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THE STRUCTURE OF SOME SODIUM AND CALCIUM ALUMINOSILICATES

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Two years ago it was pointed out[1] that the electrostatic valence rule requires that the aluminum ions in alkali aluminum silicates have the coördination number 4 rather than 6, oxygen ions in the crystal then being common to a silicon tetrahedron, an aluminum tetrahedron, and one or more alkali-ion polyhedra. Since that time examples of such structures have been found. Thus the cubic crystal sodalite,[2] $Na_4Al_3Si_3O_{12}Cl$, has a framework composed of tetrahedra, each of which shares its corners with four others, silicon and aluminum tetrahedra alternating. The three parameters determining the position of the oxygen atoms were evaluated from the x-ray data, and it was found that both the silicon and the aluminum tetrahedra are approximately regular, with the distances Si–O = 1.60 Å and Al–O = 1.74 Å. The sodium and chlorine ions are arranged in cavities in the tetrahedral framework.

We have found that many other alkali and alkaline-earth aluminosilicates have similar tetrahedral structures. Three of these, shown by natrolite, the scapolites, and davynite-cancrinite, are described in this communication.

Natrolite.—The zeolite natrolite, $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, forms orthorhombic pseudotetragonal crystals with axial ratios $a:b:c = 0.97852:1:$-0.35362. Data from oscillation and Laue photographs lead to the unit

$$a = 18.19\ \text{Å},\quad b = 18.62\ \text{Å},\quad c = 6.58\ \text{Å},$$

containing $8Na_2Al_2Si_3O_{10}\cdot 2H_2O$. The lattice is face-centered, and the space-group is shown to be C_{2v}^{19} by the absence of certain prism plane reflections.

The nature of the framework of the crystal can be deduced with some rigor from this information and the assumptions that aluminum and silicon tetrahedra of approximately the size of those found in sodalite exist in this crystal, and that they share corners but not edges or faces.[3] 8Si must then be placed in Wyckoff's position 8a, and the parameter can be taken as zero without loss of generality. Thus there are tetrahedra at 000, $^1/_2{}^1/_2 0$, $^1/_2 0\,^1/_2$, $0\,^1/_2{}^1/_2$, $^1/_4{}^1/_4{}^1/_4$, $^3/_4{}^3/_4{}^1/_4$, $^3/_4{}^1/_4{}^3/_4$, $^1/_4{}^3/_4{}^3/_4$. The distance from 0 0 0 to $^1/_4\,^1/_4\,^1/_4$ is 6.67 Å, too far to be spanned by a single tetrahedron. Hence two silicon and two aluminum tetrahedra must be attached to each of these silicon tetrahedra. In order for each tetrahedron to share all its corners it is necessary for each of these groups to form a string with those obtained from it by the translational operation *c*, as shown in figure 1. The strings are rigid, and the dimensions given above for the tetrahedra lead to $c = 6.57$ Å, in agreement with the observed 6.58 Å. The strings combine by sharing tetrahedron corners as shown in figure 2.

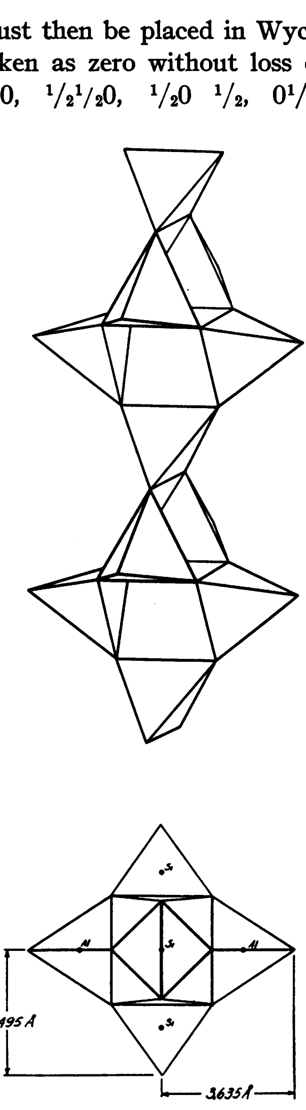

FIGURE 1

The natrolite string. Each tetrahedron has an oxygen ion at each corner and a silicon or aluminum ion at its center. Below is shown the projection of the string on (001).

The structure as a whole is not rigid; it collapses, the strings rotating about their axes until certain minimum interionic distances are reached. If all the tetrahedra were the same (silicon tetrahedra, say) the structure would have tetragonal symmetry. The introduction of the slightly larger aluminum tetrahedra reduces the symmetry to that of the orthorhombic space group C_{2v}^{19}. With the angle Θ shown in figure 2 equal to 20° 50′, the assumed tetrahedron dimensions give calculated values $a = 18.22$ Å, $b = 18.56$ Å, in good agreement with the observed $a = 18.19$ Å, $b = 18.62$ Å.

The sodium ions and water molecules occupy certain positions between the strings, such that the minimum Na–O and H_2O–O distances are about 2.6 and 3.2 Å, respectively. The channels along (001) are of such a size that on heating the crystal water molecules can escape along them without the rupture of the framework. In this way our determination of the structure of a zeolite leads to a simple explanation of their most characteristic property. The phenomenon of base-exchange is similarly accounted for; the sodium ions can run along the channels and out of the crystal as other cations run in to replace them.

The monoclinic pseudotetragonal zeolite scolecite, $CaAl_2Si_3O_{10}.3H_2O$, with $a:b:c = 0.97636:1:0.34338$, $\beta = 89° 18'$, has no doubt a closely similar structure, with the same tetrahedral framework, but with $2Na^+$ replaced by Ca^{++} and H_2O, this replacement lowering the symmetry. The change in composition is of considerable interest—the four cavities occupied by $2Na^+$ and $2H_2O$ in natrolite are still occupied, but in this case by $1Ca^{++}$ and $3H_2O$.

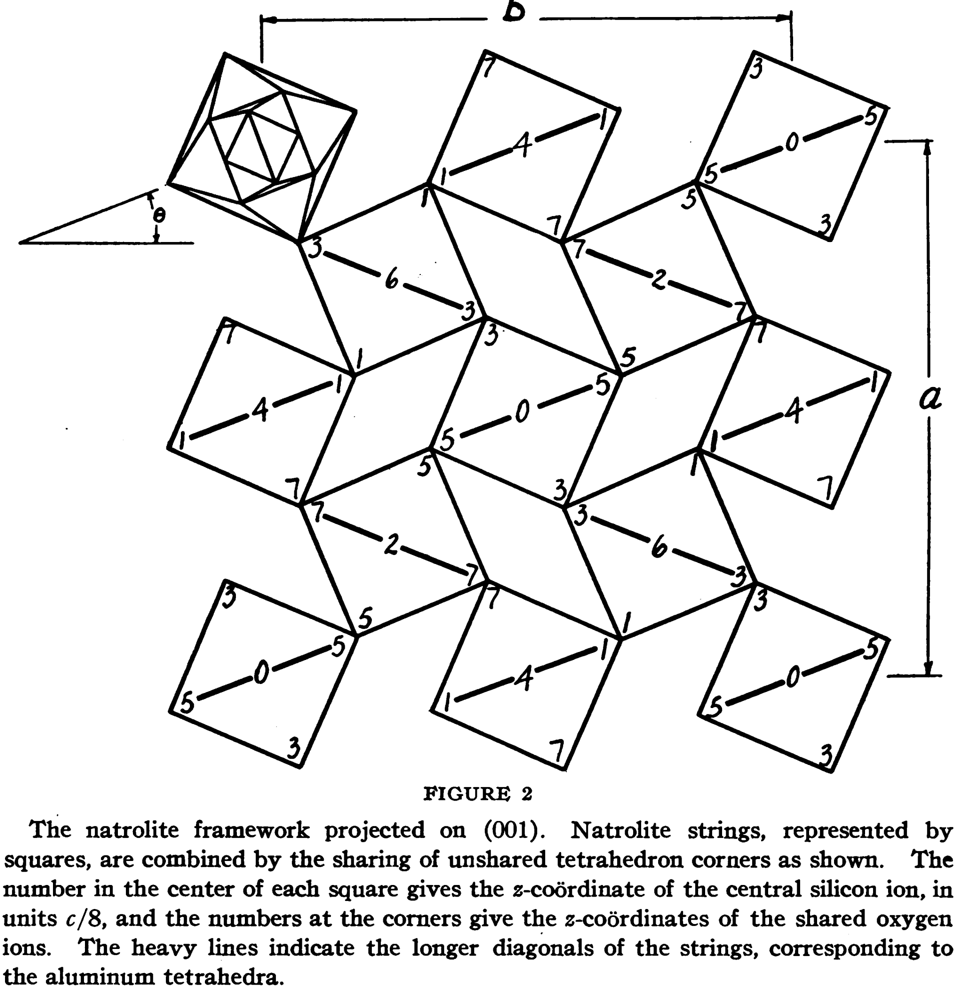

FIGURE 2

The natrolite framework projected on (001). Natrolite strings, represented by squares, are combined by the sharing of unshared tetrahedron corners as shown. The number in the center of each square gives the z-coördinate of the central silicon ion, in units $c/8$, and the numbers at the corners give the z-coördinates of the shared oxygen ions. The heavy lines indicate the longer diagonals of the strings, corresponding to the aluminum tetrahedra.

The Scapolites.—The minerals of the scapolite group can be considered as solid solutions of two end-members, marialite, $Na_4Al_3Si_9O_{24}Cl$, and meionite, $Ca_4Al_6Si_6O_{24}(SO_4, CO_3)$, in various proportions. They are tetragonal, with a:c = 1:0.43925. Data from oscillation and Laue photographs of carbonate meionite from Vesuvius and wernerite (of intermediate composition) from Bedford County, Ontario, Canada, show that the true unit has axes rotated 45° from the crystallographic ones, with

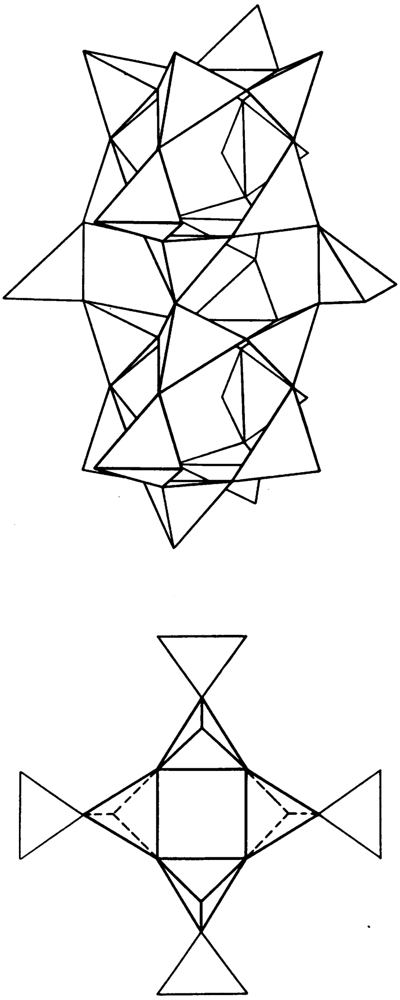

FIGURE 3

The scapolite string. (The distortion of the tetrahedra in the upper figure has no significance.)

$$a = 12.27 \text{ Å},$$
$$c = 7.66 \text{ Å}.$$

The lattice is body-centered, the space group being C_{4h}^5, C_4^5, or S_4^2. There are two molecules of the above composition in the unit.

The unit accordingly contains 24 tetrahedra, of which between 6 and 12 are aluminum tetrahedra. A rigid string of 12 tetrahedra can be built as shown in figure 3; if the (Si, Al)–O distance is given the average value 1.65 Å, the identity distance along the c-axis of the string is found to be 7.7 Å, in good agreement with the observed 7.66 Å. These strings combine by sharing still unshared corners as shown in figure 4. The structure is collapsible. When expanded as far as possible it has a = 13.6 Å, and, moreover, shows vertical symmetry planes, which the crystals do not possess. Collapse takes place by rotation of the strings, accompanied by loss of the vertical symmetry planes. When the angle Θ (figure 4) is about 25° the edge of the unit becomes equal to the observed 12.27 Å.

Assuming all tetrahedra alike, the framework is based on the body-centered tetragonal lattice, with space-group C_{4h}^5. The space-group symmetry may be changed as aluminum tetrahedra are introduced.

There are two large cavities in the unit, occupied by the 2 (Cl, SO_4, CO_3) groups, and there is also room for the 8 (Na^+, Ca^{++}) ions.

TABLE 1

CALCULATED AND OBSERVED INTENSITIES OF REFLECTION OF SCAPOLITE

(*hkl*)	ESTIMATED INTENSITY	CALCULATED INTENSITY = $A^2/7120$
0.0.2	1.5	1.57
0.0.4	50	(50.0)
0.0.6	10	9.37
0.0.8	0.5	1.45
0.0.10	2.0	2.54
0.0.12	0.0	0.24
0.0.14	0.2	0.38

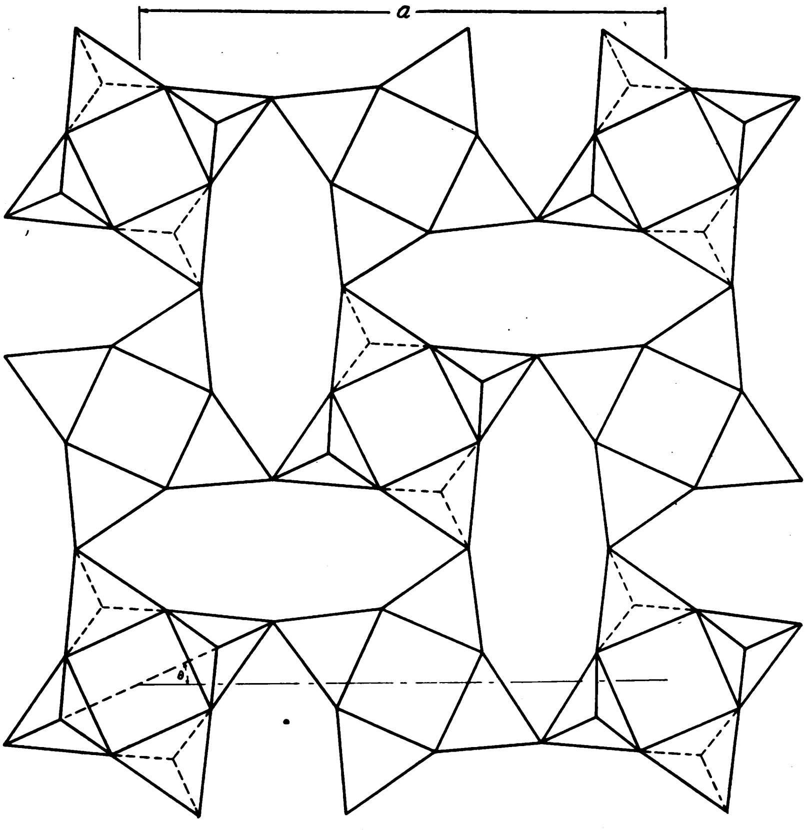

FIGURE 4

The scapolite framework, projected on (001). Scapolite strings are combined by the sharing of unshared tetrahedron corners as shown.

A first test of the structure is easily made by calculating the intensities of reflection from (00 *l*) with *l* even (the odd orders vanish), using the expression

$$I \sim A_{00l}^2$$

with $A_{00l} = 8A_{\mathrm{Ca}} + 8A_{\mathrm{Si}} + 2A_{\mathrm{CO_3}} + 16A_{\mathrm{O}}\left\{1 + (-1)^{l/2} + \cos 2\pi l z_1\right\}$

$+ 16A_{Si} \cos 2\pi l z_2$, in which Al and Si are grouped together. The predicted parameter values are $z_1 = 0.175$ and $z_2 = 0.205$. The agreement with the observed relative intensities, obtained by the visual comparison of films of varying exposure time, is excellent, and provides strong substantiation of the structure (table 1).

Davynite and Cancrinite.—The hexagonal minerals davynite and cancrinite are reported by Gossner and Mussgnug[4] to have $a = 12.80$ Å, $c = 5.35$ Å and $a = 12.60$ Å, $c = 5.18$ Å, respectively, the space group being D_{6h}^4. The davynite unit contains 2 molecules of the composition (Na, Ca)$_4$Al$_2$Si$_3$O$_{12}$(CO$_3$, SO$_4$, Cl). Cancrinite is similar, usually having somewhat more silicon than aluminum and containing some water.

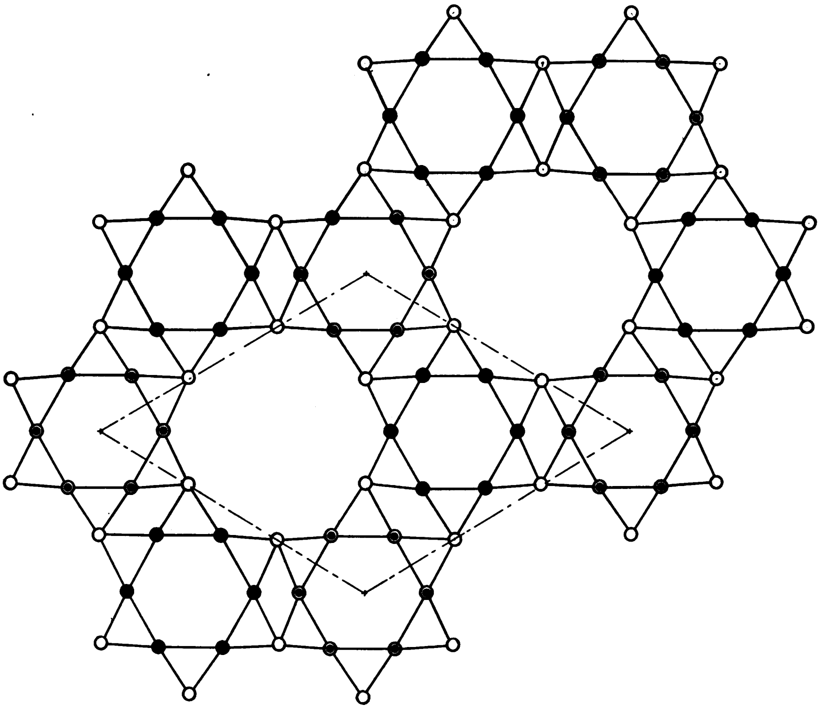

FIGURE 5

The davynite-cancrinite framework, projected on (001). The circles represent oxygen ions at tetrahedron corners; open circles, those with $z = 0$ and $^1/_2$; solid circles, with $z = {}^1/_4$; and ringed circles, with $z = {}^3/_4$.

A framework containing 12 tetrahedra in a unit of these dimensions can easily be built. The fundamental unit is the ring of six tetrahedra, also found in sodalite, beryl, tremolite, and other silicates. If such rings are joined by sharing corners as shown in figure 5 there is obtained a hexagonal structure with $a = 12.8$ Å and $c = 5.4$ Å. The tetrahedra may be silicon and aluminum tetrahedra alternately, each oxygen being common to one of each kind. The space-group of this structure is D^4_{6h}. There are cavities in which the other constituents of the crystal may be placed. Indeed, it will be seen that there are tunnels along the c-axis in the form of circular cylinders with a diameter of 6 Å (after allowing 3.0 Å for the oxygen ions of the framework). The experimental study of possible unusual properties caused by these large tunnels is planned.

The Cleavage of Tetrahedral Framework Crystals.—The physical properties of alkali aluminosilicates are determined in the main by the tetrahedral framework of the crystals, for the strength of the electrostatic bond from an alkali ion with coördination number 6 or 8 is $^1/_6$ or $^1/_8$, which is small compared with that of an aluminum or silicon ion with coördination number 4 (of value $^3/_4$ and 1, respectively). This is strikingly shown by the cleavage of these crystals. In table 2 are given the density of Al—O—Si bonds (shared tetrahedron corners) which must be broken in order to break the framework along the indicated planes, together with the observed cleavage of the crystals. The correspondence is complete; in every case ease of cleavage decreases as bond-density increases.

TABLE 2

CLEAVAGE OF TETRAHEDRAL FRAMEWORK CRYSTALS

	PLANE	NUMBER OF BONDS	AREA	BONDS PER 100 Å²	OBSERVED CLEAVAGE
Natrolite	(110)	4	$c\sqrt{2ab}$	2.34	Complete
	(100), (010)	4	bc, ac	3.30	Incomplete?
	(001)	16	ab	4.74	None
Scapolite	(110)	4	$c\sqrt{2ab}$	3.01	Good
	(100)	4	bc	4.26	Less good
	(001)	8	ab	5.31	None
Davynite-Cancrinite	(10.0)	2	ac	2.92	Complete
	(11.0)	4	$ac\sqrt{3}$	3.36	Less complete or none
	(00.1)	12	$a^2\sqrt{3}$	4.22	Less complete or none
Sodalite	(110)	4	$a^2\sqrt{2}$	3.59	More or less distinct
	(111)	6	$a^2\sqrt{3}$	4.39	None
	(100)	4	a^2	5.09	None

A detailed account of the investigation of these minerals will appear in the *Zeitschrift für Kristallographie.*

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[1] Linus Pauling, *J. Am. Chem. Soc.*, **51**, 1010 (1929).

[2] Linus Pauling, *Zeit. Krist.*, in press.

[3] Ref. 1, Rule 3.

[4] B. Gossner and F. Mussgnug, *Zeit. Krist.*, **73**, 52 (1930).