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THE CRYSTAL STRUCTURE OF MIZZONITE, A CALCIUM- AND CARBONATE-RICH SCAPOLITE[1]

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Abstract

The crystal structure of a 70.1% meionite scapolite (mizzonite, $a=12.169\pm0.004$ and $c=7.569\pm0.003$ Å) from Grenville, Quebec has been refined in space group $I4/m$ using three-dimensional x-ray intensities collected by integrated Weissenberg film techniques. Starting with positional parameters of a refined marialite scapolite structure reported by Papike and Zoltai (1965), the model was completed by Fourier methods and refined by least squares. The refined structure is basically the same as that of marialite with interesting differences concerning the aluminum distribution in the tetrahedral framework and the crystal-chemical role of the carbonate ion.

The average T-0 distances are 1.648 ± 0.008 Å in the T-1 tetrahedron and 1.680 ±0.006 Å in the T-2 tetrahedron. A determinative curve for aluminum tetrahedral occupancy based on scapolite data indicates the following assignments: T-1 (29% Al, 71% Si); T-2 (52% Al, 48% Si).

The results concerning the structural role of carbonate indicate that the group is disordered in the (001) plane and takes one of four possible positions in space and time in the scapolite structure.

Introduction

Refinement of the crystal structure of a sodium- and chlorine-rich scapolite (Papike and Zoltai, 1965) confirmed the structure model proposed by Pauling (1930) and Schiebold and Seumel (1932). Although this investigation led to a well-refined structure which in turn permitted the assignment of aluminum to one of two possible equipoints in the structure, several interesting crystal-chemical problems necessitated a crystal-structure refinement of a calcium- and carbonate-rich scapolite:

> (1) the distortions of the structure with composition, (2) the distribution of Al in the tetrahedral framework, consistent with the higher Al/Si ratios of meionite-rich scapolites, (3) the crystal-chemical role of carbonate, and (4) the environment of the calcium atom.

With these questions in mind we selected a 70.1% meionite scapolite, from Grenville, Quebec, for structural analyses and refinement.

Unit Cell and Space Group

The 70.1% meionite scapolite selected for study displays nearly perfect diffraction symmetry $4/m$ I-/- and shows no piezoelectric indication of polarity. A few very weak and diffuse reflections were observed which

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[1] Studies of silicate minerals (II). Publication authorized by the Director, U. S. Geological Survey.

apparently violate body-centered symmetry, however, these reflections were too poorly defined to be treated in the refinement. The occurrence and significance of reflections violating body-centered symmetry in scapolite are presently being investigated by M. G. Bown (Cambridge, England) and J. J. Papike (U. S. Geological Survey, Washington, D. C.). The unit-cell dimensions obtained from Debye-Scherrer photographs and refined by a least-squares method (Britton, 1964) are $a=12.169 \pm 0.004$, $c=7.569 \pm 0.003$ Å. These cell dimensions together with the specific gravity 2.703 (Shaw, 1960, p. 241) and the chemical analyses of Ingamells (quoted by Shaw, 1960), enabled us to calculate the unit-cell contents (Hey, 1939). The results are presented in Table 1.

TABLE 1. UNIT-CELL CONTENTS OF GRENVILLE MIZZONITE

Cation 1	Number Per Cell	Cation 2	Number Per Cell	Anion 1	Number Per Cell	Anion 2	Number Per Cell
Si Al	13.93 10.08	Ca Na K Mg	5.12 1.44 0.86 0.21	O^{2-}	47.85	CO_3^{2-} SO_4^{2-} Cl^{1-}	1.19 0.21 0.03
Totals	24.01		7.63		47.85		1.43

INTENSITY DATA

Single-crystal x-ray diffraction data were collected by integrated Weissenberg film techniques, using Ni-filtered Cu radiation. The hkl levels from $l=0$ through $l=6$ were photographed, giving 488 observed reflections. Photometrically measured intensities were corrected for Lorentz and polarization factors, but no absorption corrections were applied.

STRUCTURE ANALYSIS AND REFINEMENT

A set of three-dimensional electron-density sections were calculated using the refined marialite scapolite parameters for the (Ca, Na, K), (Si, Al), and (O) atomic positions. The contribution to the calculated structure factors from the carbonate group was not included in this calculation. In addition to the peaks in the electron density corresponding to the atoms included in the calculation, electron-density highs at and around (0,0,0) in the (001) plane were revealed. This density was interpreted as the contribution from the carbonate group with the high at (0,0,0) resulting from the (C,S) atom.

Using the marialite scapolite starting parameters, and including the contribution from the (C,S) atom, four cycles of least-squares refinement were executed utilizing the full matrix of the normal equations. During this calculation all weights were assigned as one, and temperature factors were fixed at $B=1.3$ Å^2 for (Ca, Na, K), $B=0.5$ Å^2 for (Si, Al), $B=0.8$ Å^2 for (O), and $B=1.0$ Å^2 for (C,S). The R value dropped from 28% to 20% for $|F_0|>0$ during this treatment.

Refinement was continued for four more cycles allowing isotropic temperature factors to vary, and R dropped to 16.6%. Electron-density maps using the parameters from the last refinement cycle still showed four peaks around the origin (0,0,0), and their contribution was included but not refined in four additional cycles, giving an $R=15.9\%$. Interatomic distance calculations permitted assignment of silicon and aluminum between two possible equipoints, and using this assignment four additional least-squares cycles were run, giving a final $R=15.7\%$ for $|F_0|>0$.

The scattering factors used during the refinement were as follows: Ca^{2+}, Na^{1+}, K^{1+}, Si^0, Al^0, C^{3+}, S^0, and O^{1-} (*International Tables for X-ray Crystallography*, Vol. III, 1962, p. 202–205), and the programs used in the crystallographic calculations were all contained in *"X-Ray 63" Program System for X-Ray Crystallography* (Stewart and High, 1964).

Calculations of the errors of the interatomic distances were made by using the diagonal elements of the variance-covariance matrix, as were the errors in the marialite scapolite structure.

DISCUSSION OF THE CRYSTAL STRUCTURE

The atom positional parameters and temperature factors for the refined mizzonite structure and the positional parameters of marialite are listed in Table 2. Selected interatomic distances and angles are presented in Tables 3, 4, 5 and may be interpreted by referring to Figs. 1a and 1b.

Distortions of the structure with composition. The basic features of the mizzonite crystal structure are the same as those of marialite (Papike and Zoltai, 1965); however, some significant changes in the positional parameters are observed.

As viewed along *c* (Fig. 1), the structure may be considered to be made up of two types of four-membered rings. The (type 1) rings are centered at (0,0,0), have apparent symmetry $4/m$, and are composed of tetrahedra having one edge parallel to *c*. The (type 2) rings are centered at (1/2, 0, 1/4), have apparent symmetry $\bar{4}$, and are composed of tetrahedra pointing alternately up and down. The geometry of mizzonite may be thought of as being derived from the marialite structure by rotating

TABLE 2. ATOM POSITIONAL PARAMETERS AND TEMPERATURE FACTORS

Atom	Coordinate	Marialite[1] Cycles Papike and Zoltai (1965)	Total Change	Mizzonite Cycles Present Study	B (Å^2)
(Ca, Na, K)	x	0.1340	+0.0088	0.1428±0.0003	1.13
	y	0.2113	+0.0057	0.2170±0.0003	
	z	0	0	0	
$(Si, Al)_1$	x	0.3388	+0.0003	0.3391±0.0003	−0.08
	y	0.4104	−0.0020	0.4084±0.0003	
	z	0	0	0	
$(Si, Al)_2$	x	0.3374	+0.0019	0.3393±0.0002	0.03
	y	0.0851	+0.0015	0.0866±0.0002	
	z	0.2060	+0.0009	0.2069±0.0004	
O_1	x	0.4587	−0.0006	0.4581±0.0007	0.58
	y	0.3483	−0.0003	0.3480±0.0007	
	z	0	0	0	
O_2	x	0.3066	+0.0054	0.3120±0.0008	0.87
	y	0.1206	+0.0074	0.1280±0.0008	
	z	0	0	0	
O_3	x	0.0517	−0.0007	0.0510±0.0005	0.84
	y	0.3500	−0.0011	0.3489±0.0005	
	z	0.2148	−0.0067	0.2081±0.0010	
O_4	x	0.2293	+0.0039	0.2332±0.0005	0.79
	y	0.1289	+0.0065	0.1354±0.0005	
	z	0.3281	−0.0018	0.3263±0.0011	
(Cl, C, S)	x	0	0	0	1.80
	y	0	0	0	
	z	0	0	0	

[1] For standard errors of marialite parameters note Papike and Zoltai (1965).

(type 1) rings in a counterclockwise direction while rotating (type 2) rings in a clockwise direction (Fig. 2). These rotations have the effect of a relative decrease in the short diameter of the oval-shaped "cation channels."

Aluminum distribution in the tetrahedral framework. In order to determine the distribution of aluminum in the tetrahedral framework of mizzonite,

TABLE 3. COMPARISON OF INTERATOMIC DISTANCES FOR TETRAHEDRA OF MIZZONITE AND MARIALITE

(a) *T*-0 Distances

Tetrahedron	Oxygen Atom	Multiplicity	*T*-0 Distance (Å)	
			Mizzonite	Marialite[1]
T-1	O_4	2	1.670±0.008	1.610
	O_1	1	1.623±0.009	1.628
	O_1'	1	1.628±0.009	1.584
		Average	1.648	1.608
T-2	O_3	1	1.677±0.007	1.660
	O_3'	1	1.679±0.007	1.660
	O_2	1	1.678±0.004	1.660
	O_4	1	1.684±0.007	1.682
		Average	1.680	1.665

(b) 0-0 Distances Within Tetrahedra

Tetrahedron	Oxygen Atoms	Multiplicity	0-0 Distances (Å)	
			Mizzonite	Marialite
T-1	O_4-O_4	1	2.630±0.012	2.639
	O_4-O_1	2	2.682±0.010	2.630
	O_4-O_1'	2	2.713±0.010	2.605
	O_1-O_1'	1	2.713±0.012	2.682
T-2	O_2-O_4	1	2.651±0.009	2.655
	O_2-O_3'	1	2.725±0.010	2.691
	O_2-O_3	1	2.782±0.009	2.776
	O_3-O_4	1	2.645±0.009	2.671
	O_3-O_3'	1	2.817±0.009	2.757
	O_4-O_3'	1	2.815±0.009	2.757

[1] For standard errors of marialite parameters note Papike and Zoltai (1965).

the method of Smith and Bailey (1963) was used. Three points were used to establish a determinative curve for tetrahedral site occupancies in scapolite:

(1) the value of 1.608±0.005 Å for a pure SiO_4 tetrahedron, a value obtained for the *T*-1 tetrahedron in marialite (Papike and Zoltai, 1965); (2) the average *T*-0 distance of the marialite structure which equals 1.646±0.004 Å; (3) the average *T*-0 distance of the mizzonite structure which equals 1.669±0.007 Å.

TABLE 4. SELECTED INTERATOMIC DISTANCES IN MIZZONITE

Type	From	To	Multiplicity	Distance (Å)
Environment of (Ca, Na, K)	(Ca, Na, K)	(C, S)	1	≃3.16
		O_5	1	≃2.37
		O_5'	1	≃2.46
		O_3'	2	2.511
		O_4'	2	2.689
		O_2	1	2.327
Anion Cage Diagonals[1]	O_1	O_1	2	8.486
	O_4	O_4	2	8.214
	O_2	O_2	2	8.208

[1] Atoms related by inversion center at 1/2, 1/2, 1/2.

Using this determinative curve (Fig. 3), the following assignments for individual tetrahedral occupancies were made: *T*-1 (29% Al, 71% Si); *T*-2 (52% Al, 48% Si). These results when compared with the tetrahedral assignments for the marialite scapolite structure provide some interesting crystal-chemical information.

These data indicate that in the solid-solution series between ordered marialite $Na_4Al_3Si_9O_{24}Cl$, and ordered meionite $Ca_4Al_6Si_6O_{24}CO_3$, aluminum is distributed between the (type 1) and (type 2) four-membered rings as follows. In ordered marialite-rich scapolites the aluminum atoms

TABLE 5. SELECTED INTERATOMIC ANGLES IN MIZZONITE

Type	Atoms	Angle
0-*T*-0 angles, *T*-1 tetrahedra	O_4-T_1-O_1	109.03°
	O_4-T_1-O_1'	110.69°
	O_1-T_1-O_1'	113.09°
	O_4-T_1-O_4	103.91°
0-*T*-0 angles, *T*-2 tetrahedra	O_4-T_2-O_3'	113.70°
	O_4-T_2-O_3	103.86°
	O_4-T_2-O_2	104.08°
	O_3-T_2-O_3'	114.16°
	O_3-T_2-O_2	112.05°
	O_3'-T_2-O_2	108.54°
T-0-*T* angles	T_1-O_1-T_1'	156.91°
	T_1-O_4-T_2	135.61°
	T_2-O_2-T_2	137.87°
	T_2-O_3'-T_2	145.97°

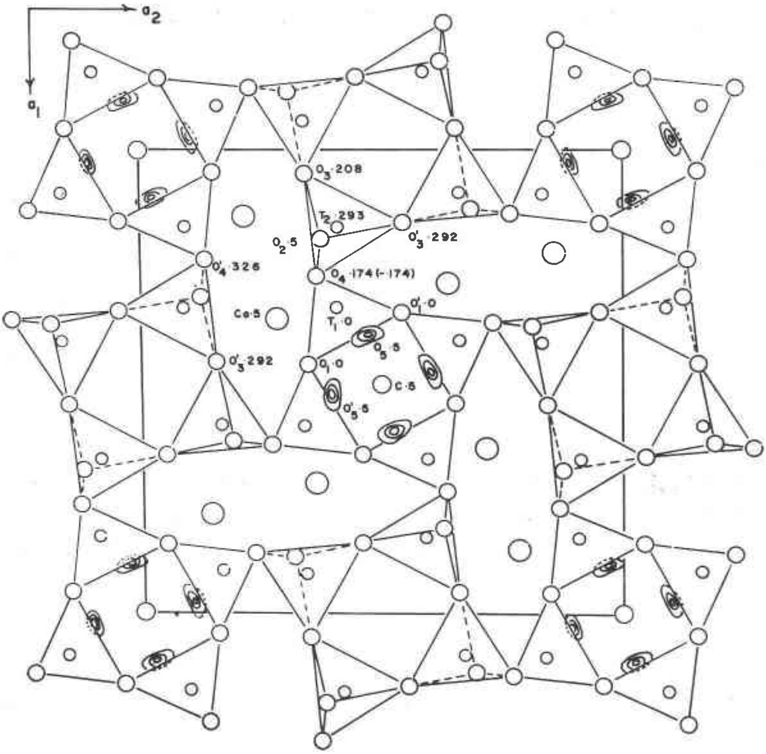

FIG. 1a. Projection of the crystal structure of mizzonite.

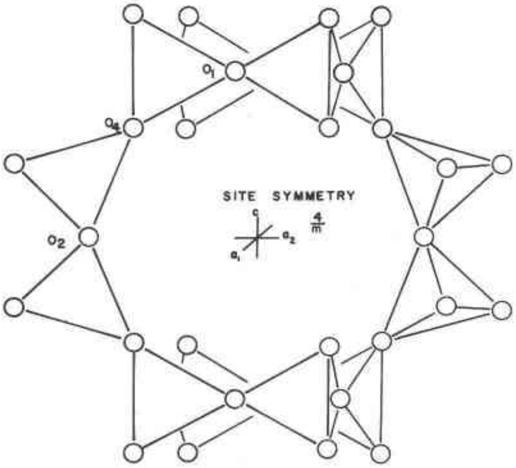

FIG. 1b. Scapolite anion cage.

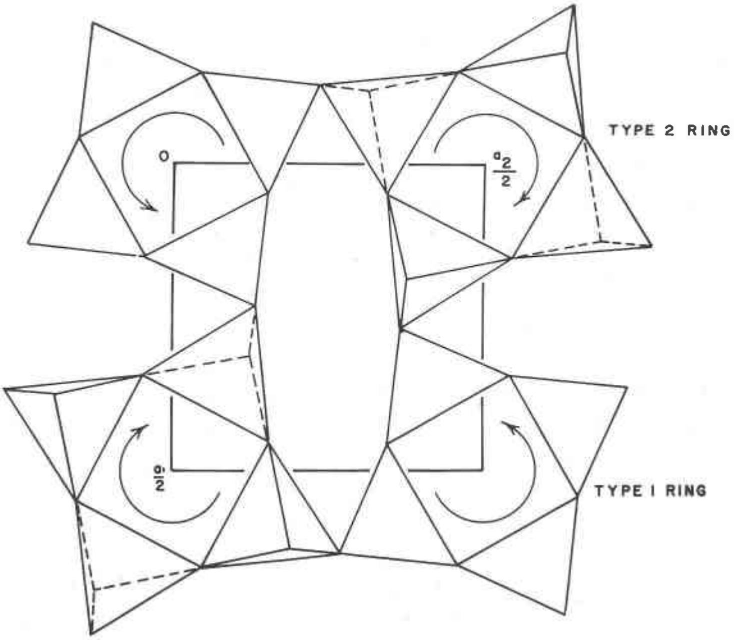

FIG. 2. Distortion of scapolite structure by ring rotation.

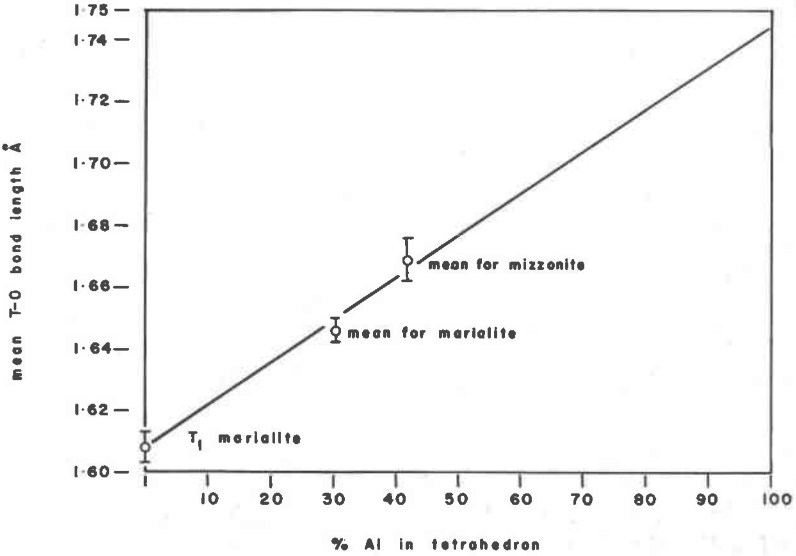

FIG. 3. Determinative curve for aluminum tetrahedral occupancies.

concentrate in the tetrahedra (T-2) making up the (type 2) four-membered rings with an end-member marialite having 37.5% Al in these rings. With an increasing proportion of the meionite end-member in the scapolite solid-solution, the aluminum occupancy in these rings will increase to 50%. Beyond this point, compositionally, the (type 2) rings would have to start forming Al-O-Al linkages, a situation which Loewenstein (1954) has called unstable in framework silicates. The present study appears to support Loewenstein's conclusion, since the density of Al-O-Al linkages may be decreased by having additional aluminum substitute into the (type 1) four-membered rings, and this behavior is observed in mizzonite where approximately 29% of the type 1 tetrahedra are occupied by aluminum.

If Al-O-Al linkages are unstable in scapolite, it is possible to speculate on why pure meionite scapolites are rare and why so commonly scapolites are deficient in aluminum (Shaw, 1960). The reason for this might be based on the fact that in pure end-member meionites with an Al/Si ratio of one, it is impossible to have all Si-O-Al linkages, and some Al-O-Al linkages would have to form. The reason for this situation in meionite as contrasted with the ordering scheme in anorthite plagioclase is that scapolites contain a five-membered ring (Fig. 4). The same types of ordering problems would be expected to result in any framework silicates with Al/Si ratio of one, and containing rings made up of an odd number of tetrahedra. It should be noted that the ordering scheme illustrated in Fig. 4, which is based on alternating AlO_4 and SiO_4 tetrahedra, is not consistent with $4/m$ symmetry. Several possibilities might explain this discrepancy:

(1) Scapolites may contain Al-O-Al linkages and the ordering scheme in Fig. 4 is incorrect; (2) The apparent $4/m$ symmetry of scapolites may be an averaging effect resulting from ordered domains of lower symmetry; (3) Combination of (1) and (2).

The intercepts of the determinative curve based on scapolite data are 1.608 ± 0.005 Å for the mean T-0 distance in a SiO_4 tetrahedron and an extrapolated value of 1.745 Å for an AlO_4 tetrahedron. These values are in good agreement with the 1.610 Å and 1.75 Å values given by Smith and Bailey (1963) for the feldspars and indicate that scapolites and feldspars behave similarly with respect to mean sizes of tetrahedra.

The role of carbonate in the scapolite structure. The results concerning the crystal-chemical role of carbonate in the scapolite structure, although not conclusive, do put some limitations on the behavior of the group. Carbon is believed to be present in scapolite in the form of carbonate groups not only on the basis of chemical analyses, but also on the basis of infrared absorption spectra, where absorption bands at 1530 cm^{-1} and 1425 cm^{-1} are present (Papike, 1964). The main problem is concerned with locating a group with essentially three-fold symmetry in a crystallographic site requiring $4/m$ symmetry. The portion of the electron density of interest is illustrated in Fig. 5. Since the electron density of the peaks in question is maximized in the *ab* plane ($Z=0$) and falls off continuously in the [001] direction, several conclusions concerning the behavior of the carbonate group can be made. First, the carbonate group is confined to the *ab* plane, rather than being tilted outward. Second, at room temperature the group is not spinning, for this should give rise to a toroid-shaped electron-density high which does not appear. Third, the carbon atom is apparently displaced from (0,0,0) in the *ab* plane. The evidence for this conclusion is based on the fact that a trigonal carbonate group with carbon at the origin and disordered in a four-fold field should give rise to twelve equally spaced peaks, rather than four.

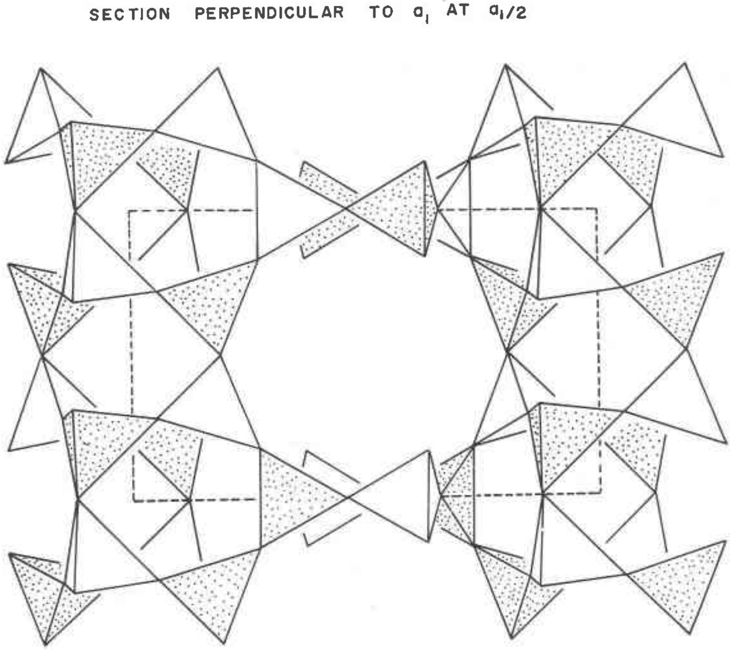

FIG. 4. Hypothetical ordering scheme in end-member meionite. AlO_4 tetrahedra designated by stippling.

These data, therefore, indicate that the carbonate group is disordered in the *ab* plane, taking one of four possible positions in space and time in the scapolite structure (Fig. 6). This interpretation is consistent with the observed electron-density distribution. However, it is possible that the correct solution to the carbonate group problem is beyond the resolution of the x-ray data.

The environment of calcium. Part of the interpretation of the environment of the calcium atom is based on the validity of the interpretation of the carbonate group behavior. Five oxygen atoms in the tetrahedral framework (two O_3', two O_4', and one O_2), together with a sixth oxygen atom of the carbonate group, appear to coordinate calcium in mizzonite. Of the three oxygen atoms in the carbonate group, two are coordinated to one calcium atom each and one oxygen is shared by two calcium atoms, for each one of the four possible orientations of the group (note Fig. 7).

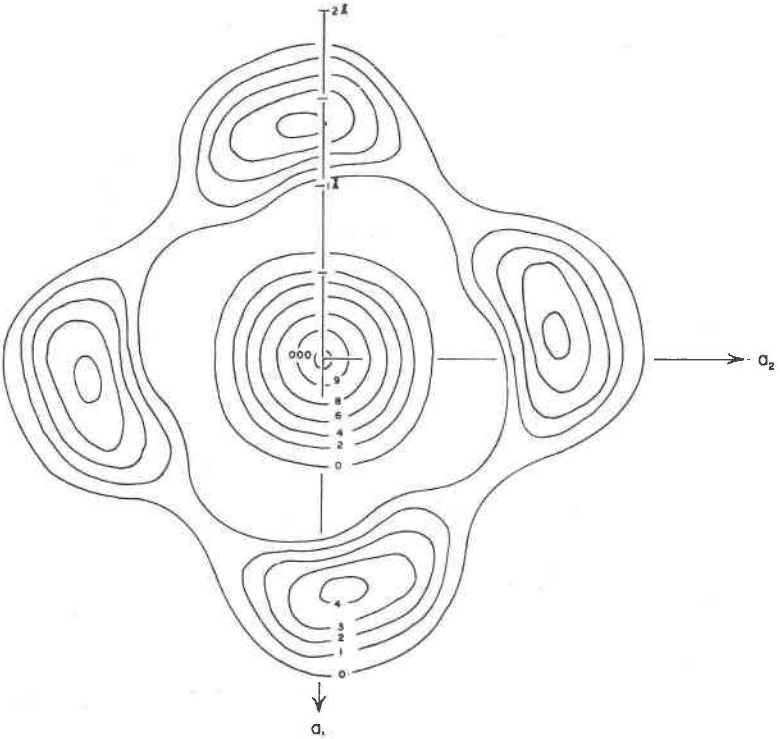

FIG. 5. Portion of electron density $\rho(xy0)$. Contours in electrons per cubic Angstrom.

The main difference between the coordination of calcium in mizzonite and sodium in marialite is that in marialite the sixth atom in the cation-coordination polyhedra is chlorine, while in mizzonite the sixth atom is oxygen (O_5). Both chlorine in marialite and oxygen (O_5) in mizzonite are located in the (001) plane and account for the significant difference between the x, y parameters of sodium in marialite and calcium in mizzonite.

CONCLUSIONS

Results concerning the aluminum distributions in the scapolite solid-solution series and the crystal-chemical role of carbonate in scapolite indicate that the $4/m$ symmetry of scapolites is an average symmetry of the structure as contrasted to a lower short range symmetry consistent with a given aluminum distribution and one of the four possible orientations of the carbonate group. This type of false symmetry in scapolite was recognized by Schiebold and Seumel (1932), who suggested that scapolites consist of submicroscopically twinned aggregates.

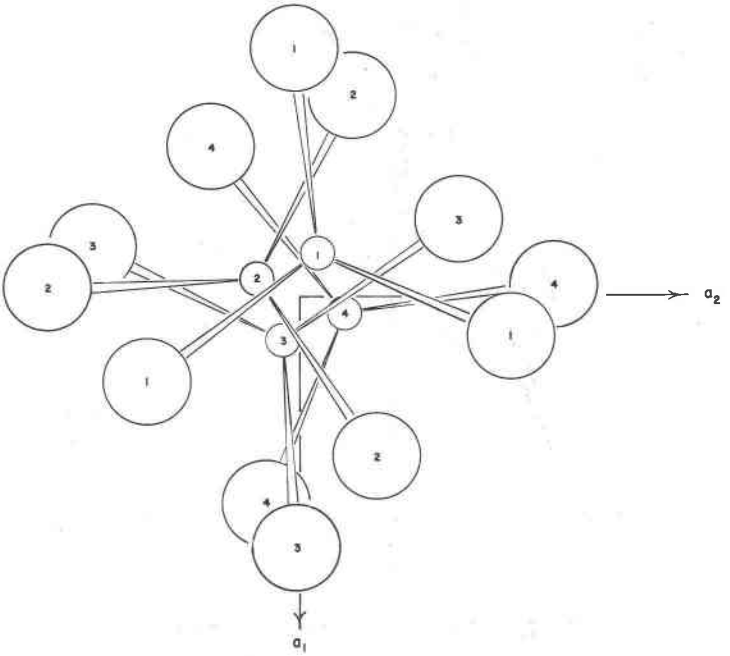

FIG. 6. Suggested interpretation of portion of electron density $\rho(xy0)$.

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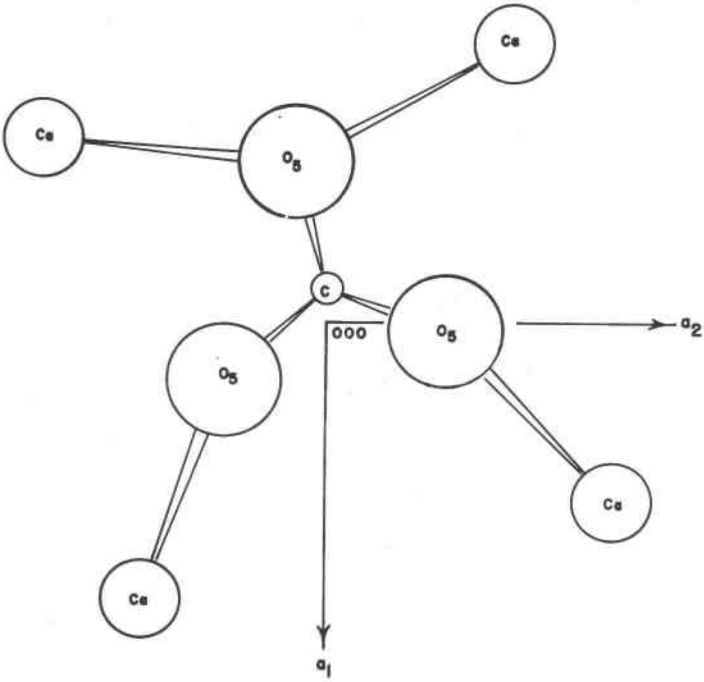

FIG. 7. Environment of calcium in the (001) plane.

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