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Liebau, F.; National Research Council of Canada. Division of Building Research

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TECHNICAL TRANSLATION 1479

CONTRIBUTION TO THE CRYSTAL CHEMISTRY
OF THE LAYER SILICATES

BY

F. LIEBAU

FROM

ACTA CRYSTALLOGRAPHICA, B24: 690 - 699, 1968

TRANSLATED BY

D. A. SINCLAIR

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PREFACE

The Division of Building Research is engaged in the basic study of the properties of dicalcium and tricalcium silicates and their respective hydrates in connection with its studies of the nature and the behaviour of hydrated portland cement. These compounds are in the same class as the layer silicates, and for this reason the discussion of the crystal chemistry of the layer silicates in this paper by F. Liebau is of special significance and interest.

The Division wishes to record its thanks to Mr. D. A. Sinclair, Translations Section, National Research Council of Canada, for translating this paper, and to Mr. P. J. Sereda of this Division who checked the translation.

Ottawa
August 1971

N. B. Hutcheon
Director

NATIONAL RESEARCH COUNCIL OF CANADA

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layer silicates

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CONTRIBUTION TO THE CRYSTAL CHEMISTRY
OF THE LAYER SILICATES

Abstract

The great number of $[\text{Si}_2\text{O}_5]$ layer silicates is primarily due to the differences in size and charge of the cations. Anhydrous layer silicates show an increasing degree of convolution of layers with decreasing radius/charge ratio of cations, the size of cation sites between layers decreasing at the same time. This explains why $1+$ cations form anhydrous layer silicates and $2+$ cations of small or medium size and $3+$ cations do not. In hydrous layer silicates the $[\text{MeO}(\text{OH})_n]$ polyhedra are 'effective' cations. The deviation from a plain conformation increases with increasing ratio radius/charge, from $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ and the bent serpentines to the ruffled ones of pyrosmalite and apophyllite.

The large group of layer or phyllosilicates includes, as we know, all those silicates in which the $[\text{SiO}_4]$ tetrahedrons are linked through common oxygen atoms into two-dimensional layers. Although the character of the linkage of the tetrahedrons into layers, and hence their symmetry, can differ widely [Liebau has given a systematic review (1962)], nevertheless all hitherto described silicate layers are similar inasmuch as each of their $[\text{SiO}_4]$ tetrahedrons is bound through common oxygen atoms to three others*, so that the composition $[\text{Si}_2\text{O}_5]^{2-}$ results. No more loosely constructed tetrahedral layers with a ratio of $\text{O}:\text{Si} > 2.5$ have been discovered.

Survey of Known Layer Silicates

When we compare the crystal structures of the layer silicates with each other, they appear to fall into two groups:

* As the one known exception, prehnite $\text{Ca}_2\text{Al}[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$ contains just as many tetrahedrons, which are linked with others through two bridging oxygen atoms as through three, so that again the composition $[(\text{Si},\text{Al})_2\text{O}_5]$ results (Preisinger, 1965).

- (1) Anhydrous layer silicates of the general formula $A_m(Si_2O_5)_n$.
- (2) Hydrous* layer silicates of frequently very complex composition, in which the water may be contained in the form of hydroxyl groups, or frequently also in the form of H_2O molecules.

Table I summarizes the anhydrous layer silicates hitherto described in the literature. Compared with those of the hydrous layer silicates they are relatively few in number. Hitherto, only $BaSi_2O_5$ (sanbornite), $BaFeSi_4O_{10}$ (gillespite) and $CaCuSi_4O_{10}$ (cuprorivaite) have been found as natural minerals.

Insofar as the crystal structures of the anhydrous layer silicates are known, they possess the following common characteristic properties:

- (a) $[Si_2O_5]$ layers are more or less strongly folded;
- (b) Half the oxygen atoms which are bound to only one silicon atom (free tetrahedral corners) point in one direction, and half in the other;
- (c) The $[Si_2O_5]$ layers have tetragonal, rhombic or pseudorhombic symmetry.

Figure 1 gives a schematic presentation of the types of layers of a number of anhydrous layer silicates, the structures of which have already been investigated quite closely. The group of hydrous layer silicates include above all the very numerous micas and clay minerals which are very widely distributed in nature. Their $[Si_2O_5]$ layers differ only slightly from the type represented in Figure 2, and are characterized by the following properties:

- (a) $[Si_2O_5]$ layers are flat;
- (b) The free tetrahedral corners point only towards one side of the layer;

* The terms "hydrous" and "anhydrous", as used in the present paper, have no reference to the form in which the "water" is present in the structure in question.

- (c) The layers have hexagonal or pseudo-hexagonal symmetry.

The few exceptions to (a) and (b) are discussed more fully on pages 8 and 9. At first glance, this comparison of the structures of hydrous and anhydrous layer silicates leaves the impression that we have two groups of structures here which differ in principle, but which have in common the absence of layers of the composition $[\text{Si}_2\text{O}_5]_x^{2x-}$.

This impression is at first strengthened when we seek to determine what cations form layer silicates of the respective groups. Examination of Table II and the first three columns of Table I shows that the monovalent cations form anhydrous layer silicates regardless of their size*. While only the large barium ions among the bivalent cations are capable of forming anhydrous phyllosilicates of the formula $\text{A}^{\text{II}}\text{Si}_2\text{O}_5$, sanbornite, no such silicates of the formula $\text{A}_2^{\text{III}}(\text{Si}_2\text{O}_5)_3$ is known. The small bivalent cations like Mg^{2+} , Ca^{2+} , Fe^{2+} , Mn^{2+} , and trivalent cations like Al^{3+} , therefore, do not form anhydrous layer silicates; however, these are precisely the cations of the typically hydrous phyllosilicates.

While this result still further confirms the difference between the two groups of layer silicates, at the same time it provides a key to an understanding of their structures, inasmuch as it reveals the importance of the valency and size of the cations in determining to which of the two groups they belong.

Relationship of the Size and Valency of the Cations to the Structure of the $[\text{Si}_2\text{O}_5]$ Layers

Anhydrous layer silicates

A layer of the composition $[\text{Si}_2\text{O}_5]_x^{2x-}$ is the carrier of one negative charge per $[\text{SiO}_4]$ tetrahedron. A monovalent cation can balance the negative charge of one tetrahedron; a bivalent cation

* In Table II the radii of the most important cations are given after Ahrens (1952).

can balance the charge of two tetrahedrons, etc. Since the negative charges are localized on the oxygen atoms which are bound to only one silicon atom, the cations are bound to these free tetrahedron corners.

In order to saturate a flat tetrahedral layer of the form sketched in Figure 2 with monovalent cations, the latter should require about as much space, neglecting the repulsion forces, between the cations as those of a $[\text{SiO}_4]$ tetrahedron of this layer. A rough calculation shows that this is the case for a cation radius of about $1.8 \overset{\circ}{\text{A}}$. Since all non-complex cations except francium Fr^+ are smaller, flat $[\text{Si}_2\text{O}_5]$ layers in silicates with monoatomic, monovalent cations should be unstable.

In the case of smaller monovalent cations, the tetrahedral layers adhere to the layer of cations by electrostatic attraction in such a way as to cause undulation of the layer. The smaller the cations, the more pronounced this undulation will be. Where the cations are extremely small, the layers would display definite folding. Again, disregarding cation-cation repulsion, this situation is indicated by Figure 3(b) and (c). Because of the mutual repulsion of the cations which actually is present, the latter distribute themselves alternately on both sides of the $[\text{Si}_2\text{O}_5]$ layer [Figure 3(d)], so that the free corners of the $[\text{SiO}_4]$ tetrahedron point alternately towards opposite sides of the layer.

This clearly derived picture of the structure of the layer silicates agrees closely with the results of the crystal structure determinations $\text{Li}_2\text{Si}_2\text{O}_5$, $\text{H}_2\text{Si}_2\text{O}_5$, $\text{Na}_2\text{Si}_2\text{O}_5$, and $\text{Ag}_2\text{Si}_2\text{O}_5$. As is evident from Figure 4(a), (b), (c), (d), the depth of folding of the $[\text{Si}_2\text{O}_5]$ layers in fact decreases with increasing cation radius.

Since one bivalent cation A^{II} must balance the charges of two $[\text{SiO}_4]$ tetrahedrons, then for equal cation size the folding of the layers $\text{A}^{\text{II}}\text{Si}_2\text{O}_5$ is considerably deeper than in a silicate $\text{A}_2^{\text{I}}\text{Si}_2\text{O}_5$ for the same size of cation A^{I} . The depth of folding of the $[\text{Si}_2\text{O}_5]$ layers in sanbornite BaSi_2O_5 [Figure 5(a)] is about midway between that of α - and β - $\text{Na}_2\text{Si}_2\text{O}_5$.

The noteworthy fact, already mentioned, that anhydrous silicates of the formula $A^{II}Si_2O_5$ do not form from the small alkaline earth ions Be^{2+} , Mg^{2+} , Ca^{2+} and Sr^{2+} any more than layer silicates of trivalent ions, is explained by the same argument as that developed above. The deeper the folding of the layers, the less space is available between the oxygen atoms for the cation. Thus, the co-ordination numbers of the cations decrease from six in $\beta-Na_2Si_2O_5$ through five in $\alpha-Na_2Si_2O_5$, four in $Li_2Si_2O_5$ to two formally in phyllosilicic acid $H_2Si_2O_5$. The deeper folding of layers necessary, owing to the greater distance between the bivalent cations of an $A^{II}Si_2O_5$ structure, would result in the gaps between the oxygen atoms being so small that small to medium size alkaline earth ions could not be accommodated in them. Only in the case of $BaSi_2O_5$ do these gaps become just large enough to accommodate Ba^{2+} ions, but now the latter must be reconciled to a co-ordination number of 7, which is unusually low for Ba^{2+} .

The small ions of the transition metals Fe, Co, Ni and Cu, like the alkaline earth ions, only give anhydrous layer silicates of the formula $A^{II}B^{II}(Si_2O_5)_2$ by adopting planar four co-ordinations in these structures owing to the deep folding of the $[Si_2O_5]$ layers [Figure 5(b)]. This planar four co-ordination was hitherto unknown, at least in the case of Fe^{2+} . In the case of petalite, $LiAlSi_4O_{10}$, the middle valency of the cations is $(1+3)/2 = 2$. The deep folding of the layers of this material [Figure 5(c)] leaves only tetrahedral gaps which, while they may be large enough for the otherwise often tetrahedrally co-ordinated Li^+ and Al^{3+} ions, do not suffice for the larger Ca^{2+} and Sr^{2+} ions.

Anhydrous layer silicates $A_2^{III}(Si_2O_5)_3$ with trivalent cations are unknown, and indeed on the basis of the arguments advanced here cannot be expected, since such a cation would have to balance the charge of three $[SiO_4]$ tetrahedrons, so that either the $[Si_2O_5]$ layers would have to be so deeply folded that the resulting available space for the cation would be too small, or else very loose and therefore unstable structures would necessarily result.

In $K_4Ca(Si_2O_5)_3$ and $K_8Ca(Si_2O_5)_5$ the ratio of the number of cations to the number of $[SiO_4]$ tetrahedrons is greater than in the compounds with only bivalent cations, so that here the medium-size Ca^{2+} ions can be accommodated in the lattice along with the larger K^+ ion.

Hydrous layer silicates

As is evident from Tables I and II, there are no anhydrous layer silicates of the small bivalent cations, Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Ca^{2+} or of the trivalent cations such as Al^{3+} and Fe^{3+} . Now, these are precisely the cations which are typical of the formation of hydrous layer silicates. In these hydrous layer silicates of the micas and clay minerals, the polyvalent cations are co-ordinated not only by the oxygen atoms bound to only one silicon atom, but also by hydroxyl ions, so that $[Me(O,OH)_6]$ octahedrons are formed. These octahedrons are linked to layers of hexagonal symmetry by common edges. The mesh size of the layers is commensurate with those of the $[Si_2O_5]$ layers, so that one or two, as the case may be, tetrahedral layers add themselves in each case to one octahedral layer (Figure 6). In the structures of the silicates in question, the negative charges of the tetrahedral layers are partially or completely neutralized by the positive charges of the octahedral layers. Thus, in these hydrous layer silicates the small, polyvalent bare Mg^{2+} , Fe^{2+} , Al^{3+} ions, etc. do not act as cations but rather, the $[Me(O,OH)_6]$ octahedrons are to be regarded as cations.

As shown by comparison of the lattice a_{hex} of cristobalites, SiO_2 and hydrargillites, $Al(OH)_3$, the structures of which are built up from $[Si_2O_5]$ tetrahedral layers or layers from $[Al(OH)_6]$ octahedrons (Table III), the space required by an $[Al(O,OH)_6]$ octahedron is about the same as that required by an $[SiO_4]$ group of the tetrahedral layer. Therefore, the $[Al(O,OH)_6]$ octahedrons are just the right size in order to balance the charge of a flat $[Si_2O_5]$ layer of the kind shown in Figure 2. Examples of aluminium layer silicates with flat $[Si_2O_5]$ layers are the three modifications of $Al_4[Si_4O_{10}](OH)_8$ kaolinite, dickite and nacrite.

The $[\text{Mg}(\text{O},\text{OH})_6]$ octahedrons are somewhat larger, so that layers formed from them have a larger mesh size than the $[\text{Si}_2\text{O}_5]$ layers of cristobalites (cf. Table III, column 3). The stresses resulting from the mutual addition of the octahedral and tetrahedral layers are compensated by the fact that the octahedral layer is broken up into narrow strings. Since the tetrahedral layer cannot be broken into strings without changing its chemical composition, the stresses in the tetrahedral layer are absorbed by reason of the fact that the free tetrahedral chains of three or two neighbouring two-chains* point to one side, while those of the next three or two two-chains, as the case may be, point to the other side of the tetrahedral layer. We find structures of this sort in sepiolites, $\text{Mg}_4[\text{Si}_6\text{O}_{15}](\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and in palygorskite (= Attapulgitite), $\text{Mg}_5[\text{Si}_8\text{O}_{20}](\text{OH})_2 \cdot \text{H}_2\text{O}$ [Figure 7(b), (c)].

The stresses arising as a result of the different amounts of space occupied by $[\text{SiO}_4]$ tetrahedrons in the $[\text{Si}_2\text{O}_5]$ layer and $[\text{Mg}(\text{O},\text{OH})_6]$ octahedrons in the octahedral layer may also be absorbed by the tetrahedral layer with the smaller mesh size having a smaller radius of curvature than the octahedral layer with a larger mesh size, similar to the way in which the double layer is curved in a bimetallic strip. As in the case of sepiolite and palygorskite, the free tetrahedral corners within rather large areas can face now in one direction, now in the other from the $[\text{Si}_2\text{O}_5]$ layers, so that double layers arise after the fashion of corrugated sheet metal [Figure 7(d)]. This occurs in the case of antigorite $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$. On the other hand, if the curvature of the double layer comprising tetrahedral and octahedral layers continues without a change of direction, they roll up into small tubes, as is known in the case of chrysotile of the same composition $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ [Figure 7(e)].

The greater the difference in mesh width of the octahedral and tetrahedral parts of the layer, i.e., the larger the $[\text{Me}(\text{O},\text{OH})_6]$ octahedrons, the smaller should be the diameter of the chrysotiles

* A two-chain is a chain with an identity period of two tetrahedrons.

tubes. This was confirmed in the electron microscopic investigations of Noll, Kircher and Sybertz (1960) where it was found that, in the layer silicates listed in Table III with tubular structure, in fact the average tube diameter decreased with increased cation radius and increasing lattice constants a_{hex} of the hydroxides crystallizing in the hexagonal C6-Type, from 650 Å in metahalloysite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ to about 100 Å in synthetic cobalt chrysotile $\text{Co}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$. At the same time, the average wall thickness of these tubes decreases from 35 double layers to four double layers. The cobalt chrysotile tubes are so unstable that, despite many attempts, the various authors were unable to synthesize chrysotile with cations larger than Co^{2+} .

If some of the silicon atoms in the $[\text{Si}_2\text{O}_5]$ layers are replaced by the larger Al^{3+} , Fe^{3+} or even Zn^{2+} ions, the mesh size of the tetrahedral layer is thereby increased so that considerable quantities of larger cations can be incorporated, at the same time retaining the flat, non-curved $[\text{Si}_2\text{O}_5]$ layer in the octahedral layer, as may be seen in the example of annites $\text{KFe}_3^{\text{II}}[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$, the synthetic phases $\text{KFe}_3^{\text{II}}[\text{Fe}^{\text{III}}\text{Si}_3\text{O}_{10}](\text{OH})_2$, $\text{KCo}_3^{\text{II}}[\text{Co}^{\text{III}}\text{Si}_3\text{O}_{10}](\text{OH})_2$, $\text{KNi}_3^{\text{II}}[\text{Ni}^{\text{III}}\text{Si}_3\text{O}_{10}](\text{OH})_2$ (Lindqvist, 1966) and sauconite $\text{Zn}_6[\text{Si}_{8-x}\text{Zn}_x\text{O}_{20}](\text{OH})_4$ (Roy & Mumpton, 1956).

Owing to the absence of polarity in the layers of mica type, in which two tetrahedral layers are added to an octahedral layer, there is no possibility of the layers being curved, so that here flat $[\text{Si}_2\text{O}_5]$ layers occur, even with cations somewhat larger than $[\text{Al}(\text{O},\text{OH})_6]$ octahedrons and especially in the case of $[\text{Mg}(\text{O},\text{OH})_6]$. Talc, $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$, which occurs only in very small and poorly ordered crystals, is an important example of this.

Whereas hydrous layer silicates with medium-size cation octahedrons $[\text{Fe}(\text{O},\text{OH})_6]$ and $[\text{Zn}(\text{O},\text{OH})_6]$, without incorporating larger cations in the tetrahedral layers, have not yet been discovered, since these octahedrons are too large for the development of rolled layers, another principle of adaptation of the $[\text{Si}_2\text{O}_5]$ layers to the cation polyhedrons is found in the transition to still larger cation polyhedrons. To be sure, only two examples

of this principle have so far been examined closely.

In the case of manganese pyrosmalite $\text{Mn}_{16}[\text{Si}_{12}\text{O}_{30}](\text{OH})_{18}\text{Cl}_2$ it can be imagined that the tetrahedral layer is constructed by continued mutual addition of $[\text{Si}_6\text{O}_{18}]$ rings [Figure 8(a)] (Takeuchi, 1966). While the free tetrahedral corners of one six-ring point to one side of the layer, those of the neighbouring six-ring point to the other side. This results in a curled $[\text{Si}_2\text{O}_5]$ layer, which adapts itself to the hexagonal layer consisting of $[\text{Mn}(\text{O},\text{OH})_6]$ octahedrons. The "unit of curl", the free tetrahedral corners of which point to one side of the layer, is therefore the six-ring.

The second example of a layer silicate constructed on the "curl principle" is apophyllite $\text{Ca}_4\text{K}[\text{Si}_8\text{O}_{20}]\text{F} \cdot 8\text{H}_2\text{O}$, the crystal structure of which has long been known. In this mineral we can imagine $[\text{Si}_2\text{O}_5]$ layers to be constructed in an entirely analogous way by the reciprocal addition of $[\text{Si}_4\text{O}_{12}]$ rings. These rings point alternately with their free tetrahedral corners to either side of the tetrahedral layers [Figure 8(b)]. In this case, therefore, the unit of curling is a four-ring. The curling of the layer is thus tighter than in the case of manganese pyrosmalite. The curled tetrahedral layers fit themselves to the layers consisting of $[\text{Ca}(\text{O},\text{OH},\text{F})_7]$ and $[\text{K}(\text{OH})_8]$ polyhedrons.

A still more tightly curled tetrahedral layer would result from the reciprocal addition of $[\text{Si}_3\text{O}_9]$ rings with free tetrahedral corners disposed half on one side and half on the other side of the layer. Such layers with three-rings as their units of curling [Figure 8(c)] might be expected in the presence of somewhat larger cation polyhedrons, i.e. in hydrous strontium layer silicates, for example. However, layers of this type would be very loosely constructed and for this reason have probably not hitherto been observed, so that this principle of adaptation of $[\text{Si}_2\text{O}_5]$ layers appears to be limited by cation layers, i.e., in the direction of large cation polyhedrons.

No case is known where $[\text{Si}_2\text{O}_5]$ layers are adapted to the layer consisting of polyhedrons of the still larger polyvalent

cations Pb^{2+} or Ba^{2+} , and indeed would be difficult to imagine. The fact that hydrous layer silicates of strontium, barium and bivalent lead have not been observed despite a strenuous effort to prepare them in some instances, appears to indicate that no adaptation occurs on the basis of this principle.

Semi-quantitative Relationship

A quantitative relationship between the roughness of the tetrahedral layers and the size and charge of the cation is depicted in Figure 9.

The roughness, i.e. the tightness of folding, waving or curling of the $[\text{Si}_2\text{O}_5]$ layers is given by the area F_T of a $[\text{SiO}_4]$ tetrahedron, which is obtained from the lattice constants of the structure in the plane of the layer, the number n_T of $[\text{SiO}_4]$ tetrahedrons and the number n_S of $[\text{Si}_2\text{O}_5]$ in the elementary cell:

$$F_T = \frac{a_1 \cdot a_2 \cdot \sin \alpha_3 \cdot n_S}{n_T}$$

On the abscissa is plotted the quantity r/z , where r is the radius, and z the charge of the naked cation (after Ahrens, 1952), when the latter is co-ordinated only by oxygen atoms of the $[\text{Si}_2\text{O}_5]$ layers (i.e. in the anhydrous layer silicates). In the hydrous layer silicates of the mica and clay mineral group the effective radius of $[\text{Me}(\text{O},\text{OH})_6]$ octahedrons is put equal to half the octahedral edge,

$$r_{\text{eff}} = \frac{r_{\text{cat}} + r_{\text{O}^{2-}}}{\sqrt{2}}$$

where in the case of isomorphous substitution in the octahedral layer r_{cat} is the arithmetic mean of the various cation radii calculated according to the chemical composition. Interlayer cations, such as K^+ or Ca^{2+} in the micas, etc., have not been taken into account as they do not belong to the octahedral layer which is added to the $[\text{Si}_2\text{O}_5]$ layer. In the case of apophyllites $\text{Ca}_4\text{K}[\text{Si}_4\text{O}_{10}]\text{F} \cdot 8\text{H}_2\text{O}$, the $[\text{CaO}_7]$ and $[\text{KO}_8]$ polyhedrons are oriented with respect to the layer in such a way that it appears more

reasonable for this consideration to choose the mean distance from the cation centre to the centre of the polyhedral area as the polyhedron radius.

In the anhydrous layer silicates, z is equal to the charge of the cation, but in the hydrous silicates in place of this we get the charge of the polyhedron, i.e., in the case of antigorite $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$, for example, there are six $[\text{Mg}(\text{O},\text{OH})_6]$ octahedrons to four $[\text{SiO}_4]$ tetrahedrons, so that the effective charge z_{eff} of such an octahedron is $4/6 = 0.67$. In the case of kaolinite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ and other dioctahedral layer silicates, where in comparison with the trioctahedral layer silicates two thirds of the octahedral places are unoccupied, these empty polyhedrons are taken into account approximately in calculating the quotient r/z . Similarly, in the case of apophyllites, where there are only five cations for 8 $[\text{SiO}_4]$ tetrahedrons, six empty polyhedrons (two rhombic and four triangular prisms) have to be taken into account, as is evident from closer examination of the structure.

In the hydrous layer silicates, the empty polyhedrons are approximately of the same size as the filled ones, but in the anhydrous layer silicates of polyvalent cations the empty polyhedrons are generally smaller and more irregular, so that it is difficult to take them into account quantitatively for purposes of the present considerations. Thus, they are disregarded, and this explains why the points for $\beta\text{-Na}_2\text{Si}_2\text{O}_5$, sanbornite BaSi_2O_5 and petalite $\text{LiAlSi}_4\text{O}_{10}$ are situated to the left of the hatched area in Figure 9.*

It is also clear from Figure 9 that anhydrous and hydrous layer silicates show the same dependence of the area occupied per $[\text{SiO}_4]$ tetrahedron on the size and charge of the cations or cation polyhedrons, which is further reason for claiming that this view of the structures is a logical one.

* The deviation of $\text{Ag}_2\text{Si}_2\text{O}_5$ from the hatched area is probably due to the fact that the Ag-O bond is decidedly covalent, and no longer just ionogenic.

Conclusion

While the detailed influence of comparatively small differences in the size and charge of the cations on the structure of flat $[(\text{Si}, \text{Al})_2\text{O}_5]$ tetrahedral layers of clay minerals was recently investigated by Bailey (1966), and Noll, Kircher & Sybertz (1960) have shown the relationship between cation radius and the diameter of chrysotile tubelets, the present investigation shows that the great variety of hitherto known tetrahedral layer types of anhydrous and hydrous layer silicates can be partially explained by taking into account the influence of these two properties - cation radius and cation charge. With increasing quotient r/z we get the following sequence of layer types: folded, flat, corrugated, rolled, curled.

The present view is only a first attempt at constructing a general picture of the layer silicates. A desirable next step might be to calculate the electrostatic components of the lattice energies of various cation-tetrahedral layer arrangements in order to come to some conclusions about their stabilities from a comparison of these values for different arrangements. These electrostatic potentials can be calculated and compared without much difficulty for topologically similar cation-tetrahedral layer arrangements; however such calculations are more difficult for topologically dissimilar arrangements.

The purely qualitative relationship between size and charge of the cations given in the present paper, on the one hand, and the structure of the layer silicates, on the other, nevertheless shows the chemist from what cations still unknown anhydrous or hydrous layer silicates have some prospect of being successfully prepared. At the same time, by taking into account certain regularities recently described (Liebau, 1962) in the construction of silicates, crystallographers may be able to arrive at certain assumptions concerning the form of the tetrahedral layers of a layer silicate of unknown structure.

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Table I

Survey of known anhydrous layer silicates

$A^I_2Si_2O_5$	$A^{II}Si_2O_5$	$A^I_mB_n(Si_2O_5)_p$	$A^{II}B^{III}(Si_2O_5)_2$
$H_2Si_2O_5$ (1)	$BaSi_2O_5$	$LiKS_2O_5$ (7)	$MgBa(Si_2O_5)_2$ (9)
$Li_2Si_2O_5$		$Li_2K_4(Si_2O_5)_3$ (7)	
$Na_2Si_2O_5$ (2), (3)			$CaMe(Si_2O_5)_2$ (10)
$K_2Si_2O_5$ (4)		$K_4Ca(Si_2O_5)_3$ (8)	$SrMe(Si_2O_5)_2$ (10)
$Tl_2Si_2O_5$ (4)			
$Rb_2Si_2O_5$ (5)		$K_4Ca(Si_2O_5)_3$ (8)	$BaMe(Si_2O_5)_2$ (10)
$Cs_2Si_2O_5$ (7)			[Me = Fe, Co, Ni, Cu]
$Ag_2Si_2O_5$ (6)		$LiAl(Si_2O_5)_2$	

- (1) Liebau (1964)
 (2) Willgallis & Range (1964)
 (3) Williamson & Glasser (1966)
 (4) Schweinsberg & Liebau (1967)
 (5) Kracek (1932)
 (6) Liebau (1961)
 (7) Sheybany (1948, 1949)
 (8) Morey, Bowen & Kracek (1930, 1931)
 (9) Grebenstschikow (1962)
 (10) Grebenstschikow (1961)

Table II

Relation between cation size and valency and the water content of layer silicates

Me ^I			Me ^{II}			Me ^{III}		
1	2	3	1	2	3	1	2	3
H ⁺		F	Be ²⁺	0,35	-	Al ³⁺	0,51	H
Li ⁺	0,68	F	Mg ²⁺	0,66	H	Ga ³⁺	0,62	-
Na ⁺	0,97	F	Ni ²⁺	0,69	H	Cr ³⁺	0,63	(H)
Ag ⁺	1,26	F	Co ²⁺	0,72	H	Fe ³⁺	0,64	(H)
K ⁺	1,33	F	Fe ²⁺	0,74	(H)	Mn ³⁺	0,66	-
Rb ⁺	1,47	F	Zn ²⁺	0,74	(H)	V ³⁺	0,74	H
Tl ⁺	1,47	F	Mn ²⁺	0,80	H	Ti ³⁺	0,76	-
Cs ⁺	1,67	?	Sn ²⁺	0,93	-	In ³⁺	0,81	-
Fr ⁺	1,80	-	Cd ²⁺	0,97	-	Sc ³⁺	0,81	-
			Ca ²⁺	0,99	H	Bi ³⁺	0,96	-
			Sr ²⁺	1,12	-	Lanthanides ³⁺	0,85 to 1,06	-
			Pb ²⁺	1,20	-	Ce ³⁺	1,07	-
			Ba ²⁺	1,34	F	Hg ³⁺	1,10	-

- Column 1 Element, ionic charge
 Column 2 Cation radius in Å after Ahrens (1952)
 Column 3 Water content of the layer silicate
 [F = anhydrous, H = hydrous, (H) = hydrous layer silicate only if fairly large cations are included in the tetrahedron sheet, - = no layer silicate known]

Table III

Hydrous layer silicates with rolled or curled $[\text{Si}_2\text{O}_5]$ layers

1	2	3	4	5	6	7
Si	-	5,03	-	-	Cristobalite	SiO_2
Al	0,51	5,06	650	35	Metahalloysite	$\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$
Mg	0,66	5,40	156	11	Chrysotile	$\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$
Ni	0,69	5,40	154	9	Garnierite	$\text{Ni}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$
Co	0,72	5,48	101	4	synthetic	$\text{Co}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$
Fe*	0,74	5,65	-	-	-	-
Zn	0,74	-	-	-	-	-
Mn	0,80	5,79	-	-	Manganese pyrosmalite	$\text{Mn}_{16}[\text{Si}_{12}\text{O}_{30}](\text{OH}_{18}\text{Cl}_2)$
Ca	0,99	6,22	-	-	Apophyllite	$\text{Ca}_4\text{K}[\text{Si}_8\text{O}_{20}]\text{F} \cdot 8\text{H}_2\text{O}$

Column 1 Cation

Column 2 Cation radius (in Å) after Ahrens (1952)

Column 3 Lattice constant a_{hex} or $a_{\text{hex}} \sqrt{3}$ (in Å)

Column 4 Mean tube diameter (in Å)

Column 5 Average number of layers (wall thickness of tubelets)

Column 6 Name of mineral

Column 7 Chemical composition

* Greenalite $(\text{Fe}^{\text{II}}, \text{Fe}^{\text{III}})_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$, an ion antigorite, always contains varying quantities of Fe^{3+} ions in addition to the Fe^{2+} ions ($r = 0.64$ Å)

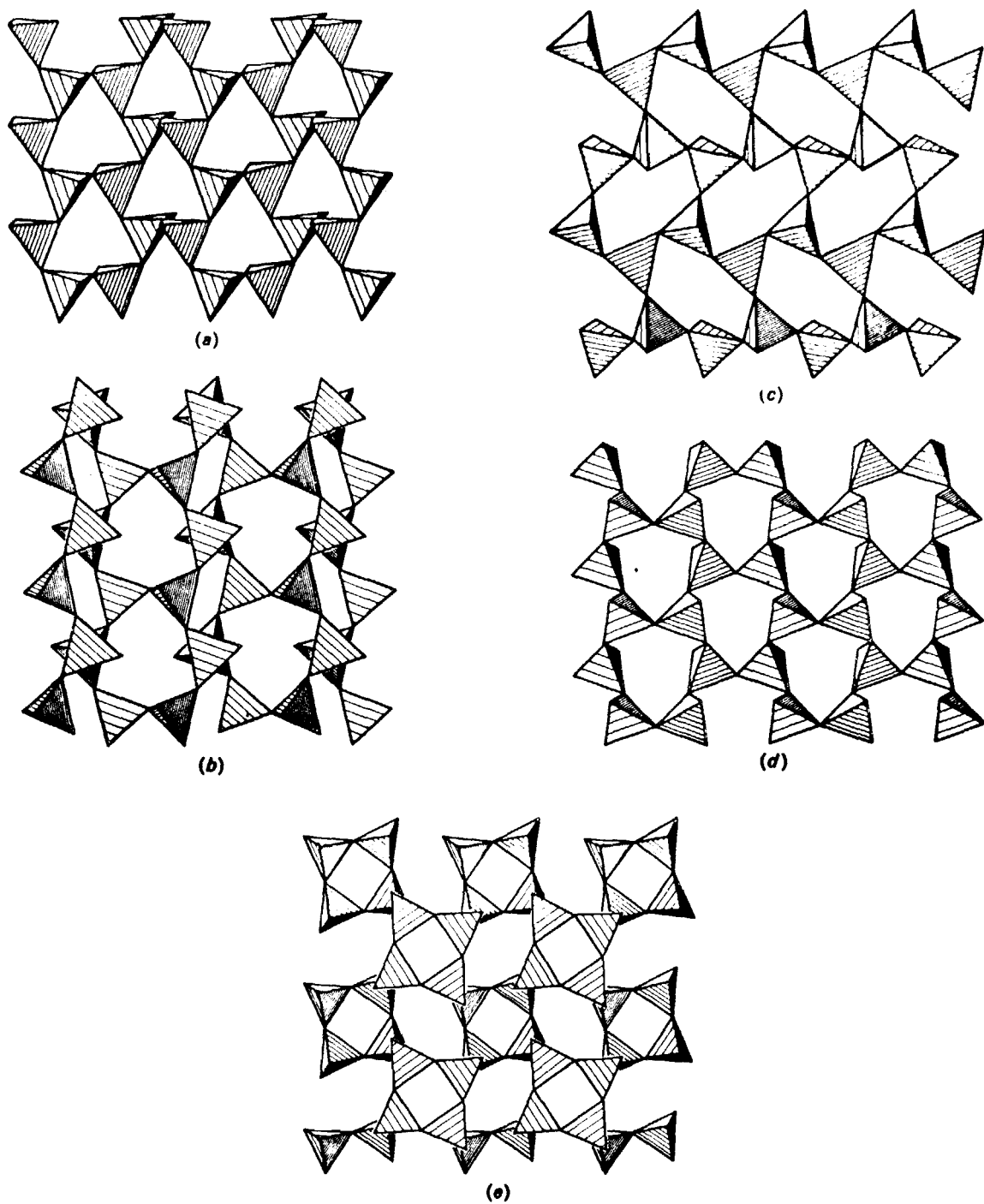


Fig. 1

$[\text{Si}_2\text{O}_5]$ types of layers of anhydrous silicates

- (a) $\text{Li}_2\text{Si}_2\text{O}_5$, (b) petalite, $\text{LiAlSi}_4\text{O}_{10}$,
(c) $\beta\text{-Na}_2\text{Si}_2\text{O}_5$, (d) sanbornite BaSi_2O_5 ,
(e) gillespite $\text{BaFeSi}_4\text{O}_{10}$

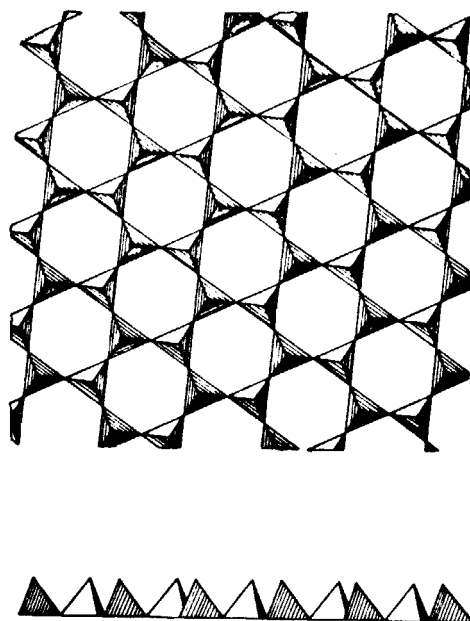


Fig. 2

The $[\text{Si}_2\text{O}_5]$ layer type of the micas and many clay minerals

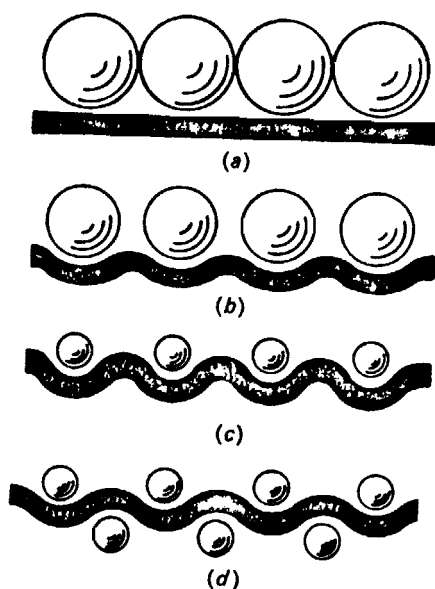


Fig. 3

Schematic representation of the adhesion
of $[\text{Si}_2\text{O}_5]$ layers to cations
of different size

(a) cation radius about 1.8 \AA (Fr^+), (b) cation radius 1.4 \AA (K^+), (c) and (d) cation radius 0.7 \AA (Li^+)

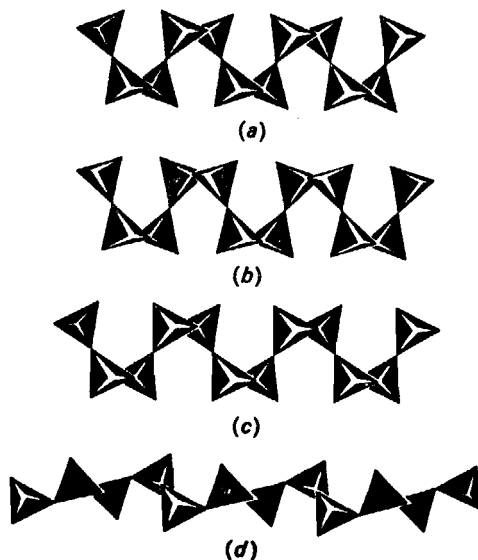


Fig. 4

Folding of $[\text{Si}_2\text{O}_5]$ layers of anhydrous layer silicates of monovalent cations

- (a) $\text{Li}_2\text{Si}_2\text{O}_5$, (b) $\text{H}_2\text{Si}_2\text{O}_5$, (c) $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$
 (d) $\beta\text{-Na}_2\text{Si}_2\text{O}_5$

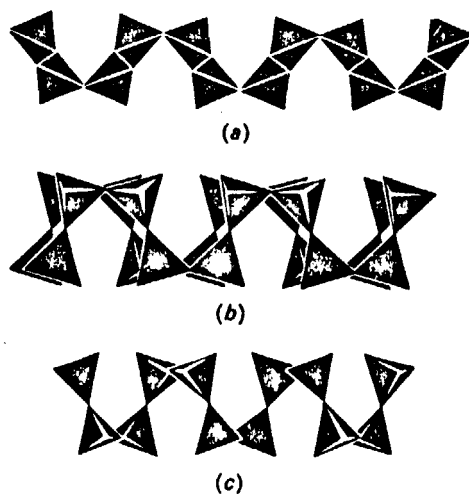


Fig. 5

Folding of $[\text{Si}_2\text{O}_5]$ layers of anhydrous layer silicates of polyvalent cations

- (a) sanbornite BaSi_2O_5 , (b) gillespite $\text{BaFeSi}_4\text{O}_{10}$,
 (c) petalite $\text{LiAlSi}_4\text{O}_{10}$

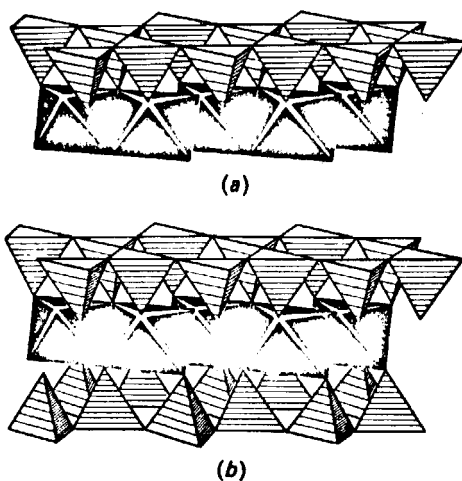


Fig. 6

Combination of tetrahedral
and octahedral layers

- (a) kaolin type layers
(b) mica type layers

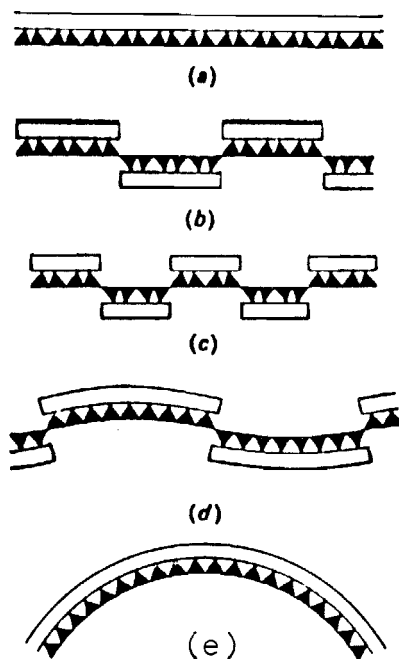


Fig. 7

Waving and rolling of the layers
of some hydrous layer silicates

- (a) kaolinite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$,
(b) sepiolite $\text{Mg}_4[\text{Si}_6\text{O}_{15}](\text{OH})_2 \cdot 4\text{H}_2\text{O}$,
(c) palygorskite $\text{Mg}_5[\text{Si}_8\text{O}_{20}](\text{OH})_2 \cdot \text{H}_2\text{O}$,
(d) antigorite $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$,
(e) chrysotile $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$

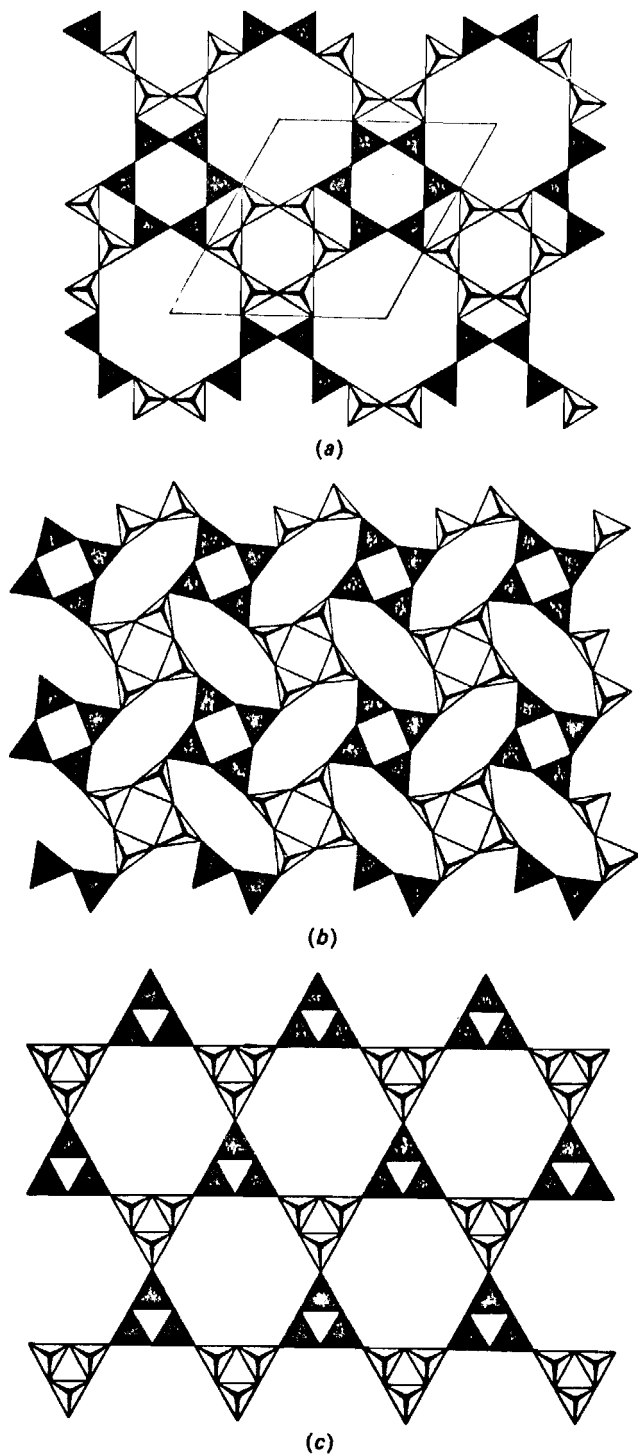


Fig. 8

"Curled" tetrahedron layers

- (a) manganese pyrosmalite $\text{Mn}_{16}[\text{Si}_{12}\text{O}_{30}](\text{OH})_{18}\text{Cl}_2$
- (b) apophyllite $\text{Ca}_4\text{K}[\text{Si}_8\text{O}_{20}]\text{F} \cdot 8\text{H}_2\text{O}$,
- (c) hypothetical type of layer with 3-rings
as the "unit of curl"

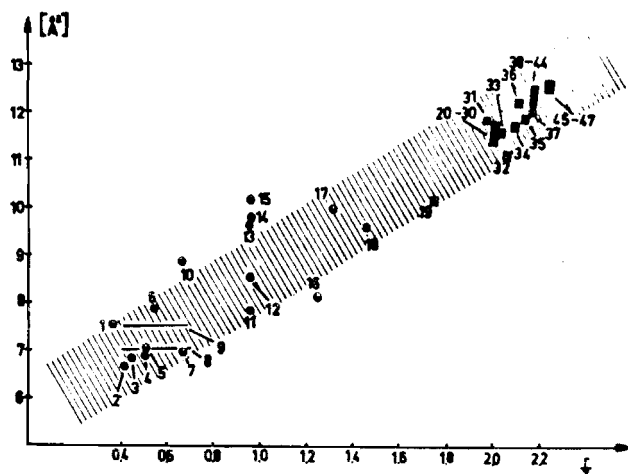


Fig. 9

Relation between area required by each $[\text{SiO}_4]$ tetrahedron F_T and the radius and charge of the cation in layer silicates

● anhydrous layer silicates; ■ hydrous layer silicates

- (1) petalite $\text{LiAlSi}_4\text{O}_{10}$, (2) cuprorivaite $\text{CaCuSi}_4\text{O}_{10}$, (3) $\text{SrCuSi}_4\text{O}_{10}$, (4) $\text{BaCuSi}_4\text{O}_{10}$, (5) gillespite $\text{BaFeSi}_4\text{O}_{10}$, (6) dalyite $\text{K}_{1.7}\text{Na}_{0.3}\text{ZrSi}_6\text{O}_{15}$ (Fleet, 1965), (7) $\text{Li}_2\text{Si}_2\text{O}_5$, (8) $\text{H}_2\text{Si}_2\text{O}_5\text{II}$ (Liebau, 1964), (9) $\text{H}_2\text{Si}_2\text{O}_5\text{I}$ (Liebau, 1964), (10) sanbornite BaSi_2O_5 , (11) $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$, (12) $\gamma\text{-Na}_2\text{Si}_2\text{O}_5$ (Hoffmann, 1965), (13) $\beta\text{-Na}_2\text{Si}_2\text{O}_5$, (14) $\text{C-Na}_2\text{Si}_2\text{O}_5$ (Williamson & Glasser, 1966), (15) $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ (Williamson & Glasser, 1966), (16) $\text{Ag}_2\text{Si}_2\text{O}_5$ (Liebau, 1961), (17) $\text{K}_2\text{Si}_2\text{O}_5$ (Schweinsberg & Liebau, 1967), (18) $\text{Tl}_2\text{Si}_2\text{O}_5$ (Schweinsberg & Liebau, 1967), (19) apophyllite $\text{Ca}_4\text{K}[\text{Si}_8\text{O}_{20}]\cdot 8\text{H}_2\text{O}$, (20) paragonite $\text{NaAl}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$, (21) margarite $\text{CaAl}_2[\text{Si}_2\text{Al}_2\text{O}_{10}](\text{OH})_2$, (22) - (24) kaolinite, dickite, nakrite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$, (25) halloysite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8\cdot 4\text{H}_2\text{O}$, (26) pyrophyllite $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2$, (27) sudoite $\text{Al}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2\cdot \text{Al}_{2.33}(\text{OH})_6$, (28) cookeite $\text{Al}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2\cdot \text{LiAl}_2(\text{OH})_6$, (29) beidellite $\text{Al}_2[\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}](\text{OH})_2\cdot (\text{Ca}, \text{Na})_{0.3}(\text{H}_2\text{O})_4$, (30) muscovite $\text{KAl}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$, (31) gyrolite $\text{Ca}_2[\text{Si}_4\text{O}_{10}]\cdot 4\text{H}_2\text{O}$, (32) manganese pyrosmalite $\text{Mn}_{16}[\text{Si}_{12}\text{O}_{30}](\text{OH})_{18}\text{Cl}_2$, (33) montmorillonite $(\text{Al}_{1.67}\text{Mg}_{0.33})[\text{Si}_4\text{O}_{10}](\text{OH})_2\cdot \text{Na}_{0.33}(\text{H}_2\text{O})_4$, (34) palygorskite $\text{Mg}_5[\text{Si}_8\text{O}_{20}](\text{OH})_2\cdot \text{H}_2\text{O}$, (35) nontronite $\text{Fe}_2^{\text{III}}[\text{Si}_{3.67}\text{Al}_{0.33}\text{O}_{10}](\text{OH})_2\cdot \text{Na}_{0.33}(\text{H}_2\text{O})_4$, (36) amesite $\text{Mg}_2\text{Al}[\text{SiAlO}_5](\text{OH})_5$, (37) talc $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$, (38) prochlorite $(\text{Mg}_{1.75}\text{Fe}_{1.15})[\text{Si}_{2.2}\text{Al}_{1.8}\text{O}_{10}](\text{OH})_2\cdot (\text{Mg}_{0.75}\text{Al}_{1.50}\text{Fe}_{0.50})(\text{OH})_6$, (39) phlogopite $\text{KMg}_3[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$, (40) magnesium vermiculite $(\text{Mg}_{2.83}\text{Fe}_{0.17}^{\text{III}}\text{Al}_{0.15})[\text{Si}_{2.86}\text{Al}_{1.14}\text{O}_{10}](\text{OH})_2\cdot (\text{Mg}_{0.48}\text{K}_{0.01})(\text{H}_2\text{O})_4$, (41) - (44) clinoptilgite, ortho-clinoptilgite, clinochrysotile, orthochrysotile $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$, (45) annite $\text{KFe}_3^{\text{II}}[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$, (46) hendricksite $\text{KZn}_3[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$ (Fron del & Ito, 1966).