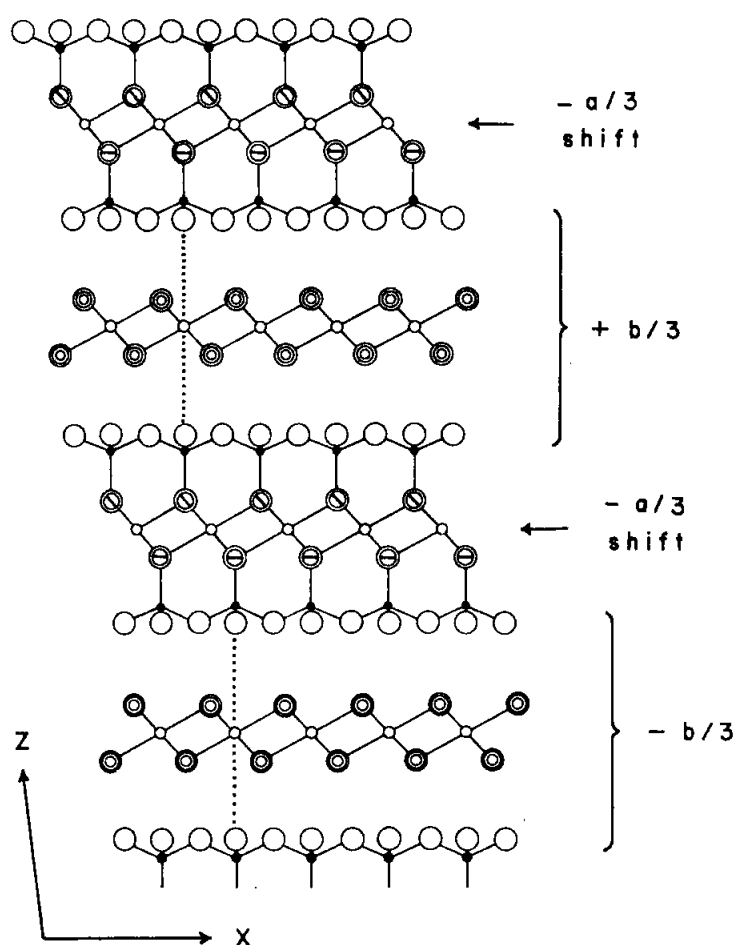


FIG. 1.30. [010] view of Llano vermiculite-s structure, with $-a_1/3$ intralayer shifts (L-type) and alternation of $\pm b/3$ shifts between adjacent 2:1 layers. Vertical dots show alignment of interlayer cations between tetrahedra above and below.

TABLE 1.24. X-ray powder data for vermiculite; spacings in Å (Bailey, unpublished)

<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (obs.)	<i>d</i> (calc.)
002	100	14.34	14.327	1,3,16	10	1.447	{1.446
004	10	7.180	7.164	2,0,18			{1.444
006	15	4.776	4.776	0,0,20	5	1.434	1.433
1,1, $\bar{1}$	40	4.604	4.601	338	10	1.359	{1.359
008	30	3.582	3.582	3,3,12			{1.357
0,0,10	40	2.866	2.865	0,6,10			{1.357
200	18	2.649	{2.652	402	15	1.333	{1.335
132			{2.649	262			{1.334
204	30	2.592	{2.592	404			{1.333
132			{2.591	260			{1.332
202	30	2.552	{2.553	1,3,18			{1.331
134			{2.549	2,0,20			{1.330
204	50	2.392	{2.394	400	10	1.321	{1.326
136			{2.390	264			{1.324
0,0,12			{2.388	406			{1.320
136	5	2.265	{2.268	262			{1.319
208			{2.261	2,0,18	8	1.297	{1.297
206	10	2.205	{2.207	408			{1.296
138			{2.203	3,3,10			{1.296
138	15	2.075	{2.078	264			{1.296
2,0,10			{2.077	1,3,20			{1.295
0,0,14	5	2.048	2.047	3,3,14			{1.295
208	15	2.015	{2.017	404	6	1.276	{1.276
1,3,10			{2.014	268			{1.274
2,0,10	5	1.837	{1.838	2,6,10	2	1.180	{1.181
1,3,12			{1.835	4,0,14			{1.180
0,0,16	2	1.790	1.791	3,3,14	2	1.169	{1.169
1,5, $\bar{1}$	15	1.744	{1.746	0,6,16			{1.168
2,4, $\bar{1}$			{1.742	3,3,18	5	1.135	{1.168
3,1, $\bar{1}$			{1.737	2,6,12			{1.134
2,0,12	20	1.675	{1.676	4,0,16			{1.134
1,3,14			{1.673				
1,3,14	7	1.575	{1.576				
2,0,16			{1.576				
332	30	1.541	{1.542				
060			{1.541				
330	30	1.534	{1.534				
334			{1.533				
062			{1.532				
332	5	1.506	{1.508				
336			{1.507				
064			{1.506				

$a = 5.344$, $b = 9.245$, $c = 28.870$ Å, $\beta = 97^\circ$.

Specimen from Llano Co., Texas, has 2-layer *s* structure.

Indices such as 1,1, $\bar{1}$ indicate edges of two-dimensional bands.

by streaked $k \neq 3n$ X-ray reflections, well crystallized Mg-vermiculites examined to date have shown a 2-layer periodicity along *Z*. Mathieson and Walker (1954) deduced that two different 2-layer *Ia* 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 alternately by $\pm b/3$ relative to one another. If 2:1 layers with intralayer 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 $+b/3$. This description neglects the interlayer water which is joined by long hydrogen bonds to each 2:1 layer surface and coordinates the exchangeable cations in a Ia configuration relative to the 2:1 layers.

Shirozu and Bailey (1966) were able to determine more details of 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 specimen was found to have a 2-layer structure of the type designated s by Mathieson and Walker. In this structure the shift within each 2:1 layer is always along $-X_1$ (L layers), the interlayer sheet has the Ia configuration, and successive 2:1 layers are displaced alternately by $+b/3$ and $-b/3$ along the Y axis (Fig. 1.30). The X-ray powder pattern is listed in Table 1.24.

The results of refinement of the Llano vermiculite indicate that the tetrahedral network is distorted by rotation of the tetrahedra by an average angle of 5.7° , as shown in Fig. 1.31. The direction of rotation is such that each basal oxygen moves towards the position of the nearest water molecule in the adjacent interlayer space, exactly analogous to the situation in chlorite. It was determined by least squares fit 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 at the time of investigation that 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 (Fig. 1.31). Large observed thermal parameters for the water are interpreted to be due mainly to random displacements of the water molecules from their average positions.

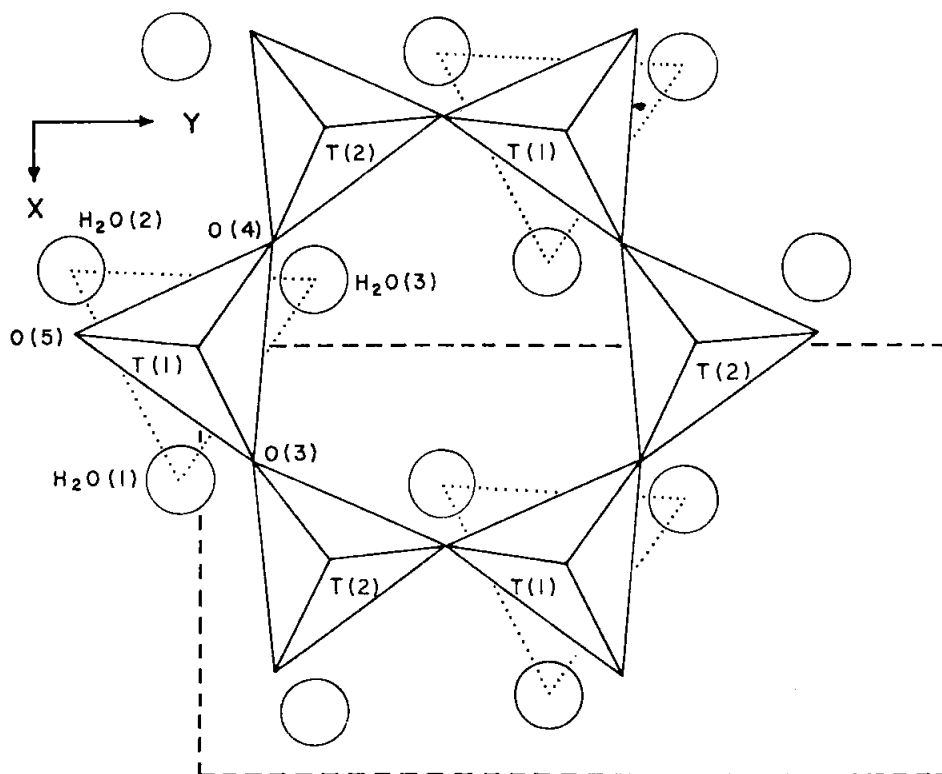


FIG. 1.31. Layer-interlayer relations in Llano vermiculite after 5.7° tetrahedral rotation and 3.3° rotation of water molecule triads (from Bailey, 1975a). Interlayer exchangeable cations lie under the Al-rich T(1) tetrahedra only and are coordinated octahedrally by six water molecules, only three of which are shown.

Perhaps the most interesting structural feature noted by Shirozu and Bailey is partial tetrahedral cation ordering with definite control of the exchangeable cation position by the sites of tetrahedral Al. Tetrahedral cation ordering is indicated both by the difference in average T—O bond lengths [T(1)—O = 1.673 Å and T(2)—O = 1.641 Å] 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 are assumed for both. The exchangeable cations are localized 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 (Figs. 1.30, 1.31). This provides local charge balance that should make this structural arrangement especially stable. The Ia structure in chlorite is believed to be less stable than the IIb and Ib types because of cation repulsion between the superposed tetrahedral and interlayer cations in the former. In the case of vermiculite the amount of cation repulsion is minimized by the small number of interlayer cations and by their concentration in the particular site where the best local charge balance can be obtained. A similar charge balance was demonstrated for Cr-chlorite by Brown and Bailey (1963).

No long-range ordering of the interlayer cations and H_2O over adjacent unit cells was noted by Shirozu and Bailey, but Alcover, Gatineau, and Méring (1973) were able to demonstrate short-range order in local domains in Kenya vermiculite by study of diffuse reflections present in the regions between the normal Bragg reflections on single crystal X-ray patterns. The abnormal scattering is concentrated along lines parallel to Z^* and disappears upon dehydration at 500°C, so that it must be attributed to the arrangement of the interlayer materials. The interpretation by Alcover *et al.* confirms the general outline of the local ordering patterns predicted by Mathieson and Walker (1954) and by Bradley and Serratos (1960) in which exchangeable Mg and

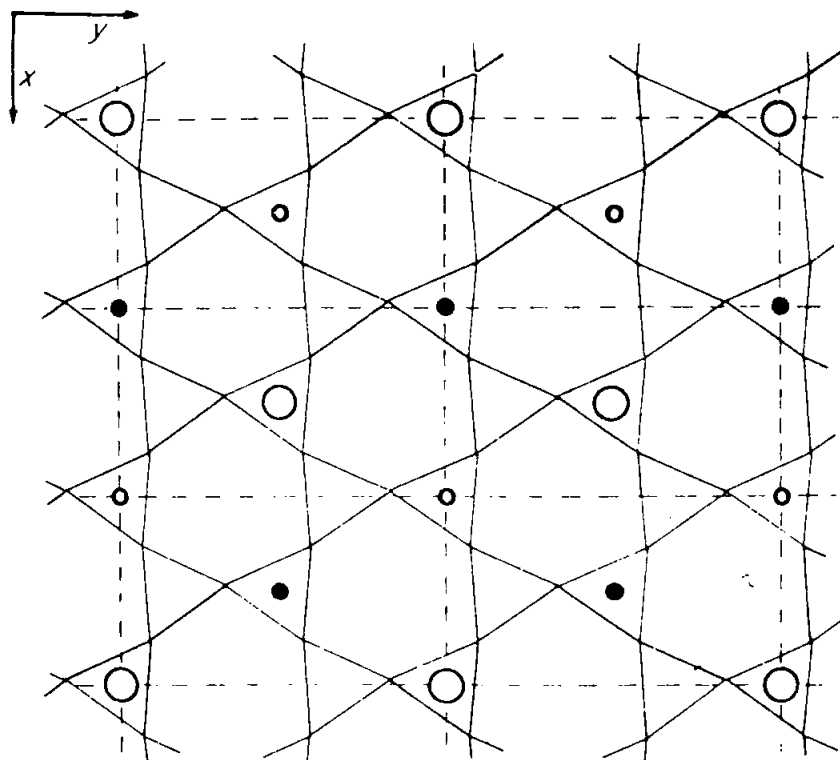


FIG. 1.32. C-centered superlattice of dimensions $3a \times b$ caused by orderly short-range distribution of exchangeable Mg cations (large circles) in local domains of vermiculite (from Alcover *et al.*, 1973). In neighboring domains the cations occupy one of the other two positions (smaller solid and open circles), which form similar centered superlattices but with the local charge balance involving different T(1) tetrahedra (superimposed triangles).

associated water molecules are distributed over the lattice points of a large *C*-centered cell having dimensions $3a \times b$, where a and b are the dimensions of the normal vermiculite unit cell. The ordering is two-dimensional in that there is no coupling between adjacent interlayers.

The possible positions for the exchangeable cations in the local supercell are divided into three sets, as shown in Fig. 1.32. Only one set of positions can be occupied in a given domain, but different sets can be occupied in different domains. Full occupancy of one set of possible positions requires 2 Mg^{2+} per supercell interlayer, or 0.33 Mg^{2+} per formula unit. The precise distribution of the interlayer water molecules over the three cells, which would be required to distinguish between the Mathieson-Walker and Bradley-Serratosa models, was not determined in this study. It is inferred, but not demonstrated, by the authors that local Si,Al ordering accompanies the interlayer Mg^{2+} ordering so that local charge balance is retained. If true, this would explain the rather small amount of *long-range* Si,Al order found by Shirozu and Bailey in Llano vermiculite, for which the *average* composition of tetrahedron T(1) was determined as $\text{Si}_{0.65}\text{Al}_{0.35}$. If there is complete local Si,Al order in each of the three domain types so that only the T(1) positions adjacent to the exchangeable cations are occupied by Al, the average over all domains would be $\text{T}(1) = \text{Si}_{0.67}\text{Al}_{0.33}$ and $\text{T}(2) = \text{Si}_{1.0}$ for the case of an ideal tetrahedral composition of $\text{Si}_{3.0}\text{Al}_{1.0}$.

De la Calle *et al.* (1976) have pointed out that the actual structure of the Llano vermiculite is less perfect than the ideal structure given by Shirozu and Bailey (1966). They show that the observed intensities and diffuseness of the $k \neq 3n$ reflections indicate a large number of stacking faults to be present. These faults break up the regular alternation of $+b/3$ and $-b/3$ interlayer shifts, as shown in Fig. 1.30 for the ideal *s* structure, so that a $+b/3$ shift is as apt to be followed by another $+b/3$ shift as by a $-b/3$ shift. The same authors have shown experimentally that the *s* vermiculite structure can be derived from an original phlogopite-1*M* by treatment with Mg^{2+} solutions, whereas the mixed *q* and *r* structures studied in Kenya vermiculite by Mathieson and Walker (1954) come from alteration of a phlogopite-2*M*₁. Because the $\text{K}^+ \leftrightarrow \text{Mg}^{2+}$ exchange is reversible, the parentage of a given vermiculite can be determined. About 90% of natural Mg-vermiculites are believed to have 1*M* parentage. The authors show also that treatment of phlogopite with Ca^{2+} or Na^+ solutions results in a 1-layer vermiculite of the 1*a*-2 type (Bailey and Brown, 1962) if the parent is a 1*M* polytype and in a 2-layer vermiculite of the type termed *p* by Mathieson and Walker if the parent is a 2*M*₁ polytype. These latter two vermiculite structures, not yet identified in natural specimens, are both characterized by retaining the relative positions of the silicate 2:1 layers of the parent so that successive hexagonal rings remain exactly superimposed. This is in contrast to the Mg^{2+} species where adjacent layers are shifted by $\pm b/3$ as a result of the interlayer cation exchange.

8. SEPIOLITE-PALYGORSKITE

8.1 General

Although sepiolite and palygorskite (= attapulgitite) may take a variety of macroscopic forms from massive to papyraceous to fibrous, they invariably are lath-like or fibrous on a microscopic scale. The laths are elongate along the $5.3 \text{ \AA}$ axis, which has been labeled *Z* in much of the literature but will be called *X* in this chapter in order to be in accord with the axes of other layer silicates. Electron diffraction of individual sepiolite laths has shown the flat lath surfaces usually to be parallel to (001) so that the *Z*-axis is normal or quasi-normal to the thinnest dimension. Because of a shorter *b*-dimension than in sepiolite, palygorskite laths tend to have a more equidimensional *YZ* cross section than sepiolite.

The structures of sepiolite and palygorskite are alike in that both contain continuous planes of tetrahedral basal oxygen atoms approximately 6.5 Å apart. The apical oxygens point alternately up and down relative to the planes of basal oxygens in a pattern such that the tetrahedra pointing in the same direction form tetrahedral ribbons that extend parallel to the length of the laths (X). The ribbons have an average width along Y of three linked pyroxene-like single chains in sepiolite and two linked chains in palygorskite (See Figs. 1.34 and 1.35). Ribbons with apices pointing up are linked vertically to ribbons with apices pointing down by forming octahedral coordination groups around Mg and Al. The linked ribbons thus form a 2:1 layer that is continuous along X but of limited lateral extent along Y. That is, the tetrahedral sheet is continuous across ribbons, but with apices pointing in different directions in adjacent ribbons. The octahedral sheet is discontinuous. A small number of exchangeable Ca^{2+} or Mg^{2+} cations and variable amounts of zeolitic water are contained in rectangular channels that lie between the backs of opposing 2:1 ribbons and extend parallel to the lath direction. In addition to the zeolitic water there are four bound water molecules (OH_2) per formula unit that lie at the edges of the ribbons and are more tightly held because they participate in the coordination of the octahedral Mg and Al.

Structural variety in sepiolite and palygorskite is possible by variation in the intralayer shifts at the octahedral interface region, as in all other 2:1 layer types, and by variation in the width

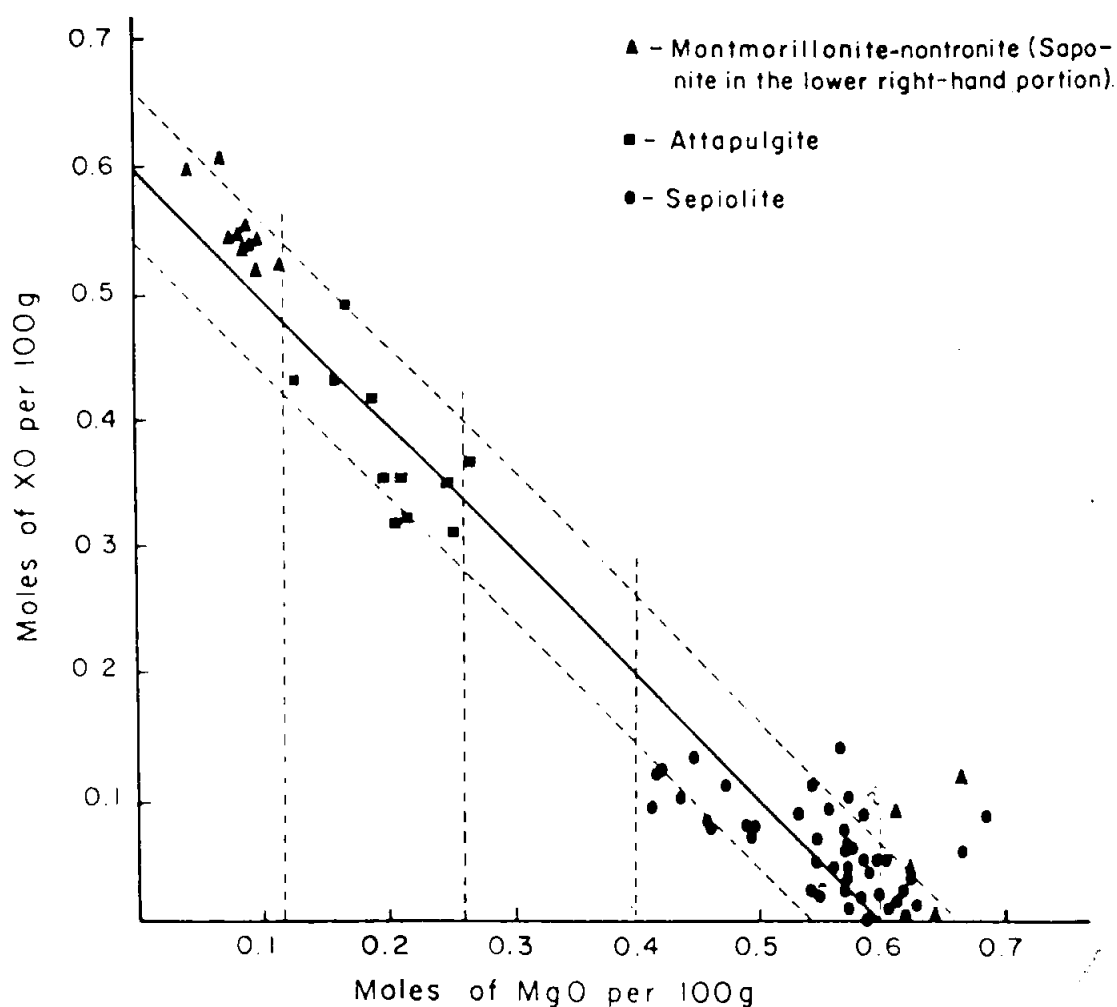
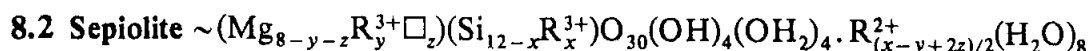


FIG. 1.33. Relationship of sepiolite, palygorskite (= attapulgite), and smectite analyses on a plot of moles MgO with respect to moles XO (= moles $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO}$, expressed as MgO). Number of octahedral vacancies increases right to left along diagonal line. From Martin-Vivaldi and Cano-Ruiz (1956).

and the manner of side linkage of the 2:1 ribbons. Although the direction of the $a/3$ intralayer shift appears to be restricted to the X_1 axis parallel to the fiber direction, the sense of this shift may be $-$ or $+$ depending on occupation of the I or II octahedral cation sets (as defined for the micas). If the octahedral cation sets occupied are the same in all 2:1 ribbons so that the sense of the intralayer shifts is always the same, the resultant ideal symmetry is monoclinic with an ideal β angle of about 105.5° . If the octahedral cations alternate regularly between the I and II sets so that the sense of intralayer shift is alternately $-$ and $+$ in adjacent ribbons, the resultant symmetry is orthorhombic. The precise space groups depend on the width of the 2:1 ribbons and the manner of lateral linkage of adjacent ribbons.

The differing widths of the 2:1 ribbons lead directly to differing numbers of octahedral cation positions per formula unit, 8 for sepiolite and 5 for palygorskite. Not all available positions need be occupied. Martin-Vivaldi and Cano-Ruiz (1956) have suggested that the sepiolite-palygorskite group with inverted 2:1 ribbons occupies the region of discontinuity between the planar structures of dioctahedral montmorillonite and trioctahedral saponite. Inherent differences in the lateral dimensions of the tetrahedral and octahedral sheets cannot be used, as in antigorite, to explain the tetrahedral inversions found in sepiolite and palygorskite. The authors postulate instead that the inverted ribbon pattern is a structural motif that is energetically favorable for accommodation of certain ratios of octahedral cations to vacancies in a regular pattern, for example 4:1 in palygorskite and 7-8:2-1 in sepiolite. Their compositional plot of the relations of sepiolite and palygorskite to montmorillonite and saponite is shown in Fig. 1.33. No specimens are shown between the sepiolite and palygorskite regions of the diagram, where the ratio of cations to vacancies is not favorable for any regular pattern of tetrahedral inversion. Martin-Vivaldi and Linares-Gonzalez (1962) have described intermediate composition specimens, however, for which they postulate a random intergrowth of 2:1 ribbons of different widths.

Sepiolite is identified by a strong 011 X-ray reflection at $12 \text{ \AA}$ and a b repeat of $27 \text{ \AA}$ whereas the corresponding values for palygorskite are $10.5 \text{ \AA}$ and $18 \text{ \AA}$.



Space group = $Pnan$ $a \cong 5.28$, $b \cong 26.95$, $c \cong 13.37 \text{ \AA}$, $\beta = 90^\circ$

Only one crystalline form of sepiolite has been recognized to date, but several slightly different structural models have been put forth in interpretation of the diffraction data. Nagy and Bradley (1955) utilized the $0kl$ reflections from an X-ray fiber photograph to propose a projection of the structure parallel to the fiber length. The atomic parameters parallel to the fiber length were not given (defining the intralayer shifts), so the structure could be either orthorhombic or monoclinic. The preferred space group is given as the monoclinic $C2/m$, which would be $A2/m$ in the orientation used in this chapter.

The Nagy-Bradley model of sepiolite differs from the later model of Brauner and Preisinger (1956) in that adjacent 2:1 ribbons are joined to each other by two common basal oxygens, instead of one, as a result of inverting apical directions along the middle of a zig-zag single chain of linked tetrahedra rather than along one edge of the chain. This leads to nine octahedral cation positions in a ribbon instead of eight as in the Brauner-Preisinger model, six OH instead of four, and six zeolitic water molecules instead of eight. Allocation of available sepiolite analyses to structural formulas by Caillère and Hénin (1961a) clearly favors the composition implied by the Brauner-Preisinger model, as listed at the head of this section.

Brauner and Preisinger (1956) and Preisinger (1959) utilized three-dimensional data from X-

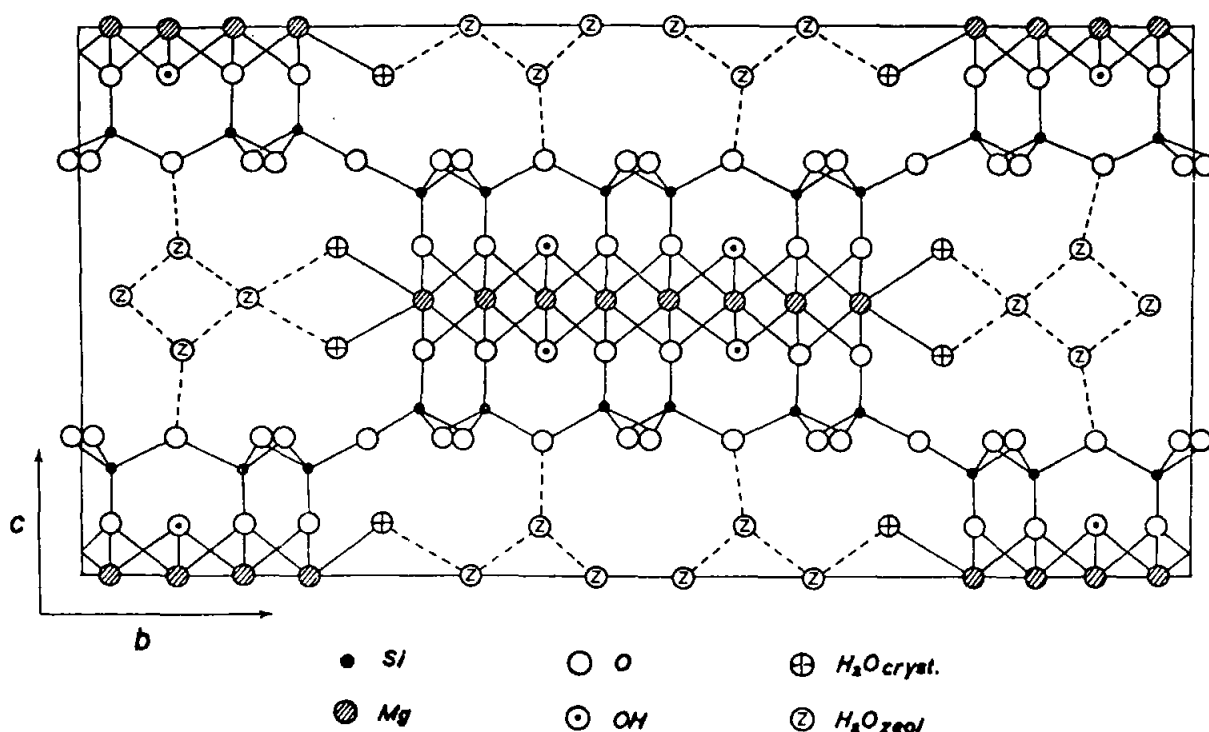


FIG. 1.34. [100] projection of sepiolite structure. Modified from Caillère and Hénin (1961a). Five-fold "spoke-pattern" of 2:1 ribbons has been called a quincunx arrangement.

ray fiber photographs in trial and error methods to propose an orthorhombic structure of space group *Pncn* (or *Pnan* in the orientation used here). This model, shown in Fig. 1.34, differs from the Nagy-Bradley model primarily in inversion of tetrahedra along a line between two adjacent zig-zag single chains, rather than within a chain, so that adjacent inverted ribbons are joined by a single basal oxygen. The ribbon width along Y of three single chains is the same in both models. A theoretical monoclinic structure of space group *A2/a* results if the same set of octahedral cation positions (I or II) is occupied in each 2:1 ribbon of the Brauner-Preisinger model, instead of alternating regularly between the two sets in adjacent ribbons. Electron diffraction studies of single laths of sepiolite by later investigators, however, have indicated only orthorhombic symmetry in specimens examined to date.

Rautureau, Tchoubar, and Méring (1972), Rautureau and Tchoubar (1974), and Rautureau (1974) have confirmed and refined further the Brauner-Preisinger model by a series of electron density and difference electron density maps using *h0l*, *0kl*, and *hk0* data derived from electron microdiffraction of a single lath of sepiolite from Ampandrandava, Madagascar. They were able to show that the tetrahedral sheets are 0.134 Å thicker than in the ideal model and participate in a nearly ideal intralayer shift of $a/3$. The 0.45 atoms of Fe + Mn substituting for Mg are ordered in one specific octahedral site. They also were able to show under conditions of dehydration of the zeolitic water that Mg atoms at the edges of each ribbon are distributed statistically in a 1:2 ratio between two octahedral sites, one of which lies on an ideal site just within the 2:1 ribbon and the other is attached to the outer edge of the ribbon where it is coordinated between adjacent apical oxygens and waters of crystallization.

Substitution of Al or Fe³⁺ for Si in tetrahedral sites is usually small (range 0.2 to 1.3 atoms per 12 sites). The total of the octahedral cations usually ranges from 7.0 to 8.0. The octahedral cations are primarily Mg, but aluminian, ferrian, manganoan, and nickeloan varieties are known. The name *falcondoite* has been approved for the Ni end member (Springer, 1976). The name *loughlinite* has been approved for a Na-rich variety. Preisinger (1963) has shown that 2 Na

TABLE 1.25. X-ray powder data for sepiolite* and loughlinite; spacings in Å

		A. Sepiolite (Brindley, 1959)				B. Loughlinite (Fahey <i>et al.</i> , 1960)	
hkl	d(calc.)	d(obs.)				d	I
		1	2	3	4		
020	13.48	—	—	—	—	12.9	100
110	12.07	12.05 (100)	12.1 (100)	12.1 (100)	12.3 (60)	7.63	5
130	7.482	7.47 (10)	7.5 (7)	7.7 (5B)	7.6 (5)	6.46	1b
200	6.750	—	—	—	—	—	—
040	6.742	6.73 (5)	6.7 (4B)	6.7 (5B)	—	5.04	1.5
220	6.036	—	—	—	—	4.81	5
001	5.255	—	—	—	—	4.51	7b
150	5.008	5.01 (7)	5.04 (3B)	5.0 (5B)	4.9 (6B)	4.34	18n
021	4.896	—	—	—	—	4.15	1.5
111	4.818	—	—	—	—	4.00	1
240	4.780	—	—	—	—	3.83	6b
060	4.495	4.498 (25)	4.49 (25)	4.47 (18)	4.5	3.63	7b
310	4.438	—	—	—	—	3.31	5
131	4.301	4.306 (40)	4.29 (35)	4.31 (25)	4.3	3.21	1
201	4.146	—	—	4.17 (5)	—	3.09	2
041	4.145	—	—	—	—	2.92	5
330	4.023	4.022 (7)	4.02 (7)	—	—	—	—
221	3.963	—	—	—	—	2.64	6
260	3.741	3.750 (30)	3.738 (25)	3.738 (20)	3.746 (20B)	2.60	5
170	3.705	—	—	—	—	2.55	7n
151	3.626	—	—	—	—	2.48	5
241	3.532	3.533 (12)	3.506 (5)	—	3.49 (5)	2.44	5
350	3.455	—	—	—	—	2.32	2
061	3.416	—	—	—	—	2.23	1
311	3.391	—	—	—	—	2.16	3
400	3.375	—	—	—	—	2.11	3
080	3.370	3.366 (30)	3.339 (45)	3.339 (35)	3.34	2.06	1
420	3.274	—	—	—	—	2.02	1
331	3.195	3.196 (35)	3.181 (15B)	3.187 (12)	—	1.907	1.5
261	3.048	3.050 (12)	—	3.048 (5)	—	1.804	1.5
171	3.028	—	—	—	—	1.774	1.5
440	3.018	—	—	—	—	1.732	2
280	3.016	—	—	—	—	1.695	3
370	2.928	2.932 (4)	2.950 (5)	—	2.98	1.675	3
190	2.925	—	—	—	—	1.634	1
351	2.887	—	—	—	—	1.608	1
401	2.840	—	—	—	—	1.567	2
081	2.837	2.825 (7)	—	—	—	1.550	3
421	2.778	2.771 (4)	—	2.79? (4)	—	1.517	3
460	2.699	—	—	—	—	1.491	1
0.10.0	2.697	—	—	—	—	1.471	1
510	2.687	2.691 (20)	2.66 (8NR)	2.675 (8NR)	2.67	1.413	1
002	2.627	—	—	—	—	1.380	1b
441	2.618	—	—	—	—	1.318	1
281	2.617	2.617 (30)	2.59	2.59	—	1.293	1.5
530	2.586	2.586 (NR)	—	—	—	—	—
022	2.580	—	(45NR)	(40NR)	—	—	—
112	2.567	—	—	—	—	—	—
371	2.557	2.560 (55)	—	—	—	—	—
191	2.556	—	2.56	2.56	—	—	—
2.10.0	2.505	—	—	—	—	—	—
390	2.495	—	—	—	—	—	—
132	2.479	2.479 (5)	—	—	2.49	—	—
202	2.448	—	—	—	—	—	—
042	2.448	2.449 (25)	2.43	2.44	2.43	—	—
550	2.414	—	(20NR)	(15NR)	(10NR)	—	—
1.11.0	2.412	—	—	—	—	—	—
222	2.409	2.406 (15)	2.395	2.39	2.36	—	—
461	2.401	—	—	—	—	—	—
062	2.268	—	—	—	—	—	—
312	2.261	2.263 (30)	2.256 (20)	2.259 (18B)	2.24 (20B)	—	—
2.10.1	2.260	—	—	—	—	—	—
620	2.220	—	—	—	—	—	—
570	2.211	2.206 (3)	—	—	—	—	—
332	2.200	—	—	—	—	—	—
640	2.134	—	—	—	—	—	—
2.12.0	2.130	2.125 (7)	2.117 (4B)	2.117 (5)	—	—	—
4.10.0	2.107	—	—	—	—	—	—

TABLE 1.25.—*continued*

<i>hkl</i>	<i>d</i> (calc.)	A. Sepiolite (Brindley, 1959)				B. Loughlinite (Fahey <i>et al.</i> , 1960)	
		<i>d</i> (obs.)				<i>d</i>	<i>I</i>
		1	2	3	4		
402	2.073						
082	2.072	2.069 (20)	2.060 (10)	2.071 (7B)	2.08 (6B)		
501	2.069						
571	2.038	2.033 (4)	—	—	—		
		1.957 (4)	—	—	—		
		1.921 (2)	—	—	—		
		1.881 (7)	1.873 (4)	—	—		
		1.818 (2)	—	—	—		
		1.760 (6)	—	—	—		
		1.700 (10)	1.716 (7)	1.722 (5)	—		
		—	1.691 (10)	1.692 (8)	1.69 (5B)		
		1.637 (3)	—	—	—		
		1.592 (10)	1.598 (4)	1.583 (9B)	1.58 (7)		
		1.550 (15)	1.578 (7)	1.548 (10)	1.551 (10)		
			1.540 (8)	—	—		
		1.518 (15)	1.517 (15)	1.517 (15)	1.517 (14)		
		1.502 (8)	—	—	—		
		1.468 (4)	1.465 (3)	—	—		
		1.416 (9)	1.406 (4)	1.412 (4B)	—		
		1.349 (6)	—	—	—		
		1.312 (6)	—	1.310 (4B)	—		
		1.299 (15)	—	1.296 (10)	—		

A. Experimental data for sepiolites from:

- 1 Little Cottonwood, Utah.
- 2 Vallecas, Spain.
- 3 Kenya.
- 4 Eski Chehir, Asia Minor.

Intensities in ().

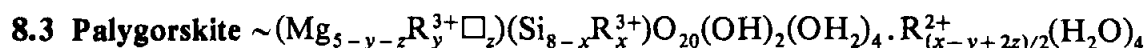
B signifies "broad"; NR "not resolved".

Indices and *d*(calc.) from *a* = 13.50, *b* = 26.97, *c* = 5.255 Å, β = 90°.* Note that *a* and *c* are interchanged relative to text.

B. Specimen from Sweetwater Co., Wyoming.

b = broad line, *n* = narrow line, | = band.*d* values for measurements at each edge of band.

substitute for 2 Mg at the edges of the octahedral sheet of loughlinite with an additional 2 Na coordinated octahedrally by water molecules in the channels between the backs of the 2:1 ribbons in order to balance the charge. The X-ray powder pattern of loughlinite is only slightly different from that of sepiolite (strong line at 12.8 Å rather than 12.0 Å, Table 1.25), but the fiber patterns and chemistry are distinctive (Fahey, Ross, and Axelrod, 1960).



Space groups: *Pnmb*, *A2/m*, *P2/a*, *Pn* $a \cong 5.21$, $b \cong 17.9$, $c \sin \beta \cong 12.7$ Å,
 $\beta \cong 90^\circ, 96^\circ, \text{ or } 107^\circ$

Considerably more structural diversity has been confirmed for palygorskite than for sepiolite in that at least one orthorhombic and three different monoclinic geometry unit cells have been identified. Provisional structures have been suggested for three of these forms, but no detailed refinements have been made. Confirmation of their validity, therefore, must await the results of further structural work.

Bradley (1940) proposed provisional details of a projection of the palygorskite structure onto the YZ plane using *Ok**l* reflections from an X-ray fiber photograph of material from Attapulgis, Georgia, U.S.A. The fiber axis is always the 5.2 Å X-axis, as in sepiolite, but the fiber pattern is different otherwise than for sepiolite. The proposed two-dimensional structure contains 2:1 ribbons that are linked to each other laterally by single basal oxygens (Fig. 1.35). The structure is similar to that of sepiolite except that the shorter *b* dimension incorporates only two linked

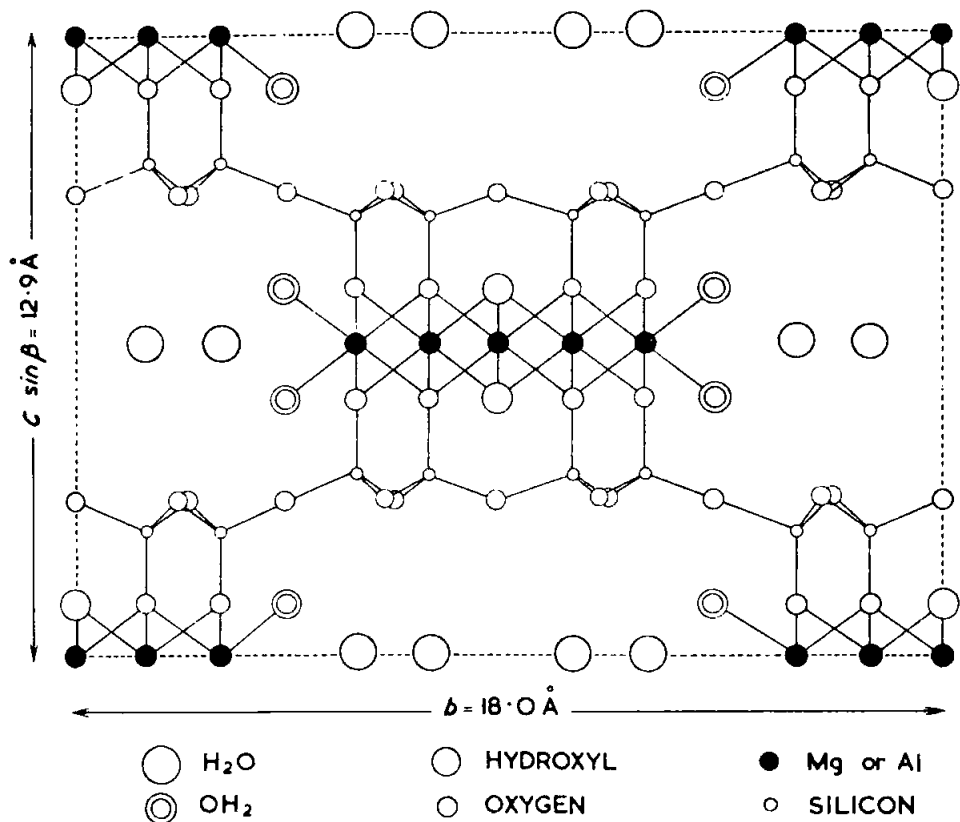


FIG. 1.35. [100] projection of palygorskite structure. Modified from Caillère and Hénin (1961*b*).

pyroxene-like single chains in the ribbon width, instead of three. There are five cation positions in the octahedral strip, not necessarily all occupied, with bound water at the edges and zeolitic water plus a few exchangeable cations in channels between the backs of the ribbons. Because only a two-dimensional model was proposed, the resultant symmetry could be either monoclinic

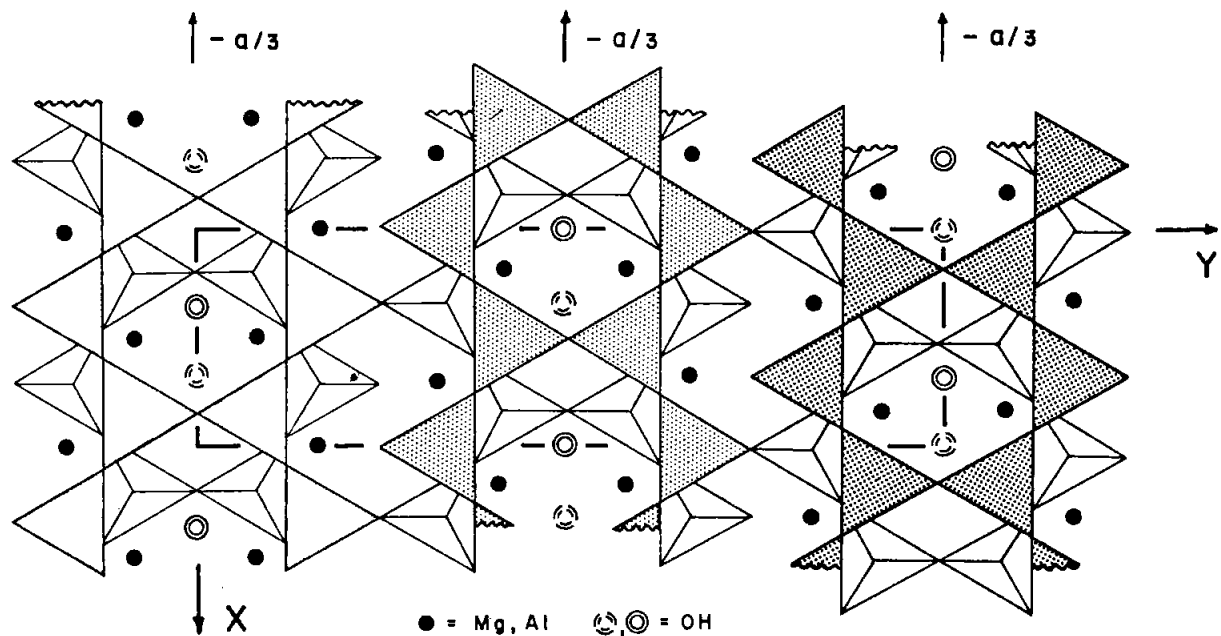


FIG. 1.36. Plan view of $A2/m$ palygorskite structure. Octahedral cations occupy set I positions in each 2 : 1 ribbon, so that all intralayer shifts are $-a/3$. The octahedron on a symmetry center along the median line of each ribbon is shown as vacant. Relative to Fig. 1.35, only the lowest 2 : 1 ribbon is shown on the left side and the highest 2 : 1 ribbon on the right side so that the bonding between ribbons can be illustrated.

or orthorhombic depending on the octahedral cation sets occupied in the 2:1 ribbons. The space group was listed as probably the monoclinic $C2/m$, which is transformed to $A2/m$ in this chapter, but the β angle was not given.

Drits and Aleksandrova (1966) calculated structure amplitudes for Bradley's monoclinic model as well as for a second monoclinic model of space group $A2/a$ in which adjacent ribbons are linked to one another by two basal oxygens instead of one. The lateral linkage in this second model is similar to that proposed by Nagy and Bradley (1955) for sepiolite. Comparison of these calculated F values with the observed values for a specimen from Dzhezdy, Kazakh, U.S.S.R., showed best agreement for the Bradley model, so that the side linkage by two oxygens appears excluded for both sepiolite and palygorskite. Drits and Aleksandrova also showed by compilation of chemical analyses of palygorskite that on the average four of the five octahedral cation positions are occupied. A two-dimensional electron density map for the Dzhezdy specimen showed that the vacancy octahedral site is ordered in a typical dioctahedral pattern.

Drits and Sokolova (1971) have confirmed further the Bradley model for the Dzhezdy palygorskite and have measured a β angle of 107° . This model requires an intralayer shift along $-X_1$ in all 2:1 ribbons (Fig. 1.36). The magnitude of β suggests a slight overshift of $0.027a = 0.28 \text{ \AA}$ from the ideal value.

Preisinger (1963) reported an orthorhombic space group $Pnmb$ for palygorskite from the type locality Palygorskaja, U.S.S.R. Although no structural details were given, this is the symmetry that would result if Bradley's monoclinic model were modified so that the intralayer $a/3$ shifts alternate in $-$ and $+$ directions along X_1 as a result of alternating octahedral cation sets I and II in adjacent 2:1 ribbons. Thus, this orthorhombic palygorskite model is exactly similar to the orthorhombic sepiolite model of Brauner and Preisinger (1956), except for ribbon width. A plan (001) view of the 2:1 ribbons shifts is shown in Fig. 1.37. The (100) side view is identical to that of the Bradley monoclinic model (Fig. 1.35).

Christ, Hathaway, Hostetler, and Shepard (1968) determined the unit cells for five palygorskites by powder X-ray diffractometry (Table 1.26). Three samples could be indexed on

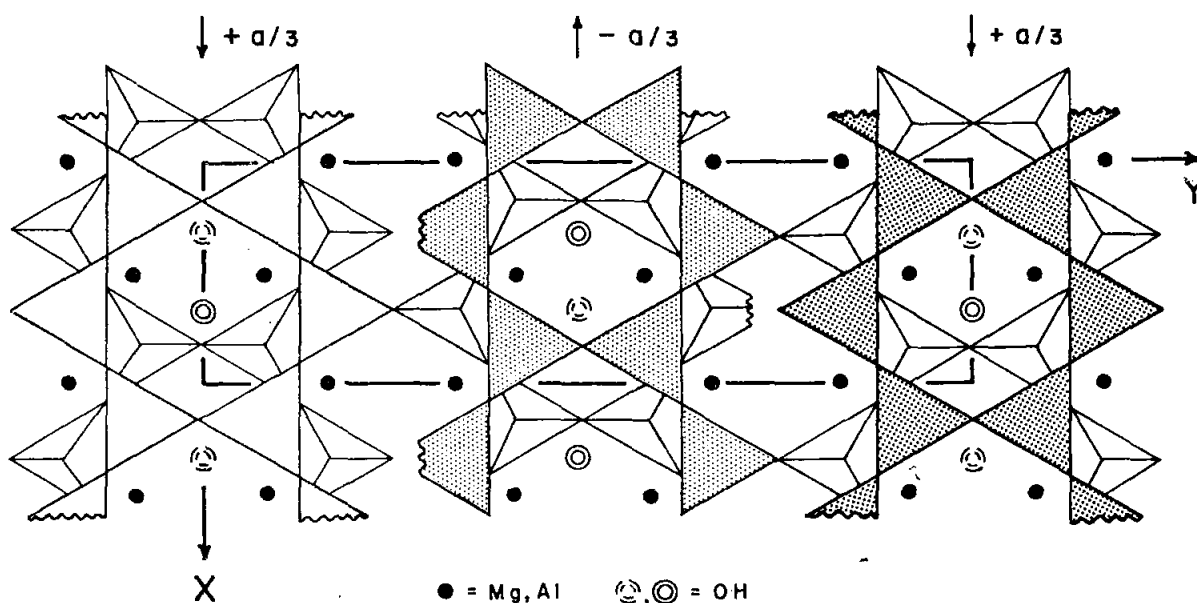


FIG. 1.37. Plan view of $Pnmb$ palygorskite structure. Octahedral cations alternately occupy I and II sets in adjacent 2:1 ribbons so that the directions of intralayer shift alternate between $-a/3$ and $+a/3$. The octahedron on a symmetry center along the median line of each ribbon is shown as vacant. Relative to Fig. 1.35, only the lowest 2:1 ribbon is shown on the left side and the highest 2:1 ribbon on the right side so that the bonding between ribbons can be illustrated.

TABLE 1.26. X-ray powder data for

A. Christ <i>et al.</i> (1969) palygorskite															
Sapillo, N. M., No. 21				Zaachila, Mexico				Attapulugus, Ga.				Glasgow, Va.			
<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)
110	10.37	10.44	100	110	10.40	10.42	100	110	10.43	10.54	100	110	10.34	10.35	100
200	6.362	6.36	13	200	6.390	6.38	15	200	6.411	6.42	10	200	6.341	6.33	19
130	5.395	5.395	9	130	5.403	5.385	15	130	5.416	5.418	7	130	5.387	5.382	13
040	4.468	4.466	20	040	4.471	4.464	31	040	4.481	4.479	23	040	4.463	4.462	29
121	4.260	4.262	22	121	4.240	4.262	34	121	4.244	4.258	15	121	4.258	4.258	11
310	4.127 s	4.129	2	310	4.144	4.146	6	310	4.158 s	4.137	10	121	4.132	4.129	15
				201	4.033 s	4.004	3					201	3.985	3.988	4
				131	3.746	3.753	14								
131	3.760	sh						131	3.751	sh					
221	3.686	3.679	15	221	3.676	3.678	64	221	3.682	3.681	7				
								240	3.673	sh		240	3.649	3.648	10
150	3.441 s	3.440	2	150	3.445 s	3.436	11	150	3.453 b	3.444	5	131	3.649		
231	3.347	3.348	7	231	3.340	3.347	47			Q		150	3.436 s	3.436	3
311	3.243	sh		311	3.241	3.250	34	311	3.247	3.246	20	231	3.358	3.351	7
												311	3.222	3.223	16
400	3.181	3.179	12	400	3.195	3.191	23					311	3.194	sh	
321	3.094	3.096	16	321	3.092	3.104	23	400	3.206	3.205	18	400	3.170	3.170	23
331	2.885	2.889	4	241	2.995	2.992	3	321	3.098	sh		321	3.087	3.088	11
411	2.689	sh		411	2.691	2.698	6	411	2.698	2.698	4	331	2.890 s	2.885	3
251	2.679	2.679	8	251	2.676	2.680	9	251	2.681	sh		411	2.674	2.673	6
421	2.602	sh		421	2.604	2.603	10	421	2.610			341	2.602	2.605	10
012	2.593	sh		440	2.600			440	2.607	b 2.601	10	421	2.596		
440	2.591							061	2.590			440	2.584	2.585	15
061	2.590	2.589	10												
102	2.567	2.567	12	012	2.573	2.566	14					421	2.566	sh	
								102	2.548			161	2.563	sh	
112	2.541			161	2.535	2.536	34	161	2.539	2.548	13b	012	2.550	sh	
161	2.538	2.539	20									061	2.530	2.536	17
												102	2.511	2.507	12
												112	2.500		
												161	2.481	sh	

A. Plus many additional lines, mostly weak and broad, for all samples; s = peak poorly resolved because of low ratio of peak intensity to background; sh = peak present, but as shoulder on adjacent, more intense peak; b = broad; Q = peak due to quartz present.

Sapillo, N.M. No. 21 $a = 12.725$, $b = 17.872$, $c = 5.242$ Å, Orthorhombic.

Zaachila, Mex. $a = 12.781$, $b = 17.885$, $c = 5.199$ Å, Orthorhombic.

Attapulugus, Ga. $a = 12.823$, $b = 17.925$, $c = 5.199$ Å, Orthorhombic.

Glasgow, Va. $a = 12.681$, $b = 17.864$, $c = 5.127$ Å, $\alpha = 92.23^\circ$, Monoclinic.

Metaline, Wash. $a = 12.78$, $b = 17.83$, $c = 5.24$ Å, $\beta = 95.78^\circ$, Monoclinic.

* Note interchange of a and c relative to text.

the basis of orthorhombic symmetry Pn^{**} consistent with Preisinger's model. An interesting point is that a sample from Attapulugus is included in this orthorhombic group. This suggests either that both structures occur at this locality or that the orthorhombic version of Bradley's model (identical to Preisinger's model) is valid for his Attapulugus sample, rather than his preferred monoclinic version. The monoclinic version, however, has been shown to be valid for other specimens (Drits and Sokolova, 1971).

palygorskite* and yofortierite; spacings in Å

Metaline, Wash.				B. Bradley (1940) palygorskite					C. Perrault <i>et al.</i> (1975) yofortierite	
				Attapulgis, Georgia					St-Hilaire, Quebec	
<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (obs.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i> (calc.)	<i>I</i> (obs.)	<i>d</i>	<i>I</i>
110	10.35	10.35	100	110	10.48	10.50	330	ss	10.5	100
200	6.357	6.36	19	200	6.45	6.44	17	ms	6.39	5
130	5.384	5.382	15	130	5.44	5.42	12	m	5.27	7
040	4.457	4.459	21	220	5.24	—	1	—	4.41	18
12 $\bar{1}$	4.364	4.364	4	040	4.50	4.49	66	s	4.13	13
121	4.132	4.137	17	310	4.18	4.18	13	w	3.793	5
				240	3.69	3.69	18	m	3.680	15
				330	3.49	3.50	12	w	3.302	90
				150	3.47		2		2.978	5
				400	3.23	3.23	120	ss	2.779	5
				420	3.04	3.03	3	ww	2.621	30
				350	2.76	—	2	—	2.526	15
240	3.650	3.649	9	440	2.62	2.61	43	s	2.510	20
150	3.433 s	3.441	3	510	2.56	2.55	8	w	2.360	8
		Q		530	2.38	2.38	5	w	2.273	5
231	3.229	3.228	14	080	2.25	—	1	—	2.173	8
32 $\bar{1}$	3.228			600	2.15	2.15	15	m	2.122	12
				550	2.10	—	1	—	1.937	5
				480	1.845	—	1	—	1.792	5
400	3.179	3.179	17	390	1.815	1.82	3	ww	1.713	8
				660	1.75	—	1	—	1.674	7
				800	1.615	1.62	3	ww	1.610	10
				680	1.555	1.56	17	w	1.564	15
				0,12,0	1.50	1.50	40	m	1.511	10
									1.480	13
									1.425	3
251	2.615	2.609	6						1.380	6
10 $\bar{2}$	2.606								1.315	10
440	2.588	2.585	9							
061	2.582									
012	2.580									
16 $\bar{1}$	2.555	2.555	9							
161	2.506	2.506	12							
102	2.505									
20 $\bar{2}$	2.502									

B. Attapulgis, Georgia $a \sin \beta = 12.9$, $b = 18.0$, $c = 5.2$ Å, $\beta = ?$.

Space group = $C2/m$.

* Note interchange of a and c relative to text.

The other two specimens in the Christ *et al.* study showed splitting of several "orthorhombic" X-ray reflections and thus must have lower symmetry. Both were reported to have primitive monoclinic cells and an n -glide plane parallel to (100). One specimen from Glasgow, Virginia, U.S.A. has the Z-axis as the unique monoclinic axis and γ as the unique monoclinic angle ($\gamma = 92.23^\circ$). No structural interpretation of this unusual geometry has been put forth. The other specimen from Metaline, Washington, U.S.A. has more conventional monoclinic geometry

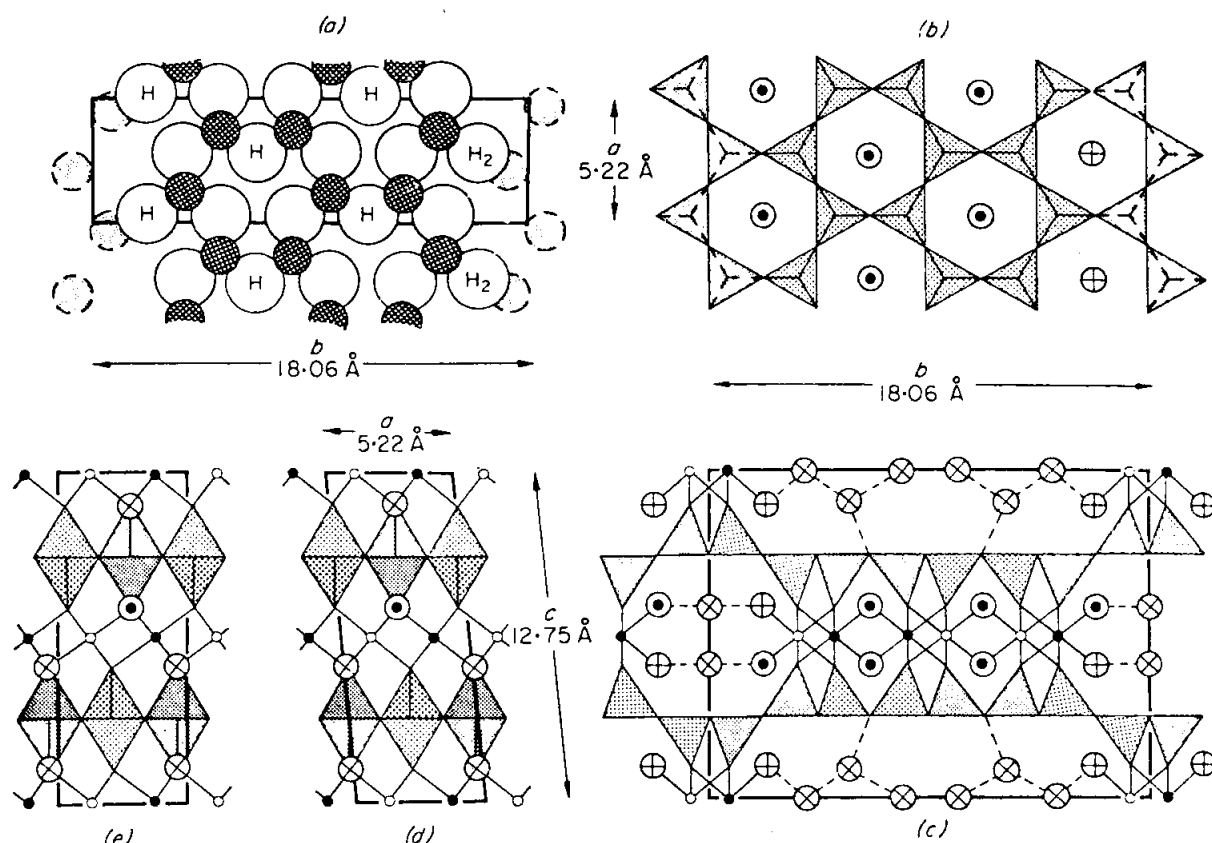


FIG. 1.38. Model of *P2/a* palygorskite structure proposed by Gard and Follett (1968) with alternation of 2:1 ribbons containing three and one pyroxene-like chains. (a) Projection on (001) of lower part of octahedral sheet with cations in set I positions. (b) Tetrahedral sheet below (a). (c) [100] projection of structure. (d) [010] projection of structure. (e) [010] projection of hypothetical *Pmam* orthorhombic palygorskite structure with octahedral cations alternating between set I and II positions in adjacent 2:1 ribbons. In (b)–(e); •, ○, cations at $x = 1/4, 3/4$, respectively; ○, OH[−]; ⊕, “bound” water; ⊗, zeolitic water in the sites proposed by Brauner & Preisinger (1956) for sepiolite.

with Y as the unique axis and β as the unique angle. The measured β value of 95.77° could be interpreted in two ways. It is within 0.5° of agreeing with the geometry of the $\beta = 107^\circ$ model if an alternative Z -axis is chosen that slopes in a direction opposite to the direction of intralayer shift in the 2:1 ribbons. Secondly, the geometry is nearly identical to that of another monoclinic unit cell determined by Zvyagin, Mishchenko, and Shitov (1963) by texture electron diffraction patterns of palygorskite ($\beta = 95.83^\circ$; space group = *P2/a*). The diffraction symmetry of *Pn* determined by Christ *et al.*, however, does not agree with either of these two interpretations so that further investigation of these two samples by electron diffraction or X-ray fiber patterns is desirable.

Gard and Follett (1968) have proposed a structural model in accord with the *P2/a* symmetry found by Zvyagin *et al.* They point out that the *P* cell requires that adjacent ribbons differ in width and that the *a*-glide requires an equal number of octahedral cations in each row parallel to Y . Their proposed model (Fig. 1.38a–d) has an alternation of 2:1 ribbons containing three zig-zag tetrahedral single chains with those containing just one chain. This model approximates more closely a normal 2:1 layer in that only 1/4 of the tetrahedra are inverted. The octahedral cations occupy the same set of positions in each 2:1 ribbon, and only four out of five positions are filled. A hypothetical orthorhombic version of symmetry *Pmam* is also possible by alternating occupation of I and II octahedral cation sets and, thus, of the − and + directions of intralayer shift (Fig. 1.38e). If either of these models can be verified by more detailed structural work, the

intergrowths of different ribbon widths proposed by Martin-Vivaldi and Linares-Gonzalez (1962) to explain observed intermediate X-ray spacings become more feasible.

Palygorskite is considerably more aluminous than sepiolite, and is closer to a true dioctahedral composition. The Mg:Al ratio varies approximately from 3:1 to 1:3 in different specimens. Sodian, ferrian, and manganoan varieties also have been reported. The Mn analogue has been named *yofortierite* (Perrault *et al.*, 1975). Caillère and Hénin (1961*b*) have pointed out that the palygorskite model with ribbon widths of two single chains (both monoclinic and orthorhombic versions) predicts less structural OH and more bound water OH₂ than seems to be present according to interpretation of thermogravimetric curves. The ideal formula of the Gard and Follett model is $\text{MgAl}_3\text{Si}_8\text{O}_{20}(\text{OH})_3(\text{OH}_2)_3 \cdot (\text{H}_2\text{O})_{4-5}$. The deviation of these ideal OH and OH₂ contents from the observed is in the same direction as for the 2-chain ribbon models but of smaller magnitude. The authors suggest hydroxylation of certain tetrahedral oxygens to explain the high OH content.

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Chapter 2

Order–Disorder in Clay Mineral Structures

G. W. BRINDLEY

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1. INTRODUCTION

CHAPTER 1 has reviewed the regular or ordered structures of layer silicates determined mainly by single crystal, X-ray diffraction methods. The present chapter and the two following chapters are concerned with irregular and disordered structures mainly in the 0.1–10 μm particle size range. X-ray powder diffraction methods are commonly used in studying these clay-grade materials, but single crystal, electron diffraction analysis furnishes additional important information (see Gard, 1971; Zvyagin, 1967).

Structural disorder is so prevalent in clay minerals that its recognition and evaluation are important aspects of the identification process. Some acquaintance with the fundamental concepts of diffraction by disordered systems is very helpful in understanding the phenomena involved. A full treatment would go far beyond what can be given in the present monograph, but from the simple treatment presented it is hoped that the main features of powder patterns from disordered layer structures will be more clearly recognized and interpreted than would be possible from a purely descriptive treatment.

The theoretical discussion is presented in Sections 3, 4, 5 and 6 and its application is given in Sections 7 and 8. Inevitably there will be some overlap between the theoretical sections and their application to different mineral groups.

It may be remarked that macro-crystalline minerals are not devoid of structural disorders, but in single crystal methods of structure analysis the investigator can usually select “good” crystals with a minimum of disorder. In studying clay minerals it is usually necessary to study them as formed in Nature and without the option of selecting “good” materials.

2. TYPES OF DISORDER IN CLAY MINERALS

Structural disorders in layer silicates, particularly in clay minerals, are of many kinds.

2.1 Thermal disorder

Disorder due to thermal motion of atoms is present in all materials and generally is not isotropic. It reduces the intensities of X-ray reflections and the reduction increases with the angle of diffraction and with the temperature. The thermal movements of the atoms in a crystal are

coupled and can be considered as thermo-elastic waves within a structure. Normally their effects outside the range of Bragg reflections are negligible but highly exposed diffraction patterns of single crystals reveal scattering effects between the Bragg reflections.

2.2 Disorder in the distribution of cations

Disorder of this type is common in silicate minerals and is mentioned frequently in Chapter 1. When Al replaces Si in tetrahedral sites, and Mg, Fe(II), Al, Fe(III), and other ions occupy octahedral sites, ordered or disordered arrangements may occur. Usually order-disorder of this kind is studied by meticulous single crystal, diffraction analysis and therefore falls outside the domain of clay mineralogy except in so far as electron diffraction by single crystals of clay size can be used. Other methods, such as infrared analysis, may be applicable. The results of single crystal, X-ray analysis (as discussed in Chapter 1) are applicable in so far as we can assume that macro-crystalline and micro-crystalline minerals are structurally similar.

2.3 Long-range and short-range order

Short-range order is compatible with long-range disorder. Silica glass is an extreme example; every Si atom is surrounded by a tetrahedral group of four O atoms, but little or no order occurs over a long range. Cation replacements in crystals may possibly be ordered within small domains, but may change from one domain to another so that over a crystal composed of many domains there is apparent disorder. A crystal as small as $1\text{ }\mu\text{m}$ is also as large as $10^4\text{ }\text{\AA}$, and therefore could contain many domains of $10^2\text{--}10^3\text{ }\text{\AA}$ size; if the size of a unit cell is of the order of $10\text{ }\text{\AA}$ many unit cells will occur within a domain. Therefore even in clay mineral crystals short-range order, long-range disorder may occur. An important example is the case of muscovite where tetrahedral cations per formula unit are near (Si_3Al) . As discussed in Chapter 1, Section 4.5.4, refined structure analyses indicate a random distribution of these cations. From observations of diffuse scattering by single crystals outside normal Bragg reflections Gatineau (1964) concluded that the Al ions tend to lie in linear bands parallel to a and $\pm 120^\circ$ to a in small domains, with different directions in different domains so that the resultant long-range effect is equivalent to a random distribution. Experiments of this kind require single crystals and in the case of clay minerals are possible only by electron diffraction.

2.4 Disorder in layer stacking

This type of disorder is frequent, indeed almost universal, in clay mineral structures and is a major topic of the present chapter.

2.5 Order-disorder in mixed-layer systems

Mixed-layer systems arise in two ways. A major characteristic of many clay mineral structures is their ability to swell by incorporating inorganic and organic material between the layers. Water is the most important of these materials. Generally the swelling (and conversely the shrinking) does not take place equally between all layers at the same time. Consequently situations arise involving mixed spacings and the resulting diffraction phenomena are those of disordered systems. Chapter 3 treats the nature of these systems and their application in clay mineral identification.

Mixed-layer systems arise in a second way. The geometrical similarity of the layer silicate structures, particularly as regards the quasi-hexagonal arrangement of the silicon-oxygen sheets, facilitates the formation of structures containing different kinds of layers. Both ordered and, more generally, disordered sequences of layers of many different kinds are found. Chapter 4

discusses X-ray diffraction by these mixed-layer sequences, particularly in relation to the statistics of order-disorder.

2.6 Finite crystal size as a lattice disorder

From a mathematical standpoint, the finite boundary of a crystal can be regarded as a type of disorder. A crystal lattice is defined as a homogeneous distribution of points, and to be homogeneous the point distribution must be infinite. From a physical standpoint, the distribution of atoms in and near the surface of a crystal will differ from that within the body of a crystal.

When the crystal size is less than about 10^{-6} cm, i.e., 100 Å, the X-ray diffractions are broadened and also may be measurably displaced. Both effects are important in relation to X-ray diffraction by clay minerals.

2.7 Structures with non-planar layers

Layer silicates with markedly polar layer structures, notably chrysotile (Chapter 1, Section 2.4) and halloysite (this chapter, Sections 6 and 7) have layers which curl into rolled and spiral forms. X-ray powder diffraction patterns of these minerals are somewhat similar to those of minerals with disorderly stacked layers. In so far as successive curved layers do not mesh together in the normal crystalline manner, these structures may be regarded as being disordered.

2.8 Mechanically disordered structures

Not all clay minerals occur as finely divided powders. Often they occur in hard, massive form due to some form of cementation. Many shales are of this kind. For X-ray examination the material must be reduced to a fine powder and pestle and mortar grinding is the process most often employed. Prolonged grinding of layer silicates produces marked structural disorder often leading to complete destruction of the diffraction pattern. This mechanically produced disorder is probably different from disorders formed under natural conditions. Mechanical strain in crystals causes broadened X-ray reflections. In the case of very small crystals, strain broadening and small crystal broadening can both contribute to the observed broadening of the X-ray diffractions; in some cases it will be necessary to distinguish the two effects.

2.9 Some general considerations

It is evident that many kinds of structural disorder can occur in clay minerals, and their recognition is an integral part of the process of identification and characterization of clay minerals. Sections 3, 4, 5 and 6 discuss at an elementary level the diffraction of X-rays by systems of small and disordered particles with a view to indicating the nature of the effects which may be observed in powder diffraction diagrams. For further reading the small monograph by Wilson (1949) is recommended; although the mathematical treatment is mainly simple, nevertheless many of the questions raised in this chapter are covered in more detail than is possible here. Among more advanced texts, that of James (1948) may be specially mentioned. A short mathematical discussion of the effect of structural disorders in layered systems on X-ray and electron diffraction processes was given by Gatineau and Tchoubar (1973).

3. DIFFRACTION OF X-RAYS BY SMALL CRYSTALS

3.1 Diffraction by ordered and disordered systems

The theory of X-ray diffraction by crystals treats a crystal as a regular three-dimensional array of identical unit cells, all scattering X-rays with the same amplitude in any particular direction. Fundamentally, X-rays are diffracted (scattered) by the electrons forming the atoms

which compose the unit cells and it is necessary to take account of the distribution of the electrons within the atoms, the thermal vibration of the atoms which effectively blurs this distribution, and the distribution of the atoms within the unit cell. Finally we arrive at a resultant scattered amplitude F for the unit cell expressed in terms of the amplitude scattered by a single electron.

To obtain the resultant scattered amplitude and hence the resultant intensity scattered (reflected) by a crystal, it is necessary to take account of the phase differences $\phi_1, \phi_2, \dots$ between the variously scattered waves and the wave scattered from the origin of the coordinate system. The standard procedure for adding waves of the same wavelength but different phases is as follows; see, for example, Wilson (1949, Ch. VII):

$$A e^{i\psi} = F e^{i\phi_1} + F e^{i\phi_2} + \dots \quad (1)$$

A and ψ are the resultant amplitude and phase. The resultant intensity is obtained by multiplying the complex amplitude by its conjugate complex.

$$\begin{aligned} I &= A e^{i\psi} \cdot A e^{-i\psi} = A^2 \\ &= (\sum F e^{i\phi_p}) (\sum F e^{-i\phi_q}) \\ &= F^2 \sum_p \sum_q e^{i(\phi_p - \phi_q)} \end{aligned} \quad (2)$$

Here p and q denote representative terms for the two series. If N scattering unit cells are involved, i.e., N terms in each series, and the system is irregular, then there will be N terms corresponding to $p = q$, i.e. $\phi_p = \phi_q$, and other terms will be random and tend to cancel out. In the limiting case,

$$I = NF^2 \quad (3)$$

In other words, the total intensity is $N \times$ (scattered intensity F^2 for each unit cell).

When the unit cells are arranged in a regular space lattice, we can find directions of incidence and scattering such that $\phi_p - \phi_q = 2n\pi$ where n is an integer. Since $\exp i(\phi_p - \phi_q) = \cos(\phi_p - \phi_q) + i \sin(\phi_p - \phi_q)$, there will be N^2 terms for which $\cos(\phi_p - \phi_q) = 1$ and $\sin(\phi_p - \phi_q) = 0$. Then

$$I = N^2 F^2 \quad (4)$$

The condition that $\phi_p - \phi_q = 2n\pi$ is equivalent to the Bragg reflection law. The intensity now is the total amplitude squared.

To obtain useful expressions for the scattered intensity, additional factors are involved to take into account the state of polarization of the radiation and the particular experimental arrangement, the so-called combined Lorentz-polarization factor often denoted by L_p (see also Section 3.5). In some circumstances, absorption of the radiation in the sample studied also must be considered but this aspect of X-ray scattering (diffraction) can be deferred until quantitative analysis is discussed in Chapter 7.

3.2 The one-dimensional "crystal"

It is convenient first to consider diffraction by a one-dimensional system of N equally spaced scattering units (unit cells). The results are directly relevant to the basal reflections from clay minerals with regularly spaced layers all of the same kind. Now let ϕ be the phase difference between waves scattered from successive unit cells. The total scattered amplitude is given by

$$A = F + F e^{i\phi} + F e^{i2\phi} + \dots + F e^{i(N-1)\phi}$$

The series is a geometrical series with N terms and the summation gives

$$A = F (1 - e^{iN\phi}) / (1 - e^{i\phi})$$

The resultant intensity is obtained by multiplying A by its conjugate complex (i.e., writing $-i$ in place of $+i$). The final result becomes:

$$I = F^2 \sin^2 (N\phi/2) / \sin^2 (\phi/2) \quad (5)$$

When ϕ is near an integral multiple of 2π , i.e., when the direction of scattering is near a Bragg reflection, one can write $\phi = 2\pi(n + u)$ and equation (5) becomes

$$I = F^2 \sin^2 (N\pi u) / \sin^2 (\pi u) \quad (6)$$

or, when u is small so that $\sin \pi u \simeq \pi u$

$$I = N^2 F^2 \left[\frac{\sin N\pi u}{N\pi u} \right]^2 \quad (7)$$

When u is very small and tends to zero, the expression in [] tends to unity and again $I = N^2 F^2$. The expression in [] gives the distribution of the diffracted intensity in the angular range near the diffracted maximum. The intensity falls to zero when $\sin N\pi u = 0$, i.e., when $u = 1/N$. The spread of the radiation varies inversely as the number of scattering units. A simple calculation, given in Section 3.4, shows how N is related to the breadth of the diffraction peak.

3.3 Two- and three-dimensional crystals

A formal extension of the preceding analysis to scattering systems in two, and three dimensions, leads to:

$$I = N_1^2 N_2^2 F^2 \left[\frac{\sin (N_1 \pi u)}{(N_1 \pi u)} \cdot \frac{\sin (N_2 \pi v)}{(N_2 \pi v)} \right]^2 \quad (8)$$

and

$$I = N_1^2 N_2^2 N_3^2 F^2 \left[\frac{\sin (N_1 \pi u)}{(N_1 \pi u)} \cdot \frac{\sin (N_2 \pi v)}{(N_2 \pi v)} \cdot \frac{\sin (N_3 \pi w)}{(N_3 \pi w)} \right]^2 \quad (9)$$

where N_1 , N_2 , and N_3 are the numbers of scattering units, i.e., unit cells, along the coordinate axes, and u , v , w express deviations from integral values of 2π analogous to the one-dimensional case.

Equations (7), (8), and (9) can be summarized in the form

$$I = N^2 F^2 S^2 \quad (10)$$

where N is the total number of scattering units in the one-, two-, or three-dimensional system and F is the amplitude scattered by the unit; S is the factor involving the size and shape of the assemblage of units, i.e., the crystal, and is sometimes called the "shape" factor.

3.4 Determination of crystal size and number of diffracting layers from X-ray line broadening

When a crystal is larger than a few hundred unit cells in each direction, appreciable diffraction occurs only in the immediate vicinity of the directions given by the Bragg equation, $n\lambda = 2d \sin \theta$. When crystals are of the order of 10 unit cells in one direction, the scattering becomes appreciable over an extended range of the angle θ . It was shown in Section 3.2 that the diffracted

intensity falls to zero when $u = 1/N$. The quantity u is easily converted to an angle $\Delta\theta$ as follows: For the n th order reflection, $(2d/\lambda) \sin \theta_n = n$ and for an adjacent direction $(2d/\lambda) \sin (\theta_n + \Delta\theta) = n + u$. Then

$$\begin{aligned} 1/N = u &= (2d/\lambda) [\sin (\theta + \Delta\theta) - \sin \theta] \\ &= (2d/\lambda) \cos \theta \cdot \Delta\theta \end{aligned}$$

The angular breadth, measured with respect to θ , between the directions where the intensity falls to zero is $2\Delta\theta = \lambda/Nd \cos \theta$. Since d is the spacing of the lattice planes and N is the number of planes, the crystal thickness (or size) $L = Nd$. The angular breadth, however, is always measured with respect to 2θ rather than θ . It is also measured at half the maximum (or peak) intensity. When these considerations are taken into account, the net result is that the breadth B , measured in radians on the 2θ scale, is given by

$$B = \Delta(2\theta) = \lambda/L \cos \theta \quad (11)$$

A more detailed analysis involving the shape of the line profile as expressed by equation (6) gives the well-known Scherrer equation:

$$B = K\lambda/L \cos \theta \quad (11')$$

where K is a constant near unity. For most purposes it suffices to take the constant K as unity; a more accurate value of K is 0.91.

Equation (11) or (11') is directly applicable provided no other factors affect the measured breadth of the diffraction peak. However, the angular breadth is always affected by the design of the X-ray powder camera or diffractometer. A correction for instrumental effects is obtained approximately by the following relation:

$$B(\text{obs.})^2 = B^2 + b^2 \quad (12)$$

where $B(\text{obs.})$ is the experimentally measured breadth, b the breadth arising from instrumental effects, and B the corrected breadth to be used in equation (11). The value of b is estimated by using a material such as a quartz powder; the precise particle size is unimportant provided it is considerably greater than $1 \mu\text{m}$. A coarsely crystalline mica or chlorite with a similar particle size also would be very suitable.

Usually the Scherrer equation will be used when $B(\text{obs.})$ is considerably greater than b at the same value of θ . For example, if $B(\text{obs.})/b = 5$, the correction to $B(\text{obs.})$ to obtain B is only 2%, which for most purposes is a negligible correction. If, however, $B(\text{obs.})/b = 2$, the correction is about 14%, and as $B(\text{obs.})/b$ diminishes below this value the correction rises rapidly and soon becomes unreliable.

In order to apply equation (11) to determine the number of layers in a clay mineral crystal, it is important to know if the peaks are broadened by still other causes. As will be shown in Chapter 4, random interstratification of layers of different kinds produces very broad reflections and values of L determined for such systems are totally meaningless. Therefore checks for possible interstratification are essential (see Chapter 4). To determine the number of layers in a crystal, the breadth of the basal 001 reflections will be measured. Many basal reflections may be obtained by using a well-oriented sample, as discussed in Chapter 5. Then, after making the appropriate corrections for instrumental broadening, values of L can be found from the whole sequence of basal reflections. If the same value of L is obtained from all the observed peaks, the result will probably be reliable and the number of layers in the crystals will be given by $L/d(001)$. Generally

it would not be very reliable to base the value of L on a single diffraction peak without some consideration of other possible causes of broadening.

3.5 Effect of line broadening on spacing measurements

In determining the lattice spacings of clay minerals, it is usual to measure the Bragg angle θ from the center of a diffraction peak. The intensity distribution in the neighborhood of a diffraction peak is given by equation (10), with the addition of the appropriate Lorentz-polarization factor, so that the equation becomes:

$$I = \text{const.} (L_p) F^2 \cdot S^2 \quad (13)$$

The constant factor includes all the basic electronic terms which arise from the fundamental X-ray scattering process. In equation (13), S^2 is the principal factor which determines the breadth of the diffraction peak. In applying this equation, particularly to broad, lower order basal reflections from clay minerals, the angular variation of the L_p factor and of F^2 must not be overlooked. The scattering factor F varies considerably from one Bragg reflection to another, but for any one reflection is generally taken to be constant. When broad reflections are involved, the angular variation of F may be important and is especially important for 00/ reflections at small 2θ angles (e.g. $2\theta < 15^\circ$ with Cu $K\alpha$ radiation). In Chapter 4, which treats interstratified structures, F is replaced by G to emphasize this variation of scattered amplitude with angle of scattering.

The L_p term in equation (13) for unpolarized radiation and a random powder sample has the form:

$$L_p = (1 + \cos^2 2\theta) / (\sin^2 \theta \cos \theta)$$

This factor tends to infinity as θ tends to zero, and rises rapidly towards small values of θ in the region of the first order diffraction maxima of clay materials. Consequently the low-angle side of the 00/ diffraction peak is greatly increased compared with the high-angle side, and broad peaks are measurably displaced.

Therefore while the *form* of the diffraction maximum given by equation (13) is determined in the first place by the function S^2 , the *position* of the peak can be modified appreciably by the angular variations of the L_p and F^2 functions. The apparent value of $d(001)$ from ultra-thin clay crystals can be seriously in error if taken directly from the apparent Bragg angle without correction for the variation of these factors.

Errors in basal spacing measurements of micaceous minerals have been discussed by Reynolds (1968) for illite, by Ross (1968) for micas, montmorillonites, and other minerals, by Tettenhorst and Roberson (1973) for glycol-montmorillonite, and by Trunz (1976) for kaolinite. Fig. 2.1 reproduces representative data.

4. DIFFRACTION OF X-RAYS FROM THE STANDPOINT OF THE RECIPROCAL LATTICE

The reciprocal lattice concept may seem an unnecessary complication but in fact it provides the simplest approach to the diffraction phenomena produced by clay minerals.

4.1 The reciprocal lattice

A reciprocal lattice, with axes x^* , y^* , z^* , is related to the crystal lattice, with axes x , y , z , by taking x^* perpendicular to the crystal plane (100), y^* perpendicular to (010), and z^* perpendicular to (001). The crystal lattice is developed by repetition of a unit cell with sides of

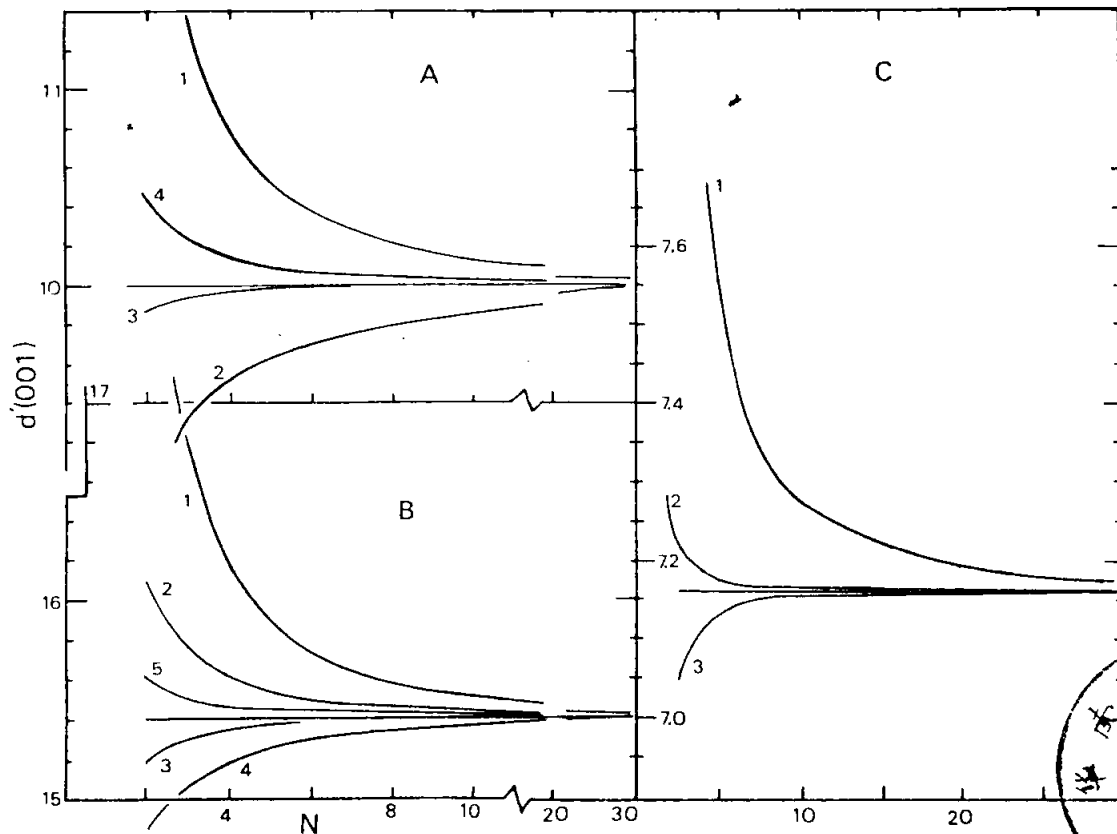


FIG. 2.1. Apparent basal spacing, $d'(001)$, in Å determined from 00l diffractions, $l = 1-5$, for crystals with N layers. A. biotite; B. montmorillonite; C. kaolinite. Data of Ross (1966 and pers. comm.) and of Trunz (1976).

length a, b, c , parallel to x, y, z . The reciprocal lattice is developed similarly from a unit with sides a^*, b^*, c^* along x^*, y^*, z^* , with magnitudes

$$a^* = 1/d(100), \quad b^* = 1/d(010), \quad c^* = 1/d(001), \quad (14)$$

where d is the spacing of the lattice planes in the crystal lattice. Fig. 2.2 illustrates the relationship between the crystal lattice and the reciprocal lattice of a monoclinic crystal oriented with b and b^* normal to the plane of the diagram. The angle β^* is supplementary to β .

A point in the reciprocal lattice has coordinates (ha^*, kb^*, lc^*) and is called the point hkl . It

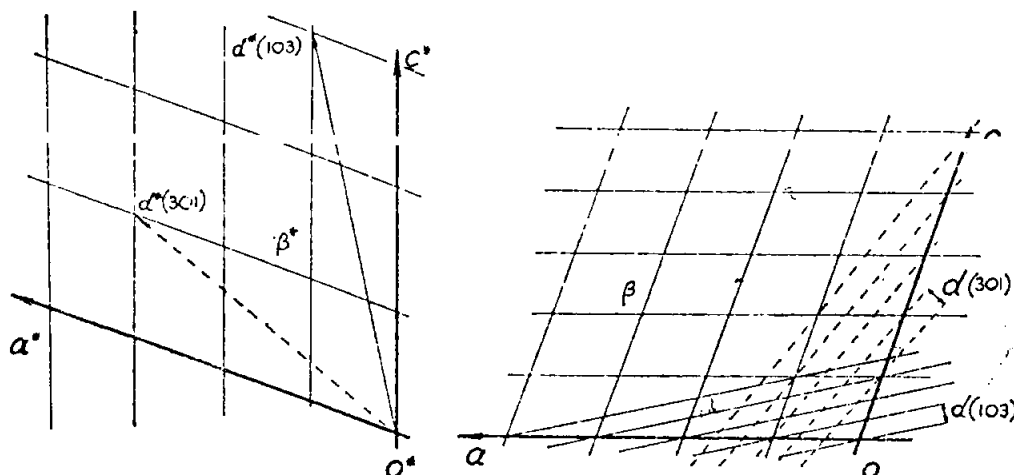


FIG. 2.2. Relation of reciprocal lattice (left) to crystal lattice (right).

can be shown that a line from O^* , origin of the reciprocal lattice, to the point hkl is perpendicular to the lattice planes (hkl) and that the distance from O^* to point hkl is given by

$$d^* = 1/d(hkl) \quad (15)$$

Equation (15) is a general statement covering the particular cases given in equations (14). Formal proof of this result will not be given here, but Fig. 2.2 illustrates the result by showing the lattice planes (103) and (301), and the corresponding reciprocal lattice vectors drawn from O^* to the points 103 and 301. In each case, d^* is seen to be perpendicular to the corresponding planes.

4.2 Bragg reflection and the reciprocal lattice

A geometrical condition in reciprocal space corresponding to Bragg reflection in crystal space is developed as follows: in Fig. 2.3, a vector O^*C is drawn opposite in direction to that of the incident radiation and of length $O^*C = 1/\lambda$. A sphere of radius $1/\lambda$ is drawn with C as center. If the sphere passes through a reciprocal lattice point $P(hkl)$, the crystal will be set correctly to reflect radiation from the lattice planes (hkl), the vector CP will be the direction of the reflected radiation, and O^*P will be perpendicular to the reflecting planes. For a reflection hkl to occur, the crystal must be rotated to satisfy the Bragg relation, and the reciprocal lattice will rotate similarly about O^* to bring the reciprocal lattice point (hkl) onto the sphere of radius $1/\lambda$.

The proof of these statements is as follows: If CO^* and CP are the forward directions of the incident and reflected radiations, then the angle O^*CP is 2θ . When this angle 2θ is bisected as shown in Fig. 2.3, then

$$O^*P = 2 \cdot O^*C \cdot \sin \theta$$

or

$$d^* = 2(1/\lambda) \sin \theta$$

and

$$1/d = 2(1/\lambda) \sin \theta$$

i.e.

$$\lambda = 2d \sin \theta$$

which is the Bragg equation for a first order reflection. If the line O^*P intersects a reciprocal lattice point before reaching P , so that $O^*P = nd^*$, (where n is necessarily integral), then

$$n\lambda = 2d \sin \theta.$$

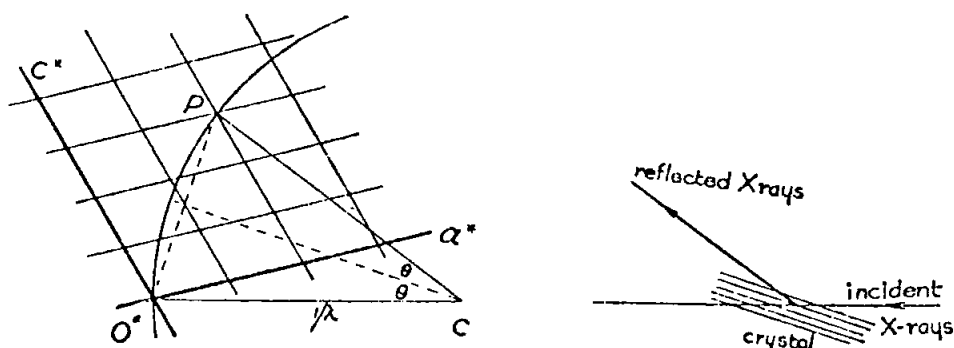


FIG. 2.3. The condition in reciprocal space (left) for Bragg reflection of X-rays (right).

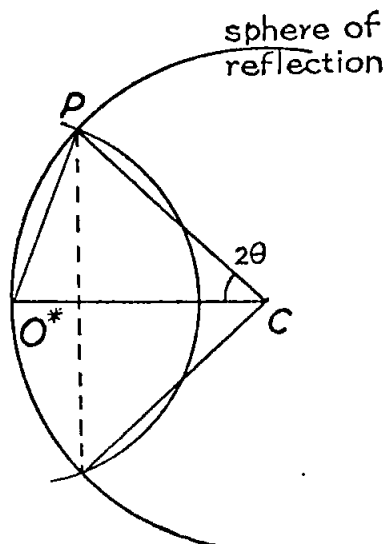


FIG. 2.4. Formation of a cone of diffraction from a random powder sample.

Thus the geometrical relation involving the sphere of radius $1/\lambda$ passing through the reciprocal point $P(hkl)$ is the necessary condition for Bragg reflection from planes (hkl) . The sphere of radius $1/\lambda$ is called the “sphere of reflection”, or the Ewald sphere after Ewald (1921, 1923) who first recognized the importance of the construction. The various ways of recording X-ray diffraction data are different ways by which reciprocal lattice points are brought into coincidence with the sphere of reflection.

In the X-ray powder diffraction method, the crystals are randomly oriented and the reciprocal lattice points trace out concentric spheres each of radius O^*P , or d^* , which intersect the sphere of reflection, centered at C , in a series of circles. The reflected radiation, in direction CP , lies on a conical surface with semi-vertical angle 2θ , as illustrated in Fig. 2.4. It is often convenient to regard the point C as signifying both the center of the sphere of reflection in reciprocal space, and the diffracting crystal or powder in real space.

4.3 Representation of reflected X-ray amplitude or intensity in reciprocal space

The amplitude or intensity of an X-ray reflection can be included in the reciprocal lattice by “weighting” the reciprocal lattice points with F , or F^2 . The finite spread of the diffracted radiation is incorporated by a diffusion of the points around the mathematical positions (ha^*, kb^*, lc^*) , in accordance with the shape function, S ; (see equations 9 and 10). Since S is a function of u, v, w , the diffusion of the reciprocal lattice points is the same for all points (hkl) . Unless the crystals are exceedingly small and the diffusion of the reciprocal lattice points correspondingly great, the structure factor F can be treated as constant within a small domain surrounding the point (hkl) in reciprocal space, but in the case of very small or very thin crystals, the variation of F becomes of major importance.

4.4 Reciprocal lattice for two-dimensional crystals

Certain clay minerals, notably those of the smectite group, exhibit highly disordered stacking arrangements resembling a pile of playing cards lying flat on each other but with little or no alignment of the edges. Such an arrangement is called turbostratic. In the extreme case, which will be considered here, each layer scatters X-rays as a two-dimensional crystal and only the basal $00l$ reflections are exceptions. The reciprocal lattice consists of points, ha^*, kb^* , or simply hk , that are diffused within the x^*y^* plane in accordance with the dimensions (shape) of the two-

dimensional layer crystal as indicated in equation (8). In the third dimension, normal to the layer plane, the diffracted intensity varies along z^* for a given hk pair only through the variation of F . The reciprocal lattice consists of diffuse lines or "rods" with the intensity varying as F^2 in the z^* direction. The only exception is along the z^* axis itself where the $00l$ reciprocal lattice points occur and they are diffused along z^* in accordance with the number of layers stacked on each other in a particle; this is the one-dimensional case considered previously.

4.5 X-ray diffraction by two-dimensional crystals

To determine the diffracted intensity for a system of randomly oriented, two-dimensional crystals, the reciprocal lattice is visualized as consisting of hk reciprocal lattice rods extending continuously in the z^* direction, and with a diffusion in the x^* and y^* directions determined by the size of the two-dimensional crystals. For a system with randomly oriented crystals, the reciprocal lattice must be rotated randomly around O^* . The result is difficult to visualize and it is much easier to proceed as follows: in Fig. 2.5, a point such as P on the sphere of reflection corresponds to a reciprocal spacing $1/d$ or to $2 \sin \theta/\lambda$. If point P is rotated around O^* to trace out a spherical surface of radius $2 \sin \theta/\lambda$, the total diffracted intensity in the direction θ (or scattering angle 2θ) is determined by the integrated intersection of this spherical surface with the hk rod.

This integration is difficult; not only the variation of F^2 in the z^* direction, but also the variation of $S^2 F^2$ normal to z^* must be taken into account. Equation (8) relates to a rectangular crystal, but for other shapes different forms of the function S arise. Wilson (1949, Ch. IV) has developed more general methods for treating these problems.

Certain general conclusions can be seen from Fig. 2.5. For each hk rod, $2 \sin \theta/\lambda$ has a minimum value such that the spherical surface developed by P barely touches the hk rod. At a slightly greater value of θ , the spherical surface intersects the $hk0$ point, and the integrated intensity increases rapidly. As θ increases still further, P moves further from O^* and smaller

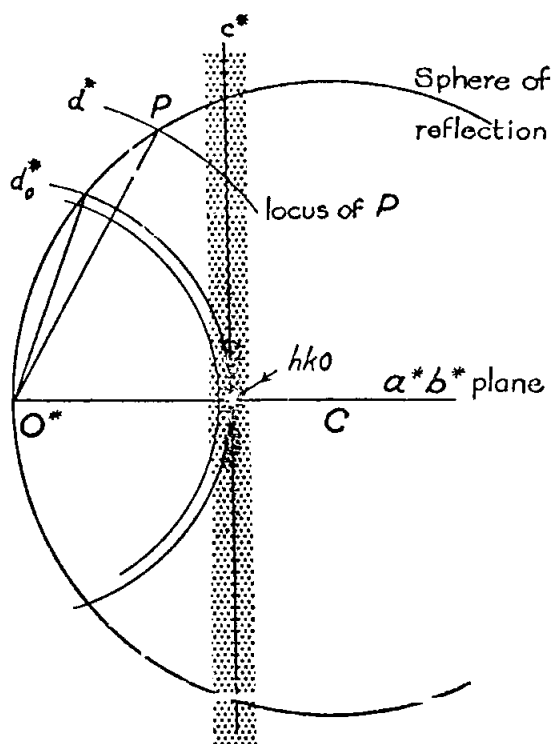


FIG. 2.5. Reciprocal lattice representation of diffraction by two-dimensional crystal layers.

intersections of the sphere with the rod occur. Therefore the diffracted intensity consists of a band of scattering with a sharp low-angle termination corresponding closely (but not exactly) with the $hk0$ diffraction position, and tailing out to higher angles of θ . Variations of intensity within the diffuse band are related to the variation of F^2 along the z^* direction.

Laue (1932) first considered these two-dimensional diffraction effects for large two-dimensional crystals for which the reciprocal lattice could be treated as lines rather than as rods parallel to z^* . Warren (1941), in work on graphite which has a simpler layer structure than the clay minerals, simplified the integration problem by replacing the interference function S by a Gaussian function of the form $\exp(-\pi\rho^2L^2)$ where ρ is the radial distance from the line through $hk0$, and by assuming F to be constant for each integration across a reciprocal lattice rod. This assumption is good for the larger θ values when the spherical integration surface cuts the reciprocal lattice rod over a short length, but is less satisfactory when the spherical surface comes close to the point $hk0$.

Warren's results merit a detailed description here. The intensity $I(2\theta)$ diffracted at an angle 2θ from a powder of randomly oriented, two dimensional crystals, is given by:

$$I(2\theta) = C \Psi(\theta) \sum F^2(hkl) \quad (16)$$

In equation (16), C is a constant, F is the structure factor for an index pair hk , and l is a continuously variable third index corresponding to the distance along the hk rod.

$$l = (2c/\lambda)(\sin^2\theta - \sin^2\theta_0)^{1/2} \quad (17)$$

where θ_0 corresponds to the point $hk0$. Here c is taken as the unit cell thickness, and $c^* = 1/c$ is the corresponding unit along the reciprocal lattice rod. Distance along the reciprocal lattice rod, lc^* or l/c , is given by $(d^{*2} - d_0^{*2})^{1/2}$ or $(2/\lambda)(\sin^2\theta - \sin^2\theta_0)^{1/2}$. Also in equation (16)

$$\Psi(\theta) = 2 \left(\frac{L}{\sqrt{\pi} \cdot \lambda} \right)^{1/2} \left(\frac{1 + \cos^2 2\theta}{(\sin \theta)^{3/2}} \right) f(x)$$

$f(x)$ = an integral evaluated by Warren, see Table 2.1

$$x = 2\sqrt{\pi} \cdot L (\sin \theta - \sin \theta_0) / \lambda$$

L = crystal size measured in the same units as λ

The $\sum$ sign is necessary because the layer structures of clay minerals are pseudo-hexagonal and $b = \sqrt{3} \cdot a$. Consequently the diffraction from various hk pairs, such as 02, 11, $1\bar{1}$, overlap. These overlapping reflections do not have the same F values, unless the layer symmetry is truly hexagonal. The various overlapping reflections are calculated as follows: With orthogonal axes and with $b = \sqrt{3} \cdot a$, the lattice spacing d and reciprocal spacing d^* are given by

$$d^{*2} = \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{3h^2 + k^2}{b^2} + \frac{l^2}{c^2}$$

TABLE 2.1. Values of $f(x)$, after Warrên (1941)

x	-1.2	-1.0	-0.8	-0.6	-0.5	-0.4	-0.3	-0.2	-0.1	0
$f(x)$	0.12	0.21	0.32	0.46	0.53	0.61	0.69	0.77	0.84	0.91
x	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0	2.0	3.0
$f(x)$	0.96	1.01	1.04	1.06	1.07	1.06	1.04	0.99	0.67	0.52

TABLE 2.2. hk index pairs giving the same $d(hk0)$ spacings for an ortho-hexagonal system, i.e. with $b = \sqrt{3} \cdot a$

$3h^2 + k^2$	hk index pairs
4	02, 11, $\bar{1}\bar{1}$
10	20, 13, $\bar{1}\bar{3}$
16	04, 22, $\bar{2}\bar{2}$
28	24, 24, 31, $3\bar{1}$, 15, $\bar{1}\bar{5}$
36	06, 33, $\bar{3}\bar{3}$
48	40, 26, $\bar{2}\bar{6}$
52	42, $4\bar{2}$, 35, $3\bar{5}$, 17, $\bar{1}\bar{7}$
76	28, $2\bar{8}$, 37, $3\bar{7}$, 51, $\bar{5}\bar{1}$
84	46, $4\bar{6}$, 53, $5\bar{3}$, 19, $\bar{1}\bar{9}$
108	60, 39, $\bar{3}\bar{9}$
124	64, $6\bar{4}$, 57, $5\bar{7}$, 11, $\bar{1}\bar{1}$

For layer silicate structures, $(h + k)$ has only even values because the layer structure is centered on the C -face. Table 2.2 lists the various hk pairs for which $(3h^2 + k^2)$ has the same value, and which give superimposed diffraction bands in randomly oriented powder diffraction patterns.

For $x > 3$, Warren gave the following approximation:

$$\Psi(\theta) = \frac{1 + \cos^2 2\theta}{\sin \theta (\sin^2 \theta - \sin^2 \theta_0)^{1/2}} = \frac{2c}{l\lambda} \left(\frac{1 + \cos^2 2\theta}{\sin \theta} \right) \quad (18)$$

This approximation covers a considerable part of the diffraction band given by equation (16). As an illustration, consider the following data for montmorillonite: With $L \simeq 300 \text{ \AA}$, $\lambda = 1.54 \text{ \AA}$, then $x = 3$ corresponds to $(\sin \theta - \sin \theta_0) \simeq 0.005$, or $(\theta - \theta_0) \simeq 0.30^\circ$. This result is practically unchanged over the diffraction range up to $2\theta = 62^\circ$. For larger values of L , the interval $(\theta - \theta_0)$ is proportionally decreased. In other words, for each of the hk diffraction bands of smectites, up to and including the important 06 band, the approximate expression (18) can be used to calculate the band profiles for angles $2\theta > 2(\theta_0 + 0.30^\circ)$.

A more accurate calculation of two-dimensional band profiles near the low-angle termination was developed by Brindley and Mering (1951). When the spherical surface of integration intersects an appreciable length of an hk rod, they divided the surface of integration into a series of

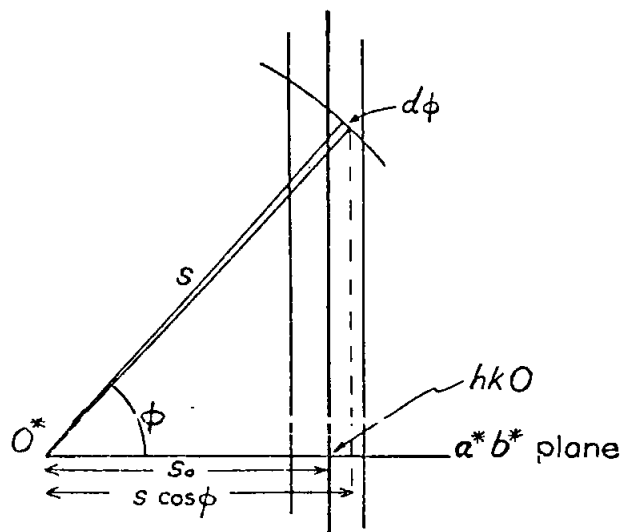


FIG. 2.6. To illustrate the numerical integration method of Brindley and Mering (1951).

strips parallel to the x^*y^* plane and at different heights (therefore different F values) from this plane. For details of this procedure, the original paper must be consulted. It is shown that

$$I(2\theta) = \frac{(1 + \cos^2 2\theta)\lambda}{16 \pi \sin \theta} \int F^2(hkl) T(X) d\phi \quad (19)$$

where $X = s \cos \phi - s_0 = 2(\sin \theta \cos \phi - \sin \theta_0)/\lambda$. The variables s , s_0 , and ϕ are illustrated in Fig. 2.6. The spherical integration surface is replaced by a cylinder divided into narrow strips subtending $d\phi$ at the reciprocal lattice origin. Values of the function $I(X)$ are tabulated for a range of values rX where r is the radius of a circular crystal or the radius of an equivalent circular area. Values of X are given for crystals of circular, hexagonal, and square shapes.

4.6 Effect of crystal size on diffraction by two-dimensional crystals

The smaller the crystal size, the greater is the lateral diffusion of the hk rods in reciprocal space, and the broader are the bands in the powder diffraction pattern. By assuming F to be constant, or to vary slowly with respect to l , for a given hk pair, Warren derived an approximate formula relating the angular width at half-maximum intensity, $B_{1/2}$, to the crystal size L ,

$$B_{1/2} = 1.84 (\lambda/L) \sec \theta \quad (20)$$

This equation is analogous to the Scherrer equation (11), with the constant $K = 1.84$ in place of a value near unity for three-dimensional crystals. The angle θ corresponds to $hk0$. A more accurate expression has been given by Warren and Bodenstein (1966), with 1.91 in place of 1.84 in equation (20).

A second method of estimating L is based on a displacement of the intensity maximum in a diffraction band from the position corresponding to the $hk0$ reflection. From Fig. 2.5, it is evident that the maximum intensity depends on the total intersection of the spherical integration surface with the reciprocal lattice rod, and occurs at a value of d^* (i.e. of $2 \sin \theta/\lambda$) slightly greater than $d^*(hk0)$. If $\sum F^2$ is constant or varies only slowly with l , then the displacement of the maximum intensity away from $d^*(hk0)$ can be related to the lateral diffusion of the hk rod, i.e., to crystal size L . If $\sum F^2$ varies rapidly with l (as happens for some hk rods), no simple relation can be derived. Warren gave an approximate formula for the apparent change of spacing Δd from $d(hk0)$ due to crystal size:

$$\Delta d = 0.32 d^2(hk0)/L \quad (21)$$

As an example of the use of equations (20) and (21), data obtained by Brindley and Robinson (1948) for the 7 Å form of halloysite may be quoted. Using the prominent 02, 11, $1\bar{1}$ diffraction band, for which $\sum F^2$ varies slowly, they found $L = 200$ Å from the half-width of the diffraction band using equation (20), and from the peak position, they found $\Delta d = 0.028$ Å and $L = 230$ Å, using equation (21). Since Δd is not accurate to better than ~10%, L likewise is known only to this order of accuracy. The two estimates of L are seen to be reasonably consistent in this favorable application† of equations (20) and (21).

5. DISORDER IN LAYER STACKING

For any particular type of layer structure and interlayer bonding mechanism, a great variety of theoretical polytype structures can be developed; see, for example, one- and two-layer

† In other respects, however, it has to be admitted that halloysite is not the best material to choose as an illustration of two-dimensional X-ray diffraction because electron microscopy shows most halloysites to be tubular, or rolled, or quasi-spherical, information which was not available when the original X-ray study was made.

kaolinite-type structures (Newnham, 1961; Dornberger-Schiff and Āurovič, 1975), one- to six-layer serpentine-type structures (Bailey, 1969), one- to six-layer and other more complex mica-type structures (Smith and Yoder, 1956; Ross *et al.*, 1966), one- and two-layer chlorite polytypes (Bailey and Brown, 1962; Lister and Bailey, 1967). See also the discussions in Chapter 1. Evidently many more theoretical structures can be developed than have so far been found in nature or prepared in the laboratory. These studies generally assume idealized forms of the layers with the SiO_4 tetrahedra arranged hexagonally and the octahedral sheets in a close-packed arrangement. The bonding mechanisms also are treated in a simple manner. It is evident from the relatively small number of actual structures compared with the large number calculated theoretically that the finer details of the layer structures and the bonding mechanisms must be quite important in determining the actual stacking arrangements of layers.

It is characteristic of clay minerals that they exhibit considerable variations in layer stacking order-disorder. Disorders commonly arise from the presence of variable amounts of intercalated material between the layers, such as variable hydration from layer to layer, and from the presence of layers of other kinds irregularly distributed, as in the many forms of interstratified structures. These aspects of order-disorder are treated in Chapters 3 and 4. In the present chapter, consideration is given to order-disorder in structures containing layers of a single kind and with a constant or nearly constant layer spacing.

The analysis of layer stacking order-disorder in clay minerals by X-ray powder diffraction methods is difficult. Two general approaches are possible. When a direct approach is used, corrections to the observed diffraction profiles for instrumental and small crystal size broadening of the diffraction peaks are necessary prior to a consideration of the nature of the disorders. An indirect approach consists of setting up models with different kinds and degrees of disorder and with appropriate values for sizes of crystal domains and calculating their diffraction patterns for comparison with observed data. Both methods have been used and both are highly mathematical. Considerable attention also must be given to the experimental aspects of the work.

5.1 Layer displacements of type $pb/3$

One type of disorder has been recognized which is amenable to simple treatment, namely random displacements of layers parallel to the y -axis by integral multiples of $b/3$ (Brindley and Robinson, 1946, 1947). In ideal models of 1:1 type layers, the OH ions in the external plane of the layer are arranged at intervals of $b/3$ so that displacement of a layer by $pb/3$, p being integral, brings the OH ions into the original positions and near-neighbor relations are unchanged. In real structures, these conditions are not exactly obeyed and the model represents a considerable oversimplification, but it has been useful in the development of ideas on the nature of the disorder commonly found in 1:1 type structures. Therefore a short account is worthwhile. Later work shows that considerable modifications are required and in fact the concept of displacement of entire layers may be a misrepresentation of the situation.

It is necessary to consider values of $p = 0$ and ± 1 only because other values involve movements of whole unit cell lengths; the case $p = 2$ is equivalent to $p = -1$. If displacements with the different values of p occur randomly, then reflections with the index $k = 3n$ are unaffected and those with $k \neq 3n$ are weak or absent. The following explanation can be given: The phase difference between radiation reflected from a unit cell at a position x, y, z and a unit cell at the origin of the coordinate system is given by

$$\begin{aligned}\Delta\phi &= 2\pi(hx/a + ky/b + lz/c) \\ &= 2\pi(hU + kV + lW)\end{aligned}\tag{22}$$

where h , k and l are indices of the reflecting planes and U , V , W are the coordinates expressed in units of cell parameters. Since U , V and W , and h , k , and l are normally all integers, $\Delta\phi$ is a multiple of 2π and the waves are in phase. If a cell or a whole layer is displaced by $pb/3$ parallel to y , the phase change is

$$\Delta\phi = 2\pi kp/3.$$

When $k = 3n$, the phase change is (an integral number) $\times 2\pi$, and it has no effect on the scattered waves. When $k \neq 3n$, the phase change is (an integral number) $\times (2\pi/3)$, i.e., 0° , 120° , 240° depending on the values of k and p . For random displacements, the resultant three-dimensional scattering is zero. Two-dimensional scattering from the layers is still possible and takes the form already discussed in Sections 4.4 and 4.5. These two-dimensional scattering effects generally are weak and diffused and most of them are not obvious by comparison with the stronger $k = 3n$ reflections. Often only the $11l$, $02l$ band is clearly seen.

Chlorites have similar arrangements of adjacent planes of O and OH ions as are found in the 1:1 layer structures, i.e., within the limitations of the idealized structure models. Therefore similar stacking disorders can be expected, and indeed are found not only in clay-grade chlorites but also in crystals of macroscopic size. When a single crystal, X-ray rotation pattern of a disordered chlorite is recorded by rotation around z^* , the direction normal to the layer plane, sharp reflections occur along all hk rows with the index $k = 3n$, and continuous lines of scattering along rows with $k \neq 3n$. These continuous lines are exactly analogous to the continuous "rods" in reciprocal space discussed in Section 4.4. Chlorites showing these effects are excellent examples of X-ray diffraction by systems disordered in this particular way. Being trioctahedral minerals, chlorites have planes of hydroxyl ions more nearly in a hexagonal arrangement than dioctahedral minerals such as gibbsite and kaolinite, and this feature of the chlorite structure probably facilitates layer displacements of the $pb/3$ type. Examples of chlorite rotation diagrams showing layer stacking disorder are given by Brindley *et al.* (1950) and by Bailey (1975).

5.2. More general treatments of layer stacking order-disorder

A detailed general treatment of X-ray diffraction by defective layer structures goes much beyond what can be presented in detail here. Wilson (1949) has given a useful introduction in his monograph *X-ray Optics—Diffraction of X-rays by finite and imperfect crystals*; Chapters V and VI are specially relevant. Here we shall present a very brief general survey.

The first attempts to provide a more detailed picture of order-disorder in clay minerals were made by Mitra (1963) and with Bhattacharjee (1969a,b, 1970) and by Noble (1971), and were oriented towards kaolinite. These studies, useful at the time they were made, have now been largely surpassed by the more fundamental approach of Plançon and Tchoubar (1975a,b, 1976, 1977a,b).

5.2.1 The direct approach of Mitra (1963)

Mitra (1963) studied disorders in kaolinite. The observed X-ray line profiles were corrected for the L_p factor and for instrumental broadening and the resulting profiles were attributed to the combined effect of small crystal size and disorder. From estimates of the effective crystal size, the diffraction effects of small crystal size and disorder were separated by a mathematical process of deconvolution. The resulting defect profiles were then analyzed by means of Wilson's treatment of diffraction by defect structures. The intensity distribution in a diffraction profile, $I(u)$, is related to the probability α of $\pm b/3$ shifts by the relation (Wilson, 1949, p. 65):

$$I(u) = \frac{12NF^2 \alpha}{9\alpha^2 + (4\pi u)^2}$$

In this equation u measures the departure from the precise Bragg angle as described in Section 3.2. From the 020 and 040 reflections, an average value of $\alpha = 0.046$ was obtained. For the 00/ reflections, an additional problem arose. In the ideal case, these reflections should not be affected by layer displacements parallel to the xy plane, and therefore the breadths of these diffractions should obey the Scherrer equation (equation 11 or 11'), $B = K\lambda/L \cos \theta$. The results showed that B did not vary linearly with $\sec \theta$. Still applying the theoretical treatment of Wilson, Mitra interpreted the data as showing a probability $\alpha = 0.057$ for a fractional increase of 0.126 in $d(001)$ or an actual increase of 0.90 Å in a basal spacing of 7.15 Å.

This study made a significant advance in the quantitative understanding of the defects in kaolinite, but the method was clearly limited to minerals with a small proportion of defects. With higher proportions of defects, the reflections with $k \neq 3n$ are considerably broadened and the profiles of the separate reflections are not accessible to study. Also the deconvolution procedure to separate the crystal size and defect broadening adds further uncertainty. The possibility that expanded basal spacings may occur and that the layer displacements may be related to these expansions, since both have the same order of probability, about 0.050, were very interesting results.

5.2.2 *The indirect approach by Noble (1971)*

Noble also was concerned with disorders in kaolinites. His approach assumed that layer displacements of $pb/3$ sub-divide a crystal into smaller domains of coherent scattering for reflections with $k \neq 3n$ but leave unaffected those with $k = 3n$. The 00/ reflections should not be affected by layer shifts "except insofar as such disorder may cause minor changes in the $d(001)$ spacing". Noble limited his considerations to the 02/, 11/ reflections of kaolinite which deteriorate into a continuous band of scattering as the frequency of layer shifts increases. Various distributions of domain sizes were assumed and the resulting diffraction patterns were calculated using the three-dimensional equivalent of equation (6). Additionally, two-dimensional scattering was assumed "in proportion to the number of disorders present in the crystal". Noble calculated the diffraction patterns for reasonable models of the distribution of domain sizes and compared the results with the observed diffraction patterns. Close agreements were obtained which seemed to verify the models chosen. The method had the advantage that it was applicable to a wide range of order-disorder in layer stacking and avoided the difficult step of separating diffraction effects due to crystal size and defects.

5.2.3 *Studies by Plançon and Tchoubar (1975–1977)*

These authors have made detailed calculations of the diffraction patterns of kaolinites with various kinds and proportions of layer stacking disorders and crystal sizes, and also have carried out carefully designed experiments aimed at reducing or eliminating those experimental factors which modify the form of the diffraction profiles. The experimental factors include the use of crystal-monochromatized $\text{Cu } K\alpha_1$ radiation, the use of freeze-dried samples by which preferential orientation is almost completely eliminated and of transmission rather than surface diffraction so that the degree of preferential orientation can be assessed, the limitation of beam divergence and height to eliminate the confusion arising from the so-called "umbrella effect" which is more noticeable in X-ray powder photography, the "step-counting" of diffracted intensity instead of continuous recording. These and other features of the experiments guarantee the high quality of the observed diffraction data which is necessary in making significant distinctions between different models of order-disorder.

The theoretical aspects of the work also have been made in a rigorous manner. The approach is to consider the effect of disorder on the reciprocal lattice representation of a layer structure. It has been seen already that the reciprocal lattice of a regular structure consists of a distribution of points diffused to an extent which depends on the crystal size and shape. When the layers are displaced randomly so that there is no phase coherence between radiation scattered from different layers then the points of the reciprocal lattice are diffused into continuous lines in directions normal to the layers but remain more or less sharp in directions parallel to the layers. Between these two extremes of complete order and complete disorder in the stacking of the layers, various degrees of order are possible which have the effect of modulating the continuous lines. Increasing order sharpens the modulations so that eventually they become sharp points. Conversely, as the stacking disorder increases, the sharp spots begin to broaden and to "fuse" into a modulated line and finally to become a continuous line but of varying intensity according to the value of the structure amplitude F .

The primary problem is the calculation of these modulated distributions for a given model. The calculations begin essentially with equation (1) for the summation of waves with phases $\phi_1, \phi_2, \dots$. The derivation of an intensity function involves phase differences of the form $(\phi_p - \phi_q)$ as in equation (2) which must now take account of the probability of a layer displacement occurring between the unit cells, or layers, denoted by P and Q. A further consideration is that the amplitude F scattered in a particular direction by two unit cells P and Q may not have the same values. If the disorder involves a relative rotation of one cell with respect to the other, then the values of F in a particular external direction, will be changed. The value of F also can change if the disorder involves Al ions occupying different octahedral cation sites. It has been seen already in Chapter 1 (Section 2.5) that there are two Al ions to occupy three cation sites. If the sites occupied change from layer to layer, or within a layer, then the scattered amplitudes also change. If ideal models of the layer structure are used, rotation of layers by $p(2\pi/3)$ is equivalent to changing the cation sites occupied but the two processes are not equivalent when the real structures are considered.

It has been seen in Section 3.2 that the calculated intensity in a general direction, defined by u in the one-dimensional case (equations 5 and 6) and by u, v, w in the two- and three-dimensional cases (equations 8 and 9), involves the crystal size and shape by involving the numbers of unit cells in the coordinate directions. Similar considerations are involved in treating the more general situations where disorders are present.

When the form of the reciprocal lattice for an assumed distribution of defects and an assumed crystal size has been calculated, the remaining steps involved in calculating the X-ray powder diffraction pattern are relatively straight-forward. They involve considering the intersections of spheres of radius $2 \sin \theta / \lambda$ with the modulated reciprocal lattice rods exactly in the same manner as described in Sections 4.4 and 4.5, and as illustrated in Fig. 2.4.

The extensive research of Plançon and Tchoubar is presented in a series of publications as follows: the basic theoretical treatment is contained in two papers published in 1975a and 1976 dealing respectively with defects of translation only, and of rotation as well as translation. Both general and special types of displacements are considered. A short account (1975b) is contained in the published volume of the International Clay Conference in Mexico City. The doctoral thesis of Plançon (1976) presents many details of the earlier calculations and of the experimental arrangements. Two further publications (1977a,b) discuss the calculations involved and the nature and proportion of the defects in natural kaolinites. A further publication (Barrios *et al.*, 1977) provides a very significant comparison of X-ray data and infrared spectroscopic data in relation to the nature of the defects.

The comparison of observed and calculated data, and the conclusions which can be drawn from these comparisons are deferred to Section 7.

6. DISORDER DUE TO CURVATURE OF LAYERS

Other types of disorder arise from the bending or curvature of layer structures. Layers can bend or curl not only from mechanical causes but also from inherent structural features. The theoretical problems arising in treating diffraction by rolled and curved structures are considerably greater than those related to planar structures. Some preliminary remarks on the origin of curved structures can be given.

6.1 Origin of, and evidence for rolled and tubular structures

Pauling (1930) recognized the possible tendency for 1:1 type layers to curl because of inherent misfits between the component octahedral and tetrahedral sheets. Chapter 1 (Section 2.4), has discussed the mismatch of the magnesian octahedral sheet and the silica tetrahedral sheet in serpentine minerals and the development of spiral, cylindrical and conical stacking arrangements in chrysotiles. Partial replacement of the Mg and Si ions in the ideal serpentine composition by Al ions decreases the dimensions of the octahedral sheet and increases those of the tetrahedral sheet and thereby facilitates the formation of stable planar layers (Roy and Roy, 1954; Gillery and Hill, 1959). A somewhat similar situation arises in the kaolinite group of minerals where the aluminum octahedral sheet is inherently on a smaller scale than the silica tetrahedral sheet. Nevertheless the commonest of these minerals, kaolinite, has a planar layer structure, but halloysite is seen in electron micrographs to have various rolled forms.

Curvature of layers has generally been considered to be a means by which internal stresses in a layer structure may be relieved. This advantage will be optimized at one radius only. In the case of chrysotile, Whittaker (1957) calculated that if the b parameter lies round the circumference of a cylinder and the a parameter is parallel to the axis of the cylinder, the optimum radius will be about 88 Å (see also a discussion by Wicks and Whittaker, 1975). Yada (1967, 1971) obtained high magnification, electron-optical images of thin sections of chrysotile tubes and found a minimum inner radius of about 35–40 Å and a maximum outer radius of about 140 Å. The average value, $(40 + 140)/2 = 90$ Å agrees very well with Whittaker's calculated value. Presumably the range of values, 40 to 140 Å, corresponds to the maximum stresses the layer structure will tolerate.

The mechanism of forming a cylindrical system of layers composed of unit cells requires that certain geometrical conditions be satisfied if the spacing of the layers is to be about the same as in planar structures. Let r_0 be the radius of a cylinder developed with the b parameter around the circumference. Then $2\pi r_0/b$ must be an integral number of unit cells. Let $(r_0 + c)$ be the radius of the next cylinder, so that c is the layer spacing, and let there be n more unit cells in this second layer. Then

$$2\pi(r_0 + c)/b - 2\pi r_0/b = 2\pi n/b.$$

With $b = 9.20$ and $c = 7.32$ Å, n has the value 4.9992, or 5 unit cells within the accuracy of the assumed parameters. Evidently these parameters permit a cylindrical structure to be developed with about the usual unit cell dimensions. Around the circumference the unit cells of successive layers will be alternatively in-step and out-of-step five times around the cylinder, but from layer to layer, the in-step and out-of-step domains need not coincide.

6.2 X-ray diffraction by curved and tubular structures

The theoretical evaluation of X-ray diffraction by tubular structures is mathematically very difficult. The usual linear framework within which three-dimensional diffraction is studied is no longer valid. Within a thick, rolled form the radius of curvature is not constant; consider, for example, the radii found by Yada for chrysotile tubes mentioned in the previous section. If, in the process of bending, fractures or faults of any kind are developed then the domains of coherent scattering will be smaller than the macroscopic system, even when the latter is only a few hundred angstroms in size. Cowley (1961) especially has emphasized the importance of considering "coherently diffracting regions in which the lattice is elastically bent"; the bending within such a region may be quite small. Thus a particle may appear in an electron micrograph as a tubular object, yet coherent diffraction may come only from small curved sections of the system. In the present context little more can be done than to refer the reader to some of the basic theoretical studies. Extensive studies by Whittaker (1952–1957), Jagodzinski *et al.* (1953, 1954) and Kunze (1956) were oriented particularly towards an understanding of chrysotile. Mitra (1965) and Mitra and Bhattacharjee (1968, 1971, 1975) dealt with the basic theoretical questions and applications to halloysite. Cowley (1961) also discussed diffraction by halloysite and in a further study (Cowley and Goswami, 1961) considered the effect of layer curvature on the symmetry of electron diffraction patterns of montmorillonite. Güven (1975) considered the effect of spherical and cylindrical bending on the form of the interference function, i.e., the function $\sin^2(N\pi u)/\sin^2(\pi u)$ as given in equation (6) and the analogous function in three dimensions.

Because of its technical importance, chrysotile has received more detailed study than halloysite. A single fiber of chrysotile yields an X-ray diffraction pattern resembling a rotation diagram of a single crystal (Fig. 2.7). In the case of halloysite, single fibers can be studied only by electron diffraction: the resulting pattern also is like a rotation diagram. The main feature of a fiber diffraction diagram is that the diffraction effects lie along parallel lines (so-called "layer lines") and from their separation the crystallographic parameter parallel to the fiber axis is obtained immediately. Most chrysotile fibers have the crystallographic x -axis along the fiber, and reflections on successive layer lines have the index $h = 0, \pm 1, \pm 2, \dots$, with $0kl$ reflections along the central layer line, and so on. For halloysite, the y -axis is usually along the fiber, and reflections on successive layer lines have the index $k = 0, \pm 1, \pm 2, \dots$ with $h0l$ diffractions along the central layer line.

In these fiber diffraction patterns, some reflections are sharp and others are diffuse or "tailed" and spread out in directions corresponding to increasing values of 2θ . In the case of chrysotile, reflections of type $h0l$ are sharp and of type $0kl$ or hkl are diffuse. Sharp reflections lie on even-order layer lines with $h = 0, \pm 2, \pm 4$. Odd-order layer lines, with $h = \pm 1, \pm 3, \dots$, have reflections with k non-zero, because $(h + k)$ must be even; the structure is centred on the (001) face. These observations indicate that the structure is disordered with respect to the y -axis, which is round the circumference of each cylindrical layer, and ordered with respect to the x - and z -axis, respectively along the fibre axis and along radial directions. Consequently, by considering only the sharp $h0l$ diffractions, one can derive the projection of the structure on the xz plane, which includes the x - and z -axis and the β -angle between them. Most chrysotiles, as discussed in Chapter 1 (Section 2.4.2) have β near 93 – 94° ; in other words, they are monoclinic and are called clino-chrysotile. The layers are arranged in an orderly way radially but with a small regular displacement parallel to the x -axis, the tube axis. The unit cell also contains two structural layers. In ortho-chrysotiles the displacements parallel to x from layer to layer are alternately $+$ and $-$ so that the two-layer unit cell has $\beta = 90^\circ$.

Evidently much useful information can be obtained from fiber-type diffraction patterns. However, when a full interpretation is required of the diffraction effects and particularly of the "tailed" diffuse reflections with the index $k \neq 0$, it becomes necessary to consider the more difficult questions relating to the curvature of the structure and the nature of the domains of coherent scattering.

6.3 Comparison with diffraction by two-dimensional crystals

A randomly oriented powder of tubular particles with the x -axis along the fiber axis gives sharp $h0l$ diffractions and tailed hk diffractions. Likewise if the y -axis is the fiber axis, the sharp reflections are $0kl$ reflections and the tailed reflections again hk diffractions. In general terms, these results are not very different from those for randomly stacked layer structures, where only $00l$ reflections are sharp, and hk diffractions tailed.

It is emphasized that the sharp $h0l$ (or $0kl$) reflections from tubular systems require successive layers of the tubular systems to be ordered with respect to the tube axis. The difference between clino- and ortho-forms lies in the ordering of the layers parallel to the tube axis. Any disorder in the way the layers are successively arranged would immediately reduce the sharpness of the $h0l$ (or $0kl$) reflections and much disorder would reduce the pattern to sharp $00l$ diffractions and all hk diffractions would be "tailed". The net result therefore might be very similar from random tube arrangements and random planar arrangements. It is questionable if powder diffraction data can distinguish these situations. Fiber diffraction patterns, taken with X-rays for chrysotile and with electrons for halloysite, will be much more useful than random powder data in deciding between such possibilities. The importance of these arguments will be made clear in Section 7 where order-disorder from the experimental standpoint is discussed.

7. ORDER-DISORDER IN 1:1 TYPE LAYER SILICATES

Earlier sections of this chapter have been oriented towards theoretical aspects of X-ray diffraction by crystals of small size and with variously disordered layer arrangements. It is necessary now to review order-disorder in different mineral groups from the experimental standpoint. Consideration will be given first to minerals having the 1:1 type layer structure.

7.1 Kaolinites and halloysites

X-ray powder photographs and diffractometer patterns reveal the variety of order-disorder effects in these minerals. Fig. 2.8 shows five such patterns ranging from the very well-ordered geode kaolinite from Keokuk, Iowa (Hayes, 1963; Keller *et al.*, 1966) to a typical halloysite (7 Å form). These diffraction patterns, recorded with a Philips Norelco diffractometer at $1^\circ(2\theta)/\text{min}$ with Ni-filtered Cu $K\alpha$ radiation, show the transition from the sharp diffractions in the first pattern to the mainly diffuse, "tailed" reflections in the last pattern. The sequence can be regarded as one of increasing layer stacking disorder. The main features of the diagrams are as follows.

The prominent basal reflections 001 and 002 near 12.4° and 24.9° $2\theta(\text{Cu } K\alpha)$ become less sharp and less intense with increasing disorder. Crystal size effects and preferential orientation contribute in part to the observed intensities. The sequence of 02l, 11l reflections in the range 20° – 33° (2θ) becomes increasingly blurred until with halloysite only a smooth diffraction band with the superimposed 002 basal reflection is obtained. In the range 35° – 40° (2θ), reflections with indices 13l, 20l occur together with the 003 basal reflection. These reflections form two groups of triplets in the less disordered kaolinites; they become two doublets in the disordered Pugu (Tanganyika) kaolinite, and finally appear as a continuous band in the halloysite pattern.

The first attempts to understand this sequence of changes aimed at a broad understanding of the structural disorders involved. From considerations of the reflections with the index $k = 3n$ and with $k \neq 3n$, as discussed in Section 5.1, Brindley and Robinson (1946, 1947) recognized the importance of layer displacement of type $pb/3$. Quantitative evaluation of the halloysite pattern by the same authors in 1948 led to the conclusion that the layers were randomly stacked and the diffractions were of the two-dimensional type apart from the basal reflections. The diffraction pattern of the Pugu kaolinite, illustrated in Fig. 2.8 was discussed rather fully by Robertson *et al.* (1954). From these studies, the concept of progressive disordering was developed, with mainly specific layer displacements of $pb/3$ -type parallel to y and equivalent directions at $\pm 120^\circ$ to y in less disordered forms and more general displacements in more highly disordered forms. This concept provided a useful general background for the next two decades, but with the gathering of more experimental data it became clear that more detailed evaluations were required.

In the early studies, many of the kaolinites which appeared to show $b/3$ -type displacements were materials used commercially as refractory clays or fireclays, and consequently the term "fireclay" came to be used for this kind of kaolinite. This unfortunate use of "fireclay" has been largely replaced by the term " b -axis disordered kaolinite", but this also is not entirely suitable. Probably the best term is simply "disordered kaolinite" with appropriate qualifications such as "slightly disordered", "highly disordered", . . . Douillet and Nicolas (1969) discussed the various schemes of nomenclature and classification of kaolinites and halloysites and their final recommendation also was to use "kaolinite" as a general term with suitable adjectival qualifications.

The basic difficulty in classifying kaolinites and halloysites according to a scheme of progressive disordering lies in the various kinds and degrees of disorder which can be present. Crystal size and shape are important variables. Layers can be planar, curved, rolled, cylindrical, and quasi-spherical, and each kind modifies the X-ray pattern differently. Basal spacings are not always and perhaps are seldom strictly uniform. Furthermore, any one sample of kaolinite or halloysite may not have a single type of disorder. All these factors combine to produce a very complex situation. The work of Mitra and his colleagues and of Noble, as described in Section 5.2, made important progress, but it is the fundamental work of Plançon and Tchoubar which has given the most detailed picture of the kinds of disorder present in kaolinites.

It is unnecessary to review in detail the vast amount of interim work, but a few references to representative studies can be given. Engelhardt and Goldschmidt (1954) and Fleurbaey and Nicolas (1964) described disordered kaolinites from Provins and from Charentes in France which are similar to the Pugu kaolinite. Murray and Lyons (1956) gave diagrams showing the variations of structural order in the sedimentary kaolins of Georgia; patterns of two Georgia kaolinites are shown in Fig. 2.8.

The importance of sample homogeneity has been stressed in several studies. Brindley and Santos (1963) showed by using artificial mixtures of kaolinite and halloysite that large proportions of halloysite in the presence of kaolinite can easily be overlooked, especially when the kaolinite is well-ordered; the composite diffraction pattern would be interpreted as a more-or-less disordered kaolinite. While electron microscopy can often give a clear indication of the presence of halloysite because of its fibrous morphology, careful procedures are necessary to avoid mistaken conclusions. Partial separation of platy and fibrous components can occur in sample preparation, such that X-ray diffraction will show mainly the platy kaolinite and electron microscopy the fibrous halloysite. Several descriptions of tubular kaolinites have been given which probably arose from such effects (see discussions by Brindley and Comer, 1956; Brindley and Santos, 1963; Santos *et al.*, 1964). Fibrous kaolinite, however, has been found with a macro-

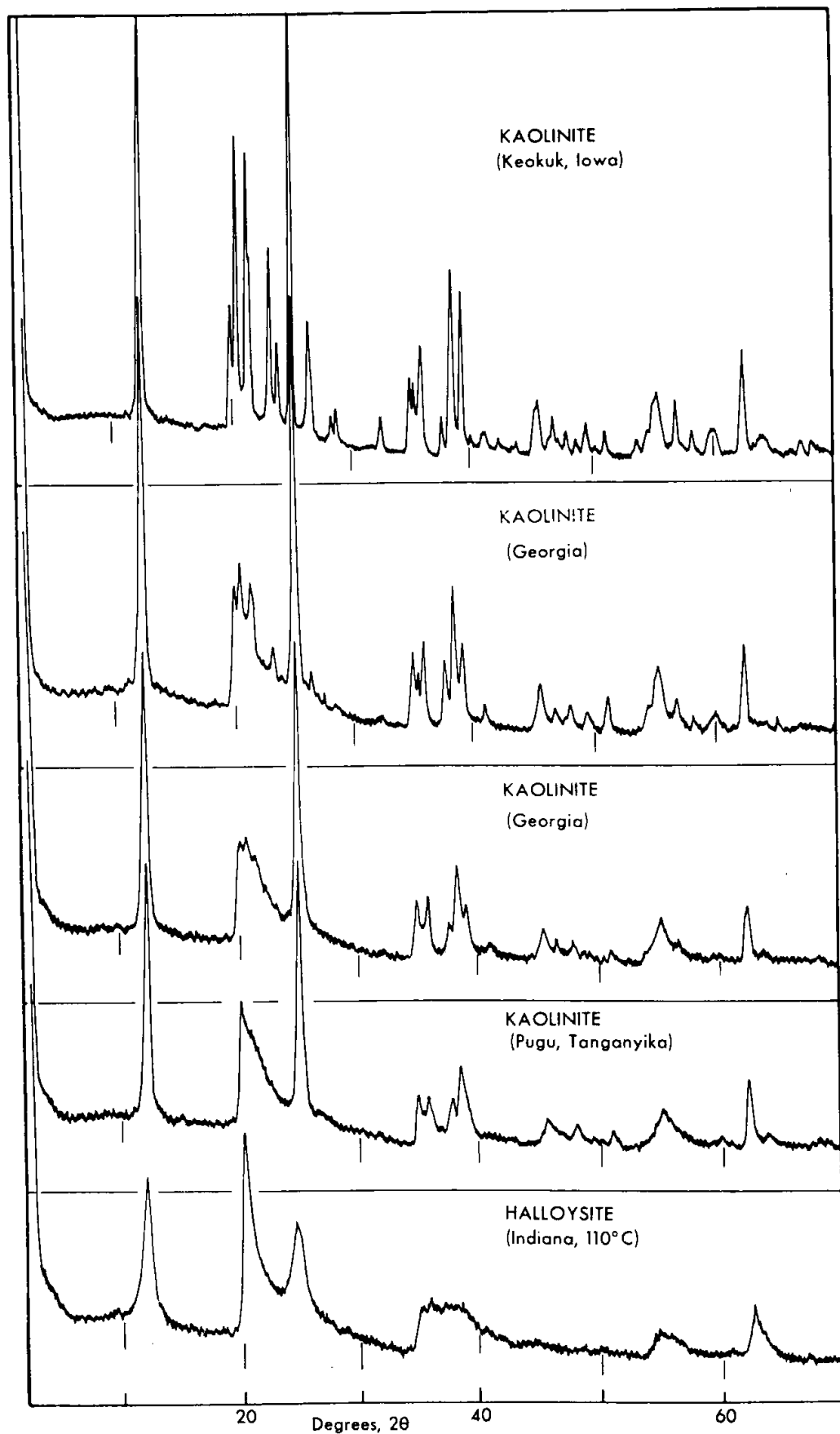


FIG. 2.8. X-ray diffractometer patterns (Cu $K\alpha$ radiation) of four kaolinites and one halloysite (7 Å form).

scopic fibrous habit and yielding an X-ray fiber diagram resembling somewhat that given by fibrous chrysotile (Santos *et al.*, 1965). Kaolin minerals have been found having a platy morphology and swelling properties like those of halloysite (Kunze and Bradley, 1964; Santos *et al.*, 1966). These minerals have been called "tabular halloysites". The existence of these unusual forms of kaolinite and halloysite causes awkward problems of nomenclature so that the suggestion of Douillet and Nicolas (1969) to use kaolinite as a general name, accompanied by suitable adjectives to cover particular varieties, may indeed be the best solution. Then many halloysites might be called tubular kaolinites, but this terminology goes beyond what is generally accepted.

7.2 Kaolinites; quantitative evaluations of disorder

The theoretical work of Plançon and Tchoubar (1975, 1976, 1977) has been described in Section 5.2.3 and it is necessary now to review in detail the results they have obtained. They have studied the following models:

- (i) Stacking faults by linear displacements only, with arbitrary displacements with probability P_a and $b/3$ displacements with probability P_b .
- (ii) Stacking faults by rotation of layers; various rotations were considered.
- (iii) Faults involving displacement of Al cation vacancies with probability P_d ; in the notation of Bailey (1963), the vacant sites may be only B and C sites, as found in kaolinites and dickites (see Chapter 1, Sections 2.5.1 and 2.5.3) or possibly A, B and C sites may all be involved.

The calculations involve considerations of the profiles of the 02 l , 11 l reflections and of the 13 l , 20 l reflections. Reflections with $k = 3n$ are affected only by the arbitrary displacements and rotations, those with $k \neq 3n$ are affected by both arbitrary and special displacements. Dimensions of the crystal domains of coherent scattering are required. From the breadth of the 001 reflection the number of layers M_z is obtained by applying the Scherrer equation; the mean effective radius of the layers, R_1 for the 02 l , 11 l reflections and R_2 for the 13 l , 20 l reflections, is obtained from the best fit of observed and calculated profiles. The radius R_2 is appreciably less than R_1 for reasons related to diffraction theory which, however, are not easily explained in a few words.

Studies have been made of four kaolinites as follows: Kaolinite 1, from Georgia, a well-ordered kaolinite, kaolinites 2, 3, and 4 from Charentes, France, with increasing amounts of disorder.

TABLE 2.3 Disorder parameters for four kaolinites (Plançon and Tchoubar, 1977b)

Sample	Source	C_M	P_a	P_d	P_b	R_1	R_2	M_z	Figure
1	Georgia	0	0.03	0.08	—	750 Å	250 Å	75 layers	2.9A,B
2	Charentes	0	0.07	0.47	—	1000	250	40	2.9C,D
				0.42	0.06				
3	Charentes	0.25	0.15	0.42	—	500	125	30	2.9E,F
				0.30	0.12				
4	Charentes	0.25	0.17	0.53	—	600	150	25	2.9G,H

C_M = measure of monoclinic character.

P_a = proportion of arbitrary displacements = P (Plançon and Tchoubar).

P_b = proportion of $b/3$ defects = η_t (Plançon and Tchoubar).

P_d = proportion of Al vacancy displacements = η_d (Plançon and Tchoubar).

R_1 = effective radius of coherent scattering domains for 02 l and 11 l diffractions.

R_2 = effective radius of coherent scattering domains for 20 l and 13 l diffractions.

M_z = number of layers per domain.

Values of M_z are respectively 75, 40, 30 and 25. Close agreements between observed and calculated data are obtained using appropriate values of P_a and P_d as listed in Table 2.3. Fig. 2.9 shows the agreements obtained. For kaolinites 2 and 3, somewhat better agreements were obtained by assuming a small proportion of $b/3$ displacements and diminishing the P_d values correspondingly.

From these results it is evident that Al vacancy displacements constitute the most important type of defect. This type of defect is consistent with the conclusions of Mansfield and Bailey (1972) relating to twinning in kaolinite which can be described in terms of domains in which Al vacancies occupy the positions labeled A, B, and C. Models involving rotations of layers led to no satisfactory agreements so that rotation of layers was rejected as an important cause of disorder in kaolinites. Displacements of type $pb/3$ appear to play a minor role. From the data in Table 2.3, it appears that $P_d \gg P_a \sim P_b$. In all the models considered, kaolinite layers were assumed to interact only between adjacent layers; Plançon and Tchoubar quoted data by Giese (1974 and per. comm.) for interaction energies between layers in support of this assumption.

As regards the physical nature of the random defects, Plançon and Tchoubar (1977b, p. 444) point out that $d(001)$ calculated from hkl diffractions is always 7.15 Å, but from $00l$ diffractions reaches 7.20 Å or even higher values in highly disordered kaolinites. The value 7.15 comes from the coherent domains between random defects, while the larger values include the layers with random shifts. Electron optical images, Fig. 2.10, show directly the layer stacking imperfections which are responsible for the larger spacings; they appear as folds, bubbles, or other inclusions. Thus, a proportion of adjacent layers may be 8 or 9 Å apart. This result is reminiscent of the earlier work of Mitra (1963). Similar observations were reported also by Lee, Jackson and Brown (1975).

An important aspect of the results is that displacements of the Al vacancy sites from position B to position C, or vice versa, correspond to the formation of a dickite element within a kaolinite structure. Chapter 1, Section 2.5.3, has shown that in dickite the layers are arranged in a regular succession with B and C octahedral cation sites vacant in alternate layers, i.e., a succession ...B C B C B..., whereas in kaolinite there is a regular succession ...B B B B... or ...C C C C.... The A site is not vacant in either the kaolinite or the dickite structure, but conceivably may be vacant in disordered kaolinites. See also the discussion of disordered dickites in Section 7.4.

Table 2.3 includes another variable, C_M , hitherto not explained. It has been seen that in the fully ordered kaolinite structure, successive layers are displaced mainly by $-a/3$ which results in a β angle for the unit cell of about 104.8° , but additionally by a small displacement parallel to y which gives an α angle of 91.8° . The unit cell is triclinic in both shape and symmetry. The precise values of these displacements arise from interactions between adjacent layers and are determined by the precise structural arrangements which include the rotation, tilting, and even some distortion of the SiO_4 tetrahedral groups and distortions of the octahedral groups around Al ions and vacant sites. In the two-layer monoclinic unit cell of dickite, the layer-to-layer displacements parallel to y are in opposite directions and thereby cancel, so that $\alpha = 90^\circ$. In a mixture of kaolinite and dickite stacking arrangements, the average α -angle must have some intermediate value between 91.8° and 90° . This aspect of the disordered kaolinite stacking is incorporated in the intensity calculations by the parameter C_M which has the value zero for a triclinic kaolinite and 1 for a monoclinic kaolinite; C_M is a measure of "monoclinicity". It may be recalled that Brindley and Robinson (1946) recognized the apparent monoclinic character of the powder patterns of disordered kaolinites and the same idea was discussed further for the disordered kaolinite from Pugu, Tanganyika, by Robertson *et al.* (1954).

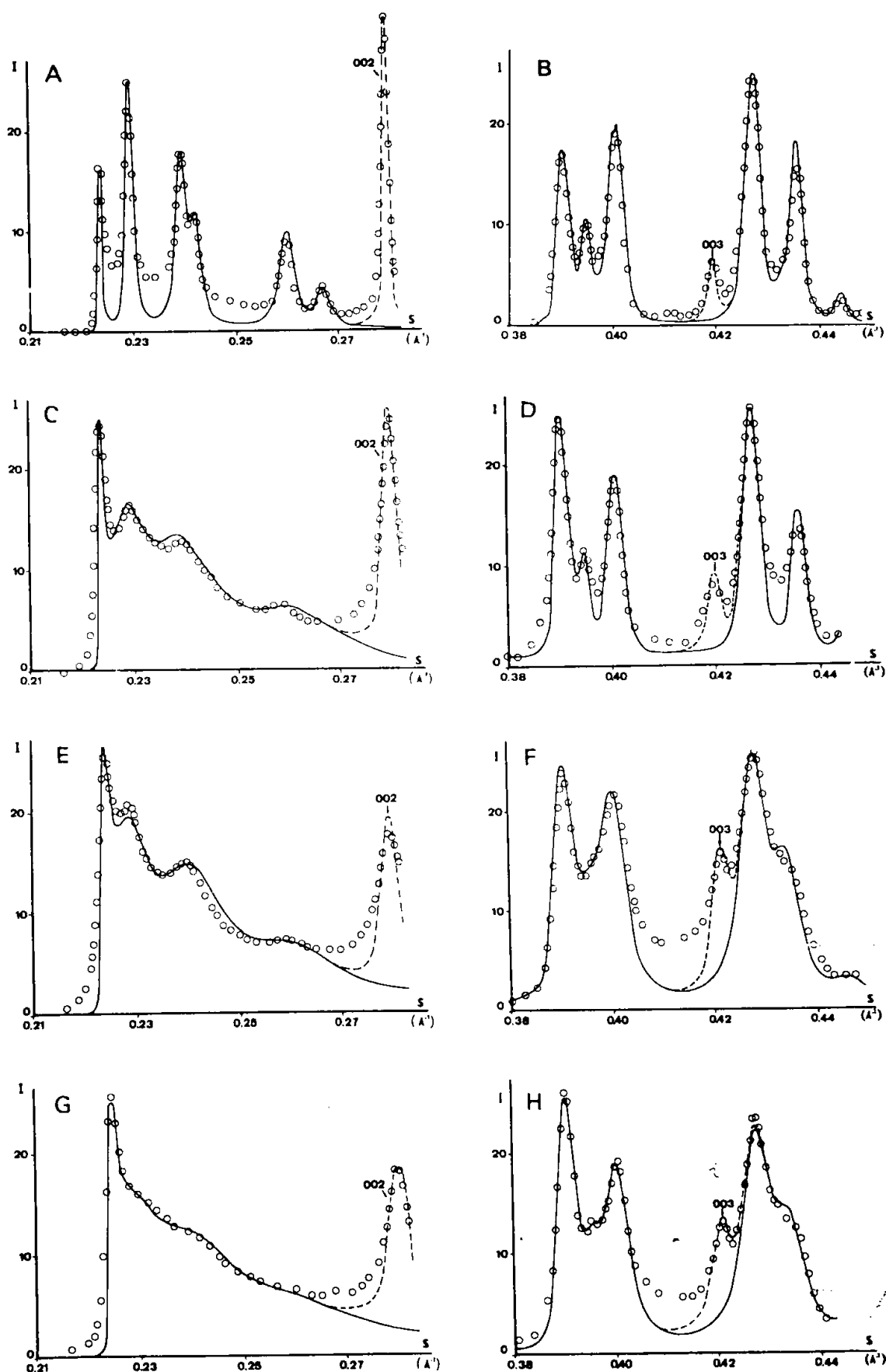


FIG. 2.9. Comparison between calculated diffraction patterns (continuous lines) and observed data (circles) for four kaolinites listed in Table 2.3. Horizontal scale $s = 2 \sin \theta / \lambda$. (Figures supplied by Dr. A. Plançon.)

It is evident from the foregoing discussion and from the data summarized in Table 2.3 that there is no simple way by which the nature of the disorder in a particular kaolinite can be determined quantitatively by applying the methods of Plançon and Tchoubar. Table 2.3 lists seven parameters of which only P_b might perhaps be neglected or combined with P_d . An atlas of curves calculated for selected values of six parameters would be a first step towards making these studies more generally applicable. There are dangers, however, in attempting to simplify a problem which, by its very nature, is not simple. The experimental aspects are as important as the theoretical when comparisons of observed and calculated intensity curves are made. The homogeneity of the sample studied is of primary importance as the results of Brindley and Santos (1963) clearly showed and as Keller and Haenni (1978) have emphatically endorsed.

Before concluding this account of disorder in kaolinites, a brief mention can be made of a so-called "crystallinity index" described by Hinckley (1963), which measures essentially the clarity of the closely spaced 02l, 11l diffractions. The heights of the $1\bar{1}0$ and $11\bar{1}$ diffraction peaks are measured above the local background drawn through the minima between these peaks. These heights, h_1 and h_2 , are not the true peak intensities. The *true* height of the $1\bar{1}0$ peak, $h(1\bar{1}0)$, is measured above the true background determined outside the range of these reflections. Then the crystallinity index is taken as $(h_1 + h_2)/h(1\bar{1}0)$. This index may have some practical value in comparing kaolinites, but only when all the data are recorded under the same experimental conditions. Fig. 2.11 illustrates the measurements used for the Hinckley index.

7.3 Halloysites

Many problems arise in determining the structural character of halloysites from X-ray diffraction data. Electron diffraction of single particles provides a better chance of determining structural details than X-ray powder diffraction. It is well established that two principal modifications exist, a less hydrous form with composition near that of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and with basal spacing near 7.2 Å, and a more hydrous form with composition near $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and basal spacing near 10.1 Å. The existence of these two forms was clearly recognized by Mehmel (1935), who used the terms "halloysite" and "metahalloysite", respectively, for the more hydrous and the less hydrous forms. Hofmann, Endell and Wilm

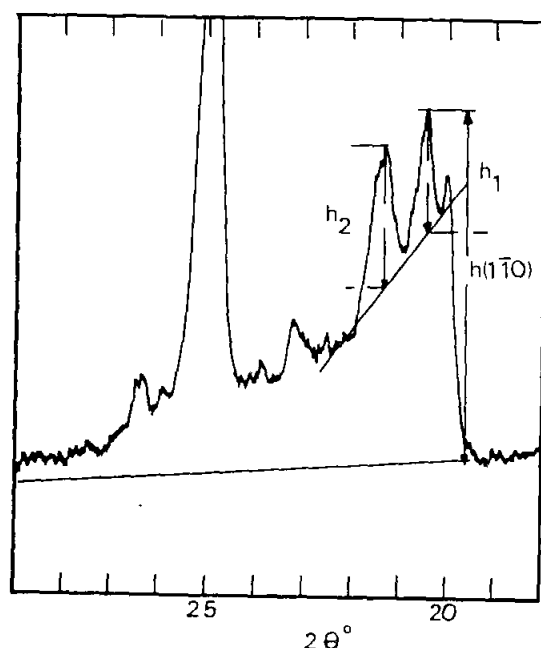


FIG. 2.11. To illustrate the Hinckley index, $(h_1 + h_2)/h(1\bar{1}0)$, as a measure of disorder in kaolinite; Cu $K\alpha$ radiation.

(1934) had found that the more hydrous form passed to so-called "kaolinite" at 105°C. In fact, the 10 Å form may transform to the 7 Å form at temperatures as low as about 70°C or in vacuo at ordinary temperatures.

7.3.1 Nomenclature

Various schemes of nomenclature have been suggested for the two forms of halloysite which have resulted in considerable ambiguity. The following can be considered:

1	2	3	4	5
7 Å-halloysite or halloysite (7 Å)	Metahalloysite	Dehydrated halloysite	Halloysite	Halloysite
10 Å-halloysite or halloysite (10 Å)	Halloysite	Halloysite	Hydrated halloysite, or Hydrohalloysite	Endellite

Terms (2) and (3) suggest that the 10 Å-form is primary and the 7 Å-form derived from it. Terms (5) were suggested to make a clear distinction between the two forms. MacEwan (1947) suggested that "halloysite" be used in a general sense and prefixed appropriately for particular forms. The net result of these various usages and definitions is that the precise meaning of the term "halloysite" is now quite uncertain unless the nomenclature is defined explicitly, or implicitly by use at the same time of a term such as endellite. The only unambiguous nomenclature is to indicate the basal spacing, as in terms (1). It suffices to give the spacings with no higher precision than 7 Å and 10 Å, although, in fact, there are some variations in the exact values. Churchman and Carr (1975) have reviewed the various nomenclatures and finally endorsed the recommendation of MacEwan (1947). This also is the opinion of the present writer, with the additional recommendation that "7 Å-" and "10 Å-" are the clearest prefixes to employ.

7.3.2 Dehydration of 10 Å-halloysite

The transformation of the 10 Å- to the 7 Å-form in atmospheres of controlled relative humidities was studied by Brindley and Goodyear (1948) by applying the treatment of Hendricks and Teller (1941) for diffraction by interstratified layer structures. The initial spacing of about 10.1 Å diminished to an average value of about 9.5 Å as a result of interstratification of dehydrated layers among mainly hydrated layers. Likewise, spacings between about 7.9 and 7.5 Å were interpreted as interstratifications of the remaining hydrated layers among mainly dehydrated layers. Between the 9.5 Å stage and the 7.9 Å stage it was thought that mixtures were present. Churchman and Carr (1972) and Churchman, Aldrich and Carr (1972) have followed the transformation in somewhat greater detail and are of the opinion that a continuous series of interstratified states exists between the 10 Å- and 7 Å-forms, each state being in equilibrium with the ambient atmosphere. The final reduction to the 7.2 Å state requires gentle heating. Chapter 3, Section 6.1 also discusses the dehydration of halloysite.

It is probably optimistic to consider that any clay mineral transformation proceeds in a wholly homogeneous manner because of differences in particle size and form. Some particles may dehydrate more readily (or less readily) than others so that even if equilibrium is established, there may still be differences between the precise state of dehydration reached by different particles.

7.3.3 X-ray diffraction data for halloysites

The X-ray powder pattern of 7 Å-halloysite is compared with patterns for variously ordered-disordered kaolinites in Fig. 2.8. On the basis of this comparison and the chemical composition, one may conclude that 7 Å-halloysite is a highly disordered, even randomly disordered form of kaolinite. Quantitative data pointing towards this conclusion are presented later.

The X-ray patterns of the 7 Å- and 10 Å-halloysite are compared in Fig. 2.18. Evidently they differ mainly in the basal reflections and rather little in the broadly spreading diffraction bands. The 10 Å-peak is considerably more intense than the 7 Å-peak and this result must be kept in mind in assessing ratios of the two forms in a mixture; any assessment based simply on the ratio of the intensities will greatly over-estimate the 10 Å component. The greater intensity of the 10 Å reflection is a consequence partly of the Lp factor which increases rapidly towards smaller 2θ values, and partly of the particular structure.

Hendricks (1938) and Hendricks and Jefferson (1938) showed that the extra water in the 10 Å-halloysite probably forms a planar arrangement with $4\text{H}_2\text{O}$ per unit cell, or $2\text{H}_2\text{O}$ per formula unit. The difference in basal spacing, $10.1 - 7.2 = 2.9$ Å, is sufficient to accommodate a plane of water molecules arranged in a hexagonal network and linked to each other and to O and OH ions of the adjacent kaolinite-type layers by hydrogen bonds (Fig. 2.12). The planar arrangement of water molecules in 10 Å-halloysite is probably more nearly regular than interlayer water in vermiculites and smectites because of the absence of interlayer exchangeable cations.

The X-ray powder data for halloysites are listed in Table 2.4. The principal distinguishing characteristics of the two forms are the 001 and 002 reflections of the 7 Å-halloysite, and the 001 and 003 reflections from the 10 Å-halloysite. The basal reflections are broad for several possible reasons including small crystal size, layer spacings not constant (which may be attributed to interstratifications of the two forms), and curvature of layers, discussed later. The remaining

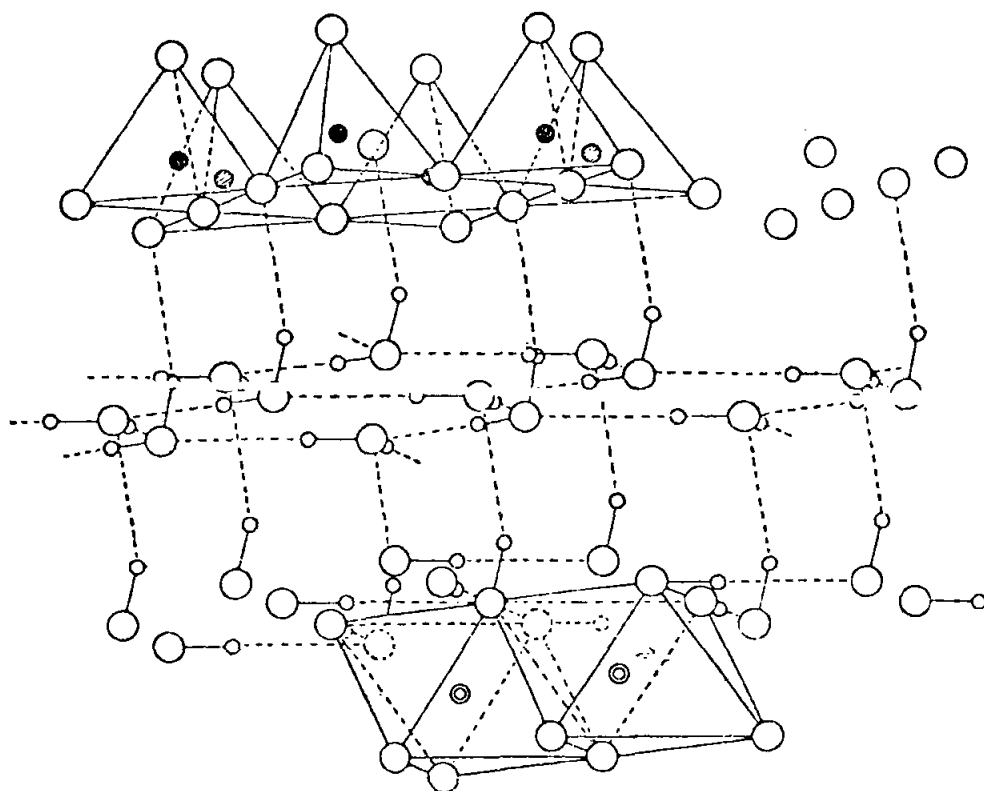


FIG. 2.12. Structure of halloysite (10 Å form) with hydrogen-bonded interlayer water. (after Hendricks and Jefferson, 1938).

TABLE 2.4. X-ray powder data for halloysites

7 Å-halloysite				10 Å-halloysite		
00 <i>l</i> and <i>hk</i> indices	<i>d</i> (obs.)	<i>I</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i>	00 <i>l</i> indices
				10.1	10	001
001	7.41	6	7.21			
02, 11	4.43	10	4.460	4.46	8	
002	3.603	4	3.607			
				3.40	5	003
13, 20	2.562	4	2.575	2.56	5	
?	2.493	—	—			
003	2.405	1	2.405			
?	2.340	—	—	2.37	3	
04, 22	2.222	$\frac{1}{2}$	2.229	2.23	3	
004	1.805	$\frac{1}{2}$	1.803			
15, 24, 31	1.680	2	1.685	1.67	3	
06, 33	1.484	5	1.487	1.48	5	
26, 40	1.283	$\frac{1}{2}$	1.287	1.28	1	
17, 35, 42	1.233	$1\frac{1}{2}$	1.236	1.23	1	
006	1.203	$\frac{1}{2}$	1.202			
08, 44	1.110	$\frac{1}{2}$	1.114			
28, 37, 51	1.023	$\frac{1}{2}$	1.023			
19, 46, 53	0.970	$\frac{1}{2}$	0.973			
39, 60	0.858	$\frac{1}{2}$	0.859			
2, 10; 48, 62	0.842	$\frac{1}{2}$	0.843			

7 Å-halloysite (Lawrence Co., Missouri), data by Brindley and Robinson (1948).

10 Å-halloysite (Herrenberg, near Aachen), data by Mehmel (1935).
d(calc.) based on *a* 5.15, *b* 8.92, *d*(001) 7.214 Å.

diffraction peaks are broad and can be described as *hk* diffractions. Spacings for these broad bands can be listed as *hk*0 diffractions from the low-angle terminations, which are more or less sharp, but they do not correspond exactly to *hk*0 positions in reciprocal space, as discussed already in Sections 4.4 and 4.5.

The first approach to a quantitative interpretation of the 7 Å-halloysite pattern (Brindley and Robinson, 1948) assumed that 7 Å-halloysite was the end-member of an order-disorder series in the stacking of kaolinite-type layers. Calculations of the diffraction profiles were made on the basis of Warren's (1941) treatment of two-dimensional diffraction. Fig. 2.13 shows the essential data. Fig. 2.13A shows the function $\psi(\theta)$ vs. θ for the 02,11 band (see equation 16 and the following discussion). Similar curves of $\psi(\theta)$ are obtained for the other bands. Fig. 2.13B summarizes the data for $\sum F^2$ as a function l' . The form of the X-ray diffraction bands depends on the product of these two functions. For the prominent 02,11 band, $\sum F^2$ is nearly constant and the profile of the band depends largely on $\psi(\theta)$. For the important 06,33 band, important because it is commonly used to obtain the *b*-parameter, $\sum F^2$ diminishes rapidly and consequently this band is sharp and has the appearance of a three-dimensional diffraction; however, it is essentially two-dimensional and has an asymmetric profile. Fig. 2.13C compares the observed and calculated data for three values of *L*, the crystal size parameter. The agreement shown confirms the general validity of the model. Further discussions have been given by Cowley (1961) and by Mitra and Bhattacharjee (1975). It should not be overlooked, however, that the semi-focusing X-ray camera used in the early work lacked the better focusing of modern instruments.

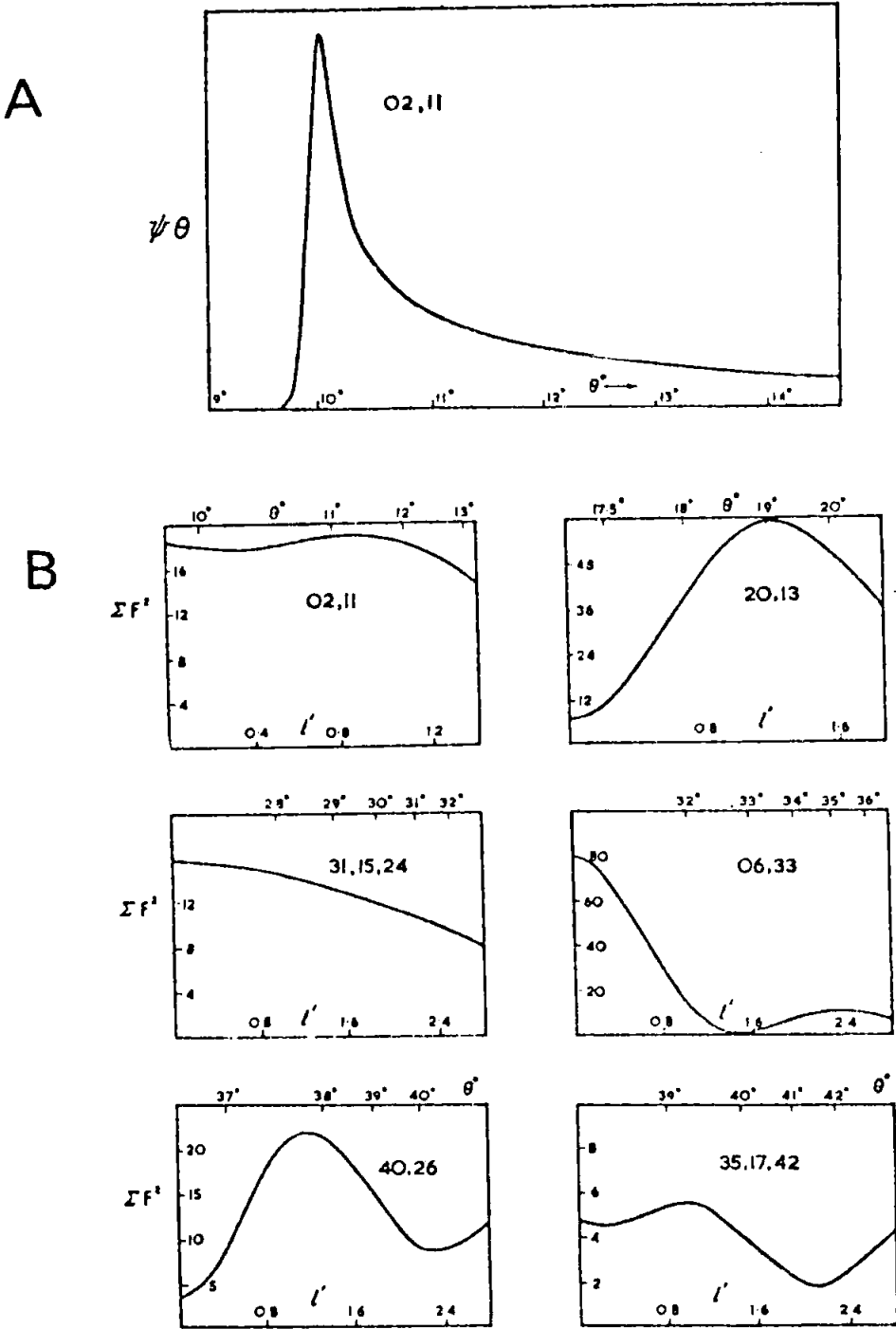


FIG. 2.13. Calculation of X-ray diffraction hk bands for 7 Å form of halloysite (after Brindley and Robinson, 1948); Cu $K\alpha$ radiation. A. The function of $\psi(\theta)$ vs. θ for the 02,11 band (see equation 16). B. Variation of $\sum F^2 (hkl)$ for the principal bands of halloysite.

7.3.4 Electron-optical data for halloysites

Before discussing further the X-ray data on halloysite, the information obtained by electron microscopy and diffraction should be considered. The tubular nature of halloysites and chrysotiles, first clearly recognized by Turkevich and Hillier (1949), Bates *et al.* (1950*a,b*), Noll and Kircher (1950, 1951), Bates and Comer (1959), raised doubts regarding the validity of the random layer model. Electron diffraction patterns of single fibers indicated that halloysites may have structures essentially different from those of other kaolinite group minerals. As further

C

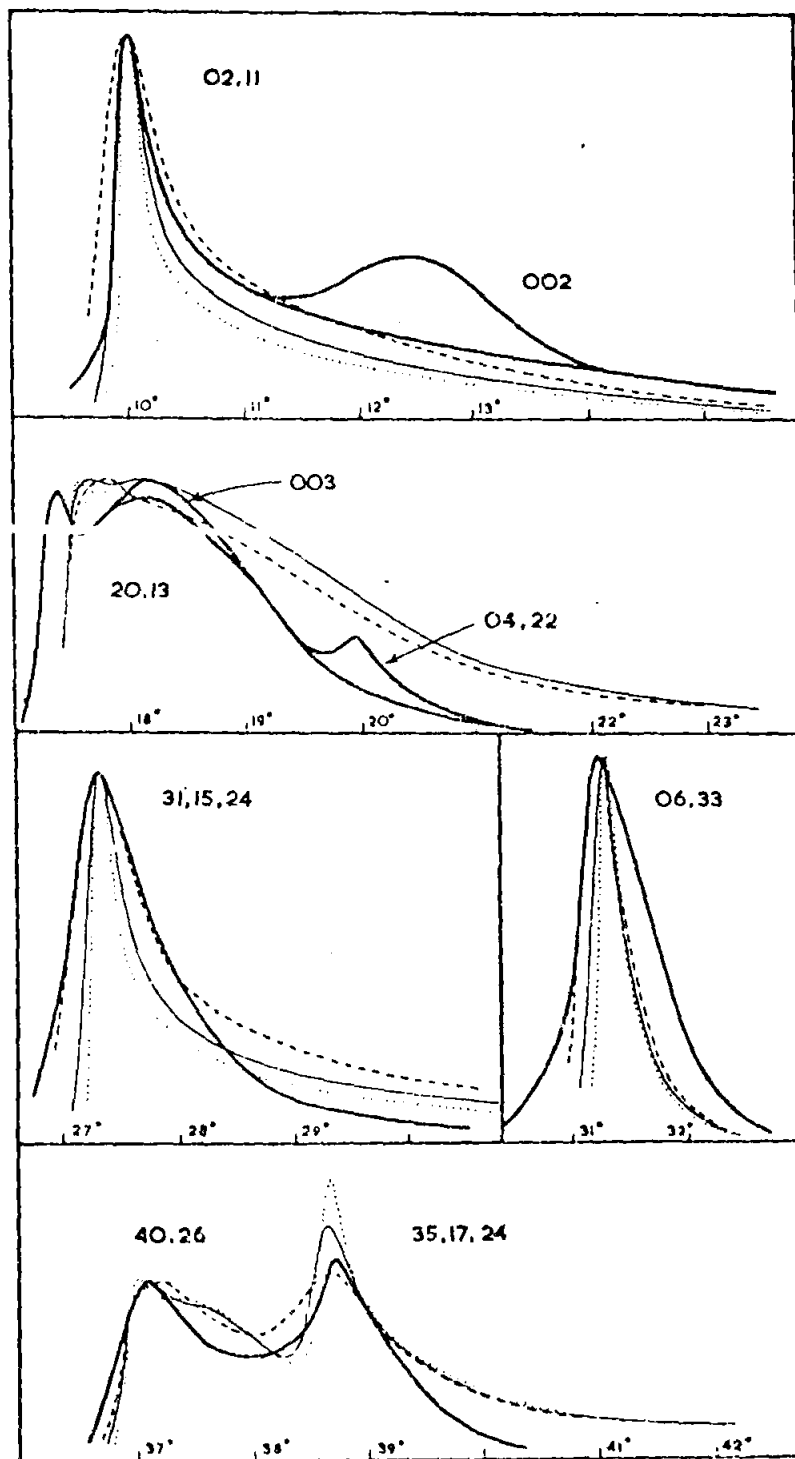


FIG. 2.13C. Comparison of calculated bands and observed data; $L = 300 \text{ \AA}$. . . , $L = 200 \text{ \AA}$ —, $L = 100 \text{ \AA}$ ----.

X-ray powder data accumulated, it appeared that details of the patterns were not adequately explained by the random layer model. The net result is that the random layer model can be regarded only as a first approximation and it is questionable if a continuous order-disorder sequence exists between fully ordered kaolinite and randomly ordered 7 Å-halloysite.

The electron-optical data need be reviewed only briefly since extensive accounts have been given by Bates (1971) and Gard (1971). Halloysites have a wide variety of morphological forms including: (i) Tubular forms of various types which can be long and thin, short and stubby, tubes

emerging from tubes. (ii) Rolled forms, sometimes showing serrated edges suggesting crystallographic planes or directions. (iii) Prismatic forms which may be hollow or solid, and having various numbers of sides to the prisms (Hofmann *et al.*, 1962). (iv) Pseudo-spherical forms which have been illustrated by Dixon and McKee (1974). (v) Platy and tabular forms of 10 Å-halloysite also have been described (Kunze and Bradley, 1964; Santos *et al.*, 1966).

Electron diffraction patterns of single halloysite particles show fiber diffraction characteristics similar to those described for chrysotile in Section 6.2. Honjo and Mihama (1954) and Honjo *et al.* (1954) showed that most halloysites have the fiber axis in the direction of the crystallographic y -axis, with $b = 8.95$ Å; a few particles have the x -axis, $a = 5.14$ Å, parallel to the fiber axis and a few have other orientations. Relatively well-defined $02l$ reflections are found in positions which correspond, as regards the l index, with positions midway between the $00l$ basal reflections. This means that the $00l$ reflections must be indexed as $002, 004, \dots$ instead of $001, 002, \dots$. The unit cell must then contain two structural layers. These results are very similar to those reported for chrysotiles, except that the fiber axis of halloysite is generally the y -axis. Honjo and Mihama indexed the diffraction pattern with a monoclinic cell, $a = 5.14, b = 8.93, c = 14.7$ Å, $\beta = 104^\circ$, but in their second paper they considered the cell might be triclinic with $\alpha = 91.8^\circ$. The structure was shown to be neither that of dickite, nor of kaolinite but a distinctive two-layer structure. Waser (1955), in a paper mainly concerned with a theoretical treatment of diffraction by tubular structures, also gave a short discussion of the electron diffraction pattern of halloysite.

Santos, Brindley and Santos (1965) studied a very unusual form of kaolinite (or halloysite, the correct name is uncertain) from Piedade, São Paulo, Brazil. This material forms macroscopic fibers and small, hair-like bundles can be selected for X-ray examination. The resulting X-ray pattern gave many more reflections than would be expected from halloysite considered as a randomly stacked layer structure. After dispersion in water, single fibers suitable for electron diffraction patterns gave results very similar to those of Honjo *et al.* (1954) with the y -axis parallel to the fiber axis and with similar evidence for a two-layer monoclinic (or possibly triclinic) unit cell.

The most detailed studies of halloysite are those of Chukhrov and Zvyagin and their colleagues (1966, 1969). They found a great variety "differing in degree of hydration, structural order, and other features". The variations are seen most clearly in electron diffraction patterns of single particles but some differences also can be seen in X-ray powder patterns. They confirmed again the two-layer structure of halloysite, which differs from those of dickite and nacrite. They gave the unit cell parameters: $a = 5.14, b = 8.90, c = 14.7$ Å, $\beta = 96^\circ$, but a triclinic cell also is possible. Their clearest results were obtained with prismatic particles; each prism face was a (001) plane. The two-layer structure proposed by Chukhrov and Zvyagin was recognized by them as being unusual in the disposition of the kaolinite-type layers, particularly as regards the superpositions of Al and Si ions from one layer to the next. Two arrangements were found which alternated; in one case, half the Al ions of one layer were superposed on Si ions, and in the other case, all the Al ions were superposed on Si ions. Values of F^2 calculated by Chukhrov and Zvyagin for the proposed two-layer halloysite structure are listed in Table 2.5 where they are compared with values by the same authors for triclinic kaolinite. It should be remarked that the structure factor F has a somewhat different significance in electron diffraction than in X-ray diffraction, because electrons are scattered by the combined potential field of the nucleus and the surrounding electrons (see for example Murr (1970) for a simple description, Vainshtein (1964) for a more detailed description of electron scattering).

In calculating the intensity of radiation diffracted by curled, rolled, cylindrical, and other kinds of deformed layers, an important consideration is the shape and size of the coherently diffracting

TABLE 2.5. Calculated values of F^2 for electron diffraction by kaolinite group minerals (from Chukhrov and Zvyagin, 1966)

hkl	$d, \text{\AA}$	Monoclinic halloysite model	Triclinic halloysite model		Dickite	Kaolinite	hkl	$d, \text{\AA}$ (X-ray data)
			hkl	$h\bar{k}l$				
020	4.45	90	15	15	65	55	0 $\bar{2}$ 0	4.46
						55	020	
110	4.43	40	70	140	40	150	1 $\bar{1}$ 0	4.37
$\bar{1}$ 11	4.35	60	40	3	120	10	110	4.33
021	4.25	170	110	10	40	150	1 $\bar{1}$ 1	4.17
111	4.13	10	40	20	190	75	111	4.12
$\bar{1}$ 12	3.95	230	30	30	35	130	0 $\bar{2}$ 1	3.84
022	3.80	10	35	15	170	65	021	3.74
112	3.64	125	80	5	30	5	1 $\bar{1}$ 1	3.42
$\bar{1}$ 13	3.43	35	2	25	75	95	111	3.37
023	3.28	25	35	70	20	24	1 $\bar{1}$ 2	3.14
113	3.14	45	6	6	30	25	112	3.10
$\bar{1}$ 14	2.97	10	30	50	20	5	0 $\bar{2}$ 2	2.84
024	2.82	25	1	15	40	55	022	2.75
114	2.70	55	3	40	15	50	1 $\bar{1}$ 2	2.52
$\bar{1}$ 15	2.54	5	15	5	60	20	112	2.48
025	2.44	55	5	30	10	20	1 $\bar{1}$ 3	2.34
115	2.34	2	5	10	45	35	113	2.30
$\bar{1}$ 16	2.22	40	20	1	10	25	0 $\bar{2}$ 3	2.13
026	2.14	10	10	0	20	1	023	2.09
116	2.08	5	20	10	5			

The halloysite data correspond to the two-layer unit cells discussed by Chukhrov and Zvyagin.

regions. Cowley (1961) gave special attention to this question and his arguments should be read in their entirety rather than as a brief summary here. Very briefly, his argument suggested that the coherently scattering domains may be considerably smaller than the whole tubular particle, and that a model involving curved layers rather than entire cylinders may be validly used. Furthermore the coherence domains depend on the wavelength of the radiation as well as on other experimental factors. As regards the wavelength dependence, electrons may "see" smaller domains than X-rays and consequently these systems may appear more ordered to electrons than to X-rays. Cowley proceeds to re-calculate the band profiles for X-ray diffraction by 7 Å-halloysite, taking into account a bending of the layers such that the average deviation in orientation from the average is of the order of 10°. His calculated profiles show somewhat closer agreement with the experimentally determined profiles given by Brindley and Robinson (1948) than those calculated with a planar model. However, it should not be overlooked that in those experiments a semi-focusing X-ray camera was used.

Several general conclusions emerge from this discussion. If electrons "see" structure over smaller domains than X-rays, then electron diffraction has a better chance to see the local ordering. It seems well established that at least the better ordered 7 Å-halloysites, perhaps those with prismatic forms, have a characteristic two-layer structure. The picture provided by random powder, X-ray diffraction emphasizes disorder over longer ranges and the model of randomly stacked layers can be accepted only as a first approximation. There are, however, variations in the X-ray powder diffraction patterns of halloysites and great care must be exercised in their interpretation. In particular, there is always the possibility that the material examined may be a mixture of halloysite and some form of kaolinite.

Finally a brief reference can be made to a paper by Mitra and Bhattacharjee (1975) which suggests a different model for 7 Å-halloysite in which layer curvature does not arise from bending of the structural layers, but from displacements of flat layers parallel to y ($b = 8.95$ Å) thereby causing a bending of the z -axis. (It should be noted that they interchange the usual x - and z -axes which may confuse the reader.)

7.3.5 Identification of halloysites

Several characteristics facilitate the X-ray identification of halloysites. The 10 Å-form is recognized by the broad 10.1 Å 001 diffraction peak which collapses to about 7.2 Å when heated for an hour or more at around 100°C; the conditions are not critical. This 10 Å peak, although usually broad because of the nature of the mineral and/or because of incipient dehydration, also less commonly appears as a sharp, strong reflection. This easy collapse of the basal spacing differentiates 10 Å-halloysites from other clays with basal spacings near 10 Å. The 003 reflection ($d = 3.40$ Å) of the 10 Å-form is then replaced by the 002 reflection ($d = 3.60$ Å) of the 7 Å-form. Organic complexes of the 10 Å-halloysite produce characteristic expansions which are discussed by MacEwan and Wilson in Chapter 3, Section 6.2.

The 7 Å-form of halloysite is easily recognized when it is the only component or a dominant component. The broad basal reflections, 001 and 002, and the broadly spreading diffraction bands are indicative of halloysite. The relatively sharp 06 diffraction peak, with $d \approx 1.48$ – 1.49 Å, indicates a dioctahedral mineral with $b \approx 8.9$ Å. The non-planar morphology of most

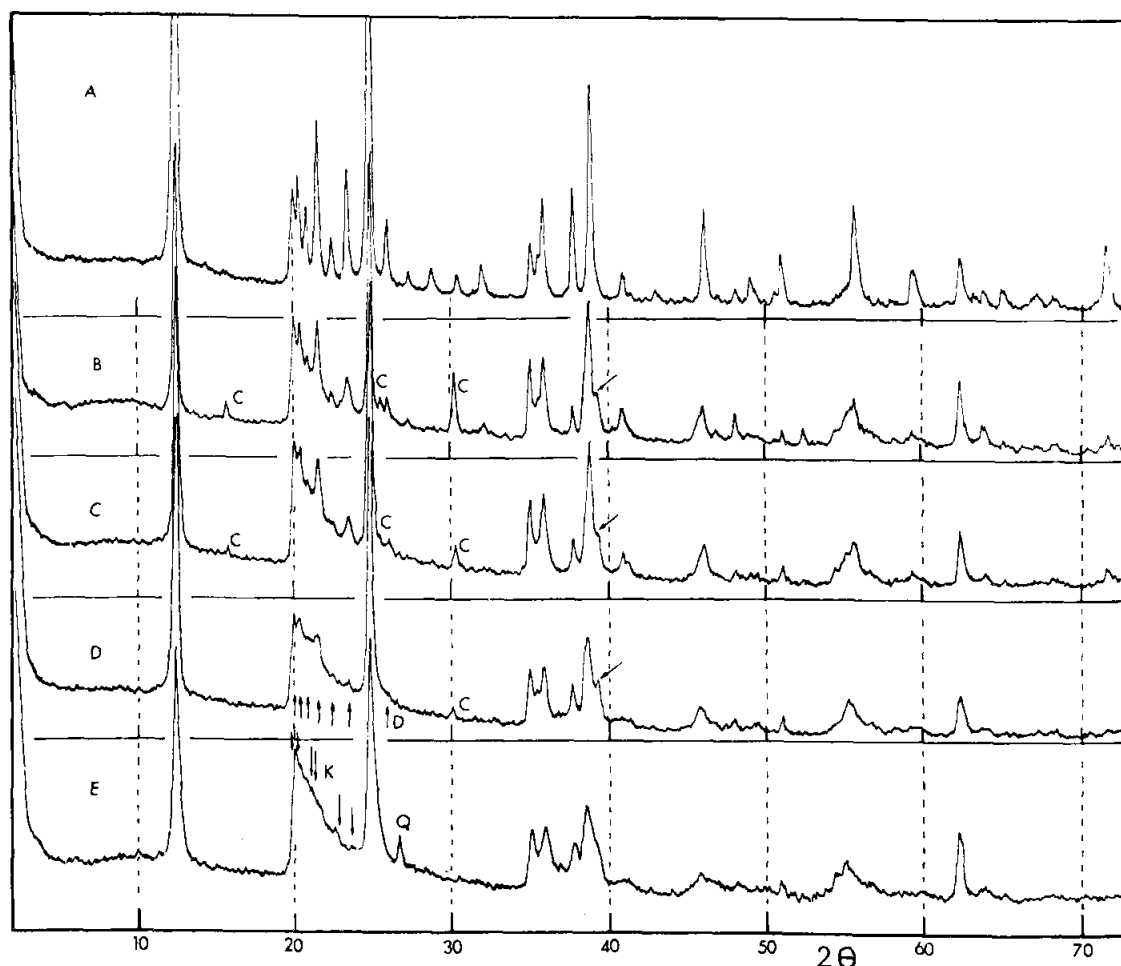


FIG. 2.14. X-ray diffractometer patterns (Cu $K\alpha$ radiation) of four dickites with various degrees of disorder (A–D) and of disordered kaolinite (E). (After Brindley and Porter, 1978).

halloysites is such that basal plane orientation generally is absent and consequently the sharp peak of the 02,11 diffraction band is often stronger than the maximum intensity of the 001 peak. All these characteristics point strongly to 7 Å-halloysite rather than to other kaolinite group minerals.

Halloysites also occur, probably rarely, in platy or tabular form (Kunze and Bradley, 1964; Santos *et al.*, 1966). The 10 Å-form presents no special problem: the easy collapse on heating and the expansion in ethylene glycol provide clear identification. The platy character is recognized by basal plane orientation, but additional confirmation should be obtained by an electron micrograph. A 7 Å-form with platy morphology could be mistaken for some form of disordered kaolinite, more particularly if some kaolinite also is present.

Mixtures of kaolinite and 7 Å-halloysite may not be obvious as mixtures. Brindley and Santos (1963) prepared mixtures of kaolinites and 7 Å-halloysites in various proportions and showed that high proportions, as much as 50%, of 7 Å-halloysite could be overlooked by an investigator who might well identify the mixture as a disordered form of kaolinite.

Miller and Keller (1963) showed that a differentiation can be made by utilizing the expansion of all kaolinite group minerals in strong potassium acetate solutions or by grinding the clay with potassium acetate added. The wet, K-acetate treated clay expands to about 14 Å. The potassium acetate is then removed by washing and, without allowing the clay to dry, ethylene glycol is added. Kaolinites and dickites return to a basal spacing of about 7.1–7.2 Å after this treatment, but all 7 Å- and 10 Å-halloysites examined, nine altogether, retained an expanded spacing of 10.4–10.9 Å. Miller and Keller studied a variety of so-called hard and soft flint clays and fire clays and found they all behaved as kaolinite in the K-acetate + ethylene glycol test. Further discussion of the intersalation process is given by MacEwan and Wilson, Chapter 3, Section 6.4; see also discussions by Deeds *et al.* (1967).

7.4 Dickite and nacrite

The structures of these minerals are discussed in Chapter 1, Sections 2.5.3 and 2.5.4. They are polytypic varieties of kaolinite with different stacking arrangements of essentially the same layers as in kaolinite itself. The precise conditions favouring their formation rather than kaolinite are not known with certainty and the writer is unaware of any laboratory synthesis of either of these polytypes. Higher temperatures and hydrothermal pressures are sometimes thought to favor dickite rather than kaolinite formation. The order of occurrence is kaolinite $\gg$ dickite $\gg$ nacrite.

Disorder in dickite has received little attention. Dickites usually appear to be structurally well-ordered and morphologically well-formed. An occurrence of dickite in Jamaica, described by Davis *et al.* (1970), has been examined further by Brindley and Porter (1978) who found a wide range of order-disorder in dickites from this area. The better ordered samples show all the X-ray powder diffraction lines expected from the two-layer monoclinic structure as described by Newnham and Brindley (1956) and Newnham (1961). With increasing disorder, reflections with the index $k \neq 3n$ become increasingly weakened and the most highly disordered samples can scarcely be distinguished from highly disordered kaolinite. Fig. 2.14 shows diffractometer patterns of dickites with various degrees of disorder.

Disorder in dickite can be interpreted probably along the same lines as disorder in kaolinite, namely in terms of "mistakes" in the positions not occupied by Al ions. In the notation of Bailey (Chapter 1, Section 2.5.3), a well-ordered dickite can be described as having a sequence of vacant octahedral sites ...B,C,B,C,... A mistake in this sequence, such as ...B,C,B,B,B,C,B,... is equivalent to a kaolinite element B,B,B, within a dickite matrix. If the number of B layers is even, then the two dickite sequences are "out-of-step". However, it is

questionable if two dickite sequences apparently "in-step", as in the example given above, will diffract coherently. The kaolinite element which separates them can be expected to have the triclinic system of axes with $\alpha \simeq 91.8^\circ$. Consequently the separated dickite units will be off-set in the y -direction. It remains to carry out theoretical studies on disordered dickites analogous to those of Plançon and Tchoubar on disordered kaolinites.

Little can be said about disorder in nacrite because too few examples of nacrite have been studied. The experience of the writer is that nacrites are seldom as well ordered as most dickites.

7.5 Serpentine minerals

The serpentine minerals are 1:1 type layer silicates with principally magnesian trioctahedral compositions. They exist with various structural forms and compositions as described in Chapter 1, Section 2.4. Comparisons can be made with the 1:1 dioctahedral structures but such comparisons are necessarily inexact. The trioctahedral minerals have a range of chemical compositions whereas the dioctahedral minerals have little or no chemical variation. In the present section, attention is given mainly to aspects of order-disorder.

7.5.1 Chrysotiles

Chrysotiles, with compositions near that of the magnesium end-member $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, have various rolled and tubular forms as discussed in Chapter 1, Sections 2.4.2–2.4.4. They give characteristic X-ray and electron fiber diffraction patterns which have been discussed already in Section 6.2 in relation to diffraction by curved and tubular systems. It has been seen that successive rolled layers can be stacked in clino- and ortho-forms and probably also in less precisely ordered arrangements. Fiber diffraction patterns, with X-rays or with electrons, furnish the best data for identifying the different structural arrangements. With powder diffraction methods, differentiation is difficult and uncertain. Whittaker and Zussman (1956) gave diagrams of calculated X-ray powder patterns for mixtures of clino- and ortho-chrysotile in the range 30° – 70° 2θ ($\text{Cu } K\alpha$). The dominant end-members of the series might be recognized under favourable circumstances, but estimation of mixtures is likely to be very uncertain. An unusual form of chrysotile, called "potato-like asbestos", has been described by Jehan and Khan (1973). The macroscopically rounded forms when crushed and dispersed yield long flexible fibers similar to those of other chrysotiles.

7.5.2 Lizardite and amesite

From the standpoint of order-disorder, these minerals can be considered together. Their compositions and structures are discussed in Chapter 1, Sections 2.4.6 and 2.4.7. Lizardite $(\text{Mg}_{3-x}\text{Al}_x)(\text{Si}_{2-x}\text{Al}_x)\text{O}_5(\text{OH})_4$, with $x \sim 0.05$ – 0.12 , is the most abundant variety of serpentine in massive materials. Amesite, with a similar formula and $x \sim 1.0$, is relatively uncommon. The structures can be considered with respect to ortho-hexagonal unit cells, with $a \simeq 5.31$ – 5.32 , $b \simeq 9.19$ – 9.21 and $c \simeq 7.31$ (lizardite) and 14.05 Å (amesite). These unit cells correspond respectively to one-layer and two-layer structures. The fact that $c(\text{amesite}) < 2c(\text{lizardite})$ can be attributed to the net positive and negative charges on the octahedral and tetrahedral sheets of the amesite structure which produce an additional force of attraction between the layers.

Disorder in these structures is related to the two sets of positions which the octahedral cations can occupy; in Bailey's notation (see Chapter 1, Section 2.2) these positions are labeled I and II. In the ordered one-layer structure, one set of sites is occupied in all layers, entirely set I or entirely set II. In ordered amesite, sets I and II are occupied alternately from layer to layer. These situations are reminiscent of those found in kaolinite and dickite.

Disorder in lizardite was discussed rather fully by Rucklidge and Zussman (1965) who showed on the basis of single crystal diffraction data that "the layers are most probably stacked in domains some of which are in one-layer sequences in either orientation, and others in alternating sequences". Reflections with index $k \neq 3n$ are streaked parallel to c^* and indicate random layer displacements of $\pm b/3$ with an estimated probability of 0.4. In powder diffraction patterns, the disorder shows as tailed reflections. In the light of the work of Plançon and Tchoubar (Section 7.2) we must be cautious in relating tailed reflections to random $b/3$ shifts of layers. There is, however, a significant difference between the di- and tri-octahedral 1:1 layer structures, for whereas the kaolinite disorder is related principally to the unoccupied octahedral positions, in lizardite it is related to the one or the other set of octahedral positions; with each set there are particular positions for the hydroxyl ions. Consequently it is quite probable that whole layer shifts of $b/3$ do occur in lizardites.

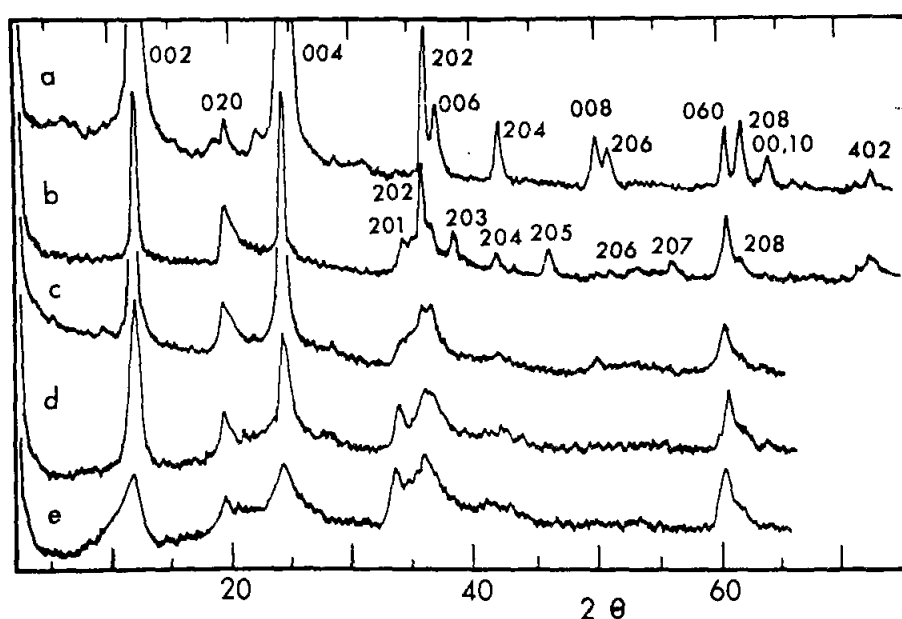


FIG. 2.15. X-ray diffractometer patterns (Cu $K\alpha$ radiation) of (a) lizardite, (b), (c) nickel lizardites, (d), (e) nepouites. Indexed patterns based on two-layer orthogonal cell (after Brindley and Wan, 1975).

Order-disorder in amesite involves not only layer stacking order but also cation ordering in both the octahedral and tetrahedral cation positions. Bailey in Chapter 1, Section 2.4.7, discusses cation ordering in these positions.

7.5.3 Lizardite-nepouite series

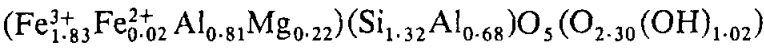
Nepouite is the end-member nickel analog of lizardite (Maksimovic, 1973; Brindley and Pham Thi Hang, 1973; Brindley and Wan, 1975). Fig. 2.15 compares X-ray powder diffraction patterns of lizardite from the type locality, two nickel-lizardites and two nepouites. The patterns are indexed with respect to the two-layer orthogonal unit cell. The lizardite pattern shows only l -even reflections, which implies a c -parameter of about 7 Å. A nickel-lizardite from Madagascar, pattern *b*, shows l -odd as well as l -even reflections and the unit cell evidently contains two layers. The streaked 020 reflection and the general absence of reflections with $k \neq 3n$ indicates the type of disorder associated with $b/3$ displacements. The nickel-rich minerals appear to be highly disordered; pattern 2.15(e) shows broad asymmetric basal reflections suggesting some interstratification of expanded layers.

7.5.4 Berthierine, brindleyite, greenalite, cronstedtite

These minerals are discussed in Chapter 1, Sections 2.4.10–2.4.14, and only a few remarks related to aspects of disorder will be added here.

Berthierine. This mineral, formerly called chamosite or chamosite-7 Å, commonly occurs as a physical mixture of trigonal (or orthohexagonal) and monoclinic forms. Interstratifications of ortho and clino stacking arrangements also occur. X-ray powder diffraction data permit only limited recognition of the structural characteristics and single crystals seem not to be available. Physical mixtures are recognized from the presence of reflections from the two components (Brindley, 1951). Although many reflections are common to both components, some are attributable to one component only (see Chapter 1, Table 1.7). From the intensities of these diagnostic reflections, the relative proportions can be estimated. Disordered layer stacking due to displacements of $pb/3$ type are common and are recognized by absence or weakness of reflections with the index $k \neq 3n$. Displacements parallel to x correspond to a mixing of ortho and clino stacking arrangements; their presence is seen from the $20l$ reflections. With the exception of the 200 reflection, $d = 2.678$ Å, which is usually sharp, other $20l$ reflections vary from sharp lines to weak diffuse bands with increasing disorder (Youell, 1955).

Disorder may be chemical as well as physical. Although berthierine can be given the “ideal” formula $(\text{Fe}^{2+}, \text{Mg})_{3-x}(\text{Fe}^{3+}, \text{Al})_x(\text{Si}_{2-x}\text{Al}_x)\text{O}_5(\text{OH})_4$, the actual formulae commonly show fewer than three octahedral cations. For a predominantly ferrous form, Brindley and Youell (1953) obtained $(\text{Fe}_{1.82}^{2+} \text{Mg}_{0.23} \text{Al}_{0.83} \text{Fe}_{0.01}^{3+})(\text{Si}_{1.32} \text{Al}_{0.68})\text{O}_5(\text{OH})_{3.96}$ with an octahedral cation deficiency of 0.11. Similar formulae with larger cation deficiencies up to 0.3 have been reported (Thurrell *et al.*, 1970). When berthierine is oxidized by laboratory heating, partial dehydroxylation occurs. For the ferrous mineral mentioned above, the formula after oxidation was the following:



This formula was derived by keeping the tetrahedral cations unchanged. Youell (1955, 1958) reported that structural disorder appears to increase when there is less ferrous and more ferric iron or more aluminum in the composition. Thus disorder may be related to a mixing of octahedral cations of various ionic sizes. Porrenga (1965, 1966) commented on the highly disordered chamosite (i.e., berthierine) in Recent Sediments as compared with the better ordered forms in older formations.

TABLE 2.6. Lattice parameter changes of berthierine and cronstedtite by oxidation

Chamosite (Brindley & Youell, 1953)			
	Ferrous form	Ferric form	Percent contraction
<i>a</i>	5.41 Å	5.25 Å	3.0
<i>b</i>	9.38	9.10	3.0
<i>d</i> (001)	7.11 _s	7.06	0.8

Cronstedtite (Steadman & Youell, 1957)			
	Ferrous form	Ferric form	Percent contraction
<i>a</i>	5.40	5.25	4.4
<i>b</i>	9.52	9.10	4.4
<i>d</i> (001)	7.08 _s	7.0 _s	0.4

Oxidation of berthierine, by replacing Fe^{2+} by smaller Fe^{3+} ions, decreases the lattice parameters. Similar effects are observed with cronstedtite. Relevant data are given in Table 2.6.

Brindleyite. This mineral is a nickel-rich analog of berthierine with a structural formula near $(\text{Ni}_{1.75}\text{Al}_{1.0}\square_{0.25})(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_5(\text{OH})_4$ (Maksimovic and Bish, 1978). Mixtures of ortho and clino polytypes are found in about equal proportions. The layer stacking is partially disordered and crystalline development poor. The deficiency in octahedral cations resembles that in berthierine.

Greenalite. This mineral has a formula near $(\text{Fe}^{2+}, \text{Mg})_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ and resembles berthierine in that mixtures of trigonal and monoclinic forms occur (see Chapter 1, Section 2.4.12). Steadman and Youell (1958) observed that oxidation is accompanied by dehydroxylation on heating in air; the resulting ferric form is less well ordered than the ferric form of berthierine.

Cronstedtite. This iron-rich mineral exhibits a wide variety of polytypic forms which are discussed in Chapter 1, Section 2.4.14. The mineral forms single crystals suitable for detailed structure analysis. Single crystals exhibiting layer stacking disorder also are found and were studied by Shaw, Steadman and Pugh (1965) by applying Wilson's treatment of diffraction by disordered layer structures (see Section 5.2.1). The problems encountered by Mitra (1963, see Section 5.2.1) in applying this procedure to kaolinite due to overlapping reflections did not arise with the single crystals of cronstedtite. The results showed considerable variation in the probability of layer displacements which ranged from 0.08 to 0.30 in six crystals studied in detail.

7.6 Chrysocolla, medmontite and copper-halloysite

These are poorly ordered layer silicates containing copper. Chrysocolla and medmontite have been described as 1:1 type layer structures but appear to be essentially different from other minerals with this type of layer structure. Chrysocolla often gives only two broad X-ray diffractions with $d \simeq 2.8$ and 1.74 Å. From selected area, electron diffraction patterns taken with normal and oblique incidence of the electron beam, Chukhrov, Zvyagin *et al.* (1969) concluded that the layer structure contains dioctahedral $(\text{Cu}, \text{Al})\text{O}$, OH sheets joined by $\text{Si}-\text{O}$ tetrahedral sheets with the tetrahedra pointing alternately towards the octahedral sheets on the two sides. The structural formula was given as $(\text{Cu}_{2-x}\text{Al}_x)\text{H}_{2-x}\text{Si}_2\text{O}_5(\text{OH})_4$. The unit cell parameters are $a = 5.70$, $b = 8.85$, $c = 6.70$ Å. The axial ratio, $b/a = 1.55$, is considerably less than a value near 1.73 found in most other layer silicates.

Medmontites at an earlier date were thought to be copper-containing smectites; they appear to be variable mixtures of chrysocolla and a hydromica. Medmontite, therefore, is not strictly a mineral name. Materials thought to be copper-halloysites were found to consist of two kinds of fibrous particles. Selected area diffraction showed that one type was chrysocolla, the other a true halloysite. The results of these studies suggest that, at low concentrations of copper, Cu or Cu and H may substitute for Al in a halloysite structure. As the concentration of Cu increases, a mixture of Cu-halloysite and chrysocolla develops in the form of intergrowths, and eventually only chrysocolla is formed. In the presence of clay-grade micas, intimate mixtures of chrysocolla and micas may be developed and form the material called medmontite. Evidently this system is highly complex. Chukhrov *et al.* (1969) give references to earlier Russian work on these minerals.

A different interpretation of the diffraction data for chrysocolla has been given by Oosterwyck-Gastuche (1970). She found unit cell parameters $a \simeq 5.8$, $b \simeq 17.8$ and $c \simeq 8.2$ Å, where b is about twice the value given by Chukhrov *et al.* and c is appreciably greater. With a formula $4[\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_3 \cdot 2\text{H}_2\text{O}]$ per unit cell, based on analyses of eight samples, a calculated

density of 2.67 is obtained in good agreement with a measured density of 2.62. The unit cell given by Chukhrov *et al.* with the smaller c parameter gives a correspondingly larger calculated density of 3.27. In the structure described by Oosterwyck-Gastuche, the Si–O tetrahedral sheets are continuous and the tetrahedra point half in the $+z$, half in the $-z$ direction, but unlike the arrangement in the Chukhrov model they alternate so as to form narrow ribbons running parallel to a and of width $b' = b/2$. The octahedra do not form continuous sheets as in the Chukhrov model but form bands of width $b/2$ linked to the tetrahedral bands. The bands or ribbons consist, therefore, of 1:1 type structures. The ribbons are thought to be curved and consequently $b'/a = 1.54$ which is considerably less than a value near $\sqrt{3}$ normally found in planar layer structures. This ribbon-like arrangement is somewhat similar to that found in palygorskite, and the curvature of the layers is reminiscent of that in antigorite. A more precise structure analysis must await the discovery of better-organized crystals.

8. ORDER-DISORDER IN 2:1 TYPE LAYER SILICATES

8.1 General considerations

Table 1.1 in Chapter 1 presents a classification of 2:1 type layer silicates based on the layer charge x per formula unit. Between pyrophyllite and talc with $x = 0$ and the micas, muscovite and phlogopite, with $x \simeq 1$, are two mineral groups of major importance in clay mineralogy, smectites and vermiculites with x in the range 0.25–0.6, and 0.6–0.9 respectively. These values of x are not precisely defined limits and when $x \simeq 0.6$ it is not clear whether a distinction can be made between high-charge smectites and low-charge vermiculites.

Ordered structures of pyrophyllite, talc, vermiculites, micas and chlorites, and their chemical compositions have been discussed already in Chapter 1 and for these minerals attention can be focused immediately on aspects of order–disorder. Smectites, however, are generally highly disordered and are omitted from Chapter 1. Therefore not only order–disorder but also the general chemistry of smectites and their subdivision into chemical species must be considered.

Smectites and vermiculites exhibit intracrystalline swelling by incorporation of water and organic materials between the layers. In humid atmospheres, the degree and regularity of the swelling varies with the nature of the interlayer cations and the relative humidity. These topics are discussed fully in Chapter 3. In the present chapter, attention is directed towards aspects of

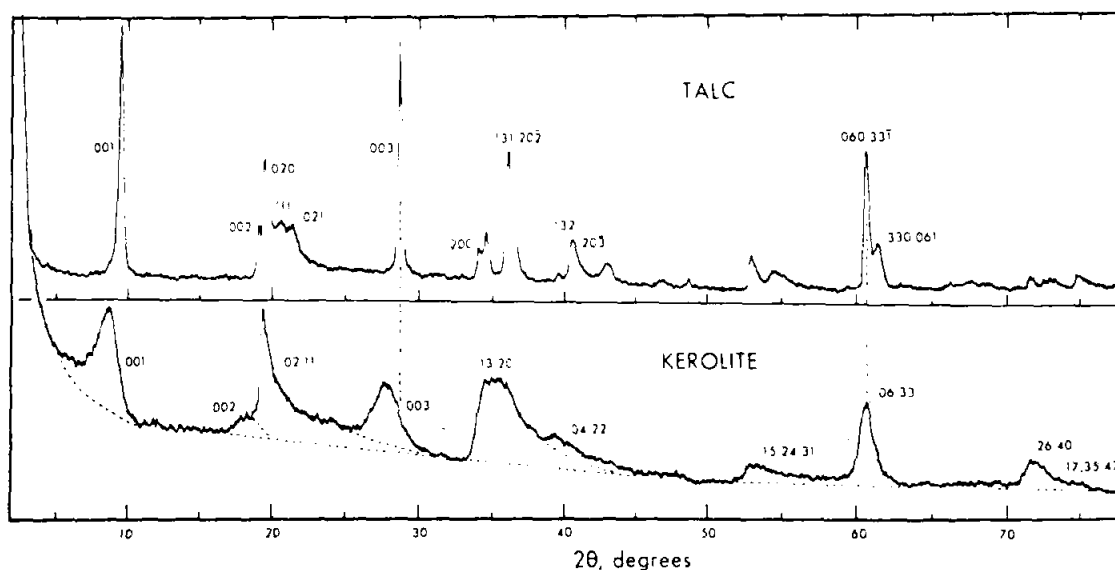


FIG. 2.16. X-ray diffractometer patterns of talc and kerolite (Cu $K\alpha$ radiation) (after Brindley, Bish and Wan, 1977).

order-disorder when the layer spacings are regular and also to questions relating to structural order within the layers themselves.

8.2 Pyrophyllite and talc

These electrically neutral, 2:1 layer structures have relatively weak interlayer bonding, i.e., weak compared with the ionic bonding in micas. However part of the cohesion between layers arises from long-range ionic forces as Giese (1975) has shown from ionic potential energy calculations. These minerals are distorted easily by mechanical treatment and distortion-free crystals suitable for single crystal analysis are not easily obtained. The descriptions of both minerals as two-layer monoclinic structures rather than as one-layer triclinic structures (see discussions in Chapter 1, Sections 3.2 and 3.3) persisted for many years probably because most samples exhibit partially random layer stacking and diffuse reflections when the index $k \neq 3n$. In their study of pyrophyllite, Rayner and Brown (1965) were limited to the analysis of a sub-cell based on the sharp reflections with $k = 3n$.

8.3 Kerolite and pimelite

Kerolite (also spelled cerolite) is an extremely fine-grained, non-expanding, magnesium silicate chemically and structurally similar to talc. The elucidation of the nature of kerolite has a long and confusing history. It is often closely associated with serpentine minerals, mainly lizardite, so that neither the chemistry nor the structural characteristics can be readily ascertained. However, from studies of mainly monomineralic materials, the essential nature of kerolite has been determined. D'yakonov (1963*a,b*) and Maksimović (1966) recognized that kerolite is close to talc and generally contains few if any swelling layers. Further data were obtained by Brindley and Pham Thi Hang (1973) and by Brindley, Bish and Wan (1977). The composition is close to $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ with $n \sim 0.75-1.2$. The fact that kerolite is non-expanding in water, and only partially and with difficulty expandable in ethylene glycol (if expandable at all) distinguishes kerolite from stevensite, with which it has been confused in the past. The additional water in the composition is probably mainly surface-held water, but some may occupy interlayer positions. The broad 001 basal reflection gives an apparent spacing of about 10.0–10.1 Å which is displaced by the effect of the L_p factor (Section 3.5). The corrected spacing is near 9.6 Å. Kerolite has a fully turbostratic structure; a typical diffraction pattern is shown in Fig. 2.16. Individual crystals contain no more than about 4–5 layers and the surface area determined by gas adsorption methods, about 200 m² g⁻¹, is consistent with the small crystal size. The enhanced basal spacing of 9.6 Å compared with 9.35–9.40 Å for talc can be attributed to the disordered layer stacking which does not permit the degree of close-packing of adjacent planes of oxygen ions found in well-ordered talc (Rayner and Brown, 1973). These authors pointed out that random stacking with the same O–O distances would increase the basal spacing by 0.27 Å.

A brief remark can be made on the terms α - and β -kerolite which have been applied to mixtures probably similar to deweylites (see Section 8.4) with a serpentine mineral predominant in the α -form and a 2:1 layer structure predominant in the β -form (Ginzburg and Rukavishnikova, 1950, 1951; Rukavishnikova, 1956). With the serpentine mineral now seen to be generally lizardite, the term kerolite can be applied to the 2:1 layer structure and the β designation becomes superfluous.

Pimelite is a nickel-containing analog of kerolite. Maksimović (1966) described a kerolite-pimelite series and more extensive data have been obtained by Brindley and Pham Thi Hang (1973) and Brindley, Bish and Wan (1979). Pimelites have the same structural characteristics as kerolites, with a broad 001 reflection, apparently near 10 Å but with a true spacing near 9.6 Å.

The structure is turbostratic with rather few layers per particle and gives broad basal reflections; it is essentially non-expanding. Substitution of as little as 1–2% NiO in the kerolite composition gives a distinct green coloration and Ni- or nickeloan kerolite is the appropriate term. When Ni atoms exceed Mg atoms the mineral has a dark green color and pimelite is then the appropriate name; the NiO content is then about 25 or more weight percent.

8.4 Deweylites and garnierites

Materials called deweylites appear to be intimate mixtures of very poorly ordered, mainly magnesian 1:1 and 2:1 layer silicates in variable proportions (Speakman and Majumdar, 1971). Faust and Fahey (1962, see p. 32, 37, 78) recognized the composite nature of deweylites and described them as serpentine–stevensite mixtures, but the non-expanding nature of the 2:1 component points to kerolite rather than to stevensite as the correct description. The composite nature of the material is shown in chemical analyses by compositions which do not conform to either a 1:1 or 2:1 type formula. The X-ray diffraction patterns show diffuse hk bands in

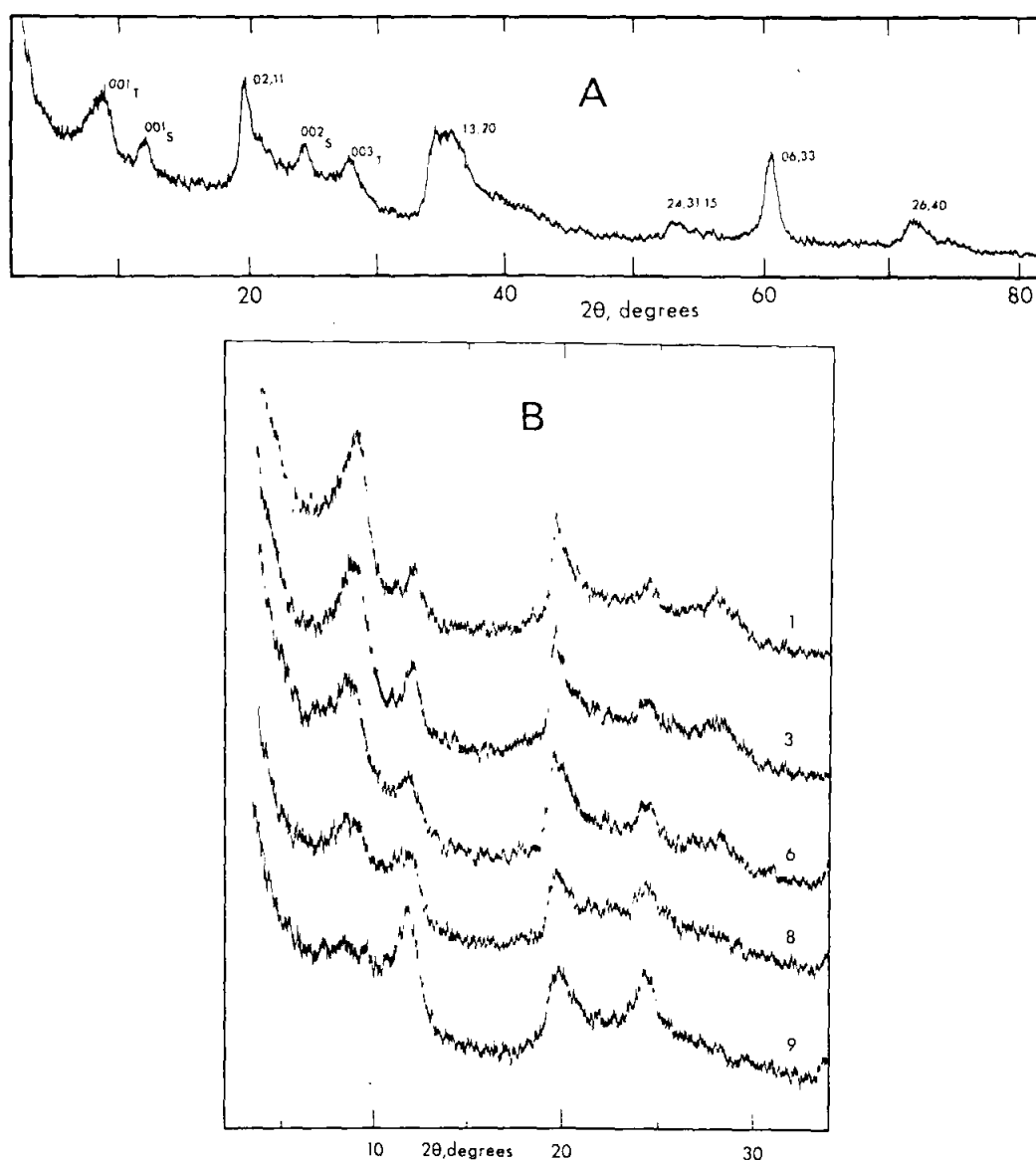


FIG. 2.17. X-ray diffractometer patterns of deweylites (Cu $K\alpha$ radiation). A. Indexed pattern with talc (T) and serpentine (S) basal reflections marked. Unmarked diffraction bands are common to both components. B. Lower angle diffraction patterns of deweylites with various proportions of the two components (after Bish and Brindley, 1978).

positions corresponding to the usual a - and b -parameters of these minerals and which overlap completely. The basal reflections corresponding to 7.2 and 10 Å spacings are generally broad and provide the only X-ray evidence for the individual components. If either component is present to a minor extent, for example less than 20%, its basal reflections may not be obvious. Also the basal reflections may be so broad, due to small crystal size and/or structural disorder, that they are barely recognizable or not recognizable as separate reflections. Chemical and X-ray data (Fig. 2.17) for a range of deweylites with different ratios of the components are given by Bish and Brindley (1978). The 1:1 component is probably related most closely to lizardite, but chrysotile is not excluded, and the 2:1 component is probably kerolite.

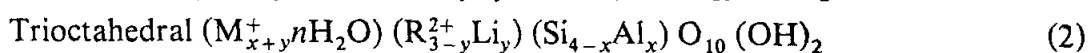
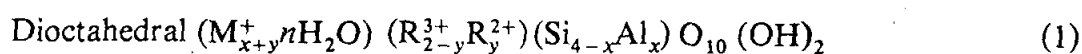
Garnierites, like deweylites, are generally intimate mixtures of 1:1 and 2:1 type layer silicates. They contain a nickel content sufficient to give an obvious green coloration, pale green when the NiO content is no more than 1–2%, but dark green when the NiO is a major chemical component. Similar difficulties exist in identifying the component minerals as in the case of deweylites. Commonly the 1:1 type mineral, a serpentine mineral, is likely to belong to the lizardite–nepouite series, and the 2:1 type mineral is talc-like and will belong to the kerolite–pimelite series. Garnierites therefore can be regarded in many cases as nickel-containing deweylites. The term garnierite is used also as a field term in a broad general sense to describe any fine grained, clay-like material containing nickel and with characteristic green color; in this broad sense it may cover nickel-containing smectites and sepiolite, minerals which are easily recognized by appropriate X-ray diffraction tests. This broader use of garnierite has been recommended particularly by Pecora *et al.* (1949) and Faust (1966). The term “garnierite group” also is sometimes used to cover all fine-grained, nickel-containing hydrous silicates, but this usage of “group” is not recommended because it groups together minerals which are structurally different and have only a common chemical feature. However, the main problem in describing garnierites lies in recognizing mixtures of 1:1 and 2:1 layer silicates and their respective proportions when only the first order basal reflections are likely to resolve the components. The other diffraction features are the broadly spreading hk diffraction bands which overlap completely for the two components. The nomenclature of the nickel-containing layer silicates was reviewed by Brindley and Maksimovic (1974).

8.5 Smectites—general considerations

8.5.1 Chemical compositions and mineral species

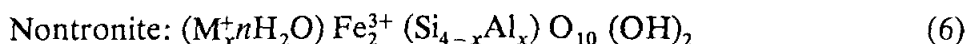
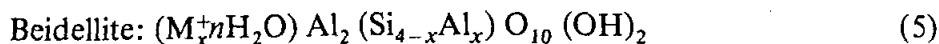
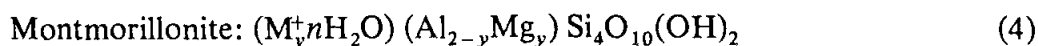
The 2:1 type layers of smectites have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions of ions of the same valence, notably Mg–Fe(II) and Al–Fe(III) substitutions, are common in octahedral positions. Coupled substitutions also occur such as $\text{Fe}^{3+} + \text{O}^{2-}$ replacing $\text{Fe}^{2+} + (\text{OH})^-$ which is equivalent to a combined oxidation–dehydration process. Anion substitutions, particularly F^- for $(\text{OH})^-$, are not common in natural smectites but are utilized in synthetic materials. Substitutions by ions of lesser charge, notably Si^{4+} by Al^{3+} in tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, produce resultant negative charges on the layers which are balanced by interlayer cations; these are commonly Na^+ , Ca^{2+} and Mg^{2+} ions but a wide range of other cations, including organic ions, can be introduced by exchange reactions.

General formulae for di- and trioctahedral smectites are as follows:



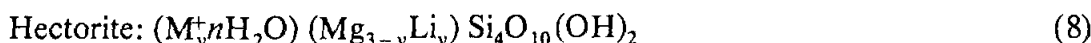
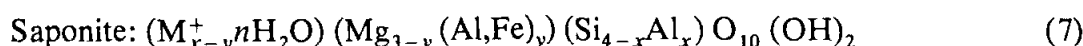
The exchangeable cations are shown as monovalent ions, M^+ , but equivalent numbers of other valent ions can be substituted; they are shown hydrated by nH_2O which also includes interlayer water not specifically associated with the ions. R^{2+} ions are commonly Mg and Fe(II) but other ions such as Ni and Zn can enter these positions. R^{3+} ions are commonly Al and Fe(III). Li^+ is the only monovalent ion to enter octahedral positions.

The following are end-member compositions for the more important dioctahedral smectites:



Intermediate compositions are common. In the montmorillonite-beidellite series, most compositions are on the montmorillonite side of the 1:1 mole ratio and compositions near the beidellite end-member are rare.

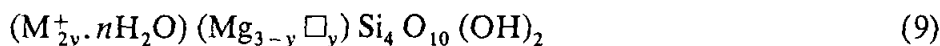
The following are the more important trioctahedral smectites:



Hectorite is analogous to montmorillonite. Saponite with a negative tetrahedral charge is, in this respect, analogous to beidellite; the negative charge is balanced partly by a positive octahedral charge and in this respect saponites resemble vermiculites (see later).

Structural formulae are derived from chemical compositions usually by assuming a total cation valence of +22 in accordance with the anion ratio $O_{10}(OH)_2$. This procedure was used by Ross and Hendricks (1945) in their now classical study of the "*Minerals of the montmorillonite group*" with "montmorillonite" used in the general sense. Allocation of cations to tetrahedral, octahedral and interlayer positions follows the usual principles of crystal chemistry but care must be taken in the allocation of ions such as Mg^{2+} which can occupy both octahedral and interlayer positions, as Foster (1951) emphasized. Méring (1975, p. 106) showed that small proportions of impurities can have large effects on structural formulae.

Stevensite has a formula of the type



according to Faust and Murata (1953) and Faust *et al.* (1959), and the layer charge appears to arise from a deficiency of octahedral cations. However, there is evidence for inhomogeneity in the sequence of layers which makes a detailed interpretation of the structure difficult to obtain (Brindley, 1955). Further discussion of stevensite is given in Section 8.10.

8.5.2 X-ray data

X-ray powder patterns of smectites show mainly basal 00 l diffractions and two-dimensional hk diffraction bands. The character of the observed pattern depends on whether a thin, well-oriented layer or a randomly oriented powder is used. The identification of smectites as a group turns mainly on the basal reflections (spacings) which depend on the nature of the interlayer cations, the degree of hydration of the cations, and the presence of liquids other than water purposely introduced as part of the identification process (see Chapter 3). Unless particular care is taken to control the ambient humidity, the interlayer hydration is likely to be variable from layer to layer and the resulting basal reflections will not conform to integral orders of diffraction in accordance with the Bragg reflection law. Therefore the use of a liquid such as ethylene glycol

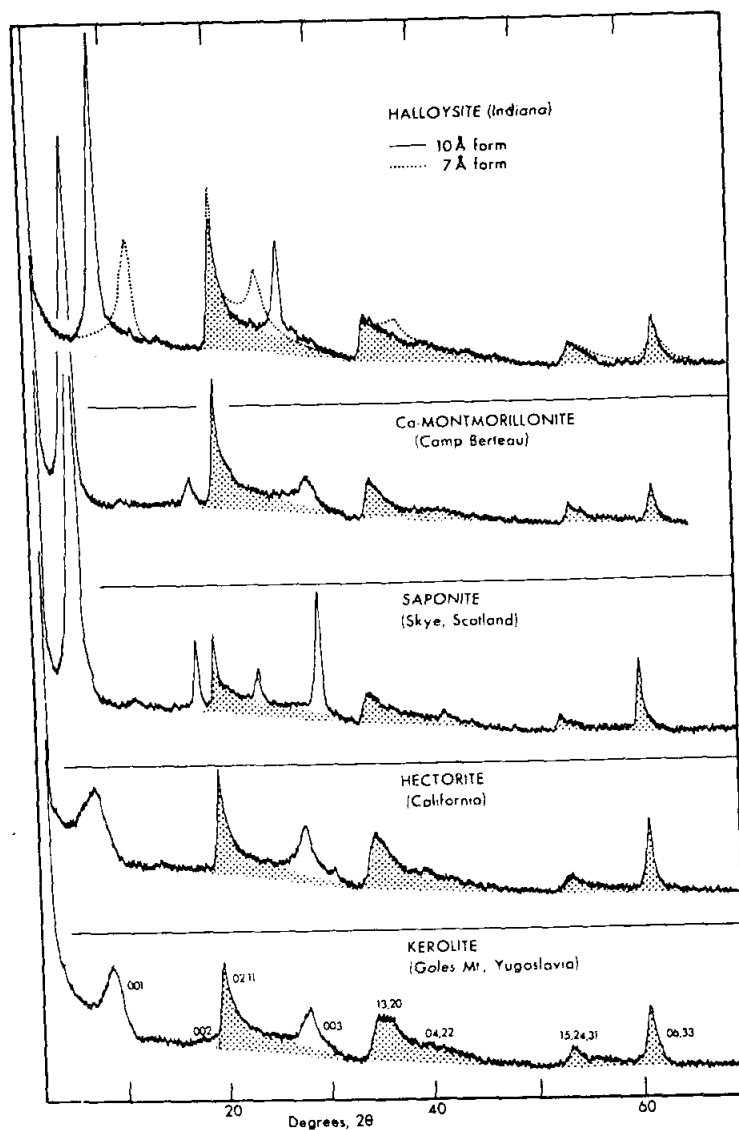


FIG. 2.18. X-ray diffractometer patterns of halloysite, 7 Å and 10 Å forms, of three smectites, Ca-montmorillonite, saponite, and hectorite, and of kerolite. The two-dimensional diffraction bands are stippled to emphasize their similarity. Cu $K\alpha$ radiation.

or glycerol which expands the basal spacings to constant values near 17 Å is an important step in the identification process.

The two-dimensional hk bands arise from the random stacking of the layers in most smectites. These bands are seen in the patterns shown in Fig. 2.18 which were recorded under ambient conditions of temperature and humidity and with the powders more-or-less randomly oriented. Certain smectites, however, have been found which exhibit ordered stacking arrangements and give hkl diffractions, but they seem to be exceptional cases. Beidellite and saponite samples have been found which show this higher degree of order; both of these minerals have layer charges which arise from tetrahedral substitutions. Apart from these exceptional cases, smectites generally show only $00l$ and hk diffractions. Many of the hk bands do not provide sharp features which permit precise measurements. Table 2.7 records the spacings corresponding to the low-angle termination of the bands. As we have seen already in the discussion of halloysite, the 06,33 band is usually sufficiently sharp to permit a measurement of $d(060)$ accurate to about 0.25% and from this result the b -parameter is obtained; $b = 6 \times d(060)$. Hence a distinction can be made between dioctahedral and trioctahedral smectites. However, it is important not to overlook

TABLE 2.7. Non-basal diffractions from smectites; spacings in Å

1 <i>hk</i> indices	2 <i>d(hk0)</i> calc.	Montmorillonites						6 Nontronite		7 Hectorite		8 Stevensite		9 Saponite	
		3 <i>d</i>	<i>I</i>	4 <i>d</i>	<i>I</i>	5 <i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
02, 11	4.51	4.61	10	4.51	10	4.49	8	4.56	10	4.58	10	4.54	10	4.51	8
13, 20	2.065	2.56	8	2.61 2.55	10	2.57	4	2.64 2.56	8	2.66	8	2.618	9	2.58	5
04, 22	2.255	2.22	3	2.244 2.159	2	2.242	1			2.289	1	2.279	2	2.26	1
15, 24, 31	1.706	1.692	6	1.711 1.685	5	1.699	2	1.718 1.671	2	1.751 1.692	5	1.725	4	1.72	3
06, 33	1.503	1.492	10	1.500	10	1.504	6	1.521	10	1.530	10	1.520	9	1.52	9
26, 40	1.302	1.289	6	1.295	5	1.294	1	1.321 1.302	1	1.323 1.304	7	1.314	7	1.31	5
17, 35, 42	1.252	1.244	6	1.250	5	1.250	1	1.260	1	1.269	1	1.265	2	1.26	1
08, 44	1.127	1.120	3	—						—		—			
28, 37, 51	1.036	1.029	3	—						—		1.047	1	1.05	1
19, 46, 53	0.984	0.976	4	0.972	1					0.992	2	0.994	3	0.99	3
0, 10; 55	0.902	—		—						—		—			
39, 60	0.868	0.864	2	0.865	1					0.880	2	0.879	3	0.88	4
	<i>a</i> 5.21	5.17		5.18		5.21		5.24		5.25		5.26			
	<i>b</i> 9.02	8.95		9.00		9.02		9.13		9.18		9.12		9.12	

2 Calculated with *a* 5.21, *b* 9.02 Å.

3 Montmorillonite, Wyoming. MacEwan (1961).

4 Montmorillonite, Unterrupsroth, Nagelschmidt (1938), with Å in place of kX units.

5 Montmorillonite, Chambers, Arizona. Earley, Osthaus and Milne (1953).

6 Nontronite, Nontron, France. Nagelschmidt (1938).

7 Hectorite, Hector, California. Nagelschmidt (1938). Previously named Mg-beidellite.

8 Stevensite, Springfield, New Jersey. Brindley (1955).

9 Saponite, Milford, Utah. Cahoon (1954).

that this diffraction feature is still a two-dimensional diffraction effect and the profile usually shows some asymmetry related to the process by which it is formed. Measurements of *b* claimed to be accurate to 0.1% or better must be viewed cautiously.

8.6 Montmorillonite

8.6.1 X-ray studies

Montmorillonite is by far the commonest of the smectite group of minerals, and for many years was used as the group name. However, to avoid possible confusion between the general and the specific use of the term, smectite is now generally preferred as the group name and montmorillonite is used for a dioctahedral Al,Mg smectite with the layer charge arising mainly from the Mg-for-Al substitutions in the octahedral positions.

X-ray diffraction studies of the swelling of montmorillonite in water, in humid atmospheres, and in organic liquids are described in Chapter 3. X-ray studies of interstratified minerals in which montmorillonite is one component are described in Chapter 4. The nature of the mineral, particularly its turbostratic structure, is such that purely structural studies (apart from those which involve swelling) are very restricted.

The layer structure of montmorillonite described by Hofmann, Endell and Wilm (1933), Marshall (1935), Maegdefrau and Hofmann (1937), Hendricks (1942), Hofmann and Hausdorf (1942), consists of a dioctahedral 2:1 layer with charge-balancing and exchangeable cations

located between the layers. Precise confirmation of the structure by the usual methods of diffraction analysis is difficult because of the variable basal spacings usually found and the turbostratic stacking of the layers.

By using carefully prepared thin layers of montmorillonite and controlled humidity conditions Pezerat and Méring (1954, 1967), using monochromatic Mo $K\alpha$ radiation, recorded up to 18 orders of basal reflections for Na- and Ca-montmorillonite. This number of reflections is many more than are usually obtained and is an indication of the regularity of the basal spacing under the conditions used. Fourier syntheses of electron density normal to (001) confirmed the 2:1 layer structure and allowed some conclusions regarding the interlayer arrangements but the small number of interlayer cations as compared with those in micas made precise evaluation of the interlayer structure uncertain. However, by using difference Fourier series, the Na ions were located at nearly the same levels in the anhydrous and hydrated phases and close to or partially within the hexagonal cavities of the Si—O tetrahedral sheets. The interlayer water molecules, even in the "single layer" hydrate, were found to lie at two levels. Mamy (1968) suggested that the water molecules may be organized in a tetrahedral manner with respect to the oxygens of the 2:1 layers. For Ca-montmorillonite, Pezerat and Méring found that the Ca ions were located in the hexagonal cavities in the anhydrous mineral but entered the water layers in the hydrated mineral. Evidently the higher hydration energy of the Ca^{2+} ion as compared with that of the Na^+ ion causes the Ca^{2+} ions to form hydration complexes with the water molecules.

The hk diffraction bands of montmorillonite (and of other smectites) are not well suited to structure analysis. X-ray structure factors cannot be evaluated directly because of the nature of the diffraction process (see Section 4.5) and also because each observed band is a summation for several hk index pairs. Only a "trial and error" procedure is possible in which bands are calculated for different structure models and compared with the observed data. The process is rendered uncritical by overlapping of many index pairs. Despite these shortcomings, the method was applied by Longuet-Escard *et al.* (1960) and Méring and Brindley (1967) to Na-, Ca-, Cs-, and Ba-montmorillonite in the anhydrous state and in several states of hydration. The main results were as follows: monovalent ions tend to remain more or less associated with the silicate layers when hydration occurs but divalent ions tend to move into the water layers. This conclusion agrees with that obtained from the basal reflections. The band profiles vary with the state of hydration in a manner which indicates some degree of organization of the water molecules; the results do not support a random or liquid-like arrangement of the water. The different swelling behaviors of monovalent and divalent ion montmorillonites are consistent with the monovalent ions remaining near the silicate layers and the divalent ions entering the water layers. Thus the silicate layers and their associated monovalent ions behave more or less like neutral entities; the layers become fully dispersed in water and basal spacings are no longer observed. Divalent ion clays dispersed in water retain a basal spacing; the clay is dispersed in small packets and surface area determinations in the dispersed state, for example by methylene blue adsorption measurements (Pham Thi Hang and Brindley, 1970; Brindley and Thompson, 1970) indicate that the packets generally comprise about 4–5 layers. X-ray diffraction measurements utilizing the Scherrer equation also indicate similar small packets. Divalent ions link pairs of layers together by satisfying two negative charges in a manner which monovalent ions cannot copy.

Dispersion studies show that K-saturated montmorillonites behave differently from other monovalent ion montmorillonites in that the K^+ ions tend to be "fixed" i.e., not easily replaceable, by the usual cation exchange reactions. Mamy and Gaultier (1975) demonstrated that when K-montmorillonite was subjected to alternate wetting and 80°C drying cycles, the basal spacing

diminished irreversibly to about 10 Å, the exchange capacity diminished to about one-third of its initial value and the initially disordered stacking of the layers became increasingly ordered. This ordering requires rotations of layers up to 30° so that they fit together more or less in the manner found in micas. The high degree of order, although still retaining arbitrary rotations from layer to layer of $n \times 60^\circ$, is shown in both X-ray and selected area electron diffraction patterns.

8.6.2 Electron optical data

Electron optical methods furnish valuable additional information on the crystal form and structure of montmorillonite and of smectites generally. In the electron microscope, montmorillonites are seen as finely divided, platy forms usually with poorly defined outlines and very crumpled layers. When suitably dilute dispersions are allowed to dry on a substrate, the individual crystals lie with their basal surfaces well oriented but randomly arranged with respect to each other. Electron diffraction patterns show sharply defined rings corresponding to $hk0$ indices from which the b parameter of the mineral can be accurately determined. The results may be more accurate than X-ray powder measurements based on the relatively sharp 06,33 diffraction band which is not strictly the 060 reflection. The electron diffraction ring pattern is not directly applicable to structure analysis because each ring is a superposition of several hk index pairs.

Two methods can be used to obtain more detailed information and both provide partial single crystal data. Extremely thin dispersions of montmorillonite and the selected area diffraction method enable single crystal spot patterns showing individual $hk0$ diffractions to be obtained. The resulting pattern indicates the symmetry of the layer structure when projected on (001). This method has been used by Oberlin and Méring (1962) and Méring and Oberlin (1967). Since montmorillonite is a dioctahedral mineral, three arrangements of the two octahedral cations per formula unit are possible; if the possible octahedral positions are labeled A, B and C, the occupied sites may be A and B, B and C, or C and A. In projection on (001), two of these arrangements have the symmetry cm and the third has the symmetry $c2mm$. These symbols define two-dimensional symmetry groups. Oberlin and Méring found the symmetry cm for a Wyoming montmorillonite. Single particles of other montmorillonites, however, gave patterns showing hexagonal symmetry both in the distribution and in the intensities of the diffractions. The generally accepted 2:1 layer structure of montmorillonite cannot exhibit hexagonal symmetry. Oberlin and Méring suggested that edge-to-edge associations of primary particles randomly rotated through $n \times 60^\circ$ might be the cause of the apparent higher symmetry. Cowley and Goswami (1961) also obtained similar hexagonal patterns and they suggested that owing to curvature of the layers (montmorillonite particles often show such curvature) the octahedral and tetrahedral sheets may diffract incoherently, i.e., behave as independent diffracting units. The suggestion of edge-to-edge associations is equivalent to a process of twinning and similar results were obtained by Mansfield and Bailey (1972) for kaolinite (see Chapter 1, Section 2.5.2).

However, whether or not the hexagonal patterns are correctly explained, the pattern with symmetry cm has still to be considered. Roberson and Towe (1972) failed to obtain confirmatory evidence and suggested that the layer symmetry may be lower, namely triclinic, with a projected symmetry $p2$. Güven (1973, 1974) emphasized that in experiments where the SAD technique is used to isolate individual crystals showing good spot patterns, there is a possibility that the selected crystals giving the best patterns may be impurities of mica or other layer silicates present in very small amounts. Zvyagin (1967, p. 327) also cautioned that "the possibility of finely dispersed sericite impurity . . . should not be ruled out."

The second approach uses the method of oblique incidence on a thin layer of well-oriented

particles, i.e., the sample giving the concentric ring pattern with normal incidence is turned to give oblique incidence. This method gives information with respect to the z^* direction in reciprocal space, but is still limited in its usefulness because of the superposition of data for several hk index pairs. In the case of montmorillonite, however, it is confirmed that the dehydrated layer structure formed by the high vacuum of the instrument is indeed turbostratic.

8.7 Beidellite, nontronite

These minerals have layer charges which arise principally from Al-for-Si substitutions in the tetrahedral sheets. Beidellite has principally Al ions in octahedral sites, and nontronite principally Fe(III) ions in these positions; a beidellite-nontronite series with intermediate compositions is found.

Pure or nearly pure end-member beidellite is rare. The best known example, from the Black Jack Mine, Idaho, was studied in detail by Weir and Greene-Kelly (1962). It has the formula $R_{0.46}^+ (Al_{1.98}Fe(III)_{0.02}Mg_{0.01}) (Si_{3.48}Al_{0.52}) O_{9.98} (OH)_2$. X-ray powder data by photographic recording showed 00 l and hkl diffractions which indicated an unusually well-ordered layer stacking arrangement (Table 2.8). For a Ca-saturated and glycerol expanded sample, 02 l , 20 l , 04 l and 24 l diffractions were recorded and were indexed with an orthogonal cell with $b = \sqrt{3}.a = 8.99 \text{ \AA}$, $c = 17.6 \text{ \AA}$. A similar beidellite from New South Wales studied by Hamilton (1971)

TABLE 2.8. X-ray powder data for beidellite; spacings in $\text{\AA}$

1	2	3	4	5	6
$d(\text{obs.})$	$d(\text{calc.})$	hkl	$I(\text{obs.})$	$d(\text{obs.})$	$I(\text{obs.})$
17.57	17.57	001	10		
4.42	{ 4.48 4.35 }	{ 020, 110 021 }	10	4.48	10+
3.95	3.99	022	10	band	
3.54	3.56	023	10	3.5	—
3.17	3.15	024	2		
2.76	2.77	025	1		
2.57	{ 2.59 2.56 }	{ 200, 130 201 }	8	2.564	10
2.52	2.48	202	10	band	
2.36	2.37	203	8	2.37	5
2.24	{ 2.23 2.24 }	{ 204 040, 220 }	2	{ 2.24 band }	2
2.19	{ 2.22 2.17 }	{ 041 042 }	2	{ band 2.12 }	1
1.693	{ 1.695 1.687 }	{ 240, 310, 150 241 }	6	1.691	1
1.663	1.664	242	8	1.662	4
1.623	1.628	243	6	1.62	
1.573	1.581	244	1		
1.528	1.526	245	1		
1.498	1.498	060, 330	10	1.497	4
1.293	1.295	400, 260	8 band	1.290	2
1.243	1.244	420, 350, 170	8	1.244	1½
1.122	1.121	440, 080	2	1.120	½
1.028	1.028	370, 510	2	1.029	2
0.979	0.979	460, 530, 190	2 band	0.971	3½
0.864	0.863	390, 600	4	0.896	1

Columns (1)–(4). Ca-beidellite, glycerol saturated, Black Jack Mine (Idaho). $d(\text{calc.})$ from orthorhombic cell, a 5.18, b 8.99, c 17.57 $\text{\AA}$, Weir and Greene-Kelly (1962). Intensities from A. H. Weir, Thesis (London) 1960.

Columns (5), (6). NH_4 -beidellite, air-dry condition, Swansea (N.S.W.). Hamilton (1971).

showed many *hkl* reflections sufficiently well for the parameters *a*, 5.16 Å, and *b*, 8.98 Å, to be determined. Basal spacings for hydration complexes and glycerol complexes were measured up to high orders of diffraction, up to 0,0,21; regrettably, Fourier syntheses were not derived. The net layer charge, $-0.44/\text{O}_{10}(\text{OH})_2$, was very similar to that of the Black Jack Mine beidellite, but was distributed with -0.29 in tetrahedral positions and -0.15 in octahedral positions. Hofmann *et al.* (1955) previously had recognized *hkl* diffractions from a beidellite from Unterrupsroth, Bavaria, with tetrahedral charge -0.45 , octahedral charge -0.13 , but another sample with tetrahedral charge -0.28 , octahedral charge -0.15 , showed only *hk* diffraction bands. Glaeser *et al.* (1967) found layer stacking order in a beidellite from the same locality when saturated with Na^+ or Li^+ ions, in the anhydrous state and when expanded homogeneously with one or two water layers, but not when saturated with Ca ions. Formation of *hkl* diffractions requires not only orderly stacking of layers, but also uniform layer spacings. With Na^+ and Li^+ ions in the inter-layer positions, regular layer spacings were obtained, but not with Ca^{2+} . No explanation was given for the lack of regular spacings with Ca ions.

Nontronites with similar tetrahedral layer charges appear to be turbostratic structures, i.e., without orderly layer stacking arrangements. Hofmann (1955, 1956) recorded only *hk* diffraction bands from nontronites. Méring and Oberlin (1967) examined individual ribbon-like crystals of nontronite from Pfaffenreuth, Germany, by electron diffraction, using the SAD technique, and obtained a spot pattern consistent with a projected layer symmetry *c2mm*. The observed and calculated *hk0* intensities were not in good agreement when the idealized layer structure was used, but better agreement was obtained when the tetrahedral groups were given rotations of $\pm 12^\circ$ (cf. discussion in Chapter 1, Section 1) and the octahedral groups were modified in the manner found in other dioctahedral layer structures. Evidently electron diffraction spot patterns obtained by the SAD technique can provide data suitable for a partially refined structure analysis at least for the *x*- and *y*-coordinates of atoms, but they give no information about *z*-coordinates.

The oblique incidence technique gave results very similar to those for montmorillonite and confirmed the turbostratic nature of the structure indicated by the X-ray powder data.

8.8 Saponite

The general formula of this trioctahedral smectite is given in Section 8.5.1. With principally tetrahedral substitution, saponite is analogous to beidellite and like beidellite may exhibit partial order in the stacking of the layers, at least when appropriate interlayer cations are present and appropriate conditions of hydration are used. A saponite from Utah, with randomly stacked layers and with mainly tetrahedral substitution was described by Cahoon (1954). Weiss, Koch and Hofmann (1955) indexed the powder diagram of a saponite from Groschlattengrün with a monoclinic cell, *a* 5.3, *b* 9.2, *c* 30.7 Å, $\beta \simeq 97^\circ$, with two hydrated layers per unit cell, and very similar to vermiculite. Broadening of reflections with the index $k \neq 3n$ was attributed to random layer displacements of type *pb*/3. Oblique incidence electron diffraction data (Zvyagin, 1967, p. 311) indicated a unit cell with *a* 5.29, *b* 9.19, *c* 10.3 Å, $\beta = 100^\circ$, with one anhydrous layer per unit cell. Suquet *et al.* (1975) studied in detail an exceptionally well-ordered saponite from Kozákov, Czechoslovakia, with approximate formula $\text{Ca}_{0.22}(\text{Mg}_{2.50}\text{Fe}_{0.26}^{2+}\text{Fe}_{0.24}^{3+})(\text{Si}_{3.30}\text{Al}_{0.68}\text{Fe}_{0.02}^{3+})\text{O}_{10}(\text{OH})_2$. The sodium-saturated form gave exceptionally good patterns corresponding to a unit cell with *a* 5.333, *b* 9.233, *c* 15.42 Å, $\beta = 99.66^\circ$, containing one silicate layer and two sheets of interlayer water molecules. Table 2.9 gives the powder diffraction data for this exceptional saponite. Fully random, partially random and well-ordered layer stacking arrangements were found to depend on the degree of hydration

TABLE 2.9. X-ray powder data for Na-saponite, monoclinic with two water layers, from Kozákov, Czechoslovakia (Suquet *et al.*, 1975); spacings in Å

<i>d</i> (obs.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i> (obs.)
15.29	15.32	001	10+
7.65	7.66	002	3
5.10	5.10	003	3
4.61	{ 4.616 4.595 }	{ 020 110 }	10
4.529	4.528	$\bar{1}11$	1
4.418	4.420	021	1
4.284	4.284	111	5
4.125	4.127	$\bar{1}12$	5
3.954	3.954	022	2
3.828	3.829	004	2
3.599	3.600	$\bar{1}13$	1b
3.424	3.424	023	2
3.256	3.256	113	2
3.063	3.063	005	5b
2.662	2.662	$\bar{2}01$	1
2.648	2.648	200	7
2.598	2.598	$\bar{2}02$	5
2.560	2.560	201	8
2.418	2.418	202	8
2.307	2.307	$\bar{2}04$	3
2.245	2.247	203	3b
2.126	2.128	134	1b
1.745	1.746	$\bar{3}11$	5
1.726	1.726	$\bar{2}42$	2
1.715	1.714	241	2
1.702	1.702	311	2
1.5389	1.5288	060	10
1.5320	1.5317	$\bar{3}32$	9
1.5092	{ 1.5093 1.5090 }	{ $\bar{3}33$ 331 }	3

d(calc.) from monoclinic cell, *a* 5.333, *b* 9.233, *c* 15.42 Å, β 96.66° Monochromatic Co *K* α radiation. Guinier-DeWolff camera. Si as standard.

and on the nature of the interlayer cations. Random stacking increases in the following cation sequences for different hydration states:

With 3 sheets of interlayer water: Mg < Ba < Ca

With 2 sheets of interlayer water: Na < Mg < Ca < Ba < Li

With 1 sheet of interlayer water: Na = K < Ca = Ba < Mg < Li

With 0 sheets of interlayer water: K = Ba < Na

Thus the sodium form gives optimum ordering with one or two sheets of interlayer water and the potassium form with anhydrous saponite. The Kozákov saponite, with high tetrahedral charge -0.70 partly compensated by an octahedral charge $+0.24$, comes close to being a vermiculite, but on the basis of the net layer charge it is classified as a smectite.

The diminished ordering in the cation sequences listed previously is not easily explained. Large monovalent cations with small electrostatic fields evidently favor layer stacking order, and cations with high fields and therefore with strong hydration tendencies give less ordered or even turbostratic stacking. Evidently, in some manner not yet known, the ordering is governed by the

water molecules. Suquet *et al.* suggest that chains of water molecules form links between the silicate layers, but the model so far is hypothetical.

In a later study, Suquet *et al.* (1977) prepared synthetic saponites in order to explore the dependence of layer stacking order on the magnitude and distribution of the layer charges. Unfortunately the "theoretical" layer charges derived from the gel compositions used did not always agree with the observed cation exchange capacities, possibly because amorphous materials were formed in some of the syntheses. The results show some correspondence with those obtained from the Kozákov saponite as regards the effect of different cation substitutions. Three-dimensional order decreases, and the expansion of the basal spacing by solvation, whatever liquid is used, increases as the charge decreases. At present it seems scarcely possible to draw any firm conclusion regarding the role of tetrahedral charge as compared with total charge in determining the degree of order-disorder in layer stacking. Generally the synthetic products gave less well-ordered layer stacking than the natural Kozákov material.

8.9 Hectorite

Hectorite is a trioctahedral smectite with principally octahedral substitutions of Li^+ for Mg^{2+} ions and is the trioctahedral analog of montmorillonite. A continuous series between hectorite and saponite, analogous to that between montmorillonite and beidellite or nontronite is unlikely because of the unusual Li-for-Mg substitution in hectorite. All available evidence points to fully random stacking of layers in hectorite. However, this random stacking does not inhibit the regularity of basal spacings; Kadi-Hanifi and Méring (1972) made a one-dimensional Fourier synthesis of an anhydrous, Li-saturated hectorite from Hector, California, using eleven orders of 00l. The results agree very well with a synthesis calculated from the accepted 2:1 layer structure.

Electron optical studies of hectorite (Oberlin and Méring, 1966) show that individual crystals form long laths extending parallel to the x -axis which often are associated parallel to their length with small rotations of the order of 8° about the common x -axis. With normal beam electron diffraction on thin layers the parameters $a = 5.25 \pm 0.01$ and $b = a\sqrt{3} = 9.09 \pm 0.02$ Å were determined. With the oblique incidence technique, elliptical patterns were obtained which showed variations of intensity that at first sight might suggest some degree of layer stacking order. Detailed analysis, however, showed that these variations represented only the variations of the layer structure factors and were consistent with random layer stacking. Synthetic hectorites including fluorine-substituted varieties have been prepared by several investigators including Granquist and Pollack (1960), Neumann (1965), Neumann and Sanson (1970, 1971), Barrer and Jones (1970, 1971). For synthetic fluor-hectorite Neumann (1965) gave a formula of the type $\text{M}_{0.35}^+ (\text{Mg}_{2.68}\text{Li}_{0.30}) \text{Si}_4\text{O}_{10}(\text{F}_{1.25}\text{OH}_{0.75})$. This material to which the name "Laponite" has been given, gives an X-ray diffraction pattern comprising 00l basal reflections and hk diffraction bands; the estimated lattice parameters are a 5.23 Å, b 9.08 Å and c is variable with values depending on the exchangeable cations and the relative humidity or solvating liquid. These materials have interesting rheological properties, but their structural characteristics are essentially the same as those of natural hectorites.

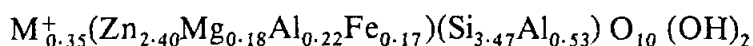
8.10 Other smectites

Under this heading, some less common smectites can be mentioned briefly. For the most part they are chemical varieties involving cations such as Cr, Ni, Cu, Zn. Their a and b lattice parameters are not strikingly different from those of other smectites and their identification depends on chemical analyses, with supporting X-ray diffraction data.

Volkhonskoite. This mineral, which appears with various spellings in the literature, is a

chromium-bearing dioctahedral smectite. The name is properly used when chromium is the dominant octahedral cation; the Cr_2O_3 content is then likely to exceed 15 weight percent. From a survey of published analyses (Brindley and Bish, in preparation), it appears that the layer charges arise from both tetrahedral and octahedral substitutions. Distinctions can be made between volkhonskoite, where chromian ions are dominant in octahedral positions, and chromian forms of other minerals, montmorillonite, beidellite, nontronite in which chromium is a significant but not dominant component. Important references to volkhonskoite include: Ross and Hendricks (1945), Weiss *et al.* (1954), Ross (1960), Bentor (1966). From the "best available analysis" quoted by Ross (1960, p. 226), the following formula is derived: $\text{Ca}_{0.28}(\text{Cr}_{1.01}\text{Fe}_{0.41}^{3+}\text{Al}_{0.36}\text{Mg}_{0.07}\text{Ni}_{0.04})(\text{Si}_{3.38}\text{Al}_{0.12})\text{O}_{10}(\text{OH})_2 \cdot 1.08\text{H}_2\text{O}$. The octahedral cations add to only 1.89, so there are some doubts regarding the purity of the material or the analysis. The *a*- and *b*-parameters of this sample are not known, but for other samples, values of *b* in and near the range 8.95–9.05 Å are consistent with the dioctahedral structure; the precise value will be related to the proportions of Cr and other ions present, but a definitive relation between Cr content and *b*-parameter is not available.

Sauconite. A zinc-containing, trioctahedral smectite was studied by Ross (1946). As in saponite, the layer charge arises principally from Al-for-Si substitutions. A typical formula is:



The parameters *a* 5.35, *b* 9.28 are from data by Faust (1951). Other samples give *b* in the range 9.27 ± 0.02 Å which is consistent with the trioctahedral character of the mineral.

Medmontite. Although medmontite was, at one time, thought to be a copper-containing smectite (Chukhrov and Anosov, 1950), subsequent work has shown that medmontites are variable mixtures of chrysocolla and mica (see further discussion in Section 7.6).

Stevensite. This trioctahedral magnesian smectite was studied by Faust and Murata (1953) who gave the formula $\text{M}_{0.15}^{+}(\text{Mg}_{2.88}\text{Mn}_{0.02}\text{Fe}_{0.02}\square_{0.08})\text{Si}_4\text{O}_{10}(\text{OH})_2$. The formula indicates that the layer charge arises from a small deficiency in octahedral cations rather than from cation substitutions. An apparently similar material was synthesized earlier by Strese and Hofmann (1941). Further examination by Brindley (1955) of stevensite from the same locality as that studied by Faust and Murata showed that the structure was interstratified in a partially regular manner with non-swelling and swelling layers, for which at that time talc and saponite seemed adequate descriptions. Faust, Hathaway and Millot (1959) disagreed with this interpretation and preferred to describe the mineral as "a random or statistically disordered distribution of the vacant sites in the sheets of octahedrally coordinated atoms which would give a small proportion of domains with few or no vacancies and which have the attributes of talc". However, a "statistically disordered distribution" of a few talc-like domains does not account for the partially ordered distribution of two kinds of layers necessary to explain the observed long spacing, the existence of which has been re-confirmed. Stevensite from Japanese sources was studied extensively by Imai *et al.* (1970); they gave a formula showing 2.72 octahedral cations per formula unit and also found evidence for a long spacing indicating again a partially ordered interstratification of non-identical layers. They noted also a close relationship between stevensite and sepiolite discussed previously by Randall (1959). This relationship has been studied further by Güven and Carney (1977, 1979) who have followed the hydrothermal alteration of sepiolite to stevensite (or a similar smectite) and then to talc. The reaction is probably topotactic and gives rise to domains of talc and smectite. In so far as the domains have a tendency to alternate in the stacking sequence, a possible explanation is obtained for the observed long spacing.

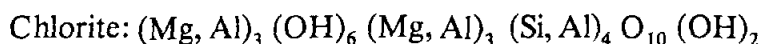
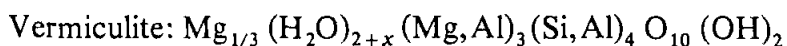
Lembergite. This name was given by Sudo (1954) to a ferrous iron-rich form of saponite. The composition of the sample studied was given as $(\text{Fe}_{1.45}^{2+}\text{Mg}_{1.52})(\text{Si}_{3.62}\text{Al}_{0.38})\text{O}_{10}(\text{OH})_2 \cdot (\text{Ca}/2)_{0.46}$. It could be objected that a special name is required only when $\text{Fe}^{2+} > \text{Mg}$ and that the composition is adequately described as a ferroan saponite. However, a similar mineral analyzed by Lemberg (1877, quoted by Sudo) has a somewhat higher iron content which would justify a particular name.

8.11 Vermiculites

Ordered structures of vermiculites are discussed in Chapter 1, Section 7.2. The present discussion is directed towards aspects of order-disorder in these minerals. On the basis of their resultant layer charge, vermiculites are intermediate between smectites and micas, and resemble smectites in showing reversible swelling in water and organic liquids. Vermiculites are usually trioctahedral minerals, though clay grade dioctahedral forms are known. Vermiculites have important tetrahedral and octahedral substitutions; the negative tetrahedral charge is compensated partly by the octahedral substitutions, and partly by the interlayer exchangeable cations and in this respect they are comparable with saponites.

The division between smectites and vermiculites is generally taken at a layer charge of -0.6 per formula unit. The identification of a mineral with respect to this division can be made on the basis of a total chemical analysis in which the interlayer cations are differentiated from those in the layers, or by a determination of the cation exchange capacity, or by determining the swelling of the basal spacing in water and in glycerol after saturating the clay with appropriate cations (Walker, 1957). When saturated with Mg^{2+} ions, vermiculites expand to about $15 \text{ \AA}$ in water and also in glycerol, whereas smectites similarly saturated expand to about $17\text{--}18 \text{ \AA}$. With K saturation, vermiculites may retain a $10 \text{ \AA}$ spacing in water whereas smectites will expand to $15 \text{ \AA}$. These properties are related to the electrostatic attractions between the layers and the interlayer ions, and expansion in water depends on the hydration energy of the interlayer ions. The division between smectites and vermiculites on the basis of a layer charge of -0.6 per formula unit corresponds therefore to an important difference in the physico-chemical properties. The question arises whether any distinction can be made between smectites with high layer charge and vermiculites with low charge. Mering and Pedro (1969) suggested that order or disorder of the isomorphous substitutions might be another distinguishing feature of these minerals, smectites having disordered arrangements and vermiculites ordered or partially ordered arrangements. The concept is interesting but difficult to apply as a practical method, and it also leaves a "blurred boundary" in so far as a degree of order is involved.

Vermiculites also have some similarities with chlorites, which is shown by writing the formulae as follows:



Whereas chlorites have interlayer sheets of octahedrally coordinated ions in a brucite-like arrangement, vermiculites have discrete octahedrally coordinated ions, $\text{Mg}(\text{H}_2\text{O})_6$, and the interlayers are more or less filled with water molecules. In the vermiculite formula as written above, $\text{Mg}_{1/3} (\text{H}_2\text{O})_2$ represents $1/3[\text{Mg} \cdot 6\text{H}_2\text{O}]$. The uncoordinated water has values of $x \approx 3$ so that $(2 + x) \text{ H}_2\text{O}$ in vermiculites approaches the $6(\text{OH})$ of chlorites. Minerals of intermediate type, such as swelling chlorites, may have both hydrated cations and hydroxide material in the interlayers, and their properties as regards swelling and thermal behaviour depend on the proportions of vermiculitic and chloritic material.

The formulae given above show that the interlayer cations in vermiculites are about 1/9 of those in chlorites. With $\text{Mg}_{1/3}$ per formula unit, there are statistically $\text{Mg}_{2/3}$ per unit cell or two Mg ions distributed over three unit cells. This number suggests a possible superlattice arrangement with the Mg ions occupying the centre and corners of a cell $3a \times b$. In this arrangement the Mg ions are distributed in a hexagonal manner at distances of b from nearest neighbors. Such a distribution could be generated by the mutual repulsions between the Mg^{2+} ions. Experimental evidence pointing to such an arrangement has been obtained by Alcover, Gatineau and Méring (1973). They recorded abnormal diffuse reflections between normal Bragg reflections for Mg- and Ni-vermiculite. The experiments used single crystal flakes, $4 \times 4 \times 0.3$ mm size, and monochromatic Mo $K\alpha$ radiation. A doubly-curved LiF monochromator gave almost point focusing of the X-ray beam. The diffraction patterns showed diffuse spots corresponding to a $3a \times b$ superlattice superimposed on the usual hexagonal pattern corresponding to the orthogonal $a \times b$ unit cell. The diffuse nature of the superlattice spots indicated ordering over small domains. The superlattice effects disappeared with dehydration and reappeared with rehydration. Evidently "these scatterings are indeed connected with the organization of the interlamellar layer (cations and water molecules)". The results suggest that on dehydration, the superlattice ordering is lost because the interlayer cations "take refuge" randomly in the nearest hexagonal cavities of the Si, Al-O tetrahedral sheets. A further interesting question is the possible relation of the interlayer cations to the distribution of negative layer charges. Alcover *et al.* concluded their discussion as follows:

"It must be accepted that the distribution of the exchangeable cations is connected with the distribution of the charges which they neutralize" and therefore "that the distribution of effective negative charges must also be at least partially ordered."*

Extensive studies by de la Calle, Suquet and Pezerat (1975) and by de la Calle *et al.* (1975) indicate interesting relations between layer stacking arrangements and the nature of the interlayer cations. Cations with high polarizing power such as Mg^{2+} and Ni^{2+} can form compact octahedral groups of water molecules with O-O distances sufficiently small to permit hydrogen bonding between the water molecules and between these molecules and the surface oxygens of the silicate layers. A relatively strong bonding mechanism develops from layer to layer favoring orderly stacking. The hydration groups tend to occupy positions opposite three-fold groups of surface oxygens and the resulting structure, as described in Chapter 1, has a two-layer unit cell in which successive layers are displaced alternately $+b/3$ and $-b/3$.

Cations with lower polarizing power and larger ionic radii such as Na^+ , Ca^{2+} , Ba^{2+} ions form less compact hydration groups which tend to lie opposite hexagonal holes of the silicate layers. Consequently they link successive layers together in somewhat the same way as the K ions in micas, with hexagonal holes of adjacent layers facing each other. Thus cation exchange reactions in vermiculites are less simple than exchange reactions in smectites and are likely to involve modifications of the layer stacking arrangements.

Similar considerations arise when a K-phlogopite is treated with strong salt solutions to produce vermiculites, or vermiculites are treated with strong KCl solutions and then heated at about 100°C to produce phlogopites. Phlogopites commonly have a $1M$ type structure, but $2M_1$ type phlogopites also occur. A $1M$ phlogopite treated with Mg^{2+} ions develops a V_1 type Mg-vermiculite (notation of de la Calle *et al.*) which resembles most natural vermiculites and exhibits layer stacking disorders; reciprocal lattice rows parallel to c^* , with indices hk , become diffused when $k \neq 3n$. In other words, the layers do not have a regular succession of displacements $+b/3$, $-b/3$, $+b/3$, ..., but there are "mistakes" in the sequence. Possibly the alteration from phlogopite to V_1 vermiculite takes place in domains, "out-of-step" with respect to each other.

* See also papers by Besson *et al.* (1973, 1974).

When treated with Na^+ or Ca^{2+} ions, $1M$ phlogopite develops a V_{III} type vermiculite which has an ordered structure corresponding to the Ia-2 chlorite structure in the Bailey-Brown notation. The reaction is a replacement of K^+ ions by hydrated Na^+ or Ca^{2+} ions without lateral displacement of layers; the structure expands normal to (001). When the initial phlogopite has the $2M_1$ structure, successive layers are rotated by $+120^\circ$, -120° . Replacement of K^+ ions by Mg^{2+} ions again involves $\pm b/3$ displacements with the possibility of disordered sequences occurring. Replacement of K^+ ions by Na^+ or Ca^{2+} ions lead to an ordered structure; $\pm b/3$ translations are not required and the resulting structure retains the 2-layer mica polytype character. Transformations between vermiculites of the same "parentage", such as $V_{\text{I}} \rightleftharpoons V_{\text{III}}$ derived from $1M$ phlogopite and $V_{\text{II}} \rightleftharpoons V_{\text{IV}}$ derived from $2M_1$ phlogopite, are relatively easy but there are differences in the kinetics; $V_{\text{III}} \rightarrow V_{\text{I}}$ goes more readily than the reverse process.[†]

8.12 Chlorites and intermediate structure types

Disorder in chlorites has been recognized since the first structure analyses of these minerals were made. Single crystal rotation diagrams taken with the crystal rotating around the z^* axis commonly show sharp spots on rows with $k = 3n$ and blurred spots or even continuous scattering along rows with $k \neq 3n$. These phenomena, already discussed in Section 5.1, indicate random layer displacements of $pb/3$ type, p being integral.

Between vermiculites and chlorites, there are wide possibilities for intermediate type minerals with properties which are likely to depend on the dominant character, vermiculitic or chloritic, of the interlayer material. Identification of such minerals will depend considerably on their behavior with respect to swelling agents, particularly water and ethylene glycol, and to heat-treatment. The importance of the interlayer material in determining the layer stacking mechanism is clearly shown by the data for vermiculite and from these results it is reasonable to expect that intermediate forms will show considerable layer stacking disorder.

8.13 Miccas, illites‡

A discussion of disorder in 2:1 type layer silicates cannot be complete without reference to miccas, and especially to illites which are clay-grade miccas usually resembling muscovite but with more SiO_2 , more H_2O and less K_2O than in the normal muscovite composition. Many names have been used in the past for these more hydrous miccas including hydromuscovite, hydromica, Glimmerton (German), etc., which are now covered by the name illite, suggested by Grim, Bray and Bradley (1937) as a non-specific term for clay-grade miccas. When attempts were made to give more precise definitions difficulties arose which Yoder and Eugster (1955) discussed critically. They recommended that the original broad description be retained and Bradley and Grim (1961) restated the original definition. In this sense, the term remains a useful one.

Most illites are dioctahedral and $2M_1$, $1M$, $1Md$, and $3T$ varieties are recognized (Levinson, 1955, and many later studies). Trioctahedral illites also are known (see, for example, Weiss *et al.*, 1956). Difficulties arise in determining the chemical and structural characteristics of illites, particularly those of $1Md$ type. Besides the difficulties inherent in obtaining suitably pure material for chemical analysis, there are also problems in finding a satisfactory basis for calculating structural formulae. Many illites are mixed-layer structures and the mixed-layering is not obvious when the proportion of admixed layers, usually montmorillonite, is small, 10% or less. An average chemical formula derived for an essentially inhomogeneous structure is of questionable value and may be seriously misleading.

[†] Further details of these interesting studies are given by C. de la Calle (1977) in her Thèse de Doctorat, *Structures des Vermiculites, Facteurs conditionnent les Mouvements des Feuilletts*, Paris.

[‡] See also Chapter 1, Section 4.5.2.

Weaver and Pollard (1973) provided a valuable survey of chemical analyses of illites. The data commonly show less K_2O , more SiO_2 , MgO and H_2O than in muscovites so that illites may resemble phengites rather than muscovites (Güven, 1970; see also Chapter 1, Sections 4.5.1, 4.5.2). The content of K^+ and equivalent ions relative to a total cation valence of +22, which corresponds with $O_{10}(OH)_2$ in the formula, is often about 0.7–0.8. Interstratification with montmorillonite layers will decrease the average number of interlayer cations and increase the water content. However if the mixed-layering is not obvious from the usual tests (i.e., observing the effect of mild heat-treatment and of ethylene glycol treatment on the profiles of the basal reflections) and therefore is probably less than about 10% (Hower and Mowatt, 1966), then interstratification is unlikely to be the whole explanation for the low interlayer cation content. The high value of H_2O , in excess of that required for the hydroxyl ions ($O_{10}(OH)_2$ is equivalent in the chemical analysis to $O_{11}.H_2O$), can be “written off” as surface sorbed water, either physically sorbed or chemically sorbed by so-called broken bonds, and/or as molecular water occupying interlayer positions not filled by K^+ and equivalent ions. The supposition that surface-held water may be appreciable is supported by the evidence that when muscovite is finely ground the water content is increased and the excess water is not removed by the usual drying process at $110^\circ C$. Illites have a large surface area and surface-held water may well be an appreciable part of the excess water. Güven (1972) has shown that some illites have fine lath-shaped particles possibly formed by splitting mica layers parallel to (110). Broken bonds may take up water; for example, $Si-O-Si$ may become $Si-OH$ $OH-Si$ to satisfy valence requirements. An alternative hypothesis suggested by Brown and Norrish (1952) was that the deficiency of K^+ ions might be made up with H_3O^+ (hydronium) ions. Some analyses appear to support this hypothesis, while others are opposed to it or are equally well interpreted without this assumption.

A few examples may be described of illites which have been studied carefully; many others could be given. Mankin and Dodd (1963) examined a $2M_1$ -illite from the Ouachita Mountains, Oklahoma, and suggested it might serve as a “reference” illite because of its purity. Formulae were developed assuming a total cation valence of +22, and also according to the Brown-Norrish model; the first method gave 2.05 octahedral cations and 0.63 (K^+, Na^+, Ca^{2+}) interlayer ions, while the second gave 1.95 octahedral cations and 0.97 ($K^+, Na^+, Ca^{2+}, H_3O^+$) interlayer ions; therefore the extra “water” might form H_3O^+ ions. Gaudette, Eades and Grim (1966) and Gaudette (1965) presented data for five illites and on the basis of twelve 00 ℓ diffractions derived one-dimensional Fourier syntheses, but these results and the chemical analyses gave no grounds for preferring either method of calculating the formulae. An extensive study by Hower and Mowatt (1966) of the mineralogy of illites and mixed-layer illite-montmorillonites based on some thirty samples, including size-fractionated materials, led them to the following conclusion: “With some temerity it is now suggested that the excess H_2O in illites is present as neutral H_2O trapped in non-expandable layers. The H_2O molecules may be present either in the interlayer structural positions not occupied by K^+ and/or as lenses of water. This may cause the less regular basal repeat distance in illites (as shown by broader basal reflections) and also the higher scattering intensity at low angles.”

A remarkable clay-like mineral called gümbelite, studied by Aruja (1944), can be called a $2M$ -illite. It consists of fine fibers about 1 cm long. From X-ray fiber diagrams the cell parameters a 5.21, b 9.02, c 20.12 Å, $\beta = 96.0^\circ$ were obtained; many reflections with l odd indices testify to the two-layer structure. The [110] direction was predominantly parallel to the fiber axis. The chemical formula relative to $12(O + OH)$ was given as: $(K, Na)_{0.72}(Al_{1.48}Mg_{0.40})(Si_{3.19}Al_{0.77}Ti_{0.04})O_{9.18}(OH)_{2.82}$ but the anion part of the formula can be written $O_{10}(OH)_{1.18}(H_2O)_{0.82}$ which indicates that almost half the hydroxyls normally present are

replaced by water molecules. This result suggests yet another way by which additional water may be present in a mica-like structure.

Structurally disordered illites are commonly described as *1Md* illites thereby implying a disordered one-layer monoclinic structure. Table 2.10 lists X-ray powder data for a synthetic *1M* muscovite given by Yoder and Eugster (1955) and for two *1M* and two *1Md* illites. Obviously some reflections are missing from the *1Md* patterns, but these are mainly weak reflections. In column 4 of the table, many *1Md* reflections are marked D = diffuse. The correspondence between the *1Md* and the *1M* patterns is such that a one-layer monoclinic lattice seems justified for the disordered materials. However, there is no obvious general rule that the missing reflections correspond to particular *hkl* indices (as in the case of kaolinite, for example) and therefore no particular pattern of disorder is discernible.

It could well be the case that the disorder is related to a small degree of mixed layering. If an illite-montmorillonite contains 10% of montmorillonite layers, the illite part of the structure will

TABLE 2.10. X-ray powder data for *1M* and *1Md* micas (illites)

<i>hkl</i>	1		2		3		4		5	
	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
001	10.08	>100	10.1	0	10.1	9	10.1	9	10.0	10
002	5.04	37	4.98	5	4.98	3	4.98	3	5.0	5
020	4.488	90	4.50	9	4.48	9	4.48	9	4.46	10
11 $\bar{1}$	4.349	27	4.35	2						
021	4.115	16	4.10	2	4.09	2				
			3.85	2*	3.87	2*				
11 $\bar{2}$	3.660	60	3.62	7	3.65	5				
003, 022	3.356	>100	3.32	9	3.34	9	3.33	9	3.32	10
112	3.073	50	3.08	7	3.07	5	3.07	2	2.97	2
11 $\bar{3}$	2.929	6	2.89	4	2.88	1	2.85	2	2.80	2
023	2.689	16	2.67	3	2.67	4				
130	2.582	50								
			2.57	10	2.56	9	2.57	10	2.55	10
13 $\bar{1}$	2.565	90								
200	2.550	22								
131	2.450	11	2.47	3	2.46	3	2.46	3D	2.44	3
13 $\bar{2}$	2.405	4								
114	2.380	12	2.38	5	2.38	4	2.38	3D	2.37	4
040	2.246	8	2.25	4	2.25	4	2.25	3D	2.23	3
220	2.219	7								
041	2.191	4							2.17	
13 $\bar{3}$	2.156	20	2.14	5	2.13	4	2.14	3D	2.14	5
202	2.109	6								
005	2.013	32	1.99	9	2.00	5D	1.99	3D	1.98	5
133	1.957	7								
134	1.900	4								
11 $\bar{6}$	1.668	18	1.71	2						
151	1.653	12	1.65	5D	1.64	3D	1.65	3D	1.64	5
204	1.635	12	1.58	1						
135	1.514	4								
060	1.499	33	1.50	9	1.50	7	1.50	9	1.49	10

1. Yoder and Eugster (1955) Synthetic *1M* muscovite
 2. Levinson (1955) *1M* illite, St. Austell, Cornwall
 3. Levinson (1955) *1M* "hydromuscovite"
 4. Levinson (1955) *1Md* illite, Fithian, Illinois
 5. Nagelschmidt and Hicks (1943) *1Md* illite, South Wales
- D = diffuse reflection. * Possibly 3*T* spacing; see ref. 1.

consist of small packets of about ten mica layers which diffract coherently, but incoherently from packet to packet. This model resembles that suggested by Noble (1971) (see Section 5.2.2) for disordered kaolinites. The diffraction peaks from these effectively thin crystals will be broadened and weakened. Shirozu and Higashi (1972), in a study concerning particularly the breadths of the 10 Å and 5 Å diffraction peaks from a variety of illites and illite-montmorillonites, claimed that the $1Md$ polytype was found only with interstratified structures. In their study of disordered kaolinites, Plançon and Tchoubar (Section 5.2.3) considered that arbitrary layer displacements were related to small proportions of abnormal spacings. Likewise in illites small proportions of abnormal spacings due to mixed-layering or to lenses of water (as suggested by Hower and Mowatt, 1966) might be the cause of the structural disorder. Conversely, structural disorder may be a more sensitive indicator of small proportions of "foreign" layers (e.g. <10%) than the customary tests using the basal reflections.

TABLE 2.11. Basal spacing variations in four Japanese muscovites (Kodama *et al.*, 1971)

Sample source	Polymorphic form	Interlayer		$d(001)$, Å	$(\bar{\delta}^2)^{1/2}$
		charge	Σ cations		
Nasu, Tochigi	$2M_1$	0.913	0.907	10.006	0
Yoji, Gumma	$2M_1$	0.853	0.853	10.012	0.096
Miyori, Tochigi	$2M_1 + 1M$	0.848	0.842	10.012	0.096
Shiraishi, Tochigi	$2M_1 + 1M$	0.837	0.782	10.045	0.189

$(\bar{\delta}^2)^{1/2}$ = root mean square variation in basal spacing.

A more detailed study of the line profiles of the basal reflections of micas was undertaken by Kodama (1965) by applying a treatment developed by Houska and Warren (1954) for the study of variable spacings in graphites. The method involves a Fourier analysis of diffraction line profiles. A subsequent study by Kodama, Gatinneau and Méring (1971) applied a similar but more fully developed theoretical treatment evolved originally by Maire and Méring (1960), again in relation to graphite. Kodama *et al.* (1971) studied the diffraction profiles of four muscovites of hydrothermal origin, with particle size <20 μm and with no detectable expanding layer components. To avoid analytical difficulties due to the α_1 , α_2 components in Cu $K\alpha$ radiation, the investigation was carried out with Cu $K\beta$ radiation. The results, summarized in Table 2.11 show that the root mean square variation of the average basal spacing determined from a series of 001 reflections varies almost linearly with the number of interlayer cations. Spacing variations are essentially absent when the number of interlayer cations approaches unity, but when the interlayer cations are insufficient to fill the interlayer positions, variable spacings are found and the variation increases as the number of vacancies increases. The mechanism causing the variable spacing is uncertain, but may arise from unequal distributions of the cations. The muscovites studied were all judged to be well-ordered, either $2M_1$ or $2M_1 + 1M$ polytypes. Therefore some degree of inhomogeneity can be present even when the structure is not obviously of $1Md$ form.

This discussion can be concluded by re-affirming that illite is a useful non-specific term for clay-grade micas. Illites generally contain less K_2O and more H_2O than normal muscovites. There are fewer K^+ and equivalent ions in interlayer positions but it remains uncertain if the additional H_2O is molecular water which, in part, occupies otherwise unfilled interlayer positions or occurs as H_3O^+ ions. Disorder appears not to be specific but probably is related to interstratification commonly of montmorillonite or similar layers. Even micas (illites) with apparently well-ordered $2M_1$ and $1M$ structures can have inhomogeneous basal spacings.

8.14 Glauconite, celadonite

These minerals are discussed in Chapter 1, Section 4.5.3, and only aspects of order-disorder need be mentioned here. Hendricks and Ross (1941) discussed in detail the chemical analyses and structural formulae of these minerals, and confirmed the close relationship between them.

The structures observed are $1M$ and $1Md$, and the disordered forms are commonly mixed-layered minerals. According to Manghnani and Hower (1964), who examined 48 glauconites of widely different geological ages, the proportion of expandable layers ranged from <5 to approximately 55%. The layer charge arises from both octahedral and tetrahedral substitutions and interlayer K^+ ions are generally fewer than in micas; in fact, the K^+ ions appear to be related almost linearly with the proportion of non-expanding layers. The Fe(III) content diminishes and the octahedral Al increases with the proportion of expandable layers. The resulting picture is one of ferric iron-rich mica-like non-expanding layers with fewer than normal interlayer K^+ ions interstratified with varying proportions of expanding montmorillonite-like (or at least smectite-like) layers. It would seem appropriate to limit the term glauconite (like illite) to situations where the proportion of expandable layers is less than some minimum but recognizable proportion (for example, 5%) of expandable layers.

The relations of glauconite to celadonite have been discussed by Buckley *et al.* (1978). From a total of 57 glauconite and 25 celadonite samples, those containing more than 5% interstratification or other impurities were rejected, leaving 22 glauconites and 15 celadonites for detailed analysis. They considered that these minerals are indeed separate mineral species. Celadonites have a composition near $K(Fe^{3+}, Al)(Mg, Fe^{2+})Si_4O_{10}(OH)_2$ while glauconites have an average composition near $K_{0.85}(Fe^{3+}, Al)_{1.34}(Mg, Fe^{2+})_{0.66}(Si_{3.76}Al_{0.24})O_{10}(OH)_2$. They can be differentiated by X-ray diffraction data "particularly when $d(060)$ spacings are plotted against Fe(III) content"; celadonites have $d(060)$ mainly in the range 1.507 – 1.509 Å (with one sample at 1.510 Å), and glauconites in the range 1.512 – 1.517 Å. All the celadonites examined gave sharp $00l$ and hkl reflections indicating a $1M$ type structure and glauconites gave broader basal reflections (due to disorder or interstratification) and reduced hkl reflections. In an earlier study, Warshaw (1957) remarked that all samples she examined had strong to medium reflections of types $00l$ and $hk0$ or hk and that "many have few other reflections than these"; also $0kl$ reflections "are missing in all but the best crystallized glauconites." The "201 reflections are always fairly strong, though broad." It may be remarked that Buckley *et al.* considered that "the term 'glauconite' should be reserved for use in the specific mineralogical sense, that both constituents be specified in naming mixed-layer clays, and that the adjective 'glauconitic' be used in all other contexts."

8.15 Sepiolite, palygorskite

By including these minerals in this section of Chapter 2, the section which deals with order-disorder in $2:1$ type layer silicates, it is implied that although they have important fibrous and chain-like structural features (see Chapter 1, Section 8) they can still be validly regarded as $2:1$ type layer structures. The structures have continuous sheets of linked tetrahedral groups, so that they qualify as phyllosilicates, but unlike most of the layer silicates considered in this monograph the tetrahedral groups of any one sheet do not all point in one direction, but in any one sheet some point in the $+z$ directions, others in the $-z$ direction. Because of this alternation, the tetrahedral sheets are divided into ribbons which can have various widths. Somewhat similar situations exist in antigorite (Chapter 1, Section 2.4.5) and possibly in chrysocolla (this chapter, Section 7.6). The a parameter, parallel to the long axis of the ribbons, is about 5.2 – 5.3 Å in both minerals. The b parameter is a multiple of $b' = \sqrt{3}a \simeq 9.0$ Å. For sepiolite, $b \simeq 27$ Å and for

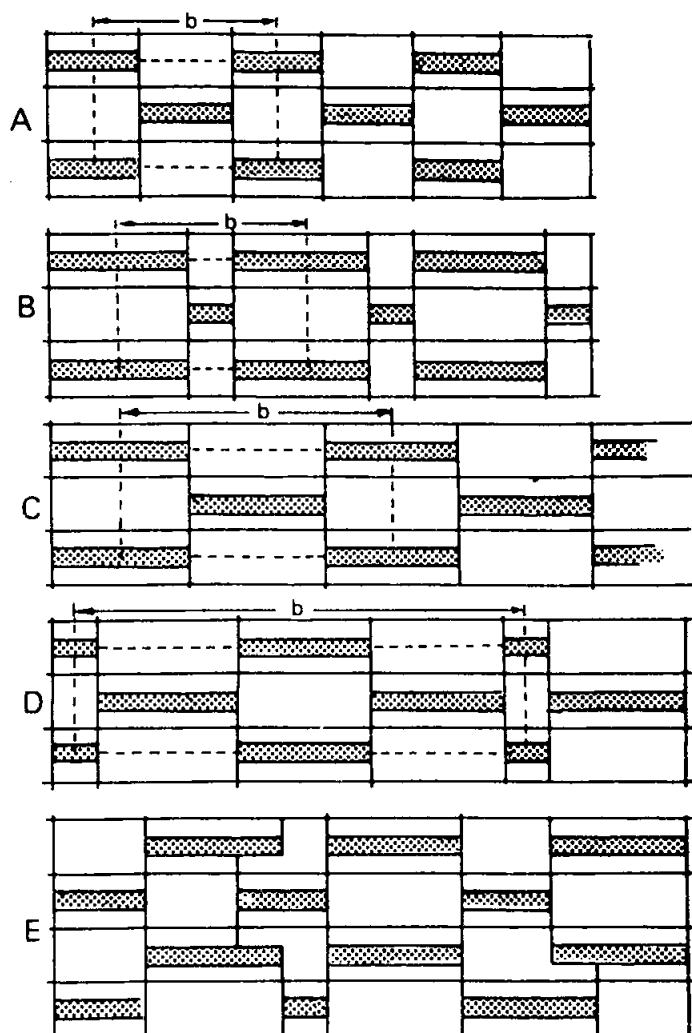


FIG. 2.19. Schematic diagrams comparing the structures of palygorskite and sepiolite minerals. The stippled areas represent cross-sections of octahedrally coordinated sheets; non-stippled areas, tetrahedrally coordinated sheets. In structures A–D, unit cells are outlined with dashed lines. A represents the accepted structure of palygorskite, with $b \simeq 18 \text{ \AA}$; B a possible alternative structure, also with $b \simeq 18 \text{ \AA}$. C represents sepiolite, $b \simeq 27 \text{ \AA}$, and D a possible combination of B and C with $b \simeq 45 \text{ \AA}$. E represents a possible disordered arrangement combining various $9 \text{ \AA}$ and $13.5 \text{ \AA}$ wide units.

palygorskite $b \simeq 18 \text{ \AA}$. The long b parameter results from the alternation of the tetrahedra. These are the broadly accepted features of the sepiolite and palygorskite structures.

Other possible structural arrangements have been suggested which are of interest in relation to possible disorders in these minerals. Gard and Follett (1968) suggested that the ribbon-like units of palygorskite might consist not of equal units, each about $9 \text{ \AA}$ wide, but rather of unequal units respectively $13.5 \text{ \AA}$ and $4.5 \text{ \AA}$ wide which together generate the $18 \text{ \AA}$ b parameter. The $13.5 \text{ \AA}$ wide unit is similar to that in sepiolite (except that palygorskites may be less clearly trioctahedral than sepiolites) and the $4.5 \text{ \AA}$ wide unit resembles the chain structure in pyroxenes. Chapter 1, Section 8, discusses the Gard-Follett model. At an earlier date, Martin Vivaldi and Linares Gonzalez (1962) examined sepiolite–palygorskite clays which gave diffraction patterns not exactly characteristic of either mineral, but “compromise” diagrams which suggested to them the possibility of ribbon-like units of various widths fitting together and producing a partially ordered–partially disordered arrangement. The a parameter and probably also the c parameter will be unaffected by this disorder. Martin Vivaldi and Robertson (1971) suggested that other combinations of “ribbons” might be the cause of the “fringes” seen in electron micrographs of

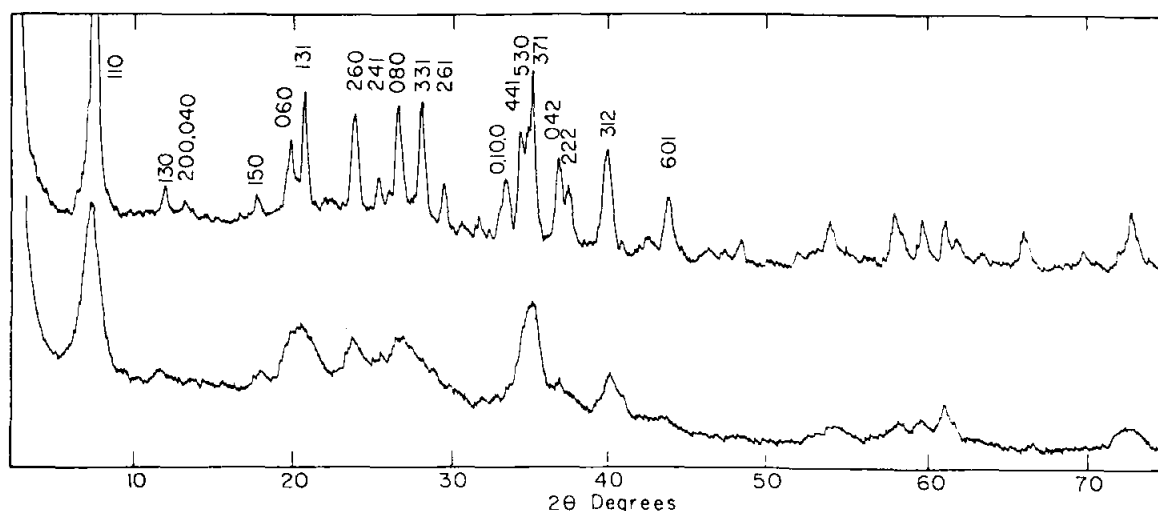


FIG. 2.20. X-ray diffractometer patterns (Cu $K\alpha$ radiation) of well-ordered and poorly ordered sepiolite (after Brindley, 1959).

individual fibers of sepiolite and of palygorskite taken at high magnifications. These fringes may be lattice images of long spacings produced by particular groupings of different ribbon components. Fig. 2.19 illustrates some of the regular and irregular arrangements which have been suggested.

Diffractometer powder patterns of sepiolites, Fig. 2.20, show considerable variation in the number of observed diffractions, their intensities and line profiles (Brindley, 1959). So far there has been no suggested explanations for these diffraction features; it is difficult to decide whether or not they are similar to those observed by Martin Vivaldi and Linares Gonzalez. Further research into these problems may be worthwhile.

9. CONCLUDING REMARKS

Some general observations on order-disorder in layer silicates, particularly in clay minerals, can be given to conclude this chapter. It is evident from a comparison of Chapters 1 and 2 that disordered states cannot be described with the same precision that is possible for the ordered states, with accurately measured unit cell parameters, symmetry relations and atomic positions. Most clay minerals have appreciable disorder and many are highly disordered. Small crystal size and structural disorder together produce X-ray powder patterns which are difficult to evaluate in detail and investigators must often limit the identification process to the recognition of the structure types involved. Minerals are then placed in categories such as kaolinite, illite, smectite, illite-montmorillonite (see Chapter 5), etc. Wide variations in the degree of order and disorder are found in each of these categories. Qualifying terms, such as well-ordered, highly disordered, etc., provide better descriptions but are far from being precise.

The early descriptions of disorder in terms of layer displacements, such as $b/3$ displacements, took account of important features of the X-ray diffraction patterns and were consistent with the weaker bonding between layers as compared with that within layers. Later work, however, has shown that a better description is in terms of a variable occupancy of octahedral cation sites from one domain to another. Random disorders also are important and may arise from incorporation of "foreign matter" between layers, not necessarily as complete layers but probably as "islands" which disturb the regularity of the layer spacings and also disorder their stacking sequence. Such defects have been seen in high-resolution, electron-optical images (cf. Fig. 2.10) and also are indicated by the mathematical analyses of diffraction line profiles, as in

the work of Mitra and of Plançon and Tchoubar on kaolinites and of Kodama *et al.* on muscovites. Thus the interlayering or interstratification which is discussed in succeeding chapters may also be present but to a much smaller extent in structures not ordinarily considered as being interstratified.

There is a wide gap between those who study crystal structures in minute detail and who apply highly mathematical methods to analyze diffraction data from disordered systems on the one hand, and those who are concerned with geological and soil science problems on the other. The process of identification however calls for a useful interaction between these extremes, and indeed progress in clay mineralogy demands this interaction. Identification of clay minerals often will not proceed much beyond the recognition of the mineral category and a qualitative assessment of the degree of order-disorder. It is very desirable that further studies of a fundamental character be undertaken similar to those of Plançon, Tchoubar, Gatinéau, Mering, Kodama, Güven and others. It is also desirable that continued efforts be made to relate these fundamental studies to the wide range of naturally occurring minerals.

The basic philosophy of studying disordered minerals is different from that of studying ordered minerals. To study the ideal crystal structure of any particular mineral it suffices to obtain one supremely well-ordered crystal. To study disorder calls for consideration of tens (or hundreds) of mineral samples. The nature of illite, for example, cannot be determined from one supremely good illite. Many illites must be studied to assess their structural and chemical variations. In fact, one sees a strong tendency in this direction, which is likely to increase in the future. Much valuable cooperative work can be done by geologists, crystallographers, mineralogists and investigators concerned with clay mineral applications. The study of disorder is likely to continue when the basic ordered structures have all been solved.

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Chapter 3

Interlayer and Intercalation Complexes of Clay Minerals

DOUGLAS M. C. MAC EWAN and M. J. WILSON

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1. INTRODUCTION

INTERLAMELLAR complexes of clay minerals are formed by the introduction of inorganic and organic materials between the structural layers, the relatively weak bonding between the layers as compared with the strong ionic-covalent bonding within the layers facilitating their formation. The most common of the interlayer materials is water which is normally present between the layers of smectites and vermiculites, and in the hydrated form of halloysite. The extent to which

inorganic and organic materials enter the silicate structures varies greatly and depends on many factors related to the detailed structure and composition of the layers, and the nature of the materials.

In the early stages of the structural study of these complexes attention was focused principally on the swelling–shrinking behaviour with respect to water, and the complexes formed with simple organic liquids, notably ethylene glycol and glycerol. The use of these liquids became a standard identification test. From these simple beginnings, a wide range of investigations has developed oriented towards the understanding of the formation, structure and properties of the complexes, as well as the refinement of identification procedures and the development of new procedures. Both aspects will be treated in this chapter. As regards research on the complexes themselves, X-ray diffraction is the major method of investigation, but other techniques, notably infrared absorption spectroscopy, are being increasingly applied. In keeping with the particular theme of this monograph, X-ray studies will be considered with rare references to other methods.

For purposes of X-ray identification of clay minerals, it will often be necessary to utilize no more than a fraction, possibly a small fraction, of the total knowledge now available on the interlamellar complexes of clay minerals. Nevertheless, it would be short-sighted to ignore, certainly in the present text, the wealth of information now available. As an example of the use of detailed information, the following may be cited. It has become evident that the charge distribution and swelling behaviour of smectites are often highly inhomogeneous from layer to layer and that the extent of the inhomogeneity can be studied in detail by observing the swelling behaviour with a sequence of long chain amines with increasing numbers of carbon atoms. From these basic studies, an identification (or characterization) technique has emerged giving information on the homogeneity of a smectite which at present cannot be obtained in any other way. The suitability of a smectite for a particular technological application may well depend on knowing more about the mineral than its average chemical composition, average cation exchange capacity and average layer charge. The extent of the inhomogeneity may be of major importance. With considerations of this kind in mind, we consider that no apology is required for discussing in detail the nature of the complexes formed by organic and inorganic materials in clay minerals.

An interlamellar complex is a form of association between lamellar clay minerals and other substances, in which the substance reacted with the clay occurs between the layers of the clay mineral. In the 2:1 clays forming these associations, three basic components should be distinguished. These are:

- (a) The clay mineral layer itself, which may be called the substrate and which has an overall negative charge due to ionic substitutions in the structure.
- (b) The exchangeable cations which compensate the overall negative charge of the layer and occur between the layers.
- (c) Neutral molecules including H_2O , which also occur between the layers and are associated with the cations and the layers.

Interlamellar complexes can be formed by replacement of either of the interlamellar constituents of such natural clays by extraneous substances. The naturally occurring cations may be replaced by any other inorganic cations, monovalent or polyvalent, or by complex cations, such as NH_4 . They may also be replaced by organic cations of any degree of complexity ranging, for instance, from methyl ammonium to long chain poly-functional cations. With neutral molecules, the water in the natural clay may be replaced by other neutral molecules belonging to a wide variety of types, such as alcohols, glycols, amines, ketones, sulphur compounds, etc. It

has been shown also by Bloch (1950) that these neutral molecules may be replaced, following a suitable technique, by inorganic salts. Finally, there exists the possibility of mixed complexes in which there are present, for instance, two or more cationic species and/or two or more types of neutral molecule.

In the 1 : 1 clays, which have a very much smaller overall negative charge compared with the 2 : 1 minerals, only neutral molecules are capable of penetrating between the layers. Indeed, in certain of these clays water molecules are already present under natural conditions. It is also possible with the 1 : 1 clays to form interlamellar complexes with inorganic salts.

Interlamellar complexes show a definite interlayer spacing or in certain cases a mixture of a limited number of interlayer spacings. In certain circumstances, however, with an aqueous medium between the layers, a different type of complex can occur in which instead of a definite interlayer spacing there is a continuous distribution of interlayer distances. The mean spacing is capable of increasing indefinitely and varies as the reciprocal of the square root of the concentration of the solution. In this case we have normal liquid, or something approaching normal liquid, between the layers and the interlayer spacing is determined by osmotic forces. Although generally the spacings given by these osmotic complexes are larger than those for the regular interlamellar complexes, they do in fact overlap.

This chapter is dedicated to the memory of Dr G. F. Walker, whose Chapter 7 in the second edition of this Monograph has been extensively used. One of us (D.M.C.M.) records here, with much gratitude, his receipt of grants from the Aberdeen County Education Department (now Grampian Region), from the Nicol Trust, Aberdeen, and from the Carnegie Trust for the Universities of Scotland.

2. AQUEOUS COMPLEXES WITH 2 : 1 CLAY MINERALS

2.1 Arrangement of interlamellar water and cations

Before considering the arrangement of water molecules and exchangeable cations in expanding layer silicates it will be useful to discuss briefly the structure of water itself. In the structure of ice at atmospheric pressure (Owston, 1958), the water molecules are linked by strong hydrogen bonds to four nearest neighbours in an overall tetrahedral configuration, the resultant structure being a very open one (Fig. 3.1). In each molecule the net charge distribution resembles a tetrahedron with two positive and two negative corners. The centre of positive charge is located midway between the protons and the centre of negative charge near the oxygen nucleus on the side next to the protons (see review by Low, 1961). A radial analysis of X-ray scattering by liquid water shows that some features of the network are retained although there are different concepts as to the exact arrangement.

The structure of interlayer water has been studied by a number of investigators and the picture now emerging is one in which the water molecules are more-or-less regularly arranged and interact with each other, with the surface anions of the silicate sheets and with the compensating exchangeable cations (Farmer and Russell, 1971). The nature of the exchangeable cations and the composition of the adjoining silicate sheets are of great importance in this respect and to appreciate this situation more fully the structure of the interlamellar region of vermiculite is described as deduced from X-ray studies of single crystals. Hendricks and Jefferson (1938) first postulated a hexagonal network of water molecules which were linked to the silicate sheet surfaces by hydrogen bonds, but this arrangement did not take into account the existence of interlayer cations. Grudemo (1954) later established that the water molecules and exchangeable cations were in fact arranged in an ordered manner. With more complete data, Mathieson and

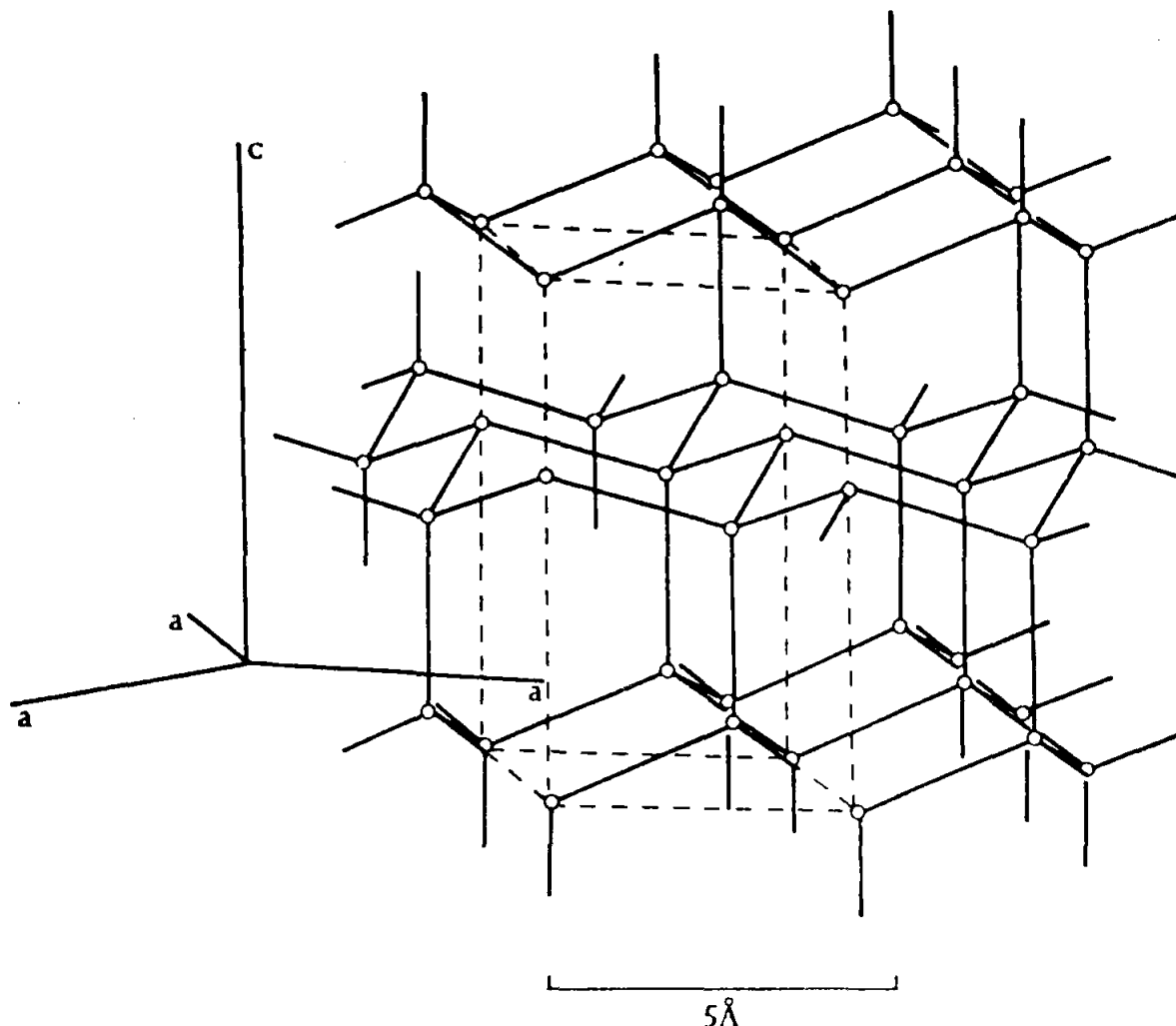


FIG. 3.1. The arrangement of oxygen atoms in ice I. The unit cell outlined in dashes contains four molecules. Redrawn from Owston (1958) (Eisenberg and Kauzmann, 1969).

Walker (1954) and Mathieson (1958) demonstrated that for a Mg-vermiculite the exchangeable cations lie midway between the silicate layers and that the water network consists of two sheets on either side of the cation arranged in a distorted hexagonal array (Fig. 3.2). Shirozu and Bailey (1966) confirmed the location of the exchangeable cations and showed that the cation occupies only one of three possible octahedral sites. This site is positioned vertically between the ordered Al tetrahedra of the adjoining silicate sheets so that the exchangeable cations tend to be controlled directly by the sites of Al-for-Si substitution. Such a local charge balance should enhance the stability of the arrangement.

The exact configuration adopted by the interlayer cations and H_2O molecules in vermiculite is still uncertain and different models have been proposed by Mathieson and Walker (1954) and Bradley and Serratosa (1960). The general outline of the local ordering patterns predicted by both models has recently been confirmed by the experimental work of Alcover *et al.* (1973) and the reader is referred to Chapter 1 for details.

2.2 Relationship of interlayer cations to silicate sheet structure

Recent work has shown that the distribution of the exchangeable cations in the interlayer space must be connected with the distribution of the charges on the silicate sheet which they neutralize. For vermiculite, the control of the exchangeable cation positions by the sites of

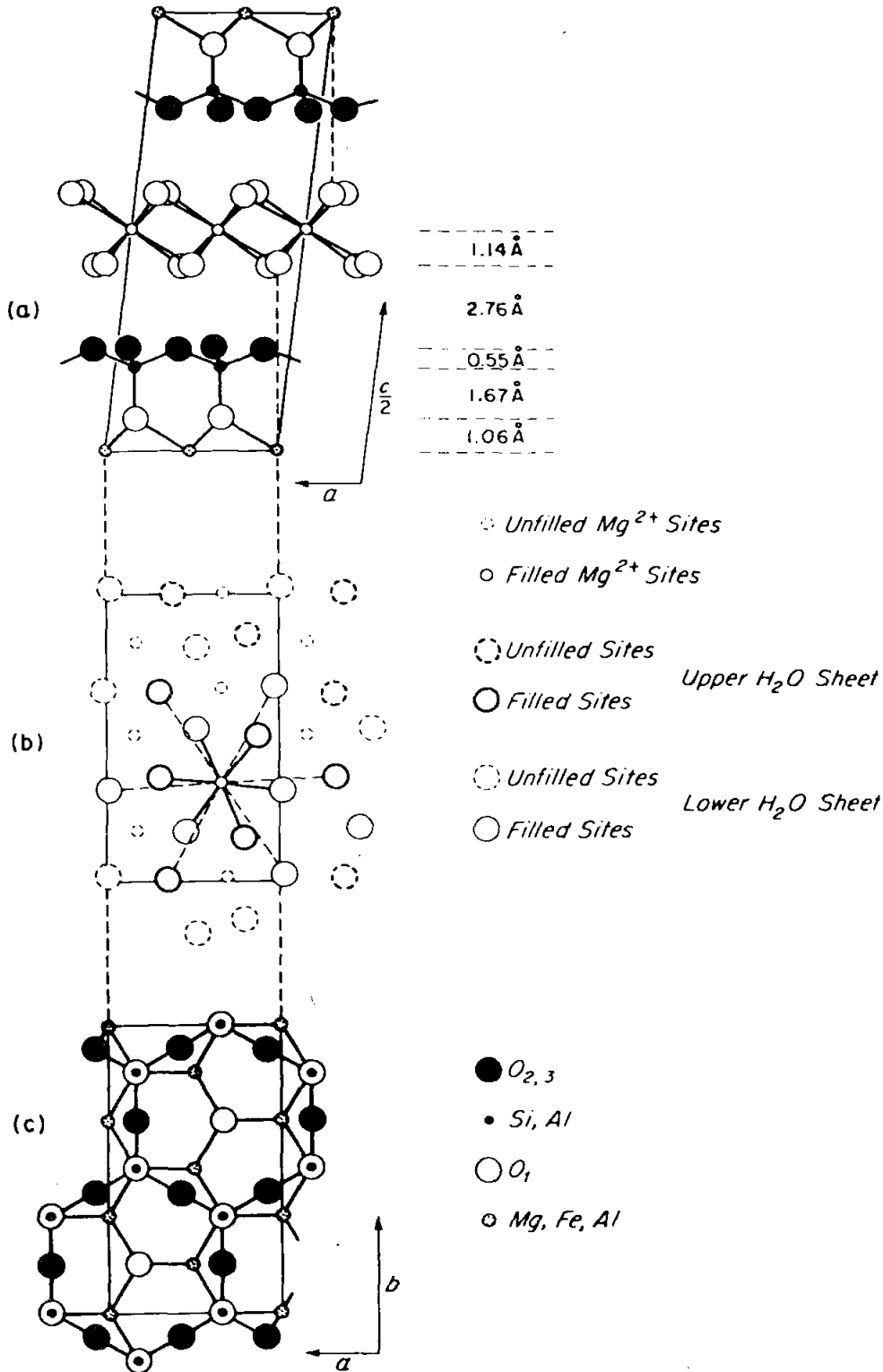


FIG. 3.2. The crystal structure of Mg-vermiculite (a) Projection normal to ac plane; (b) projection normal to ab plane interlayer region (c) projection normal to ab plane showing one half of a silicate layer ($z = 0$ to $c/8$) (from Walker, 1961).

tetrahedral Al has already been mentioned and Suquet *et al.* (1975) have further emphasized this point with saponite. Suquet *et al.* (1975) propose that the ordered or semi-ordered structure of saponite can be accounted for by the existence of interlayer “chains”—mediated through exchangeable cations and interlayer water—anchoring adjacent silicate sheets into positions

which remain fixed relative to each other. This effect is related to charge localization at the sheet surface which in tetrahedrally substituted minerals allows the oxygens of aluminium tetrahedra to act as specific points of attachment for the interlayer "chains". Such a link is relatively weak and can easily be disrupted by grinding. It is not found in octahedrally substituted smectites, because the negative surface charge is distributed over all the surface oxygens in a diffuse manner.

Suquet *et al.* (1975) also showed that the interlayer cations strongly influence the three-dimensional order of the structure as deduced by the number of random stacking faults and $b/3$ translations. This point was again illustrated by a study of vermiculite (de la Calle *et al.*, 1975) in which it was shown that there are two main types of layer stacking, one characteristic of the Mg-form and the other of the Ca- and Na-forms. In Mg-vermiculite, diffuse scattering along the $0kl$ reciprocal rows where k is not a multiple of 3 indicates that successive layers are shifted by $\pm b/3$, but with Ca or Na as the exchangeable ions a $1a-2$ stacking sequence (in the nomenclature of Bailey and Brown, 1962*) was obtained. These structures are fundamentally different. In Ca- and Na-vermiculites, the pseudo-hexagonal cavities at the surfaces of the two adjoining sheets face each other directly rather than being moved by $\pm b/3$ as in Mg-vermiculite. It is possible to obtain both structures from the same vermiculite crystal merely by exchanging the interlamellar ions, thus showing that these ions create an environment which modifies the relative positions of the silicate sheets. According to de la Calle *et al.* the cations which yield different stacking sequences fall into a strongly polarizing group, which includes Mg^{2+} and Ni^{2+} , and a weakly polarizing group which includes Na^+ , Ca^{2+} and Ba^{2+} (see also Chapter 2, Sections 8.8 and 8.11).

The influence of the interlayer region upon the structure of the silicate sheet is also reflected to some extent by the effect of the exchange cations upon the length of the b axis. Following the work of Radoslovich (1961) on micas, Leonard and Weed (1967) observed that the b dimension of laboratory-produced dioctahedral vermiculite varied with the exchange ion and with its hydration state. For example, in the hydrated state Li- and Mg-saturated samples showed an increase in the b dimension compared with that of the parent mica. After dehydration at $350^\circ C$ there was a decrease in this parameter. These observations can be accounted for on the assumption that dehydration involves rotation of the surface oxygen triads of the silicate sheet, whereas in the hydrated state the Li and Mg ions hold a water network with sufficient energy to limit such rotation. However, it should be noted that Eirish and Tret'yakova (1970) reported that the b dimension of montmorillonite saturated with a variety of cations increased on being heated at 100 to $260^\circ C$.

2.3 Types of complex formed with water and inorganic cations

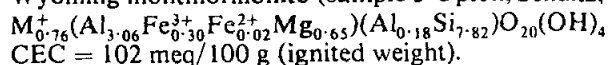
Extensive studies have shown that sorption of water into the interlamellar space is governed both by the size and charge of the saturating cation as well as by the value and localization of the layer charge of the adjacent silicate sheets. Early studies of smectites (Nagelschmidt, 1936; Hofmann and Bilke, 1936) showed what appeared to be a continuous variation of $d(001)$ with water content but it is now clear that this variation results from a random interstratification of two (or more) successive hydrates. Bradley *et al.* (1937) showed that water molecules could be sorbed in monomolecular sheets in montmorillonite, and that one, two, three and four layers of water are possible. The occurrence of "steps" in the basal spacings of swelling minerals as a function of water content is now a generally accepted phenomenon. Mooney *et al.* (1952) and Norrish (1954) showed how the water content is related to the saturating cations.

Table 3.1 shows the basal spacings obtained for various smectites and vermiculites saturated with different cations at particular relative humidities. These data do not show the range of

* See Chapter 1, Sections 6.2 and 6.3.

TABLE 3.1. Effect of interlayer cations on basal spacings (Å) of smectites and vermiculites at 32, 52 and 79% relative humidities and immersed in water

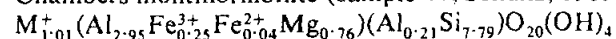
1. Wyoming montmorillonite (sample 5 Upton, Schultz, 1969)



CEC = 102 meq/100 g (ignited weight).

Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.5	12.5	14.8 (br)	Ind
NH ₄	11.7	11.7 (br)	11.9	12.4 (asymm high)
K	11.9	11.9	12.1	Ind
Li	12.9 (br)	14.1 (br)	15.1 (br)	27.0
Cs	12.5	12.4	12.4	12.5
Ca	15.2	15.1	15.5	19.0
Mg	15.1	15.1	15.2	19.5
Sr	15.1	15.3	15.6	19.0
Ba	13.2 (br)	14.5 (br)	15.6	18.8

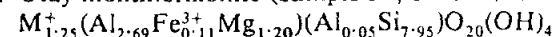
2. Chambers montmorillonite (sample 47, Schultz, 1969).



CEC = 159 meq/100 g (ignited weight).

Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.8	12.8	14.5 (br)	18.8
NH ₄	12.1	12.2	12.3	12.4
K	12.2	12.2	12.2	Ind
Li	13.7 (br)	14.7 (br)	15.1 (br)	15.9 (br)
Cs	12.5	12.3	12.5	12.5
Ca	15.2	15.1	15.1	19.0
Mg	14.9	14.9	15.1	19.5
Sr	15.1	15.3	15.3	19.2
Ba	12.7	12.7	12.7	19.0

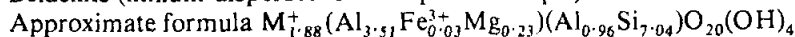
3. Otay montmorillonite (sample 34, Schultz, 1969).



CEC = 137 meq/100 g (ignited weight).

Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.5	12.5	12.8 (br)	19.0 (br → Ind)
NH ₄	12.4	12.4	12.4 (br)	12.4 (br)
K	11.9 (br)	11.9 (br)	12.1 (br)	12.2 (br → Ind)
Li	12.8 (br)	12.6 (br)	13.7 (br)	19.0
Cs	12.4	12.4	12.4	12.4
Ca	15.1	15.2	15.2	18.7
Mg	14.9	14.9	15.1	19.5
Sr	15.1	15.3	15.6	18.7
Ba	12.8	12.8	12.8	18.7

4. Beidellite (lithium-dispersed Unterrupsroth sample).



Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.5	12.5	12.5	14.8
NH ₄	11.8	11.9	11.9	12.0
K	11.8	11.9	11.9	12.1 (br)
Li	12.4	13.5 (br)	14.8	Ind
Cs	11.9	11.9	11.9	12.1
Ca	15.1	15.1	15.1	15.1
Mg	14.7	14.7	15.0	15.9
Sr	14.5 (asymm low)	14.7 (asymm low)	15.4	16.0 (asymm high)
Ba	12.5	12.5	14.7 (br)	16.0 (br)

TABLE 3.1 (Cont).

5. Saponite (St. Cyrus, Kincardineshire, Scotland, Mitchell, 1954). Approximate formula $M_{0.70}^{+}(Al_{0.6}Fe_{0.5}Mg_{4.9})(Al_{1.3}Si_{6.7})O_{20}(OH)_4$. CEC = 99 meq/100 g.				
Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.5	12.5	12.8 (asymm high)	15.5 (br → Ind)
NH ₄	12.2	12.7	12.7	13.5 (br)
K	12.4	12.4	12.5	15.4 (br)
Li	12.4	12.4	14.1 } 16.6 }	Ind
Cs	12.4	12.2	12.3	12.5 18.8 (w)
Ca	15.1	15.2	15.2	15.8
Mg	14.7	14.7	14.7	19.0
Sr	15.2	15.2	15.2	18.7
Ba	12.8	12.8	12.9 (br asymm high)	18.7
6. Vermiculite (Kenya, Mathieson and Walker, 1954). $M_{1.60}^{+}(Al_{0.32}Fe_{0.96}^{3+}Mg_{4.72})(Al_{2.56}Si_{5.44})O_{20}(OH)_4$ CEC = 130 meq/100 g.				
Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.3	12.6 (asymm high)	14.6	14.9
NH ₄	10.8 (br)	10.8 (br)	11.0 (br)	12.9 (br)
K	10.4 (v.br asymm high)	10.4 (v.br asymm high)	10.5 (v.br asymm high)	10.5 } 14.3 } (v.br)
Li	12.5	12.5	12.5	14.8 (→ Ind)
Cs	12.6 (br)	12.6 (br)	12.6 (br)	12.6 (br)
Ca	14.8	14.9	14.9	14.9
Mg	14.3	14.4	14.4	14.6
Sr	14.9	14.9	14.9	15.2
Ba	12.4	12.5	12.6	15.4
7. Loch Scye vermiculite (Smith Aitken, 1965). Low iron, high charge vermiculite CEC = 180 meq/100 g				
Interlayer cation	32% RH	52% RH	79% RH	in water
Na	12.1	14.7	14.7	14.9
NH ₄	10.8	10.8	10.8	11.0
K	11.0	11.0	11.0	11.0
Li	12.1	12.4	12.0 (asymm high)	14.6 } 13.0 }
Cs	11.4 (br)	11.4 (br)	11.4 (br)	11.5 (br)
Ca	14.9	14.9	14.9	15.1
Mg	14.4	14.4	14.4	14.6
Sr	14.9	14.9	—	15.2 } 13.2 }
Ba	12.3	12.4	12.0 (asymm high)	14.9 } 13.0 }

KEY. (br) = broad, probable indication of interstratification; asymm high/low = asymmetrical towards high/low spacings; → Ind = tendency to indefinite swelling; w = weak; CEC = cation exchange capacity.

relative humidities over which the different hydration states are stable, nor the regions where interstratification between two hydration states are likely to occur, but they do indicate what one might reasonably expect under most laboratory conditions.

More detailed studies by Glaeser and Méring (1968) and Suquet *et al.* (1975) reveal differences which can be illustrated with Na as the exchangeable ion.(Fig. 3.3). Montmorillonite,

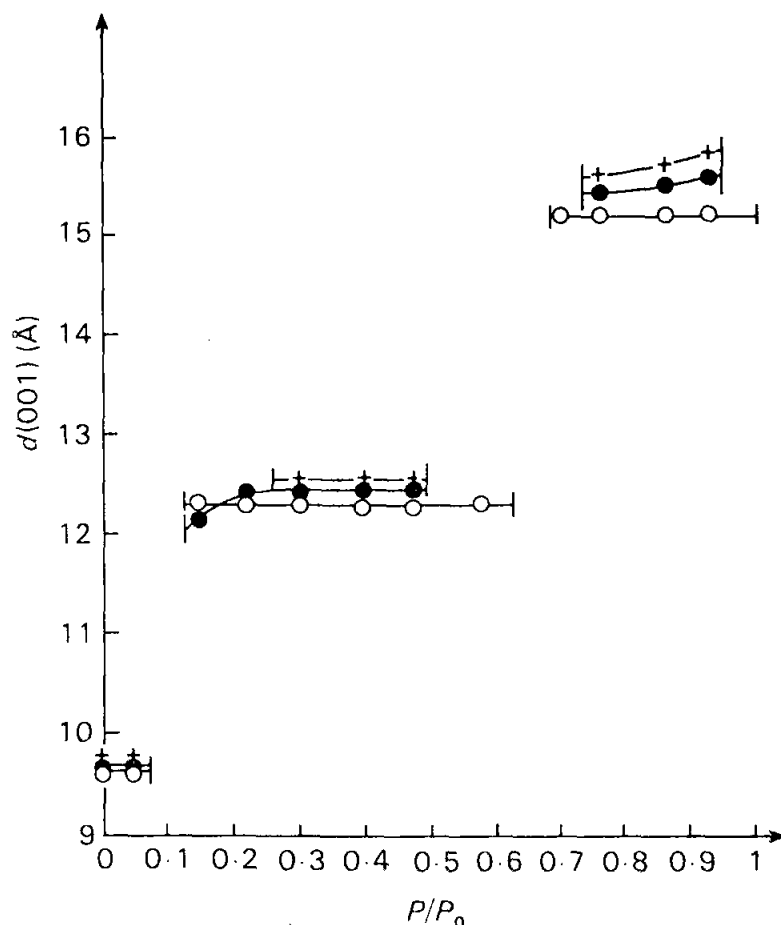


FIG. 3.3. Basal spacings (Å) of Na-saturated montmorillonite (●—●), beidellite (O—O) and hectorite (+—+) at different relative humidities (after Glaeser and Méring, 1968).

hectorite and beidellite exhibit several homogeneous states of hydration (characterized by a rational series of reflections) the one-layer being predominant. In the one- and two-layer hydration states of montmorillonite and hectorite, the basal spacing may vary, whereas that of beidellite remains constant. Interstratification between two hydration states is more extensive for montmorillonite and hectorite than for beidellite. Na-saponite behaves in exactly the same way as beidellite (Suquet *et al.*, 1975) and in this respect closely resembles Na-vermiculite (Mamy and Le Renard, 1970). K-saturated smectites apparently behave in a similar way to Na-saturated samples, although most K-vermiculites retain a spacing of about 10.4 Å at all relative humidities. However, according to Walker (1961), structural contraction on K-saturation may be absent or only partial with low-charge vermiculites. Here a distinct 12.5 Å spacing is possible and in many vermiculites a broad intermediate spacing indicates interstratification between contracting and non-contracting forms.

Somewhat more complicated behaviour is shown by the expanding minerals saturated with other cations. With Ca, the two layer hydrate predominates over an extensive range of relative humidities (Fig. 3.4). The spacing is stabilized by the formation of octahedrally co-ordinated hexahydrate groups of composition $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ (Méring, 1946). However, the basal spacing varies in both octahedrally- and tetrahedrally-charged smectites as is shown by the sloping steps of the hydration curve. For Mg-saturation a sloping curve for the two-layer hydrate is observed for both saponite and montmorillonite but the slope is somewhat steeper for the latter mineral. According to Suquet *et al.* (1975) Li-saponite has five possible hydration states, none of which is characterized by a horizontal step. On the other hand, the basal spacing of Li-vermiculite with a

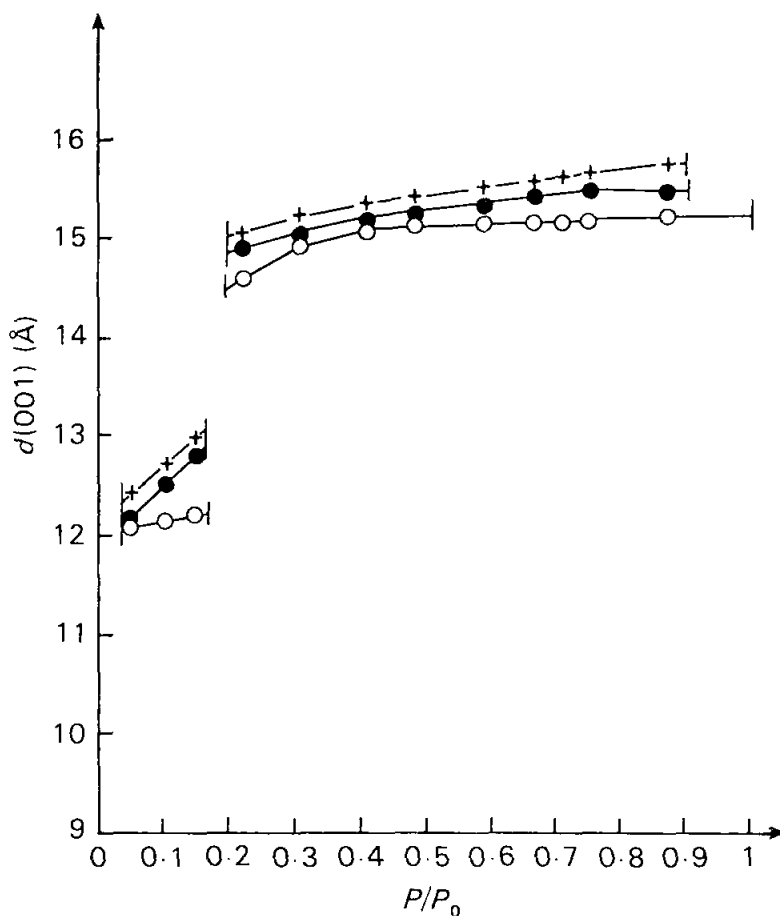


FIG. 3.4. Basal spacings (Å) of Ca-saturated montmorillonite (●—●), beidellite (○—○) and hectorite (+—+) at different relative humidities (after Glaeser and Méring, 1968).

single water layer remains constant up to 55% relative humidity, after which interstratification between various hydration states predominates.

2.4 Hydration and osmotic swelling of vermiculites and smectites

Vermiculites and smectites when saturated with certain ions are capable of swelling to give much larger spacings between the layers than those normally observed with interlamellar complexes. This type of swelling may be called osmotic swelling or type 2 swelling (MacEwan, 1960). The essential features of it are not only the large spacings observed but also the different nature of the forces between the layers. These forces are osmotic and result from a balance of electrostatic forces, van der Waals forces and osmotic pressure of the interlamellar ions. The distance between the layers is not even approximately constant but shows a distribution covering a fairly considerable range of distances.

The transition from normal or type 1 interlamellar swelling to type 2 swelling is a sharp one. The swelling in the type 2 range is dependent on the concentration of electrolyte in the solution. The silicate-layer separation normally increases linearly with the reciprocal of the square root of the salt concentration. Normal electrical double layers are presumably developed between the silicate layers.

In Na- and Li-montmorillonite Norrish (1954) and Foster *et al.* (1955) showed that individual layers dissociate completely as the water content is increased. Norrish (1954) immersed a small flake of montmorillonite in salt solutions of progressively decreasing concentration and followed the spacing changes by using a long spacing X-ray camera. His results for Na-clays are shown in

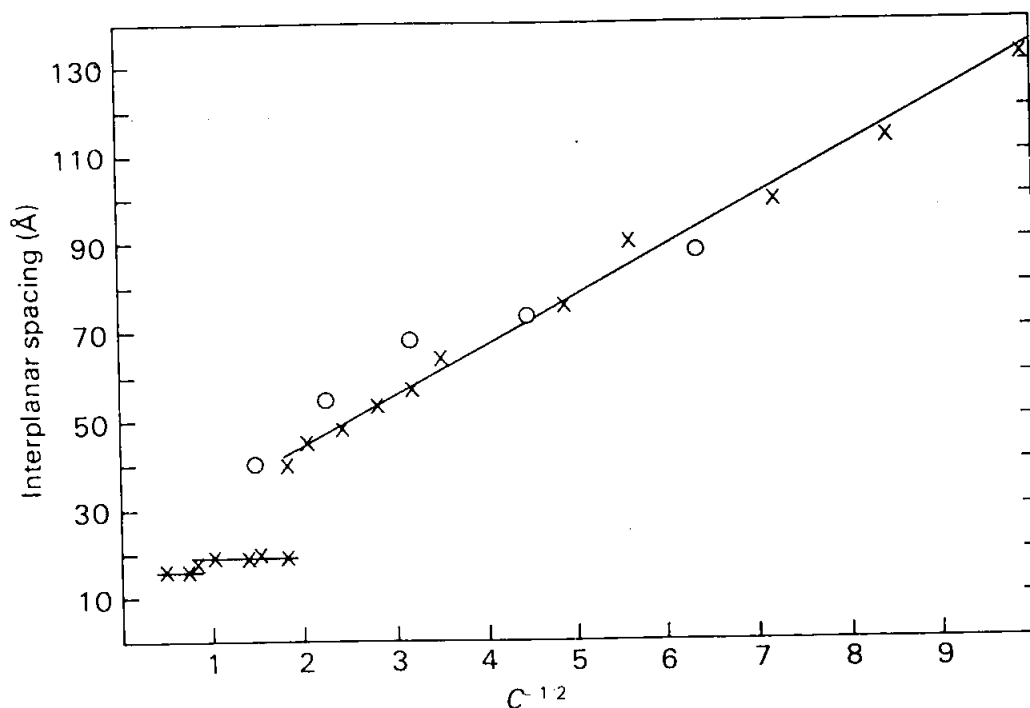


FIG. 3.5. Change of approximate mean spacing between layers of montmorillonite with reciprocal of square root of concentrations for Na-saturated clay (after Norrish, 1954). x in NaCl solutions, O in Na_2SO_4 solutions.

Fig. 3.5. The spacing first increases in steps corresponding to various organized structures of water molecules until 20 Å is reached and then jumps to 40 Å, after which it increases steadily, Foster *et al.* (1955) recorded diffraction patterns at various water to clay ratios, as is illustrated in Fig. 3.6 for Li-montmorillonite.

In the zone of large spacing, (*i.e.* >40 Å), no single spacing occurs but instead there is a statistical distribution; the spacings plotted in Fig. 3.5 are mean values. This point is illustrated in Fig. 3.7, which is a Fourier transform (see Chapter 4) from the intensity data for one sample, and shows the probability $W(R)$ of occurrence of different interlayer distances R in the system having a mean spacing of 50 Å. The first maximum occurs in the neighbourhood of the mean spacing, the second and subsequent maxima are distances between layers which are not nearest neighbours. The system is therefore highly irregular as regards interlayer spacings. Parallelism of the layers is, however, probably well preserved within regions containing an appreciable number of layers; even in the most highly swollen preparations, the orientation of the aggregate is preserved and the whole sample remains birefringent.

Rausell-Colom and MacEwan (1964) have shown that the expansion of Na-montmorillonite in decreasing electrolyte concentrations is not reversible and that on bringing the expanded clay through a series of increasing electrolyte concentrations the spacing follows a different path and remains expanded to a relatively high concentration of electrolyte. Rausell-Colom and MacEwan ascribed this behaviour to the formation of edge-to-edge and edge-to-face bonds between the montmorillonite layers. These cross-links bring about the development of a non-reversible frictional force between layers in addition to the forces due to the electrical charges and the hydration of the layers and the ions.

2.5 Factors affecting osmotic swelling

In the expanding minerals, osmotic swelling depends largely upon the surface charge density and charge localization as well as on the nature of the exchangeable cation. Complete

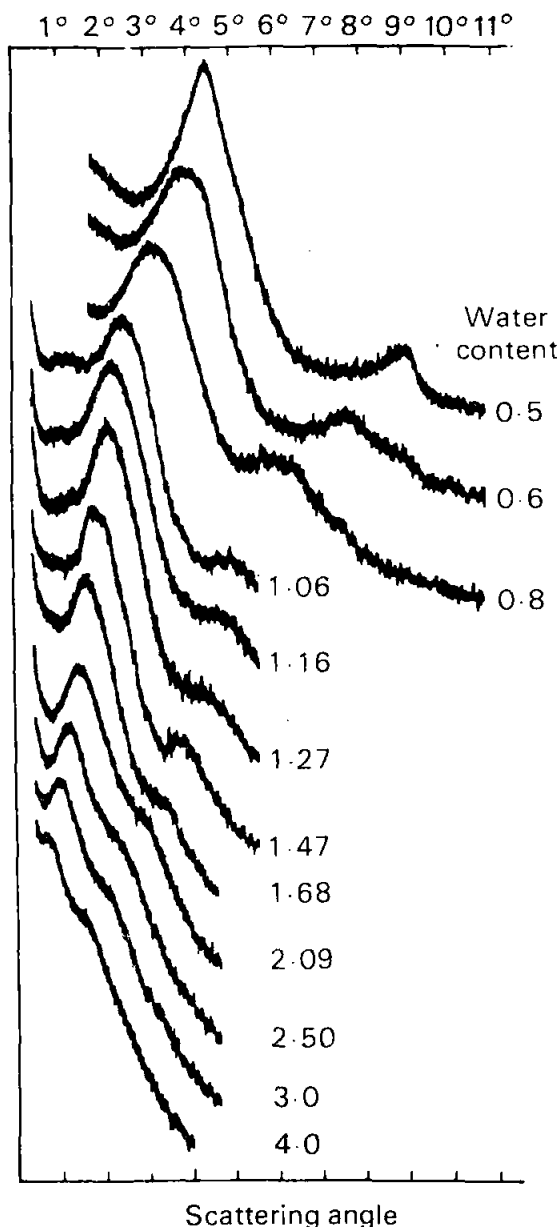


FIG. 3.6. Diffraction pattern (Cu $K\alpha$) of 001 and 002 from Li-montmorillonite containing various amounts of water (after Foster *et al.*, 1955).

dissociation of the layers may or may not occur in Na-saturated forms when the layer charge derives primarily from tetrahedral substitution. Thus, some beidellites expand in this way whereas others yield a spacing of about 15 Å (Table 3.2). According to Suquet *et al.* (1975) saponite and vermiculite yield spacings of 15.2 and 14.9 Å respectively in the fully hydrated Na forms. However, all these minerals show unlimited swelling (except for vermiculites of very high charge) when saturated with Li, which illustrates the importance of ion size in this respect. Dispersion of the layers may also occur with K-saturated montmorillonite, although K-beidellite and K-saponite usually (but not always) form single layer hydrates, yielding a spacing of 12.6 Å, approximately. The behaviour of vermiculite varies according to its layer charge as described previously.

With divalent cations unlimited swelling is not observed probably because these ions provide a link between the charged sites on the facing silicate sheets. A three-layer hydrate occurs with Ca-montmorillonite and a two-layer hydrate with vermiculite, yielding spacings of 19.1 and 14.9 Å respectively. Beidellite and saponite appear to provide a transition between these two forms.

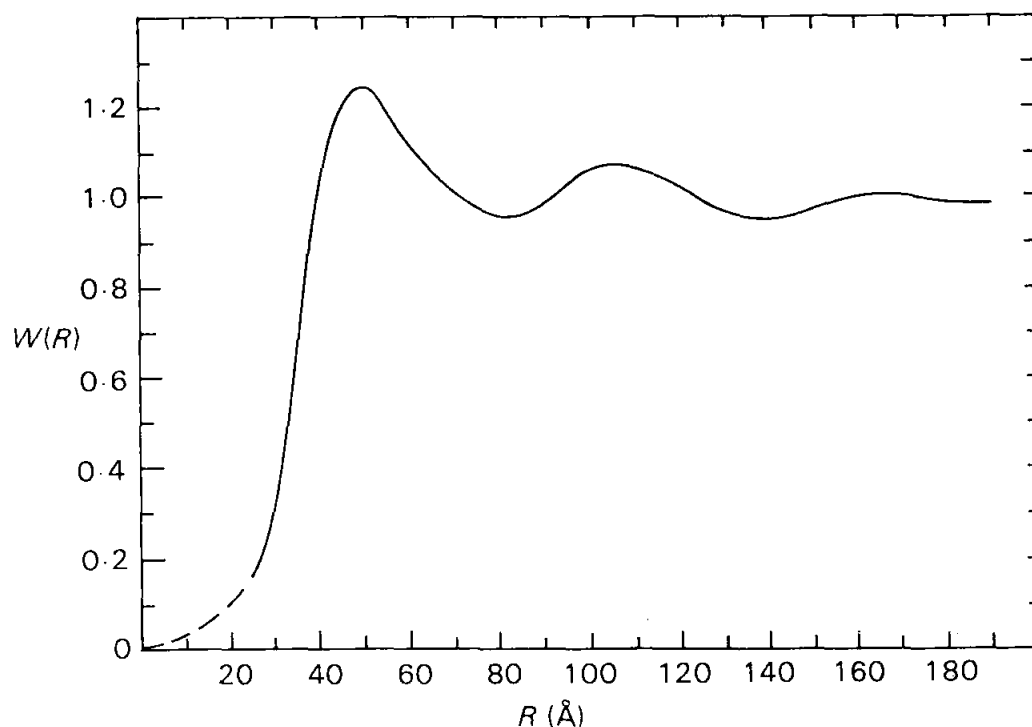


FIG. 3.7. One-dimensional Fourier transform of scattering from montmorillonite in 0.13N NaCl showing distribution of silicate layers (after Norrish, 1954).

According to Suquet *et al.* (1975) Mg- and Ba-montmorillonite and beidellite sorb three layers of water in their maximum hydration states as opposed to the two layers sorbed by vermiculite. In Mg- and Ba-saponite, however, although a three-layer hydrate is dominant a small proportion of the two-layer form may remain.

It is interesting to note that an expanded Na-clay, if treated with a K^+ solution of low concentration, does not contract, whereas if treated with Ca^{2+} solution, it does. The "expanded" Ca^{2+} system is thus absolutely unstable, the K^+ system metastable. If the expanded clay is

TABLE 3.2. Mean values of basal spacings, $d(001)$ (Å), of water solvation complexes of smectites and vermiculites after Suquet *et al.* (1975)

Clay mineral	Exchangeable cation					
	Li	Na	K	Ca	Mg	Ba
Montmorillonite	Ind	Ind	(1) { Ind 15.5 }	19.1	19.4	18.7
Beidellite (2)	Ind	15.2	12.7	{ 18.7s 15.4vw }	18.6	
(3)	Ind	Ind	12.55	18.6	18.58	18.38
Saponite	Ind	15.2	12.6	{ 18.6vw 15.4s }	{ 18.9s 15.7s }	{ 18.5s 15.9vw }
Vermiculite	{ Ind 15 }	14.9	(1) { 12.6 10.4 }	14.9	14.7	15.7

(1) According to the origin and history of the sample.

(2) Beidellite from Rupstoth, Germany; unpublished data of R. Glaeser.

(3) Beidellite from Black Jack Mine (Idaho); Weir, 1960.

Ind = indefinite swelling, s = strong, vw = very weak.

TABLE 3.3 Classification of 2:1 minerals according to the swelling in water and the exchangeable cation after Suquet *et al.* (1975)

Hydration state	Exchangeable cation					
	Li	Na	K	Ca	Mg	Ba
Indefinite	MBSV	MB	M			
3 water layers				MB(S)	MBS	MBS
2 water layers	V	BSV	M	(B)SV	(S)V	(S)V
1 water layer			BSV			
0 water layer			V			

M = Montmorillonite, B = Beidellite, S = Saponite, V = Vermiculite.

treated with an H^+ solution (acid) an interesting phenomenon occurs. The system remains expanded at first, and then, after a period of days, it contracts. Norrish (1954) suggested that this contraction is due to the release of polyvalent ions by attack of the clay mineral structure.

In summary, it can be seen that the mineral exhibiting least swelling is vermiculite where there is a high layer charge residing mainly in the three surface oxygens co-ordinated to tetrahedral aluminium. The most hydrated mineral is montmorillonite with a lower layer charge related mainly to octahedral substitution of Mg^{2+} for Al^{3+} . Here the Mg^{2+} is linked to four silicon-oxygen tetrahedra which in turn expose 10 of their oxygens on the surface layer. Beidellite and saponite exhibit intermediate hydration behaviour because they have a similar layer charge to that of montmorillonite but the localization of this charge is more closely related to vermiculite. A classification of the expanding minerals taking into account their hydration states with various exchangeable cations is shown in Table 3.3.

The study of osmotic swelling in vermiculites and smectites is an important means of obtaining data regarding the forces which exist between charged colloidal particles in suspension in an electrolyte. It has become a highly developed and specialized branch of research which lies outside the scope of this monograph. It is desirable, however, to note that the existence or non-existence of this type of swelling is diagnostic for the distinction between vermiculites and smectites and also for distinguishing between vermiculites of different layer charge. With diminishing layer charge, the osmotically non-swelling vermiculites pass into vermiculites which swell osmotically when saturated with Li-ions, and then into the smectites which swell in this way when saturated with Li- or Na-ions.

2.6 Osmotic swelling of vermiculites with substituted ammonium cations

Vermiculite shows type 2 swelling when saturated with butyl and propyl ammonium cations and then immersed in dilute solutions of the corresponding chlorides. By reducing the concentration of electrolyte, swelling of typical type 2 nature takes place between the layers of the vermiculite. A single crystal of vermiculite subjected to this treatment will maintain its coherence and for a suitably low concentration of electrolyte the macroscopic swelling of the crystal can easily be observed and photographed. Examples of this phenomenon have been described by Walker and collaborators (Walker, 1960; Garrett and Walker, 1962). Similar effects are produced by certain amino acids in the cationic form (Walker and Garrett, 1961). A study of the swelling of butyl ammonium vermiculite has been made by Rausell-Colom (1964) in which the effect of the application of mechanical loads to the swollen crystal could be measured, thus giving a direct measurement of the swelling pressure as a function of interlayer distance. The results agree with the supposition that the repulsive forces between the layers arise from the

interaction of diffuse double layers. The difference between calculated repulsion and the measured swelling pressure is of the order of magnitude of the van der Waals attraction between the layers. The results obtained are similar in their general lines to those obtained by Norrish and Rausell-Colom (1963) with Li-vermiculite. The mean interlayer spacing varies linearly against the logarithm of the applied load. This method provides a useful technique by which direct information may be obtained on the pressure acting between charged colloidal particles due to double layer interaction, and the information is fundamentally important for the theory of the forces between colloidal particles.

3. DEHYDRATION AND REHYDRATION

When hydrated layer silicates are heated to successively higher temperatures, a progressive contraction of the basal spacing occurs. The mechanism involved in the dehydration of vermiculite has been studied in some detail (Walker, 1956*a*) and the description given here is taken from Walker's chapter on vermiculite in the previous edition of this monograph.

3.1 Dehydration of vermiculites

Progressive removal of interlayer water from vermiculite leads to the development of a series of less hydrated phases illustrated in Fig. 1.29 (p. 99) which have been studied by single-crystal X-ray methods (Walker, 1956*a*). Phases encountered during the dehydration of the normal 14.36 Å Mg-vermiculite lattice include a 13.82 Å phase corresponding to a structure containing double sheets of interlayer water with a different arrangement from those in the 14.36 Å lattice; an 11.59 Å phase in which single sheets of water molecules are interleaved with the silicate layers; a 20.6 Å phase consisting of approximately regular alternations of 11.59 Å and 9.02 Å components; and a 9.02 Å phase from which all interlayer water has been excluded. Although structural data on most of these phases are incomplete, the *c* dimension of the unit cell and the stacking sequence of the silicate layers are known for each phase, allowing a provisional attempt to be made at tracing the mechanism of the dehydration process. It should be noted that the β angle changes progressively as water is removed from the lattice. Since the configurations of the interlayer regions of phases other than the 14.36 Å phase have not been determined in detail, these are not shown in this figure, but postulated structures are given by Walker (1956*a*).

Starting from the fully hydrated 14.81 Å phase, which contains approximately sixteen water molecules per cation, removal of water at first produces a regular contraction of the lattice along the *c* axis without lateral displacement of the silicate layers with respect to each other (Fig. 1.29*a,b*, p. 99). During this initial stage, gradual introduction of vacant sites causes the remaining water molecules to be displaced increasingly from their regular hexagonal sites so that a distortion of the network develops (Fig. 1.29*b*). When the spacing reaches 14.36 Å, contraction ceases temporarily while the number of water molecules per cation falls from about twelve to about nine. At this point an abrupt contraction of the lattice to 13.82 Å takes place, during which the stacking sequence of the silicate layers changes (Fig. 1.29*c*). In the 13.82 Å phase, the location of the cations and water molecules has not been finally established, but it appears that the cations are displaced from their central position, and occupy a less perfect octahedral environment consisting of three interlayer water molecules and three oxygens of the silicate layer surface.

A further abrupt contraction to 11.59 Å, representing a lattice containing single sheets of water molecules, follows when the water molecule to cation ratio is reduced to about eight to one (Fig. 1.29*d*). In this transition, the silicate layer relationships are preserved as in the 13.82 Å phase and it is probable that the interlayer cation sites remain unchanged. Withdrawal of further

TABLE 3.4. Basal spacings (Å) of heated vermiculite powders after Barshad (1948, 1950 and 1952)

Temperature (°C)	Interlayer cations					
	Mg	Ca	Ba	Li	Na	K
Room	14.3	15.1	12.6	12.6	12.6	10.4
170	11.8	11.8	10.3	11.0	10.3	10.5
250	10.1	10.1	10.3	10.3	10.1	10.4
410	10.0	10.0	10.1	9.7	10.0	10.4
610	9.4	9.6	10.1	9.4		10.4

Vermiculites from Macon Co., North Carolina, less than 140 mesh (ASTM); samples sealed in glass capillaries at indicated temperature and photographed after cooling.

water molecules proceeds without accompanying structural changes until about three water molecules per cation remain. The gradual development of an approximately regular alternation of 11.59 Å and 9.02 Å components is then observed as an intermediate stage before complete contraction of the lattice to 9.02 Å takes place. A further lateral displacement of the silicate layers with respect to one another is associated with 11.59–9.02 Å contraction (Fig. 1.29e). During the final stage, individual water molecules tend to be trapped in the interior of the crystal by the convergence of the silicate layers near the edges. Other hydrated vermiculite structures (samples saturated with Li⁺, Na⁺, Ca²⁺, Sr²⁺, Ba²⁺) have been studied in less detail but show similar, although not identical, phase-changes on dehydration (Walker, unpublished).

The diffusion of water molecules into the interlayer region of vermiculite can be followed readily under the microscope, or in sufficiently large crystals, by direct observation (Walker, 1956b). Diffusion in Mg-vermiculite during the 11.59–13.82 Å and 13.82–14.36 Å phase transitions takes place in a highly regular manner (Fig. 3.8). Phase boundaries are represented by dark lines moving across the planar surfaces of the crystals and, at intermediate stages, all three phases may coexist in a single crystal.

The conditions of temperature and humidity at which the partially hydrated phases of Mg-vermiculite are stable have not been fully determined, but limited data for the specimen from West Chester, Pennsylvania, are available. Air at 50% relative humidity and at 20°C was passed continuously over the specimen during examination. Under these conditions the 14.36 Å phase in this specimen is stable to about 60°C at which temperature it is replaced by the 13.28 Å phase, while at 70°C the 11.59 Å phase develops. In the vicinity of 110°C indications of the development of the 9.02 Å component gradually appear, and the 20.6 Å phase (which gives a strong second-order reflection at 10.3 Å) can be observed at about 200–250°C. Spontaneous rehydration of the 13.28 Å and 11.59 Å phases (and of the 11.59 Å component of the 20.6 Å phase) occurs in moist air, whereas those layers which have collapsed to 9.02 Å do not rehydrate readily. As a consequence, heating the specimen in air followed by cooling before examination normally produces interstratification of 14.36 Å and 9.02 Å components, which is observed as a progressive displacement of the 14 Å reflection towards 9 Å with increasing temperature. With macroscopic crystals, displacement of the basal reflection of the West Chester vermiculite below 10 Å occurs by about 300°C but the last traces of interlayer water are held tenaciously and complete removal is not effected till about 700°C. Corresponding temperatures for batavite (iron-free vermiculite) are approximately 400°C and 800°C respectively.

Table 3.4 shows basal spacings at different temperatures from vermiculite saturated with various exchangeable cations.

3.2 Dehydration of smectites

All montmorillonites lose interlayer water in the range 100–200°C giving a “collapsed” structure. The details of the dehydration depend on the exchangeable cation and also on the structure of the smectite. This conclusion has been well illustrated by the infrared studies of Farmer and Russell (1967). They showed that stable water complexes remain in Li-, Mg- and Ca-montmorillonite and saponite heated at 80°C but, whereas they begin to break down in montmorillonite above 120°C, in saponite they decompose much more slowly.

In fact, co-ordinated water is retained above 300°C, first as a trihydrate which with Mg²⁺ persists up to 190°C, and then as monohydrate. The spacings found are similar to those found in the different stages of dehydration of vermiculite but they are less well defined. Water is less strongly retained with Na⁺ and K⁺ as exchangeable ions but again Na- and K-saponites dehydrate less readily than the corresponding montmorillonites. Table 3.5 shows the spacing obtained from montmorillonite saturated with various cations and heated at different temperatures.

3.3 Rehydration in vermiculites and smectites

The rehydration characteristics of the expanding minerals also show differences which can be related to structure. After heating at 700°C, Li-, Na- and K-saponite will rehydrate readily when the mineral is exposed to moist air. Divalent cations only fail to rehydrate substantially when the mineral is heated above 450°C. In contrast none of the cations rehydrate substantially above 450°C in montmorillonite, whilst with Mg²⁺ and Li⁺ rehydration is insignificant above 250°C (Russell and Farmer, 1964), a fact probably due to the penetration of these small ions into empty sites in the octahedral layer where they neutralize the layer charge (Hofmann and Klemen, 1950). This reaction is used in distinguishing montmorillonite and beidellite and will be described in more detail later (Section 5.4). These differences in rehydration behaviour are probably connected with charge localization at the oxygen surfaces adjoining the interlamellar region. The diffuse distribution of negative charge on this surface in montmorillonite means that, after dehydration, the layer charge is concentrated upon those oxygens which are in direct contact with the interlayer cation. In saponite, however, such flexibility is not available because the negative charge is related to three surface oxygens co-ordinated to an aluminium ion, so that a

TABLE 3.5. Spacings, $d(001)$, Å, obtained from diffraction photographs of oriented aggregates of montmorillonite (0.3–0.7 μm)—after Martin-Vivaldi *et al.* (1963)

Temperature (°C)	Interlayer cations									
	Mg	Ca	Ba	Li	Na	K	NH ₄	Rb	Cs ^(a)	Sr
110	10.4	(10.9)	10	(10.9)	9.6	10.0	10.4	10.3	(11.2)	12.6 ^(b)
150	10.4	9.8	10	(9.7)	9.6	10.0	10.4	(10.3)	—	(9.8)
200	10.1	9.8	(10.1)	9.5	—	10.0	10.4	10.3	—	9.8
250	(10.1)	(9.6)	10.1	—	—	10.0	10.4	(10.3)	(11.5)	9.8

^(a) For Cs, spacings were deduced from powder photographs.

^(b) A value of 12.6 was obtained in two experiments but lines are very broad.

Figures in parentheses represent interstratified structures.

cation lying in the hexagonal holes in the surface makes direct contact with only two of these (Farmer, 1978). Vermiculite resembles saponite in its rehydration characteristics except that its K^+ and NH_4^+ forms do not hydrate.

4. ORGANIC COMPLEXES WITH 2:1 CLAY MINERALS

These complexes may be introduced by considering the complexes formed with aliphatic compounds with polar groups, which can be divided into α - and β -complexes (Aragón *et al.*, 1959). In the α -complexes the chain of the molecule is parallel to the layer, whereas in the β -complexes the chain stands either perpendicular or at a steep angle to the layer. For successive members of an aliphatic series, the α -complexes give a constant spacing, or in some cases, two spacings where both one-layer and two-layer interlamellar complexes can be formed; the β -complexes give a more-or-less linear increase in spacing with the number of carbon atoms in the chain. It follows that whereas the α -complexes give relatively small interlayer spacings, the β -complexes can lead to very large spacings. Generally, a given series of compounds, such as alcohols or amines, can form both α - and β -complexes, and the occurrence of the one or the other depends on a variety of factors. It is further possible to distinguish between $\alpha_{||}$ and $\alpha_{\perp}$, in which the plane of the zig-zag of the carbon chain is either parallel to or perpendicular to the plane of the layer (Brindley and Hoffmann, 1962).

The types of organic complex formed can be classified according to the bonding mechanism involved. The classification of Mortland (1970) is followed.

4.1 Types of bonding

4.1.1 Cationic bonding

In this type of complex, first studied by Hendricks (1941), the organic material enters the interlamellar space in the form of a positive ion, as, for example, the alkylammonium ion (Leonard *et al.*, 1962; Weiss, 1963; Brindley, 1965; Kinter and Diamond, 1963). In fact these complexes may form so easily that under appropriate conditions the absorption of the organic molecule can be used to measure the cation exchange capacity of the clay, as with methylene blue (Robertson and Ward, 1951; Pham Thi Hang and Brindley, 1970).

Some compounds such as urea and amines are adsorbed in the cationic form because of protonation of the oxygen of the carbonyl group. These organic cations replace the normal metal cations but their adsorption is modified by their pH dependence. Other forces, such as van der Waals forces, also influence the adsorption of these large cations. Organic cations also interact with water and this interaction varies with the ion. Theng *et al.* (1967) showed that the affinity of the clay for an organic cation is linearly related to the molecular weight, with the exception of the smallest, methyl-ammonium, and the largest quaternary-ammonium ions. As the length of an alkyl-ammonium chain increases, the contribution from physical, non-electrical adsorption forces also increases.

Mortland and Barake (1964) have shown that in systems in which both organic and inorganic cations are present, the cations are not distributed uniformly, but tend to segregate themselves in various layers so that, for instance, a metal ion displacing ethyl-ammonium will replace the latter ion in one layer before replacement proceeds in other layers. Barrer and Brummer (1963) suggest a possible explanation based on the idea that a continuous layer of metal cations permits a regular water structure in the interlayer space. Similar segregation was observed by Méring and Glaeser (1953) with mixtures of inorganic cations.

Weed and Weber (1968) find that the polyvalent cations of paraquat (1,1'-dimethyl-4,4'-dipyridilium dichloride) and diquat (1,1'-ethylene-2,2'-dipyridilium dibromide) are selectively

adsorbed by minerals on which the charge density is such that the separation of charges corresponds to that of the organic cation, suggesting that the negative charges on the clay mineral surface are effectively discrete. Similarly, Serratosa (1966) found that in pyridinium-montmorillonite the ring is parallel to the clay layer giving a 12.5 Å spacing, whereas in pyridinium-vermiculite it is perpendicular giving a 13.8 Å spacing.

Many organic substances become protonated in the interlamellar position due to the acidity of the adsorbing clay surface. The protons may also be donated by water associated with metal cations, especially the more electro-negative ions such as Al^{3+} as, for example, $[\text{Al}(\text{H}_2\text{O})_6]^{3+} \rightarrow [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}^+$. A third method is by proton transfer from a protonated species already present, an example being when the NH_4^+ in an NH_4 -montmorillonite transfers its proton to 3-aminotriazol forming 3-aminotriazolium (Russell, Cruz and White, 1968). Raman and Mortland (1969) have observed these reactions with pyridine, methylamine, 3-aminotriazol, NH_3 as proton acceptors and NH_4^+ , pyridinium, ethylammonium, methylammonium and urea cations as donors. The general reaction can be represented as $\text{AH}^+ + \text{B} \rightleftharpoons \text{BH}^+ + \text{A}$ where AH^+ represents the protonated species (proton donor) and B represents the base (proton acceptor) with which it reacts.

When the amount of organic base adsorbed is more than enough to satisfy the charge of the clay mineral, then a phenomenon known as hemi-salt formation may occur in which the molecules are adsorbed in the form (B_2-H^+) , *i.e.* the proton is held equally by two neighbouring basic groups. Examples of these are ethylammonium-ethylamine-montmorillonite (Farmer and Mortland, 1965), pyridinium-pyridine-montmorillonite (Farmer and Mortland, 1966).

4.1.2 Anionic bonding

With substances adsorbed from the vapour phase, anions occasionally occur in the interlamellar space, *e.g.* benzoate (Yariv *et al.*, 1966), the $\text{HCN}-\text{CN}^-$ complex studied by Cruz *et al.* (1974) (following section), and the mixed complexes with aliphatic acids studied by Aragón and Andrés (1973).

4.1.3 Ion-dipole and co-ordination bonding

Infrared studies have shown that the nature of the saturating cation plays an essential role in the process of adsorption of neutral molecules, for example, the square-planar 4 to 1 complex formed with ethylamine in Cu-montmorillonite (Mortland, 1970). It is clear now that co-ordination around the cation plays an important role even with the complexes of alcohols and glycols. Dowdy and Mortland (1967, 1968) have shown by means of infrared studies that water and alcohols can compete for positions surrounding the cation. Co-ordination around the cation has been observed for many polar molecules, such as ketones, amides, pyridine, amino-acids, etc. (Mortland, 1970).

The complexes of 2 : 1 clay minerals saturated with transition metal ions and then treated with polar organic liquids typically show structures in which the organic molecules are co-ordinated around the exchangeable cations in a regular arrangement, and such complexes may be used very conveniently for studying the forms in which polar molecules can co-ordinate such cations. Typical examples include the nickel-acetonitrile complex studied by Rodríguez *et al.* (1966), in which the organic molecules are arranged in pseudotetrahedral form around the cations. The 13.5 Å spacing of this complex is substantially larger than the 12.9 Å spacing obtained with Ba-montmorillonite, an increase which is ascribed to the tetrahedral configuration. Free complexes of Ni(II) with acetonitrile show octahedral co-ordination.

Ethylenediamine is adsorbed from aqueous solution by Cu-montmorillonite to form an

interlamellar complex $[(\text{EDA})_2\text{Cu}]^{2+}$, with a spacing of about $12.5 \text{ \AA}$ (Laura and Cloos, 1970). Cruz *et al.* (1974) suggest that in the HCN complex of Cu-montmorillonite CN^- ions are present as well as neutral molecules. These ions are strongly held by the cations.

Partially dehydrated Cu(II)-montmorillonite forms three types of complex with benzene, respectively red, green and brown in colour. The red complex shows a loss of the aromatic character of the benzene nucleus. The red and green forms are interconvertible following the degree of humidity of the clay. The brown complex develops in conditions where probably CuOH^+ ions are present. It is suggested that the green complex is a π -complex in which there is a reaction with the entire π -electron cloud of the nucleus, and consequently no symmetry modifications (Doner and Mortland, 1969; Mortland and Pinnavaia, 1971; Van der Poel *et al.*, 1973). The red complex, however, may contain associated radical cations formed by electron transfer from the parent molecule to the metal cation (Rupert, 1973; Pinnavaia *et al.*, 1974).

4.1.4 Hydrogen bonding

Hydrogen bonding can be important as a stabilizer of the adsorption of all those molecules containing OH, NH_2 and NH_3 groups. When the study of organic complexes was commenced, Bradley (1945a) and MacEwan (1948) suggested that hydrogens attached to α -carbon atoms could become active in hydrogen bond formation with the oxygens of the clay mineral layer. Infrared studies, however, do not confirm this type of bonding in smectites and vermiculites although this does not exclude some sort of ion-CH dipole interaction. It is now clear that in all complexes with polar molecules an important factor involved in their stabilization is the coordination of the molecules around the metal cations (previous section).

Infrared studies have also shown that active organic groups may be linked to the metal cations by so-called "water bridges", that is to say, a structure in which the cation is linked to an organic molecule by a hydrogen bond formed with a water molecule coordinated to the cation (Farmer and Mortland, 1966; Parfitt and Mortland, 1968; Yariv *et al.*, 1966; Tahoun and Mortland, 1966). This phenomenon is of most importance for cations such as Mg^{2+} which have a sufficient solvation energy to retain the primary hydration shell.

Organic molecules may also associate with each other by hydrogen bonding, a phenomenon important in mixed complexes.

There is evidence that hydrogen bonding to the clay surface is more powerful in 2:1 clays having their source of charge in the tetrahedral layer than in those that have the charge in the octahedral layer.

4.1.5 Van der Waals bonding

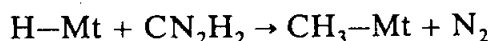
This is a type of bonding which acts in all complexes and is particularly important for complexes with high-molecular-weight organic compounds. Greenland (1965) suggests that with large cations the van der Waals interaction may predominate. In the case of β -complexes van der Waals interactions between the adsorbed molecules may be a major factor in the stability of the complex.

4.1.6 π bonding

With transition metals, complexes may be formed by donation of π -electrons to the organic compound. Such complexes are observed with benzene, xylene, toluene, etc. (Doner and Mortland, 1969). They are formed by octahedrally charged Cu(II)-clays in the anhydrous state (Section 4.1.3). Clays with tetrahedral charge apparently have a much more stable hydrated form.

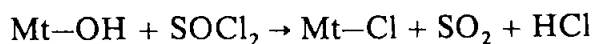
4.1.7 Covalent complexes

In these complexes, the interlamellar material is fixed directly to the montmorillonite layer by covalent or homopolar bonds. Such material takes the form of a radical, which in the cases studied is organic. The complexes are formed by treatment of dry montmorillonite with active organic reagents. The first work of this type was due to Berger (1941) who methylated H-montmorillonite by use of diazomethane:



The hydrophobic product was found to have a basal spacing of 14.1 Å.

Deuel (1952) and collaborators (1950, 1951, 1952, 1953) studied a variety of similar reactions, notably the formation of montmorillonite chloride by reaction of hydrogen or sodium montmorillonite with thionyl chloride. Here hydroxyl of the clay mineral is assumed to be replaced:



From the chloride it is claimed that esters, alkyl and aryl derivatives may be prepared by standard chemical methods.

These complexes have been studied further by Aragón and Castro (1969). It is not certain which OH groups contribute to the formation of these complexes. Deuel considered that the presence of reactive OH was evidence for the existence of the Edelman-Favejee structure, but this structure is excluded by consideration of the X-ray data for smectites and vermiculites. The formation of such complexes necessitates the preparation of the acid clay, *i.e.*, an H-saturated clay, and it has been shown that such clays cannot form without some degradation of the clay mineral structure, and the formation of hydroxyls on the surface of the clay by alteration of the superficial SiO_4 tetrahedra.

Uytterhoeven and Fripiat (1960) have observed the formation of complexes of this type by reaction of the clay with the anhydride of an aliphatic acid. Uytterhoeven (1962) has used methyl lithium for detection of active hydrogen, belonging either to H_2O 's co-ordinated around the interlamellar cations, or to OH groups on the clay mineral surface. Li is fixed and CH_4 evolved.

The reality of the methylation produced by this treatment has been contested by Brown *et al.* (1952), and by Greenland and Russell (1955), but has been affirmed by Aragón (1965) who, unlike Brown *et al.*, found that after methylation the adsorptive properties of the montmorillonite were substantially changed, and that the spacing of 12.35 Å obtained remained constant after treating with polar and non-polar organic substances. Greenland and Russell, like Martin-Vivaldi and Hendricks (1952), suggest that the diazomethane used as a reagent becomes polymerized in the interlayer position, and Aragón admits this as a possible explanation of the modifications observed. However, Barrer and Reay (1958) examined a phenyl-montmorillonite prepared by Deuel, and accepted the genuineness of this sample. The question, therefore, remains open.

A further study of a phenyl-montmorillonite has been made by Aragón and Espinoza (1966). Their sample was prepared following the method recommended by Spencer and Giesekeing (1952), which consists of treatment with thionyl chloride and phenyl magnesium bromide, ether washing and drying *in vacuo*. They obtained a spacing of 13.08 Å, slightly modified by treatment with aromatic and aliphatic hydrocarbons. On heating to 200°C the measured spacing decreases, but unlike that of ordinary montmorillonite, recovers on treatment with toluene and benzene.

Aragón and Castro (1969) also claim to have methylated and acetylated vermiculites, as a

result of which the expansion with aliphatic amines is eliminated (methylated sample) or severely restricted (acetylated sample). In view of the known instability of acid vermiculites, the exact nature of these samples is subject to doubt.

4.2 Arrangement of sorbed molecules in interlamellar complexes

The orientation and packing of aliphatic chain molecules on montmorillonite have been investigated by Hoffman and Brindley (1960) and the general principles involved reviewed by Brindley and Hoffmann (1962). They divide the α or flat-lying complexes into $\alpha_{\parallel}$, those with the zig-zag of the carbon chain parallel to the silicate surface, and $\alpha_{\perp}$, those with the plane of the zig-zag perpendicular to the surface. They suggest that the $\alpha_{\parallel}$ arrangement is adopted where there are strongly polar groups so that the dipole is placed parallel to the two silicate surfaces, whereas with weakly polar molecules the $\alpha_{\perp}$ arrangement is adopted because it provides a favourable environment for organic-organic interactions. Geometrical packing involves keying of the molecules into the surface structure and results in the so-called "shortening of contact distances" between organic molecules and the silicate surface. Such packing is equally possible with either the $\alpha_{\parallel}$ or $\alpha_{\perp}$ arrangements.

We can illustrate these concepts with the ethylene glycol complex which has been widely used for identification purposes and which is discussed more extensively later. This complex was first described in the classical work of Bradley (1945a) and MacEwan (1944, 1948) and it was initially concluded that the zig-zag of the O—C—C—O chain lay parallel to the surface oxygens of the silicate sheet. Brindley (1956) and Brindley and Hoffmann (1962) later presented evidence to show that, in fact, this plane lay parallel to the c axis, a view subsequently confirmed for the one-layer complex with vermiculite (Bradley *et al.*, 1963) and for the two-layer complex with montmorillonite (Reynolds, 1965). These studies indicate that the methylene groups of the glycol

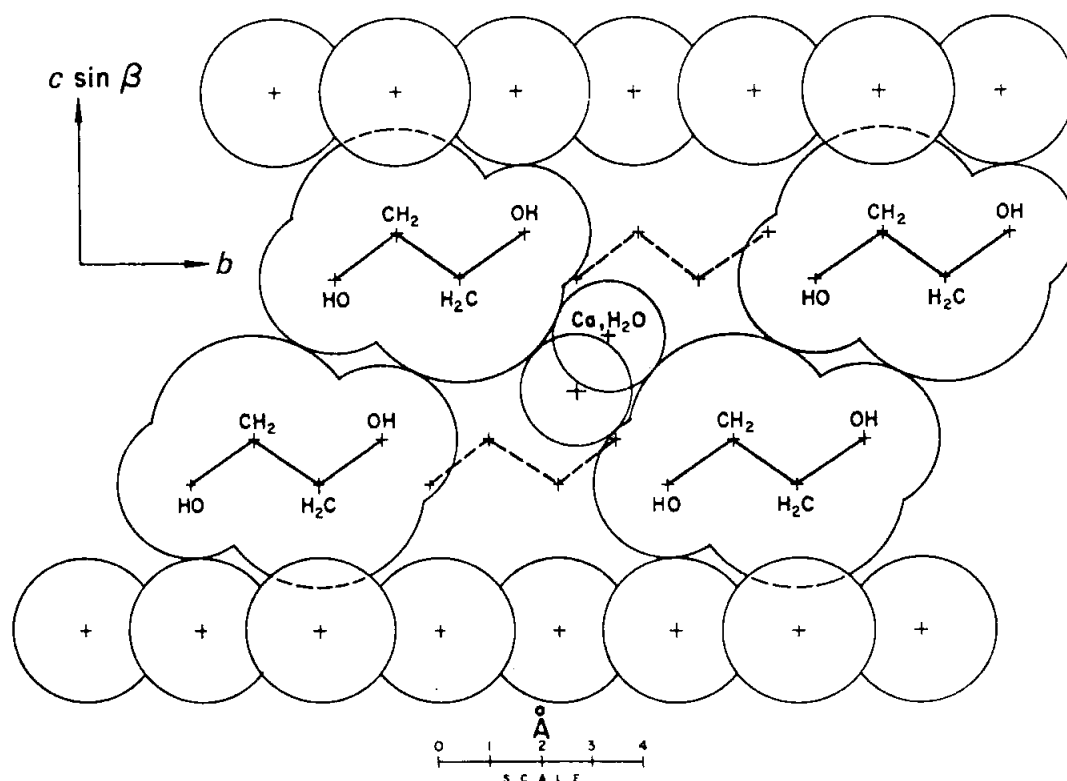


FIG. 3.9. Proposed structure of the glycol layer projected on to a plane parallel to bc . Water calcium positions may be at either position shown at the centre of the figure. Glycol molecules at the distance $a/2$ in front of and behind the plane of the projection are indicated by dashed O—O—C—C—O chains (after Reynolds, 1965).

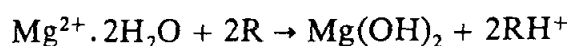
molecules key into the holes of the surface oxygen network with exchangeable cations fitting into the interstices (Fig. 3.9).

The packing involved in long-spacing complexes of montmorillonite with alcohols (Brindley and Ray, 1964) and with fatty acids (Brindley and Moll, 1965) illustrates the concepts which have since been used by Weiss and his co-workers in their detailed studies of the complexes with amines (Section 5.2). With alcohols, reversible complexes are obtained, one series (C_6 – C_{18}) at temperatures above the alcohol melting points and a second (C_{12} – C_{18}) at temperatures below the alcohol melting points. It was concluded that in the latter series the fully extended chain molecules were arranged in double layers inclined at 77° to the silicate surfaces, an angle consistent with covalent bonding between the $-OH$ group and the surface oxygens. In the above-melting-point series a bending of the molecules may occur, although the molecules apparently remain anchored to the silicate surface by the $O-H \dots O$ bonds. With fatty acids, Brindley and Moll (1965) obtained stable long-spacing complexes with montmorillonite only at temperatures above the acid melting points. From the change of spacing of $d(001)$ with the number of carbon atoms it was concluded that the organic molecules are arranged in single layers between the silicate sheets at about $65^\circ \pm 6^\circ$ to (001). Packing considerations suggest that the molecules extend in opposite directions across the interlamellar space with active (OOH) terminations being closely associated with the silicate surfaces. This leads to the so-called "head-to-tail" arrangement where the molecules are arranged in pairs displaced relative to one another along the length of the carbon chain. The stacking angle of the molecules can be related to intermolecular packing and to packing with respect to the silicate surface with which $OH \dots O$ bonds are formed.

With vermiculites a full three-dimensional Fourier synthesis may be possible and has been attempted, for example, on complexes of pyridine-vermiculite (Susa *et al.*, 1967) and piperidine-vermiculite (Iglesias and Steinfink, 1974). In both studies the organic molecules were statistically distributed over crystallographically equivalent positions in the unit cell. Iglesias and Steinfink concluded that such a statistical distribution is inherent in the nature of these complexes and that in all probability crystallographically ordered complexes could not be prepared by the usual ion-exchange techniques.

4.3 Role of interlamellar water and exchangeable cations

A central role in the adsorption process is played by interlayer water and the nature of the exchangeable cation. Interlamellar water in montmorillonite adjacent to cations of high field strength is much more dissociated than water in the bulk state—the NMR studies of Touillaux *et al.* (1968) give a factor of 10^7 —and is capable of protonating organic molecules so that they are retained in the cationic form. The polarizing influence of the cation decreases in the sequence $Al > Mg > Ca > Li \approx Na > K$ and the reaction is favoured by low water contents since, in this case, only water molecules in direct contact with the cations will be present. Brindley (1970) represents the process in the extreme form as follows:



where R is a neutral basic organic molecule and magnesium is shown with two co-ordinated water molecules. Where $R = NH_3$ the process can be followed by determining the amount of NH_4^+ formed so that the influence of the inorganic cations and the amount of residual water can be readily assessed (*e.g.* Mortland *et al.*, 1963; Russell, 1965). Mortland and Raman (1968) have shown that, during dehydration, clay surfaces behave as if they become more acidic. Many other studies illustrate the key role of the saturating cation in the adsorption process. For example,

Farmer and Mortland (1965) have shown that where the neutral organic molecule is ethylamine then ethylammonium ions are formed, whereas with pyridine, a situation arises where the organic molecule is bonded to Mg^{2+} or Ca^{2+} cations via water molecules (Farmer and Mortland, 1966).

4.4 Sorption in excess of cation exchange capacity

Greenland and Quirk (1961) have shown that, with the long-chain pyridinium bromides (over 8 C-atoms in the chain), excess adsorption occurs over and above that given by the CEC of the mineral, accompanied by adsorption of the Br^- ion. This excess adsorption presumably arises from van der Waals interaction between the organic chains. Cloos and Laura (1972) find that ethylene-diamine is adsorbed as $(\text{EDA})_2^{2+}$ in amounts up to the CEC of the clay, and thereafter is adsorbed as the monoprotinated ion $(\text{EDA})\text{H}^+$. Farmer and Mortland (1965, 1966) have pointed to the occurrence of hemi-salt formation when adsorption occurs in excess of the CEC, *i.e.* the formation of ions of the type $(\text{B}_2-\text{H})^+$. This process has been further illustrated by the investigations of Brindley and Tsunashima (1972) who showed that hemi-salt formation occurs with montmorillonite complexes of morpholine and piperidine, leading to a total absorption about twice that found for cation exchange alone.

4.5 Mixed complexes

A considerable number of studies have been made of mixed sorbates. If a 2:1 clay is saturated with a substituted ammonium ion it is possible, by treatment with a neutral organic liquid, to obtain further expansion, the introduced molecules generally distributing themselves in a regular way around the existing interlamellar organic ions. Thus in triethylammonium

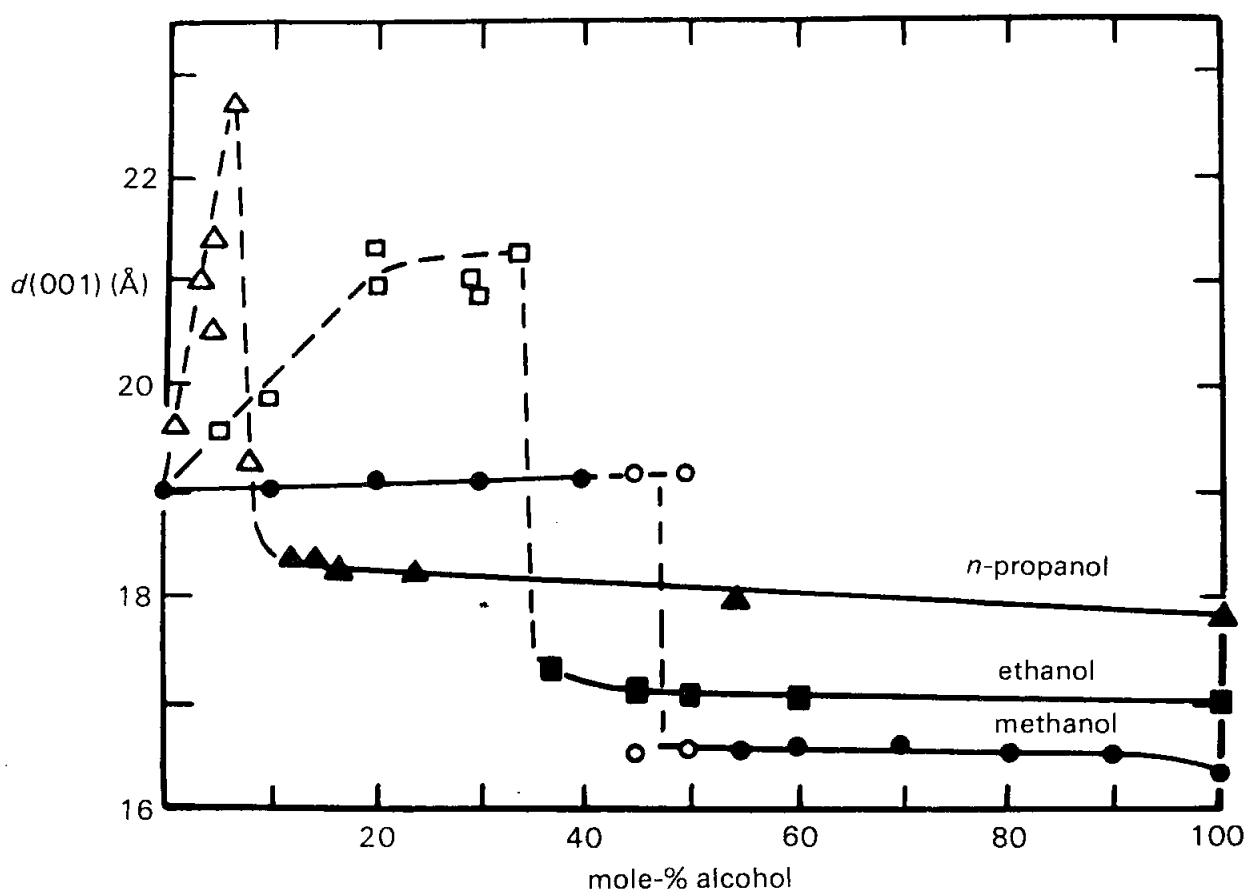


FIG. 3.10. Basal spacings of Ca-montmorillonite in equilibrium with water-alcohol mixtures. Solid symbols for well-ordered phases, open symbols for poorly-ordered or mixed-layer phases (after Brindley *et al.*, 1969).

montmorillonite, the effect of various introduced amines is in general to cause a further increase in swelling (Gutiérrez Ríos *et al.*, 1967). The increase in spacing due to the introduced molecules varies from practically zero to 1.8 Å for cyclohexylamine. Aragón and Andrés (1973) have shown that mixtures of aliphatic alcohols and amines sorbed on vermiculite form definite mixed structures. With montmorillonite there is a transition, at a definite proportion, from the value for the alcohol to that for the amine. The relative molecular concentrations in the interlayer region are, however, unknown. This problem was circumvented by Heydemann and Brindley (1968) in their investigations of *n*-alkyl alcohol-alkyl bromide mixtures by establishing equilibrium with montmorillonite *via* the vapour phase. A strong preference for the absorption of alcohol was found which was regarded as evidence for different absorption mechanisms, the alcohol molecules being attached by OH...O bonds to the silicate surface and the bromides being absorbed mainly by cation-dipole attractions. This work therefore illustrates the importance of the polar OH⁻ termination as compared with the Br⁻ termination in complex formation.

The intracrystalline swelling of Ca-montmorillonite when immersed in progressively changing water-organic mixtures was investigated by Brindley *et al.* (1969). With water-monohydric alcohol mixtures the basal spacings, which indicate a poorly ordered structure, increase up to a

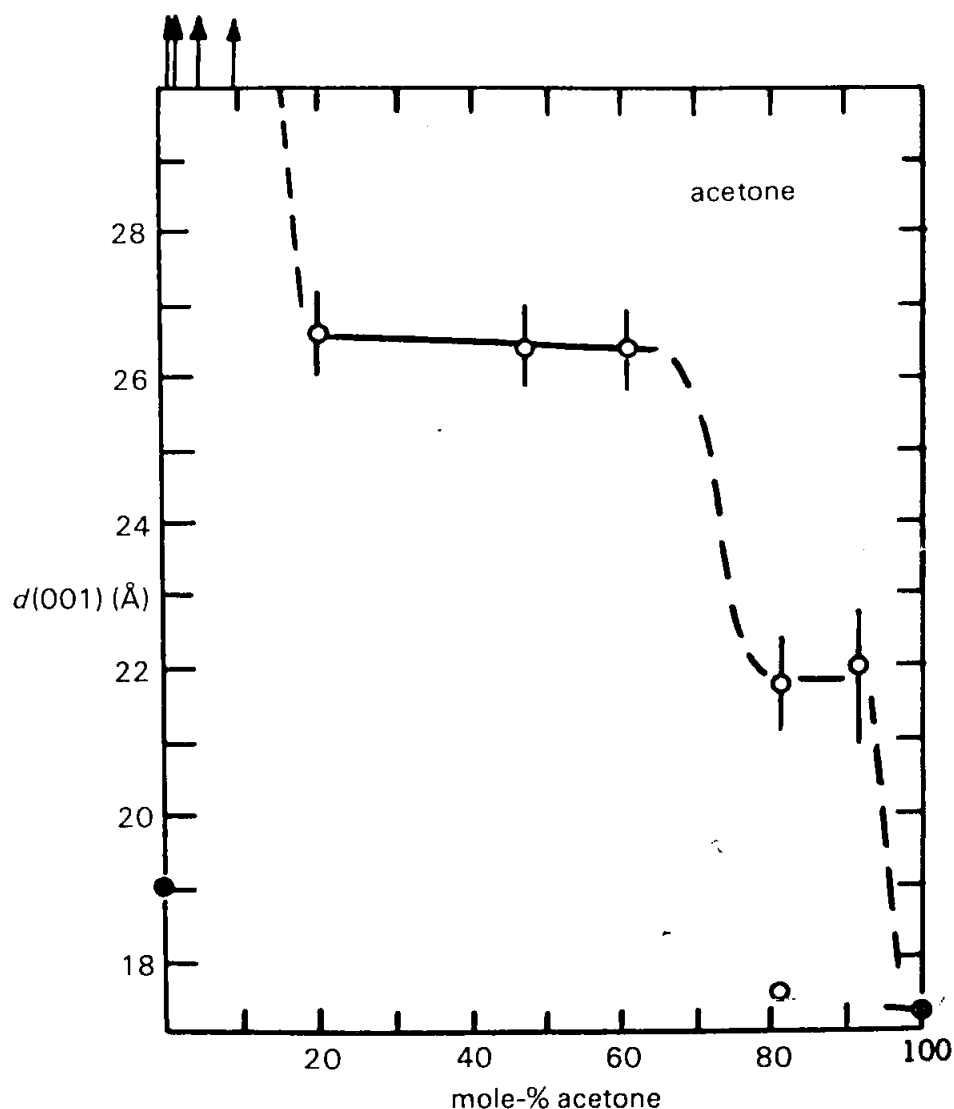


FIG. 3.11. Basal spacings of Ca-montmorillonite in equilibrium with water-acetone solutions. Arrows pointing upward indicate spacings outside the range of measurement (after Brindley *et al.*, 1969).

limit as the mole fractions of alcohol are increased. After this concentration the basal spacings diminish abruptly and indicate well-ordered structures (Fig. 3.10). A similar phenomenon is observed with water–dihydric alcohol mixtures but with a water–acetone system there is complete dispersion of the Ca-montmorillonite in the range 0–10 mole% and expansion to well-defined complexes at 26.5 and 22 Å up to 90 mole% (Fig. 3.11). Similar results were obtained by Ruiz-Amil and MacEwan (1957) with Na-montmorillonite but the dispersion of Ca-montmorillonite (which yields a stable water complex of 19 Å) is more surprising. With water–dioxane and water–morpholine systems constant spacings were recorded over the entire range of mixtures.

These studies indicate that the interactions of compounds in mixtures—either in solution or after being absorbed by the clay mineral—severely limit the extent to which deductions concerning absorption behaviour can be made when these deductions are based upon the absorption of the compounds separately. This point was highlighted by Lailach and Brindley (1969) who showed that the pyrimidines, thymine and uracil, although not absorbed by montmorillonite from solutions containing these compounds alone, are appreciably absorbed from solutions containing adenine or 2,6-aminopurine. This specific co-absorption is of great interest because the interactions are between the same pairs thought to interact in the double-helix structure of DNA.

Numerous studies of mixed complexes have been made by Weiss and his collaborators, one type being used for the determination of layer charge (Weiss and Lagaly, 1967). The work is described more fully in Section 5.2.

4.6 Demixing of cations

Méring and Glaeser (1953) showed that in a mixed Na–Ca montmorillonite “demixing” or segregation of the cations may occur so that some interlayer spaces have only Na^+ and others only Ca^{2+} . This demixing was shown by using conditions such that the Ca^{2+} layers have two interlamellar water layers and the Na^+ layers only one. It was noted (Glaeser and Méring, 1954, 1958) that there is a critical Ca^{2+} ion fraction (f value) at which demixing occurs and below which only the spacing of a pure Na^+ clay is evident. Differentiation may be easier to observe with a suitably chosen organic liquid. Thus Mortland and Barake (1964) found segregation of ethylammonium and Ca^{2+} ions and used X-ray data to distinguish such a system from one where there is a homogeneous mixture of interlayer cations. In mixed alkylammonium-exchanged smectite McBride and Mortland (1973) found that the different ion species segregated into randomly interstratified layers whereas in vermiculite segregation into crystallites was observed, probably as a result of structural inhomogeneity. They concluded that segregation appears to be a direct result of differences in cationic properties such as ion size and hydration properties.

5. IDENTIFICATION OF 2:1 CLAY MINERALS

The smectite and vermiculite mineral groups grade into each other with respect to layer charge and on this basis may be considered as forming part of a single series. The position of an unknown mineral within this series is indicated by commonly used diagnostic tests. Such tests frequently yield unequivocal results but it is not uncommon to encounter “borderline” cases. Here there is no alternative but to use a combination of tests and to report the results in detail. As emphasized by Walker (1975) “information of this type is likely to be far more useful than the mere allocation of a given specimen to one or other of the groups without confirmatory evidence”.

Organic complexes have been used extensively to characterize the 2:1 clay minerals and are now considered in detail.

5.1 Complexes with glycerol and ethylene glycol

To be of use in identification, organic complexes should be readily formed from a hydrated clay, should be stable, and should provide an unequivocal spacing. These requirements point to the use of polyhydric alcohol complexes, and in fact glycerol (MacEwan, 1944) and ethylene glycol (Bradley, 1945*b*) were recommended at an early date, and are still the most-used substances for the purpose. With smectites, glycerol was alleged to give a spacing of 17.7 Å, independent of cation saturation, and ethylene glycol 16.9–17.1 Å. Tables 3.6 and 3.7 show that this is broadly true, but the actual spacing is dependent mainly on the charge of the layer. Many minerals classified as vermiculites can also give a large spacing (~16 Å) with ethylene glycol, and with certain ions, can give a large spacing with glycerol. If we consider smectites and vermiculites as forming part of a single series the results in Tables 3.6 and 3.7 suggest that minerals having a charge, x , up to 1.2 per $\text{O}_{20}(\text{OH})_4$ formula unit may be regarded as smectites, and those with a charge 1.2–1.8 as vermiculites. This division will correspond to the current usage of these names.

Table 3.6 shows that ethylene glycol gives two-layer complexes (complete or nearly so) with a number of minerals classified as vermiculites and is also liable to form interstratified complexes. The result holds for all vermiculites in Table 3.6 except those of the highest charge approaching that of mica. It is also seen that the spacings decrease for values of layer charge above *ca* 1.0 and that with Mg as the exchangeable cation, interstratification sets in at $x = 1.2$ and a one-layer complex is obtained for $x = 1.4$. Several ions give interstratification for $x = 1.6$. Jonas and Thomas (1960) have shown that with ethylene glycol the proportion of K^+ ions influences the uptake of the organic molecules, as does the total layer charge of the mineral. High-charge smectites which are K-saturated will fail to expand with ethylene glycol as will vermiculites in general (Walker, 1961).

With glycerol complexes a more regular picture emerges. All the large monovalent cations give a one-layer complex with the minerals of low charge and no complex or a low-spacing complex with those of high charge. The small ions (Li, Mg, Na) change from two-layer to one-layer around $x = 1.2$ and the large divalent ions remain two-layer up to $x = 1.5$. Apparently, beidellite can give either a one- or a two-layer glycerol complex, indicating that the swelling behaviour of smectites may depend not only on the total layer charge but on its location (Harward and Brindley, 1965). Glycerol complexes of saponite may also behave in a slightly different way. Suquet *et al.* (1975) observed that saponite saturated with Li^+ , Na^+ , Ca^{2+} and Mg^{2+} shows a weak reflection at 14.3 Å in addition to the reflection at 18 Å. The supplementary reflection can be eliminated by grinding for 5 minutes. It seems, therefore, that with glycerol the swelling behaviour of both beidellite and saponite may be intermediate between that of montmorillonite and vermiculite.

In general, however, it is evident from Table 3.7 that glycerol solvation using suitable ions is likely to provide a fairly sound basis for an empirical separation between smectites and vermiculites at about the layer charge suggested. Walker (1957, 1958) suggested that differentiation should be made by pretreating with Mg^{2+} before the addition of glycerol and this procedure still seems to be the best. As emphasized by Walker (1975), no simple diagnostic test based on ethylene glycol has yet been developed. Once the presence of smectites has been established, however, then ethylene glycol treatment may be useful in establishing the simultaneous presence of vermiculite and chlorite. Table 3.6 shows that Na-saturation clearly distinguishes vermiculites (except those of highest charge) from chlorites.

The identification of smectites and vermiculites may be complicated by the presence of minerals which are chloritic in nature but which expand with ethylene glycol and with glycerol. Such minerals have been noted by Stephen and MacEwan (1950, 1951) under the name of

TABLE 3.6. Basal spacings (Å) of ethylene glycol solvation complexes of smectites and vermiculites after Brindley (1966) and Suquet *et al.* (1975)

Cation (<i>r</i>)	Smectites					Vermiculites						
	M1	B1	B2	B4	H1	S1	V1	V2	V3	V4	V5	V6
CEC = <i>x</i> = 0.7			1.25-1.35		1.33	1.19						
		0.92(c)	0.95(a)		1.0-1.1(a)	0.92(c)	1.2(a)	1.2(a)	1.3(a)	1.4(a)	1.6(a)	2.00
												1.60(c)
												1.80(a)
	Li (0.60)	16.9-17.1	—	16.6	—	16.4	16.1	16.1	16.2	16.1	16.0	—
	Mg (0.65)	16.9-17.1	—	17.1	16.9	16.7	16.3	(15.5)	(15.2)	14.3	14.3	—
	Na (0.95)	16.9-17.1	16.8 _s	16.9	16.9	16.7	16.3	16.2	16.3	16.1	(14.8)	12.9
	Ca (0.99)	16.9-17.1	16.8 _s	16.7	16.8	16.6	16.2	16.1	16.1	16.1	(15.6)	—
Sr (1.13)	16.9-17.1	—	—	—	—	16.1	16.1	16.2	16.1	(15.6)	—	
Ba (1.35)	16.9-17.1	—	—	—	—	16.7	16.2	16.2	16.1	(15.6)	—	
K (1.33)	16.9-17.1	—	—	14	16.9	16.5	16.2	16.2	16.2	16.0	—	

r = ionic radius (Å) CEC = cation exchange capacity, meq/g clay.
x = layer charge per O₂₀(OH)₄ formula unit: (a) estimated from CEC, (c) from chemical analysis.
M1 = data for montmorillonites generally found; given by MacEwan (1961 p. 184).
B1 = Beidellite, Black Jack Mine (Idaho); Weir and Greene-Kelly (1962).
B2 = Beidellite, synthetic; CEC on Ca-saturated material dried at 65°C; Harward and Brindley (1965).
B4 = Beidellite, Rupsroth, Germany; unpublished data from R. Glaeser; Suquet *et al.* (1975).
H1 = Fluorhectorite, synthetic; CEC on Ca-saturated material dried at 65°C; Thompson and Brindley (unpublished data).
S1 = Saponite, Kozakov, Czechoslovakia; Suquet *et al.* (1975).
V1, 2, 3, 4, 5 = Vermiculites from Young River (Western Australia); Nyasaland; Kenya; West Chester, Pennsylvania; Macon County, North Carolina; Walker (1958).
V6 = Vermiculite, Llano, Texas, Bradley *et al.* (1963). Also van Olphen (1965).
Values in parentheses are average values for irregular layer sequences.

TABLE 3.7. Basal spacings (Å) of glycerol solvation complexes of smectites and vermiculites after Brindley (1966) and Suquet et al. (1975)

Cation (<i>r</i>)	Smectites					Vermiculites								
	M1	M2	M3	B1	B2	B3	B4	S1	V1	V2	V3	V4	V5	V7
CEC = 0.90 <i>x</i> = 0.68(c)			1.20	0.92(c)	1.21-1.35 0.95(a)	1.27 0.98(c)		1.19 0.92(c)	1.2(a)	1.2(a)	1.3(a)	1.4(a)	1.6(a)	1.90 1.45(a)
Li (0.60)	17.8	17.7	16.8	—	—	—	18.0	18.1	14.2	14.2	14.3	14.3	14.3	14.3
Mg (0.95)	17.8	17.7	17.6	—	17.8*	17.7	17.9	18.1s 14.3vw	14.3	14.3	14.3	14.3	14.3	14.3
Na (0.95)	17.8	17.7	16.4	17.65	—	—	18.0	18.1	14.8	14.8	14.8	14.8	14.8	14.3
Ca (0.99)	17.8	17.7	16.8	17.6	17.8*	—	17.7	17.9s 14.4vw	17.6	17.6	17.6	17.6	14.3	14.2
Sr (1.13)	17.8	—	—	—	—	—	—	—	17.6	17.6	17.6	17.6	15.8	—
Ba (1.35)	17.8	17.7	17.2	—	—	—	—	18.1	17.6	17.6	17.6	17.6	14.3	14.3
K (1.33)	(18)	14.2	13.2	—	—	—	13.7	18.2	—	—	—	—	—	10.6
Rb (1.48)	—	14.4	14.0	—	—	—	—	—	—	—	—	—	—	11.2
NH ₄ (1.48)	—	14.5	—	—	—	—	—	—	—	—	—	—	—	11.2
Cs (1.69)	—	15.4	14.5	—	—	—	—	—	—	—	—	—	—	12.0

r = ionic radius (Å) CEC = cation exchange capacity, m-eq/g clay.

x = charge per $\text{O}_{20}(\text{OH})_4$ formula unit: (a) estimated from CEC; (c) from chemical analysis.

M1 = Montmorillonite, Wyoming; Greene-Kelly (1953b); for CEC, see Greene-Kelly (1952).

M2 = Montmorillonite, Otay, California; Barshad (1950).

M3 = Montmorillonite, Goldfield, Nevada; Barshad (1952).

V7 = Vermiculite, Macon County, North Carolina, Barshad (1950, 1952).

B1, 2, 4, S1, V1, 2, 3, 4, 5 as in Table 6.

Values in parentheses are average values for irregular layer sequences.

*These values were obtained with liquid glycerol; with glycerol vapour, 14.25 Å (Mg) and 14.55 Å (Ca) were obtained.

TABLE 3.8. Basal spacings (Å) of swelling chlorite and various related minerals.

Treatment	A	B	C	D	E	F
Air dry	14	13.6	14.9	28.3	29.1	12–15
Glycerol	17.8	14.8	17	32–33	32	17.8
Ethylene glycol		14.2				16.9
110°C			14.7†			10b
300°C			10			9.6
500°C	14	13.7	10	28b	23.7	9.6

Key: A Swelling chlorite (Stephen and MacEwan (1951)).

B Random interstratification of chlorite and swelling chlorite from the Middle Muschelkalk, Périgny, Jura (Martin-Vivaldi and MacEwan, 1957).

C Sample from red band of Middle Muschelkalk, Olesa, Catalonia (Martin-Vivaldi and MacEwan, 1957).

D Original "corrensite" from Zaiserweiher (Lippmann, 1954).

E Interstratified montmorillonite-chlorite from Ward County, Texas (Earley *et al.*, 1956).

F Montmorillonite.

† Powder photograph of sample in sealed tube.

b = broad.

"swelling chlorites". Their characteristics are that they give a spacing of about 14 Å, which is heat-stable, perhaps not to the degree of well-crystallized chlorites, but at least up to 430°C. The nature of these "swelling chlorites" has been debated, and Bradley and Weaver (1956) have regarded them as a variant of vermiculite, and have referred to them as "vermiculite/swelling chlorite". This question has been discussed by Martin-Vivaldi and MacEwan (1960), who insist that swelling chlorite is distinct from vermiculite, but postulate a series of intermediate minerals between the two. Table 3.8 gives diagnostic criteria for swelling chlorite and various related minerals.

5.2 Complexes with amines

Adsorption of amines proceeds by a cation exchange reaction and the numerous investigations of Weiss and his co-workers have shown that in the 2:1 minerals both the magnitude of the layer charge and the homogeneity of the charge distribution may be deduced from swelling behaviour in relation to the number of carbon atoms in the amine chain.

Lagaly and Weiss (1969) described complexes with various smectites, vermiculites and micas, in which the layer charge varied from 0.5 to 2.00 per $(\text{Si,Al})_8\text{O}_{20}$ unit. Details of the experimental procedure are given by Weiss and Lagaly (1967). The orientation of the alkylammonium ions between the silicate sheets depends mainly on layer charge and in low-charge minerals on the chain length of the cations. Short chains are arranged in monolayers with the chain axis parallel to that of the silicate sheet (α -complexes) and yield a spacing at approximately 13.5 Å (Fig. 3.12). A double layer of similarly oriented ions is formed when the area covered by a flat-lying cation, A_{fc} exceeds the "equivalent area", A_e , available to each univalent cation in a monolayer. The area covered by a flat-lying cation is given by

$$A_{fc} = n_c(1.26)(4.5) + 9 (\text{\AA}^2)$$

where n_c is the number of carbon atoms in the alkylammonium ion and the "equivalent area" is given by

$$A_e = \frac{d(100) \times d(010)}{2(x + y + z)}$$

where $(x + y + z)$ is the number of fixed negative charges on the silicate layer.

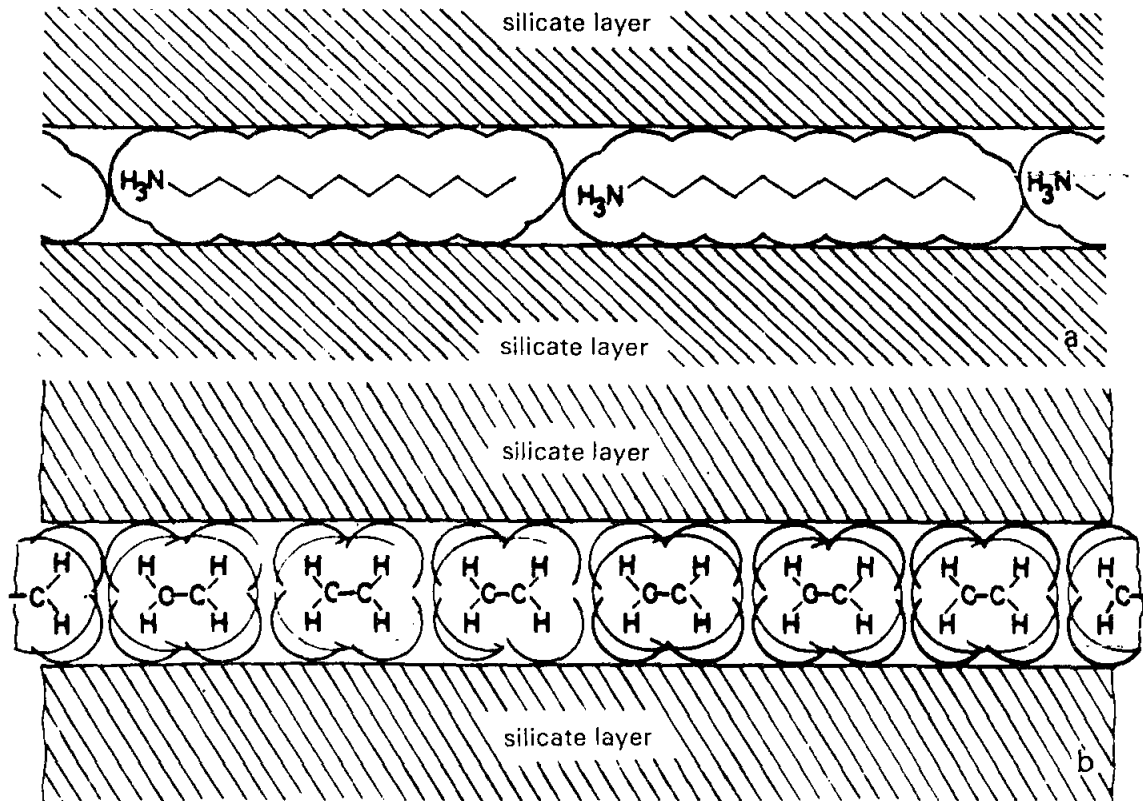


FIG. 3.12. Monolayers of *n*-alkylammonium ions in the interlayer space of *n*-alkylammonium silicates. (a) chain zig-zag plane perpendicular to the silicate layers; (b) chain zig-zag plane parallel to the silicate layers (after Lagaly and Weiss, 1969).

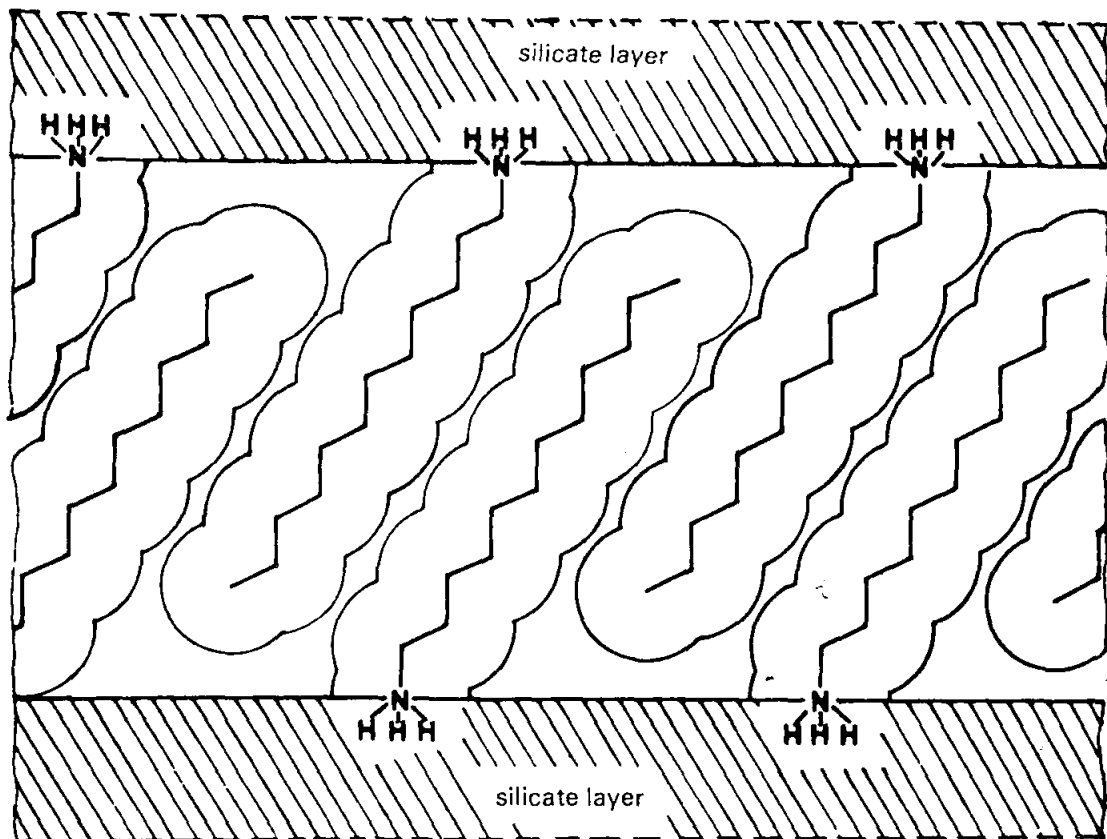


FIG. 3.13. Paraffin-like structures of the alkyl chains in the interlayer space of *n*-alkylammonium silicates (after Lagaly and Weiss, 1969).

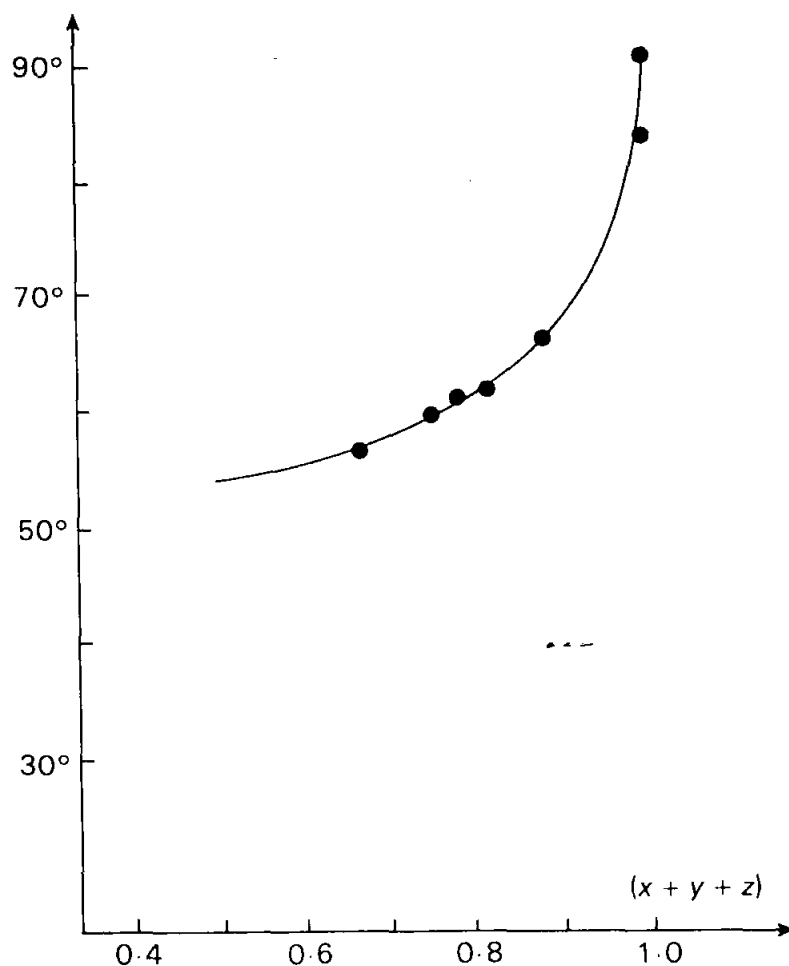


FIG. 3.14. Dependence of tilting angle β upon layer charge $(x + y + z)$ (after Lagaly and Weiss, 1969).

When $A_{fc} \geq 2A_e$ the double layer arrangement becomes unstable and the alkyl chains form “paraffin-type” structures (Fig. 3.13) in which the angle β between the chain axes and the silicate sheet increases with layer charge. In vermiculite, β ranges from 50–60° and approaches 90° in micas. Lagaly and Weiss described a number of different methods for estimating layer charge making use of the various transitions described above and achieved impressive agreement with layer-charge values derived from chemical analysis. For example, when a “paraffin-type” structure is formed the basal spacing increases linearly with increasing chain length of the cation, the mean increase per carbon atom Δd being related to the tilting angle β of the alkyl chain by

$$\sin \beta = \frac{\Delta d}{1.26}$$

Lagaly and Weiss gave an empirically determined standard curve relating tilting angle to charge density (Fig. 3.14).

Lagaly and Weiss (1969) also used a mixed complex for the determination of layer charge. Expanding layer silicates previously complexed with n -alkylammonium are swollen in long-chain primary alcohols, the number of carbon atoms in the alkyl chain of the alcohols n_a being related to basal spacing in a definite manner (Fig. 3.15). When $n_a > n_c$ the basal spacing increases linearly with n_a , the alkyl chains of both the alcohols and the cations being arranged in a paraffin-type double layer structure with their chain axis perpendicular to the silicate layers (Fig. 3.16).

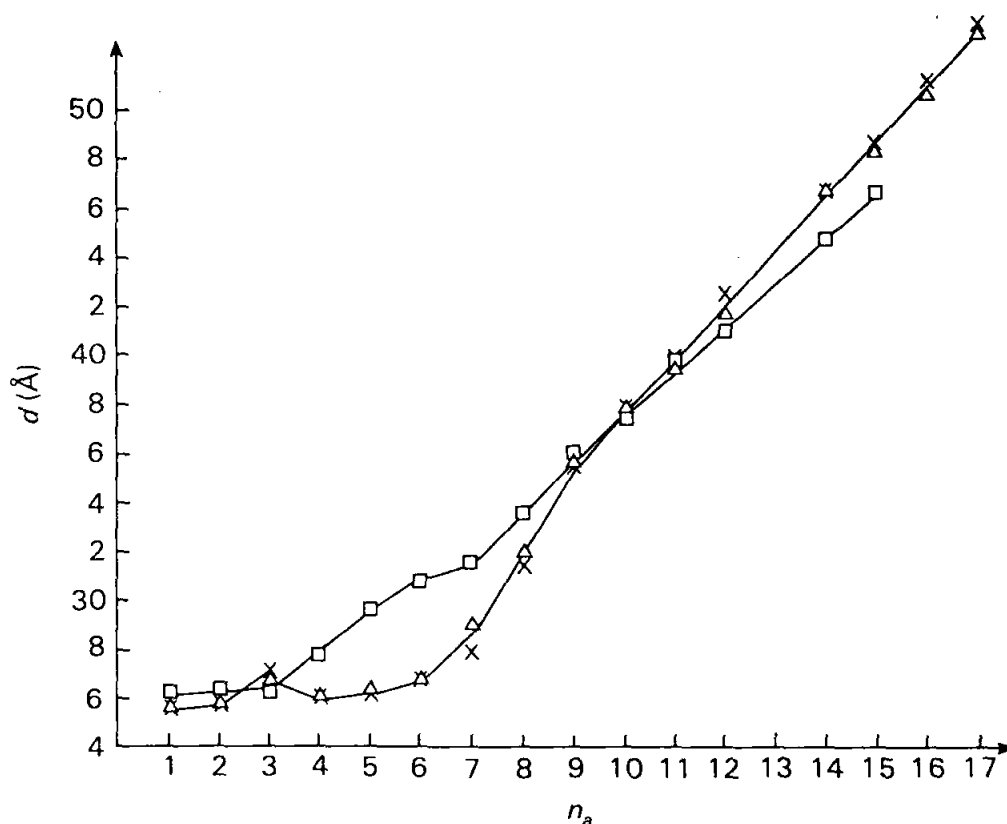


FIG. 3.15. Basal spacings of n -alkylammonium silicates swollen under primary n -alcohols. n_a = number of carbon atoms in the alkyl chain of the n -alcohols. $\square$ —vermiculite from South Africa. Δ —beidellite-II from Unterrupstoth (Rhois), Germany. $\times$ —montmorillonite from Cyprus (after Lagaly and Weiss, 1969).

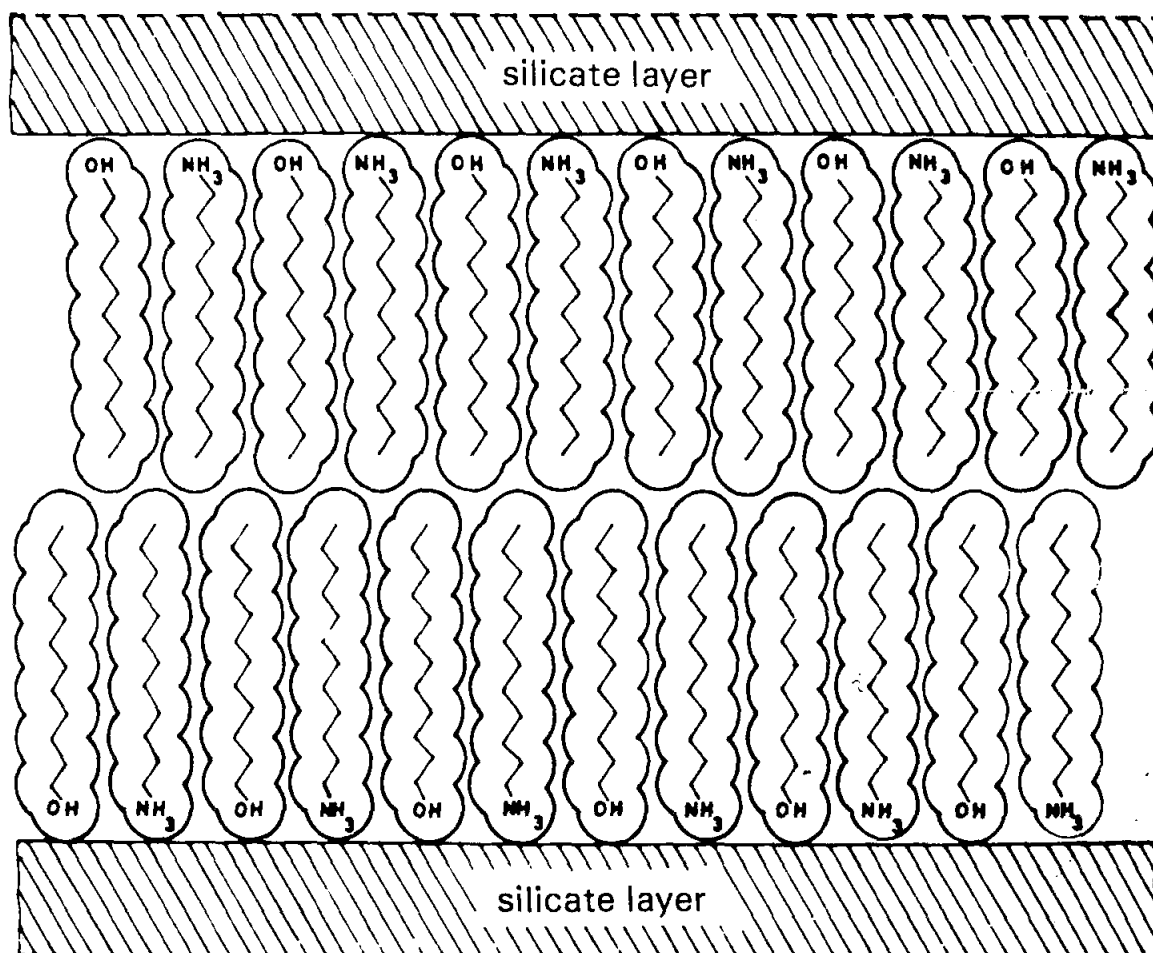


FIG. 3.16. Arrangement of alkyl chains in the interlayer space of n -dodecyl-ammonium silicates swollen under n -dodecanol (after Lagaly and Weiss, 1969).

Lagaly and Weiss (1970) also used *n*-alkylammonium complexes for assessing the homogeneity of charge distribution in expanding minerals, particularly montmorillonite. It was pointed out that layer charge may vary throughout individual crystallites because silicate layers having different charge densities may be arranged in a regular, random or segregated fashion, in a way exactly analogous to interstratification with different components. Where charge distribution is homogeneous the mono-to-double layer transition occurs sharply between two members of the homologous series (Fig. 3.17). With inhomogeneous charge distribution (which seems to be the rule with natural montmorillonite) the transition occurs over a range (Fig. 3.18) marked by interstratification between mono- and double-layer complexes yielding a non-integral series of reflections. Completion of the double layer is recognized by the reappearance of a rational series of basal reflections. The upper and lower limits of cation density are determined from the n_c values which mark the beginning and end of the random interstratification.

There still appears to be some dispute concerning the deductions and conclusions which may be drawn from *n*-alkylammonium layer silicate complexes. One source of difficulty lies in

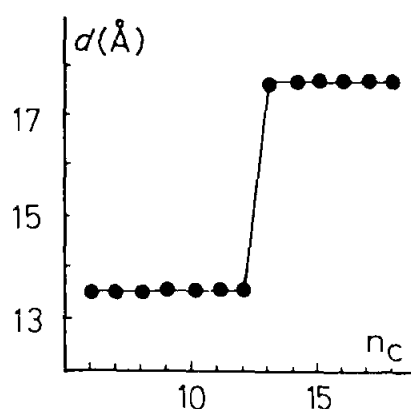


FIG. 3.17. Dependence of basal spacing upon the chain length in *n*-alkylammonium montmorillonites with a homogeneous charge distribution (after Lagaly and Weiss, 1970).

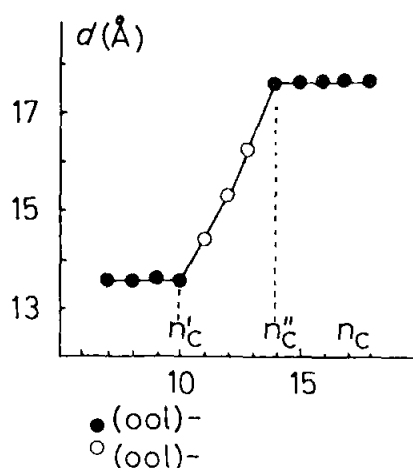


FIG. 3.18. Calculation of the limit values of the cation density ξ from the basal spacings of the *n*-alkylammonium derivatives

$$\xi = \frac{1/2a_0 \cdot b_0}{5.7n_c + 9}$$

for $n_c = n'_c$, ξ = upper limit of cation density; for $n_c = n''_c$, ξ = lower limit of cation density (after Lagaly and Weiss, 1970).

obtaining reproducible data. The method of drying the complexes appears to be particularly important and Walker (1967) suggested that too rapid drying of "paraffin-type" complexes with vermiculite induces a tendency for the alkyl chains to stick as they interpenetrate, thus yielding anomalously high spacings. Indeed, using unidimensional Fourier analysis, Johns and Sen Gupta (1967) showed that alkyl chain orientation is maintained at $55^\circ \pm 5^\circ$ with vermiculites of varying layer charge complexed with a range of alkyl ions. They showed that for any given alkyl ion there may be a series of complexes of differing 001 periodicities due to interpenetration of the alkyl chains. These complexes formed as a result of particular washing and drying sequences.

5.3 The effect of heat on ethylene glycol and glycerol complexes

Table 3.9 from Brindley (1966) summarizes the main data regarding the effects of heat on ethylene glycol and glycerol complexes with 2:1 minerals. In parts (a) and (b), three samples are listed, a hectorite and two montmorillonites. These data refer to observations made with the X-ray diffractometer using the oscillating-heating method introduced by Bradley *et al.* (1958). Table 3.9(a) shows the temperatures at which the complex collapses to a single-layer one, that at which the single-layer complex is optimally developed (sharp basal reflection, successive orders visible), and finally, the temperatures at which the single-layer complex breaks down, leaving the desolvated clay "skeleton".

Table 3.9(c), from Greene-Kelly (1953b) refers to the re-solvation after heating, and shows the

TABLE 3.9(a). Thermal stabilities of ethylene glycol and glycerol complexes of three smectites, from Brindley (1966)

Cation	Ethylene glycol			Glycerol		
	H	A	C	H	A	C
I. Temperatures at which first layer of organic material is removed ($^\circ\text{C}$)						
Ca	110	80	70	135	120	120
Na	110	75	75	150	115	170
II. Temperatures for optimum formation of single-layer complexes ($^\circ\text{C}$)						
Mg	125	125	140	175	170	180
Ca	110	115	100	175	145	180
Ba	105	110	100	160	145	170
Li	105	100	95	175	100	155
Na	120	80	90	160	120	190
K	80	95	90	140	145	135
III. Temperatures of collapse of single-layer complexes ($^\circ\text{C}$)						
Mg	285	255	340	290	280	350
Ca	210	210	200	260	250	300
Ba	180	270	175	220	230	290
Li	180	175	225	270	240	225
Na	155	105	120	210	160	210
K	95	140	100	170	170	150

H = Hectorite; CEC = 0.80 m-eq/g.

A = Montmorillonite (Argentina); CEC = 1.05 m-eq/g.

C = Montmorillonite (Cheto, Arizona); CEC = 1.30 m-eq/g.

From Tettenhorst *et al.* (1962) and Brunton *et al.* (1963).

TABLE 3.9(b). Basal spacings (Å) of single-layer ethylene glycol and glycerol complexes of smectites (to nearest 0.05 Å) (Brindley, 1966)

Cation	Ethylene glycol			Glycerol		
	H	A	C	H	A	C
Li	13.5	13.55	13.55	14.25	14.05	14.15
Mg	14.05	13.85	13.95	14.3	13.75	13.95
Na	13.9	13.5	13.8	14.05	13.85	13.9
Ca	13.9	13.55	13.8	14.5	14.05	14.1
Ba	13.6	13.35	—	14.3	13.85	14.0
K	14.0	13.65	13.55	14.7	13.9	13.75

H, A and C as Table 3.9(a).

TABLE 3.9(c). Basal spacings (Å) of Wyoming montmorillonites pre-heated at various temperatures and then treated with glycerol for several hours (Greene-Kelly, 1953b)

Cation	Cation radius (Å)	Pre-heating temperature (°C)					
		103	200	330	430	540	640
Li	0.60	17.8	(17.8)	9.5	9.5	9.5	9.5
Mg	0.65	17.8	17.8	(9.5)	9.5	9.5	9.5
Na	0.95	17.8	17.8	17.8	(17.8)	9.5	9.5
Ca	0.99	17.8	17.8	17.8	17.8	9.5	9.5
Sr	1.13	17.8	17.8	17.8	17.8	9.5	9.5
La	1.15	17.8	17.8	17.8	17.8	9.5	9.5
K	1.33	(18)	(18)	(18)	(18)	9.9	9.9
Ba	1.35	17.8	17.8	17.8	17.8	17.8	9.8

Figures in parentheses, irregular structures.

degree of uptake of glycerol, following pre-treatment at selected temperatures for several hours. It will be noted that, with this technique, either a two-layer complex is formed, or else none at all.

The temperature for optimum formation of the single-layer complex correlates well with the type of cation, following the series Mg^{2+} , Ca^{2+} , Ba^{2+} , Li^+ , Na^+ , K^+ . This sequence, however, is neither an ionic size series nor a field strength series, but corresponds to a series cited by Barshad (1952) for the effect of cations in determining the ease of expansion of montmorillonite in polar liquids.

In (c), the main interest is in the low-temperature loss of expansion of Li- and Mg-montmorillonites. This result forms the basis of the Hofmann-Klemen (1950) and Greene-Kelly (1953a) test for the location of charge deficiency in smectites (see Section 5.4).

5.4 Distinction between beidellite and montmorillonite

The Hofmann-Klemen and Greene-Kelly test consists in heating a Li-saturated sample of a mineral known to belong to the montmorillonite-beidellite series to 250–300°C overnight. The sample is then saturated with glycerol, and an X-ray diagram recorded. A 001 spacing of about 9.5 Å indicates a montmorillonite, and a spacing of 17.7 Å a beidellite. It should be checked that the diagram shows a regular series of higher orders. An irrational sequence of basal reflections would indicate interstratification, and would suggest that the mineral is of an intermediate

composition. The diagram in this case can be analysed by the methods described in Chapter 4, to obtain an estimate of the composition. Saponite, as well as beidellite, gives the expanded spacing of 17.7 Å after this treatment, so that the test may be diagnostic for montmorillonite in distinction from the other members of the montmorillonite–beidellite–saponite group. The Hofmann-Klemen test may give anomalous results if the Li clay is mounted on ordinary soda-lime glass slides and it is therefore advisable to use silica glass (Byström-Brusewitz, 1975). The irreversible collapse following heating to 250–300°C overnight is considered by Greene-Kelly (1953a) to be an indication that the seat of the negative charge is in the octahedral layer, and that there are vacant sites there, thus allowing the Li ions to migrate from the interlamellar positions to the octahedral positions. Montmorillonite alone fulfils this condition if one ignores the small number of vacancies which may be present in trioctahedral minerals of the group.

The Hofmann-Klemen effect can be used to prepare a series of montmorillonites of variable mean layer charge. A dispersed clay is treated with appropriate volumes of mechanically mixed bi-ionic solutions containing Li^+ and another cation, usually Na^+ . The dried clay is then heated at about 250°C for 24 hours in air. (Special care is required for the preparation of mixed Li^+ – Ca^{2+} clays because Ca-montmorillonite does not expand beyond 19 Å in water—Brindley and Ertem, 1971.) The bi-ionic clay contains variable proportions of Li^+ ions in the exchange positions which, after heating, move into the layer structure thereby reducing the layer charge and the number of interlayer cations. According to Glaeser *et al.* (1972) such preparations can be used for the evaluation of the number of tetrahedral charges in montmorillonite or beidellite. The method consists essentially of plotting residual charge (as a percentage of initial charge) against the fraction of the exchange capacity saturated by Na^+ . With an ideal montmorillonite containing only octahedrally derived charge the experimental points lie on a straight line which passes through the origin. With beidellite, however, the line intersects a point which is proportional to the tetrahedral charge. Inherent assumptions of the method are that all the residual charge is accessible to measurement (by complexing with $\text{Cu}(\text{EDA})_2^{2+}$ in this case) and that the Li^+ which does not migrate into the structure is equal to the tetrahedral charge. Glaeser *et al.* state that the results obtained are preferable to those based upon chemical analysis because the latter are strongly influenced by small amounts of free oxides. For example, the presence of 2% free alumina in a montmorillonite leads to the attribution of about 20% of the exchange capacity as tetrahedral charge.

Bi-ionic montmorillonites are also highly convenient for the investigation of the relationship between layer charge and hydration and solvation properties. Several such studies have been made (Glaeser and Méring, 1971; Calvet and Prost, 1971; Brindley and Ertem, 1971) from which it is apparent that the theoretical basis for the Hofmann-Klemen effect is still the subject of some discussion. Infrared observations have been interpreted as showing that some Li^+ ions migrate partly into the hexagonal holes of the silicate sheet surface rather than into vacant octahedral sites (Tettenhorst, 1962; Russell and Farmer, 1964; Farmer and Russell, 1967) and Calvet and Prost (1971) envisage this situation as a transitional state during the migration of Li^+ . These ions are, therefore, less firmly fixed with respect to subsequent cation exchange reactions than the Li^+ in the octahedral sheets (Brindley and Ertem, 1971).

5.5 Dehydration

The dehydration characteristics of the expanding minerals have been discussed in Section 3.1 and 3.2 and it is sufficient to state here that normally all the minerals in this group will contract to about 10 Å after heating at 300°C for 2 hours. Any detailed study should of course be made with a selected cation. If the cation is strongly hydratable like Mg^{2+} , then the basal reflection

must be measured before the specimen has cooled or precautions taken against rehydration. Walker (1961) points out that the latter requirement must not be underestimated since clay-size Mg-vermiculite may take up moisture from the air within a few seconds if the sample is allowed to cool. The rehydrated vermiculite would then be falsely diagnosed as a chlorite. For routine purposes it would seem advisable to minimize the chance of rehydration by pretreating the sample with a poorly hydratable cation such as K^+ although, as shown in Section 3.3, this procedure by no means removes the possibility altogether.

5.6 Interlayer contaminants

Expanding minerals do not always show complete contraction after heating because they contain so-called interlayer contaminants which prop open adjacent silicate sheets. This phenomenon is particularly common in soil clays and typically the basal reflection becomes rather broad or more diffuse after heating. The properties of such materials are intermediate between chlorite and montmorillonite or vermiculite and for this reason they are frequently described as "intergrade", or "intergradient" (Jackson, 1963). The interlayer material most frequently consists of polymerized hydroxy-hydrates of Al and Mg ions (often referred to as hydroxyl-Al and Mg) and the presence of iron in this form also has been suggested. In acid soils both smectites and vermiculites often contain hydroxyl-Al, although it appears that optimum development in each mineral may be favoured by slightly different conditions (Rich, 1968). On the other hand the precipitation of interlayer Mg would normally be associated with alkaline soils and may also occur extensively in marine sediments. So far there is little evidence for naturally occurring hydroxy-Fe interlayers. The possibility of interlayer organic material has also been suggested (e.g. Maun *et al.*, 1973).

Various chemical methods have been proposed for the removal of interlayer material and these are summarized in Table 3.10. With all such methods, however, it is inevitable that the silicate structure itself is also attacked and hence the possibility that the original characteristics of the expanding mineral have been modified should always be borne in mind.

5.7 Acid treatment

When the 2:1 minerals are treated with dilute acid the H^+ ions attack the silicate layers via the interlayer region and exposed edges, so displacing octahedral ions, such as Al and Mg, which

TABLE 3.10. Reagents employed for removing interlayer material (after Rich, 1968)

Reagent	Reference
(1) KOH + KCl	Brown, 1953
(2) Heating at 400°C followed by boiling in NaOH	Dixon and Jackson, 1959
(3) NH_4F	Rich and Obenshain, 1955
(4) NaF	Glenn, 1960
(5) $NH_4F + NH_4Cl + HCl$	Rich and Cook, 1963; Rich, 1966
(6) F-saturated resin	Huang and Jackson, 1966
(7) Acetic acid	Klages and White, 1957
(8) Citric acid	Klages and White, 1957
(9) Ammonium citrate	Klages and White, 1957
(10) Na-dithionite-citrate	Tamura, 1956, 1957
(11) Na-citrate	Tamura, 1958; Sawhney, 1960

then occupy the interlayer sites. Consequently, it is difficult to prepare an H-saturated form that is stable for more than a few hours. Treatment with strong acid attacks the structure more vigorously and when combined with X-ray examination may be of some diagnostic value. Trioctahedral minerals are often destroyed by such treatment, leaving a residue of amorphous silica, which gives only a diffuse background on an X-ray diagram. Dioctahedral smectites are more resistant, although nontronite and other ferruginous forms are more readily dissolved than the highly aluminous species. Many montmorillonites will resist treatment even with concentrated mineral acids. Such treatments (corresponding to the industrial process of "activation") alter the character of the X-ray diagram of the dehydrated mineral which no longer gives a regular series of orders but a diffuse band in the region 12–15 Å, suggesting irregular interstratification. The glycerol complex of a montmorillonite treated in this way may show a regular series of orders.

6. COMPLEXES WITH 1:1 MINERALS

Interlamellar complexes formed with the kaolinite group minerals are becoming more widely used for identification purposes and form the subject of a growing volume of work. Amongst these minerals, only halloysite occurs in a naturally hydrated form but, as will be shown later, hydrates of kaolinite can be prepared experimentally. With halloysite, organic complexes can be formed by treating the mineral with an excess of an organic liquid but with kaolinite this can be done only indirectly by first forming and then replacing an intercalation complex.

The hydrated form of halloysite yields a strong basal reflection at 10.1 Å which on heating at temperatures of 60–70°C contracts to 7.2 Å. There is, therefore, sufficient space for a single layer of water molecules between the adjacent aluminosilicate sheets of the hydrated form, thus accounting for the additional 2H₂O in the composition formula. Hendricks and Jefferson (1938)

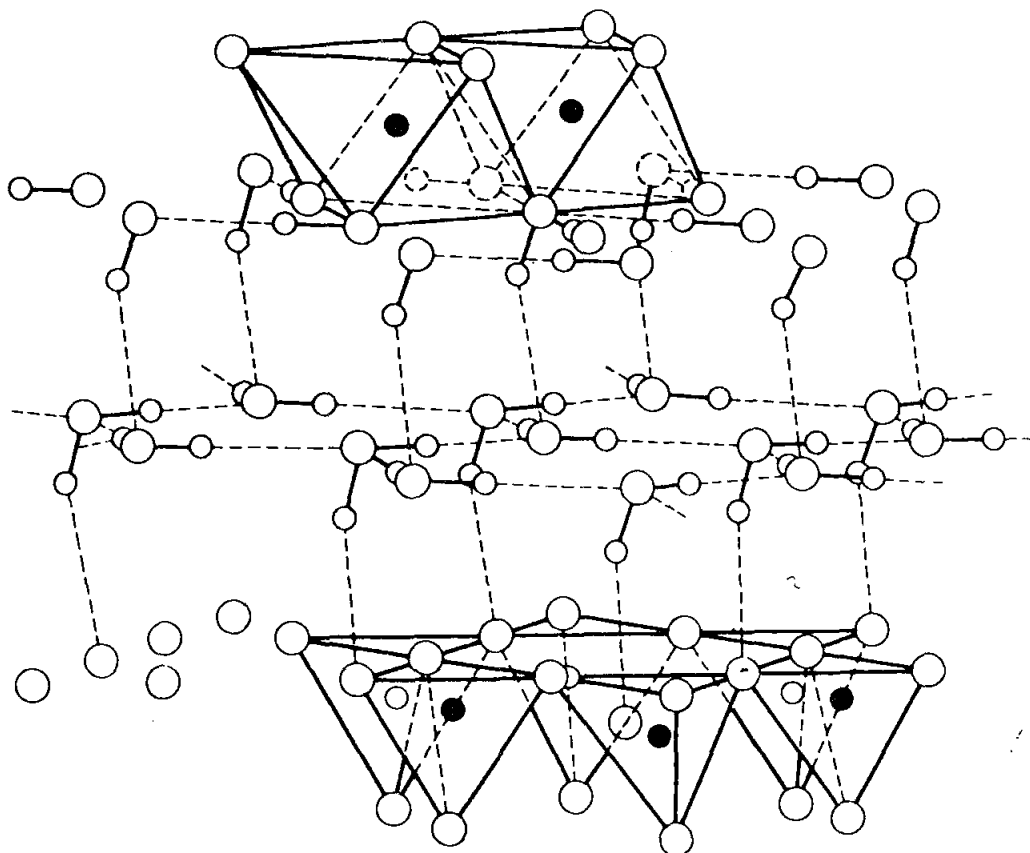


FIG. 3.19. Diagrammatic sketch of a portion of the halloysite 4H₂O structure showing the configuration of a single layer of water molecules (suggested by Hendricks and Jefferson, 1938).

showed that such a layer of water molecules could be arranged in a hexagonal pattern, and linked by hydrogen bonds to each other and to the adjacent silicate sheets (Fig. 3.19). This model is still generally accepted.

6.1 Dehydration of halloysite

The dehydration of fully hydrated halloysite was first studied comprehensively by Brindley and Goodyear (1948) who followed the changes of weight and of basal spacing when the mineral was dehydrated in atmospheres of different relative humidity (0–30%). The fact that basal spacings occurred in two ranges, 10.1–9.5 Å and 7.9–7.5 Å, corresponding to the hydrated and dehydrated forms of the mineral, was interpreted as indicating an interstratification of hydrated and dehydrated layers; there was no evidence for the existence of intermediate forms of halloysite with spacings between 9.5 and 7.9 Å. With some refinement these conclusions have been substantially confirmed by later workers. Harrison and Greenberg (1962), who extended the

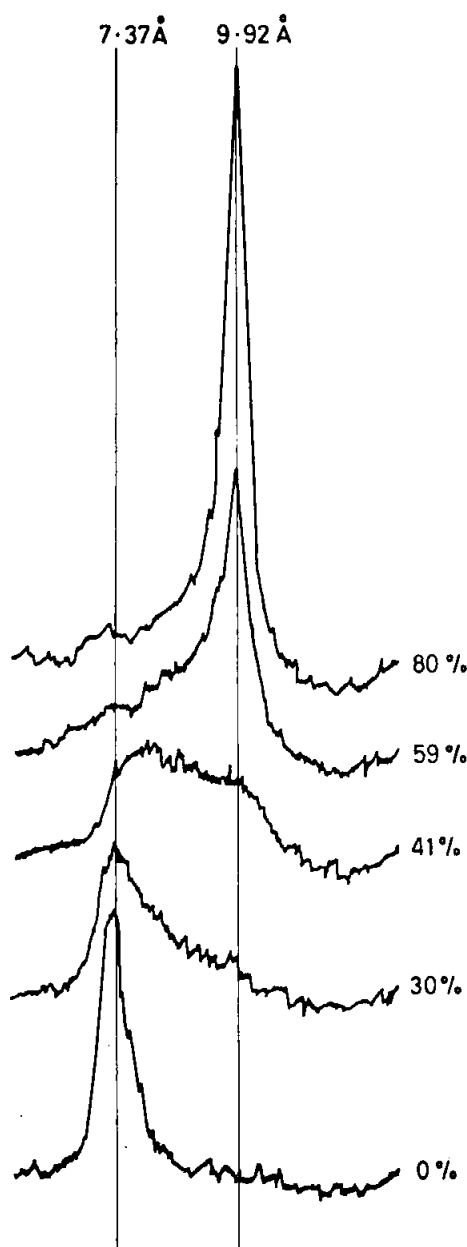


FIG. 3.20. Change in the 001 reflections of hydrated halloysite with decrease in relative humidity (after Hughes, 1966).

range of relative humidities used to 100%, observed some dehydration of the fully hydrated form even at a relative humidity of 90%, as manifested by the appearance of a diffuse shoulder on the high angle side of the 10.1 Å reflection. Hughes (1966) found that halloysite dehydrated rapidly in the 70–30% relative humidity region and suggested that samples of different origin may dehydrate over widely differing humidity ranges, the upper limit of the range possibly depending on the past drying history of the sample. A further study by Churchman *et al.* (1972) showed that the profiles of the basal reflections from partially hydrated forms could be most satisfactorily analysed by assuming that there was a strong tendency for the hydrated and dehydrated layers to be segregated with only a slight degree of random interstratification. The X-ray traces of Hughes (1966) are typical of the changes observed in the basal reflection of halloysite during progressive dehydration (Fig. 3.20). The dehydration of hallosite is practically irreversible except by passing through an intersalation complex. Thus, halloysite dehydrated to any degree shows no detectable rehydration even when exposed to 100% relative humidity for up to two months (Harrison and Greenberg, 1962).

6.2 Organic complexes with halloysite

The formation of organic complexes of halloysite was studied first by MacEwan (1946, 1948, 1949) and later by Weiss and Russow (1963), Camazano and Garcia (1966) and Olejnik *et al.* (1968). In general, organic substances enter in such a way as to form a single flat molecular layer.

TABLE 3.11. Organic complexes of halloysite after Carr and Chih (1971) and MacEwan (1948)

Compound	X-ray reflections	Δ observed	Δ min (calc.)	Δ MacEwan
Methanol	001 asymm	2.5	3.7	3.4
Ethanol	001d asymm	<0.3	4.0	2.8d
1-propanol	001d asymm	<0.3	4.0	0.3
1-butanol	001d asymm	<0.3	4.0	0.3
Ethane 1,2 diol	001, 002, 003	3.6	4.0	3.7
Propane 1,3 diol	001, 003	3.8	4.0	4.4
Butane 1,3 diol	001d asymm	3.5d	4.0	4.0d
Glycerol	001, 003	4.0	4.4	3.8
1,4 dioxane	001 asymm	n.c.	4.2	d
Methyl cellosolve	001, 003	3.8	4.4	3.5
Ethyl cellosolve	001, 003	3.7	4.4	3.6d
Butyl cellosolve	001d asymm	d	4.4	3.1d
Diethylene glycol	001, 003	3.9	3.9	3.6
Triethylene glycol	001, 003	3.8	4.0	3.5
2-chlorethanol	001, 003	3.6	4.0	3.6
Ethane 1,2 diamine	001, 003	4.5	4.0	4.5
Propane 1,2 diamine	001, 002	4.2	4.5	d
Diethylamine	001d asymm	0.3	4.0	0.3
Acetone	001d asymm	1.2d	4.0	3.9
Acetaldehyde	001 asymm	n.c.	4.0	3.6
Acetonitrile	001d asymm	0.5	3.7	3.4
Nitromethane	001, 003	3.0	3.7	3.3
Nitrobenzene	001 asymm	n.c.	3.7	d

Key: Δ is the clearance space (Å) occupied by the organic material measured as the difference between the observed $d(001)$ basal spacing and the $d(001)$ of metahalloysite *i.e.* 7.2 Å.

Δ min (calc.) values obtained by Carr and Chih (1971) from 'Catalin' molecular models.

d = diffuse (Carr and Chih, 1971; MacEwan, 1948) or double peak (MacEwan, 1948) asymm = asymmetrical peak shape.

n.c. = no complex.

A certain degree of contraction is shown by the basal spacing, but Carr and Chih (1971) have shown that the complexes generally show some interstratification with the unexpanded material. They suggest that a sample can only be accepted as being fully complexed when, besides a sharp symmetrical 001 reflection, higher rational orders are present.

TABLE 3.12. Basal spacings (Å) of kaolinite complexes prepared (a) directly from a liquid melt or concentrated aqueous solution (b) by solution in an "entraining" agent and (c) by displacement of a previously formed complex

(a) Direct Intercalation. Data from Weiss *et al.* (1963a) and Olejnik *et al.* (1970).

Intercalated Compound	Basal Spacing
Formamide	10.1
Hydrazine	10.4
Dimethylsulphoxide	11.2
Urea	10.7
Acetamide	10.9
Pyridine <i>N</i> -Oxide	12.5
<i>N</i> -Methylformamide	10.7
Dimethylformamide	12.1
Potassium acetate	14.0
Cesium acetate	14.7
Rubidium acetate	14.4
Ammonium acetate	14.05
Sodium acetate	10.1
Lithium acetate	9.5
Calcium acetate	10.4
Potassium cyanoacetate	13.0

(b) Intercalation via "entrainment" in 24% aqueous hydrazine solution.
Data from Weiss *et al.* (1963a).

Intercalated Compound	Basal spacing	
	In presence of "entraining" agent	After removal of "entraining" agent
Potassium acetate	10.4	14.0
Sodium acetate	10.4	10.1
Potassium oxalate	10.4	10.3
Potassium salt of glycine	10.7	12.4
Potassium salt of alanine	10.7	12.45
Potassium salt of lysine	10.6	14.9
Potassium lactate	10.6	11.2
Glycerol	10.4	10.5
<i>n</i> -Octylamine	31.7	31.7
Benzidine*	10.6	20.8†

* entrained in 24% solution of hydrazine in water ethanol.

† after treatment with the melt.

(c) Intercalation via displacement of pre-formed complex. Data from Camazano and Garcia (1966) and Olejnik *et al.* (1970).

Intercalated Compound	Displaced Compound	Basal Spacing
Ethylene glycol	Dimethylsulphoxide	10.9
Glycerol	Dimethylsulphoxide	11.1
Acetonitrile	Dimethylsulphoxide	11.0
Nitrobenzene	Dimethylsulphoxide	11.0
Acetone	Dimethylsulphoxide	11.2
Dimethylacetamide	<i>N</i> -methylformamide	12.3

The results obtained by various investigators are summarized in Table 3.11. Certain complexes which MacEwan observed with Hungarian halloysite were not observed by Carr and Chih (1971) with the Te Puke specimen, notably the complexes with ethanol, acetone, acetaldehyde and acetonitrile. Evidently, particular specimens of halloysite may react in different ways and kinetic factors may also play an important role (Theng, 1974). Thus, Carr and Chih (1971) observed that the Kauri tubular halloysite forms complexes more slowly and reaches equilibrium at a lower basal spacing than the tabular Te Puke material. They also failed to obtain any interlamellar complex with dimethylsulphoxide (DMSO), whereas Camazano and Garcia (1966) and Olejnik *et al.* (1968) obtained positive results. It has further been observed that several compounds not reacting with halloysite in the natural state were capable of reacting with a rehydrated specimen. Rehydration was achieved by first forming an intersalination complex with ammonium or potassium salts (Wada, 1959; Garrett and Walker, 1959) and then washing with water.

There seems to be no simple relationship between complexing ability and either dielectric constant or dipole moment of the organic molecule (Carr and Chih, 1971). The most obvious mechanism to explain the stability of these complexes involves the formation of hydrogen bonds between the organic molecule and the clay surface, intercalation being favoured by the presence of OH or NH₂ groups. Infrared measurements (Olejnik *et al.*, 1968) show that the hydroxyl stretch vibration at 3690 cm⁻¹ weakens in the spectrum of the interlamellar organic complex, suggesting that the hydroxyls in the mineral responsible for this band become bonded to the organic molecules.

6.3 Complexes with kaolinite

Kaolinite has a structure with a three-dimensional regularity and does not form interlamellar complexes so readily as halloysite. However, Wada (1961) showed that salts such as potassium acetate can penetrate into the interlayer space of kaolinite and expand the basal spacing from 7.2 to 14.2 Å. Similarly, a considerable number of polar organic molecules such as urea, hydrazine and formamide can also react with kaolinite in this way (Weiss *et al.*, 1963a, 1966). One-dimensional Fourier syntheses of the resulting complexes, indicate that the N—H...O distances are of the order of 2.81–2.84 Å, and that the carbonyl group is directed towards the hydroxyl surface thus suggesting N—H...O—Si and C=O...H—O hydrogen bonding. This work has been continued by Olejnik *et al.* (1971).

Complexes with kaolinite can be divided into three classes (Weiss *et al.*, 1963a; Olejnik *et al.*, 1970)—namely: (1) with substances introduced directly from a liquid, melt, or concentrated aqueous solution; (2) with substances introduced in the form of a solution in a so-called “entraining agent” (*i.e.* a substance capable of opening the interlamellar space and permitting the entry of the solute molecules); (3) with substances introduced by displacement of a previously formed complex. Table 3.12 gives a list of the spacings obtained with various substances which have been introduced into kaolinite according to these three procedures.

Generally, the intercalation of kaolinite is incomplete and some kaolinites cannot be intercalated at all. Wiewiora and Brindley (1969) prepared mixtures of intercalating and non-intercalating kaolinites and after submitting the mixtures to potassium acetate treatment made semi-quantitative X-ray diffraction measurements of the amount of the intercalated phase. In its simplest form the intercalation ratio is

$$\frac{I(001) \text{ complex}}{I(001) \text{ complex} + I(001) \text{ kaolinite}}$$

but Mata-Arjona *et al.* (1970) have derived a complete expression for the intercalation ratio, taking into account the structure factor and the Lorentz and polarization factors. The ratio increases with temperature and with the addition of water to the system.

For complexes formed by process (2), the solute is highly solvated below a certain limiting concentration so that few unsolvated molecules are present for intercalation. On increasing the solute concentration the rate of intercalation first increases, and then falls because of the self-association of the organic molecules at high concentrations; addition of water at this stage once again increases the reaction rate. The rate of complex formation thus passes through a maximum with concentration of complexing molecules and/or water content.

The basal spacings of the kaolinite complexes indicate that a single flat layer of organic molecules is present with a considerable amount of keying. For pyridine-*N*-oxide (PNO) complexes, Weiss *et al.* (1966) suggest two possible arrangements: (1) a double layer of molecules with the aromatic ring lying flat; (2) a single layer with the ring perpendicular to the substrate layer and the oxygen atom of the organic molecule in contact with the substrate hydroxyl. The latter orientation, however, is incompatible with the pleochroic behaviour of the PNO bands in the infrared spectrum. Fourier analyses (Weiss *et al.*, 1963*a*) and infrared data (Ledoux and White, 1966*a,b*) indicate that the ring is probably tilted in these complexes.

Olejnik *et al.* (1968) have extended their observations with DMSO to include dickite as well as kaolinite and halloysite, their work indicating that the intercalation rate for DMSO increases in the order dickite < kaolinite < halloysite. Individual kaolinites, however, show differences in reactivity which appear to be due not merely to particle size (Wiewiora and Brindley, 1969) but also to structural factors, as suggested by Weiss *et al.* (1963*a*). The spacing of the kaolinite-DMSO complex is approximately 11.2 Å, the amount of DMSO introduced being equivalent to one and a half molecules per unit cell layer; the proportion of complexed material, however, never exceeds 90% (Olejnik *et al.*, 1968). Infrared studies of the complex (Jacobs and Sterkx, 1970) show that the S=O band is normal to the basal plane, in agreement with the Fourier analysis of Weiss *et al.* (1966). It has further been suggested that the powerful interaction between the organic molecules and the clay mineral results in an enlarged kaolinite unit cell and disordered stacking of the layers and that after the removal of the intercalated DMSO a small proportion of the layers are arranged as in the dickite structure (see also Farmer and Russell, 1967).

TABLE 3.13. Characterization of the various reaction types of kaolinite (after Range *et al.*, 1969)

	Type I	Type II	Type III	Type IV	Halloysite
Reaction with hydrazine	fast reaction	fast reaction	slow reaction	no reaction	fast reaction
Basal spacing (Å)					
after treatment with hydrazine	10.42	10.42	9.5–9.6	7.2–7.3	10.0–10.2
after leaching the hydrazine compound with water	7.2	10.04	10.2	7.2–7.3	9.95
after replacement of water by ethylene glycol	7.2	10.85	10.85	7.2–7.3	10.85
after replacement of water by glycerol	7.2	7.2	7.2	7.2–7.3	11.10

Examples of different reaction types in natural kaolinite clays are:

- Type I. Georgia kaolin, moderately ordered,
- Type II. Georgia kaolin, poorly ordered,
- Type III. Pugu kaolin, K. (Robertson *et al.*, 1954),
- Type IV. Pugu kaolin, D. (Robertson *et al.*, 1954).

6.4 Identification of kaolinite group minerals using intercalation complexes

Intercalation complexes can be used to distinguish the kaolinite group minerals from serpentine or chlorite and also to differentiate between the various members of the group. Wada (1961) first pointed out that, whereas halloysite and kaolinite complexed readily with potassium acetate (and to a lesser degree with many other salts), no such complex could be formed with antigorite, chrysotile or chlorite. Such a difference in behaviour between the kaolinite and serpentine minerals is difficult to understand considering their structural similarities. The potassium acetate-kaolinite complex yields a strong basal reflection at 14 Å which does not offer a direct differentiation from chlorite, but new complexes can be readily formed by washing with saturated salt solutions. Thus, washing with ammonium nitrate gives an 11.6 Å reflection which is stable at room temperature; the full procedure is given by Andrew *et al.* (1960). Other methods for distinguishing kaolinite from chlorite have been described using hydrazine (Wada and Yamada, 1968) and DMSO (Gonzalez Garcia and Sanches-Camazano, 1968). The latter yields a spacing of 11.18 Å so that further treatment is unnecessary. However, caution is advisable in the use of these methods since it is now known that certain kinds of disordered kaolinites do not seem to form intercalation complexes (Range *et al.*, 1968; Alietti, 1970).

Differentiation between the various kaolinite group polymorphs using intercalation complexes is suggested by the studies of Wada (1965). He attempted to prepare hydrates from these minerals by first making potassium acetate complexes, converting these to ammonium chloride

TABLE 3.14. Procedure for distinguishing different reaction types of kaolinite and halloysite minerals (after Range *et al.*, 1969)

Procedure	Observed basal spacings (Å)
Drying at 110°C	7.2-7.4
Treatment with hydrazine hydrate (65°C, 7 days)	10.4₂ 9.5-9.6 7.2-7.3 10.0-10.2
Leaching of the hydrazine compound with water	7.2 10.04 10.2 sharp 8 diffuse 9.95
Replacement of water by ethylene glycol	10.85 10.85 10.85
Replacement of water by glycerol	7.2 7.2 11.10
	Kaolinite (Type I) Kaolinite (Type II) Kaolinite (Type III) Fire-clay mineral (Type IV) Halloysite

complexes and displacing the ammonium chloride by water. Halloysite forms the well-known water complex with a 10.1 Å spacing whereas kaolinite forms only a partial complex and dickite none at all. Nacrite, however, forms another well-defined water complex with an 8.5 Å basal spacing. Range *et al.* (1969) used intercalation properties with hydrazine as a means of classifying halloysite and kaolinites with varying degrees of structural disorder. Several types of kaolinite can be distinguished on the basis of the spacings observed after treatment with hydrazine, water, ethylene glycol and glycerol (Table 3.13). A flow sheet for the procedure is given in Table 3.14 and further details by Range *et al.* (1968). The initial hydrazine complex is formed by sealing the hydrazine-kaolinite mixture in a glass ampoule for 7 days at 65°C.

The type of kaolinite which does not react with hydrazine is of some interest and Range *et al.* (1969) suggested that it should be regarded as a distinct "fire-clay mineral" since it is affected by a particular type of disorder. Weiss *et al.* (1963*b*, 1967) had earlier concluded that, whereas a translational type of disorder involving layer displacement along the *a*, *b* axes does not affect intercalation, a type of disorder due to distortion of the layers around interlayer cations is inhibiting in this respect. On the other hand, Wiewiora and Brindley (1969) found no simple correlation between intercalation and the degree of structural order in the samples they studied; potassium acetate intercalation indeed diminished with particles less than about 0.5 µm in diameter, where a slight increase in structural order was observed. At the present time, therefore it seems that several factors affecting the intercalation process in the kaolinite group minerals are not fully understood.

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