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THE CRYSTAL STRUCTURE OF A MARIALITE SCAPOLITE

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ABSTRACT

The crystal structure of an 80.6% marialite scapolite, with $a = 12.060$ Å ± .003, $c = 7.572$ Å ± .003, and space group $I4/m$ was determined and refined. Three-dimensional intensities were collected with an equi-inclination, single-crystal diffractometer on a spherical crystal of scapolite from Gooderham, Ontario.

After several unsuccessful attempts at refining the model proposed by Pauling (1930), and Schiebold and Seumel (1932), the three-dimensional Patterson function was computed and solved for an approximation of the structure with the minimum function method. This model was completed and refined by Fourier and least squares methods. The refined structure is similar to that of Pauling and of Schiebold and Seumel, however, most of the atomic coordinates have been shifted substantially.

Average T–O distances are 1.608 Å in the first and 1.665 Å in the second tetrahedron. Comparison with known Si, Al–O distances indicates that Al must be restricted to the second tetrahedral position.

INTRODUCTION

Research on the crystal structure of scapolite was carried out by Gossner and Brückl (1928), Pauling (1930), Schiebold and Seumel (1932), and Scherillo (1935). Among these investigators Pauling was the first to propose a reasonably complete structure model and Schiebold and Seumel to present a complete set of atom coordinates. These two models were essentially identical, and for over thirty years they provided the only structural information on scapolites. Although this structure has now been proven to be correct in its basic features, it did not provide sufficient detail for modern mineralogical research and the need for its refinement was obvious.

The present investigators have undertaken the refinement of the scapolite structure and have selected an 80.6% marialite scapolite from Gooderham, Ontario. This particular scapolite was chosen because: (1) it had been carefully analyzed by Ingamells (quoted by Shaw, 1960), (2) suitable crystals for single crystal work were obtainable from Dr. D. M. Shaw, and (3) it was about as close to the sodium end-member of the series as can be found in nature. This latter criterion was believed to be advantageous since marialite scapolites are known to contain less CO_3 than meionite scapolites and, therefore, are expected to yield fewer structural complications. Determination of the meionite structure and of the position of the carbonate group was postponed to a later stage of the project.

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UNIT CELL AND SPACE GROUP

Preceson photographs of marialite display diffraction symmetry $4/mI^{-}/_{-}$, which is consistent with space groups *I*4, $I\bar{4}$, and *I*4/*m*, where *I*4/*m* is the only one possessing a center of symmetry. In order to determine the presence or absence of a center of symmetry in scapolite, piezoelectric tests have been run by Schiebold and Seumel (1932), Hettich and Steinmetz (1932), Greenwood (1935), and Gibbs and Bloss (1961). The only positive effect was obtained by Greenwood on a crystal from Mogok, Burma. Burley *et al.* (1961) ran a statistical test for centrosymmetry and concluded from the results that their scapolites were centric. The statistical test for centrosymmetry proposed by Wilson (1949) and Howells *et al.* (1950) was carried out using a computer program written by Gorres and Jacobson (1963). Results of this test (Fig. 1) correspond to a centric distribution, and therefore, the most probable space group of the Gooderham scapolite appeared to be *I*4/*m*.

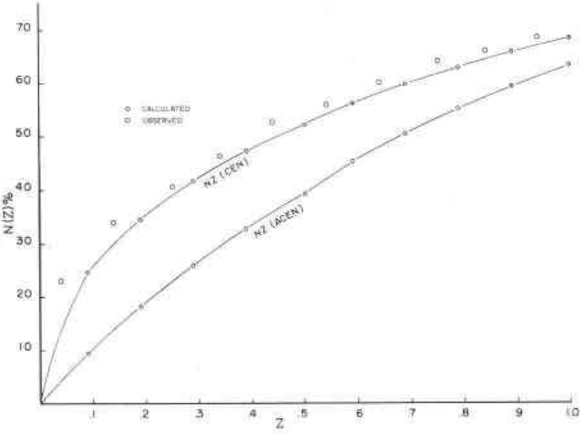

FIG. 1. Acentric-centric statistics

The unit-cell dimensions were determined from carefully prepared Debye-Scherrer photographs and refined with a least squares technique (Britton, 1964). The final cell dimensions obtained are:

$$a = 12.060 \pm .003 \text{ Å}$$
$$c = 7.572 \pm .003 \text{ Å}$$

Using these cell dimensions, the specific gravity of 2.619 (Shaw, 1960), and the chemical analysis of Ingamells (quoted by Shaw, 1960) the unit cell contents were determined by the method described by Hey (1939). The results are shown in Table I.

INTENSITY COLLECTION

A single crystal of the Gooderham marialite was ground into a sphere .179 mm in diameter and oriented with a crystal sphere orienter (Papike *et al.* 1962). A set of three-dimensional intensities was collected by a direct counting method with an equi-inclination single crystal diffractometer equipped with a proportional counter. Values of Υ, ϕ, Sin θ, and 1/LP were calculated using Prewitt's (1960) computer program. The asymmetric unit in reciprocal space for copper radiation contains 684 reflections of which 490 were within the recording range of the apparatus. These intensities were corrected for Lorentz and polarization factors, and for absorption corrections using the tables of Evans (1952).

TABLE 1. UNIT CELL CONTENTS OF GOODERHAM MARIALITE

Cation 1	No. Per Cell	Cation 2	No. Per Cell	Anion 1	No. Per Cell	Anion 2	No. Per Cell
Si Al	16.75 7.37	Na Ca K Mg Fe	5.89 1.49 .43 .01 .02	0	48.03	Cl CO_3 SO_4	1.45 .44 .01
Totals	24.12		7.84		48.03		1.90

TABLE II. APPROXIMATE PEAK WEIGHT FOR SYMMETRIC INTERACTIONS

Interaction	Peak weight
(Na,Ca,K) – (Na,Ca,K)	143
(Si,Al) – (Si,Al)	140
Cl – Cl	440
O – O	81

STRUCTURE ANALYSIS

Initial tests on the validity of the Pauling-Schiebold-Seumel structure model showed rather poor correlation between calculated and observed structure factors. It was decided, therefore, to attempt a complete structure determination.

The three-dimensional Patterson synthesis was computed using a Fortran program written by Mr. Larry Finger. Since the space group in both fundamental and vector space was assumed to be $I4/m$ and the asymmetric unit is 1/16 of the unit cell, the Patterson function was calculated for the range 0-*a*/2, and 0-*c*/4. Sampling intervals of *a*/50 and *c*/40 were used.

Taking into account the unit cell contents listed in Table I, the approximate weights of the Patterson peaks for symmetric interactions can be predicted and are listed in Table II. Since the equipoints of space group *I*4/*m* have ranks 2, 4, 8, and 16, the only atoms which are expected to be in a general position without disordering are (Si, Al) and O. Since the (Si, Al) atom is the heavier of the two, a (Si, Al)–(Si, Al) inversion peak appeared to be the most desirable starting place for the minimum function method (Buerger, 1959). Coordinates for symmetric interactions of an atom in general position for space group *I*4/*m* are:

		Weight
Power Rotation Peaks	2x, 2y, 0	2
Rotation Peaks	x−y, x+y, 0	4
Inversion Peaks	2x, 2y, 2z	1
Reflection Peaks	0, 0, 2z	4

In an attempt to locate an inversion peak, correlation minimum function maps were made by directly superimposing Patterson levels 1/40 to 20/40 on a half scale zero-level map and tracing the minimum of the two maps. Level 17/40 was the only one which showed a strong reflection interaction at 0,0 and its correlation map showed several inversion peak candidates. However, only one of these peaks had the corresponding rotation satellite peaks at the zero level (Fig. 2).

All Patterson maps separated by 17/40 along the *c*-axis were superimposed with appropriate shifts required by the space group symmetry and their minimum function was traced. In this manner a complete set of M_2 maps was constructed. M_4 maps were made by taking the minimum of portions of the M_2 maps related by a 180° rotation. M_8 maps were constructed from M_4 maps by taking the minimum of portions of the M_4 maps related by a 90° rotation. The resulting M_8 maps (Fig. 3) revealed peaks which were assumed to represent 24 (Si,Al) atoms, 8 (Na,Ca,K) atoms, 2 Cl atoms, and 8 oxygen atoms. The remaining 40 oxygen peaks, however, did not appear in the M_8 maps. The reason for this could be a combination of setting the zero line of the Patterson function too high, and of low peak height for the oxygen atoms because of high thermal motion. High thermal motion of oxygen was indicated later in the refinement by high temperature factors for oxygen.

An implication map I4 (xy0) was next prepared (Fig. 4). This map is a projection of an approximation of the structure, with ambiguities on (001) (Buerger, 1959). There are peaks on this map corresponding to all

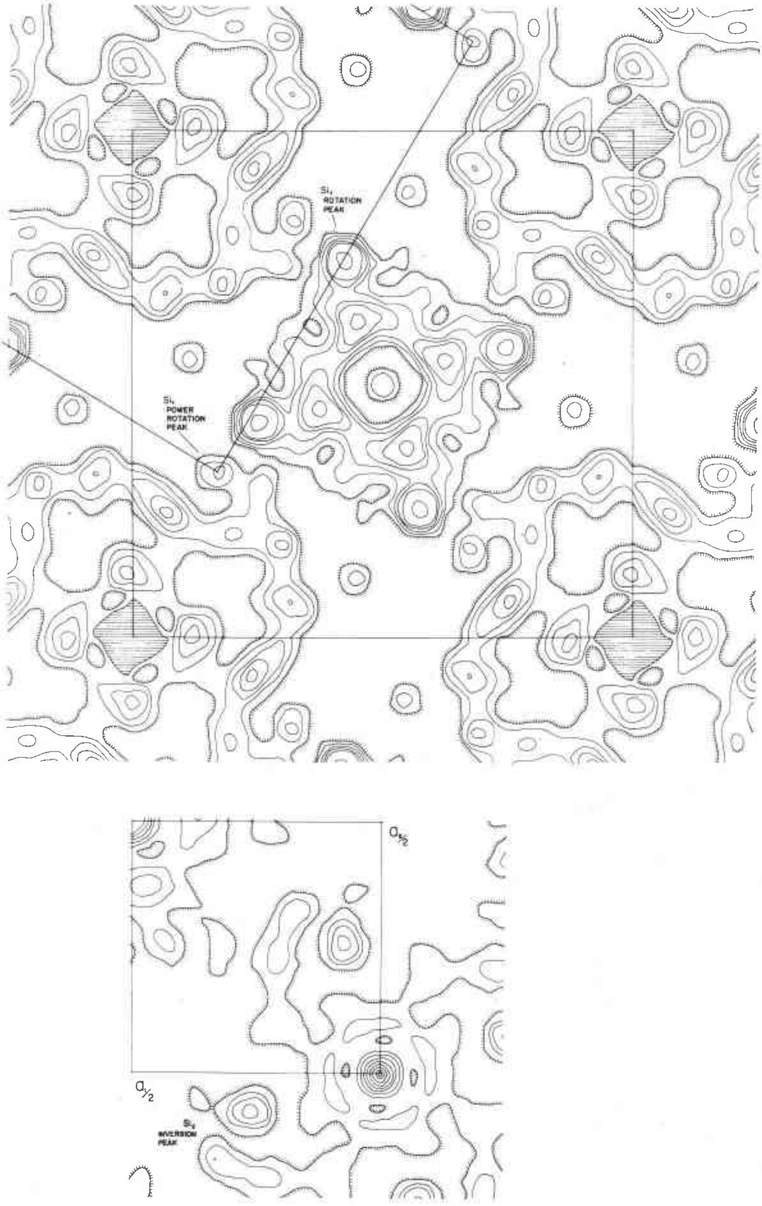

FIG. 2. Patterson maps of levels 0/40 (top) and 17/40 (bottom).

of the peaks of the minimum function analysis, thereby substantiating the trial model.

Using the trial model as revealed by the minimum function, three cycles of Fourier maps were run using a Fourier program written for the Control Data Corporation 1604 computer (Muller and Jacobson, 1963). The first cycle revealed the missing oxygen positions and their coordinates were included for the preparation of a second set of Fourier maps. The R value for this set of maps was 36% for scaled F_{obs} values >20. A third set of Fourier maps was run using the atom coordinates as revealed in the second map set and the corresponding R value decreased to 33%.

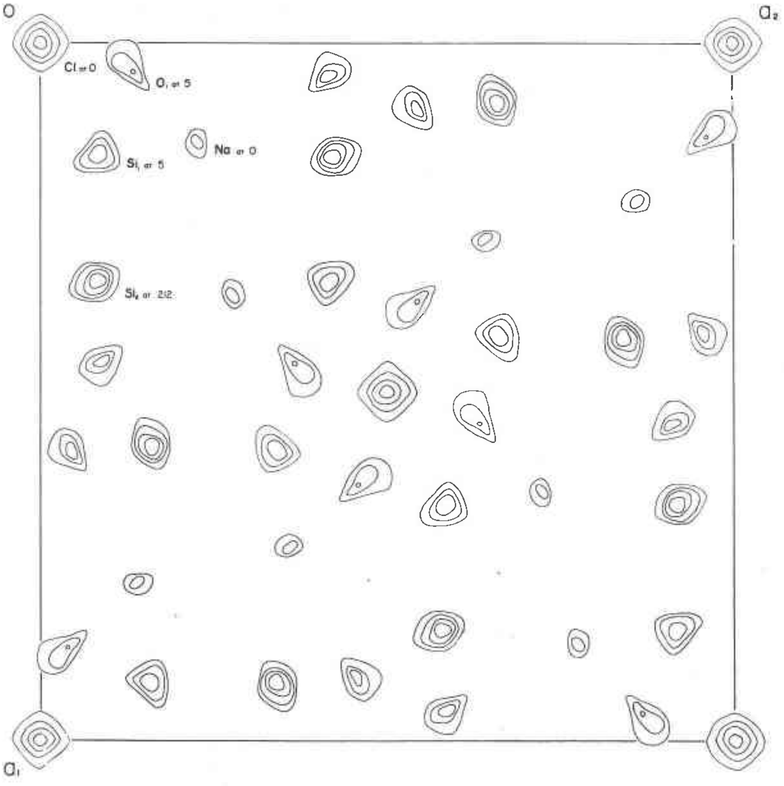

FIG. 3. Composite M_8 map.

Refinement. The coordinates as revealed in the Fourier maps were submitted for eleven cycles of full matrix least squares refinement using a program written for the Control Data 1604 computer by Muller and

Jacobson (1963). The R value dropped to 15.29% for scaled $F_{obs} > 10$. The refinement was continued with all Al assigned to the $(Si,Al)_2$ position and with all reflections included. The R value dropped to 11.97% after 6 additional cycles. A three-dimensional electron-density function was then prepared and a composite projection of it is shown in Fig. 5.

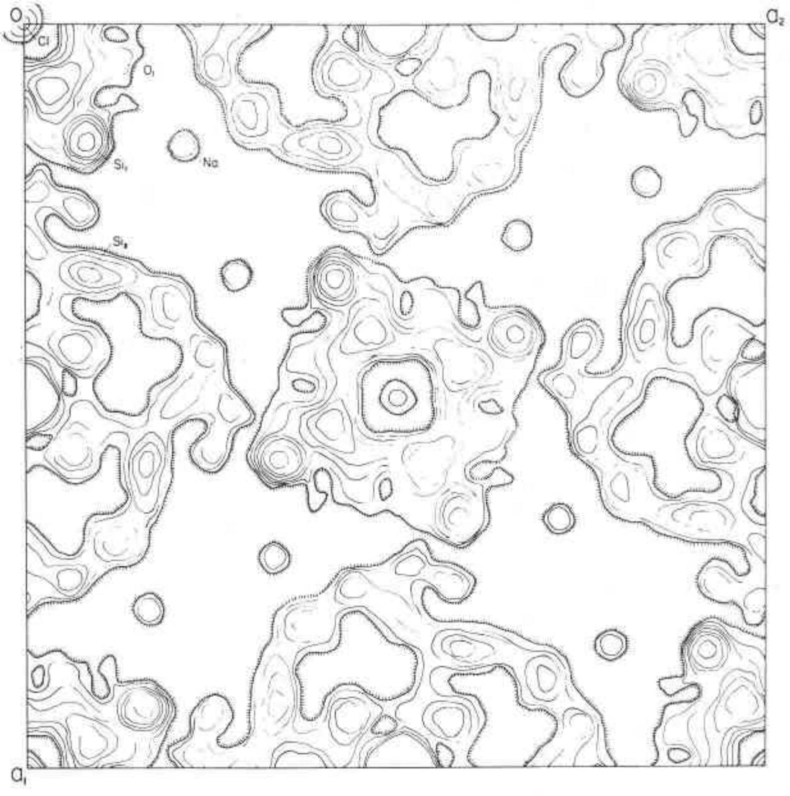

FIG. 4. Implication map 14 (xy0).

The isotropic temperature factor for (Na,Ca,K) was found to be 2.65. This fairly high temperature factor suggested the possibility that Na could be considered as a split atom. This assumption could be justified on crystal chemical grounds since (Na,Ca,K) could be bound to Cl, CO_3, or SO_4 groups, all of which could result in different positions for the (Na,Ca,K) atom. The Na atom was accordingly split into two equal parts with the two halves being placed on opposite sides of the mirror plane. The vertical separation of the two half atoms was .76 Å. The starting isotropic temperature factors were 1.3 for each half. After 6 cycles of full matrix least squares refinement cycles the two half atoms moved back toward the mirror plane and the individual temperature factors increased to >2.

The possibility still remained that some of the atoms did not conform to $I4/m$ symmetry. The refinement was therefore continued with symmetry common to all possible space groups consistent with $4/mI^{-}/_{-}$ symmetry. The origin was shifted from an inversion center so that the B terms of the structure factors would be calculated, six cycles of full matrix least squares were run, and all the atoms retained $I4/m$ symmetry.

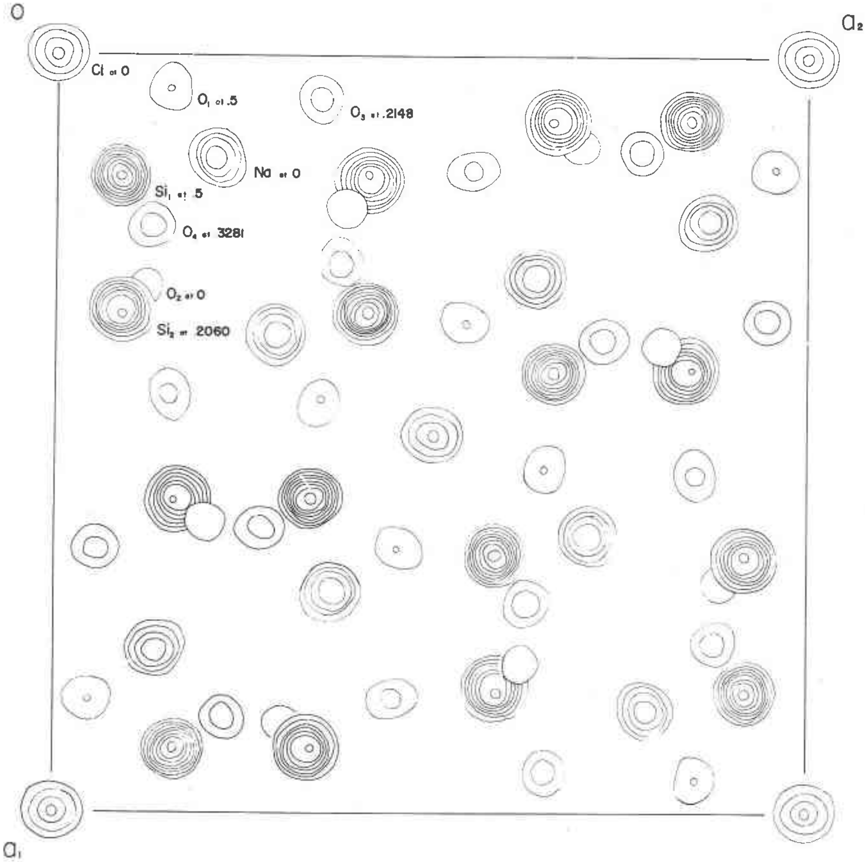

FIG. 5. Electron density composite projection.

Table III. Marialite Atom Coordinates and Temperature Factors

Atom	Coordinate	Schiebold-Seumel (1932)	Total Change	Final	B
Na	X	.13	+0.004	0.1340 ± .0003	2.65
	Y	.23	−0.0187	0.2113 ± .0002	
	Z	0	0	0	
Si_1	X	.334	+0.0048	0.3388 ± .0001	.82
	Y	.409	+0.0014	0.4104 ± .0001	
	Z	0	0	0	
$(Si,Al)_2$	X	.358	+0.0206	0.3374 ± .0001	.76
	Y	.069	+0.0161	0.0851 ± .0001	
	Z	.177	+0.0290	0.2060 ± .0002	
O_1	X	.456	+0.0027	0.4587 ± .0005	1.60
	Y	.350	−0.0017	0.3483 ± .0004	
	Z	0	0	0	
O_2	X	.307	−0.0004	0.3066 ± .0006	2.14
	Y	.093	+0.0276	0.1206 ± .0004	
	Z	0	0	0	
O_3	X	.051	+0.0007	0.0517 ± .0003	1.55
	Y	.353	−0.0030	0.3500 ± .0002	
	Z	.250	−0.0352	0.2148 ± .0006	
O_4	X	.234	−0.0047	0.2293 ± .0003	1.37
	Y	.129	−0.0001	0.1289 ± .0002	
	Z	.323	+0.0051	0.3281 ± .0006	
Cl	X	0	0	0	—
	Y	0	0	0	
	Z	0	0	0	

DISCUSSION OF THE CRYSTAL STRUCTURE

The atomic coordinates and isotropic temperature factors are given in Table III, which also gives the coordinates of the Schiebold-Seumel model, and the R values of both the Schiebold-Seumel model and the refined model are given in Table IV. The refined temperature factors and scale factor were used in calculating the R values for both models.

The important interatomic distances and angles are listed in Table V. This table should be used in conjunction with Fig. 6 for ease in interpretation. Details of the marialite structure are illustrated in Fig. 7.

The structure is best described as a framework of (Si,Al)-O tetrahedra with a spherical opening at the center which is surrounded by four oval shaped channels running parallel to the *c*-axis. The large central opening is occupied by Cl and the vertical channels are occupied by (Na,Ca,K). The framework can be considered to be made up of two types of four-membered rings of tetrahedra which are both parallel to the (001) plane.

TABLE IV. R VALUES FOR MARIALITE

$$r = \frac{(|Fo| - |Fc|)^2}{|Fo|^2} \times 100$$

$$R = \frac{(|Fo| - |Fc|)}{|Fo|} \times 100$$

	Schiebold-Seumel (1932)	Refined
r(HKL)	46.37	2.05
R(HKL)	59.55	11.97
R(HK0)	57.63	9.50
R(HK1)	47.38	10.19
R(HK2)	53.35	9.92
R(HK3)	64.67	13.00
R(HK4)	63.33	13.85
R(HK5)	55.19	13.08
R(HK6)	94.51	17.72
R(0KL)	54.07	8.34
R(1KL)	48.40	10.40
R(2KL)	59.01	12.34
R(3KL)	54.37	10.46
R(4KL)	54.89	11.63
R(5KL)	70.88	13.95
R(6KL)	62.00	10.44

One ring is made of tetrahedra having one edge parallel to the *c*-axis (type 1) while the other four-membered ring is comprised of tetrahedra pointing alternately up and down (type 2). The type 2 rings are joined together into multiple chains running parallel to *c*, and are held together by type 1 rings.

Each (Cl, CO_3, SO_4) atom is coordinated by 4 (Na,Ca,K) atoms, and the Na atoms are coordinated by 1 Cl atom and 5 oxygen atoms. One can easily test Pauling's electrostatic valency principle with respect to the (Na,Ca,K) atoms. Considering chemical substitution and the aluminum distribution in the framework, the negative charge contributions to the (Na,Ca,K) can be considered to be as follows:

TABLE V. SELECTED INTERATOMIC DISTANCES IN MARIALITE

From	To	Multiplicity	Distance Å
Si_1	O_4	2	1.610 ± .004
	O_1	1	1.628 ± .006
	O_1'	1	1.584 ± .006
O_4	O_4	1	2.639 ± .006
	O_1	2	2.630 ± .007
	O_1'	2	2.605 ± .006
O_1	O_1'	1	2.682 ± .008
$(Si,Al)_2$	O_3	1	1.660 ± .004
	O_3'	1	1.660 ± .004
	O_2	1	1.660 ± .003
	O_4	1	1.682 ± .004
O_2	O_4	1	2.655 ± .005
	O_3'	1	2.691 ± .006
	O_3	1	2.776 ± .006
O_3	O_4	1	2.671 ± .005
	O_3'	1	2.757 ± .004
O_4	O_3'	1	2.757 ± .005
(Na,Ca,K)	Cl	1	3.018
	O_4	2	2.849
	O_2	1	2.352
	O_3'	2	2.535

Si-O-Si Angles

Atoms	Bond Angle
Si_1-O_4-Si_2	138.3°
Si_1-O_1-Si_1	156.8°
Si_2-O_3-Si_2	139.0°

TABLE VI. MEAN Al-O DISTANCES

(Smith and Bailey, 1963)

Mineral	Mean Al-O Distance Å
Maximum microcline (Pellotsalo)	1.741
Maximum microcline (Pontiskalk)	1.734
Primitive anorthite	1.749
Low albite	1.744
Natrolite	1.747
Gismondine	1.735
Cordierite	1.747

$$\begin{array}{lcr} (\mathrm{Cl}, \mathrm{CO_3}, \mathrm{SO_4}) & = & -.291 \\ \mathrm{O_4}\ 2\mathrm{x}(-.114) & = & -.228 \\ \mathrm{O_3}\ 2\mathrm{x}(-.228) & = & -.456 \\ \mathrm{O_2} & = & \underline{-.228} \\ & & -1.203 \end{array}$$

This negative charge compares favorably with a +1.170 for the (Na,Ca,K) ion.

The average (Si,Al)-O bond lengths of the two types of tetrahedra are:

Type 1 (Si, Al)-O = 1.608 Å
Type 2 (Si, Al)-O = 1.665 Å

Comparison with known (Si,Al)-O distances (Smith and Bailey, 1963) indicates that Al must be restricted to the second tetrahedral position. Assuming that all Al is in the $(\mathrm{Si,Al})_2$ position and is disordered within

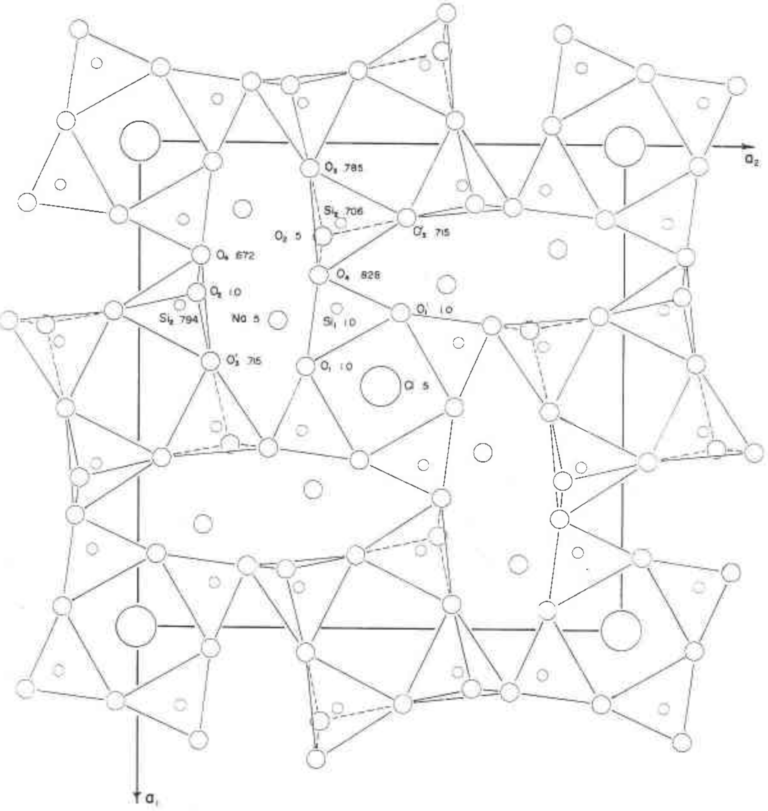

FIG. 6. Projection of the crystal structure of marialite.

the type 2 rings, each tetrahedron contains on the average 46% Al based on the calculated unit cell contents. This ordering scheme makes available two points on a plot of % Al in a tetrahedron versus average T-O distance (Fig. 8). If the relation between mean T-O distance and % Al in a tetrahedron is linear as has been implied for the feldspars (Smith and Bailey, 1963), the extrapolation to 100% Al gives a theoretical mean T-O distance for a pure AlO_4 of 1.732 Å. The same type of extrapolation for the feldspars gives 1.75 Å, and mean Al-O distances determined for ordered structures are given in Table VI. As compared with other reported mean Al-O distances the value of 1.732 Å appears a little low, however, with more structure determinations in the scapolite group the significance of this number can be more fully assessed.

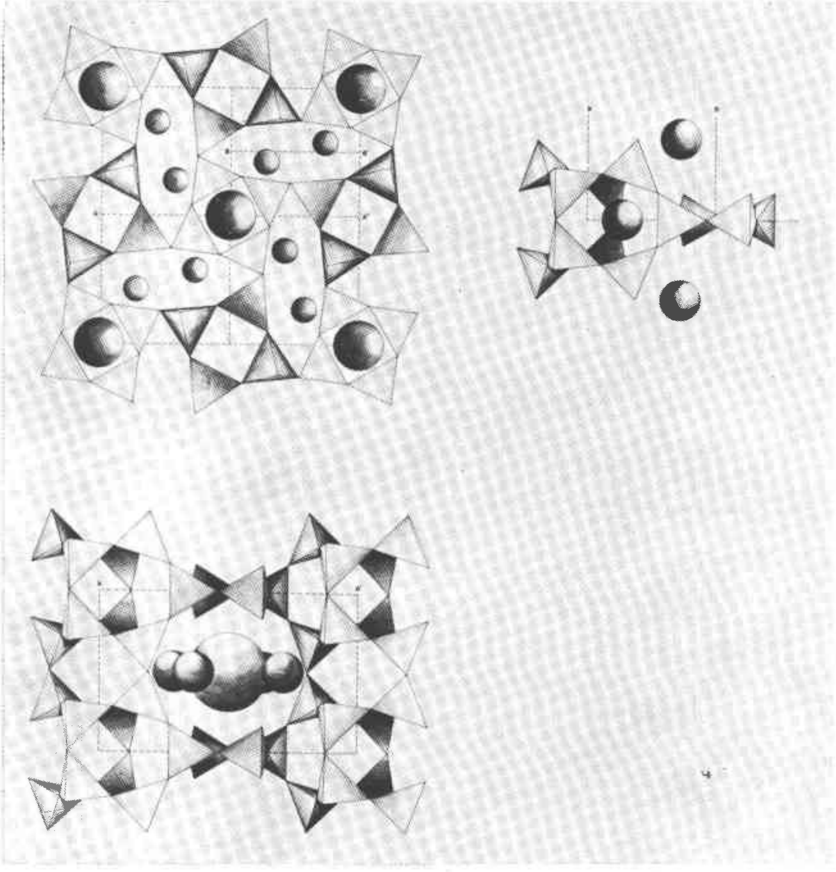

FIG. 7. The crystal structure of marialite.

The question remains as to what is responsible for the Al concentration in the $(Si,Al)_2$ position. There appears to be an obvious explanation for ordering of this type for the composition and space group in question. The chlorine atom is symmetry-fixed at 0, 0, 0 and ½, ½, ½, and the Na atom would also be expected to be at $z = 0$ and $z = 1/2$. From the standpoint of electrical neutrality, therefore, the aluminum would be expected to be concentrated in the type 2 tetrahedra which are closer to the Na atoms. This should be true even if the bonds are only partially ionic in nature.

The 80.6% marialite scapolite used in this structure analysis was chosen partly because of its low CO_3 content. Nevertheless, approximately ¼ of the central opening could be occupied by carbonate groups for the composition in question, and this is evidenced by Fourier difference maps. However, the peak heights and distribution in these maps were not well enough defined for any definite conclusions concerning the structural role of CO_3. Structural work on high carbonate scapolites is expected to throw light on this problem.

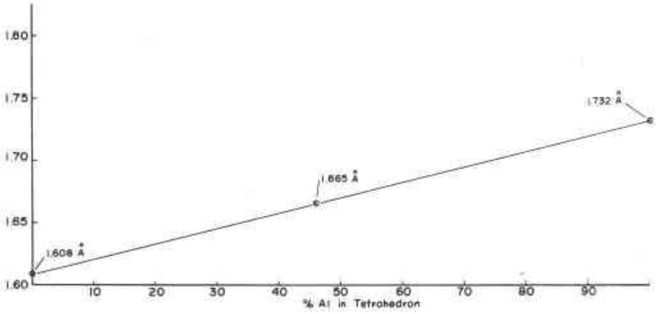

FIG. 8. Aluminum tetrahedral occupancy.

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