

# STRUCTURAL IRREGULARITIES IN HYDROUS MAGNESIUM SILICATES \*

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## ABSTRACT

The crystal structures of chrysotile, antigorite, attapulgite, sepiolite, vermiculite, and montmorillonite are discussed in the light of the degree to which they resemble chlorite.

The proposal is advanced that the perfection of articulation between tetrahedrally and octahedrally coordinated layers is temperature-sensitive, and that the several crystallizations reflect the degree to which difficulty of articulation limits the growth of particular compositions.

It is widely known that at the same time that Pauling (1930, pp. 123, 578) was taking advantage of his observations of approximate dimensional fits between silica mineral- and hydroxide-coordination schemes to elucidate the structures of the hydrous layer silicate minerals, he also took cognizance of the fact that brucite layer dimensions were rather larger than would be expected to make a strain-free articulation with a silica layer. Subsequent analyses have not altered this impression and some, such as Jagodzinski and Kunze's (1954, pp. 137-150) analysis of chrysotile, have greatly strengthened it.

In considering the crystalline silica minerals themselves, certain generalities are established in principle, although actual intimate details of low symmetry forms are lacking. The three basic minerals (quartz, cristobalite, and tridymite) have in common the property that they are composed of three-dimensional nets of silica tetrahedra, each silicon being tetrahedrally surrounded by four oxygens and each oxygen shared by two silicons. An important degree of covalent bonding nature is inherent in each of these associations, and each mineral is subject to rapid high-low inversions which involve only the extension or contraction of the networks with no disruption of the covalent bonds. Each high-form is notably less dense than the corresponding low-form.

In the silica minerals the electron population affords an environment of eight valence electrons to each kernel. For each silicon, with four bonded neighbors, the consistent disposition of the four negative maxima which constitute the bonds is the regular tetrahedron, with the positions of high probability of occupancy by electron pairs equal in density and in density distribution. For each oxygen only two of the negative maxima are sharpened by bond character, and their disposition is open with respect to the

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tetrahedral angle. The two unbonded more diffuse maxima, representing the two unshared electron pairs, are closed to compensate, but still constitute a restraint upon the degree to which the oxygen bond angle can open.

It seems a fair presumption that this restraint upon bonding angle is temperature-sensitive, and that it affords a mechanism in the light of which the remarkable temperature-dependent extensibilities of the silica mineral networks may be viewed. It is an equally valid factor whether the scheme be a detail in one of the actual silica crystallizations as in tridymite or cristobalite, or whether it be arranged for articulation with other neighbors as in the layer silicate crystallization.

The over-all linear extension of tridymite layers is about one and one-half percent laterally and negligible vertically up to the temperature of its thermal transition. Brucite is relatively insensitive laterally, but the various common octahedral compositions have a latitude of a few percent. Figure 1 illustrates diagrammatically the relative courses of thermal expansion for several magnitudes of "brucite" layer compositions and for pure and substituted tetrahedral compositions.

Isomorphous substitutions are presumed to cause characteristic increases or decreases in average lateral dimensions for either tetrahedral or octahedral layers, but cannot alter the kind of bonding scheme which characterizes the host. The size effects have recently been authoritatively reviewed

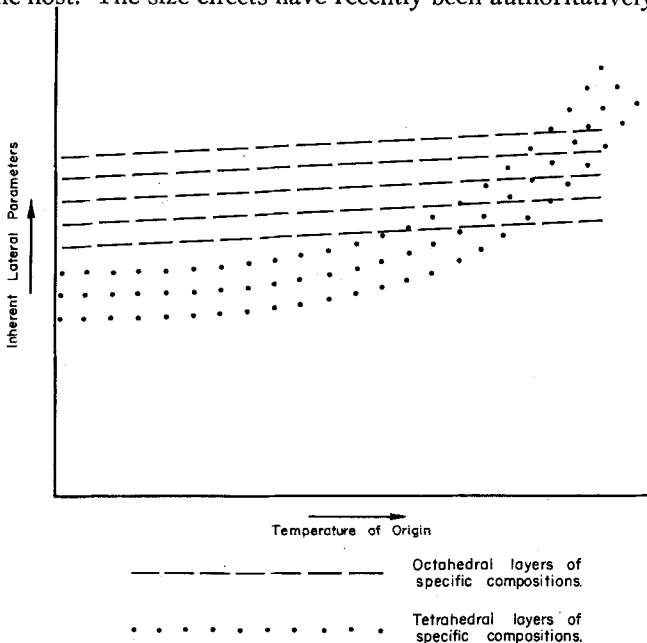


FIGURE 1.—Diagrammatic illustration of curves representing the natural lateral extents of some tetrahedral compositions crossing those of octahedral compositions with increasing temperature.

by Brindley and MacEwan (1953, 34 *et seq.*). Their analysis is made from a quite different point of view than the one taken here, but it is not basically at variance with this analysis.

In the chlorite minerals the tetrahedral network is at or near the limit of its lateral extensibility, and the octahedral layer at or near its limit of compressibility. Compositions which exist as macrocrystals in the typical chlorite crystallization in nature must have fitted strain-free at the temperatures at which they achieved such regularity. It is further to be noted that such macrocrystals have a low resistance to weather, as would be anticipated for compositions put under strain by reversion to ordinary temperatures. Compositions of excessively poor fit, as the highly ferriferous, do not exist in sizes comparable with those of the more favorable compositions, and they exhibit diffraction effects interpretable as departure from the ideal chlorite scheme. All compositions in the minerals of unquestioned low-temperature origin exist as fine-grained, and frequently faulty, manifestations of the chlorite crystallization, or perhaps only a chlorite-like crystallization.

For the purposes of the discussion to follow, it is probably desirable to adopt a stylized drawing of layer crystallizations which can schematically represent both the crystallo-chemical aspects and the X-ray diffraction character. A view of the projection of chlorite onto the *bc* plane is depicted in Figure 2a. Sets of narrow black lines represent the levels of open hexagonally packed oxygens of linked bases of tetrahedra and the silicons bonded to them. These levels represent the strongest bonding in the structure, and the two kinds of atoms are not normally resolved in one-dimensional Fourier syntheses of routine X-ray diffraction data. The broad shaded lines represent the more loosely bonded octahedral layers. These either may or may not be resolved into components in one dimensional syntheses, depending on the quality of diffraction data. This stylized drawing is an analogue of a two-dimensional *bc* plane electron density plot for a chlorite. Figure 2b is the comparable representation of the "chrysotile structure." It actually indicates only what chrysotile would be if it were a perfect analogue to kaolinite; *i.e.*, if it did not suffer from the misfit being discussed. The 2a and 2b plans differ only in that the second is a polar structure. Tetrahedral silica nets are linked to octahedral layers by Si-O bonds disposed alternately up and down in the chlorite arrangement, leaving one-half of the "brucite" layers without primary bonds to silica, and one tetrahedral layer is bonded to each "brucite" layer in the polar arrangement.

With some license to disregard details, the above arrangements are now to be compared with two structures for fibrous magnesian minerals. Figures 3a and b are stylized electron density plots, respectively, of the *ab* planes for attapulgite and for sepiolite. Usage has been to call the approximately 5.2 Å period *a* in the layer structures and *c* in the fibres. Although these structure analyses are merely schematic (Bradley, 1940, p. 405; Nagy and Bradley, 1955, p. 885) they suffice for this discussion. The tetrahedral

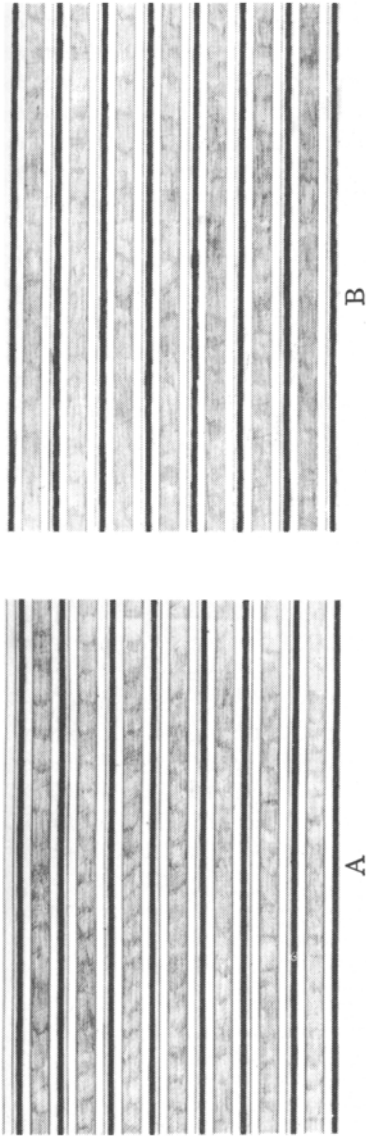


FIGURE 2. — Schematic illustrations of the crystal structures of (A) chlorite and (B) a kaolin analogue with the chlorite composition.

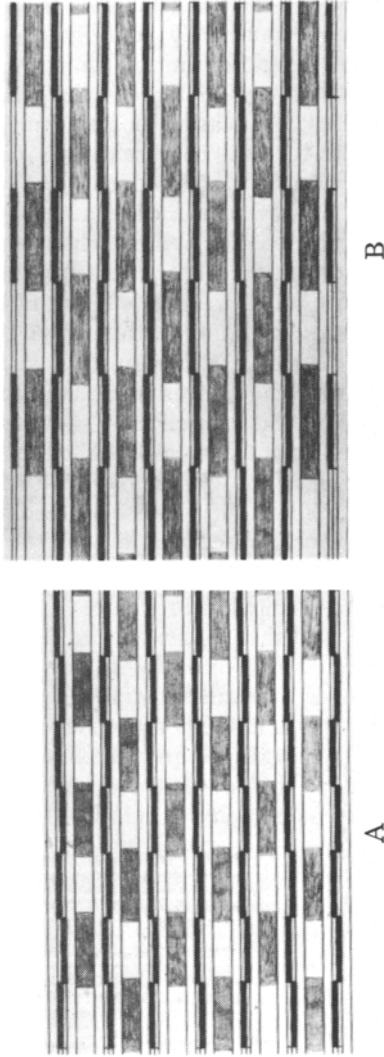


FIGURE 3. — Schematic illustrations of the crystal structures of (A) attapulgite and (B) sepiolite.

linked nets dominate the structures just as in the chlorites, but the sites of silicons, and the directions of the Si-O bonds to neighboring octahedral layers are disposed in grouped linear arrays, alternating up and down so that the articulated octahedra form ribbons in an ab face-centered array. Between octahedrally coordinated ribbons in these structures are water channels, disposed in environments analogous with that of the unbonded "brucite" layers of the chlorite structure. All of these structures are encountered on occasion as clay minerals. Any strain that might have been inherent in local composition is dissipated by the multiple terminations represented by ribbon edges.

The phenomenon of alternation in disposition of tetrahedra seems to be one which could exist in the chlorite crystallization, as a fault, just as readily as it does in the fibrous structure, and the centered arrangement of series of such faults is a highly efficient mechanism for dissipation of strain.

If frequent faults of this type were regularly disposed, as illustrated for a hypothetical case in Figure 4, a structure distinct from that of chlorite and resembling the fibrous minerals would obtain even for a chlorite composition. The real existence of such a structure in a chlorite composition has not been conclusively established, but an analysis of 001 intensities only for a chloritic mineral in the daphnite composition presented last year by Brindley and Gillery (1954 these proceedings) could have represented such a case.

Reciprocal space relations of the pertinent diffraction effects in the respective *okl* or *hko* sections corresponding to the stylized electron density plots are compared in Figure 5. On the left the 001 nodes of chlorite are shown, and the position of the 021 row line, along which nodes are distributed differently according to polytypism, is only indicated. The attapulgite and sepiolite details illustrate the effect of the cell centering on the comparable regions in reciprocal space for the two known degrees of multiplicity along the *b*-axis. A greater multiplicity, as was implied in Figure 4, would only move the odd-odd nodes nearer to the vacant odd order 001 positions depicted as occupied in chlorite. The dashed lines in the right-hand diagram

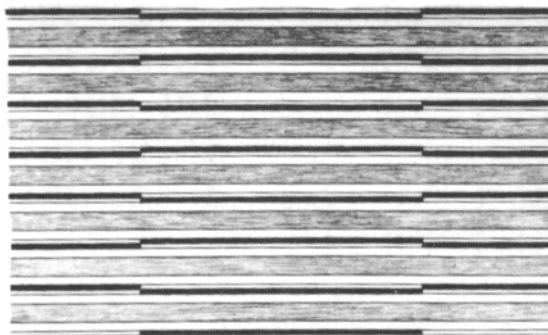


FIGURE 4. — Schematic illustrations of a hypothetical structure which could accommodate the chemical composition of the chlorites.

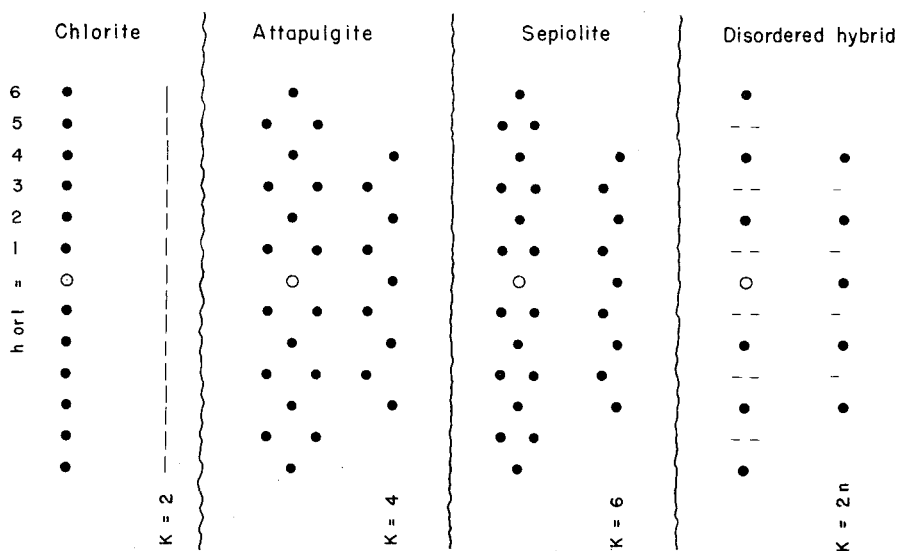


FIGURE 5. — Sketches in the pertinent sections in reciprocal space which illustrate the relations between the chlorite, attapulgite, sepiolite, and proposed faulty structure.

indicate the locus of such nodes with increasing  $b$ -axis length. Actually, it is my feeling that widely dispersed tetrahedral faults would not be disposed with perfect regularity, but would only tend to appear at some average displacement from each other. In this case the reciprocal space designation for the odd-odd nodes would be the actual dashed lines shown. In powder diffraction and in the only approximately parallel aggregates which come to hand in fine-grained specimens, these features would appear only as diffuse maxima alternating in nearly integral sequence with the sharper maxima equivalent to even-order chlorite nodes.

In the attapulgite and sepiolite crystallizations, intensities of odd-odd reflections are substantial, but they arise mainly from the difference in scattering power between "brucite" ribbons and water channels. The chlorite compositions distributed in the same geometry would afford only the moderate amplitudes due to the centered nature of the tetrahedral arrangement.

In taking the attitude that "faults" of the kinds which occur so frequently in the two fibrous minerals that they constitute structures may also well be the controllers of anomalous diffraction features encountered in some chlorite compositions and their derivatives, a serious indeterminacy is encountered. It is not known how widely such faults can be separated and still remain within coherently scattering domains. It would seem that with increasing dispersal of faults (equivalent with decreasing degree of strain for variable compositions), diffraction effects should grade from those of the

hybrid character to those of typical chlorites. In this latitude four degrees of fault abundance and its consequences may be enumerated:

1. Faults so regular as to constitute a structure and to impose a fibrous habit; exemplified by attapulgite and sepiolite.
2. Faults sufficiently frequent to afford diffraction effects anomalous with respect to the chlorite structure, and at least in some cases to introduce a secondary pinacoidal cleavage; exemplified by some iron-rich chlorites.
3. Faults frequent enough to foster lath-shaped habits, but not enough to modify drastically the diffraction effects which would be anticipated from typical layer structure; exemplified by nontronite, saponite, bowlingite, and some vermiculites.
4. Faults so infrequent as to permit equidimensional flake layer structures and typical layer structure diffraction effects; exemplified by the typical high-magnesian chlorite and most vermiculites and montmorillonite group minerals.

These degrees are thought of as proportional to the difference between the degree of misfit inherent in the composition and the differential expansion effect which obtained at the temperature of origin.

To illustrate the latitude of variability which appears to be reasonable in faulty regions within chloritic structures of unfavorable composition, two additional hypothetical plots are depicted in Figures 6a and b. The first is an instance in which the approximate composition of a chlorite is maintained through a faulted region, and the second illustrates the presumed easier local simulation of vermiculite or montmorillonite at these localities where the primary bonding of both tetrahedral neighbors is directed away from a given octahedral environment.

It is probably desirable to make a short appraisal of the relationships of the foregoing concept to a few of the most closely related postulates and analyses concerned with faulty crystallizations.

The montmorillonite structure proposed by Edelman and Favajee (1940, p. 417 *et seq.*) embodied these present features on a unit scale. Diffraction evidence has been considered adequate to refute the original proposal, but Edelman's later modification (1947, p. 4) proposed a less frequent incidence of the same type of fault. The third and fourth degrees of abundance cited above constitute a presumption that the faults are of like nature but still far less frequent than those of Edelman's second estimate.

Analyses of tubes have established that the polar configuration of Figure 2b exists in a macaroni-shaped, but crystalline state (Jagodzinski and Kunze, 1954, pp. 137-150; Honjo and Mihama, 1954, p. 511). The aspect of a local detail in such a tube, viewed in the direction of a radius, is comparable with a system of edge dislocations in the octahedral levels extending parallel with the tube axis. The condition has been ascribed by Bates (1951, pp. 83-91) to inherent misfits between tetrahedrally and octahedrally coordinated layers of the compositions at hand. In some cited instances *a* has been the curved axis with *b* the axis of curvature; in others the reverse is true.

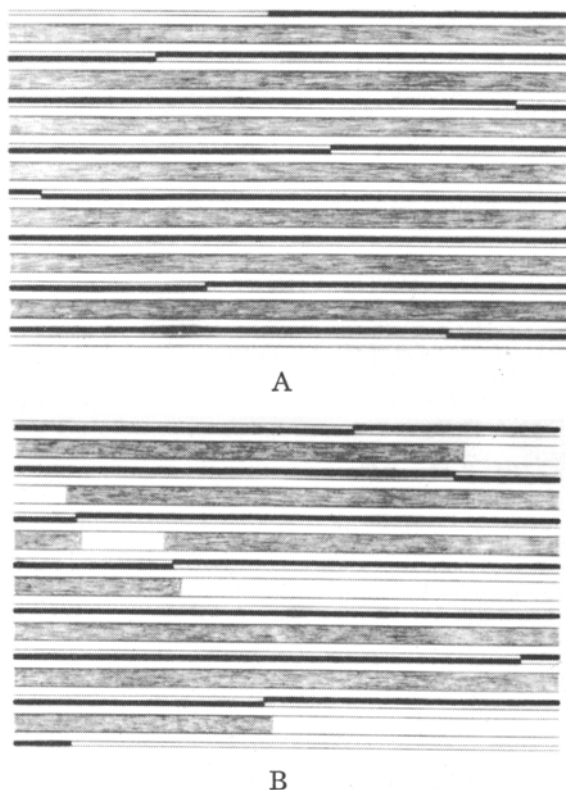


FIGURE 6. — Schematic illustrations of irregularly faulted regions in a chlorite structure (A) retaining the chlorite composition and (B) a more hydrous composition.

Zussman (1954, p. 498) has elaborated the concept of curvature of structural grade in crystals to note that the superstructure effects of antigorite described by Aruja (1945, pp. 65-74) can be accounted for by a corrugation of entire layers such that a super-period is superposed onto the a-axis.

The centered array of silica tetrahedra arranged in ribbons pointing alternately up and down is, in a sense, a corrugation which is imposing a super-period on the b-axis for the attapulgus and sepiolite structures, and for the hypothetical "chlorite" illustrated. Corrugation in this sense is necessary to the actual existence of the two reasonably established structures. Zussman's analysis and the concept being advanced here are both predicated on a degree of misfit in the structure. I think that I would be approximately paraphrasing Zussman's analysis to say that he describes a system in which, from a chosen origin, a sequence of oversize octahedral layers articulate with increasing difficulty with the tetrahedral, an absence of one row of oxygen intervenes (equivalent to an edge dislocation), and



articulation is again permitted to a sequence equally extensive with the original. The strain of regular alternation of crowded strips with underpopulated strips dissipates itself in the corrugation. If this is true, there is very little difference between Zussman's explanation of the observed a-axis compensation, and multiplicity of antigorite and the present hypotheses for relief along the b-axis. The Zussman analysis could also be extended to include tetrahedra pointed both directions if such a structure were sometime encountered.

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