

substrats et stabiliser des formes 'actives' légèrement différentes de celles trouvées par les méthodes de calcul conformationnel pour le cation isolé.

Nous retiendrons donc de notre comparaison l'existence à l'état solide d'une torsion préférentielle  $\varphi_4$  de  $-50$  à  $-75^\circ$ , les autres angles étant beaucoup plus variables.

#### Relations intermoléculaires

La chaîne contient deux atomes d'hydrogène particulièrement liants, H(35) et H(36) fixés sur l'azote quaternaire. D'autre part celui de l'hydroxyle, H(31), est souvent actif.

Dans le propranolol, l'alprénolol et l'éphédrine, tous trois forment des liaisons avec l'anion  $\text{Cl}^-$ . Dans l'isoprénaline, le groupement quaternaire se lie soit à l'anion  $\text{SO}_4^{2-}$ , soit aux groupements  $-\text{OH}$  phénoliques tandis que les groupements hydroxyle fixés sur C(13) sont en relation avec l'anion, l'eau d'hydratation ou un autre hydroxyle. Enfin dans la noradrénaline, le groupement quaternaire est lié à l'anion  $\text{Cl}^-$ .

Entre les noyaux aromatiques hydrophobes les interactions sont généralement faibles mais dans les catécholamines, les hydroxyles des radicaux  $-\text{C}_6\text{H}_3(\text{OH})_2$  sont souvent en relation avec l'anion (interactions de type  $\text{O} \cdots \text{H}-\text{N}$  et  $\text{O}-\text{H} \cdots \text{Cl}^-$ ).

#### Conclusion

Nous constatons que dans les cristaux, ces molécules forment toujours des liaisons avec des centres négatifs grâce au groupement quaternaire  $>\text{NH}_2^+$  et quelques fois grâce au groupement hydroxyle  $-\text{OH}$ . Il est possible, en milieu biologique, que les mêmes interactions interviennent entre ces molécules et leurs récepteurs adrénergiques.

De même, il est possible que la torsion préférentielle  $\varphi_4$  ( $50$  à  $75^\circ$ ), relativement stable dans les cristaux, soit caractéristique de la (ou d'une) conformation active vis à vis des récepteurs mis en jeu.

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## Crystal Structure of a Sodium and Chlorine-Rich Scapolite

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The crystal structure of scapolite with composition 19.4% Me, and  $a = 12.059$  (1) and  $c = 7.587$  (2) Å, has been refined in a newly determined space group,  $P4_2/n$ . The three-dimensional intensities were collected with an integrated precession camera using Zr-filtered Mo radiation. The structure has been completed by Fourier methods and refined by full-matrix least-squares calculations. The refined structure turned out to be similar to that previously reported but has a different symmetry with significant differences in the Al distribution and the coordinates of some sites, especially the (Na, Ca) site. The refined structure also has a lower  $R$  (7.4%) index. Average (Si, Al)-O distances are 1.608 Å in the T(1) tetrahedron, 1.693 Å in the T(2) tetrahedron and 1.651 Å in the T(3) tetrahedron, thus indicating that more Al atoms go into the T(2) than T(3) sites, but no Al atom enters the T(1) sites. The average position of the (Na, Ca) site is off the mirror plane present in the space group  $I4/m$ . The (Na, Ca) site is shown to be 8-coordinated rather than 6-coordinated as previously reported. The  $\text{CO}_3$  groups have the same horizontal disordered disposition as in meionite-rich scapolites, but in this Na, Cl-rich crystal they have a wider range of vertical disposition, suggesting that some of the planar  $\text{CO}_3$  groups tilt from the (001) plane. The present study shows that this sodium, chlorine-rich scapolite really has a distorted, pseudo body-centred structure.

#### Introduction

The natural scapolites form a solid-solution series between the two theoretical end-members,  $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$  (marialite) and  $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$  (meionite). The index of chemical composition, at. % Me, has been de-

finied as  $100(\text{Ca} + \text{Sr} + \text{Fe} + \text{Mn} + \text{Mg})/(\text{Na} + \text{K} + \text{Ca} + \text{Sr} + \text{Fe} + \text{Mn} + \text{Mg})$  and the nomenclature is accepted as marialite,  $\text{Me}_0\text{-Me}_{20}$ ; dipyre,  $\text{Me}_{20}\text{-Me}_{50}$ ; mizzonite,  $\text{Me}_{50}\text{-Me}_{80}$ ; meionite,  $\text{Me}_{80}\text{-Me}_{100}$  (Shaw, 1960; Deer, Howie & Zussman, 1963). This paper is an attempt to refine the crystal structure of a natural scapo-

lite approximating most closely to the idealized end-member marialite, in a newly determined space group.

The structures suggested by Gossner & Brückl (1928), Pauling (1930), Schiebold & Seumel (1932), and Scherillo (1935) do not differ greatly. Using the space group  $I4/m$  Papike & Zoltai (1965) determined the crystal structure of a scapolite (ON8; 19.4% Me) identical to that used in this study. Their refined structure was similar to that of Schiebold & Seumel, with a maximum shift of 0.0352 Å, or an r.m.s. shift of 0.0153 Å in the atomic coordinates and an  $R=11.97\%$ . Later, Papike & Stephenson (1966) refined the crystal structure of another scapolite (M730; 70.1% Me) in the space group  $I4/m$ . This refined structure is basically the same as that of marialite (ON8; 19.4% Me) with differences in the Al distribution and an  $R=15.7\%$ . However, problems regarding the high  $R$  value (15.7%) and the negative temperature factor for the disordered

(Si,Al) site reported, the presence of weak reflexions violating body-centred symmetry, the (Si,Al) ordering scheme, *etc.*, still remain unresolved.

Specimen ON8 (19.4% Me) from Gooderham, Ontario, Canada, actually has the space group  $P4_2/n$ , because of the presence of weak reflexions of type  $h+k+l=\text{odd}$  (Lin, 1971; Lin & Burley, 1971). It was therefore decided to refine its structure in the new space group. This particular scapolite is important because: (i) it appears to be one of the most Na, Cl-rich scapolites reported (Deer, Howie & Zussman, 1963); thus it is closest to the theoretical marialite end-member ( $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ ); (ii) the crystal structure of this scapolite has previously been studied by Papike & Zoltai (1965) in the space group  $I4/m$ , so that their structure is a useful starting model for the refinement in the newly determined space group  $P4_2/n$ ; (iii) the chemical composition, optical properties and geological occurrence of this specimen have previously been described by Shaw (1960), so that the specimen is well characterized.

#### Data collection

The unit-cell contents were determined by using the unit-cell dimensions  $a=12.059$  (1),  $c=7.587$  (2) Å (Lin, 1971) and the chemical analysis and specific gravity of 2.619 (Shaw, 1960). The cell contents of specimen ON8 are  $(\text{Na}_{5.76}\text{Ca}_{1.67}\text{K}_{0.42}\text{Fe}_{0.002}\text{Mn}_{0.005}\text{Sr}_{0.002})(\text{Si}_{16.68}\text{Al}_{7.35})\text{O}_{48.55}[\text{Cl}_{1.45}(\text{SO}_4)_{0.007}(\text{CO}_3)_{0.44}]$ .

A single crystal was ground into a sphere with an approximate diameter of 0.5 mm. The X-ray diffraction intensities were collected by integrated Buerger's precession film techniques, using Zr-filtered Mo  $K\alpha$  radiation. The  $hk0$  level and the  $hkl$  levels from  $h=0$  through  $h=6$  were photographed to give 1255 total reflexions. Of these, the unobserved reflexions were assigned values of  $I_{\text{min}}/3$  (Hamilton, 1955). These photometrically measured intensities were then corrected for Lorentz and polarization effects and converted into unscaled  $|F_{\text{obs}}|$ . No absorption correction was made, because the transmission factor is not significantly affected by the reflexion angle  $\theta$  (Evans & Ekstein, 1952).

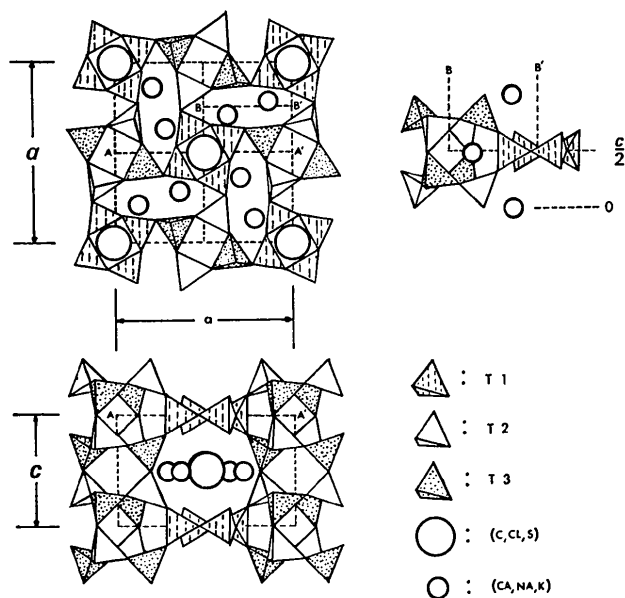


Fig. 1. The crystal structure of marialite (19.4% Me; Gooderham, Ontario).

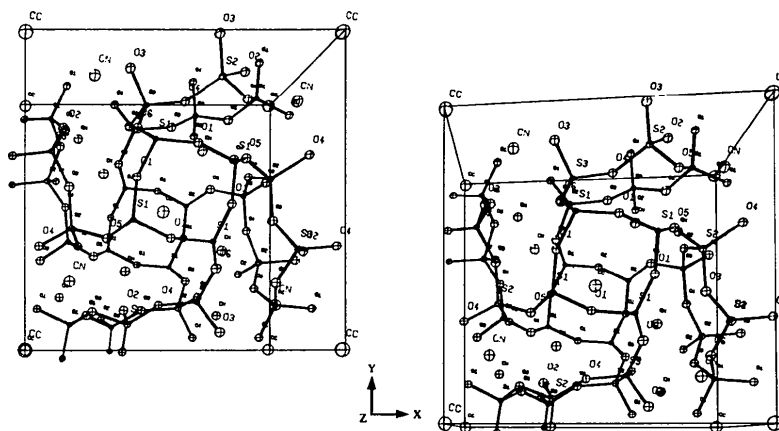


Fig. 2. A stereographic projection of the crystal structure of scapolites, where CC=(C,Cl), CN=(Ca,Na), S=(Si,Al).

## Refinement

The structure refinement was carried out by using a full-matrix least-squares program (*ORFLS*) contained in the X-RAY 67 program system for X-ray crystal-

Table 1. Atomic coordinates and temperature factors of marialite (19.4% Me; Gooderham, Ontario)

Papike & Zoltai (1965)		Present study	
	Parameters		Parameters
Na(1)	X 0.3660 (3) Y 0.2887 (2) Z 0.5 B 2.65	(Na, Ca) (1)	X 0.3659 (3) Y 0.2884 (3) Z 0.5064 (4) B 2.68 (6)
Cl(1)	X $\frac{1}{2}$ Y $\frac{1}{2}$ Z $\frac{1}{2}$ B -	(Cl, C) (1)	X $\frac{1}{2}$ Y $\frac{1}{2}$ Z $\frac{1}{2}$ B 3.85 (12)
Si(1)	X 0.3388 (1) Y 0.4104 (1) Z 1.0 B 0.82	Si(1)	X 0.3390 (1)] Y 0.4100 (1) Z 0.9989 (3) B 0.69 (3)
(Si, Al) (2)	X 0.6626 (1) Y 0.9149 (1) Z 0.7940 (2) B 0.76	(Si, Al) (2)	X 0.6621 (2) Y 0.9152 (2) Z 0.7956 (2) B 0.79 (4)
(Si, Al) (2')	X 0.4149 (1) Y 0.8374 (1) Z 0.7060 (2) B 0.76	(Si, Al) (3)	X 0.4145 (2) Y 0.8368 (2) Z 0.7085 (2) B 0.63 (4)
O(1)	X 0.4587 (5) Y 0.3483 (4) Z 0 B 1.60	O(1)	X 0.4574 (4) Y 0.3511 (4) Z 0.0011 (7) B 1.39 (8)
O(2)	X 0.6934 (6) Y 0.8794 (4) Z 0 B 2.14	O(2)	X 0.6939 (4) Y 0.8797 (4) Z 0.0048 (7) B 1.25 (7)
O(3)	X 0.3500 (2) Y 0.9483 (3) Z 0.7852 (6) B 1.55	O(3)	X 0.3486 (6) Y 0.9448 (5) Z 0.7898 (6)] B 1.48 (10)
*O(3')	X 0.5517 (3) Y 0.8500 (2) Z 0.7148 (6) B 1.55	O(4)	X 0.5499 (5) Y 0.8475 (6) Z 0.7163 (6) B 1.49 (10)
O(4)	X 0.2707 (3) Y 0.3711 (2) Z 0.8281 (6) B 1.37	O(5)	X 0.2706 (5) Y 0.3699 (5) Z 0.8277 (6) B 1.30 (9)
O(4')	X 0.3711 (1) Y 0.7293 (3) Z 0.8281 (6) B 1.37	O(6)	X 0.3710 (6) Y 0.7282 (6) Z 0.8270 (7) B 1.47 (10)
-	-	O(7)	X 0.3833 (63) Y 0.4817 (64) Z 0.5012 (101) B 4.01 (1.28)
R index	11.97 %	R index	7.4 %

\* Note that in the case of Papike & Zoltai (1965), (Si, Al) (2'), O(3') and O(4') are symmetrically equivalent to (Si, Al) (2), O(3) and O(4) respectively.

lography (Kundell, Chastain & Stewart, 1967). The scattering factor curves used were as follows: Na<sup>1+</sup>, K<sup>1+</sup>, Ca<sup>2+</sup>, Si<sup>0</sup>, Al<sup>0</sup>, Cl<sup>1-</sup>, C<sup>2+</sup> and O<sup>1-</sup> (*International Tables for X-ray Crystallography*, 1962).

Scapolite is composed of a (Si, Al)-O tetrahedral framework having a round cavity at the centre of the unit cell. The central spherical cage is open to and surrounded by four oval-shaped channels running vertically (*i.e.* ||*c* axis) and contains the large anions (Cl, CO<sub>3</sub>, SO<sub>4</sub>), while the surrounding vertical channels contain the cations (Na, Ca, K) (*cf.* Fig. 1).

Refinement was initiated using the model of Papike & Zoltai (1965), but the atomic coordinates were transformed into a set of values based on the new space group *P4<sub>2</sub>/n* with origin at  $\bar{1}$  at  $\frac{1}{2}, \frac{1}{4}, \frac{1}{4}$  from  $\bar{4}$ . As shown in Table 1, some atoms are disordered on the same sites and all atomic sites except the site of (Cl, C) are of the general site. The temperature factor of Cl was assumed to be 2.0, since it was not included in the model of Papike & Zoltai (1965) and it was expected to be high owing to the probable disordering of Cl and C atoms.

In the first two cycles of refinement, only the scale factors assigned for each level of reflexion data were refined, giving an *R* value ( $\sum ||F_o| - |F_c|| / \sum |F_o|$ ) of 14.9%. During the earlier stages of refinement, the unobserved reflexions were ignored and all the weights of reflexions were assigned as unity. Refinement was continued for three more cycles allowing atomic coordinates to vary in addition to scale factors, and the *R* value dropped to 13.6%. After three additional cycles of refinement during which scale factors, atomic coordinates and isotropic temperature factors were varied, the *R* value dropped to 8.6% and the result showed that a considerable change of temperature factors had occurred, *e.g.* that of Cl from 2.0 to 4.93. The isotropic temperature factors of all Si atoms and O atoms came within the normal range.

Subsequently, a new scattering curve of  $0.77f_{Cl^-} + 0.23f_{Ca^{2+}}$  was prepared to replace the scattering curve of Cl<sup>-</sup> to conform with the presumed disordered site occupancy, and three more cycles of refinement were executed; the *R* value dropped to 8.0% and the temperature factor of the disordered (Cl, C) site was reduced from 4.93 to 3.78. Similarly, a new scattering curve of  $0.8f_{Na^+} + 0.2f_{Ca^{2+}}$  was used for the disordered (Na, Ca) site and three cycles of refinement were run; the *R* value then dropped to 7.7% and the only prominent change was the isotropic temperature factor of the (Na, Ca) site which increased from 1.55 to 2.28. At this stage, the dimensions of the three (Si, Al) tetrahedra were calculated using the *BONDLA* program contained in the X-RAY 67 program. Using the mean T-O bond length for each tetrahedron and a curve prepared by Smith & Bailey (1963), the Al occupancy of each site was estimated. The results indicate that the T(1) tetrahedron is Al-free, and T(2) and T(3) tetrahedra are partly occupied by Al atoms. Using the estimated occupancy of Al and Si among these three

equipoints, three additional least-squares cycles were run, and the  $R$  value converged at 7.6%.

Finally, the unobserved reflexions were included and a modified Cruickshank weighting scheme was applied, of the type  $w = 1/(A + B \cdot F_o + C \cdot F_o^2)$  where the coefficients  $A$ ,  $B$  and  $C$  are all determined by least-squares methods. Then, following five more cycles in which all scale factors, positional and isotropic thermal parameters were varied, the  $R$  value finally stayed at 7.5%. However, a number of parameters were re-adjusted. Both Fourier syntheses  $q(xyz)$  and difference syntheses  $\Delta p(xyz)$  using the parameters from the last refinement cycle showed four elongated peaks around the (Cl,C) atom with a slim maximum on the (001) plane. These four peaks are formed by positional disordering of oxygen atoms of the  $\text{CO}_3^{2-}$  group (see Papike & Stephenson, 1966). The coordinates of these four peaks (Fig. 6) were used as starting parameters and included in the continued refinement. After two additional cycles in which scale factors, atomic coordinates and isotropic temperature factors were allowed to vary, the  $R$  value was lowered to 7.4% and all parameters remained unchanged within the standard deviations. The final, parameters are listed in Table 1. A table of observed and calculated structure factors is available\*.

### Discussion

In order to be consistent with previous descriptions of scapolite crystal structures, the final, refined param-

\* The table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30074. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

eters have been transformed into those based on the origin at  $\bar{4}$ . The refined model is compared with that based on the space group  $I4/m$  (Papike & Zoltai, 1965) in Table 1. As expected, the difference between the ideal structure ( $I4/m$ ) and the pseudosymmetric structure ( $P4_2/n$ ) is small (Vousden, 1954; Lin, 1971; Lin & Burley, 1971). Comparison of the two models in Table 1 shows that the  $x$  and  $y$  coordinates of most atoms are essentially the same, while the  $z$  coordinates have a small but significant difference compared with the standard deviation  $\sigma$ , especially those atoms located on the mirror plane in the space group  $I4/m$ , e.g. Na(1), Si(1), and O(2) atoms (Papike & Zoltai, 1965). These atoms migrate from the mirror plane as discussed elsewhere (Lin, 1971). Temperature factors are also re-adjusted.

The pseudo body-centered structure of this Na, Cl-rich scapolite is illustrated in Fig. 1 and its details are better presented by the stereographic drawing (Fig. 2) plotted by using the program *ORTEP* (Johnson, 1965). The (Si,Al) $\text{O}_2$  framework is still composed of two types of four-membered rings of (Si,Al)-O tetrahedra which are both parallel to the (001) plane. However, the (type 1) ring has only T(1) tetrahedra having one edge nearly parallel to the  $c$  axis but (Si,Al) atoms of alternate tetrahedra are above and below the (001) plane. The (type 2) ring has T(2) and T(3) tetrahedra, pointing alternately up and down. In the  $I4/m$  structure these two tetrahedra are equivalent. The (type 2) rings are connected vertically into multiple chains running parallel to the  $c$  axis and are held laterally by (type 1) rings.

The important interatomic distances and angles are listed in Tables 2(a), (b) and 3. Using the average (Si,Al)-O bond lengths of the three types of tetrahedra

Table 2. *Interatomic distances in marialite* (19.4% Me, ON8, Gooderham, Ontario)

(a) (Si,Al)-O and O-O distances in tetrahedra

Tetrahedron	Atoms	T-O distance (Å)		Atoms	O-O distance (Å)	
		Multiplicity	Distance		Multiplicity	Distance
T(1)	O(1)	1	1.594 (5)	O(1)-O(5)	1	2.618 (8)
	O(5)	1	1.612 (6)	O(1)-O(1')	1	2.642 (7)
	O(1')	1	1.607 (5)	O(1)-O(6')	1	2.601 (8)
	O(6')	1	1.619 (6)	O(1')-O(5)	1	2.640 (8)
	Average		1.608 (5)	O(1')-O(6')	1	2.635 (8)
T(2)	O(2)	1	1.688 (5)	O(5)-O(6')	1	2.620 (7)
	O(4)	1	1.690 (7)	Average		2.626 (8)
	O(3')	1	1.693 (7)	O(2)-O(4)	1	2.820 (8)
	O(5')	1	1.699 (6)	O(2)-O(3')	1	2.720 (8)
	Average		1.693 (6)	O(2)-O(5')	1	2.689 (7)
T(3)	O(3)	1	1.646 (7)	O(4)-O(5')	1	2.695 (9)
	O(4)	1	1.639 (7)	O(4)-O(3')	1	2.842 (9)
	O(6)	1	1.673 (7)	O(3')-O(5')	1	2.802 (8)
	O(2')	1	1.644 (5)	Average		2.761 (8)
	Average		1.651 (6)	O(3)-O(4)	1	2.754 (9)
				O(3)-O(6)	1	2.642 (9)
				O(3)-O(2')	1	2.760 (8)
				O(4)-O(6)	1	2.726 (9)
				O(4)-O(2')	1	2.653 (8)
				O(6)-O(2')	1	2.621 (7)
				Average		2.693 (8)

Table 2 (cont.)

(b) Selected interatomic distances

Type	From	To	Multiplicity	Distance (Å)
(Na, Ca, K) coordination polyhedron	(Ca, Na, K)	O(2')	1	2.350 (6)
		O(3')	1	2.516 (7)
		O(4')	1	2.500 (7)
		O(5')	1	2.868 (6)
		O(5'')	1	2.817 (7)
		O(6')	1	2.882 (7)
		O(6'')	1	2.945 (6)
		O(7)	0.24	2.289 (76)
		Cl(1')	0.76	2.85*
		Central anion cage diagonals	O(1)	O(1')
	O(5)	O(6')	4	8.055 (8)
	O(2')	O(2'')	2	7.933 (7)

\* The 3.021 Å distance of (Na, K, Ca) (1)–Cl(1) directly calculated from the mean positions of these two substitutionally and positionally disordered sites is actually the overall mean distance between the atoms involved. The (Na, K, Ca) (1) is actually not coordinated to the Cl atom but to O(7) of the CO<sub>3</sub> radical. The sum of (Na, K, Ca) (1)–O(7) and O(7)–Cl(1) is normally much larger than (Na, K, Ca) (1)–Cl(1). Furthermore, the former two distances are semiparallel to the latter one. Therefore, (Na, K, Ca) (1)–Cl(1) is in fact shorter than the above 3.021 Å and is approximately estimated to be 2.85 Å, which is quite close to its normal distance for this crystal.

[Table 2(a)] and the curve of Smith & Bailey (1963), the Al, Si occupancy of each tetrahedral site was estimated as follows: T(1) (0% Al, 100% Si); T(2) (59% Al, 41% Si); T(3) (29% Al, 71% Si). It is unknown whether Al–O–Al linkages are formed in this scapolite; however, with these site occupancies the so-called unstable Al–O–Al linkage (Loewenstein, 1954) can be avoided. The Al content in the unit cell derived from the crystal structure analysis was found to be 7.10 atoms per unit cell, which is consistent with the unit-cell content of 7.35 Al atoms, determined by chemical analysis. Applying the statistical method used by Smith & Bailey (1963) and Papike & Zoltai (1965), a plot of % Al in a tetrahedron *versus* average T–O distance (average of the tetrahedral bonds) (Fig. 3) can be constructed by using two available points:

(1) Average distance of T(1)–O:

$$[(\text{Si}_{1.0}\text{Al}_{0.0})\text{-O}] = 1.608 \text{ \AA}.$$

(2) Average distance of T(2)–O and T(3)–O

$$[(\text{Si}_{0.54}\text{Al}_{0.46})\text{-O}] = 1.672 \text{ \AA}.$$

The linear extrapolation to 100% Al gives a theoretical mean T–O distance for a pure AlO<sub>4</sub> tetrahedra of 1.748 Å which is significantly longer than 1.732 Å given by Papike & Zoltai (1965) for the same scapolite. The same type of extrapolation for the feldspars gives 1.750 Å (Smith & Bailey, 1963). This suggests that the T–O bond in scapolites behaves similarly to the T–O bond in feldspars.

In the real, pseudo body-centred structure of this scapolite the coordination polyhedra are more distorted than those in its ideal, body-centred structure.

Table 3. Interatomic angles in marialite (19.4% Me, Gooderham, Ontario)

Type	Atoms		
O–T(1)–O	O(1)–T(1)–O(5)	109.43 (31)°	
	O(1)–T(1)–O(1')	111.22 (28)	
	[T(1) tetrahedra]	O(1)–T(1)–O(6')	108.04 (31)
		O(5)–T(1)–O(1')	110.20 (31)
		O(5)–T(1)–O(6')	108.35 (32)
O–T(2)–O	O(1')–T(1)–O(6')	109.52 (31)	
	O(2)–T(2)–O(4)	113.23 (28)	
	O(2)–T(2)–O(3')	107.08 (26)	
	[T(2) tetrahedra]	O(2)–T(2)–O(5')	105.13 (28)
		O(4)–T(2)–O(3')	114.30 (34)
O–T(3)–O	O(4)–T(2)–O(5')	105.38 (31)	
	O(3')–T(2)–O(5')	111.40 (33)	
	O(3)–T(3)–O(4)	113.93 (35)	
	O(3)–T(3)–O(6)	105.47 (32)	
	[T(3) tetrahedra]	O(3)–T(3)–O(2')	114.03 (29)
T–O–T	O(4)–T(3)–O(6)	110.78 (34)	
	O(4)–T(3)–O(2')	107.79 (27)	
	O(6)–T(3)–O(2')	104.41 (29)	
	T(1)–O(1)–T(1')	158.77 (37)	
	T(2)–O(2)–T(3')	140.22 (35)	
	T(3)–O(3)–T(2')	146.61 (41)	
	T(2)–O(4)–T(3)	147.98 (42)	
	T(1)–O(5)–T(2')	137.78 (42)	
	T(3)–O(6)–T(1')	137.63 (43)	

Moreover, (type 2) and (type 3) (Si–Al)-tetrahedra are more distorted than (type 1) (Si, Al) tetrahedra. The shorter O–O distances in (type 2) and (type 3) tetrahedra are the edges that are shared with the (Na, Ca) polyhedra (Table 3). In the (type 3) tetrahedron, the T(3)–O(6) bond is considerably longer than the mean T(3)–O bond length. This is because O(6) is coordinated to T(3), T(1) and two additional (Na, Ca) sites which are shifted away from each other by the distortion from the ideal *I4/m* structure. The coordination environment of O(6) is best shown in Fig. 4. The disordered (Na, Ca) cations attract the O(6) anion and tend to pull O(6) further away from T(3) if both (Na, Ca) sites shift away from each other. T(1) contains more Si than T(3), thus T(1) is more electrically positive than T(3), and therefore T(1) has a stronger attracting force

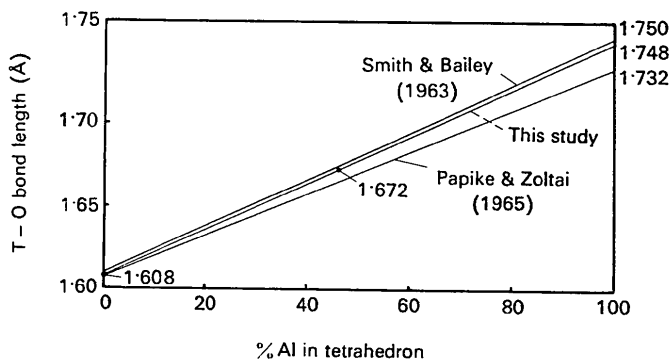


Fig. 3. Determinative curves for aluminum tetrahedral occupancies.

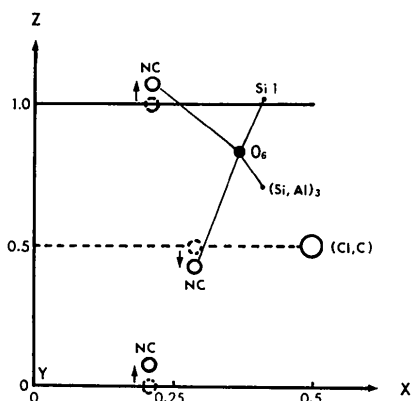


Fig. 4. The chemical bonding of O(6) ( $x=0.3710$ ,  $y=0.7282$ ,  $z=0.8270$ ). Viewed horizontally along the  $y$  direction.

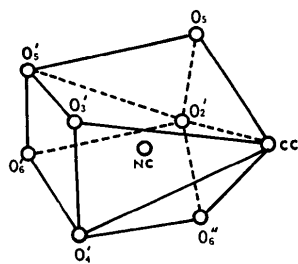


Fig. 5. Coordination polyhedron of (Na, Ca) in marialite. The (Na, Ca) atom is at  $x=0.3659$ ,  $y=0.2884$  and  $z=0.5064$  and is viewed along the  $x$  direction, *i.e.*, the long diagonal of the oval shape channel. NC=(Na, Ca), CC=(Cl, C).

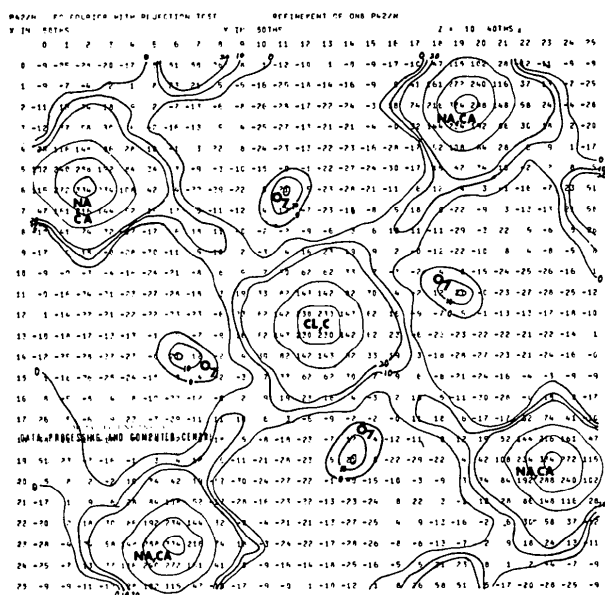


Fig. 6. Horizontal section of  $F_0$  synthesis to show the  $\text{CO}_3$  group disordered in the central anion cage. Section runs  $x=0 \rightarrow \frac{2.5}{5.0}$  down,  $y=0 \rightarrow \frac{2.5}{5.0}$  across, at  $z=\frac{1.0}{4.0}$ . Note:  $F_0$  synthesis was calculated using the space group  $P4_2/n$  with origin at  $\bar{1}$  at  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$  from  $\bar{4}$ .

for the O(6) anion. The resultant of the three attracting forces described above moves O(6) away from T(3), and thus increases the T(3)–O(6) distance. The other oxygen atoms bonded to T(3), are only bonded to one (Na, Ca) disordered site and the less electrically positive T(2) which contains 59% Al.

The (Na, Ca) coordination polyhedron (Fig. 5) is also rather distorted. The interatomic distances from the (Na, Ca) site to the coordinated atoms range from 2.289 to 2.945 Å. Papike & Zoltai (1965) report that the Na atoms are coordinated by 1 chlorine atom and 5 oxygen atoms. However, the (Na, Ca) site is actually coordinated by 7 oxygen atoms from the tetrahedral framework, together with either 1 chlorine anion or 1 oxygen atom [*i.e.* O(7)] from the carbonate radical ( $\text{CO}_3^{2-}$ ) (Table 2). Each (Cl,  $\text{CO}_3$ ,  $\text{SO}_4$ ) disordered anion site is coordinated by 4 (Na, Ca, K) disordered cation sites. The electrostatic valency principle (Pauling, 1960) holds reasonably for the (Na, Ca, K) sites in this scapolite. By taking into account the coordination of the atoms, the chemical substitution and the bond distances (Table 2), the sum of the strength of the electrostatic bonds around the (Na, Ca, K) site can be calculated to be 1.31 v.u. by using the method of Donnay & Allman (1970). However, if the bond strength of the (Na, Ca, K)–O bonds is calculated by using the empirical bond strength–bond length curves for oxides (Brown & Shannon, 1973 and personal communication), then the sum of bond strengths around the (Na, K, Ca) site will be 1.03, 1.10 and 0.98 v.u. respectively by using the individual bond strength–bond length parameters [in the expression  $S = S_0(R/R_0)^{-N}$ ], the universal bond strength–bond length parameters [in the expression  $S = (R/R_1)^{-N_1}$ ] and the bond strength–bond length parameters [in the expression  $S = S_0(R/R_0)^{-N}$ ] corrected for oxygen coordination. The parameters of the last kind are not preferred by Brown & Shannon (1973). The ideal value of the sum of bond strengths is calculated to be 1.21 v.u. from the valence and the population ratio of the atoms at the (Na, K, Ca) site.

The refined temperature factors of the atoms fall into three size groups according to the crystal-chemical nature of the atoms in marialite (Table 2). The three groups are: (1) temperature factors of the tetrahedral Si and (Si, Al) disordered sites which range from 0.63 to 0.79; (2) those of the tetrahedral framework oxygen atoms, ranging from 1.25 to 1.49; (3) those of metallic ions (Na, Ca, K), chlorine anion and oxygen atoms of the  $\text{CO}_3$  radical, ranging from 2.68 to 4.01. The abnormally high temperature factors of the (Na, Ca, K) sites and (Cl, C) sites are due to the substitutional and/or positional disordering at these sites. Each atomic species involved has only partial occupancy of its site. The abnormally high thermal parameter of the oxygens of the  $\text{CO}_3$  group is due to positional disordering (Stout & Jensen, 1968). These phenomena are, therefore, nonthermal in reality and are due to the nature of a disordered crystal. The refined isotropic temperature factors for Si, (Si, Al) and the framework oxygen

atoms (Table 2) are generally larger than the previously determined values in well refined, ordered silicate structures (Burnham, 1965). Again, this may be partly because of the disordering of the crystal and partly because of the inherent internal strain which induces the distortion of the ideal structure (Vousden, 1954; Lin, 1971). In order to confirm that atoms originally located on the mirror plane in the ideal structure ( $I4/m$ ) do migrate away from the mirror plane when refined according to  $P4_2/n$ , a vertical electron-density section was prepared and this shows a round (Na, Ca, K) peak with the centre clearly located away from the mirror plane.

In this marialitic scapolite, nearly one fourth of the central cavities are occupied by a carbonate group. This is shown in both the Fourier synthesis and the difference synthesis in which four peaks elongated parallel to the  $c$  axis and symmetrical around the origin (000) and with a density maximum on the (001) plane are present (Fig. 6). This has been previously described and explained by Papike & Stephenson (1966). However, some of the  $\text{CO}_3$  groups are believed to be tilted from the (001) plane, as evidenced by the elongated peaks present on the vertical electron-density maps and the large temperature factors. In conclusion, the crystal structure of this sodium and chlorine-rich scapolite has successfully been refined in the newly determined space group  $P4_2/n$ . The overall structure is shown to be pseudo body-centred, contrary to previous reports.

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## The Crystal and Molecular Structure of the Dimethyl Ester of *meso*-Tartaric Acid

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Crystals of the dimethyl ester of *meso*-tartaric acid are triclinic, space group  $P\bar{1}$ , with  $a=8.117$ ,  $b=9.619$ ,  $c=5.606$  Å,  $\alpha=96.8$ ,  $\beta=103.0$  and  $\gamma=73.9^\circ$  ( $Z=2$ ). Intensity data were measured on an automatic diffractometer. The structure was solved by direct methods and refined to an  $R$  of 0.096. The molecular conformation is identical with the dissymmetric conformation found in *meso*-tartaric acid and its derivatives. The hydrogen atoms of the methyl groups show a disordering over a staggered and eclipsed position with respect to the C–O bond of the ester group. The hydrogen-bond scheme is the same as in racemic acid dihydrate and two modifications of *meso*-tartaric acid.

### Introduction

In *meso*-tartaric acid and its salts the *meso*-tartaric acid molecule has a dissymmetric conformation (Boots-

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ma & Schoone 1967; Kroon & Kanters 1972; Kroon, Peerdeman & Bijvoet 1965) and both conformational antipodes are present in the unit cell, thus constituting a racemate. In order to acquire knowledge of the effect