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Crystal Structures of Clay Minerals and Related Phyllosilicates [and Discussion]

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Crystal structures of clay minerals and related phyllosilicates

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The paper reviews the structures and crystal chemistry of clay minerals, including interstratified minerals and related phyllosilicates. Brief accounts are presented of the disordered structures encountered in the different mineral groups and a conceptual structural model for interstratified minerals is outlined.

Introduction

Clays are by definition fine-grained solids and many of their properties derive from this fact. They are hydrous silicates with layer structures and they belong to the larger group of phyllosilicates of which micas are probably the most widely known. Layer silicates are so named because the ions (or atoms) in their structures are arranged in sets of parallel planes which are strongly bonded together to form layers. Their morphology, usually thin platy crystals, reflects the underlying atomic arrangement. Clay minerals have been defined (Bailey 1980*a*) as follows: 'Clay minerals belong to the family of phyllosilicates and contain continuous two-dimensional tetrahedral sheets of composition T_2O_5 ($T = Si, Al, Fe^{3+}, \ldots$) with tetrahedra linked by sharing three corners of each with a further corner pointing in any direction. The tetrahedral sheets are linked in the unit structure to octahedral sheets and to groups of coordinated cations or individual cations.'

The essential features of phyllosilicate structures are the continuous two-dimensional tetrahedral T_2O_5 sheets, the basal oxygens of which form a hexagonal (in ideal configuration) mesh pattern (figure 1*a*). The apical oxygen at the fourth corner of the tetrahedra, usually directed normal (or nearly normal) to the sheet, forms part of an immediately adjacent octahedral sheet in which octahedra are linked by sharing edges (figure 1*b*). The junction plane between tetrahedral and octahedral sheets consists of the shared apical oxygens of the tetrahedra and unshared OH groups that lie in projection at the centre of each sixfold ring of tetrahedra. Usually coordinating cations in the octahedral sheet are Al, Mg, Fe^{3+} and Fe^{2+} but other cations such as Li, Cr, Mn, Ni, Cu, Zn occur in some species. There are two kinds of octahedral sheets. If all the octahedra are occupied the sheet is called trioctahedral; if two-thirds of the octahedra are occupied and the third octahedron is vacant, the sheet is called dioctahedral.

The unit formed by linking one octahedral sheet to one tetrahedral sheet is named a 1:1 layer and the exposed surface of the octahedral sheet consists of OH groups (figure 1*c*). A similar linkage can occur on the other side of an octahedral sheet to form a 2:1 layer, both surfaces of which consist of the hexagonal mesh of basal oxygens. Structures exist in which the 1:1 or 2:1 layers are not electrically neutral. Charge balance is maintained in such structures by interlayer material which may be individual cations as in the mica group, hydrated cations as in vermiculites and smectites, or octahedrally coordinated hydroxide groups or linked sheets of the latter, as in the chlorite minerals. The composite unit layer plus interlayer forms a structure unit, e.g. a mica unit of structure: a mica unit. The terms plane, sheet, layer and

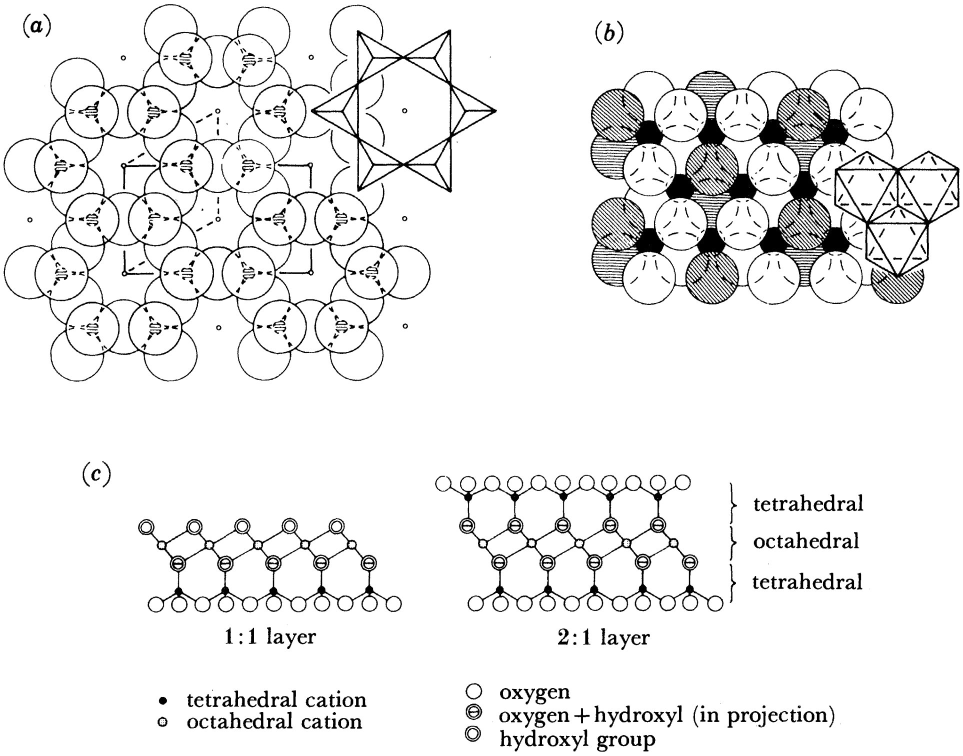

FIGURE 1. (*a*) Plan of ideally hexagonal tetrahedral sheet; alternative hexagonal *P*- (dashed) and orthogonal *C*-cells (full lines) are shown. (*b*) Octahedral sheet with inner hydroxyls of 2:1 layer shaded. (*c*) 1:1 and 2:1 layers (from Bailey 1980*b*).

TABLE 1. CLASSIFICATION OF CLAY MINERALS AND RELATED PHYLLOSILICATES

structure type	group	charge†
1:1 layer	serpentine–kaolin	*ca.* 0
2:1 layer	talc–pyrophyllite	*ca.* 0
	smectite	*ca.* 0.2–0.6
	vermiculite	*ca.* 0.6–0.9
	mica	*ca.* 1.0
	brittle mica	*ca.* 2.0
	chlorite	variable
2:1 inverted ribbons	sepiolite–palygorskite	variable

† Negative charge per formula unit layer, $O_5(OH)_4$ for 1:1 layer minerals and $O_{10}(OH)_2$ for mica, brittle mica, vermiculite and smectite.

structure unit have precise meanings and define increasingly thicker parts of the layered arrangement.

CLASSIFICATION

Phyllosilicates can be classified on the basis of layer type (2:1 or 1:1), charge on the layers, and the type of material occurring between the layers. Such a classification is set out in table 1. Further subdivision can be made based on the nature of the octahedral sheets into dioctahedral and trioctahedral subgroups, into polytypes (or polytypoids) on the basis of the way the structure units are stacked to form the crystals, and also on the basis of chemical composition into mineral species. The structures of the major groups are shown in a schematic form in figure 2.

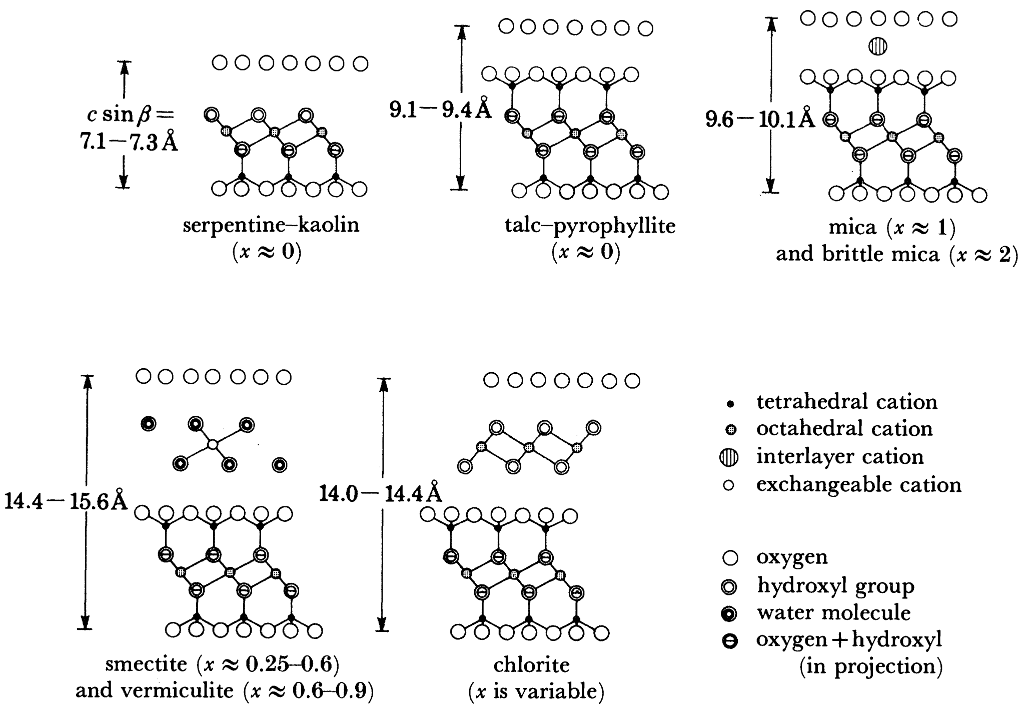

Figure 2. Structures of major clay minerals groups (from Bailey 1980*b*).

REAL STRUCTURES

The discussion so far has been limited to idealized geometrical arrangements: hexagonal arrangements of tetrahedra in the tetrahedral sheets and regular octahedra in octahedral sheets. For tetrahedral sheets to link with octahedral sheets in a common junction plane the sheets must have similar lateral dimensions.

Dimensions of free unlinked octahedral and tetrahedral sheets can be estimated. For octahedral sheets the cell parameters of brucite, $Mg(OH)_2$, and of gibbsite and bayerite, $Al(OH)_3$, lead to *b*-dimensions for the conventional *C*-face-centred orthogonal cell of 9.4 Å and 8.65 Å† respectively. Unconstrained tetrahedral sheets do not exist in minerals but an estimate of the lateral dimensions they would have can be obtained assuming undistorted tetrahedra and T–O bond lengths found in silicates. For ideal hexagonal geometry, $b = (4\sqrt{2})(\text{T–O})$. Structure determinations of many silicates have shown that Si–O = 1.618 ± 0.01 Å and tetrahedral Al–O = 1.748 ± 0.01 Å. For a tetrahedral sheet containing Si only, the lateral dimension of an ideal hexagonal array is estimated to be 9.15 ± 0.06 Å. Substitution of Al increases this and, if a linear relation between substitution of Al for Si and average T–O bond length is assumed, the corresponding *b*-dimension for a tetrahedral sheet of average composition $(Si_{1-x}Al_xO_5)$ would be close to $9.15 + 0.74x$. Thus the estimated *b*-dimension of the tetrahedral sheets in muscovite $(Si_{0.75}Al_{0.25})$ composition would be about 9.335 Å. Structural adjustments are therefore necessary to allow tetrahedral and octahedral sheets to link together. These adjustments involve distortions of both tetrahedral sheets and octahedral sheets from their ideal geometry.

Lateral dimensions of tetrahedral sheets can be decreased by twisting adjacent tetrahedra

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 0.1\ \text{nm}$.

in alternate directions through an angle α in the plane of the sheet. The resulting b-dimension is given by $b = b_{\mathrm{ideal}} \cos \alpha$. The amount of lateral decrease ranges from about 1 % for $\alpha = 8.1°$ to a maximum of 13.4 % for the maximum geometrically possible value of $\alpha = 30°$. Additional adjustment can be obtained by thinning or thickening the tetrahedral sheets by changing $\mathrm{O_{basal}}$–T–$\mathrm{O_{apical}}$ angles. An increase in this angle thickens the sheet and a decrease makes the sheet thinner. Further adjustments of tetrahedral sheets can be made by tilting of tetrahedra.

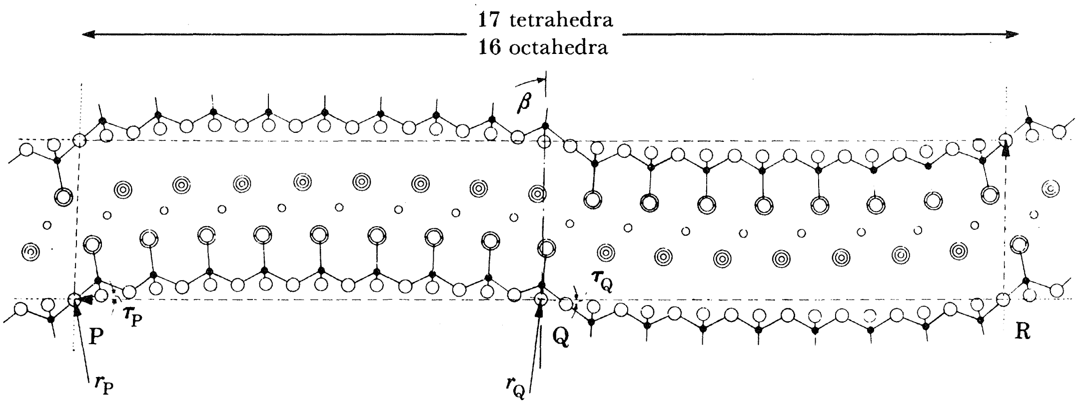

FIGURE 3. Antigorite alternating wave structure (from Bailey 1980*b*).

Octahedral dimensions are altered mainly by changes in thickness. Even when as in brucite and gibbsite, they are not linked to tetrahedral sheets, octahedral sheets are enlarged because of cation repulsion. In dioctahedral structures this leads to two types of octahedra, one larger and unoccupied and two smaller containing cations. The amount of octahedral flattening can be related to the angle between the normal to the sheet and a body diagonal. For an ideal octahedron this angle $\psi = 54.73°$ and the octahedral thickness is $2(\mathrm{M{-}O}) \cos \psi$, where M–O is the octahedral site to anion distances averaged over all the octahedra including those that are unoccupied. The lateral dimension of an octahedral sheet is given by

$$b = (3\sqrt{3})(\sin \psi)(\mathrm{M{-}O}).$$

In layer silicates ψ usually lies between 58° and 60°.

In summary, by means of the distortions from ideal geometry, tetrahedral and octahedral sheets of a wide range of composition can link together and form 1:1 and 2:1 layers.

SERPENTINE FORMULAE

Many aspects of the crystal chemistry of minerals are conveniently summarized by structural formulae. In these the species and proportion of cations in differently coordinated sites are grouped together and the formula is expressed in terms of the anion content of the unit cell (or other defined structure unit).

The anions in phyllosilicates are predominantly O and OH but F may replace some or all of the OH in some species. Comparison of the number and kinds of ions in successive planes in the structure unit of pyrophyllite and muscovite, both minerals having 2:1 layers, shows the information summarized in structural formulae. Both minerals have the same anionic framework. In pyrophyllite the succession of planes of atoms in the structure unit is

negative charge: $6\mathrm{O}:12$; $4\mathrm{O}+2\mathrm{OH}:10$; $4\mathrm{O}+2\mathrm{OH}:10$; $6\mathrm{O}:12$;
positive charge: $4\mathrm{Si}:16$; $4\mathrm{Al}:12$; $4\mathrm{Si}:16$; $6\mathrm{O}:12$.

Charge on layer is: positive, 44; negative, 44. The electrical charge on the 2:1 layer is balanced, no interlayer material is required, and the structural formula of pyrophyllite can be written

$$(\mathrm{Al}_4)(\mathrm{Si}_8)\mathrm{O}_{20}(\mathrm{OH})_4.$$

The corresponding succession of planes in the 2:1 layer of muscovite is

negative charge: 6O:12; 4O+2OH:10; 4O+2OH:10; 6O:12;
positive charge: 3Si+Al:15; Al:12; 3Si+1Al:15.

Charge on layer is: positive, 44; negative, 42. The 2:1 layer unit has a net negative charge which is balanced by 2 K^+ ions as interlayer material and the structural formula is

$$\mathrm{K}_2(\mathrm{Al}_4)(\mathrm{Si}_6\mathrm{Al}_2)\mathrm{O}_{20}(\mathrm{OH})_4.$$

The formulae given above are expressed on the basis of an $\mathrm{O}_{20}(\mathrm{OH})_4$ anion unit, the anion content of a 2:1 structure unit. The volume, V, of the structure unit in layer silicates is given by

V = repeat period normal to the plane of the layers × ac
(the area of the base of the C-face centred orthogonal cell).

For minerals with 2:1 type layers, other than chlorites, the anionic content of the ideal structure unit is $\mathrm{O}_{20}(\mathrm{OH})_4$; for minerals with 1:1 layers the content is $\mathrm{O}_{10}(\mathrm{OH})_8$. Because these structure units are face-centred, structural formulae are frequently expressed on the basis of an $\mathrm{O}_{10}(\mathrm{OH})_2$ formula unit for 2:1 layer minerals and $\mathrm{O}_5(\mathrm{OH})_4$ for 1:1 minerals.

SERPENTINE MINERALS

The serpentine minerals have 1:1 trioctahedral layers and their structural formulae are given in table 2. Their crystal forms range from platy (lizardite, amesite) to cylindrical rolls (chrysotile). Antigorite with a periodic alternating wave structure and greenalite and caryopilite with saucer-shaped domains are intermediate. These different structures have been attributed to the degree of misfit between the dimensions of the tetrahedral and octahedral sheets.

In chrysotile, magnesian lizardite and antigorite there is little or no tetrahedral substitution so the Si-rich tetrahedral sheet is smaller than the Mg-rich octahedral sheet. The linking of the tetrahedral and octahedral sheets in chrysotile is achieved by tilting the tetrahedra which causes the 1:1 layers to form cylindrical rolls with the larger octahedral sheet on the outside. In antigorite (figure 3) the tendency to curl is periodically interrupted by inverting the tetrahedral sheet and producing an alternating wave structure which allows 17 tetrahedra to link with 16 octahedra. This leads to smaller Mg/Si and OH/Si ratios than those of the ideal formula, $\mathrm{Mg}_3\mathrm{Si}_2\mathrm{O}_5(\mathrm{OH})_4$. In the region of inversion fourfold and eightfold rings with half the tetrahedra facing in opposite directions replace the normal sixfold rings (figure 4). Recently Guggenheim *et al.* (1982) have indicated that in greenalite and caryopilite a different pattern of tetrahedral inversion relieves the strain of the lateral misfit. They have postulated structures consisting of islands of six-membered rings of tetrahedra surrounded by three- and four-membered rings of inverted tetrahedra. A deficiency of octahedral cations relative to the ideal formula results and this is substantiated by chemical analysis. Structural formulae of nepouites (the Ni-rich analogues of lizardite) show similar deficiency of octahedral cations (Brindley & Wan 1975) and their powder diffraction patterns are said to be highly disordered.

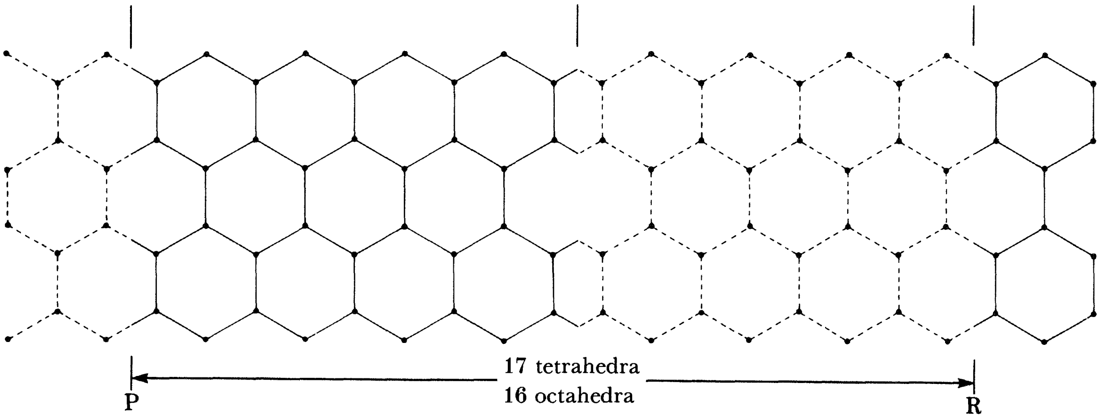

FIGURE 4. Fourfold and eightfold rings of tetrahedra in the region where tetrahedra are inverted in antigorite: sixfold rings of tetrahedra point up (full lines) and down (dashed lines) in alternating waves (from Bailey 1980*b*).

TABLE 2. STRUCTURAL FORMULAE TYPICAL OF SOME SERPENTINE–KAOLIN GROUP MINERALS

	cations		anions
	octahedral	tetrahedral	
	trioctahedral sub-group		
chrysotile	Mg_3	Si_2	$O_5(OH)_4$
lizardite	$(Mg_{2.8}Al_{0.2})$	$(Si_{1.8}Al_{0.2})$	$O_5(OH)_4$
berthierine	$[(Fe^{2+}, Mn^{2+}, Mg)_{3-x}(Fe^{3+}, Al)_x]$	$(Si_{2-x}Al_x)$	$O_5(OH)_4$
amesite	$[(Mg, Fe^{2+})_2Al_{1.0}]$	(Si_1Al_1)	$O_5(OH)_4$
cronstedtite	$(R^{2+}_{3-x}, Fe^{3+}_x)$	(Si_{2-x}, Fe^{3+}_x)	$O_5(OH)_4$
antigorite†	Mg_3	Si_2	$O_5(OH)_4$
greenalite†	Fe^{2+}_3	Si_2	$O_5(OH)_4$
	dioctahedral sub-group		
kaolinite dickite nacrite	Al_2	Si_2	$O_5(OH)_4$
halloysite – 7 Å	Al_2	Si_2	$O_5(OH)_4$ c $\frac{1}{2}H_2O$
halloysite – 10 Å	Al_2	Si_2	$O_5(OH)_4$ c $2H_2O$

† These formulae are only approximate, see text.

In the structures adopted by the planar serpentine minerals the positions of adjacent layers are governed by the pairing of the basal oxygens in the surface of the tetrahedral sheet of one layer with hydroxyls on the surface of the adjacent layer to form hydrogen bonds (figure 5). There are two possible sites for octahedral cations in a given 1:1 layer (figure 6) and there are three relative positions of adjacent 1:1 layers that allow the O–OH pairing required for interlayer hydrogen bonds (Bailey 1969). Bailey (1969) has shown that if only one of the three relative positions of adjacent layers is allowed in the same crystal there are twelve trioctahedral polytypes, i.e. structures consisting of layers of the same composition differing only in the stacking sequence. There is a tendency for certain compositions to adopt specific stacking sequences; these structures are more correctly called polytypoids rather than polytypes. Different polytypes lead to different patterns of superimposition of ions and hence to the balance of attractive and repulsive forces in the structure, and it has been found that structures that have the most energetically favourable arrangements are more abundant naturally.

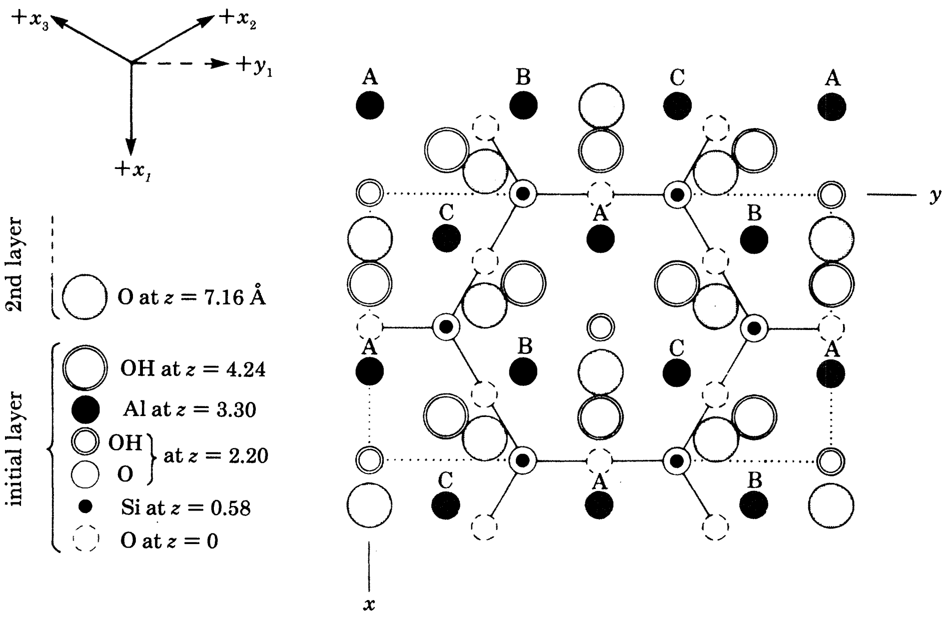

FIGURE 5. Pairing of basal tetrahedral oxygens (stippled) of upper 1:1 layer with surface hydroxyls (large double circles) of layer below (from Bailey 1980*b*).

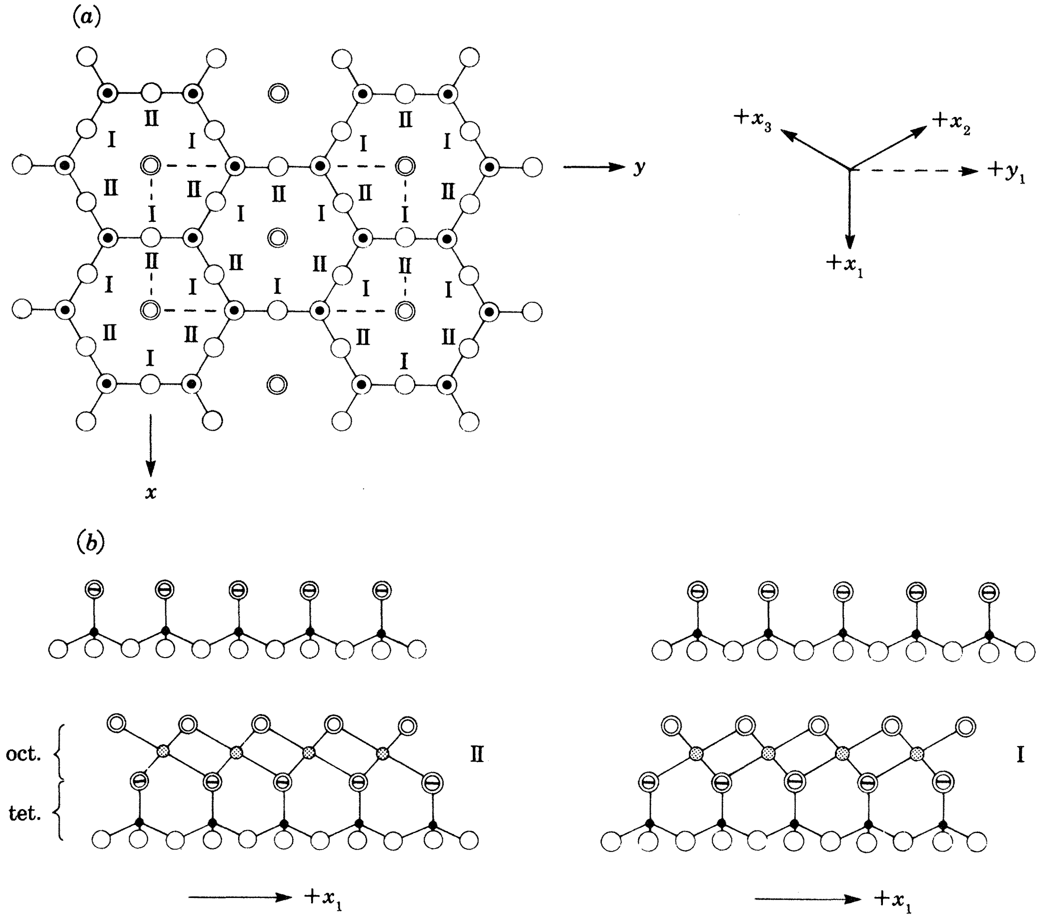

FIGURE 6. (*a*) Sets I and II of octahedral cation positions above a tetrahedral sheet of a 1:1 layer relative to a fixed set of hexagonal axes. (*b*) Octahedral sheets in different orientations due to occupancy of set I or set II octahedral cation sites (from Bailey 1980*b*).

Partly disordered layer stacking is common in serpentine minerals that arise from $\frac{1}{3}b$ displacements at interlayer junctions and disorder in the sets of octahedral cations sites that are occupied.

KAOLIN MINERALS

The kaolin minerals consist of 1:1 dioctahedral layers and their structural formulae are given in table 2. There are three polytypes kaolinite, dickite and nacrite. Only two of the three octahedral sites are occupied in any 1:1 layer and the larger vacant octahedral site is surrounded by six smaller occupied sites (figure 7). Zvyagin (1962) showed that there were 52 possible dioctahedral structures with periodicities between one and six layers. From analysis of attractive and repulsive forces between adjacent layers Newnham (1961) showed that dickite and nacrite should be the most stable 2-layer forms and kaolinite the most stable 1-layer form. Bailey (1963) has shown that the structures of kaolinite, dickite and nacrite differ in the arrangement of vacant and occupied octahedral cation sites in successive layers.

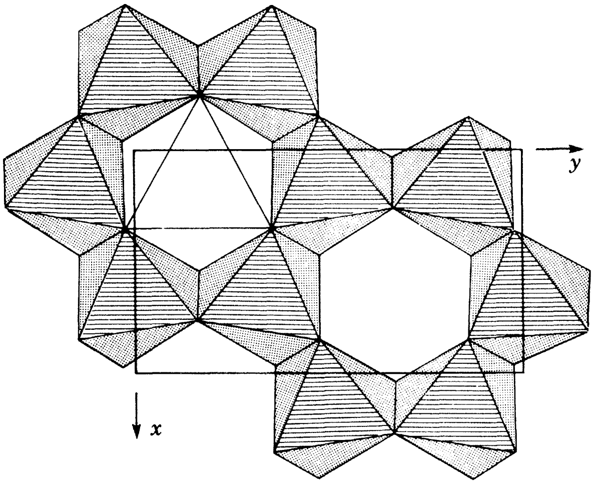

FIGURE 7. Occupied octahedra (shaded) surrounding larger vacant octahedral site in dickite structure (from Bailey 1980*b*).

Partly disordered kaolin minerals are common. Careful analysis of powder diffraction patterns by Plançon & Tchoubar (1975, 1976, 1977) showed that faults involving displacement of octahedral cation vacancies and stacking faults by linear displacements of layers by $\frac{1}{3}b$ and by arbitrary distances were involved. Their results showed that the most important type of defect was that arising from variations in occupancy of the three types of octahedral cation sites. Faults arising from linear displacements of adjacent layers occurred but were of less importance.

Halloysite minerals show morphologies that range from the most common tubular form to pseudo-spherical forms. In addition the 10 Å form has been reported to exist as in a platy form. Halloysite consists of 1:1 dioctahedral layers that are stacked turbostratically. It exists in two forms, a less-hydrated 7 Å form in which there is little or no water between the layers, and a 10 Å-hydrated halloysite which has a single sheet of water molecules between the layers. In partly dehydrated halloysite some of the interlayers contain water, others do not, and hydrated and dehydrated interlayers appear to be in a random sequence.

TALC AND PYROPHYLLITE

The minerals of this group have neutral 2:1 type layers. Structural formulae are given in table 3. Talc and the disordered fine grained varieties kerolite (Mg-rich) and pimelite (Ni-rich) have trioctahedral layers; pyrophyllite has dioctahedral layers.

The electrically neutral layers of pyrophyllite and talc are held together by van der Waals bonding reinforced by a small ionic attraction. Layer stacking is restricted neither by the need to superimpose rings of tetrahedral basal oxygens around interlayer cations nor by arrangements required for hydrogen bonding. In ordered structures oxygens in adjacent layers do not adopt the closest possible packing arrangement. In both talc and pyrophyllite four of the six basal oxygens of one layer superimpose between two oxygens of the hexagonal ring of basal oxygens in the next layer. This arrangement leads to a minimum Si–Si repulsion between adjacent layers.

TABLE 3. STRUCTURAL FORMULAE OF TALC–PYROPHYLLITE GROUP MINERALS

	cations		anions
	octahedral	tetrahedral	
	trioctahedral		
talc	Mg_3	Si_4	$O_{10}(OH)_2$
kerolite	Mg_3	Si_4	$O_{10}(OH)_2$ c $1H_2O$
	dioctahedral		
pyrophyllite	Al_2	Si_4	$O_{10}(OH)_2$

Partial disorder in layer stacking is common in pyrophyllite and talc. Layer displacements of $\frac{1}{3}b$ lead to identical positions of the atoms in the surfaces of opposing layers and hence displacements occur easily.

Kerolite is a very fine-grained material with composition identical to talc except that more water is found by analysis. Layer stacking appears to be completely turbostratic. Thus the oxygens in the surface of adjacent layers do not interweave as they do in talc and as a result the layer spacing is slightly larger than talc. It is also possible that occasional water interlayers or occluded water molecules are situated between the talc-like layers.

MICAS

The 2:1 layers in micas are negatively charged and this charge is balanced by large univalent cations, usually potassium. As in the other mineral groups discussed previously there are trioctahedral and dioctahedral subgroups. Table 4 summarizes the structural formulae of some common micas. The layer charges arise by (i) substitution of Al for Si in tetrahedral sites, as in muscovite, and (ii) substitution of univalent or divalent cations for the divalent or trivalent octahedral cations in trioctahedral and dioctahedral micas respectively, as in celadonite.

The stacking of 2:1 layers of micas is controlled by the 'keying' of the large interlayer cation into the ideally hexagonal rings of surface oxygens in adjacent layers. Frequently because of tetrahedral rotation the surface oxygen arrangement is ditrigonal. Smith & Yoder (1956) derived the possible stacking sequences that apply to both trioctahedral and dioctahedral subgroups. Based on the assumption that the same interlayer stacking angle is found between all the layers in a given crystal, they showed that there are only six possible polytypes. They used a convenient and now widely accepted nomenclature for these in terms of the symmetry of the polytype and the number of mica units in the repeat unit. These polytypes are $1M$ (one-layer monoclinic), $2M_1$ and $2M_2$ (both two-layer monoclinic structures), $2Or$ (two-layer orthorhombic), $3T$ (three-layer trigonal) and $6H$ (six-layer hexagonal). The $1M$, $2M_1$ and $3T$ structures are most abundant because in these the surface oxygen arrangement is ditrigonal (owing to tetrahedral twist), and the coordination of the large interlayer cation is octahedral with respect to its nearest oxygen neighbours. In the $2M_2$, $2Or$ and $6H$ structures, the six oxygens around the interlayer cation form a trigonal prism in which three surface oxygens of one layer superimpose on three oxygens of the adjacent layer, presumably a less energetically favourable situation.

TABLE 4. STRUCTURAL FORMULAE OF SOME MICA GROUP MINERALS INCLUDING CLAY MICAS

		cations		anions
	interlayer	octahedral	tetrahedral	
		trioctahedral		
phlogopite	K	Mg_3	(Si_3Al)	$O_{10}(OH)_2$
biotite	K	$(MgFe^{2+})_3$	(Si_3Al)	$O_{10}(OH)_2$
		dioctahedral		
muscovite	K	Al_2	(Si_3Al)	$O_{10}(OH)_2$
paragonite	K	Al_2	(Si_3Al)	$O_{10}(OH)_2$
phengite	K	$(Al_{1.5}Mg_{0.5})$	$(Si_{3.5}Al_{0.5})$	$O_{10}(OH)_2$
celadonite	K	$(AlFe^{3+})_1(MgFe^{2+})_1$	Si_4	$O_{10}(OH)_2$
glauconite	$K_{0.85}$	$(R^{3+}_{1.4}R^{2+}_{0.6})$	$(Si_{3.75}Al_{0.25})$	$O_{10}(OH)_2$
illite	$K_{0.8}$	$(R^{3+}_{1.65}R^{2+}_{0.35})$	$(Si_{3.55}Al_{0.45})$	$O_{10}(OH)_2$

If only an occasional mistake occurs in layer stacking angles, twinned crystals result. If the stacking angle varies regularly or randomly, disordered crystals are formed. In addition to variation in layer stacking angles, disorder may arise from variations in the distances between different 2:1 layers. Kodama *et al.* (1971) from a careful analysis of line profiles of basal reflections concluded that variation in layer to layer separation was related to the number of interlayer cations per formula unit, ideally 1. In the samples they studied these ranged from 0.913 to 0.837 per formula unit.

Micas that occur widely in fine grained form are illite, glauconite and celadonite. Celadonite appears to have an ordered $1M$ structure; illite and glauconite are $1M$ disordered. Illite and glauconite units commonly occur interstratified with smectite layers and it is difficult to detect with certainty the presence of less than 10% swelling interlayers. Even so, whereas celadonite appears to have close to one large cation per formula unit, glauconites and illites that show no evidence of interstratification rarely contain as many as 0.8 large cations per formula unit. Another feature of illite (and glauconite) is that chemical analyses show more structural water per formula unit than well-crystallized micas (Hower & Mowatt 1966; Cimbálníková 1971). The modern consensus is that this water is located between occasional 2:1 layers either as water molecules or lenses of water trapped between layers.

BRITTLE MICAS

Brittle micas are distinguished from true micas in having a negative charge of 2 per formula unit. Table 5 gives ideal structural formula for clintonite (trioctahedral) and margarite (dioctahedral). The layer charge may originate entirely in the tetrahedral sheet, or partly in the tetrahedral sheet and partly in the octahedral sheet. Clintonite with $SiAl_3$ in the tetrahedral sheet has the largest tetrahedral twist, $\alpha = 23°$, found in layer silicates which decreases the lateral dimensions of the sheet by about 10%. Margarite, the dioctahedral variety, is of interest because it has been shown that in one specimen the Al content of the two tetrahedral sheets in the same 2:1 layer differ by about 10% (Guggenheim & Bailey 1975).

TABLE 5. STRUCTURAL FORMULAE OF BRITTLE MICA GROUP MINERALS

		cations		anions
	interlayer	octahedral	tetrahedral	
		trioctahedral		
clintonite	Ca	(Mg_2Al)	$(SiAl_3)$	$O_{10}(OH)_2$
		dioctahedral		
margarite	Ca	Al_2	(Si_2Al_2)	$O_{10}(OH)_2$

TABLE 6. STRUCTURAL FORMULAE OF SOME CHLORITE GROUP MINERALS

	hydroxide sheet		2:1 layer		
	cations	anions	cations		anions
			octahedral	tetrahedral	
		trioctahedral			
	$(R^{2+}_{1.4}R^{3+}_{1.6})$	$(OH)_6$	R^{2+}_3	$(Si_{2.4}Al_{1.6})$	$O_{10}(OH)_2$
	$(R^{2+}_{1.1}R^{3+}_{1.5}\square_{0.4})$	$(OH)_6$	R^{2+}_3	$(Si_{3.3}Al_{0.7})$	$O_{10}(OH)_2$
		di-trioctahedral			
sudoite	$(R^{2+}_{2.1}R^{3+}_{0.9})$	$(OH)_6$	$Al_{2.1}$	$(Si_{2.8}Al_{1.2})$	$O_{10}(OH)_2$
cookeite	(Al_2Li)	$(OH)_6$	Al_2	(Si_3Al)	$O_{10}(OH)_2$
		di-dioctahedral			
donbassite	$(Al_{2.2}Mg_{0.1})$	$(OH)_6$	Al_2	$(Si_{3.2}Al_{0.8})$	$O_{10}(OH)_2$

CHLORITES

The chlorite structure consists of negatively charged 2:1 layers that are regularly interleaved with positively charged sheets of cations octahedrally coordinated to hydroxyls. In addition to the electrostatic attraction between the negatively charged 2:1 layer and the positively-charged hydroxide sheet, the hydroxyls of the hydroxide sheet form hydrogen bonds with the surface oxygens of the 2:1 layers on either side.

There are two octahedrally coordinated sheets in the chlorite structure, one in the 2:1 layer and another in the hydroxide interlayer sheet. These are either both trioctahedral (trioctahedral chlorites), dioctahedral in the 2:1 layer and trioctahedral in the hydroxide sheet (di-trioctahedral) or dioctahedral in the 2:1 layer and in the hydroxide sheet (di-dioctahedral). Structural formulae for these different chlorites are given in table 6. Tri-dioctahedral varieties may be possible but have not yet been recognized naturally.

Chlorites are usually either regular one-layer structures or more commonly irregular structures with $\frac{1}{3}b$ displacements. Bailey & Brown (1962) have shown that there are twelve possible different regular chlorite polytypes designated I or II, according to which of the two sets of octahedral cation positions are occupied in the interlayer sheet, *a* or *b*, according to the position of the interlayer sheet relative to the plane of surface oxygens of an underlying 2:1 layer, and 1–6, depending on the position of the second 2:1 layer above the interlayer sheet (figure 8).

Many chlorites have what has been termed semi-random stacking sequences. Their X-ray diffraction patterns indicate that adjacent 14 Å thick chlorite units (2:1 layer plus hydroxide sheet) are irregularly stacked but the layers and interlayers maintain hydrogen bonding and only occur in positions that are related by $\pm\frac{1}{3}b$ shifts along the three pseudo-hexagonal Y-axes. These semi-random structures allow irregular stacking sequences of either the three a or three b positions of the interlayer sheet on the original 2:1 layer and of the 2,4,6 ('even') or 1,3,5 ('odd') positions of the following 2:1 layer on the hydroxide sheet. Because of equivalence of some of the structures, there are found to be six semi-random structures. Four of these are based on a monoclinic-shaped cell with $\beta = 97°$, I*a*-even, I*b*-even, II*a*-odd, II*b*-even, and two are based on an orthohombic-shaped cell $\beta = 90°$; I*b*-odd and II*a*-even. These six semi-random sequences can be recognized from X-ray powder diffraction patterns. Four have been found to occur naturally, II*b*-even (80%), I*b*-odd, $\beta = 90°$ (12%), I*b*-even, $\beta = 97°$ (4%), I*a*-even, $\beta = 97°$ (3%). The relative abundance of these structures can be explained on the basis of differences in attractive and repulsive forces of which repulsion of the superposed interlayer cations and tetrahedral cations is probably the most important in decreasing the stability of I*a* and II*a* structural units relative to I*b* and II*b*. Bailey (1975) has given a detailed analysis of the structural factors affecting the relative stabilities of chlorite structures.

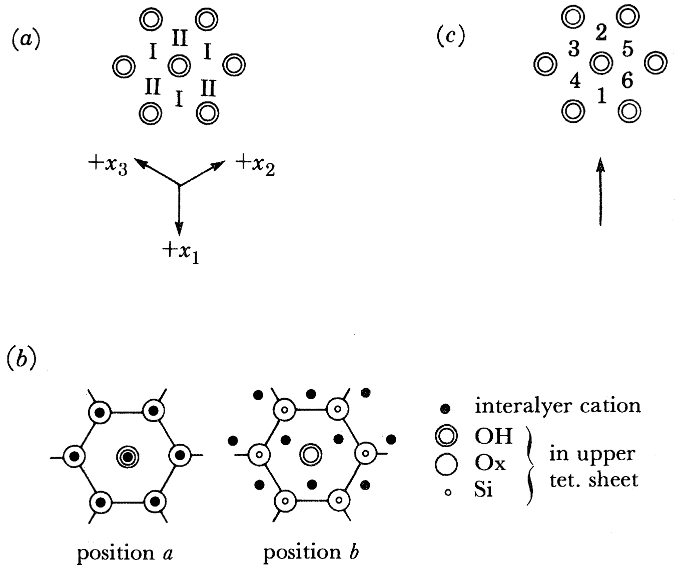

FIGURE 8. (*a*) Choice of octahedral cation sets I and II in interlayer hydroxyl sheet in chlorite. (*b*) Two different positions *a* and *b* of cations of interlayer hydroxyl sheet over upper tetrahedral sheet of underlying 2:1 layer. (*c*) Six positions for centre of hexagonal ring in 2:1 layer above interlayer relative to upper hydroxyl plane of interlayer sheet (from Bailey 1980*b*).

VERMICULITES

Vermiculites and smectites are minerals whose 2:1 layers have a smaller negative charge than micas. As indicated in table 1, the layer charge on 2:1 layers in vermiculites ranges from about 0.6–0.9 per formula unit; in smectites the layer charge lies in the range 0.2–0.6. Vermiculites are trioctahedral; dioctahedral varieties may exist but have not been found free of other minerals in nature. A typical structural formula for trioctahedral vermiculite is

$$(X^{+2}_{0.4})[(MgFe^{2+})_{2.3}(AlFe^{3+})_{0.7}](Si_{2.5}Al_{1.5})O_{10}(OH)_2.$$

Because vermiculites and smectites have smaller layer charge than micas the attractive forces between the 2:1 layers and the interlayer cation are less. The hydration energy of the interlayer cation may then be sufficient to overcome the attractive forces of the layer to the cations and allow water to hydrate the interlayer cation which causes swelling normal to the plane of the layers. The ability of vermiculites and smectites to swell in water allows cation exchange between the interlayer cation and cations in an external solution. Both groups of minerals can also sorb organic cations by cation exchange and other organic molecules by solvation of the interlayer cations. In fact a widely used diagnostic test for identifying vermiculites and smectites is based on the amount of swelling when ethylene glycol or glycerol is sorbed between the 2:1 layers. Generally, vermiculites swell less than smectites because the interlayer cation to 2:1 layer attractive force is greater.

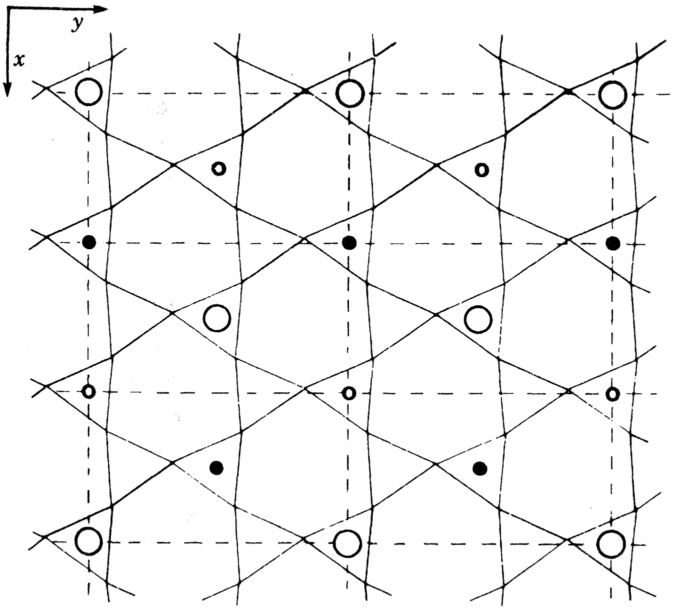

FIGURE 9. Superlattice of dimensions $3a \times b$ caused by short-range order in distribution of exchangeable interlayer cations (large circles) in local domains in vermiculite. Smaller solid or open circles are possible sets of cation positions in adjacent domains (from Bailey 1980*b*).

The crystal structure of the 14.36 Å phase of Mg-vermiculite (Mathieson & Walker 1954; Mathieson 1958; Shirozu & Bailey 1966) shows that the exchangeable Mg^{2+} cations lie in a plane midway between adjacent 2:1 layers and have a plane of water molecules on either side. The interlayer material is similar to the interlayer sheet in chlorite but with about $\frac{1}{9}$ of the cation sites occupied and $\frac{2}{3}$ of the hydroxyl sites of chlorite occupied by water molecules in vermiculite. The tetrahedral cation sites in vermiculite are ordered, the T_1 site having more Al than the T_2 site and the interlayer cations are found in those sites which lie between the Al-rich tetrahedra in adjacent layers. Although all the chlorite stacking sequences should be possible, only the I*a* chlorite structure has been found in vermiculites. I*a* chlorites are less stable than II*b* and I*b* types because of repulsion between superposed interlayer and tetrahedral cations. This cation repulsion is less in vermiculite because there are fewer interlayer cations and their situation in the sites that give local charge balance may be the factor that causes the I*a* type structure to be favoured.

The interlayer cations and water molecules in vermiculite appear on average to be randomly distributed over the possible sites. Alcover *et al.* (1973) have shown short-range ordering of interlayer cations over a face-centred superlattice with dimensions $3a \times b$ (figure 9). This ordering is two-dimensional only, so that cation distribution in one interlayer is not related to that in the next and may even change in different regions of the same interlayer.

The structural similarities of chlorite and vermiculite give rise to materials of intermediate type which may have hydrated cations and islands of hydroxide material in the interlayer. Minerals of this kind are common and appear to be formed by the alteration of micas in moderately acid environments, and give rise to materials that have been referred to as dioctahedral vermiculite, soil chlorites or smectite intergrades commonly found in soils (Brown 1953; Rich 1968).

SMECTITES

As discussed in the section on vermiculites, smectites have 2:1 layers with layer charge 0.2–0.6 per $O_{10}(OH)_2$ formula unit and have the ability to swell by absorption of water and other substances between the 2:1 layers. The interlayer cations are usually easily exchangeable with these in external solutions.

TABLE 7. IDEAL STRUCTURAL FORMULAE OF SOME SMECTITE GROUP MINERALS

	cations			anions
	interlayer†	octahedral	tetrahedral	
		trioctahedral sub-group		
saponite	$X_{0.5}^{+1}$	Mg_3	$(Si_{3.5}Al_{0.5})$	$O_{10}(OH)_2$
hectorite	$X_{0.3}^{+1}$	$(Mg_{2.7}Li_{0.3})$	Si_4	$O_{10}(OH)_2$
		dioctahedral sub-group		
montmorillonite	$X_{0.35}^{+1}$	$(Al_{1.65}Mg_{0.35})$	Si_4	$O_{10}(OH)_2$
beidellite	$X_{0.4}^{+1}$	Al_2	$(Si_{3.6}Al_{0.4})$	$O_{10}(OH)_2$
nontronite	$X_{0.4}^{+1}$	Fe_2^{3+}	$[Si_{3.6}(Al, Fe^{3+})_{0.4}]$	$O_{10}(OH)_2$

† X denotes an exchangeable cation.

Both trioctahedral and dioctahedral smectites occur with a wide range of compositions. Table 7 gives structural formulae for some of the more common varieties. The charge on the layers arises from tetrahedral substitution, octahedral substitution or a balance of both. In the dioctahedral subgroup ideal montmorillonite has octahedral substitution only; beidellite and nontronite have tetrahedral substitution. Many dioctahedral smectites show both octahedral and tetrahedral substitutions. In saponites, trioctahedral Li-poor smectites, tetrahedral substitution predominates whereas in hectorite, a Li-rich trioctahedral smectite, the charge arises from replacement of some divalent Mg^{2+} octahedral cations by Li ions. Stevensite is a trioctahedral smectite with less than the ideal octahedral occupancy of three cations and little or no tetrahedral Al for Si substitution. The deficiency of octahedral cations gives rise to the negative charge on the layers.

Layer stacking in most smectites is random, there being little or no relation in the *ab*-plane in the positions of adjacent layers. Some saponites and beidellites, notably those with higher charge on the 2:1 layers, show some ordering in layer stacking when the appropriate interlayer cations are present and when in appropriate hydration states.

Crystalline swelling of smectites in water is caused by hydration of the interlayer cation. The amount of swelling depends mainly on relative humidity and the nature of the interlayer cation. When Na is the interlayer cation, hydrates with one, two and three layers of water molecules in the interlamellar space are formed and at large relative humidities 2:1 layers may disperse. With Ca interlayer cations, swelling appears to be limited to the three water-layer hydrate in which the 2:1 layers are separated by about 9 Å. The two-layer hydrate is stable over a wide range of relative humidities (*ca.* 0.98–0.3, Ormerod & Newman 1983), and the one-layer hydrate is found at small relative humidities.

Sepiolite and palygorskite

Both sepiolite and palygorskite have a lath-like or fibrous morphology that reflects their crystal structures (figures 10 and 11). Both contain continuous planes of oxygen about 6.5 Å apart that are the basal oxygens of dominantly Si tetrahedra. Apical oxygens point up and down from the basal oxygen planes so that tetrahedra pointing in the same direction form ribbons in the 5.3 Å repeat fibre direction. The tetrahedra in the ribbons with apices facing up and down are linked via octahedral cations thus forming a 2:1 structure continuous in the fibre direction but limited in extent to the direction perpendicular to the ribbons. The ribbons have a width of three linked pyroxene chains in sepiolite and two pyroxene chains in palygorskite. Thus the basal oxygens of the tetrahedra form continuous two-dimensional planes but with apices that point either up or down in adjacent ribbons. In the ideally rectangular channels between the ribbons there are exchangeable Ca and Mg ions and and variable amounts of zeolitic water. Water molecules denoted (OH_2) in the structural formulae on table 8 are coordinated to octahedral Mg or Al at the edges of the ribbons and are more strongly held than the zeolitic water in the channels. Evidence has been presented (Yücel *et al.* 1981) that in less-well-crystallized sepiolites the silicate ribbons are not parallel but form a ‘herringbone’

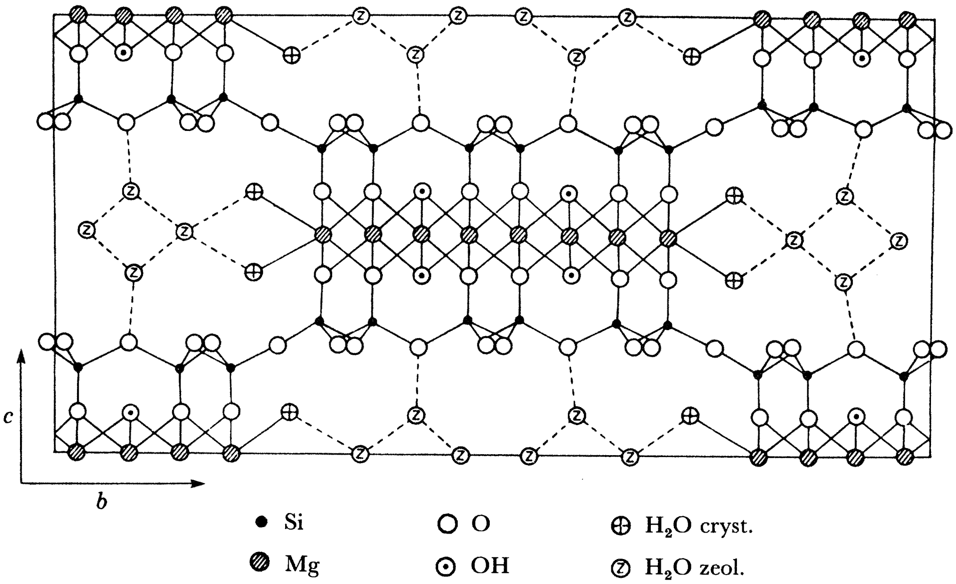

Figure 10. Structure of sepiolite projected along the fibre axis (Bailey 1980*b*).

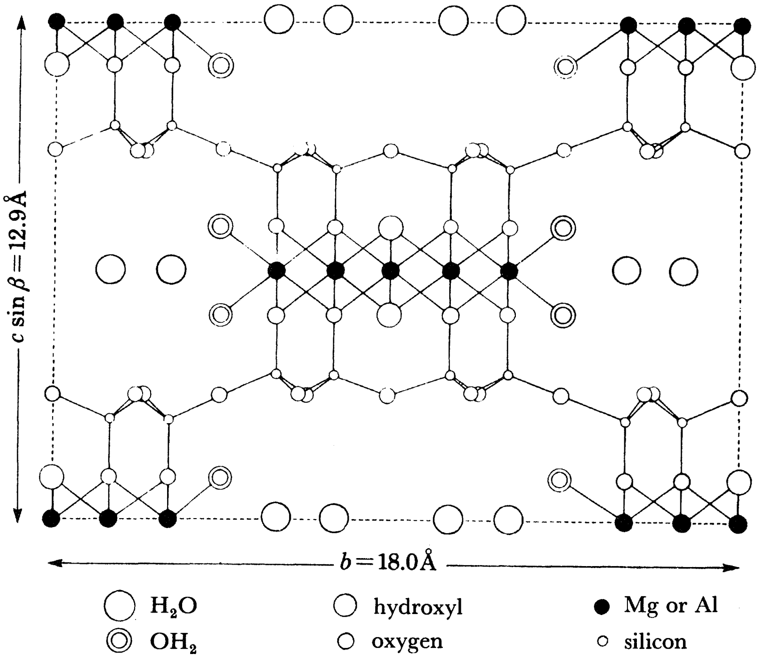

FIGURE 11. Structure of palygorskite projected along fibre axis (from Bailey 1980*b*).

TABLE 8. STRUCTURAL FORMULAE OF SEPIOLITE–PALYGORSKITE GROUP MINERALS

	2:1 ribbons			channels	
	cations		anions	exchangeable cations	
	octahedral	tetrahedral			
		trioctahedral			
sepiolite (ideal)	Mg_8	Si_{12}	$O_{30}(OH)_4(OH_2)_4$		
	$(Mg_{7.3}Al_{0.5})$	$(Si_{11.8}Al_{0.2})$	$O_{30}(OH)_4(OH_2)_4$	$X^{+1}_{0.1}$	$0.8H_2O$
		dioctahedral			
palygorskite (ideal)	Mg_5	Si_8	$O_{20}(OH)_2(OH_2)_4$		
	(Mg_2Al_2)	$(Si_{7.8}Al_{0.2})$	$O_{20}(OH)_2(OH_2)_4$	$X^{+1}_{0.2}$	$0.4H_2O$

pattern by small rotations of the ribbons in alternate directions about the fibre axis at the corners of the ribbons.

INTERSTRATIFIED MINERALS

Interstratification is the term used to describe phyllosilicate materials in which structural units of different kinds occur in the stacking sequence normal to the plane of the layers.

Interstratified materials arise in two ways. Some clay minerals (notably smectites, vermiculites and halloysite) can sorb inorganic (e.g. water and cations) or organic (cations, alcohols, etc.) material between the layers. This process may not take place equally in all the interlayers at the same time so more than one kind of interlayer separation in the same crystallite may result. Second, because the 2:1 and 1:1 layers are strongly bonded internally but relatively weakly bonded to each other and because the surface planes of the different kinds of layers and the hydroxide sheet of chlorites are geometrically similar, layers with different internal arrangements can stack together and articulate well at their interfaces.

Interstratification may be random, in which no discernible pattern exists in the stacking sequence, ordered, with regular periodic stacking schemes, and partly ordered, in which there is a tendency for ordering to exist.

Regularly ordered sequences have been found for two-component systems only. Those which were judged (Bailey 1982) to be sufficiently regular to be allocated mineral names, plus hydrobiotite (Brindley *et al.* 1983), are listed in table 9. In these the stacking sequence of structure units is ABABAB ... and the repeat distance normal to the layers is the sum of that of the components. Another two-component system, named tarasovite (Lazarenko & Korolev 1970) and described by them as an interstratification of mica and rectorite (itself a regular 1:1 interstratification of mica and smectite units) has been included although it does not quite meet Bailey's (1982) criteria. In this mineral ideally the layer sequence would be ... AAABAAABA ... in which A represents a mica unit and B represents a smectite unit. Brindley & Suzuki (1983) have examined this material and report that there is a small excess of mica units over and above those required for the ideal sequence. These they believe to be randomly interstratified among the AAAB units.

TABLE 9. REGULARLY INTERSTRATIFIED MINERALS

mineral	component layers
	1:1 *regular*
aliettite	talc–saponite
corrensite	trioctahedral chlorite–trioctahedral smectite trioctahedral chlorite–trioctahedral vermiculite
hydrobiotite	biotite–trioctahedral vermiculite
kulkeite	trioctahedral chlorite–talc
rectorite	dioctahedral mica–dioctahedral smectite
tosudite	chlorite–smectite (dioctahedral)
	2:1 *regular*
tarasovite	mica–rectorite (3:1 mica–smectite)

Less regularly ordered sequences than those in table 9 are very common ranging from partly ordered to random. The following two-component systems have been reported: illite–smectite, glauconite–smectite, mica–vermiculite, mica–dioctahedral chlorite, smectite–chlorite, chlorite–vermiculite, kaolinite–smectite, and mica–chlorite. Three component systems, illite–chlorite–smectite and illite–smectite–vermiculite are also found (Reynolds 1980). In addition Eberl *et al.* (1982) have described a kerolite-stevensite interstratification.

The need for precise use of the terms outlined earlier – 'plane', 'sheet', 'layer', 'structure unit' and 'interlayer' – for the various components of layer silicate structures is specially evident in discussion of interstratified minerals and in hypotheses about their structure and paragenesis.

A CONCEPTUAL MODEL FOR INTERSTRATIFIED MINERALS

Consider interstratifications of mica units (M) and smectite units (S). The mica units consist of 2:1 layers with a negative charge of about 1 equivalent per formula unit which is balanced by an interlayer K ion. The smectite units are 2:1 layers having a negative charge of, say, about 0.3 equivalents per formula unit balanced by a solvated interlayer exchangeable cations. The basic assumption is that local charge balance is maintained across the interlayer between adjacent 2:1 layers and that the charges on the surfaces of the 2:1 layers on either side of an interface are equal. In pure mica and smectite, the stacking sequences are ... MMMM ... and ... SSSSS ... respectively. In both mica and smectite structures (and in all non-interstratified structures) there is one kind of interlayer and one kind of interface and interlayer. Under the assumptions made above the mica 2:1 and smectite 2:1 layers must be homogeneous or nearly so, i.e. have about the same negative charge on the silicate oxygen surfaces on each side of the 2:1 layer that face each other across every interlayer. We can symbolize these by ↔↔ for mica and — — for smectite 2:1 layers, where an arrowhead represents a high-charge half-layer and no arrowhead, a low-charge half-layer, and the distance between the symbols indicates the separation of adjacent 2:1 layers.

Next consider the regularly interstratified mineral rectorite in which the unit sequence is MSMSMSMS .... To obtain two kinds of interlayer regions the material must contain polar 2:1 layers (i.e. layers with asymmetric charge distribution) that have high charge (mica-like) on one side of each 2:1 layer and low charge (smectite-like) on the other side. Layers of this type, symbolized ← can be stacked →← →← to provide an alternation of high-charged non-expanding K-containing interlayers with low-charged expanding interlayers that contain exchangeable cations and water. The rectorite structure would then have one kind of layer, two kinds of interfaces and two kinds of interlayers. An ideal tarasovite, MMMSMMMS ..., which consists of 2:1 layers in which three non-expanding interlayers are regularly followed by an expanding interlayer can be symbolized

→↔↔← →↔↔←

It has two kinds of interfaces in the proportion of three non-expanding to one expanding, and two kinds of 2:1 layers, one non-polar and the other polar, and polar and non-polar layers that are equally abundant. The sequence can be readily adjusted to include the small extra proportion of mica units found by Brindley & Suzuki (1983) in their tarasovite specimen by the addition of occasional extra non-polar high charge 2:1 layers, ↔, into the middle of the SMMMS packets. Such a sequence would be

→↔↔← →↔↔↔← →↔↔←

The reverse of this mechanism would allow for smaller proportions of non-expanding interlayers in tarasovite. The process of addition of extra non-polar high charge 2:1 layers (i.e. more than 50% mica units) could also apply to the MSMS ordered rectorite structure, but removal of such layers from the ideal rectorite (50% M 50% S units) is not possible. The fact that partly ordered MS structures appear to be found only when more than 50% of the interlayers do not expand may be related to this observation.

It is of interest to note that the regular sequence ... SMMS ... has not yet been reported and that Reynolds & Hower (1970) found that only models based on ... SMSM ... ('allevardite-type ordering') and ... SMMMS ... ordering ('Kalkberg type ordering') were required to match the X-ray patterns observed for partly-ordered natural illite–smectites.

If random interstratification of mica and smectite units is considered, two kinds of interfaces and interlayers are required. One of these is high charge and non-expanding, the other low charge and expanding. In a randomly interstratified two-component sequence, three kinds of 2:1 layers are necessary, high charge and low charge non-polar 2:1 layers, ↔ and — respectively, and a polar high–low charge 2:1 layer, ←. A short illustrative sequence is

— — →↔← — →↔← — →← →↔↔←.

For a three-component random interstratification, for example, a mica–vermiculite–smectite interstratification, six kinds of 2:1 layers are necessary; three non-polar and three polar. This provides three kinds of interfaces; high-charge non-expanding, medium- and low-charge each with different abilities to expand.

These considerations are relevant to the description of interstratified clay minerals. What do we imply when a mineral is described as a random interstratification of illite and smectite or a partly-ordered IS-type material? Unless care is exercised in terminology, the nature, properties and proportions of the different kinds of layers, interlayers and interfaces can be obscured.

Understanding the genetic changes involved when clays, rich in expanding interlayers, are buried, or clays rich in collapsed layers are altered by leaching requires careful consideration of the structural modifications in the 2:1 layers and of the resulting patterns of stacking sequences. The structural changes in 2:1 layers and their observed sequences (see, for example, Hower *et al.* 1976; Weaver & Beck 1971) seem to require the production of different kinds of 2:1 layers and their arrangement in stacking sequences similar to those described above.

The author thanks the Mineralogical Society for permission to reproduce the figures in this paper which are taken from *Crystal structures of clay minerals and their X-ray identification* (Brindley & Brown 1980). Chapter 1 (Bailey 1980*b*), chapter 2 (Brindley 1980) and chapter 4 (Reynolds 1980) in the same monograph were also invaluable in compiling this brief account of the structures of clay minerals.

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Discussion

P. Nadeau (*The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, U.K.*). Concerning the proposed interstratified mineral tarasovite, I should ask the speaker to consider a clay material composed of 40 Å thick mica particles, corresponding to 4 silicate layers coordinated by 3 planes of K^+ ions. How would the interfaces of those particles behave, as pyrophyllite, or as smectite, i.e. non-swelling or swelling? If the interfaces behave as smectite, which I suggest they do, then a sedimented aggregate of such particles would be indistinguishable from a so called ideal tarasovite structure by X-ray diffraction, that is to say 3 mica layers followed by a smectite layer.

G. Brown. Dr Nadeau's comments re-emphasize the need for precise use of terminology in discussions of the structural components of clays.

If it were possible to cleave a mica crystal, e.g. muscovite, into crystallites 40 Å thick, i.e. crystallites composed of four 2:1 layers each bearing a negative charge of about 1 equivalent per $O_{10}(OH)_2$ formula unit, the charge being symmetrically disposed about the plane of the octahedrally coordinated cations, with K^+ ions balancing the negative charge on the 2:1 layers, including the newly formed external surfaces, the resulting crystallites could be referred to as 40 Å thick mica particles. The units referred to by Dr Nadeau are not of this kind.

The existence of material consisting *entirely* of crystallites 40 Å thick, presumably obtained by dispersion in an aqueous environment, virtually presupposes that the original sample was ideal tarasovite, which consists of a stack of 2:1 layers in which the succession of interlayers is a regular sequence of three high-charge non-expanding interlayers followed by one low-charge expanding interlayer.