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The Crystal Structure of an Intermediate Scapolite – Wernerite

BY S. B. LIN* AND B. J. BURLEY

Department of Geology, McMaster University, Hamilton, Ontario, Canada

The crystal structure of a scapolite (52% M) with strong superlattice reflexions ($h+k+l=$ odd) has been determined in space group $P4_2/n$. The three-dimensional intensity data were collected with a normal beam single-crystal diffractometer using Mo $K\alpha$ radiation. Two quantitative relationships were obtained, *viz.* (1) the exponential relationship between the intensity ratio $r(r= \sum I_{h+k+l=odd}/\sum I_{h+k+l=even})$ and the atomic displacement from the imaginary mirror plane being consistent with the space group $I4/m$; (2) the linear relationship between the above intensity ratio and the difference of Al occupancy between T(2) and T(3) sites. The horizontal disposition of the disordered CO_3 groups in this scapolite is the same as those present in others, but the vertical disposition is different. In this scapolite the planar CO_3 groups are essentially tilted from the (001) plane.

Introduction

Scapolites form a solid solution series between marialite ($Na_4Al_3Si_9O_{24}Cl$) and meionite [$Ca_4Al_6Si_6O_{24}(CO_3 \cdot SO_4)$] and the basic structure has been ascertained (Deer, Howie & Zussman, 1963). The pseudo-body-centred structure of marialitic scapolite has been established by Lin & Burley (1973a). However, it still needs further confirmation by more systematic investigations because a precise determination of a pseudosymmetric structure is difficult owing to the much weaker extra reflexions and the high correlation among the structural parameters. Therefore, a gem scapolite of Tsarasaotra, Madagascar (specimen XL) was selected for further study for the following reasons.

(a) The extra, weak reflexions ($h+k+l=$ odd) of this intermediate scapolite are much stronger than those displayed by the marialitic scapolite. The relationship between the structural distortion and the intensity of the weak $h+k+l=$ odd reflexions can be further examined.

(b) Scapolite XL has an intermediate composition (52% M)† with more Al atoms than the marialitic scapolite, and it should provide information for the understanding of the relationship between the distribution of Al and the intensity of the $h+k+l$ odd reflexions.

(c) Since the scapolite XL contains chlorine and carbonate in about equal amounts, the internal strain caused by $Cl \rightleftharpoons CO_3$ substitution will become profound, and a corresponding complexity in the environment around the site occupied by Cl and CO_3 is expected.

Experimental

The space group of the scapolite XL is $P4_2/n$ with nearly three times stronger ($h+k+l=2n+1$) reflexions than those of scapolite ON8 (Lin & Burley, 1973a).

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* Present address: Department of Geology, National Taiwan University, Taipei, Taiwan, China.

† Where % M = (number of Ca, Sr, Fe, Mn, Mg atoms per unit cell/number of Na, K, Ca, Sr, Fe, Mn, Mg atoms per unit cell) × 100.

The yellowish-gem scapolites of Tsarasaotra, Madagascar have been reported to be around 50% M (Lacroix, 1922; Gossner & Brückl, 1928). The present scapolite is also a transparent, yellowish prismatic single crystal with dimensions of about $0.7 \times 0.7 \times 2.0$ cm. The cell dimensions are $a = 12.116$ (1), $c = 7.581$ (2) Å. Its refractive indices were found to be $n_o = 1.570$, $n_e = 1.549$, thus giving a composition of 49.1% M (Shaw, 1960). This scapolite was also found to be 52% M by electron microprobe analysis, using as a standard another scapolite ON70 which has a composition close to scapolite XL (Lin & Burley, 1973c). The microprobe analysis has been corrected for fluorescence, absorption and atomic number with the computer program *EMPADR* VII (Rucklidge & Gasparrini, 1969) and found to very close to that without these corrections.

The carbon content was obtained by using the relationship that the total number of anions (Cl^-) and radicals (CO_3^{2-} and SO_4^{2-}) in the unit cell is equal to two. All minor elements, such as Fe, Mg, Mn, Sr, etc., are neglected because of the practically insignificant quantities present in scapolites. With the specific gravity 2.69, and using the cell volume and the microprobe analysis, its cell formula was calculated to be $(Ca_{4.17}Na_{3.31}K_{0.46})$ $(Si_{14.99}Al_{8.69})O_{47.8}Cl_{0.73}(SO_4)_{0.37}$ $(CO_3)_{0.87}$.

X-ray diffraction intensities were collected with a normal-beam single-crystal GE XRD6 diffractometer equipped with scintillation counter and a pulse-height analyser. Zr-filtered Mo $K\alpha$ radiation was employed. Of the 1730 *hkl* reflexions measured, 360 have intensities less than three standard deviations above the background and were regarded as unobserved reflexions. Lorentz and polarization corrections were applied.

Structure analysis and refinement

The scattering curves of Na^+, K^+, Ca^{2+}, Si^0, C^{2+}, Al^0, Cl^-, S^0 and O^- were from *International Tables for X-ray Crystallography* (1962). The computer programs used were those of the X-RAY program system (Computer Science Center, University of Maryland). The unobserved reflexions were included throughout the whole process of structural analysis and full-matrix least-squares refinement. The starting model was the refined structure of the marialitic scapolite based on $P4_2/n$, in which all atomic sites are in the general position $8(g)$ except for the (Cl, S, C) site which is in $2(a)$ (see Table 1 and Fig. 2). However, some preadjustments were made; the oxygen of the CO_3 group was excluded and the z coordinates of those atomic sites, (Na, Ca, K) (1), O(1), (Si, Al) (1), O(2), which lie on the mirror plane in the corresponding ideal $I4/m$ structure, were deliberately placed on the xy planes at $z = 0$ or $\frac{1}{2}$. Two cycles of refinement of the scale factor and the coordinates reduced the R value from 27.4% to 15.7% and shifted all the atoms away from the xy planes at $z = 0, \frac{1}{2}$. The refinement was continued for six

Table 1. *Final atomic coordinates and isotropic temperature factors in scapolites*

For each atomic site the parameters x, y, z and B are given.

Atomic sites	Scapolite ON8 (19.4% M)*	Scapolite XL (52% M)	Scapolite ON45 (93% M)†
(Na, Ca, K) (1)	0.3659 (3)	0.3603 (2)	0.3565 (2)
	0.2884 (3)	0.2841 (2)	0.2807 (2)
	0.5064 (4)	0.5126 (3)	0.5001 (3)
	2.68 (6)	1.89 (3)	1.79 (4)
(Cl, C, S) (1)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	3.85 (12)	1.88 (7)	1.97 (29)
(Si, Al) (1)	0.3390 (1)	0.3390 (1)	0.3395 (2)
	0.4100 (1)	0.4092 (1)	0.4074 (2)
	0.9989 (3)	0.9978 (3)	1.0000 (3)
	0.69 (3)	0.51 (2)	0.47 (4)
(Si, Al) (2)	0.6621 (2)	0.6593 (2)	0.6599 (2)
	0.9152 (2)	0.9155 (2)	0.9129 (2)
	0.7956 (2)	0.7967 (2)	0.7930 (3)
	0.79 (4)	0.61 (3)	0.51 (5)
(Si, Al) (3)	0.4145 (2)	0.4125 (1)	0.4130 (2)
	0.8368 (2)	0.8363 (1)	0.8401 (2)
	0.7085 (2)	0.7103 (2)	0.7072 (3)
	0.63 (4)	0.57 (2)	0.51 (5)
O(1)	0.4574 (4)	0.4576 (3)	0.4593 (5)
	0.3511 (4)	0.3503 (3)	0.3475 (5)
	1.0011 (7)	1.0019 (7)	0.9999 (10)
	1.39 (8)	1.03 (5)	1.33 (9)
O(2)	0.6939 (4)	0.6902 (5)	0.6871 (4)
	0.8797 (4)	0.8757 (5)	0.8732 (5)
	0.0048 (7)	0.0088 (7)	0.9999 (9)
	1.25 (7)	1.13 (8)	0.98 (8)
O(3)	0.3486 (6)	0.3498 (4)	0.3491 (5)
	0.9448 (5)	0.9420 (4)	0.9495 (5)
	0.7898 (6)	0.7947 (6)	0.7941 (9)
	1.48 (10)	1.38 (7)	1.09 (10)
O(4)	0.5499 (5)	0.5459 (5)	0.5504 (5)
	0.8475 (5)	0.8472 (5)	0.8491 (5)
	0.7163 (6)	0.7160 (7)	0.7055 (9)
	1.49 (9)	1.25 (8)	1.11 (10)
O(5)	0.2706 (5)	0.2677 (5)	0.2674 (5)
	0.3699 (5)	0.3667 (5)	0.3645 (6)
	0.8277 (6)	0.8307 (7)	0.8245 (7)
	1.30 (9)	1.45 (8)	1.42 (12)
O(6)	0.3710 (6)	0.3703 (5)	0.3643 (6)
	0.7282 (6)	0.7287 (5)	0.7345 (5)
	0.8270 (7)	0.8256 (7)	0.8269 (7)
	1.47 (10)	1.28 (8)	1.48 (12)
O(7)		0.3978 (50)	
		0.4793 (52)	
		0.4598 (78)	
		4.63 (103)	
O(8)		0.4007 (30)	
		0.4819 (30)	
		0.5871 (46)	
		3.99 (64)	
R (%)	7.4	8.3	7.2

* From Lin & Burley (1973a).
† From Lin & Burley (1973b).

cycles to refine the scale factor, coordinates and iso-tropic temperature factors, then R dropped to 11·4%. Each reflexion had been assigned a weight of unity up to this stage.

To obtain information about the disposition of the CO_3 group, electron density sections were calculated. On the horizontal $\Delta\varrho(xyz)$ sections at $z=0.5$, four equal peaks around 0, 0, 0 and one electron-density high region at 0, 0, 0 similar to the features found in meionite and mizzonite were noted and thought to be contributed by the disordered CO_3 groups (Lin & Burley, 1973b; Papike & Stephenson, 1966). However, vertical $\Delta\varrho(xyz)$ sections parallel to (100) and inter-secting these four electron-density peaks present in the above-mentioned horizontal $\Delta\varrho(xyz)$ section, all

showed a vertical region of high electron density with two unequal peaks each at opposite ends [Fig. 1(a)]. The four stronger peaks from such four vertical re-gions of high electron density are alternately above and below the xy plane at $z=0$, $\frac{1}{2}$ and likewise the other four weaker peaks from the same four regions (Fig. 1). This is quite unlike the case in mizzonite (Papike & Stephenson, 1966) and meionite (Lin & Burley, 1973b), in which CO_3 groups are mainly disordered and con-fined to the xy plane at $z=0$, $\frac{1}{2}$. Because the orientation of the CO_3 groups was not very clear it was decided to postpone this problem to the later stages. Therefore, the refinement was continued for three more cycles with the Cruickshank weighting scheme and R dropped to 9·9%.
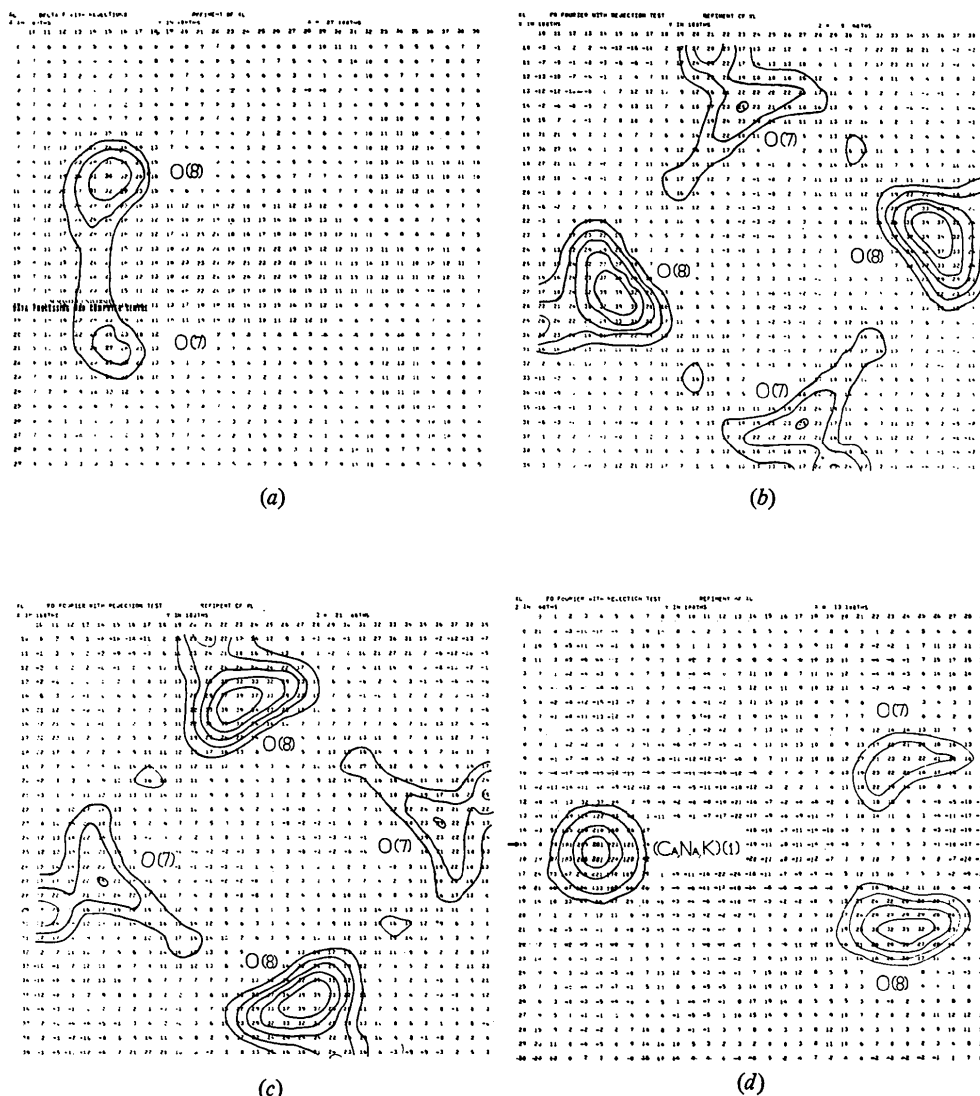

(a)

(b)

(c)

(d)

Fig. 1. (a) Section of ΔF_o synthesis, perpendicular to the a axis at $x=0.53$. (b), (c) Sections of F_o synthesis, running $x=35/100 \rightarrow 64/100$ down, $y=35/100 \rightarrow 64/100$ across, at (b) $z=0.4$ and (c) $z=0.6$. (d) Section of F_o synthesis, running $y=25/100 \rightarrow 49/100$ across $z=15/60 \rightarrow 45/60$ down, at $x=38/100$. Note: These Fourier syntheses were based on $P4_2/n$ with origin at $\bar{1}$ at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ from $\bar{4}$.

At this point, analysis of the data revealed that some intense reflexions, especially those at low reflexion angles, appeared to be seriously affected by extinction. With deletion of these poor data, the R dropped to 9·2% after one cycle of least-squares calculations. Then the same electron-density sections formerly used to reveal the CO_3 group were prepared again and still displayed the same features. As a preliminary test, the oxygen of the CO_3 group was assumed to be disordered in only one set of equivalent sites with parameters $x=0·39$, $y=0·45$, $z=0·50$, $B=6·0$. By allowing its z to vary, two cycles of least squares were executed; then, the oxygen of the CO_3 group moved away from the xy planes at $z=0$, $\frac{1}{2}$ with a significant change of z to 0·52 and its isotropic temperature factor abnormally increased to 11·96, although R decreased slightly to 8·8%.

Because of the results of the above tests and the later geometrical analysis of the possible disordered patterns of CO_3 groups and (Ca, Na, K) (1) sites (Fig. 5), the writers conclude that the trigonal-planar CO_3 group becomes inclined to (001) instead of being parallel to it as in meionite or mizzonite. The two peaks in Fig. 1(a) statistically represent oxygens of the CO_3 groups disordered in the possible tilted positions. Therefore the oxygens of the CO_3 group were separately assigned to two different sets of equivalent disordered sites. They are:

O(7): $x=0·395$, $y=0·480$, $z=0·400$, $B=6·0$, $m=0·14$
O(8): $x=0·395$, $y=0·480$, $z=0·600$, $B=6·0$, $m=0·28$

where m is the population factor and is inferred from the content of CO_3 in the crystal, the approximate ratios of areas and heights between the two peaks in Fig. 1(a), and the disordering configuration of the CO_3 group to conform to the observed electron density (see Fig. 1 and the later discussion). With the contribution from O(7) and O(8), R automatically dropped from 9·2% to 8·7%. One subsequent cycle further reduced the R value to 8·6% and the isotropic temperature factors of O(7) and O(8) to 3·1 and 4·0 respectively. $\varrho(xyz)$ sections were then calculated to show the statistical disposition of the disordered carbonate groups (Fig. 1). The corresponding peaks formerly present in the corresponding $\varDelta\varrho(xyz)$ sections largely disappeared except for the broad and much weaker ones on the section at $z=0·5$. In order to test the validity of the populations (m) of O(7) and O(8), one cycle of least-squares calculations was run in which populations of O(7) and O(8), and all positional and isotropic thermal parameters of other atoms except O(7) and O(8) were allowed to vary. The result showed that the populations and R remained nearly the same [m of O(7)=0·16, m of O(8)=0·28, $R=8·6$%].

The dimensions of the (Si, Al) tetrahedra were calculated with the parameters derived in the penultimate cycle. The Al occupancy of each tetrahedral (Si, Al) site was assigned (Smith & Bailey, 1963). Then four cycles of least-squares refinement were run, giving a

final $R(\sum||F_o|-|F_c||/\sum|F_o|)$ of 8·3% for all observations including those with $|F_o|<|F_{o\ min}|$.

Discussion

The refined parameters are listed in Table 1 together with other scapolites (Lin & Burley, 1973a,b).* The important interatomic distances and angles are in Tables 2 and 3.

Table 2. *Interatomic distances in scapolite*
(52% M; *Tsarasaotra, Madagascar*)

(a) (Si, Al)–O and O–O distances of tetrahedra

Tetra-hedron	T–O Distances (Å)		O–O Distance (Å)	
T(1)	O(1)	1·604 (4)	O(1)–O(5)	2·648 (7)
	O(5)	1·617 (6)	O(1)–O(1′)	2·666 (5)
	O(1′)	1·620 (4)	O(1)–O(6′)	2·620 (7)
	O(6′)	1·639 (6)	O(1′)–O(5)	2·674 (7)
			O(1′)–O(6′)	2·656 (7)
			O(5)–O(6′)	2·608 (8)
	Average	1·620 (5)	Average	2·645 (7)
T(2)	O(2)	1·720 (6)	O(2)–O(4)	2·847 (7)
	O(4)	1·717 (6)	O(2)–O(3′)	2·784 (7)
	O(3′)	1·730 (6)	O(2)–O(5′)	2·743 (8)
	O(5′)	1·734 (6)	O(4)–O(5′)	2·722 (8)
			O(4)–O(3′)	2·912 (8)
			O(3′)–O(5′)	2·882 (8)
	Average	1·725 (6)	Average	2·815 (8)
T(3)	O(3)	1·620 (6)	O(3)–O(4)	2·705 (8)
	O(4)	1·622 (6)	O(3)–O(6)	2·607 (8)
	O(6)	1·651 (6)	O(3)–O(2′)	2·713 (7)
	O(2′)	1·623 (6)	O(4)–O(6)	2·698 (8)
			O(4)–O(2′)	2·631 (7)
			O(6)–O(2′)	2·596 (7)
	Average	1·629 (6)	Average	2·658 (7)

(b) Selected interatomic distances

Type	Distances	Multi-plicity	Distance (Å)
Environment of (Na, Ca, K)	(Ca, Na, K) (1)–(Cl, C) (1)	1	3·117 (2)*
	(Ca, Na, K) (1)–O(2′)	1	2·347 (5)
	(Ca, Na, K) (1)–O(3′)	1	2·518 (6)
	(Ca, Na, K) (1)–O(4′)	1	2·491 (6)
	(Ca, Na, K) (1)–O(5)	1	2·842 (6)
	(Ca, Na, K) (1)–O(5′)	1	2·675 (6)
	(Ca, Na, K) (1)–O(6′)	1	2·838 (6)
	(Ca, Na, K) (1)–O(6″)	1	2·971 (6)
	(Ca, Na, K) (1)–O(7′)	1	2·391 (63)
	(Ca, Na, K) (1)–O(8′)	1	2·494 (36)
Carbonate group	C–O(7) or C–O(8)	3	≤1·345 (48)
Anion cage diagonals	O(1)–O(1′)	4	8·467
	O(5)–O(6′)	4	8·131
	O(2′)–O(2″)	2	8·091

* See remarks in the last paragraph of text.

Table 3. *Interatomic angles in scapolite*
(52 % M; *Tsarasaotra, Madagascar*)

T(1) tetrahedra

O(1)–T(1)–O(5)	110·60 (29)°
O(1)–T(1)–O(1')	111·54 (21)
O(1)–T(1)–O(6')	107·73 (28)
O(5)–T(1)–O(1')	111·32 (30)
O(5)–T(1)–O(6')	106·30 (29)
O(1')–T(1)–O(6')	109·14 (28)

T(2) tetrahedra

O(2)–T(2)–O(4)	111·82 (24)
O(2)–T(2)–O(3')	107·59 (24)
O(2)–T(2)–O(5')	105·11 (26)
O(4)–T(2)–O(3')	115·24 (28)
O(4)–T(2)–O(5')	104·10 (28)
O(3')–T(2)–O(5'')	112·56 (29)

T(3) tetrahedra

O(3)–T(3)–O(4)	113·07 (29)
O(3)–T(3)–O(6)	105·67 (29)
O(3)–T(3)–O(2')	113·50 (26)
O(4)–T(3)–O(6)	111·03 (29)
O(4)–T(3)–O(2')	108·35 (25)
O(6)–T(3)–O(2')	104·91 (26)

T–O–T angles

T(1)—O(1)–T(1')	158·43 (28)
T(2)—O(2)–T(3')	139·45 (28)
T(3)—O(3)–T(2')	145·30 (36)
T(2)—O(4)–T(3)	147·83 (35)
T(1)—O(5)–T(2')	137·07 (40)
T(3)—O(6)–T(1')	137·61 (37)

The structure of this 52% M scapolite is similar to the 19·4% M scapolite (Lin & Burley, 1973a). However the present one deviates more from the body-centred symmetry (Fig. 2). The vertical edge of the T(1) tetrahedra of which the (type 1) four-membered ring is composed, deviates from its parallel disposition with respect to the c axis, and of course, these four T(1) tetrahedra are not on the same plane. Again as in the 19·4% M scapolite the T(2) and T(3) tetrahedra are also more distorted than the T(1) tetrahedron. Even the order of the lengths of the edges and the cation–anion distances in each coordination polyhedron are similar for these two scapolites.

The distortion of the central anion cage to accommodate Cl^- and CO_3^{2-}, whose proportion mainly depends on the % M, can be evaluated from Table 4 and Fig. 2. O(2)–O(2') is the horizontal diagonal of the cage, while O(1)–O(1') is the inclined diagonal closely parallel to the c axis. It is obvious that the cage becomes more equidimensional as the composition is richer in meionite content. This is due to a corresponding adjustment of the cage in order to accommodate more of the large anions, CO_3^{2-} and SO_4^{2-}. The ratio of O(1)–O(1') to O(2)–O(2') is also related to the variation of the axial ratio c/a, and it should be noted that the distance O(1)–O(1') is equal to c in length. These distortions reflect an increase of the a axis and a decrease of the c axis as the % M increases.
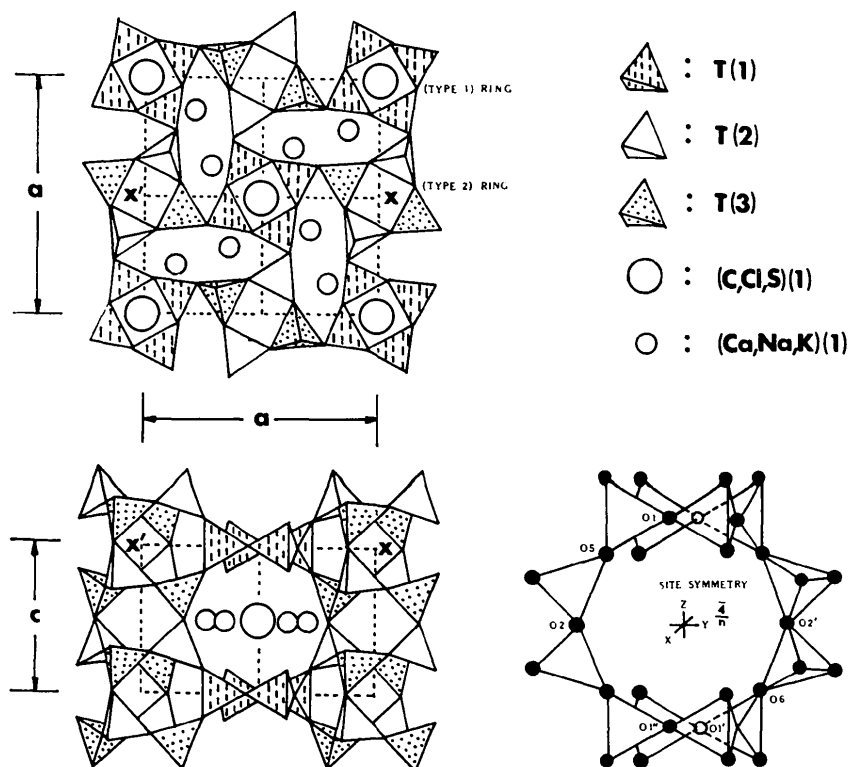

Fig. 2. The crystal structure and the central anion cage of the scapolite.

Table 4. *Distortion of the central anion cage as a function of chemical composition of scapolites*

Scapolite	ON8 (19·4% M)*	XL (52% M)	ON45 (93% M)†
O(1)–O(1′)	8·457 Å	8·467 Å	8·480 Å
O(5)–O(6)	8·055	8·131	8·223
O(2)–O(2′)	7·933	8·091	8·234
$\frac{O(1)-O(1')}{O(2)-O(2')}$	1·066	1·046	1·030
c=O(1)–O(1″)	7·587 Å	7·581 Å	7·557 Å
a	12·059	12·116	12·194
c/a	0·629	0·626	0·620

* Data from Lin & Burley (1973*a*).
† Data from Lin & Burley (1973*b*).

One of the possible factors causing the weak reflexions which violate the body-centred symmetry, is that those atomic sites (Na, K, Ca) (1), (Si, Al) (1), O(1), O(2) located on the mirror planes in the ideal $I4/m$ structure are displaced along the c-axis direction and thus move away from the xy planes at $z=0$ and $\frac{1}{2}$. Moreover, the intensity of $h+k+l$ odd reflexions will be proportional to that displacement (Lin & Burley, 1971). The structure of the Na, Cl-rich scapolite (19·4% M) has shown that those atomic sites mentioned above all migrate from xy planes at $z=0$ and $\frac{1}{2}$
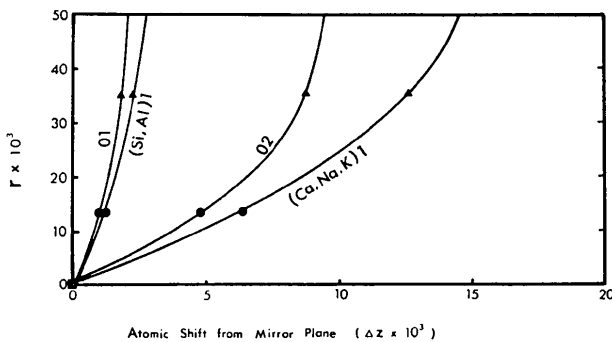

Fig. 3. Relationship between the intensity ratio $r = \sum I_{h+k+l=odd} / \sum I_{h+k+l=even}$, and the atomic displacement from the mirror plane consistent with the space group $I4/m$. Triangles stand for scapolite XL; dots for scapolite ON8 and the square for the case of scapolite with no, or extremely weak, $h+k+l$ odd reflexions, *e.g.* meionite ON45 (*cf.* Table 5).

(Lin & Burley, 1973*a*). The present intermediate scapolite (52% M) again shows that such atomic sites not only displace in the same direction along the c axis but also move farther away from those xy planes (Table 2). Fig. 3 illustrates the exponential-type relationship between the intensity of an $h+k+l$ odd reflexion and the atomic displacement from the xy planes at $z=0$ and $\frac{1}{2}$. All these curves pass through the origin (Fig. 3) because the atomic sites concerned will remain on the mirror planes at $z=0$ and $\frac{1}{2}$, if no extra reflexion violating the body-centred symmetry occurs. It also implies that the z coordinate of the (Ca, Na, K) (1) site is the most affected during the distortion of the crystal structure from the $I4/m$ symmetry.

The scapolite framework can be considered as composed of (type 2)-ring columns which are laterally connected together by (type 1)-rings to form further lateral five-membered tetrahedra rings (Fig. 2). The (type 2)-ring column is formed by a continuous vertical superposition of (type 2) four-membered rings in such a way that T(2) and T(3) tetrahedra are alternately arranged (Fig. 2). With the mean (Si, Al)–O bond lengths (Table 2) and the curve of Smith & Bailey (1963), the Al occupancy of each tetrahedral (Si, Al) site was estimated and listed together with those assigned for the other two scapolites (Table 5). The results show that in the 52% M scapolite, Al atoms already start to enter T(1) sites. This will decrease the probability of the formation of unstable Al–O–Al linkages (Lowenstein, 1954) in (type 2)-rings; otherwise these linkages must be formed within the (type 2)-ring column because the number of Al atoms per unit cell of this scapolite is greater than eight, *i.e.*, the number of the general equipoints. Of course, Al–O–Al linkages will still be formed in the five-membered tetrahedral rings, but the number of the total Al–O–Al linkages in the whole structure will be fewer (*cf.* Fig. 2).

Table 5 also shows that Al tends to concentrate in T(2) sites and Si tends to concentrate in T(3) sites in the intermediate scapolite. In other words, the intermediate scapolite has a higher degree of ordering in the distribution of Al and Si than marialite and meionite. When the scapolite structure based on the ideal space group $I4/m$ is transformed into that based on the real space group $P4_2/n$, the geometrical configuration

Table 5. *Al occupancy (%) in the tetrahedral sites and rings of scapolites*

% M = 100 [(number of Ca, Sr, Fe, Mn, Mg atoms per unit cell)/(number of Na, K, Ca, Sr, Fe, Mn, Mg atoms per unit cell)].
$r = \sum I_{h+k+l=odd} / \sum I_{h+k+l=even}$ for the 0*kl* layer reflexions (see Lin & Burley, 1971, 1973*c*).
$R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

Scapolite specimens	M (%)	$r \times 10^3$	T(1) (Si,Al) (1)	(Type 1) ring	T(2) (Si,Al) (2)	T(3) (Si,Al) (3)	(Type 2) ring	R (%)
Marialite (ON8)*	20	13·5	0	0	59·3	29·3	44·3	7·4
Intermediate scapolite (XL)	52	35·4	7·14	7·14	82·2	13·6	47·8	8·3
Meionite (ON45)†	93	‡	30·7	30·7	50·7	49·3	50·0	7·2

* See Lin & Burley (1973*a*) and Table (1).
† See Lin & Burley (1973*b*) and Table (1).
‡ Extremely small because reflexions with $h+k+l=2n+1$ could not be observed.

of the T(1) tetrahedral sites remains exactly the same (if only ordering occurs) or virtually remains unchanged (if distortion accompanies the ordering), for the following reasons (cf. Fig. 2):

(a) The total number of equivalent T(1) sites in the unit cell remains eight.

(b) All equivalent T(1) sites remain on or move slightly off their original mirror positions; thus they are still virtually symmetrical with respect to those atom sites close to the adjacent mirror planes, e.g. (Na, Ca, K) (1).

(c) T(1) tetrahedra only form the (type 1) four-membered tetrahedral rings in both ideal and real structures of scapolite.

Therefore the Al occupancy of site T(1) will not be related to the deviation from the body-centred symmetry and hence to the intensity of $h+k+l$ odd reflexions when the ideal structure ($I4/m$) is transformed into the real structure ($P4_2/n$). However, the Al occupancies of sites T(2) and T(3) are related to the ordering of Al and also to the extent of the deviation from the body-centred symmetry for the scapolite structure. In the ideal structure ($I4/m$), the (type 2) ring will contain only one kind of tetrahedral site, while in the real structure ($P4_2/n$) it contains two kinds of tetrahedral sites, namely T(2) and T(3) (Fig. 2). The smaller the difference between the Al occupancy of T(2) and T(3) the lower the ordering of the Al and Si atoms, and hence the weaker the intensity of the $h+k+l$ odd reflexions. In the extreme case in which the Al occupancies of T(2) and T(3) are equal, T(2) and T(3) become identical and the pseudo-body-centred structure ($P4_2/n$) automatically transforms into the body-centred structure ($I4/m$). Hence the superlattice reflexions violating the body-centred symmetry disappear. Thus the intensity of the $h+k+l$ odd reflexion is related to the difference between the Al occupancy of T(2) and T(3).

The ratios (r) of $\Sigma I_{h+k+l=odd}/\Sigma I_{h+k+l=even}$ of scapolite ON8, ON45 and XL (Table 5) were plotted against the corresponding differences of Al occupancy (Fig. 4). The curve connecting the points must pass through the origin which corresponds to the case of the body-centred structure ($I4/m$), and the relationship is virtually linear. Furthermore, when the line is extrapolated to 100% difference in Al occupancies, the corresponding r ratio was found to be 0·05 which is just about equal to the maximum ratio at about 37% M shown in plot of r ratio vs. % M (Lin & Burley, 1971, 1973c). This consistency indicates, first, that at 37% M, scapolite has its highest degree of ordering of Al and Si, i.e., 100% Al in T(2) and 0% Al in T(3); second, 0·05 is probably the highest ratio of $\Sigma I_{h+k+l=odd}/\Sigma I_{h+k+l=even}$ for the scapolite structures; third, the experimental results are internally consistent, and therefore reliable.

The role of the carbonate group in meionite containing very little chlorine and sulphur has been studied by Lin & Burley (1973b) and the results show

that the CO$_3$ group is disordered mainly in the xy planes at $z=0$ and $\frac{1}{2}$, taking one of four possible positions, similarly to the case in mizzonite (Papike & Stephenson, 1966). However, the disposition of the CO$_3$ group in this intermediate scapolite should be more complex than in meionite and mizzonite, because the present scapolite contains a significant amount of Cl to occupy the same sites and has relatively strong ($h+k+l$ odd) reflexions to violate body-
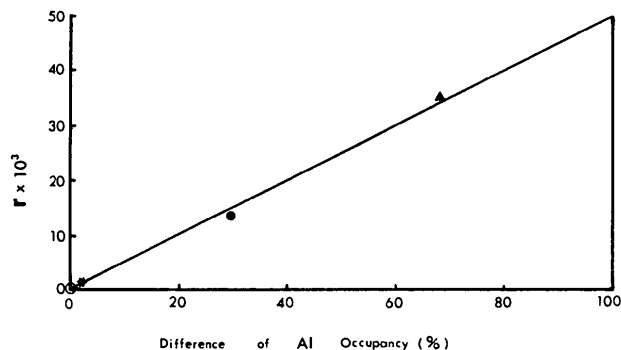

Fig. 4. Relationship between the intensity ratio $r=\Sigma I_{h+k+l=odd}/\Sigma I_{h+k+l=even}$ and the difference of Al occupancies between T(2) and T(3) sites. The triangle stands for scapolite XL, the dot for scapolite ON8 and the asterisk for meionite ON45 (cf. Table 5). The circle represents the case of $I4/m$ which has no superlattice reflexion.
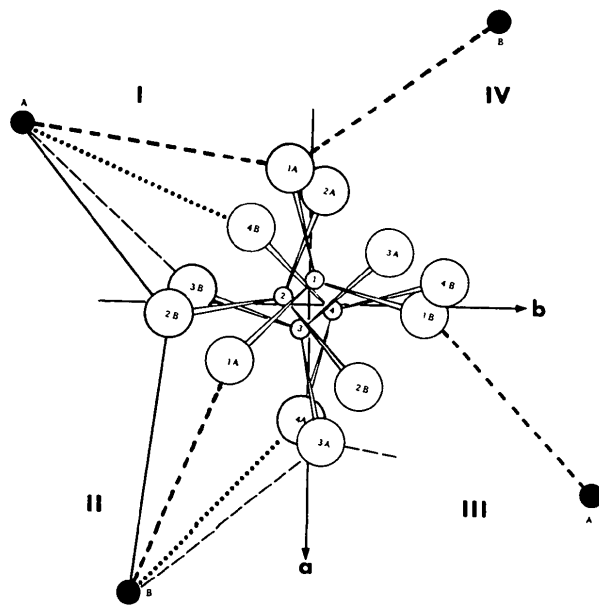

Fig. 5. The disordered scheme of the tilted carbonate groups in the intermediate scapolite, where the large open circles represent the oxygen atoms; the small open circles represent the carbon atoms while the large dots are the coordinated (Ca, Na, K) atomic sites. The arabic figures indicate each single CO$_3$ group possessing one of four disordered orientations; roman numerals indicate the quadrants; A means the oxygen or (Ca, Na, K) atomic sites are above xy planes at $z=0$ or $\frac{1}{2}$, while B means below the said planes. The horizontal crystallographic axes are indicated by a and b.

centred symmetry. There is a sympathetic relationship between the intensity of the $h+k+l$ odd reflexions and the chemical composition, specifically the Cl amount present in scapolites (Lin & Burley, 1971, 1973c). Thus it is desirable to observe the environment of these anions in order to understand this fact.

As described in the previous section, the planar CO_3 groups in this scapolite should be tilted rather than parallel to (001), and their composite disordered configuration is also consistent with the $\bar{4}$ symmetry. Various possible disordered schemes of the inclined CO_3 group have been tried and only scheme (a) has been found to be consistent with the observed electron density (Fig. 1) and the required symmetry. This scheme can be demonstrated in the following way, referring to Fig. 5.

(a) Quadrant	I	II	III	IV
Group				
1		A	A	B
2	A	B	B	
3		B	A	A
4	B		A	B
Total	$2A+B$	$A+2B$	$2A+B$	$A+2B$

where the roman figures represent each quadrant in the xy plane; the arabic figures represent each CO_3 group possessing one of the possible orientations. A means that a specific oxygen atom of the CO_3 group is above (001) and B that the said atom is below such a plane.

Another possible scheme is a combination in unequal proportions of scheme (a) and the following scheme (b) which is actually the reverse of scheme (a).

(b) Quadrant	I	II	III	IV
Group				
1	B	B		A
2	B	A	A	
3		A	B	B
4	A		B	A
Total	$A+2B$	$2A+B$	$A+2B$	$2A+B$

This combined scheme can be concordant with the $\bar{4}$ symmetry and even the observed electron density. However, a significant portion of the scheme (b) in this scapolite is unlikely because the observed electron-density ratio (Fig. 1) and the refined population ratio of O(7) to O(8) are both nearly 1:2.

The angle at which the majority of the CO_3 planar groups are inclined to the horizontal plane (001), with any of the four orientations allowed by the scheme (a) and the refined coordinates, was calculated to be 39°. Their distance off the (0, 0, 0) or $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site was found to be 0·147 Å. This displacement is concordant with the requirement that the carbon of the CO_3 groups disordered in the fourfold field should be displaced from the site 0, 0, 0 in order to give rise to eight peaks rather than 24 peaks. The real C–O bond of the CO_3 group should be slightly shorter than the mean value of the distance between O(7) and 0, 0, 0 (or

$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the distance between O(8) and the 0, 0, 0 i.e., $(\frac{1}{2})$ $(1·300+1·390)=1·345$ Å, because the planar CO_3 group is displaced off the 0, 0, 0 site by 0·147 Å. The distance between O(7) and O(8) both above or both below the horizontal plane at $z=0$ or $\frac{1}{2}$, was found to be 1·788 Å, while the distance between O(7) and O(8) both in the same quadrant was found to be 0·966 Å.

Although $\varrho(xyz)$ sections at and near $z=0$ or $\frac{1}{2}$ do not show any peak corresponding to the peaks which appear on the corresponding $\varDelta\varrho(xyz)$ sections and have similar x,y coordinates to the CO_3 group, it is believed that the inclined angle of the CO_3 group could vary in a rather wide range but with the most probable angle of 39° as evidenced by the $\varDelta F(xyz)$ and $F(xyz)$ maps. There is a difference of 0·05 between the least-squares refined z coordinate of O(7) and that of the O(7) peak on the $\varrho(xyz)$ map. It is not quite certain whether this is due to the errors in amplitudes or phases of F_o, or to the effects of series termination. According to the microprobe analysis, this intermediate scapolite also contains some SO_4^{2-} or SO_3^{2-} anions in the anion cage, but its atomic positions were not definitely revealed on the $\varrho(xyz)$ and $\varDelta\varrho(xyz)$ maps. A number of spurious peaks were, however, present in the anion cavity. In short, the environment in the anion cavity is complex; nevertheless, it is obvious that the CO_3 group in the intermediate scapolites with relatively strong $h+k+l$ odd reflexions becomes tilted to (001) plane, and the proposed disordering scheme (a) of the CO_3 group seems to be the most probable one.

The (Ca, Na, K) (1) site present in the vertical section of the F_o synthesis [i.e parallel to (100)] appear to be well defined, round, and with the centre above the xy plane at $z=0$, $\frac{1}{2}$ [Fig. 1(d)]. However, the (Ca, Na, K) (1) site present in the horizontal sections of the F_o synthesis [i.e. parallel to (001)] appears to be somewhat elongated along [110], and possibly split because the highest point is not at the centre of the whole peak. This phenomenon could be interpreted as follows. The (Ca, Na, K) (1) sites in some unit cells are coordinated to Cl atoms at (0, 0, 0) or $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the (Ca, Na, K) (1) sites in other unit cells are coordinated to the oxygens of the CO_3 group. The sum of [(Ca, Na, K)–O]+[C–O]=3·7 Å is much greater than the normal bond distance (Ca, Na, K)–Cl$\simeq$2·9 Å and again, the distance Ca–C=3·2 Å found in meionite (Lin & Burley, 1973b) is also longer than the latter. It should be noted that Cl and C are disordered on the 2(a) equivalent sites. Therefore, the (Ca, Na, K) (1) atomic sites coordinated to the Cl atom would be closer to 0, 0, 0 or $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, while those coordinated to the oxygens of the CO_3 group would be further away from these sites, even when the CO_3 planar group tilts to offset the larger sum of the vectors $\overrightarrow{(Ca, Na, K)–O}+$ $\overrightarrow{C–O}$ than the vector $\overrightarrow{(Ca, Na, K)–Cl}$. It should be remarked that the entry (Ca, Na, K) (1)–(C, Cl) (1)=

3·117 Å listed in Table 2(*a*) represents only the overall average distance between the atoms involved in that entry in this disordered crystal rather than any specific distance in the unit cell. As explained above, the (Ca, Na)–Cl distance would be shorter than 3·117 Å.

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The Crystal and Molecular Structure of Oxobis(ethane-1,2-diolato)osmium(VI): a Five-Coordinate Diester Complex

BY FREDERICK L. PHILLIPS AND ANDRZEJ C. SKAPSKI

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

Oxobis(ethane-1,2-diolato)osmium(VI), $OsO(O_2C_2H_4)_2$, a model compound for the staining and fixation of unsaturated membrane lipids by OsO_4, is orthorhombic with $a = 10·950$ (2), $b = 8·376$ (2), $c = 7·735$ (2) Å, space group *Pbcn*, $Z = 4$. Full-matrix least-squares refinement with 655 independent reflexions gave $R = 0·030$. The molecule possesses C_2 crystallographic symmetry, and a short Os–O(terminal) bond, of length 1·670 Å, lies along the twofold axis. An essentially square-pyramidal coordination is found for Os, in which four O atoms from the two chelating esters form the base of the pyramid, with a mean Os–O(ester) distance of 1·885 Å. Os lies 0·64 Å above the base. A feature of the molecule is the large O(apical)–Os–O(basal)mean angle of 110·1°. This is a consequence of the electronic repulsion by the strongly π-donating oxo ligand upon the ester O atoms.

Introduction

Osmium tetroxide is a specific reagent in organic chemistry for the *cis*-hydroxylation of olefinic double bonds (Cairns & Roberts, 1968), and it is widely used as a staining and fixation agent for the examination of biological tissues by electron microscopy (Hayat, 1970; Riemersma, 1970). Although the action of OsO_4 on tissue has been known for a long time (*e.g.* Branell, 1849), the exact nature of the processes taking place has been a subject of controversy and is still not fully understood. The most widely accepted theory involves the initial attack of OsO_4 on unsaturated tissue components with the formation of Os^{VI} mono- or diesters. The issue of whether mono- or diesters are formed has, however, been the subject of some debate, and evidence for both sides of the question has been summarized by

Riemersma (1970). A more recent theory has been put forward by Litman & Barnett (1972) who suggested that OsO_4 attaches itself by means of hydrogen bonds to aliphatic side chains and proteins in the tissue. This theory has been refuted by Collin & Griffith (1974), who showed that OsO_4 has negligible hydrogen-bonding properties.

We have carried out an X-ray structural study on relatively simple mono- and diester complexes of Os^{VI} which could serve as model compounds for the staining and fixation of unsaturated membrane lipids. We first determined the structure of a monoester complex (Collin, Griffith, Phillips & Skapski, 1973), and found this compound, $[OsO_2(O_2C_2Me_4)]_2$, to be five-coordinate and dimeric, and to have a structure quite different from that hitherto accepted. A study of the equivalent diester, $OsO(O_2C_2Me_4)_2$ (tetragonal, $a =$