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## CLASSIFICATION OF THE NATURAL SILICATES\*

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### INTRODUCTION

Many efforts have been made in the past to interpret the chemical constitution of the silicates, but views concerning them long remained largely subjective. The more recent development of the  $x$ -ray analysis has cast new and important light upon this problem. We have thought that a summary of the results bearing upon the chemical constitution and composition of the natural silicates, obtained by the various workers in this field, would be welcomed by the student.

We will deal first with the classification of the silicates as a basis for the presentation of the data assembled. In the second part we will give tables showing their composition.

### PART I. CLASSIFICATION OF THE SILICATES

#### I. BASIS OF CLASSIFICATION

*Underlying principles.* We will first consider certain principles which must underlie any sound classification of the silicates. There are three chief principles.

The first is that of ionic radii. The first determination of the radii of ions was made by W. L. Bragg and published by him in 1920.<sup>1</sup> His measurements, though inaccurate, were valuable since they suggested new and important principles. The first accurate measurements were made by J. Wasastjerna,<sup>2</sup> who determined the radii of O and F ions by the refractive indices of their compounds. V. M. Goldschmidt<sup>3</sup> continued the investigation and prepared tables giving the radii of ions of numerous other elements. Later discussions by L. Pauling,<sup>4</sup> V. M. Goldschmidt,<sup>5</sup>

\* Read before a joint session of the Mineralogical Society of America and the Geological Society of America, Dec. 30, 1936.

<sup>1</sup> Bragg, W. L., *Phil. Mag.*, vol. 40, p. 169, 1920. See also *Phil. Mag.*, vol. 2, p. 258, 1926.

<sup>2</sup> Wasastjerna, J., *Soc. Scient. Fenn.*, Comm. I, p. 38, 1923. (*Finska Vetenskaps-Societeten Commentationes Physico-Math.*)

<sup>3</sup> Goldschmidt, V. M., *Geochemische Verteilungsgesetze der Elemente: Skrifter det Norske Videnskaps-akad., Oslo, I, Matem-Naturvid Klasse*, Pt. VII, 1926, No. 2.

<sup>4</sup> Pauling, L., *Jour. Am. Chem. Soc.*, vol. 49, p. 765, 1927.

<sup>5</sup> Goldschmidt, V. M., *Krystallchemie: Fort. Min. Kryst. Petrog.*, vol. 15, p. 73, 1931.

W. H. Zachariasen<sup>6</sup> and others<sup>7</sup> have added greatly both to the accuracy of the measurements and to our knowledge of the subject.

The fundamental principle that atoms replace each other in isomorphous structures, not as long supposed, according to their chemical relations, but according to the radii of their ions, was first suggested by F. Zambonini<sup>8</sup> in 1922 and E. T. Wherry<sup>9</sup> in 1923. It was later developed more fully by V. M. Goldschmidt,<sup>10</sup> W. L. Bragg<sup>11</sup> and others. It may be termed Zambonini's Law.

The second principle, announced by L. Pauling,<sup>12</sup> affirms that the sum of all electrostatic charges is zero, not only in larger units, but in all adjacent parts of the structure, otherwise instability would result.

The third principle concerns more particularly the constitution of the silicates and is highly important. It was established by W. L. Bragg<sup>13</sup> and his co-workers and confirmed by others.

It was shown that SiO<sub>4</sub> groups occur in all the natural silicates, however varied their composition. These groups are in the form of tetrahedra, the four large O atoms occupying the solid angles of each tetrahedron and the small Si atom being found in its center.<sup>14</sup> (The apices of the solid angles of the tetrahedron are placed at the centers of the O atoms.)

It has been shown further that the tetrahedra combine by their solid angles, one oxygen atom being shared equally by two adjoining tetrahedra. *It is very important to recognize that the tetrahedra do not combine by their edges or faces, but by their solid angles only.* All the varied and complex compositions of the silicic acids are shown to be formed by the combinations of the SiO<sub>4</sub> tetrahedra in this manner.

*Development of types.* Since all the various silicates are thus made, it is possible to develop all conceivable types of silicates by considering the various ways in which the tetrahedra may combine by their solid angles. There are five such types.

<sup>6</sup> Zachariasen, W. H., *Zeits. Krist.*, vol. **80**, p. 137, 1931.

<sup>7</sup> Neuburger, M. C., *Zeits. Krist.*, vol. **93**, pp. 1-36, 1936, table.

<sup>8</sup> Zambonini, F., *Rend. Accad. Lincei*, vol. **31**, p. 295, 1922. Synopsis in *Am. Mineral.*, vol. **8**, p. 81, 1923.

<sup>9</sup> Wherry, E. T., *Am. Mineral.*, vol. **8**, p. 1, 1923.

<sup>10</sup> Goldschmidt, V. M., *op. cit.*, No. 2, 1926.

<sup>11</sup> Bragg, W. L., West, J., *Proc. Roy. Soc., A*, vol. **114**, p. 450, 1927.

<sup>12</sup> Pauling, L., *Am. Chem. Jour.*, vol. **51**, p. 1010, 1929.

<sup>13</sup> Bragg, W. L., West, J., *Proc. Roy. Soc., A*, vol. **114**, p. 450, 1927.

Bragg, W. L., *Proc. Roy. Inst.*, vol. **25**, p. 302, 1927. *Zeits. Krist.*, vol. **74**, p. 237, 1930.

<sup>14</sup> This was first shown by Sir Wm. Bragg and R. E. Gibbs in  $\beta$  Quartz (*Proc. Roy. Soc., A*, vol. **109**, p. 405, 1925), and later extended to silicates in general by W. L. Bragg and his associates.

1. Tetrahedra uncombined.
2. Tetrahedra combined by one solid angle.
3. Tetrahedra combined by two solid angles.
4. Tetrahedra combined by three solid angles.
5. Tetrahedra combined by four solid angles.

Since a tetrahedron possesses only four solid angles it is manifest that this process can go no further and hence, that there are but five fundamental types.

## II. FUNDAMENTAL TYPES

Let us consider the characteristics of these types. (See Fig. 1.)

FIG. 1. TABLE SHOWING RELATIONS OF THE FUNDAMENTAL TYPES  
Fundamental Silicate Types

Type	Name	Chemical Formula	Solid angles combined in SiO <sub>4</sub> groups	Geometric form	Valence and O per Si
I	Orthosilicates	R' <sub>4</sub> SiO <sub>4</sub>	none	Separate tetrahedra	''''SiO <sub>4</sub>
II	Orthodisilicates	R' <sub>6</sub> Si <sub>2</sub> O <sub>7</sub>	1	Pairs	''''SiO <sub>3½</sub>
III	Metasilicates	R' <sub>2</sub> SiO <sub>3</sub>	2	Chains—rings	''SiO <sub>3</sub>
IV	Metadisilicates	R' <sub>2</sub> Si <sub>2</sub> O <sub>6</sub>	3	Sheets	'SiO <sub>2½</sub>
V	Dioxide type	SiO <sub>2</sub>	4	Net-works	SiO <sub>2</sub>

### Complex Silicate Types

Made by association of two or more fundamental types in the same crystal.

1. The simplest type is manifestly one in which the SiO<sub>4</sub> tetrahedra remain separate and are not combined with others. The body in question is evidently an orthosilicate. Its formula is R'<sub>4</sub>SiO<sub>4</sub>, since the valency of the SiO<sub>4</sub> group is four. This type may be best defined as having tetrahedra with their solid angles uncombined. The structure is illustrated by the projection of olivine in Fig. 2.

2. The first step in combination is where two SiO<sub>4</sub> tetrahedra unite to form a pair. This they do by joining solid angles, one oxygen atom being shared equally by two neighboring tetrahedra. The formula of such compounds is R'<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>, instead of R'<sub>8</sub>Si<sub>2</sub>O<sub>8</sub> as in the case of the original two tetrahedra. The valency of the pair is six, their being six oxygen atoms free to unite with neighboring kations. It is clearly an orthodisilicate. The structure of this type is illustrated in Fig. 3.

3. The union of the SiO<sub>4</sub> groups by two solid angles produces an endless series of tetrahedra. This may take the form either of endless chains, or it may be curved to form rings. In either case the formula is R'<sub>2</sub>SiO<sub>3</sub>. It is a metasilicate with a valency of two. The structure of forms having chains is illustrated in Fig. 4, those with rings in Fig. 5.

4. The SiO<sub>4</sub> tetrahedra may unite by three solid angles to produce sheets of indefinite extent. One solid angle of each group remains free in this case. The free angles may turn in either direction, or all may

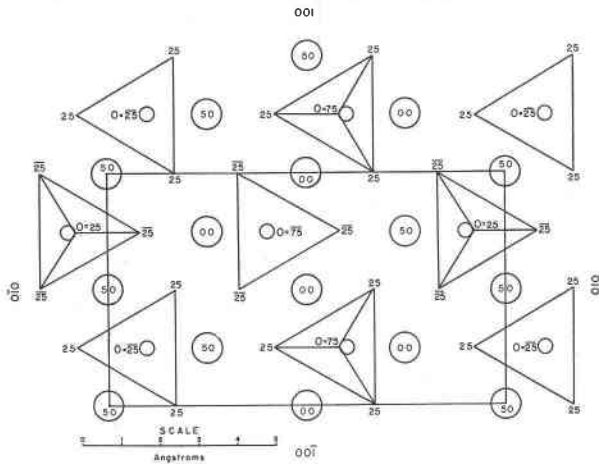


FIG. 2. Type I, Orthosilicates. Projection of olivine<sup>15</sup> upon the (100) plane, based upon the work of W. L. Bragg and G. B. Brown, (*Zeits. Krist.*, vol. 63, p. 538, 1926. Compare Fig. 2, p. 545). The rectangle outlines the unit cell. The tetrahedra are shown by triangular outlines, their three-fold axes being parallel to the *a*-axis, their apices directed alternately towards and away from the observer. The small circles within the tetrahedra represent Si atoms, the larger circles (Mg, Fe) atoms. The parameters are on the *a* axis, the origin being at the center. The separate character of the  $\text{SiO}_4$  tetrahedra, characteristic of this type, is well shown.

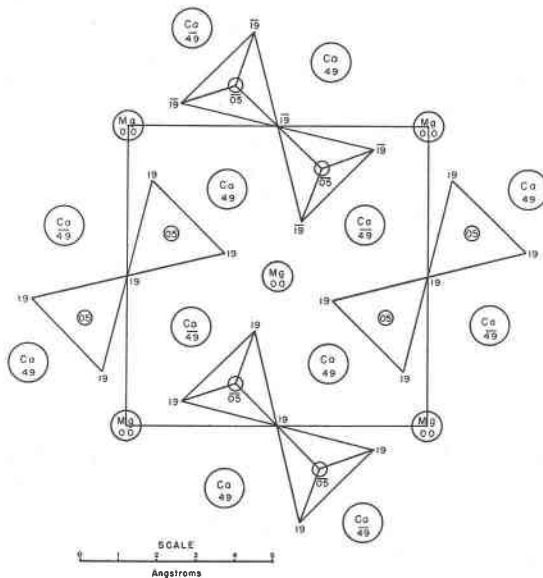


FIG. 3. Type II, Orthosilicates. Projection of melilite (akermanite) upon the (001) plane, showing the union of tetrahedra by one solid angle to form pairs. Based upon the work of B. E. Warren (*Zeits. Krist.*, vol. 74, p. 131, 1930. Compare Fig. 2, p. 135). The square outlines the unit cell. The small circles represent Si atoms. The parameters are on the *c* axis. The formula is seen to be  $\text{Si}_2\text{O}_7$ , and the valency 6 (since there are six free O atoms).

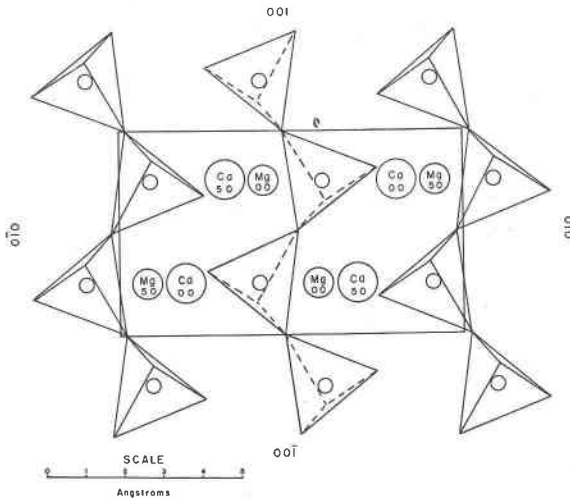


FIG. 4. Type III, Metasilicates. Projection of diopside, showing the union of SiO<sub>4</sub> tetrahedra by two solid angles to produce chains of indefinite extent. Based upon the work of B. E. Warren and W. L. Bragg.<sup>16</sup> The plane of projection is (100), the line of vision being parallel to the *a* axis. The front half, only, of the unit cell is projected. The formula is seen to be SiO<sub>3</sub>, the valency 2, since there are two free O atoms in each tetrahedron.

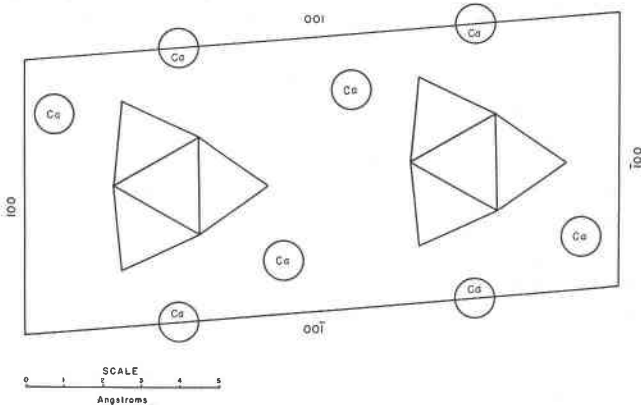


FIG. 5. Projection of monoclinic wollastonite on (010), after M. Barnick (Inaugural Dissertation, *Berlin*, Fig. p. 30, 1936). Chains formed of tetrahedra joined by two solid angles are curved to form rings.

<sup>15</sup> The characteristics of the different types are illustrated in Figs. 2 to 8. The SiO<sub>4</sub> groups are represented as tetrahedra. The oxygen atoms are not shown in the drawings, save in Fig. 8. The centers of the oxygen atoms are located at the apices of the solid tetrahedral angles, their diameters being equal, approximately, to the length of the tetrahedral edges. The small circles in the centers of the tetrahedra represent Si or Al atoms. Double circles represent two atoms. All atoms are drawn to one-half true scale, to avoid crowding.

<sup>16</sup> The projection was calculated by the author from coordinates of the atoms, given by B. E. Warren and W. L. Bragg, *Zeits. Krist.*, vol. 69, p. 189, 1928. Compare Fig. 9, p. 188. See also W. L. Bragg, *Zeits. Krist.*, vol. 74, p. 252, Fig. 8, 1930.

turn in one direction, as in the micas. The one uncombined oxygen atom gives the  $\text{SiO}_4$  group a valency of one and an oxygen: silicon ratio of two and one half. In order to write the formula of its compounds without fractional values, it becomes  $\text{R}'_2\text{Si}_2\text{O}_5$ . It is a metadisilicate. The struc-

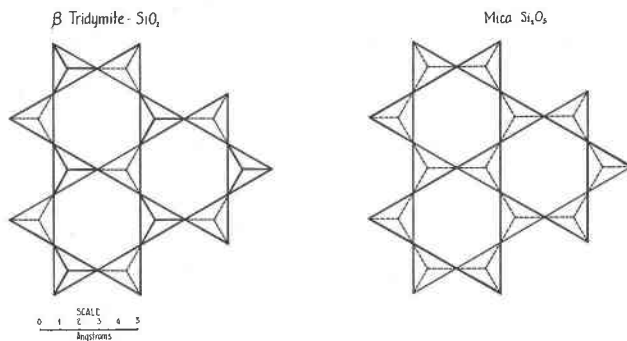


FIG. 6. Type IV, Metadisilicates. The fourth type is illustrated by Figs. 6 and 7, both of which are after L. Pauling, (*Proc. Nat. Acad. Sci.*, vol. 16, p. 124, Figs. 2 and 3, 1930). In Fig. 6 the  $\text{SiO}_4$  group of  $\beta$  tridymite (or  $\beta$  cristobalite) and  $(\text{Si}, \text{Al})\text{O}_4$  groups of mica are projected upon the basal pinacoid. The tetrahedra are united by three solid angles to form sheets of indefinite extent parallel to (001). The remaining free angles of the tetrahedra are directed alternately upward and downward in  $\beta$  tridymite and in the same direction in the micas.

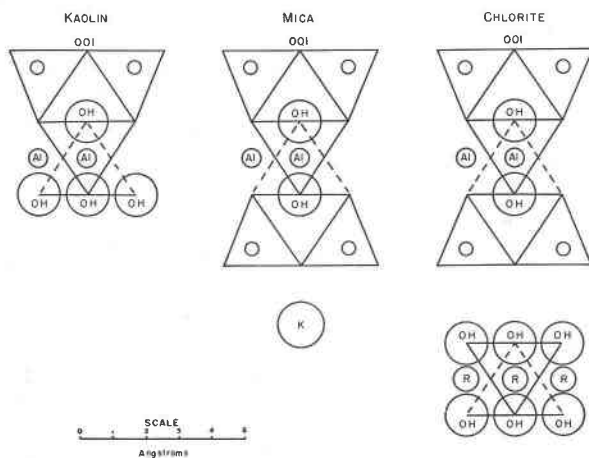


FIG. 7. Diagrammatic projection of members of the kaolin, mica and chlorite families, on a plane perpendicular to the basal pinacoid. Sheets of  $\text{Si}_2\text{O}_5$ , or  $(\text{Si}, \text{Al})_2\text{O}_5$ , are seen to alternate with sheets of  $\text{Al}_2(\text{OH})_4$  in kaolin,  $\text{Al}_2(\text{OH})_2$  and  $\text{K}$  (or  $\text{Na}$ ) in micas, and  $\text{Al}_2(\text{OH})_2$  and  $\text{R}_3(\text{OH})_6$  in chlorites. All show the sheet-like structure of these minerals.<sup>17</sup>

<sup>17</sup> Pauling, L., *Proc. Nat. Acad. Sci.*, vol. 16, p. 578, Fig. 1 and p. 580, Fig. 2 (chlorites), 1930. The diagrams of Pauling show but one Al atom in the unit cell. A second Al atom has been added in these diagrams since two are present.

ture of this type is illustrated in Figs. 6 and 7. Figure 6 shows the  $\text{Si}_2\text{O}_5$  sheets viewed perpendicular to the sheet, Fig. 7 parallel to the sheet.

5. The last step is where the tetrahedra unite with others by four solid angles. There are in this case no uncombined oxygen atoms and the formula is  $\text{SiO}_2$ . It is one of the familiar polymorphic forms of silicon dioxide. Such a group is a neutral body and can combine no further. If, however, we replace part of the Si atoms, found in some multiple of

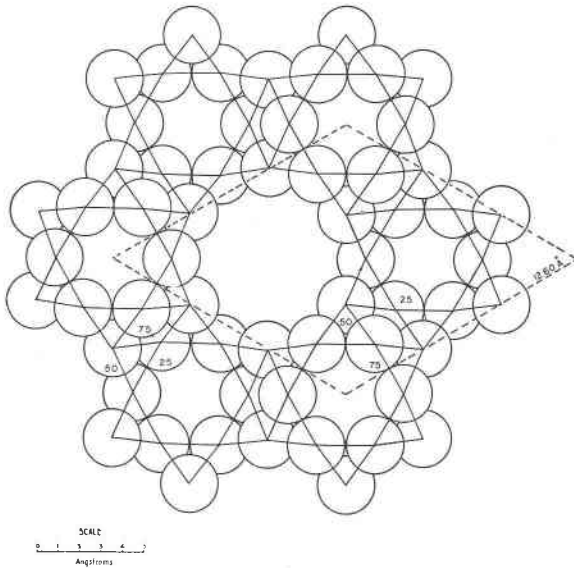


FIG. 8. Type V, Dioxide type. A single sheet of the structure of cancrinite is shown, projected on the (001) plane after L. Pauling (*Proc. Nat. Acad. Sci.*, vol. **16**, 1930. Compare Fig. 5, p. 458). The oxygen atoms are drawn in this diagram in order to show the remarkable, large, tunnel-like cavities characteristic of certain members of this type (e.g. the ultramarines) in which various kations or other anions may be placed, or even water retained, as in the zeolites. Similar successive sheets are superimposed to form three-dimensional net-works of indefinite extent.

the group, by Al atoms, the charge of the whole becomes negative. The formula of such a body is  $\text{R}(\text{Al},\text{Si})\text{O}_2$ . Its valency equals the number of the replacing Al atoms. Such groups form three-dimensional net-works of indefinite extent. Figure 8 illustrates structures of this type.

The operations are clearly at an end. We have five fundamental types of silicates. *The structures thus developed are the same as those previously recognized, but their assembling into groups and the basis upon which they are developed are not the same.*

## III. COMPLEX TYPES

The classifications of the past have been based largely upon the geometric forms of the structure, but the subject is not so simple as has been assumed. The various fundamental types we have described may unite with each other to form complex assemblages. Just as, in chemical reac-

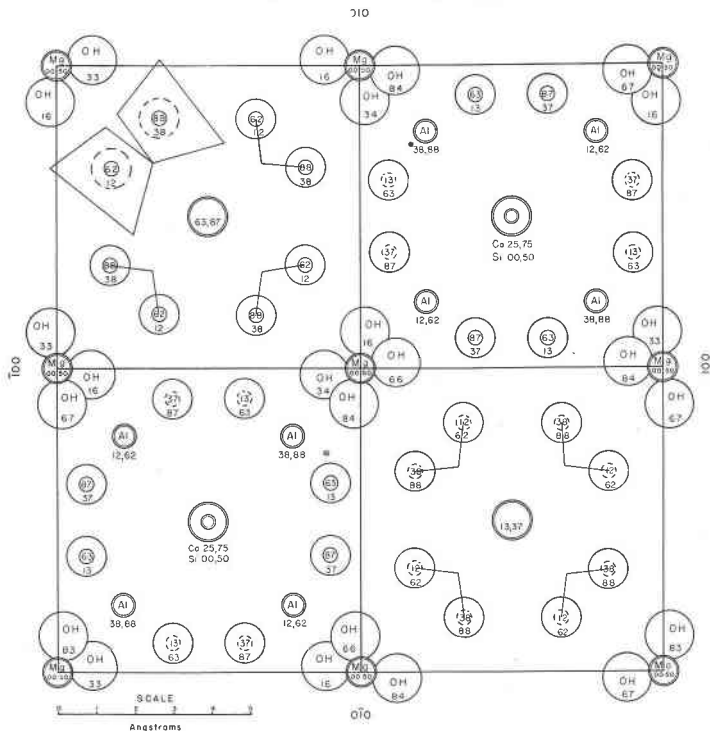


FIG. 9. Projection of vesuvianite on the (001) plane, after B. E. Warren and D. I. Modell, illustrating the characteristics of the complex silicates. Adjacent quadrants are seen to differ in both structure and composition. The  $\text{SiO}_4$  tetrahedra are separate in the upper right- and lower left-hand quadrants of the projections: (the O atoms are omitted to avoid confusion of the eye). The  $\text{SiO}_4$  tetrahedra are united by one solid angle to form pairs in the upper left- and lower right-hand quadrants. Only one pair is drawn, but the union of the others by a single O atom is represented. The small circles represent Si atoms, the larger, unlettered circles Ca atoms. The parameters are given on the  $c$  axis.

tions, elements unite to form compounds, so the fundamental types may unite to produce complex types. The fundamental types may be compared to the elements, the complex ones to the compounds resulting from their union. As the chemical elements retain their identity in their compounds so each fundamental type retains its identity in the complex ones. Their characteristics are illustrated by Figs. 9, 10 and 11.



Vesuvianite, illustrated in Fig. 9, was studied by B. E. Warren and D. I. Modell.<sup>18</sup> They showed that the unit cells may be divided into quadrants of two quite different types. The diagonally opposite quadrants are alike and symmetrical with respect to a center of symmetry, but they differ fundamentally from the other quadrants of the unit cell. The authors showed further that the portion of the cell represented in the upper right-hand quadrant of Fig. 9 has essentially the structure and composition of an orthosilicate garnet, with separate tetrahedra. The portion represented in the upper left-hand quadrant of the figure, on the contrary, has its tetrahedra united to form pairs with the formula  $\text{Si}_2\text{O}_7$ . Parts of the same unit cell thus represent two different types, an orthosilicate,  $\text{SiO}_4$ , and an orthodisilicate,  $\text{Si}_2\text{O}_7$ , respectively. The formula of vesuvianite is  $\text{Ca}_{10}\text{Al}_4 \left[ \begin{array}{l} (\text{SiO}_4)_5 \\ (\text{Si}_2\text{O}_7)_2 \end{array} \right] 2\text{Mg}(\text{OH})_2$ .

It is manifest, therefore, that vesuvianite cannot justly be put in either the orthosilicates, with separate, or orthodisilicates, with paired tetrahedra, since it is both. Nor can it be placed in any one division of any classification now in general use.<sup>19</sup> It is interesting to note that the types remain distinct, though found in the same unit cell.

Bertrandite,  $\text{Be}_2(\text{BeOH})_2 \left[ \begin{array}{l} \text{SiO}_4 \\ \text{SiO}_3 \end{array} \right]$  studied by T. Ito and J. West<sup>20</sup> illustrates the same principles. It contains separate  $\text{SiO}_4$  tetrahedra associated with chains formed of  $\text{SiO}_4$  tetrahedra combined by two solid angles, hence combined the formula  $\text{SiO}_4$  and  $\text{SiO}_3$ . Like vesuvianite it cannot properly be placed in any division of classifications now in use.

Zunyite, was studied by L. Pauling, who showed that it contains groups of five tetrahedra, united by their solid angles as illustrated in Fig. 10.<sup>21</sup> The outer tetrahedra are joined to the central one by one solid angle and the central tetrahedron is united to the outer ones by four solid angles. The formula of the group, written without fractional values is, therefore,  $\left[ \begin{array}{l} (\text{Si}_2\text{O}_7)_2 \\ \text{SiO}_2 \end{array} \right]$ . It is a three-dimensional group, but it cannot be referred to the recognized three-dimensional division, since the latter has groups of tetrahedra of indefinite ("infinite") extent. It cannot be placed with the finite, self-contained, pairs and rings, since the latter

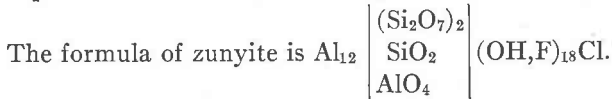
<sup>18</sup> Warren, B. E., Modell, D. I., *Zeits. Krist.*, vol. 78, p. 422, 1931. Compare Fig. 4, p. 428.

<sup>19</sup> Machatschki, F., in 1932 proposed to unite all silicates having separate or finite groups of  $\text{SiO}_4$  tetrahedra in his "Orthosilicates" division. Others have not followed him in this.

<sup>20</sup> Ito, T., West, J., *Zeits. Krist.*, vol. 83, p. 384, 1932.

<sup>21</sup> Pauling, L., *Zeits. Krist.*, vol. 84, p. 447, Fig. 2, 1933.

are one- or two-dimensional. It is manifest that it cannot be placed properly in current classifications. It is a complex silicate and consists of our types II and V in combination. Associated with the groups of five tetrahedra are also separate  $\text{AlO}_4$  tetrahedra. If the latter be viewed as representatives of  $\text{SiO}_4$  then zunyite has also an orthosilicate element.



Tremolite is another illustration of the complex silicates. It was studied by B. E. Warren.<sup>22</sup> One of the double chains, so characteristic

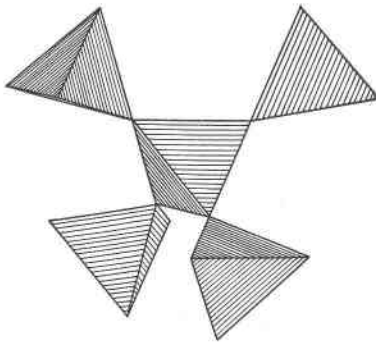


FIG. 10. A group of five  $\text{SiO}_4$  tetrahedra of zunyite, after L. Pauling (*Zeits. Krist.*, vol. 84, p. 447, Fig. 2, 1933). The tetrahedra are united by their solid angles to form a limited, three-dimensional group combining types II and V.

of the amphiboles, is shown in Fig. 11. It consists of pairs of tetrahedra alternating in sequence. The tetrahedra of the first pair are united to others by two solid angles and have altogether the formula  $\text{Si}_2\text{O}_6$ . They are succeeded by two tetrahedra united to others by three solid angles, hence with the formula  $\text{Si}_2\text{O}_5$ . It thus consists of two chains whose alternate links are united to produce incipient sheets and embraces in the same structure one-dimensional and two-dimensional elements of our types III and IV. Its general formula is  $\text{R}'_6 \left| \begin{array}{c} \text{Si}_2\text{O}_6 \\ \text{Si}_2\text{O}_5 \end{array} \right|$  which, in the case of tremolite, becomes  $\text{Ca}_2\text{Mg}_5 \left| \begin{array}{c} \text{Si}_4\text{O}_{12} \\ \text{Si}_4\text{O}_{10} \end{array} \right| (\text{OH}, \text{F})_2$ .

The last complex silicate to which we will refer is epididymite, described by T. Ito.<sup>23</sup> It is an interesting illustration of structures of this type. It was shown by Ito to consist of discontinuous sheets made

<sup>22</sup> Warren, B. E., *Zeits. Krist.*, vol. 72, p. 42, 1929.

<sup>23</sup> Ito, T., *Zeits. Krist.*, vol. 88, p. 142, 1934.

of three-dimensional bands ("triple chains" of Ito). Its formula is  $\text{NaBeOH} \begin{vmatrix} \text{Si}_2\text{O}_5 \\ \text{SiO}_2 \end{vmatrix}$ , comprising our types IV and V. It cannot be properly placed in any classification now in use.

It is manifest that the classifications of the past, based upon the geometric form, failed to provide a place for the complex structures we have

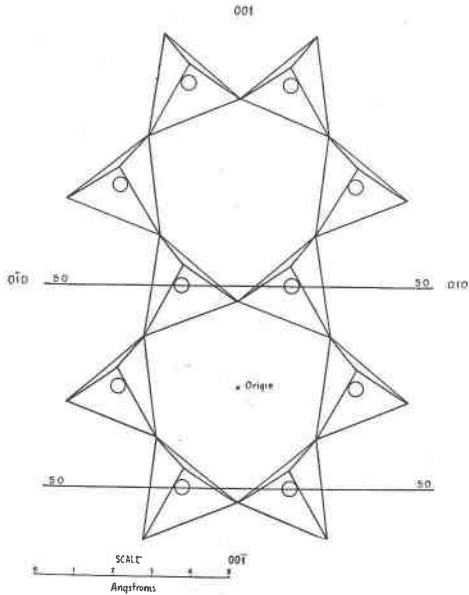


FIG. 11. Projection of a double chain of tremolite on the (100) plane, based on the work of B. E. Warren.<sup>24</sup>

described and for other similar ones. Moreover, no simple method is known for predicting the possible geometric structures. A classification based upon the manner in which the tetrahedra unite, on the contrary, remains valid, correctly expresses the chemical formulae and classifies the resulting geometric forms. It seems possible that there may be a much greater recognition of structures of complex types in the future.

#### IV. COMPARISON WITH CLASSIFICATION OF OTHERS

It seems desirable to present the relations of the classification here proposed to those that have been given by others, based upon *x*-ray study.

<sup>24</sup> The projection was calculated by the author from coordinates given by B. E. Warren, *Zeits. Krist.*, vol. 72, p. 52, 1929. Compare Fig. 1, p. 46 and Fig. 2, p. 48 (by error made diopside in original).

## 1. Classifications by Others

(a) *F. Machatschki*, 1928. The first classification upon this basis, with which I am acquainted, was proposed by Machatschki in 1928.<sup>25</sup> It seems to rest, in part only, upon *x*-ray investigations, but is singularly penetrating and suggestive. He recognized three types: an Orthotype, a Metatype and a Feldspar type, respectively.

His Orthotype comprised silicates with separate  $\text{SiO}_4$  tetrahedra, agreeing, in this respect with the usage of most others. Later, however, he used the term for a very different assemblage. His Feldspar type comprised crystals built on the pattern of silicon dioxide in which the Si atoms are replaced, in part, by Al, the valency of the group equaling the number of replacing Al atoms. The characteristics of the various divisions are shown in the following table.

Orthotype.  $\text{SiO}_4$  groups separate  $(\text{SiO}_4)^{-4}$

Metatype.  $\text{SiO}_4$  groups united by two O atoms, forming chains.  $(\text{SiO}_3)^{-2}$

Feldspar type.  $\text{SiO}_4$  groups united by four O atoms forming net-works.  $(\text{SiO}_2)$  type.

(b) *W. L. Bragg*, 1930. In 1930 Bragg added two new types<sup>26</sup> to the divisions proposed by Machatschki, with whose work he was acquainted. The first of these was his "Self-contained" group, consisting of bodies with tetrahedra united to form pairs,  $\text{Si}_2\text{O}_7$ , or rings, the latter in various multiples of  $\text{SiO}_3$ . The essential idea is that of a body containing a finite number of combining  $\text{SiO}_4$  tetrahedra, in contrast with the infinite number found in his succeeding divisions. He adds, also, a second group of crystals having the structure of the micas, with indefinitely extended two-dimensional sheets and a general formula  $\text{R}_2'\text{Si}_2\text{O}_5$ . His classification is shown in the following table.

(a) Separate  $\text{SiO}_4$  groups, Orthosilicates,  $(\text{SiO}_4)^{-4}$ .

(b) Self-contained groups, ( $\text{SiO}_4$  groups limited).

1. Pairs,  $(\text{Si}_2\text{O}_7)^{-6}$ . 2. Rings,  $(\text{Si}_3\text{O}_9)^{-6}$ ,  $(\text{Si}_4\text{O}_{12})^{-8}$ ,  $(\text{Si}_6\text{O}_{18})^{-12}$ .

(c) Silicon-oxygen chains.

1. Single chains,  $(\text{SiO}_3)^{-2}$ , 2. Double chains,  $(\text{Si}_4\text{O}_{11})^{-6}$ .

(d) Silicon-oxygen sheets,  $(\text{Si}_2\text{O}_6)^{-2}$ .

(e) Three-dimensional net-works,  $(\text{Si,Al})\text{O}_2$ .

Bragg's classification has justly had very great weight, not only because of the value of its suggestions, but also because of the brilliance of his investigations.

<sup>25</sup> Machatschki, F., *Centrbl. Min.*, A, p. 98, 1928.

<sup>26</sup> Bragg, W. L., *Zeits. Krist.*, vol. 74, pp. 300-301, 1930.

(c) In the same year, 1930, *St. v. Náráy-Szabó* presented a new classification.<sup>27</sup> He accepted all of Bragg's divisions for what he terms his "Silicates proper," but adds to them new divisions under the name "Complex silicates." The latter are characterized by the presence of accessory anions in addition to the silicon oxides. In this manner he proposes eight new groups as follows:

1. Titano-silicates.
2. Boro-silicates.
3. Carbonato-silicates.
4. Vanado-silicates.
5. Sulphato-silicates.
6. Sulpho-silicates.
7. Three-dimensional networks.
8. Silicates with several anions, (e.g. Thaumassite, with  $\text{SiO}_3$ ,  $\text{CO}_3$ ,  $\text{SO}_4$ ).

(d) *F. Machatschki*, 1932. In 1932 Machatschki offered a new and enlarged classification which has had much weight.<sup>28</sup> His divisions are:

A. Orthotype, embracing silicates with  $\text{SiO}_4$  tetrahedra separate, or united to form pairs or rings; their formulae  $(\text{SiO}_4)^{-4}$ ,  $(\text{Si}_2\text{O}_7)^{-6}$ ,  $(\text{SiO}_3)^{-2}$ .

B. Metatype,  $\text{SiO}_4$  tetrahedra united to form chains of indefinite extent, their formula  $\infty (\text{SiO}_3)^{-2}$ .

C. Mica type,  $\text{SiO}_4$  tetrahedra forming sheets of indefinite extent, their formula  $\infty (\text{Si}_2\text{O}_5)^{-2}$ .

D. Feldspar type,  $\text{SiO}_4$  tetrahedra united to form extended net-works, their formula  $\infty (\text{Si,Al})\text{O}_2$ ,  $(\text{SiO}_2)$  type).

Machatschki's classification is based, like those of his predecessors, primarily upon the number of combining  $\text{SiO}_4$  tetrahedra, whether finite or infinite, and secondarily, upon the geometric forms of the resulting structures.

(e) In 1936 *C. Hermann, O. Lohrmann, H. Philipp*, adopted a classification<sup>29</sup> that is essentially that of W. L. Bragg, save that they divide his first group, with separate  $\text{SiO}_4$  tetrahedra, into two parts. Their divisions are as follows:

- I. Separate  $\text{SiO}_4$  tetrahedra, with other anions.
- II. Separate  $\text{SiO}_4$  tetrahedra, without other anions.
- III. Finite groups of  $\text{SiO}_4$  tetrahedra forming open groups or rings.
- IV. One-dimensional infinite Si-O chains.
- V. Two-dimensional extended Si-O nets.
- VI. Three-dimensional extended (Si, Al)-O lattices.

<sup>27</sup> Náráy-Szabó, *St. v.*, *Zeits. Phys. Chem.*, Ab. B, Bd. 9, pp. 356-377, 1930.

<sup>28</sup> Machatschki, F., *Geol. Förenigens I, Stockholm Förhandlingar*, Bd. 54, pp. 447-470, 1932.

<sup>29</sup> Hermann, C., Lohrmann, O., Philipp, H., *Zeits. Krist., Ergänzungsband, Strukturbericht*, II, p. 20, 1936.

## 2. Classification Proposed

The classification proposed by the author has many features in common with those of others. It differs from them, however, in the following respects:

(a) It is based upon the manner in which the  $\text{SiO}_4$  tetrahedra combine and not upon the geometric forms of the structures resulting. We believe that the former is the cause of the latter. We hence regard it as more fundamental.

(b) It is based upon one simple, progressive method. There is no known simple method for predicting all the possible geometric forms of the structures. It is believed to be simpler.

(c) It is true chemically. All members of one fundamental type have the same general chemical formula; all bodies of the same general formula are placed in the same fundamental type. These statements are not true of the other suggested groupings.

(d) The complex types of silicates are distinguished, and their relations to those of simpler types are shown. The complex silicates which have very different structures have been placed in earlier classifications, without discrimination, in simpler types. The subject is more complex than has hitherto been recognized.

### SUMMARY

The fundamental fact in the classification of the natural silicates is the combination of the  $\text{SiO}_4$  tetrahedra by their solid angles. Five fundamental types are developed upon this basis and described. It is shown that the fundamental types may combine further to form complex types whose characteristics are considered. The relations of this classification to earlier classifications is discussed.

In the second part, to be published later, the composition and classification of the species of natural silicates will be given as far as they have been determined by *x*-ray investigation, with references to the literature in which their structures are described.

The following table gives the composition of the families of the natural silicates thus classified, as far as their structures have been determined by *x*-ray investigation.

FAMILIES OF SILICATES											
SiO <sub>2</sub> tetrahedra united by	I ORTHOSILICATES R <sub>2</sub> SiO <sub>4</sub> 0 angles. Separate		II ORTHOSILICATES R <sub>2</sub> SiO <sub>7</sub> 1 angle. Pairs		III METASILICATES R <sub>2</sub> SiO <sub>3</sub> 2 angles. Rings and Chains		IV METASILICATES R <sub>2</sub> Si <sub>2</sub> O <sub>3</sub> 3 angles. Sheets		V DIOXIDE TYPE SiO <sub>2</sub> 4 angles. Net-works		
	ANHYDROUS	ANHYDROUS	Rings	Chains	Rings	Chains	Rings	Chains	Rings	Chains	
BIVALENT	Olivine fam. (Mg,Fe) <sub>2</sub> SiO <sub>4</sub>	R <sup>+</sup> Melilites Co <sub>2</sub> (Mg,Zn)Si <sub>2</sub> O <sub>7</sub>		R <sup>+</sup> Amphiboles R <sup>+</sup> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> R <sup>+</sup> (Ca,Mg,Fe)		Wollastonite fam. R <sup>+</sup> SiO <sub>3</sub> R <sup>+</sup> Pyroxenes R <sup>+</sup> SiO <sub>3</sub> R <sup>+</sup> (Ca,Mg,Fe)					
	Phenacite fam. (Be,Zn) <sub>2</sub> SiO <sub>4</sub>										
TRIVALENT	Chondrodite fam. nMg <sub>2</sub> SiO <sub>4</sub> + Mg(OH,F) <sub>2</sub>	Calomine Zn <sub>2</sub> (OH) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O		C. Chrysothite (Mg,OH) <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> )(H <sub>2</sub> O) III, III'		Apophyllite 4CoSi <sub>2</sub> O <sub>7</sub> ·KF <sub>2</sub> ·H <sub>2</sub> O Talc Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>					
	C. Bertrandite Be <sub>2</sub> (BeOH) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> I-III										
	Garnet fam. R <sup>+</sup> R <sup>+</sup> (SiO <sub>4</sub> ) <sub>3</sub>	R <sup>+</sup> Melilites (Ca,Na) <sub>2</sub> (Mg,Al)(Si,Al) <sub>2</sub> O <sub>7</sub>		R <sup>+</sup> Pyroxenes (X,Y)(Si,Al) <sub>2</sub> O <sub>6</sub> X: (Ca,Na,K) Y: (Mg,Fe,Al,Mn,Ti,Li)							
	Cymite Group Al <sub>2</sub> O <sub>3</sub> SiO <sub>4</sub>	Thortveitite Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		Beryl Be <sub>3</sub> Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>6</sub>							
ANHYDROUS	Eulytite fam. Bi <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub>			Condrite Mg <sub>2</sub> Al <sub>3</sub> Si <sub>2</sub> Al <sub>2</sub> O <sub>8</sub>							
HYDROUS-F	Staurolite 2 Cyanite + Fe(OH) <sub>2</sub>	Meliponite fam. (Ca,Na)Be <sub>2</sub> (Si,Al)(OH) <sub>2</sub> F <sub>2</sub>									
	Topaz Al <sub>2</sub> (OH,F) <sub>2</sub> SiO <sub>4</sub>	C. Zuyevite Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH,F) <sub>2</sub> Cl II, II'		R <sup>+</sup> Amphiboles X <sub>2</sub> Y <sub>2</sub> (Si,Al) <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> X: (Ca,Na,K) Y: (Mg,Fe,Al,Mn,Ti,Li)							
ANHYDROUS	Eucrase AlBeOHSiO <sub>4</sub>										
	C. Vesuvianite Ca <sub>2</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> (ZnMgOH) <sub>2</sub> I-III	R <sup>+</sup> Melilites (Na,Ca) <sub>2</sub> Si <sub>2</sub> (Si,Al) <sub>2</sub> O <sub>7</sub>		Benitoite BaTi(SiO <sub>3</sub> ) <sub>3</sub>							
QUADRIVALENT	Zircon fam. (Zr,Th)SiO <sub>4</sub>										
	Titanite fam. Ca(TiO)SiO <sub>4</sub>										

Names of complex silicates are in italics preceded by letter C  
\* Signifies structure not adequately known