THE AMERICAN MINERALOGIST, VOL. 45, SEPTEMBER-OCTOBER, 1960

CLASSIFICATION OF SILICATES AND OTHER MINERALS WITH TETRAHEDRAL STRUCTURES

TIBOR ZOLTAI, *Crystallographic Laboratories, Massachusetts Institute of Technology, Cambridge, Massachusetts.**

ABSTRACT

The conventional geometric classification of the silicates is no longer sufficient to classify the ever-increasing number of determined ionic tetrahedral structures. More detail is desirable in the classification, and consequently, new classification criteria are necessary to provide a larger number of subdivisions. The study of the relative energies of isolated rings of tetrahedra suggests that the size of the tetrahedral loops may be used as one additional criterion. It is suggested that another criterion may be based on the different nature of the corner sharing of tetrahedra. A numerical expression, called the sharing coefficient, is derived to cover this criterion. In the proposed classification these two criteria are added to the customary silicate classification, and, consequently, the classification proposed is basically in accordance with the conventional scheme.

A large number of silicates can be classified differently depending on whether we consider all tetrahedra of the structure, or only the silicon and aluminum tetrahedra. This problem is not treated consistently in the literature. In some cases aluminum tetrahedra are disregarded or other tetrahedra, like boron, are accepted. It is suggested that all tetrahedrally coordinated cations should be considered as part of the tetrahedral frame of a silicate. This suggestion is supported by the similarity of the observed ionic radii and electronegativity of other four-coordinated cations with that of silicon and aluminum, and by the analytical data indicating the random distribution of silicon and other cations in different tetrahedra of certain silicates.

INTRODUCTION

The classification of things of scientific interest is not merely a filing system, but is also a basis for evaluation and comparison. As such, it constitutes a step in the progress of science and may lead to the better understanding of nature, and to the establishment of new directions of research. The classification conceived by Machatschki (1928) and developed by Bragg (1930) was an excellent system for classifying a large number of silicates. It also explained many of the important physical properties of silicates. Consequently, the classification was of considerable importance in the understanding of the silicates and other crystals with similar tetrahedral structures. Since 1928 the number of tetrahedral structures determined has grown so tremendously that the Machatschki-Bragg classification is no longer adequate, especially for structures with a three-dimensional network of tetrahedra. There is a definite need for an improved classification, first, to provide more subdivisions in the system of classification and, second, to point out minor, but important, similarities between different tetrahedral structures.

---

* Present address: Department of Geology and Mineralogy, University of Minnesota, Minneapolis 14, Minnesota.

After the structure of coesite was determined (Zoltai and Buerger 1959) and compared with structures of other forms of silica, the significance of tetrahedral loops in the tetrahedral structures became apparent. In the conventional classification the geometric forms of the tetrahedral structures are related to the cleavage, hardness and the optical properties of the crystals; similarly the size of the tetrahedral loops are related to the energies of the tetrahedral structures (Zoltai and Buerger 1960). The importance of the size of the tetrahedral loops in a structure and its prospective application as a natural classification criterion stimulated an investigation of tetrahedral structures and the construction of an improved classification.

Other geometric features of tetrahedral structures were observed during the course of this study. Most of them are applied in the proposed classification system. The classification criteria are discussed in detail in their order of application.

THE GEOMETRICAL FORMS

The conventional classification is based on geometrical forms created by the linkage of tetrahedra. These forms are referred to as "types" in the literature. They are: isolated tetrahedra, groups, chains, rings, sheets and three-dimensional networks of tetrahedra. These features are important, and are widely accepted. Consequently they are adopted in this classification. Minor revisions, however, are made in order to group these types systematically, and to cover all the possible ionic tetrahedral structures. Some of the types have distinct directions in which the tetrahedral structures extend to infinity. In others the tetrahedral structures are terminated in all directions. Consequently, if the tetrahedral structures are extended to infinity in zero-, one-, two- and three-dimensions, four major types of tetrahedral structures are possible. These four types are:

(1) Isolated groups of tetrahedra.
(2) One-dimensionally non-terminated structures of tetrahedra.
(3) Two-dimensionally non-terminated structures of tetrahedra.
(4) Three-dimensionally non-terminated structures of tetrahedra.

It is theoretically possible for a crystal to be composed of two or more different types of tetrahedral structures. To cover such possibilities a fifth type is established:

(5) Mixed-types of tetrahedral structures.

All these types can be divided into subtypes. In the first three types the subtypes can be defined according to the complexity of the tetrahedral structure of the type. That is, in the first type the number of tetrahedra can serve as a basis for the subdivisions and in the others the number of single chains, single rings and single sheets welded together. In the fourth type the subtypes can be defined according to an important characteristic of these structures, that is, according to the sharing of tetrahedral corners only, or the sharing of one or more tetrahedral edges or faces also.

The types and subtypes are listed in the first two columns of Table 1.

CORNER SHARING IN TETRAHEDRAL STRUCTURES

A brief study of the tetrahedral structures revealed that different number of tetrahedral corners can be shared and still make up the same type, and even the same subtype structure. For example, two single

TABLE 1. SHARING COEFFICIENTS AND CATION-ANION RATIOS OF THE TYPES AND SUBTYPES OF TETRAHEDRAL STRUCTURES

Types	Subtypes	Sharing coefficients	Cation-anion ratios
1. Isolated groups of tetrahedra	a. single tetrahedron	1.00	1:4
	b. pair of tetrahedra	1.25	1:3½
	c. large groups	1:25–1.50–(1.75)*	1:3½–1:3–(1.2½)
	d. mixed groups	1.25–1.50–(1.75)	1:3½–1:3–(1:2½)
2. One-dimensionally non-terminated structures of tetrahedra	a. single chains	1.50	1:3
	b. single rings	1.50	1:3
	c. double chains	1.50–1.75	1:3–1:2½
	d. double rings	1 50–1.75	1:3–1:2½
	e. multiple chains	(1.50)–1.75–2.00	(1:3)–1:2½–1:2
	f. multiple rings	(1.50)–1.75–2.00	(1:3)–1:2½–1:2
	g. mixed chains and rings	(1.50)–1.75–2.00	(1:3)–1:2½–1:2
3. Two-dimensionally non-terminated structures of tetrahedra	a. single sheets	1.50–1.75	1:3–1:2½
	b. double sheets	(1.50)–1.75–2.00	(1:3)–1:2½–1:2
	c. multiple sheets	(1.50)–1.75–2.00	(1:3)–1:2½–1:2
	d. mixed sheets	(1.50)–1.75–2.00	(1:3)–1:2½–1:2
4. Three-dimensionally non-terminated structures of tetrahedra	a. networks with corners shared	1.75–4.00	1:2½–1:1
	b. networks with one or more edges shared	4.00–8.00	1:1–1:½
	c. networks with one or more faces shared	8.00–	1:½–
5. Mixed types			

* Sharing coefficients in parentheses indicate theoretically possible but practically improbable ranges.

chains can be welded into a double chain if each tetrahedron of the first chain is connected to a tetrahedron of the second chain. Two single chains can also be welded into a double chain if only every second tetrahedron of the first chain is connected to every second tetrahedron of the second chain. In the former case six tetrahedral corners are shared per two tetrahedra and in the latter only five. The general geometric form, however, still remains a double chain. A similar situation exists in the sheet structures. A sheet can be constructed if each tetrahedron shares three corners with other tetrahedra. A sheet also can be constructed if certain tetrahedra share only two corners. Once again, the number of tetrahedral corners shared is the only difference between the two sheets. In the three-dimensional network usually all four corners are shared. In some structures a few corners are left unshared, and consequently the average number of tetrahedral corners shared becomes less than four.

In these examples it was tacitly assumed that only two tetrahedra can share a tetrahedral corner. This is not a necessary restriction. Several three-dimensional networks of tetrahedra are actually known in which three or even more tetrahedra share a tetrahedral corner. In order to distinguish between such structures, the number of tetrahedral corners shared is no longer sufficient. It has to be supplemented with the number of tetrahedra participating in the sharing of a corner.

It is possible to derive a single numerical value which can express both the number of tetrahedral corners shared and the number of tetrahedra participating in the sharing, if we make two assumptions:

A. The difference between the smallest and the largest number of tetrahedra participating in the sharing of a tetrahedral corner in a structure can not be more than one.

B. No edges of tetrahedra can be shared unless the corners are shared between more than four tetrahedra, and no faces can be shared unless the corners are shared between more than eight tetrahedra.

Assumption *A* means, for example, that as long as there are free corners present in a structure, no corners can be shared between more than two tetrahedra; or if some corners are shared between two tetrahedra only, no corners can be shared between more than three tetrahedra. Assumption *B* means that edges and faces can be shared only in very dense tetrahedral structures. In certain structures the density of the tetrahedra may require geometrically the sharing of edges, and in even denser structures the sharing of faces.

Under these conditions the average number of tetrahedra participating in the sharing of a tetrahedral corner in a structure also defines the number of corners shared. The average number of tetrahedra participating in the sharing of a corner in a structure is called the sharing coefficient of the structure. It can be either an integer or a fraction. An integral number defines a state in which each corner of each tetrahedron is shared between n tetrahedra, where n is the integer in question A fractional number, on the other hand, defines a state in which some corners are shared between n tetrahedra and others between $n+1$ tetrahedra, where n is the integral part of the sharing coefficient. The fractional part, further, defines the ratio of the number of corners shared between n and $n+1$ tetrahedra. A sharing coefficient of $n+\frac{1}{4}$ means, for example, that all the corners are shared between at least n tetrahedra and in addition every fourth corner is shared between $n+1$ tetrahedra; or a sharing coefficient of $n+(1/20)$ means that all the corners are shared between at least n tetrahedra and in addition every twentieth corner is shared between $n+1$ tetrahedra.

There is a simple relationship between the sharing coefficient and the cation-anion ratio in the tetrahedral radical of the chemical formula. The relationship is obvious when a tetrahedral corner is shared between two or more tetrahedra. Then the same anion simultaneously belongs to two or more cations. The cation-anion ratio in a single tetrahedron is 1:4 and in a pair of tetrahedra it is $1:3\frac{1}{2}$, and the corresponding sharing coefficients are 1:00 and 1.25 respectively. Consequently the sharing coefficient not only describes a geometric feature, but also defines part of the chemical formula. A list of possible sharing coefficient ranges for the types and subtypes of the tetrahedral structures, and the corresponding cation-anion ratios, are tabulated in the third and fourth columns of Table 1.

Assumptions *A* and *B* were found, empirically, to hold for dominantly ionic crystals. These assumptions are generalizations of Pauling's third rule which states, briefly, that the sharing of edges and particularly of faces of ionic polyhedra decreases the stability of the structure. This is because such sharing necessitates the close approach of two cations and thus increases the potential energy of the system. Assumptions *A* and *B* can be supported by similar arguments. When more tetrahedra share a tetrahedral corner, more tetrahedra come in contact, and the high valence cations approach each other, thereby increasing the potential energy of the system. Since a system tends toward the lowest energy state possible, the corners should be shared by the least possible number of tetrahedra. Thus no corner is shared by three tetrahedra unless there is no lower energy state available. Similarly no tetrahedral corners will be shared between three tetrahedra in a double chain when a multiple chain or other geometric form represents lower energy with the corners shared between two tetrahedra only. The same argument restricts the sharing of edges and of faces to structures where it is necessitated by geometry, in extremely dense three-dimensional networks.

REPEAT UNITS AND LOOPS OF TETRAHEDRA

With the exception of the isolated groups of tetrahedra, the single chains, and the three-dimensional networks with one or more faces shared, all the tetrahedral structures contain loops of tetrahedra. These loops are outstanding features. They are also important in the consideration of the energies of structures. Consequently the tetrahedral loops are simple and non-artificial criteria. Modern investigators of the tetrahedral and other polyhedral structures noticed the significance of these loops, and, in one form or other, they applied the loop concept to the subclassification of certain types of tetrahedral and polyhedral structures. Wells subdivided the polyhedral networks according to the size of the loops formed by polyhedra. Tetrahedral networks are also included in his classification (Wells 1954, Part 2). However, he considered only the highly regular tetrahedral networks with a sharing coefficient of 1.75 and 2.00.

Liebau (1956) classified the tetrahedral silicate structures on the basis of the number of tetrahedra in the periodic unit of the tetrahedral structure. Liebau's classification subclassifies the simpler tetrahedral structures very conveniently, but fails to give a sufficient number of subdivisions for the three-dimensional networks.

The combination and extension of Wells' and Liebau's principles could conveniently be applied to the subclassification of all types of tetrahedral structures. The structures containing no loops of tetrahedra can be subdivided according to the number of tetrahedra in the periodic unit of the tetrahedral structure, and structures containing loops of tetrahedra can be subclassified according to the number of tetrahedra in the loops. The former term is called the repeat unit of tetrahedra, and the latter the loop of tetrahedra.

The repeat unit of tetrahedra in the isolated groups of tetrahedra would be simply the number of tetrahedra in the groups. If there are different kinds of groups in the structure, several units will be listed and one number will represent each kind of group.

In an endless single chain the repeat unit of tetrahedra is the number of tetrahedra in the motif of the chain which is repeated by translation to form the chain. If, for example, all the tetrahedra of the chain are similarly oriented and are translation equivalents, the repeat unit is one tetrahedron. But if every second tetrahedron is oriented differently from the first one, then only every third tetrahedra are translation equivalents, and the repeat unit of the chain is two tetrahedra (Liebau 1956, p. 75).

In most of the other types of tetrahedral structures there are loops of tetrahedra, and every tetrahedron of the structure is part of one or more loops. These structures can be subclassified either (1) by the size of the

TABLE 2 CLASSIFICATION OF TETRAHEDRAL STRUCTURES

Types	Subtypes	Sharing coefficients	Repeat-units and loops of tetrahedra	Structure families	Members
1. Isoiated groups of tetrahedra	a. Single tetrahedron	1.00	1		Olivine, garnet, sphene, apatite, gypsum etc.
	b. Pair of tetrahedra	1.25	2		Ilvaite, tilleyite, ZrPO$_4$ lawsonite
	c. Large groups	1.40	5		Zunyite
	d. Mixed groups	1.111	1–2		Idocrase
		1.167	1–2	Epidote	Clinozoisite, allanite
2. One-dimensionally non-terminated structures of tetrahedra	a. Single chains	1.50	2	Pyroxenes	Enstatite, diopside, augite etc.
		1.50	3	Wollastonite	
		1.50	5	Rhodonite	
	b. Single rings	1.50	3	Benitoite	Catapleite, wadeite
		1.50	4	Axinite	
		1.50	6	Tourmaline	Dioptase, caledonite
	c. Double chains	1.583	8	Xonotlite	
		1.625	6	Amphiboles	Tremolite, hornblende etc.
		1.75	4	Sillimanite	
	d. Double rings				
	e. Multiple chains				
	f. Multiple rings				
	g. Mixed chains and rings				
3. Two-dimensionally non-terminated structures of tetrahedra	a. Single sheets	1.75	4–8	Apophyllite	Datolite
		1.75	4–8	Gillepsite	
		1.75	6	Mica	Clay, chlorite etc.
		1.75	6	Sepiolite	Beryllonite, V$_2$O$_5$
		1.833	5	Melilite	Hardystonite, gehlenite, åkermanite
	b. Double sheets	2.00	4–6	Hex. Celsian	α Celsian
	c. Multiple sheets				
	d. Mixed sheets				
4. Three-dimensionally non-terminated structures of tetrahedra	a. Networks with corners shared	1.75	10	P$_2$O$_5$	
		1.821	8–10	12CaO·7Al$_2$O$_3$	
		2.00	3–6	GeS$_2$	
		2.00	4–5–8	Scapolites	Marialite etc.
		2.00	4–6	Sodalite	Ultramarine, helvite, danalite, hauynite
		2.00	4–6–8	Paracelsian	Danburite, hurlbutite
		2.00	4–6–8	Analcite	Leucite, pollucite
		2.00	4–6–8–9	Coesite	
		2.00	4–6–8–10	Feldspars	Sanidine, orthoclase, plagioclase etc.
		2.00	4–6–8–12	Chabazite	
		2.00	4–6–8–12	Gmelinite	
		2.00	4–6–9	Beryl	Cordierite
		2.00	4–6–9	Milarite	Osumilite
		2.00	4–6–12	Faujasite	
		2.00	4–6–12	Cancrinite	
		2.00	4–8	Natrolite	Edingtonite, thomsonite
		2.00	5–6	Petalite	
		2.00	5–6–8	Heulandite	Philippsite (?)
		2.00	5–7–8	Keatite	

TABLE 2 (*continued*)

Types	Subtypes	Sharing coefficients	Repeat-units and loops of tetrahedra	Structure families	Members
		2.00	6	Cristobalite	Carnegieite, cuprite, Na_2CaSiO_4, $K_2Al_2O_4$ $Na_2Al_{24}O$,BPO_4, $BAsO_4$ etc.
		2.00	6	Tridymite	Nepheline, $BaAl_2O_4$, $BaFe_2O_4$, $KAlSiO_4$, $K_2MgSi_3O_8$ etc.
		2.00	6–8	Quartz	Berlinite, hi-eucryptite, $AlPO_4$, $AlAsO_4$ etc.
		2.75	3–4–6	Bertrandite	
		2.75	3–4–6–8	Hemimorphite	
		2.75	3–4	B_2O_3	
		3.00	3–4	Ag_2HgI_4	
		3.00	3–4–5	Phenacite	Willemite
		4.00	3	Sphalerite	BeO, MgTe etc.
		4.00	3	Wurtzite	BeS, BeTe etc.
	b. Networks with one or more edges shared	4.00	3	Cubanite	
		4.00	4	Cooperite	
		6.00	3	Zn_3P_2	Bi_2O_3
		8.00	Octahedron	Fluorite	ZrO_2, ThO_2 etc., also antifluorite structures: Na_2O, K_2O, Li_2O etc.
	c. Networks with one or more faces shared				
5. Mixed types					

smallest loop of the structure, or (2) by the list of the different sizes of loops occurring in the structure, or (3) by the list of all the symmetrically non-equivalent loops, in order of the increasing size of the loops. The first alternative has only five or six subdivisions, which is not sufficient to distinguish between a large number of possible structures, especially in the three-dimensional networks. The second alternative increases the number of subdivisions considerably. The third alternative, however, increases it to such an extent that almost every known structure has a different list of loop sizes.

Although the third alternative offers a greater number of subdivisions than the second, the second has been chosen for this classification for the following reasons: because the determination of the symmetrically non-equivalent loops is difficult and, in complicated structures, might become confusing; secondly because the number of subdivisions offered by the much simpler second alternative seems to be sufficient since only very similar structures have the same loop sizes.

The loop sizes can be determined either by simple observation or by a more systematic approach offered by the symmetry of the structure: all the possible loops of the structure must include the tetrahedra of the tetrahedral motif of the structure. The number of tetrahedra in the motif is usually less than five. Unfortunately in complicated structures there might be a very long list of loop sizes, especially for the larger loops. In order to avoid an unnecessarily long list, the loop sizes can be limited arbitrarily. At the present time it seems to be satisfactory to limit the number of loop sizes of a structure to four, and the size of the largest loop to twelve.

As the sharing coefficient increases above 4.00, tetrahedral edges are shared, and, in addition to the loops, incomplete polyhedral openings are present. When the sharing coefficient approaches 8.00 certain openings become complete polyhedra, but when the sharing coefficient reaches 8.00, all the edges are shared and all the openings are polyhedral. For example, the openings in the fluorite structure are octahedral. In structures with a sharing coefficient higher than 8.00, the polyhedral openings start to disappear, making room for solid bodies of tetrahedra. With a sharing coefficient at and above 8.00 there are no more loops of tetrahedra. Instead of units and loops these structures can be subdivided according to the shape of their polyhedral openings.

STRUCTURE FAMILIES

After the tetrahedral structures are classified according to types, subtypes, sharing coefficients, and repeat units or loops of tetrahedra, there remain only very similar structures in each category of the classification. They are in most cases isomorphic, isotypic, or derivative structures. It is theoretically possible, however, that two structures can be so similar that they have the same tetrahedral loops, yet their tetrahedral linkages are different; these should not be left in the same final group. Two such structures are apophyllite and gillepsite. They are similar in every respect, except in the linkage of tetrahedra. In both structures the tetrahedra are oriented so that they form triangular pyramids with their bases in the plane of the sheet of the layered structure. In apophyllite the three basal corners of the pyramids are shared, but in gillepsite the two basal corners and the apices of the pyramids are shared. Such structures should be separated as two different structure families, so that in the final column of the classification there are only closely related structures.

CLASSIFICATION OF SILICATES

There is a complication in the structures of the silicates which makes their classification difficult. This is the presence of tetrahedrally coordinated Al, B, Be and other cations. This complication is usually neglected by most authors and gives rise to an inconsistency in the treatment of various silicates. The problem can be illustrated briefly by three points:

(1) It is generally accepted that Al can replace Si, and when it does, the Al tetrahedra still remain part of the tetrahedral framework of the silicates. In some cases, however, the Al tetrahedra are not so regarded. For example, cordierite is usually classified as a six-membered single-ring structure, where the tetrahedra of the ring are Si tetrahedra. But Al tetrahedra connect these rings into a continuous three-dimensional network.

(2) In other cases other cations occur in tetrahedra and they are sometimes accepted as part of the frame and sometimes not. For example, B in danburite is accepted as part of the frame, and danburite is classified as a silicate with the three-dimensional network of tetrahedra. Ca occurs in tetrahedral coordination in Na_2CaSiO_4 and is accepted as part of the framework, so that the crystal is a derivative of the cristobalite structure. But tetrahedrally coordinated Be is not accepted in beryl, phenacite or bertrandite, nor Zn in willemite, hemimorphite or hardystonite.

(3) Almost every author treats this problem differently (Bragg 1930, 1937, Berman 1937, Gruner 1931, Strunz 1937, Swartz 1937). Most authors exclude cations other than Si and Al from the tetrahedral frame of the silicates. In some instances even Si atoms are excluded from the frame as in Na-melilite (Swartz 1937). On the other hand some authors (Strunz 1937, 1957, Eitel 1941) accept two alternate classifications for the silicates containing several cations in tetrahedral coordination.

Without a consistent treatment of the various four-coordinated cations, a classification of silicates based on their tetrahedral structures is somewhat artificial. In order to save the otherwise satisfactory Machatschki-Bragg classification, the problem of the cations must be treated consistently. The acceptance of all the tetrahedrally coordinated cations in the tetrahedral frames of the silicates would not only be the simplest solution, but probably the only satisfactory solution. This is the only way, for example, for the consistent classification of the melilites. The linkage of the tetrahedra in the various melilites is identical although the tetrahedra are occupied by different cations. In Na-melilite there are only Si cations in the tetrahedra, in gehlenite only Si and Al cations, but in hardystonite, there are also Zn and in melilite Mg and Fe cations.

Geometrically there are several cations which can substitute for silicon in a tetrahedron without changing significantly the size of the tetrahedron. Table 3 is a list of some cations which can be found tetrahedrally coordinated in silicate structures, and some which might conceivably be present in tetrahedral coordination. They are listed in order of increasing cation-oxygen radius ratio. The minimum radius ratio geometrically required for a tetrahedron is .225, so that any of the cations from B to Ca, listed in Table 3, can fit into an oxygen tetrahedron. Due to its large size, however, Ca distorts the tetrahedron considerably. Most of these cations also have similar electronegativity, so that their substitution for Si would not be expected to change significantly the nature of the chemical bond (Pauline 1939, p. 58). The list of the observed cation-oxygen distances indicates that the variation in the size of the tetrahedron is even less than indicated by the theoretical radius ratios. Except in the case of B and Ca

TABLE 3. SOME IMPORTANT TETRAHEDRALLY COORDINATED CATIONS IN SILICATES

Cation	Radius ratio (calculated)	Observed M—O distance ±.05 Å	Electro-negativity	Examples
B^{3+}	.25	1.50	2.0	Danburite, datolite, homolite
Be^{2+}	.28	1.60	1.5	Beryl, phenacite
As^{5+}	.30	—	2.0	—
P^{5+}	.34	—	2.1	Stillwellite
Si^{4+}	.38	1.60	1.8	Silicas, silicates
Li^{+}	.39	—	1.0	—
Al^{3+}	.41	1.78	1.5	Aluminosilicates
Ge^{4+}	.43	1.80	1.8	Many silicates
Ga^{3+}	.46	—	1.5	Many silicates
Mg^{2+}	.47	1.80	1.2	Melilite, åkermanite
Fe^{2-3+}	.48–.50	1.80	1.5–2.0	Staurolite, cordierite
Zn^{2+}	.50	1.82	1.8	Hemimorphite, hardystonite
Ti^{4+}	.55	1.82	1.6	Schlorlomite, astrophyllite
Ca^{2+}	.67	1.90	1.0	Na_2CaSiO_4

Data from Pauling (1940), Hori (1954), Smith (1954).

tetrahedra, the different cation-oxygen distances are almost equal to the cation-oxygen distances observed in the Si and Al tetrahedra.

In many silicate structures containing several tetrahedrally coordinated cations the different cations appear to occupy symmetrically different tetrahedra. In beryl the Si cations appear to occupy the tetrahedra of the hexagonal rings, and the Be cations the tetrahedra which connect these rings into continuous networks of tetrahedra. This separation of the two cations is probably not complete except in a state of high order. The milarite structure is similar to the beryl structure, except that milarite has double hexagonal rings. At room temperature there are $(Si_{.90}Be_{.10})$ cations in the tetrahedra of the hexagonal rings and $(Si_{.40},Be_{.27}Al_{.33})$ cations in the connecting tetrahedra (Ito and Sadanaga 1952). Consequently Be can be present in both tetrahedra, and the rejection of the connecting tetrahedra in the consideration of the tetrahedral frame of milarite or beryl is artificial. The only consistent treatment is the acceptance of all tetrahedra, and the classification of milarite and beryl as structures containing three-dimensional networks of tetrahedra.

There is only one important criterion which can lead to discarding a tetrahedron from consideration as part of the tetrahedral frame, namely the nature of its bonding. The tetrahedral structure of a silicate can be regarded as the frame of the crystal. This frame is a strong unit within the structure, since in each tetrahedron half or more of the cation's bond strength is expended in holding the tetrahedral frame together and less than half is expended in connecting the cation to the rest of the structure. Any tetrahedron can be part of the frame, provided that half or more of the cation's bond strength is distributed within the tetrahedral frame. If less than half of the bond strength of the cation is distributed within the frame, the tetrahedron belongs to the rest of the structure, rather than to the frame. A good example is offered by axinite. Here the four-membered rings of Si tetrahedra are connected by Al tetrahedra, but the Al's contribute less than half their bond strength to connect the Si tetrahedra and more than half to connect the Fe octahedra and B triangles.

Of course, it is expected that in a silicate a large number of tetrahedra are Si tetrahedra in order to classify the crystal chemically as a silicate. If the replacement of Si by another cation goes as far as the complete replacement of all the Si, the compound should not be called a silicate chemically, although structurally it still might be included in the silicates. An example is yttro-garnet, in which practically all the Si is replaced by Al (Yoder and Keith 1950).

By accepting the tetrahedrally coordinated cations in the tetrahedral frame of the silicates, some changes have to be made in the conventional classification of beryl, cordierite, hemimorphite, phenacite, willemite, bertrandite and melilites. Beryl and cordierite are three-dimensional networks instead of single rings, and hemimorphite, phenacite and willemite are three-dimensional networks instead of pairs of tetrahedra. Bertrandite is also a three-dimensional network instead of a complex of chains and groups of tetrahedra. In the melilites the pairs of tetrahedra become sheets of tetrahedra.

In hemimorphite, phenacite, willemite and bertrandite, all of the cations are tetrahedrally coordinated. These tetrahedra build up a neutral network, somewhat similar to that of the pure silicas. The cation-anion ratio in these minerals is higher than in SiO_2, and consequently the sharing of one oxygen by two cations would no longer give a neutral structure. In order to obtain neutrality, the oxygens are shared by up to three cations, and some of the O^{--} is replaced by $(OH)^-$.

ACKNOWLEDGMENT

The author is deeply indebted to Professor M. J. Buerger for his suggestions and constructive criticism during the preparation of this paper.

APPENDIX

The sharing coefficient of a tetrahedral structure can be obtained from the subscripts of the tetrahedrally coordinated cation (T) and anion (A) in the chemical formula. An equation has been derived for this calculation.

There is a total number of $4T$ tetrahedral corners in a chemical-formula unit, x of these are joined to anions shared by $n+1$ tetrahedra and $4T-x$ to anions shared by n tetrahedra. Then the average number of tetrahedra participating in the sharing of a corner is:

$$\begin{aligned} \text{sharing coefficient} &= \frac{x(n+1)+(4T-x)n}{4T} \\ &= \frac{x}{4T}+n \qquad (1) \end{aligned}$$

A is the number of anions per chemical formula and is the sum of the number of corners shared between $n+1$ and n tetrahedra:

$$\begin{aligned} A &= \frac{x}{n+1}+\frac{4T-x}{n} \\ &= \frac{xn+4T(n+1)-xn-x}{n^2+n} \\ x &= 4T(n+1)-A(n^2+n) \qquad (2) \end{aligned}$$

Equations (1) and (2) can be combined to obtain the sharing coefficient in terms of T, A and n:

$$\begin{aligned} \text{sharing coefficient} &= \frac{4T(n+1)-A(n^2+n)}{4T}+n \\ &= n+1-\frac{A}{4T}(n^2+n)+n \\ &= 2n+1-\frac{A}{4T}(n^2+n) \qquad (3) \end{aligned}$$

The only unknown in equation (3) is n. Fortunately, n can be obtained from the ratio of the number of available tetrahedral corners to the number of shared corners: $4T/A$. This ratio does not express the proportion of corners shared by $n+1$ and by n tetrahedra, but it is equal to the sharing coefficient when its value is an integer. Between integers the integral part of $4T/A$ is equal to the integral part of the sharing coefficient, that is, to n in equation (3). Consequently:

$$n = \text{the integer of } \frac{4T}{A} \qquad (4)$$

In conclusion, the sharing coefficient of a tetrahedral structure can be obtained from the structural chemical formula by using equations (4) and (3).

REFERENCES

BERMAN, H. (1937), Constitution and classification of the natural silicates. *Am. Mineral.* **2,** 342–408.

BRAGG, W. L. (1930), The structure of silicates. *Zeit. Krist.* **74,** 237–305.

BRAGG, W. L. (1937), Atomic structure of minerals. Cornell Univ. Press.

EITEL, W. (1941), Physikalische Chemie der Silikate. J. A. Barth Verl. Leipzig.

GRUNER, J. W. (1931), Structure of some silicates. *Am. Mineral.* **16,** 437–454.

HORI, F. (1954), On the diadochic substitution in silicates. *Mineral. Journ. Japan.* **1,** 109–125.

ITO, T., AND SADANAGA, R. (1952), The crystal structure of milarite. *Acta Cryst.* **5,** 209–213.

MACHATSCHKI, F. (1928), Zur Frage der Struktur und Konstitution der Feldspate. *Zbl. Min. Geol. Palaeo. A,* 97–104.

LIEBAU, F. (1956), Bemerkungen zur Systematik der Kristallstrukturen von Silikaten mit hochkondensierten Anionen. *Zeit. Phys. Chem.* **206,** 73–92.

PAULING, L. (1939), The nature of chemical bond. Cornell Univ. Press.

SWARTZ, C. K. (1937), Classification of the natural silicates. *Am. Mineral.* **22,** 1073–1087, 1161–1174.

SMITH, J. V. (1954), A review of the Al—O, Si—O distances. *Acta Cryst.* **7,** 585–595.

STRUNZ, H. (1937), Systematik und Struktur der Silikate. *Zeit. Krist.* **98,** 60–83.

STRUNZ, H. (1957), Mineralogische Tabellen. Akad. Verl. Geest and Portig.

WELLS, A. F. (1954–56), The geometrical basis of crystal chemistry. Part 1–6. *Acta Cryst.* **7,** 535–554, 842–853, **8,** 32–36, **9,** 23–27.

YODER, H. S., AND KEITH, M. L. (1950), Complete substitution of aluminum for silicon: the system $3MnO.Al_2O_3.3SiO_2—3Y_2O_5.5Al_2O_3$. *Bull. Geol. Soc. Amer.* **61,** 1516–1517.

ZOLTAI, T., AND BUERGER, M. J. (1959), The structure of coesite, the dense, high pressure form of silica. *Zeit. Krist.* **111,** 129–141.

ZOLTAI, T., AND BUERGER, M. J. (1960), The relative energies of rings of tetrahedra. *Zeit. Krist.* **114,** 1–8.

REFERENCES FOR STRUCTURE DATA

Strukturbericht. Band I-VII. *Zeit. Krist.* (1913–1939).

Structure Reports. Vol. 8–15. Intern. Union Cryst. (1940–1951).

BERGER, S. V. (1952), Crystal structure of B_2O_3. *Acta Cryst.* **5,** 388–389.

BERGHOFF, G., BAUER, W. H., AND NOWACKI, W. (1958), Über die Kristallstruktur des Faujasits. *Neues Jb. Min. Mh.* **9,** 193–200.

BRAUNER, K., AND PREISINGER, A. (1956), Struktur und Entstehung des Sepioliths. *Tscherm. Min. Petr. Mitt.* **6,** 120–140.

DENT, L. S., AND SMITH, J. V. (1958), Crystal structure of Chabasite, a molecular sieve. *Nature* **181,** 1794–1796.

HEIDE, H. G. (1954), Die Struktur des Dioptas. *Naturwiss.* **41,** 402–403.

HENSHAW, D. E. (1955), The structure of wadeite. *Min Mag.,* **227,** 585–595.

ITO, T., AND TAKEUCHI, Y. (1952), The crystal structure of axinite. *Acta Cryst.* **5,** 202–208.

ITO, T., AND MORI, H. (1953), The crystal structure of datolite. *Acta Cryst.* **6,** 24–32.

MIYASHIRO, A. (1956), Osumilite, a new silicate mineral and its crystal structure. *Am. Mineral.* **41,** 104–116.

SMITH, J. V. (1953), The crystal structure of paracelsian $BaAl_2Si_2O_8$. *Acta Cryst.* **6,** 613–620.

STRUNZ, H. (1956), Die Zeolithe Gmelinit, Chabasit, Levyn. *Neues Jb. Min. Mh.* **7,** 250–259.

TAKEUCHI, Y., AND DONNAY, G. (1959), The crystal structure of hexagonal $CaAl_2Si_2O_8$. *Acta Cryst.* **12,** 465–470.

VENTRIGLIA, U. (1955), La struttura della heulandite. Period. Min. **24,** 49–83.

ZEMANN-HEDLIK, A., AND ZEMANN, J. (1955), Die Kristallstruktur von Petalit $LiAlSi_4O_{10}$. *Acta Cryst.* **8,** 781–787.

ZVIAGIN, B. B. (1957), Determination of the structure of celadonite by electron diffraction. *Russ. Phys. Cryst.* **2,** No. 3, 388–394.

Manuscript received December 20, 1959.