PROGRESS IN SILICATE STRUCTURES*

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INTRODUCTION

Once a year the members of each scientific society are asked to listen to an address by its retiring president. One of the favorite subjects of such an address is a review of recent work which falls within the scope of the speaker's principal interests. My address, therefore, will be a review of the work in silicate structures of the last ten years. This decade has not been as startlingly full of discoveries in this field as the previous one, largely because many investigators equipped with better apparatus and mathematical tools, invaded organic chemistry as well as other fields unfamiliar to a mineralogist.

In the time at my disposal, I will not be able to cover more than an outline of the progress in silicate studies. I will not even touch on ceramics and cement products, interesting as they are.

CLASSIFICATION OF STRUCTURES

W. L. Bragg proposed a structural classification of the silicates in 1930 which, with a few changes, has stood the test of time. Berman (1937) followed Bragg closely with his "Constitution and Classification of the Natural Silicates." Strunz introduced a new concept in 1937 by proposing that any tetrahedra containing as cations P, As, S, B, Be, Zn, Fe, or Mg be considered structurally similar to tetrahedra of Si and Al. There is no question regarding the validity of his reasoning. This places, however, all Be silicates into other classes, the majority of them among framework structures. Boron silicates are partly affected. Willemite and hemimorphite become frameworks. The melilite group also joins the sheet structures from its former classification as finite groups, and there are other changes. Eitel (1941, page 15) in his encyclopedic work "Physikalische Chemie der Silikate," agrees with Strunz in general, though he indicates that on the basis of the infrared reflection spectrum the older classification may be better. The speaker favors the original one for the simple reason that it was designed for the silicates (including those in which Al replaces Si), regardless of the presence of other tetrahedral configurations. Our discussion will follow this older order.

* Address of the retiring President of the Crystallographic Society of America, delivered at the annual meeting of the Society at Yale University, April 1, 1948.

Isolated SiO_4 Tetrahedra

Apparently there have been no new structures discovered in this group unless those compounds are included which resemble, and are isomorphous with, phosphate structures. Ellestadite, as McConnell (1937) has shown, has the apatite structure, but contains in place of PO_4 tetrahedra, approximately equal numbers of SiO_4 and SO_4 tetrahedra. Klement (1941) has succeeded in synthesizing this mineral in the F as well as (OH) variety. Hägle and Machatschki (1939) describe the mineral britholite as a cerium silicate-apatite in which SiO_4 and PO_4 tetrahedra occur together in the ratio of 2:1.

Strunz (1942) thought that he had found another silicate with the apatite structure in the highly complex and rare earth silicate *steenstrupine*. Machatschki, in a reply in 1943, claimed that this mineral is not related to apatite but has a structure still unknown. There have been some interesting isotypic and isomorphous series described which, though only partly among the silicates, may be worthy of mention. O'Daniel and Tscheischwili (1943) found the following minerals and compounds to be isomorphous:

low-Ca orthosilicate	low-Ca_2SiO_4
glaucochroite	$(Mn, Ca)_2SiO_4$
tephroite	Mn_2SiO_4

They (1941 and 1942) were able to show with the aid of the crystal structure of sodium beryllium tetrafluoride, Na_2BeF_4, which is isotypic with low-Ca_2SiO_4, that the latter is orthorhombic and has the structure of olivine. Since Ca has a coordination of 6 in this low temperature form, they argue that the two high temperature forms which are important in slags and cements must have a lower coordination for Ca, probably of 4, which makes these silicates very reactive, a view also held earlier by Brandenberger.

O'Daniel and Tscheischwili (1942) also showed that the Ba and Sr orthosilicates, Ba_2SiO_4 and Sr_2SiO_4, are isotypic with potassium beryllium tetrafluoride, K_2BeF_4 and, therefore, with low-K_2SO_4 and a large group of other sulfates and chromates. The large cations are surrounded by 9 and 10 oxygen ions. Bredig (1945) finds that high Ca_2SiO_4 has the same structure as low K_2SO_4 and defends his view that Ca has a higher coordination in high-Ca_2SiO_4 than in low-Ca_2SiO_4, which is in opposition to the opinion of O'Daniel and Brandenberger. He also shows that merwinite, $Ca_3Mg(SiO_4)_2$, has practically the same structure as high-Ca_2SiO_4 and for this reason suggests that merwinite is not a definite compound but a high temperature isomorphous mixture of forsterite in high-Ca_2SiO_4. The forsterite component acts as a stabilizer in this instance. The dis-

cussion of these compounds of Ca_2SiO_4 and K_2SO_4 sounds confused, because Ca_2SiO_4 has four polymorphs which are named γ, β, α' and α, and K_2SO_4 has two, β and α. This is the order used from low to high temperature and, therefore, is the reverse of that customarily used for minerals.

This discussion of isolated tetrahedra structures would not be complete without mention of the isotypes of the garnet structures. Pabst (1937) described the structure of plazolite, $Ca_3Al_2(SiO_4)_2(OH)_4$, in which one of the SiO_4 groups is replaced by four hydroxyl groups. Still more unusual are the artificial hydrogarnets or garnetoids in which nearly all the tetrahedral SiO_4 positions are occupied by (OH) groups, as for example, $Ca_3Al_2(OH)_{12}$, according to Flint, McMurdie and Wells (1941).

Finite Groups

$CaSiO_3$ occurs in three modifications, pseudowollastonite, wollastonite, and parawollastonite. The structure of the latter, which is the monoclinic form, has been determined in detail by Barnick (1936). It is supposed to consist of Si_3O_9 rings which lie in planes normal to the b axis. The morphological and other properties of the mineral do not suggest such a structure, however.* As the triclinic wollastonite is very similar morphologically to parawollastonite, its structure may be assumed to resemble it closely. Bustamite (Peacock, 1935), vogtite, pectolite, and schizolite, which are isomorphous with wollastonite, should have comparable structures. Since some of these minerals contain an (OH) in place of an O, does this mean that the hydroxyls are tied to the Si ions? This has been thought unlikely in the past. It is of considerable interest that O'Daniel (1943) discovered that the sodium beryllium fluoride $NaBeF_3$ has the same structure as wollastonite and can be used as a model structure.

The detailed structure determination of rhodonite is still missing. Rhodonite possesses isomorphous relatives containing (OH) groups in babingtonite, and inesite, which have been investigated by Richmond (1937 and 1942).

According to Belov (1942), dioptase, $CuSiO_3 \cdot H_2O$, has a structure similar to beryl with hexagonal rings of SiO_4 tetrahedra. He assigns to catapleiite $Na_2Zr(Si_3O_9) \cdot 2H_2O$, a trigonal ring similar to that in benitoite. While these two structures had been predicted in these minerals, Belov seems to be responsible for complete determinations. Though the structure of cordierite, $Al_3Mg_2(Si_5Al)O_{18}$, had been known in a general way for over ten years, the details of it were not worked out until 1942 by Bystrom. He confirms its beryl-like structure.

* Several members of the Society, in particular Miss Gabrielle Hamburger, expressed the same opinion.

The structure of tourmaline in its main features has been determined by Gabrielle Hamburger and M. J. Buerger (1948).* It consists of hexagonal rings of SiO_4. The arrangement of the rings gives polarity to the structure. The rings are held together by the other cations including Al in octahedral coordination.

Chain Structures

Chain structures are largely limited to pyroxenes, amphiboles, and a few minerals which seem to provide the link between chain and layer structures. Though pyroxenes and amphiboles represent chemically highly complicated isomorphous mixtures, the structures themselves seem to display fewer complications than other silicates. Little work has been published on the pyroxenes in the last decade. It would be of interest to know, for example, what the maximum ratio of Al to Si ions in a single chain can be, and how this ratio compares with Al to Si tetrahedra ratios in other silicates. Such a statistical study might throw some light on the stability of pyroxene chains. Based on a study of pyroxenes by Niggli (1943) the speaker has computed a few of the highest ratios of Al to Si in the tetrahedra of the single chains. The highest value in a titanaugite from Aberdeenshire is 1:2.6. The next highest is about 1:3.
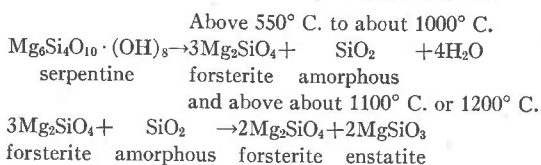
The lithium pyroxene spodumene changes to a new phase on heating to about 1000° to 1100° C. which has been called β-spodumene. This decomposition product has no chain structure but consists of a framework of tetrahedra of Si and Al similar to quartz and eucryptite, according to a still unpublished work by Gruner and Ellestad.

The amphiboles are almost the only representatives of double chain structures. Two recent papers by Hallimond (1943) and A. N. Winchell (1945) give us an excellent idea of the distribution of the ions in these complicated substitution structures. Here the maximum substitution of Al for Si tetrahedra reaches a ratio of 1 to 3 in the *Ca-bearing* amphiboles, which is probably not exceeded in any of the others.

One of the chain (or layer) structures still very imperfectly known is serpentine in its two dimorphs, antigorite and chrysotile. According to recent work by Warren (1941) and Aruja (1944) both are probably layer structures and not double chains as originally described. The layers would resemble those of kaolinite closely, but the presence of Mg in place of Al in chrysotile would cause the strained layers to grow no wider than probably 30 to 100 Å. The result would be ribbon-like fibres, according to Warren. It is very interesting that serpentine seems to change directly to forsterite without passing through the amorphous phase (except for the excess SiO_2) on heating to about 600° C. This observa-

* Described more fully in *Am. Mineral.*, **33**, 532–540 (1948).

tion, made by Gruner (1939) and Hargreaves and W. H. Taylor (1944), is particularly noteworthy, as the single chain structure of enstatite is more closely related to serpentine than is the structure of forsterite, and one might have expected enstatite for this reason. Even more surprising is the fact, first observed by Hargreaves and Taylor (1944), and confirmed and carried further by Gruner (unpublished experiments) that chrysotile fibres after decomposition above 600° C. give a fairly well defined rotation photograph, which means that forsterite now either exists as a single crystal in the fibre or as many crystals, all possessing identical orientation. These heated fibres show parallel extinction. Therefore, one of the three crystallographic axes of forsterite must be parallel to the fibres. Inspection of the rotation photograph indicates that the *c* axis of forsterite is parallel to the axis of the original fibre. In terms of structural bonds, this would mean that the SiO_4 tetrahedra separate on heating, but the MgO_6 octahedra retain their linkages. Held at a temperature of 1200° to 1300° C., one of the enstatite phases will appear as an additional compound in the fibres or powders as shown by the strongest lines of enstatite in the film. The enstatite is visible as minute grains but shows no orientation. Definite proof of the presence of enstatite may be had by dissolving out the forsterite with acid and *x*-raying the residue. The reactions in the solid state take place as follows:

$$\text{Above 550° C. to about 1000° C.}$$
$$\underset{\text{serpentine}}{Mg_6Si_4O_{10}\cdot(OH)_8}\rightarrow\underset{\text{forsterite}}{3Mg_2SiO_4}+\underset{\text{amorphous}}{SiO_2}+4H_2O$$
$$\text{and above about 1100° C. or 1200° C.}$$
$$\underset{\text{forsterite}}{3Mg_2SiO_4}+\underset{\text{amorphous}}{SiO_2}\rightarrow\underset{\text{forsterite}}{2Mg_2SiO_4}+\underset{\text{enstatite}}{2MgSiO_3}$$

Thilo (1939 and 1941) and associates made a number of experiments on the stability of talc, anthophyllite, tremolite, and enstatite. A bundle of fibres of anthophyllite after heating at 1000° C. gives a rotation photograph of enstatite fibres which shows clearly that the double chains have split lengthwise resulting in single chains. Thilo explains this division by the elimination of (OH) groups in the structure. This seems a plausible suggestion, for amphiboles with fluorine substituting for (OH) have been grown from melts, according to Scheumann and Lüdke, while (OH) amphiboles have never been synthesized.

Attapulgite, $Mg_5Si_8O_{20}(OH)_2\cdot8H_2O$, is a clay mineral with a double chain structure related to that of the amphiboles. It has large spaces between the chains, containing H_2O molecules, according to W. F. Bradley (1940). Since sepiolite and such indefinite Mg-silicates as mountain cork give very similar *x*-ray powder photographs, it may be assumed that they have practically the same structures as attapulgite. The monoclinic

structure of epidote, $Ca_2O \cdot (Al, Fe)O_2OH \cdot Al \cdot Al \cdot Si_3O_9$, has been investigated recently by Ito (1947). He arrives at an unusual chain or band structure of Si and Al tetrahedra, which is parallel to the *b*-axis of the mineral. This composite band, $(Si, Al)_4O_9$, is the basic structure. The distortions of the SiO_4 tetrahedra are so extreme that one wonders whether considerable adjustments of parameters will not be necessary in a future study. Ito regards zoisite a twinned epidote (or rather a twinned clinozoisite).

Sanbornite, $Ba_2Si_4O_{10}$, notwithstanding a similar formula, is not similar in structure to gillespite, $BaFeSi_4O_{10}$. The latter has a layer structure according to Pabst (1943). Hendricks (1942) has suggested that sanbornite is made up of sets of chains of Si_3O_8 similar to those in epididymite, which may also be interpreted as sheets of Si_4O_{10}, as pointed out under layer structures.

LAYER STRUCTURES

Many investigators have been busy on the members of this structure type. Though most of these structures have the same pattern of endless tetrahedral $(Si, Al)_4O_{10}$ layers, to which are attached octahedral metal oxygen layers, the possible combinations and variations of them appear to be inexhaustible. A. N. Winchell (1942) has classified the micas into hepta- and octophyllites, depending upon the total number of cations associated with their simplest chemical molecules. Considering the complexity of the chemical compositions, it is surprising that this classification holds good in the great majority of the structures as shown by Hendricks and Jefferson (1939), Stevens (1938) and others. In other words, any isomorphous mixing between heptaphyllites and octophyllites is not common. An interval exists between the octophyllites, which have most of their three octahedral positions occupied, and the heptaphyllites, which have only two or slightly more than two filled. The resulting holes in these pseudohexagonal layers give rise to different symmetry elements depending on the shifts, rotations and stackings of the hexagons. According to Hendricks and Jefferson (1939) hexagonal, monoclinic and triclinic unit cells result, many of superlattice dimensions. In addition to such complications, the layers also undergo rapid changes in composition in their planes as evidenced by the varying optical properties, especially the optic angles, as observed under the microscope in single continuous mica sheets.

The exceedingly fine-grained micas, which go under such names as sericite, illite, and hydromuscovite, are in a class by themselves. They are defect structures *principally* with regard to missing alkali cations. What takes the place of these ions? Analyses show definitely that as K

decreases H_2O increases. Does this mean that hydronium ions could perhaps substitute for K, a possibility which should be investigated in the infrared spectrum. Aruja (1944) has shown recently that the unusual fibrous mineral gümbelite has the muscovite structure. This makes it a hydromuscovite in which considerable Mg may replace a part of octahedral Al.

Glauconite, $(OH)_{6-10} \cdot K_{2-3}(Mg, Fe'', Ca)_{1-3} (Fe''', Al)_{3-6} (Si_{13-14}Al_{2-3}) O_{38-40}$, has a mica structure as shown by Gruner (1935) and by Hendricks (1941). Though the mineral has a composition which, while similar to the phengites, has too high a Si:Al ratio, too much ferric iron and not enough K, it does show a structure closely resembling biotite. To be sure, the ions do not fit perfectly as evidenced by the fact that the individual crystals never grow beyond microscopic size.

The preceding observation with regard to grain size could be considered a rule for the growth of silicate crystals. The greater the number of substitutions, other conditions being equal, the smaller the crystals unless they were formed at high temperature; for only heat will lend great mobility to the ions and give them an opportunity to find the most suitable neighbors and permit larger growth.

Pyrophyllite and talc, notwithstanding their relatively simple compositions, show anomalous structures which, according to Hendricks and Jefferson (1938) can be best explained with shifts of the neutral layers over one another by simple submultiples of the length of the b-axis. We used to think that talc rarely could accommodate more than a very few percent of ferrous iron in its structure. Recently Gruner (1944) has found a talc structure, however, which is made up of 75% of Fe and 25% of Mg with reference to the octahedral cations. This new mineral, minnesotaite, $(Fe'', Mg)_{11} (Si, Al, Fe''')_{16}O_{37} \cdot (OH)_{11}$, as it is called, though occurring in enormous amounts in ancient iron formations, has all the earmarks of a metastable defect structure with omissions in the octahedral positions and with considerable (OH) substitution for O.

A still less stable and very unusual structure is the iron silicate stilpnomelane, $(K, Na, Ca)_{0-1} (Fe, Mg, Al)_{7-8} Si_8O_{23-24} \cdot 2-4H_2O$. Neither mica nor chlorite, though often mistaken for either, this mineral can accommodate Fe, (OH), H_2O and K between its mica layers in a manner somewhat similar to Fe and (OH) in the orthosilicate staurolite. Its x-ray photographs indicate a very large superlattice according to Hutton and Fannkuchen (1938). The speaker, without wishing to appear facetious, would say that a hand specimen could be called one giant superlattice, so variable is the composition from point to point in one specimen. Chloritoid $Fe(OH)_2[(OH)_2 (Mg, Fe, Al)_3 (SiAl)_4O_{10}]$ seems to have a similar structure according to Machatschki and Mussgnug (1942). If it is

correct it is the most condensed layer structure known, for notwithstanding additional Fe'' and (OH) between its mica-like layers, the spacing of the layers is closer than that in pyrophyllite.

When Pauling (1930) first suggested the structure of kaolinite, it appeared that this polar lattice would remain confined to the kaolinite group. This is not the case, for Hendricks (1939) has found that cronstedtite, $(2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O)$, has this structure. Iron not only replaces Al in the octahedral layers, but also a part of the Si in the tetrahedral layers. Amesite, $(Mg, Fe)_4Al_2(Si_2Al_2O_{10}) \cdot (OH)_8$, which for many years had been considered an end member of the chlorite group, also possesses a modified kaolinite structure in which a large part of the Si in the tetrahedral layer is replaced by Al. According to Gruner (1944), a few units of chlorite are interstratified with the kaolinite units in amesite leading to superstructures over a hundred Å units thick. It has already been mentioned in another place that Warren and Aruja think that the serpentines possess a kaolinite structure.

The structure of kaolinite itself was thought to have the monoclinic symmetry m. This has been challenged very recently by Brindley (1946) who has discovered that some of the ions have slightly different parameters than determined previously, placing the unit cell in the triclinic asymmetric class. This seems to be the first instance that an important silicate mineral has been found without symmetry.

A problem still unsolved in connection with kaolinites is the high content in Si in anauxite, $Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$, a variety of kaolinite. The ratio $Al:Si$ instead of being 1 to 1 as in kaolinite proper, reaches $2:3$ in well crystallized anauxite. To explain this excess of SiO_2, Hendricks (1942) has made a novel suggestion that neutral layers of SiO_2 are interstratified with the kaolinite sheets. Each SiO_2 layer would consist of two tetrahedral SiO_4 layers facing one another and having, therefore, all corners shared. The three dimensions of these layers correspond very closely to those of kaolinite. The speaker has for years been fascinated by such a simple hypothetical structure for SiO_2 and still wonders why it should be thermodynamically less stable than talc or pyrophyllite, for example.

It is only natural that one should ask why there is not more interstratification on a molecular layer scale of any of these structures since they all have the same pattern of very similar dimensions. Most of these structures would also be stable under the same conditions. The answer may be found more likely in the relatively stationary or only slowly changing chemical environment in a system, than in any aversion on the part of the structures to change from layer to layer. In other words, if the cation supply and composition could be changed at the same rate at which the

growths of individual layers proceeded, we could conceivably get a single crystal containing any combination or all of the different layers without any more flagrant violations of the laws of symmetry than we have encountered in other structures.

So far we have not even mentioned the complicated montmorillonite and halloysite types of structures which have received almost as much attention during the last decade as all the other layer silicates combined. As more than a score of investigators of these minerals have not been able to reach agreement on these structures, it would take us too long to present the subject fairly on this occasion.

Two other minerals will be mentioned here, though their layers are quite different from the Si_4O_{10} structures discussed. Gillespite, $BaFeSi_4O_{10}$ has been described by Pabst (1943). Its layers are built of tetragonal meshes of tetrahedra which, similar to those in apophyllite, point alternately up and down if the sheet is horizontal. Unusual is the coordination of the Fe ion in the center of a *square* of O ions. Ito, who had described the structure of orthorhombic epididymite in 1934, has found recently (1947) that the structure of its monoclinic dimorph eudidymite, HNa-$BeSi_3O_8$, is very similar. The orthorhombic one may conceivably be considered an internal twin of the monoclinic modification. The layers in both structures have the composition $NaSi_3O_7$. Unusual is the sharing of faces of SiO_4 tetrahedra with faces of Na octahedra in both minerals. Sanbornite $Ba_2Si_4O_{10}$ has been mentioned as a probable layer structure by Hendricks.

FRAMEWORK STRUCTURES

The most important structures in this class are the feldspars. They have received additional attention in a more quantitative way by Chao, Smare, Hargreaves, and W. H. Taylor (1939 and 1940). According to them the lamellae of microperthite consist of monoclinic K feldspar and triclinic Na feldspar. The latter, however, is somewhat different in structure from albite. A homogeneous and stable triclinic structure can be obtained by heating the lamellae to 1075° C. The stabilization is apparently brought about by some slight modification in the structure. These investigators were able to show that there are marked differences in the sizes of the Si and Al tetrahedra. Chao and W. H. Taylor (1940) have also been able to demonstrate that the plagioclase feldspars do not form a complete isomorphous series. Miscibility is found at each end of the series but does not seem to include andesine and labradorite which seem to consist of interstratified lamellae of the other members of the series if at relatively low temperatures.

The structure of nepheline based on that of tridymite has now been

worked out by M. J. Buerger, G. E. Klein, and G. Hamburger (1947). About half of the Si positions in the tridymite-similar structure are replaced by Al. Nepheline practically always contains an excess of SiO_2 which can easily be explained now on the basis of its tridymite-similar framework in which not all the Al for Si substitutions have occurred.

M. J. Buerger and Washken have discovered recently that eucryptite, $LiAlSiO_4$, has a derivative quartz structure.* The speaker wishes to add here that β-spodumene, $LiAlSi_2O_6$, has the same kind of structure from which the lithium may be removed leaving a quartz-like framework of Al and Si tetrahedra in which hydrogen probably as hydroxyl preserves electrostatic balance. This hydrogen is driven off as water (a total of about 5.5%) between 400° and 650° C. Judging from x-ray powder patterns the structure persists though the compound has lost an O from one of its positions as indicated by the equation:

$$2HAlSi_2O_6 \rightarrow (AlSi_2)_2O_{11} + H_2O.$$

This loss reminds one of the sillimanite-mullite relationship. The structure finally collapses around 850° C. to quartz and amorphous Al_2O_3 which changes to cristobalite and mullite near 1200° C. It is possible that heating for weeks instead of days would change the transformation temperatures somewhat.

Leucite, chemically the K equivalent of β-spodumene, has a structure very similar to pollucite, $CsAlSi_2O_6 \cdot nH_2O$, and, therefore, also similar to analcite, $NaAlSi_2O_6 \cdot H_2O$, as determined by Náray-Szabó (1942) in a detailed investigation. This seems to explain why leucite can be readily changed to analcite in Na-salts solutions. But why does leucite contain no water? There seems to be room for it just as there is in pollucite which has a slightly larger cell. It is interesting in this connection that Fleischer and Ksanda (1941) could dehydrate pollucite but were unable to introduce water again at room temperature. They were partially successful when they used high pressures and temperatures.

The zeolites have come in for their share of attention particularly through publications by W. H. Taylor and M. H. Hey. As most of the more recent work deals with the behavior of zeolitic water, they will not be discussed.

CONCLUSION

Highly fascinating and important as all these contributions have been, they have advanced us only a short distance toward one of our ultimate goals. This is the fundamental relationship of structures to phase equilibria between solids as well as between solids and solutions. Why do some

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* Verbal communication.

bonds give way to others if we change the physical and chemical environment? To answer satisfactorily most questions like these may require several generations so that our present knowledge may look very insignificant to the student of the solid state of the next century.

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