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INVITED REVIEW

SIGNIFICANCE OF
RECENT STRUCTURE DETERMINATIONS OF
LAYER SILICATES FOR CLAY STUDIES

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In the last 10 years or so much work has been done to determine the crystal structures of layer silicates more precisely than previously and, as a result, ideas about these structures have had to be revised.

Around 1930 the classical studies of Bragg and his collaborators, and of Pauling, established the general geometrical features of layer silicate structures. The basic building units were found to be layers of linked tetrahedra articulated, by sharing oxygens, with layers of octahedra. In the 1 : 1, kaolinite type materials, with layer thicknesses about 7 Å, the composite layer unit was made up of one tetrahedral layer and one octahedral layer; in the mica and chlorite minerals the silicate layer was formed by joining two tetrahedral layers, one on either side, to an octahedral layer.

The individual tetrahedra consist of four oxygens disposed around a central cation, usually Si^{4+} , which can be replaced by other ions of suitable size, such as Al^{3+} . The octahedra consist of six oxygens (or OHs) surrounding larger cations such as Mg^{2+} and Fe^{2+} . Octahedra and tetrahedra were considered to be regular and no account was taken of the effect of the size of the central cation on the size of the group. Almost the only departure from a purely geometrical approach resulted from the concept of isomorphous substitution.

These early structural studies can be regarded as no more than approximations. The aim of the early workers was to define the general structural scheme of silicate structures and in this they succeeded.

Since 1954, Fourier and least squares methods have been used to determine atomic co-ordinates of layer silicates with much greater precision than before. The structures of eighteen layer silicates have been determined by these methods, with various degrees of accuracy. All eighteen (see Table 1) show considerable distortions from the previously accepted ideal structures. The main distortions are:

(i) The surface oxygen triads (the oxygens forming the bases of the tetrahedra) are rotated about c^* alternatively clockwise and anti-clockwise through an angle α

from their positions in the ideal hexagonal arrangement. Because of the effect of the vacant octahedral site, the tetrahedra are also slightly tilted in dioctahedral structures.

(ii) The octahedra are flattened in the direction normal to the layers. The octahedral layers are between 1.95 and 2.25 Å thick; thicknesses from 2.2 to 2.5 Å would be expected for regular octahedra.

These distortions have important consequences. The cavities in the surface oxygen array are deformed from the hexagonal arrangement of the ideal model to a ditrigonal array, so the interlayer cations in micas have six nearest neighbours co-ordinated in the form of a trigonal antiprism. Formerly the interlayer cations were thought to be in twelve-fold co-ordination, situated in the hole formed between two vertically opposed hexagonal rings of oxygens. As a consequence of the tilting of the tetrahedra, the oxygens of the surface layers in dioctahedral minerals are not co-planar; the raised oxygens are 0.1–0.2 Å above the others and a corrugated surface results. Thus the space available between the layers for intercalated molecules cannot be treated as the space between two plane surfaces.

The size of the angle α through which the tetrahedra twist differs for different compositions. In their undistorted forms an entirely siliceous tetrahedral layer with Si—O = 1.62 Å would have a b dimension of 9.16 Å; regular trioctahedral layer, entirely magnesian, with Mg—O distance of 2.10 Å, would have $b = 8.91$ Å. For the two types of layer to combine, the size of either or both must be adjusted. It is now generally accepted that the tetrahedra twist to decrease the lateral extent of the tetrahedral layer enough for it to fit the octahedral layer.

Radoslovich (1961) showed that the angle through which the tetrahedra are twisted can be calculated from a knowledge of the structural formula and the observed b axis of the mineral. The average length of the bond between the tetrahedral cation and the surrounding oxygen atoms can be calculated from the structural formula, and hence the length that the b axis would have in an undistorted tetrahedral layer (b tetrahedral) can be found (Radoslovich & Norrish, 1962). It is easily shown that

$$\cos \alpha = \frac{b \text{ observed}}{b \text{ tetrahedral}}$$

The octahedral layer is probably flattened by the repulsion of cations in adjacent octahedra. This is the well-known Pauling principle of shortening of edges shared between polyhedra; the limit to this shortening is set by the repulsion between anions along a shared edge. For a constant, or near constant, octahedral cation to oxygen bond length, the shortening of shared edges results in the octahedra flattening in the c^* direction and the edges that lie in the ab plane lengthening (Donnay, Donnay & Takeda, 1964a).

Radoslovich & Norrish (1962) proposed a new model for layer silicate structures on the basis of Radoslovich's structure for muscovite (1960). The main features of this model are:

(i) The dimensions of the tetrahedral layer in the plane of the layer can be

readily diminished by rotation of the tetrahedra, but the rigidity of the tetrahedral groups prevents significant extension beyond the size of the undistorted layer.

(ii) The octahedral layer can be extended or contracted, with somewhat greater difficulty than the tetrahedral layer, by changes in bond angles rather than bond lengths, so that the thickness is altered.

(iii) The surface oxygen triads in micas will rotate until they lock on to the inter-layer cation.

On the basis of this model Radoslovich (1962) proposed new formulae relating the b axis dimension to chemical composition, replacing earlier formulae, for example those of Brindley & MacEwan (1953), which were empirically based and took no account of specific structural features such as twisting of tetrahedra or interlayer cations. Radoslovich tested and refined these new formulae by statistical analysis.

Radoslovich (1963) proposed two new general principles concerning the relation between b axis length and chemical composition in layer silicates. These were that tetrahedral substitution had little or no effect on the b dimension and that therefore b was determined mainly by the size of the octahedral layer. The effect of substituting Al for Si in tetrahedral co-ordination is to lengthen the average tetrahedral cation to oxygen bond length and hence to increase the size of the undistorted tetrahedral layer. Tetrahedral layers of different composition, and hence with different b tetrahedral, can be adjusted to fit a smaller octahedral layer merely by twisting the tetrahedra by different amounts—the greater the twist the greater the contraction. For micas Radoslovich considered that the tetrahedral twisted until the surface oxygens locked on to the interlayer cation. This implies an invariant interlayer cation to surface oxygen distance for each cation species, and so Radoslovich deduced that the interlayer cation will also affect the b dimension in micas.

Later work shows that neither of these conclusions is fully justified. Comparison of the b dimensions of pairs of micas that differ only in tetrahedral substitution (Table 2) shows that substitution of Fe^{3+} ($\text{Fe—O} = 1.86 \text{ \AA}$) for Al^{3+} ($\text{Al—O} = 1.77 \text{ \AA}$) increases b by $0.05\text{--}0.08 \text{ \AA}$. Whether substitution of Al^{3+} for Si^{4+} ($\text{Si—O} = 1.62 \text{ \AA}$) has a similar effect is not known, because to maintain charge balance the structure must also change in other ways, but it seems likely that substituting Al for Si will produce a force leading to expansion of the tetrahedral layer.

From detailed structure determinations on iron micas, Steinfink (1962) and Donnay *et al.* (1964b) found K—O bond lengths in the range $2.929\text{--}2.954 \text{ \AA}$ (2.942 \AA mean) and $3.015\text{--}3.074 \text{ \AA}$ (3.054 \AA mean) for ferriphlogopite and ferriannite respectively. These, together with the values $2.832\text{--}2.886 \text{ \AA}$ (2.857 \AA mean) calculated from Gatineau's (1963) muscovite co-ordinates, show that the K—O distance is a variable in mica structures and is not the constant 2.81 \AA assumed by Radoslovich & Norrish (1962). This variability should be considered as one possible reason why micas differ in the ease with which they release potassium as reported by Raussel-Colom *et al.* (1965).

Despite limitations caused by too few structure determinations, Radoslovich's work has gone a considerable way to providing a new general model for layer silicates. Donnay *et al.* (1964a) have gone further and claimed that the structures

of one-layer trioctahedral micas can be predicted with reasonable accuracy from a knowledge of b and the chemical composition. Their approach is based on a model structure, suggested by the structure determination of ferriannite by Donnay *et al.* (1964b).

The essential features of this model are:

1. The structure is strictly orthohexagonal, $a\sqrt{3}=b$, $\beta=100^\circ$, $\cos \beta = -a/3c$ and all one-layer trioctahedral micas closely correspond to these conditions (Sadanaga & Takéuchi, 1961; Donnay *et al.*, 1964a).

2. Regular tetrahedra that can twist by rotation about the normal to the layer through an angle α .

3. The octahedra are flattened into trigonal anti-prisms. They introduce an angle ψ as a measure of the flattening of the octahedra, ψ being defined as the angle between the normal to the basal faces of the octahedron and the line that connects opposite vertices of the octahedron. The bonds from the octahedral cation to the surrounding oxygens and hydroxyls are assumed to be equal.

The angle $\psi = 54^\circ 44'$ in a regular octahedron but is greater after flattening. If the octahedral cation to oxygen bond lengths can be taken as a constant, when $\psi > 54^\circ 44'$ octahedral edges parallel to the basal plane are stretched and b is increased. From geometrical considerations these authors deduce formulae relating the b dimension to the average length of the tetrahedral cation-oxygen bond, d_t , to the average octahedral cation-oxygen bond lengths, d_o and to the angles α and ψ . The formulae are:

$$b = 4\sqrt{2} d_t \cos \alpha$$

and

$$b = 3\sqrt{3} d_o \sin \psi.$$

Both d_t and d_o can be obtained from a knowledge of the structural formulae of the mica calculated from the chemical analysis and bond lengths given in *International Tables for X-ray Crystallography* (Vol. III, 1962) and hence α and ψ can be obtained by measuring b . These relationships can be used, for example, to predict the range b can take for known chemical compositions. Donnay *et al.* (1964a) show that for their structural model b is restricted more by the K—O bond lengths, for which they allow a range from 2.72 to 3.25 Å, than by the limits set by d_t , α , d_o and ψ . They disagree with Radoslovich's conclusion that the cell dimensions are mainly controlled by the octahedral layers. Considering the effect of small changes in d_t and d_o , keeping the K—O distance fixed, they show that changes in d_t would have a much greater effect on b than changes in d_o . However the K—O bond length is also a variable in the mica structure so its length would be expected to change in response to changes in d_o and d_t and the conclusion that the size of the tetrahedra is more important than the size of the octahedra in determining b is not justified.

Donnay *et al.* (1964a) also deduce formulae for one-layer trioctahedral micas from which the co-ordinates of the atoms in the unit cell can be calculated from the cell dimensions, which can be obtained from X-ray powder patterns and the

chemical composition. They have tested these formulae by comparing the co-ordinates obtained in structure determinations for ferriphlogopite and ferriannite with those obtained by calculation. For these two minerals the agreement between the two sets of co-ordinates is good, and discrepancies are attributed to slight departures of the actual structures from the model, for example, octahedral cation to oxygen and octahedral cation to hydroxyl bonds are not equal and tetrahedra are not strictly regular, as the model assumes.

TABLE 1. Structure determinations by Fourier and/or least squares methods for layer silicates

Minerals with 1:1 type layers	
Dickite	Newnham & Brindley (1956); Newnham (1961)
Kaolinite	Drits & Kashaev (1960)
Antigorite	Zussman (1954)
Chrysotile	Whittaker (1953, 1956a, b)
Amesite	Steinfink & Brunton (1956)
Cronstedtite	Steadman & Nuttall (1963)
Micas	
Xanthophyllite	Takéuchi & Sadanaga (1959)
Muscovite	Radoslovich (1960); Gatineau (1963); Burnham & Radoslovich (1965)
Ferriphlogopite	Steinfink (1962)
Ferriannite	Donnay <i>et al.</i> (1964b)
Paragonite	Burnham & Radoslovich (1965)
Margarite	Takéuchi (1964)
Others	
Prochlorite	Steinfink (1958a, 1961)
Corundophyllite	Steinfink (1958b)
Cr-chlorite	Brown & Bailey (1963)
Orthohexagonal iron chlorite	Shirozu & Bailey (1965)
Vermiculite	Mathieson & Walker (1954); Mathieson (1958)
Pyrophyllite	Rayner & Brown (1965)

TABLE 2. Comparison of *b* dimensions for pairs of micas which differ only in their tetrahedral substitution

Mica	Composition	<i>b</i> observed (Å)	<i>b</i> calculated* (Å)
Phlogopite	K Mg ₃ (Al Si ₃)O ₁₀ (OH) ₂	9.209†	9.210
Ferriphlogopite	K Mg ₃ (Fe ²⁺ +Si ₃)O ₁₀ (OH) ₂	9.29‡	9.210
Annite	K Fe ₃ ²⁺ (Al Si ₃)O ₁₀ (OH) ₂	9.348§	9.374
Ferriannite	K Fe ₃ ²⁺ (Fe ³⁺ +Si ₃)O ₁₀ (OH) ₂	9.404¶	9.374

* Radoslovich (1962).

‡ Steinfink (1962).

¶ Wones (1963b).

† Wones (1963a).

§ Eugster & Wones (1962).

Unfortunately these formulae will be of limited application as a substitute for structure determinations. The effect of ordering of octahedral cations, which Veitch & Radoslovich (1963) have suggested is likely to occur when both divalent and trivalent octahedral cations are present, has not been considered. The effect of vacant octahedral positions has also been ignored and many natural trioctahedral micas have less than full occupancy of octahedral sites. More than 70% of the trioctahedral micas considered by Foster (1960) have less than 2.90 octahedral cations for the three available sites. The use of the formulae for the prediction of the structures of naturally occurring trioctahedral micas is therefore severely limited. They are valid only for one-layer trioctahedral micas that have full octahedral occupancy and in which the octahedral cations are not ordered.

Isomorphous substitution is common in layer silicates and hence different cation sites in the tetrahedral and octahedral layers might be favoured by different cations. Information on the distribution of different ionic species over the available sites is necessary for an understanding of the local structure.

There are usually two kinds of crystallographically distinct tetrahedral cation sites, and when Al substitutes for Si one of these sites could contain a larger proportion of Al than the other. Because Al and Si have a very similar scattering power for the X-ray wavelengths used for structure determinations, tetrahedral occupancy cannot be deduced from differences in electron density. Careful structure determinations are required to detect ordering of Al and Si because ordering is deduced from differences in cation to oxygen distances in different tetrahedra. In layer silicates, tetrahedra occupied solely by Si have an average $d_t = 1.62$ Å and tetrahedra occupied solely by Al have an average $d_t = 1.77$ Å (Smith & Bailey, 1963). There is a linear relation between these values for intermediate compositions, and so for a tetrahedron with $(\text{Si}_{0.75}\text{Al}_{0.25})$ d_t would be about 1.655 Å. To establish differences in occupancy between purely Si ($d_t = 1.620$ Å) and $(\text{Si}_{0.75}\text{Al}_{0.25})$ ($d_t = 1.655$) tetrahedra therefore requires standard deviations of <0.01 Å in bond length determinations. Substitution of Fe^{3+} for Si^{4+} in an ordered way could be detected readily by changes in scattering power.

In the six micas the structures of which have been determined, ordering of cations has been reported in muscovite only (Radoslovich, 1960) and subsequent re-examination of Radoslovich's data by Gatineau (1963) shows that both sites have similar bond lengths equivalent to an occupancy of all the tetrahedral sites by $\text{Si}_{0.75}\text{Al}_{0.25}$. This is further supported by Burnham & Radoslovich (1965) whose careful analyses of muscovite and paragonite show bond lengths for all tetrahedra close to 1.65 Å. Random occupancy of the tetrahedral sites has also been found in ferriphlogopite, $\text{K Mg}_3(\text{Fe}^{3+}\text{Si}_3)\text{O}_{10}(\text{OH})_2$ by Steinfink (1962) and in ferriannite $\text{K Fe}_3^{2+}(\text{Fe}^{3+}\text{Si}_3)\text{O}_{10}(\text{OH})_2$ by Donnay *et al.* (1964b).

Examples of tetrahedral ordering have been reported among the chlorites; Steinfink's (1958a, b, 1961) prochlorite determination suggests that one tetrahedral site with a cation to oxygen bond length of 1.73 Å contains $(\text{Si}_{0.3}\text{Al}_{0.7})$ and the other site with a bond length of 1.63 Å contains $(\text{Si}_{0.8}\text{Al}_{0.2})$. Similarly Brown & Bailey's (1963) study of a Cr-chlorite shows that the two sites with bond lengths

1.685 and 1.636 Å contain ($\text{Si}_{0.6}\text{Al}_{0.4}$) and ($\text{Si}_{0.9}\text{Al}_{0.1}$) respectively. But when decisions based on differences in bond lengths have to be made the probable error of the bond length determination must be ascertained, and there is evidence that it is easy to underestimate the error.

Ordering can occur between the three possible cation sites in an octahedral layer. Veitch & Radoslovich (1963) favour a model for octahedral layers in which the octahedral sites in any one layer are of two kinds, there being two A sites for each B site. There are strong tendencies to ordering between the three sites. In all dioctahedral structures so far determined, the cations are ordered, only two out of the three possible sites being occupied, and the cation to oxygen distances around the occupied sites are smaller than around the vacant sites. In the trioctahedral mica, xanthophyllite (Takéuchi & Sadanaga, 1959) with (Mg_2Al) as octahedral cations, one site, presumably that occupied preferentially by Al, is smaller than the other two and Takéuchi & Sadanaga suggest that this may be the reason for the invariance of chemical composition in xanthophyllite.

The situation is more complex among the chlorites, ordering is possible between the different sites in a single octahedral layer and also between the talc and brucite octahedral layers of the chlorite structure. In three of the four chlorite structures that have been determined (see Table 1) the talc octahedral layer and the brucite octahedral layer show differences in cation population, but one (corundophyllite) does not (Steinfink, 1958b). Ordering among the sites within individual octahedral layers occurs in prochlorite (Steinfink, 1958a) and Cr-chlorite (Brown & Bailey, 1963) but not in corundophyllite. In the iron chlorite (Shirozu & Bailey, 1965) stacking disorder prevents the detection of ordering within individual octahedral layers.

The ordering discussed above is long range order, that is ordering that exists regularly throughout a crystal. This is the only kind of ordering that crystal structure determinations can detect directly.

Gatineau (1964), who studied the short range ordering of Al-for-Si substitutions in muscovite, by the analysis of diffuse non-Bragg scattering, concluded that the substitutions of Al-for-Si tend to occur in rows in which every atom is substituted. These rows favour the [10] or [11] or $[1\bar{1}]$ directions in the plane of the layer. The crystal is thus divided into domains each of which is characterized by the direction of these rows. The rows of substitutions are grouped together into bands that contain equal numbers of rows of entirely Al and entirely Si atoms but without regular alternation, that is in these bands $\text{Al/Si} = 1:1$. The bands alternate with bands of equal size, in which there is no Al, thereby leading to an overall ratio of three Si to one Al. Substituted and unsubstituted bands face each other across interlayers, and this leads to local charge balance around each K ion.

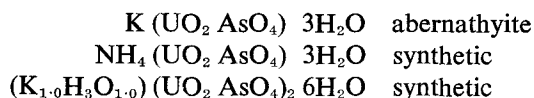
This is the only study of the short range order in layer silicates; information of this kind is necessary for the understanding of chemical processes that take place at the atomic level, such as for example the diffusion of ions between the layers, weathering, and chemical alterations.

From the results of structure determinations on layer silicates, the layers seem

to have considerable flexibility in response to interatomic forces within the crystal. This is particularly evident for the tetrahedral layer that forms both layer surfaces in 2 : 1 minerals and one surface in 1 : 1 minerals. Even in framework structures such as the zeolites, for example chabazite (see Smith, 1964, for review), there are major shifts of the atoms of the aluminosilicate framework when molecules are sorbed; for some of the oxygen atoms the shift may be as much as 0.5 Å. The degree of flexibility of the surface oxygen array in layer silicates is such that changes in structure might be expected in response to sorption. No direct X-ray structure determination has been made to test for this effect. The electron diffraction study of montmorillonite by Cowley & Goswami (1961) could be interpreted as supporting this kind of structural change. They found that after treatment with organic bases some crystals of montmorillonite had a *b* dimension about 2% greater than in the untreated material. The *b* dimension found for these crystals, 9.10 ± 0.06 Å, is similar to what would be expected for layers of untwisted tetrahedra of the montmorillonite composition. Cowley & Goswami considered the possibility that *b* increased because the substrate was modified by the sorbed organic molecules. However, they point out that only some crystals show this effect, and favour the interpretation that these are crystals of different chemical composition. Obviously more work is needed to explain these observations.

The ease with which tetrahedral layers can be deformed suggests that it would be unwise to assume that the substrate for adsorption is inert. This is particularly important for swelling clays like montmorillonite and vermiculite in which surfaces of this kind form such a large proportion of the total material. In fact, deformation from the structure characteristic of the interior of crystals may be quite general in the atomic layers near the surface. The forces that hold atoms in their positions inside a crystal, and which appear to be in delicate balance, are different in the surface layers. The results of crystal structure determinations must therefore be applied with caution to studies of surfaces.

To account for the smaller K₂O and larger H₂O content of hydrous micas, Brown & Norrish (1952) proposed the partial substitution of oxonium ion H₃O⁺ for interlayer K⁺. Structural studies by Ross & Evans (1964, 1965) on minerals of the torbernite group have shown that (H₃O)⁺ occurs in interlayers of these minerals. The torbernite group are minerals made up of layers of (UO₂ XO₄)_nⁿ⁻, with X = P or As, which take up water and exchangeable cations between the layers. They are therefore in some ways similar to clays. Detailed structural study of



showed that in the first two materials one K⁺ + three water molecules and one NH₄ ion + three water molecules were distributed randomly over four interlayer sites. In the (K, H₃O) material, (K_{0.5}H₃O_{0.5}) and 3H₂O are distributed randomly over the four interlayer sites. The interlayer sites, mainly occupied by water molecules, are linked to each other, and to the oxygens of the layers, by hydrogen bonds more

or less tetrahedrally disposed around each water oxygen. The exact position of the protons is not known—the authors suggest that they are probably distributed so that the charges on all the oxygens are as nearly neutralized as possible. These determinations show that K^+ , NH_4^+ , and H_3O^+ can all replace water molecules in a water layer. The ability of these ions and water molecules to occupy water sites in a crystal is not altogether surprising because they are all about the same size. In aqueous solution they are all thought to have four-fold co-ordination. Brady & Krause (1957) found that the hydration number of K was 4 in solutions of KOH and they say that, 'It appears that K^+ , which is close in size to the H_2O molecule, enters substitutionally into the pseudo-structure of water without disturbing the structure to any great extent'. This model for an aqueous solution, in which monovalent cations of the correct radius (such as K^+ , NH_4^+ , and H_3O^+) substitute randomly for water molecules in a tetrahedrally co-ordinately structure, resembles the structure of the interlayer region of the abernathy-like compounds. There is thus well-documented evidence for H_3O^+ substituting for K^+ in interlayer positions.

The implications of the findings of Ross & Evans to clay mineral structures are wider than the question of the K and H_2O contents of hydrous micas. They are also relevant to the structure of the interlayer sorbed water and cation films in expanding clay minerals. Hendricks & Jefferson (1938) proposed a structural model for interlayer water in which the water molecules form hexagonal layers, each water molecule forming three hydrogen bonds with other water molecules, and one hydrogen bond to an oxygen in the surface of the silicate. From recent work on the swelling of montmorillonite in salt solutions, Posner & Quirk (1964a, b) postulated the existence of ordered water layers in contact with the aluminosilicate surfaces. They base their model on the structure proposed by Walker (1956) for the 14.8 Å phase of magnesium vermiculite, in which definite cation sites are octahedrally surrounded by six water molecules. The cation–water structure found by Ross & Evans for the torbernite minerals suggests that, in clays, a structural scheme in which cations are randomly distributed over water sites in the water layers may also be possible. The ability of K^+ , NH_4^+ , and H_3O^+ to replace H_2O , and thereby enter into the water layers, suggests that structures of this kind should be considered, at least for cations of suitable size.

The importance of the interlayer cation–water structure to swelling has been shown by Greenland, Quirk & Theng (1964), who found the swelling of mixed Ca–alkyl ammonium montmorillonite was 4–5 times as great as Ca-montmorillonite. They attribute this to the effect of the large alkylammonium cations in disrupting the cation–water structure between the layers. It seems that K^+ , NH_4^+ and H_3O^+ , because of their ability to replace water molecules in water structures, might not have such a disrupting effect.

REFERENCES

- BRADY G.W. & KRAUSE J.T. (1957) *J. chem. Phys.* **27**, 304.
BRINDLEY G.W. & MACEWAN D.M.C. (1953) *Ceramics: A Symposium*, p. 15. British Ceramic Society.

- BROWN B.E. & BAILEY S.W. (1963) *Am. Miner.* **48**, 42.
- BROWN G. & NORRISH K. (1952) *Mineralog. Mag.* **29**, 929.
- BURNHAM C.W. & RADOSLOVICH E.W. (1965) *Yb. Carnegie Instn Wash.* **63**, 232.
- COWLEY J.M. & GOSWAMI A. (1961) *Acta crystallogr.* **14**, 1071.
- DONNAY G., DONNAY J.D.H. & TAKEDA H. (1964a) *Acta crystallogr.* **17**, 1374.
- DONNAY G., MORIMOTO N., TAKEDA H. & DONNAY J.D.H. (1964b) *Acta crystallogr.* **17**, 1369.
- DRITS V.A. & KASHAEV A.A. (1960) *Kristallografiya*, **5**, 224.
- EUGSTER H.P. & WONES D.R. (1962) *J. Petrology*, **3**, 88.
- FOSTER M.D. (1960) *U.S. Geological Professional Paper* 354-B, 11.
- GATINEAU L. (1963) *C.r. hebd. Séanc. Acad. Sci., Paris*, **256**, 4648.
- GATINEAU L. (1964) *Bull. Soc. fr. Minér. Cristallogr.* **87**, 321.
- GREENLAND D.J., QUIRK J.P. & THENG B.K.G. (1964) *J. Colloid Sci.* **19**, 837.
- HENDRICKS S.B. & JEFFERSON M.E. (1938) *Am. Miner.* **23**, 863.
- MATHIESON A.MCL. (1958) *Am. Miner.* **43**, 216.
- MATHIESON A.MCL. & WALKER G.F. (1954) *Am. Miner.* **29**, 231.
- NEWNHAM R.E. (1961) *Mineralog. Mag.* **32**, 683.
- NEWNHAM R.E. & BRINDLEY G.W. (1956) *Acta crystallogr.* **13**, 919.
- POSNER A.M. & QUIRK J.P. (1964a) *Proc. R. Soc. A*, **278**, 35.
- POSNER A.M. & QUIRK J.P. (1964b) *J. Colloid Sci.* **19**, 798.
- RADOSLOVICH E.W. (1960) *Acta crystallogr.* **13**, 919.
- RADOSLOVICH E.W. (1961) *Nature, Lond.* **191**, 67.
- RADOSLOVICH E.W. (1962) *Am. Miner.* **47**, 617.
- RADOSLOVICH E.W. (1963) *1st Int. Clay Conf. Proc.* (I. Th. Rosenqvist and P. Graff-Petersen, editors, Vol. 1, p. 3, Pergamon Press, Oxford).
- RADOSLOVICH E.W. & NORRISH K. (1962) *Am. Miner.* **47**, 599.
- RAUSSEL-COLOM J., SWEATMAN T.R., WELLS C.B. & NORRISH K. (1965) *Experimental Pedology* (E. G. Hallsworth and D. V. Crawford, editors), p. 40. Butterworths, London.
- RAYNER J.H. & BROWN G. (1965) *Clays and Clay Minerals. Proc. 13th Conf.*, p. 73, Pergamon Press, Oxford.
- ROSS M. & EVANS H.T. JR. (1964) *Am. Miner.* **49**, 1578.
- ROSS M. & EVANS H.T. JR. (1965) *Am. Miner.* **50**, 1.
- SADANAGA R. & TAKÉUCHI Y. (1961) *Z. Kristallogr. Miner.* **116**, 406.
- SHIROZU H. & BAILEY S.W. (1965) *Am. Miner.* **50**, 868.
- SMITH J.V. (1964) *J. chem. Soc.*, 3759.
- SMITH J.V. & BAILEY S.W. (1963) *Acta crystallogr.* **16**, 801.
- STEADMAN R. & NUTTALL P.M. (1963) *Acta crystallogr.* **16**, 1.
- STEINFINK H. (1958a) *Acta crystallogr.* **11**, 191.
- STEINFINK H. (1958b) *Acta crystallogr.* **11**, 195.
- STEINFINK H. (1961) *Acta crystallogr.* **14**, 198.
- STEINFINK H. (1962) *Am. Miner.* **47**, 886.
- STEINFINK H. & BRUNTON G. (1956) *Acta crystallogr.* **9**, 487.
- TAKÉUCHI Y. (1964) Program and abstracts of first meeting of Clay Minerals Society held at Madison, Wisconsin, October 5-8, 1964.
- TAKÉUCHI Y. & SADANAGA R. (1959) *Acta crystallogr.* **12**, 945.
- VEITCH L.G. & RADOSLOVICH E.W. (1963) *Am. Miner.* **48**, 62.
- WALKER G.F. (1956) *Clays and Clay Minerals. Proc. 4th Conf.*, p. 101. Nat. Acad. Sci.-Nat. Res. Council, Washington, Publ. 456.
- WHITTAKER E.J.W. (1953) *Acta crystallogr.* **6**, 747.
- WHITTAKER E.J.W. (1956a) *Acta crystallogr.* **9**, 855.
- WHITTAKER E.J.W. (1956b) *Acta crystallogr.* **9**, 862.
- WONES D.R. (1963a) *Am. Miner.* **48**, 1300.
- WONES D.R. (1963b) *Am. J. Sci.* **261**, 581.
- ZUSSMAN J. (1954) *Mineralog. Mag.* **30**, 498.