CURRENT PROGRESS IN SILICATE STRUCTURES

by

W. F. BRADLEY
Illinois State Geological Survey
Urbana, Illinois

ABSTRACT

Attention is called to the value to be derived from application of diffraction analysis of modern grade to specific, familiar, approximately known crystallizations. Features consequent to ordering of coordination polyhedra of differing sizes in layer structures are discussed, and their bearing upon relations between lattice parameters and chemical compositions are outlined.

In the establishment of the principles of clay mineral structures through the last 30 years, clay mineral investigators have been almost totally indebted to the earlier analyses made on the better-organized macrocrystalline silicate mineral groups. These analyses were conducted from the point of view that complex compositions need be understood in terms of few kinds of coordination polyhedra, specific ones of which could be considered as equivalent even though they represented chemically different entities. Analyses on this level of schematic basis were so successful that the major silicate groups and their coordination schemes became relatively familiar.

Current Fourier methods, aided by computing machines, now afford the opportunity to establish in detail some of the intimate complexities of these already familiar crystallizations.

The feature of greatest import which emerges from such detailed analyses relates to the sizes of silica and alumina tetrahedra. A survey by Smith (1954) established consensus values of $1.60 \pm 0.01\text{Å}$ for the Si–O bond and $1.78 \pm 0.02\text{Å}$ for the Al–O bond in tetrahedral coordination. The distinction is well within the resolving power of three-dimensional analyses. It is particularly well illustrated in Bailey and Taylor’s (1955) analysis of a potassium feldspar. One specific tetrahedron is much larger than average, one is moderately larger, and two are essentially typical for silicon occupancy.

No analyses that include three-dimensional sections are yet published for any layer silicates, but chlorite studies by Steinfink (1958) include projections in which specific large and small tetrahedra are distinguished.

Layer silicates conform substantially to hexagonal arrangement in their $ab$-planes and afford easy measurement of the reticulation periods. Frequent one-dimensional syntheses also strongly indicate that layers are essentially planar. The accommodation of polyhedra of known sizes into reticulation schemes of known lattice parameters is subject to solution.
For a purely siliceous net in open hexagonal array, the known bond lengths provide that a fully extended net have orthohexagonal $a$ and $b$ parameters of $5.22 \pm 0.04\AA$ and $9.05 \pm 0.06\AA$. In an actual mineral compound, these parameters must adjust to become commensurate with the rest of the structure. In the kaolin minerals the siliceous net is observed to reticulate at about $b_0 = 8.9\AA$. The articulated rotations of tetrahedra toward a trigonal array less open than the ideal hexagonal are illustrated in Newnham and Brindley’s (1956) dickite structure (Fig. 1) and are probably a general compacting mechanism.

![Diagram](image)

**Figure 1.**—Tetrahedral and octahedral coordination levels in dickite (after Newnham and Brindley, 1956) illustrating articulated rotations of triangular bases to modify the fundamental mesh of the respective ideal schemes.

When tetrahedral nets include both silicon and aluminum occupants, both mesh gauge and order among the species are concerned in fitting. Disordered arrays including oversize units can only approach full net extensibility if averaged over large areas. The sharp diffraction effects of many crystals indicate that (at least partial) ordering is probably the common state.

Speculative discussions of order inferences are subject to the fault that they may be found to be in error as soon as the subject mineral is actually analyzed. In spite of this danger, a paper on this subject follows in the present Proceedings (DeVore, 1958), and the temptation is presented to view one attractive aspect (not an item in the following discourse) of the subject here, which can be drawn upon later in discussion of chemical compositions.

The basis for polymorphism in the micas is the displacement of $\frac{1}{3} a_0$ inherent in the hexagonal packing of the octahedral level. For biotite compositions, observed displacements do not deviate sensibly from the exact $\frac{1}{3}$. For the muscovite crystallization the displacement does deviate perceptibly, and in Yoder and Eugster’s (1955) 1M synthetic muscovite it deviates even
further. Figure 2 illustrates the unequal observed arrangement of spacings of muscovite powder diagram 02l and 11l lines, drawn in the form of an imaginary c* rotation diagram.

It is also true that the muscovite composition involves an inherently smaller octahedral coordination scheme parameter than that of common biotites. We can look then at the possibilities of compacting an ordered tetrahedral array of muscovite composition into the observed dimensions of muscovite layers. Figure 3 represents an ordered distribution of one aluminum-bearing tetrahedron in four, articulated so that a 9.0Å hexagonal net can accommodate it in the same space which would be available to a fully extended entirely siliceous net. The normally ideally hexagonal rings which seat potassium ions are seen to be distorted into two kinds of irregularly shaped rings each of which would be presumed to displace its potassium ion from the center of the ideal scheme. The keying of two nets by potassium ions consequently introduces a small displacement of one with respect to the other which is independent of the fundamental 1/3 a₀ hexagonal displacement. In the schematic vectorial representation of polymorphs as employed by Smith and Yoder (1956) the supplementary displacement takes the form of an addition to each vector inclined at about 15° and about one-fifth as long. The displacement of reference grids in the superposition for the
assumed array of Fig. 3 is illustrated in Fig. 4. It provides an increment of 1.5° to the β angle of the 1M structure and about 0.5° to that of the 2M. If the 1M structure is truly single layer, it also introduces a deviation of about 0.5° from 90° into the γ angle for the 1M. Powder data do not permit that it be confirmed, but the probability of such a displacement was noted by Hendricks and Jefferson (1939) for their 6-layer monoclinic lepidolite, later described by Smith and Yoder (1956) on the basis of the simpler 2-layer monoclinic of a second kind.

It is to be hoped that a modern refinement of the 2M muscovite structure will be made soon.

The differing sizes of silicon- and aluminum-occupied tetrahedra bear significantly on the parameters of layer silicates of variable compositions. For any given tetrahedral aluminum : silicon ratio at a given temperature, a limit of extensibility of a hexagonal net, averaged over many cells, must exist if layers are to be maintained. The limit is lowered by order, except for the 1 : 1 ratio, order being equivalent to reduction of the number of cells over which periodicities need be averaged.

There is also a vague limit to the compressibility of nets of each composition. The articulated rotation of tetrahedron bases in the open hexagonal packing by 30° each would close the open hole and reduce layer parameters by about 15 percent. Complete closure would greatly reduce Si-O-Si bond angles, however (from about 140° to about 120°), and is probably never achieved. Average rotations of 5° or 10° are probably most favorable.

The above described elastic nets are articulated with octahedral layers which themselves have inherent layer parameters and their own degrees of elasticity, in turn dependent upon their composition and its order.
For octahedral layers, simple trioctahedral compositions are exemplified by the magnesium phases. The [111] section in periclase, with all octahedral edges equally shared, has dimensions $5.17 \times 8.95 \times 2.43\AA$ for units analogous with the layer silicates. Brucite, with six edges shared (and shortened), has dimensions $5.45 \times 9.44 \times 2.10\AA$. Synthesized talc, of cross-section $5.26 \times 9.10\AA$, would require a $2.30\AA$ octahedral thickness to maintain the same bond lengths. The latter parameter has not been specifically determined, but a thickness of this order of magnitude is suggested by the $c \sin \beta$ value of $9.26\AA$, about 0.10 greater than that for pyrophyllite.

For octahedral layers of dioctahedral composition, only three edges are foreshortened by sharing, and shorter bond lengths are accommodated in a given mesh by this mechanism, which in turn can be modified by thickening or thinning as with the trioctahedral compositions. The scheme of accommodation is well illustrated in Newnham and Brindley's (1956) dickite structure.

Brindley and MacEwan (1953) reviewed a large number of observed lattice parameters from crystals of known chemical compositions which they...
discuss in terms of three convenient quantities: a diffraction parameter which may be designated $b_{\text{obs}}$, a tetrahedral contribution which is a function of tetrahedral composition, and an octahedral contribution which is a function of octahedral composition. Their observations required two sets of tetrahedral contributions, but we can use one quantity, $b_t$, as a tetrahedral potential, and deal in terms of $b_{\text{obs}}$, $b_t$, and a $b_{\text{oct}}$ for octahedral potential.

![Figure 5](image.png)

**Figure 5.**—Relations between observed $b$-axis periods and chemical compositions of assorted layer silicates. Average tetrahedral potentials, empirical relations, and magnitudes for trioctahedral and dioctahedral compositions are indicated common with respect to observations cited in literature for analyzed specimens.

Figure 5 summarizes the relationship between all the dimensional features discussed above. Full lines bound the range of full extension and easy contraction for tetrahedral nets, hatched areas indicate common octahedral compositions, and dashed lines indicate the empirical trends observed by Brindley and MacEwan (1953) on the basis of which arithmetic averages of tetrahedral and octahedral meshes could be related to chemical composition. The indicated datum points are analyses taken largely from Brindley and MacEwan (1953) and Kovalev (1956). The larger displacements from the level of full extension are presumed to be associated with the better degrees of order.

Several of the analyses of Fig. 5 are replotted in Fig. 6 in terms suggested
by the compilation of chlorite analyses by Kovalev (1956). Some value of $b_t - b_{obs}$ near about 0.15Å probably represents a best strain-free tetrahedral mesh. Tetrahedral compositions stretched to $b_t - b_{obs}$ values less than 0.15Å have thickened the octahedral layers, and tetrahedral compositions excessively compacted (high $b_t - b_{obs}$ values) have stretched and thinned the octahedral layers. The four open circles were located without regard for probable occupancy of some tetrahedra by ferric ion, and probably all belong somewhat further to the right.

The relationships reviewed here for the layer structures are also strongly supported by the general aspects of the crystallizations of related compositions that do not maintain the layer morphology. These were discussed in an earlier conference (Bradley, 1955) and will be only briefly cited here.

Natural chrysotiles and syntheses aimed at the $2\text{SiO}_2\cdot3\text{MgO}$ composition are variously described as curved, tubular and helical. Their composition lies well off the compatibility range in Fig. 4. Antigorite near the above composition is found to be corrugated, but introduction of alumina into synthesis batches permitted the synthesis of platy polymorphs (Roy and Roy, 1954). In this case, improved fit is consequent to simultaneous intro-
duction of some larger tetrahedra and some smaller octahedra. Synthesis of material of platy habit was also accomplished by employing germanium to yield Mg₅Ge₅O₁₀(OH)₈ (Roy and Roy, 1954).

The high incidence of fibrous crystallizations in high silica magnesian compositions was also discussed before.

Consideration of the adjustment of octahedral nets discussed above leads to another interesting consideration. The foreshortening of shared edges by dioctahedral compositions leaves a regularly disposed larger unoccupied octahedral interstice. Opposite displacements of the same oxygens would provide two large interstices and one small interstice. An extension of this mechanism to mixed octahedral populations would provide a situation such that the energy of the system obviously would be improved by order among compositions near 2 : 1 or 5 : 1 ratios. Other arrangements, too, could well be imagined.

In this connection two pertinent unpublished analyses of iron-bearing chlorites have been called to my attention by the respective authors. Dr Gianco Gottardi (personal communication, 1957) has examined a chlorite of composition Mg₃.06Fe²⁺₁.62Fe³⁺₀.₆₆Al₁.₁₈Si₂.₄₁Al₂.₁₈O₁₀.₆₂OH₇.₉₈ for which a one-dimensional Fourier synthesis establishes that the iron is concentrated in the talc layer, and Dr Hugo Steinfink has a two-dimensional analysis which establishes that one specific octahedron is preferentially occupied by iron.

To summarize: order is a common phenomenon among the layer silicates, and current methods of analysis are sufficiently definitive to permit direct observation of whatever order may exist in a suitably crystallized example.

REFERENCES


DeVore, George W. (1958) These proceedings.


