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Structural Refinement of the Monte Somma Scapolite, a 93% Meionite

By *Horstpeter H. Ulbrich* (Basel) *)

With 4 figures and 3 tables in the Text

Abstract

A structural refinement, based on 778 independent reflections, was undertaken of the Monte Somma scapolite (93% meionite). The refinement was carried out with symmetry $I\bar{4}m$ to a final agreement factor of 2.96%. Atomic coordinates of atoms, although more precise, are essentially similar to those reported from structural analyses of less calcic scapolites. Anisotropic temperature factors and RMS displacements are listed. Partial ordering of (Si, Al) in the T-2 site was observed, as follows from the distribution of atoms in the positions T-1 (34% Al, 66% Si) and T-2 (53% Al, 47% Si).

Introduction

Scapolites are tetragonal framework silicates, with two formula units per cell. Structural models (fig. 1) have been proposed by several authors (e. g., PAULING, 1930; SCHIEBOLD and SEUMEL, 1932) and on the whole are confirmed by recent refinements (PAPIKE and ZOLTAI, 1965; PAPIKE and STEPHENSON, 1966). A stoichiometric model based on data from microprobe spot analysis has been set up by EVANS, SHAW and HAUGHTON (1969). These authors show that the end members of the scapolite group – marialite, $Na_4Al_3Si_6O_{24}Cl$, and meionite, $Ca_4Al_6Si_6O_{24}CO_3$ – change their compositions according to two different types of coupled substitutions. First, marialitic scapolites substitute Na_3Si_2Cl by $Ca_3Al_2CO_3$. Then, from 25% marialite to the calcic end member, the substitution is of $NaSi$ by $CaAl$.

Several space groups have been proposed for scapolites: $P4_2/n$ (GOSSNER and BRÜCKL, 1928; LIN and BURLEY, 1971 and ULBRICH, 1973, restricted that space group to intermediate compositions); $P4/m$ (BURLEY et al., 1961; PHAKEY and GHOSE, 1972); $P4_2/m$ (GOSSNER and BRÜCKL, 1928); $P4$ (PHAKEY

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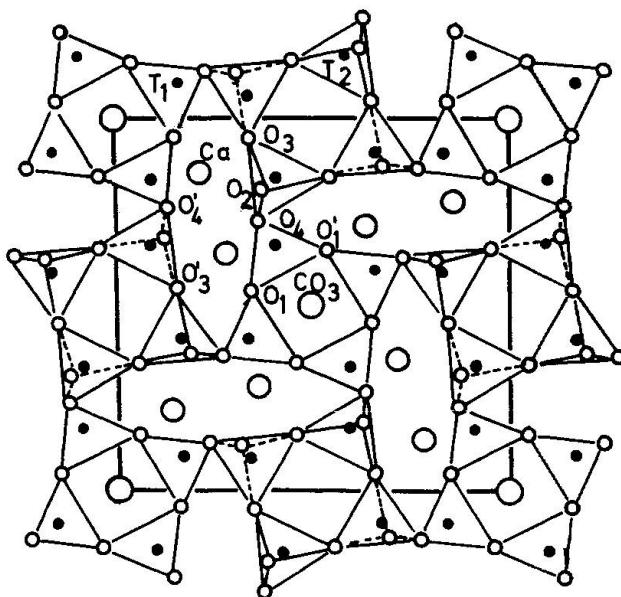


Fig. 1. Projection of the scapolite structure on (001) (from PAPIKE and STEPHENSON, 1966). Origin is at upper left corner; the CO_3 group in the center is at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. $(\text{Si}, \text{Al})_1$ tetrahedra correspond to the T-1 sites and form a fourfold ring with one of their tetrahedral edges parallel to the c-axis; $(\text{Si}, \text{Al})_2$ tetrahedra correspond to the T-2 sites.

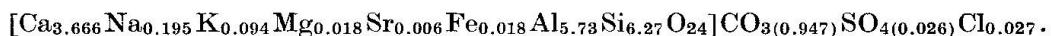
and GHOSE, 1972), and I4/m (PAULING, 1930; SCHERILLO, 1935; PAPIKE et al., 1965, 1966; while LIN and BURLEY, 1971 and ULRICH, 1973, reported it to be present only in Na- and Ca-rich scapolites). Structural refinements (PAPIKE et al., 1965, 1966; this paper) and crystallographic studies (LIN and BURLEY, 1971) indicate that end member crystals have diffraction patterns complying with the I4/m space group (presenting only a-reflections, for which $h+k+l=2n$), whereas additional spots (of the b-type: $h+k+l\neq 2n$) in specimens of intermediate compositions lower considerably the symmetry.

As part of a project of structural studies on scapolites, the Monte Somma meionite was refined. With a composition of about 93% meionite (EVANS et al., 1969), it is the most calcic scapolite reported up to date. Two were the reasons for the structural study: to provide better data on atomic positions, and to investigate the environment of the CO_3 -group. The specimen comes from an aggregate deposited at the Royal Ontario Museum (collection number M 9122) and was kindly donated by Prof. B. W. Evans.

Experimental Section

Precession photographs from several crystals of the Monte Somma meionite showed only a-reflections; the Laue symmetry is 4/m, the diffraction symbol is 4/m I-/-, and the space group was taken as I4/m (cf. PAPIKE et al., 1965, 1966). One of the crystals was ground to a spheroid with principal radii $0.1 \times 0.1 \times 0.12$ mm. Laue photographs taken after the grinding process showed

no asterism. The general formula of the Monte Somma scapolite (cf. EVANS et al., 1969) is



Since $\mu = 16.3$, no absorption corrections are necessary. Three dimensional intensity data were collected by a $\theta - 2\theta$ scan technique with a computer-controlled Picker diffractometer using monochromatic $\text{MoK}\alpha_1$ radiation. Details of the instrumental setting are given in DUESLER and RAYMOND (1971). Cell parameters were calculated with a version of a least squares program by Busing and Levy and are based on twelve carefully centered reflections. They are: $a_0 = 12.189$ (9), $c_0 = 7.576$ (6) Å¹. Intensity data were collected from the following shells: a- and b-reflections, $+h$, $+k$, $+l$, up to $50^\circ 2\theta$; a-reflections only, for $+h$, $+k$, $+l$ in the interval $50^\circ - 60^\circ 2\theta$ and up to $50^\circ 2\theta$ for $-h$, $+k$, $+l$. Lp corrections and averaging of intensities of equivalent reflections were computed with programs UCFACS and PICKOUT (Department of Chemistry, University of California, Berkeley) (cf. DUESLER and RAYMOND, 1971). The least-squares refinement, distance and error calculations and Fourier synthesis were performed with Ibers' NUCLS, Baur's SADIAN, the Busing-Levy ORFFE and Zalkin's FORDAP programs. Neutral scattering factors for atoms are based on values given in CROMER and MANN (1968); factors for Na, Sr, Fe and K were incorporated in the proper proportions into Ca, the ones for S and Cl into those for C.

Structural refinement was based on 778 independent reflections, for which $F^2 > 3\sigma(F^2)$, where σ is the standard deviation of intensity counts. All b-reflections were considered non-existent, since only one or two have intensities barely above background level. After assignment of trial parameters and isotropic temperature factors taken from PAPIKE and STEPHENSON (1966), final refinements were performed with anisotropic temperature corrections and different Al and Si occupancies in the T-1 and T-2 sites (fig. 1). These occupancies were estimated according to the method of SMITH and BAILEY (1963). The final agreement factors are as follows: conventional R-factor: 2.96%; weighted R-factor: 4.88% (for details, see DUESLER and RAYMOND, 1971). A final difference Fourier showed no predominant peak positions².

Results and Discussion

Atomic parameters (nomenclature of atoms according to PAPIKE et al., 1965, 1966; cf. also fig. 1), anisotropic temperature factors, bond lengths and

¹) Cell parameters based on Guinier powder patterns are slightly different (ULBRICH, 1973) and probably reflect some differences in composition among individual crystals of the Monte Somma aggregate.

²) A list of calculated and observed intensities can be obtained from the author.

Table 1. Positional and thermal parameters^{a, b}

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(Ca, M) ^c	14354 (6) ^c	21919 (6)	0	180 (4) ^c	249 (5)	1172 (12)	59 (4)	0	0
(Si, Al) ₁	33962 (6)	40765 (6)	0	63 (5)	87 (5)	336 (11)	-11 (4)	0	0
(Si, Al) ₂	34014 (5)	8698 (5)	20714 (6)	110 (4)	108 (4)	263 (9)	1 (2)	-2 (3)	13 (3)
O ₁	45894 (18)	34754 (19)	0	140 (13)	229 (15)	858 (32)	-9 (12)	0	0
O ₂	31303 (21)	12718 (18)	0	274 (14)	182 (14)	371 (26)	58 (13)	0	0
O ₃	5054 (14)	34928 (13)	20582 (18)	208 (10)	219 (10)	573 (21)	4 (8)	-103 (11)	18 (10)
O ₄	23379 (14)	13613 (14)	32618 (20)	249 (11)	191 (10)	903 (23)	41 (9)	261 (13)	59 (13)
(C, N) ^f	0	0	0	467 (31)	467 (31)	688 (75)	0	0	0
O ₅ ^d	10371 (56)	2166 (85)	0	902 (60)	2055 (94)	1746 (96)	-855 (72)	0	0

^a Positional parameters (fractional coordinates) and thermal parameters are multiplied by 10⁵.

^b Thermal correction is of the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

^c Standard deviations, in terms of the last significant digit, in parenthesis.

^d Oxygen atom of the CO₃-group.

^e Ca and M (= Fe + Sr + Na + K + Mg) assigned to the same equipoint.

^f Carbon, S and Cl at the origin.

Table 2. Root-mean-square displacements along principal axes (in Å × 10⁴)

	Axis 1	Axis 2	Axis 3
(Ca, M)	1049 (15)	1460 (12)	1846 (10)
(Si, Al) ₁	665 (29)	830 (24)	989 (16)
(Si, Al) ₂	850 (15)	911 (15)	925 (14)
O ₁	1023 (5)	1315 (4)	1580 (30)
O ₂	1039 (36)	1076 (54)	1508 (42)
O ₃	1059 (28)	1288 (28)	1452 (24)
O ₄	976 (32)	1174 (31)	1898 (24)
(C, N)	1415 (77)	1875 (62)	1875 (62)
O ₅	1831 (106)	2253 (62)	4352 (105)

For explanations, see table 1.

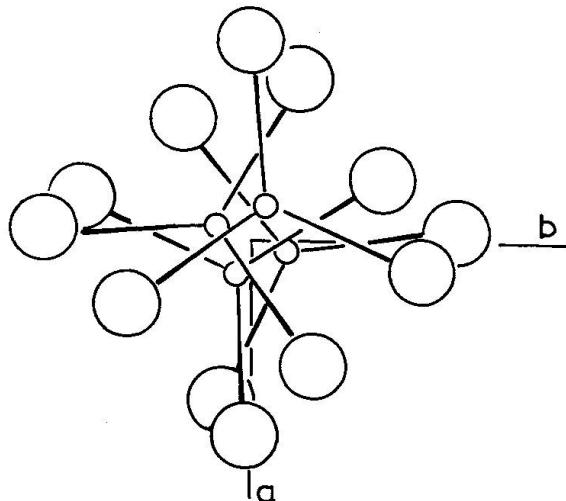
angles, and root-mean-square displacements of vibration are given in tables 1 to 3.

An anomaly results from the presence of the CO₃-group with its three-fold-symmetry at the site of a 4/m symmetry. Attempts have been made to place the carbon atoms with the proper occupancy factors into x, y, 0 and x, y, z positions, but the refinements did not converge. It has also been tried, unsuccessfully, to move O₅ away from the mirror plane. The best results were obtained with the positions indicated in table 1, conforming to a model proposed by PAPIKE and STEPHENSON (1966) (cf. fig. 2). Accordingly, thermal parameters and root-mean-square amplitudes for C and O₅ are large, since they represent the values for "average" clusters and not for real atoms. The approximate Cl-Na distance is somewhat less than 3.018 Å (based on data by PAPIKE and ZOLTAI, 1965), slightly larger than that in halite (2.8199 Å). Conversely, the C-Ca bond length is around 3.19 Å (table 3). Therefore, whenever Ca and Na coexist in a scapolite that is not exactly an end-member, a positional splitting has to be expected. Sodium is present in subordinate quantities in the Monte Somma scapolite, and it is not possible to refine slightly separated

Table 3. Bond lengths and selected bond angles

		Multiplicity	Distance (Å)
(Ca, M)	O ₂	1	2.3508 (26)
	O ₄	2	2.6607 (20)
	O' ₄	2	2.8882 (16)
	O ₅	1	2.4559 (98)
	O' ₅	1	2.4574 (106)
(Si, Al) ₁	O ₁	1	1.6286 (23)
	O' ₁	1	1.6290 (24)
	O ₄	2	1.6792 (15)
Average: 1.6540 (19)			
(Si, Al) ₂	O ₂	1	1.6769 (10)
	O ₃	1	1.6775 (17)
	O' ₃	1	1.6800 (17)
	O ₄	1	1.6889 (16)
Average: 1.6808 (15)			
(C, N)	O ₅	4	1.2913 (63)
(Ca, M)		4	3.1938 (8)
Bond angles			
Si ₁ —O ₁ —Si' ₁	156.7 (2)	O ₂ —Si ₂ —O ₃	112.9 (1)
Si ₂ —O ₂ —Si' ₂	138.7 (2)	O ₂ —Si ₂ —O' ₃	107.4 (1)
Si ₂ —O' ₃ —Si' ₂	145.2 (1)	O ₂ —Si ₂ —O ₄	104.2 (1)
Si ₁ —O ₄ —Si ₂	135.6 (1)	O ₃ —Si ₂ —O' ₃	114.3 (1)
O ₁ —Si ₁ —O' ₁	113.3 (2)	O ₃ —Si ₂ —O ₄	103.6 (1)
O ₁ —Si ₁ —O ₄	109.4 (1)	O' ₃ —Si ₂ —O ₄	114.1 (1)
O' ₁ —Si ₁ —O ₄	110.4 (1)		
O ₄ —Si ₁ —O' ₄	103.3 (1)		

For explanations, see table 1.

Fig. 2. Clustering of the CO₃-groups at the origin, according to a model proposed by PAPIKE and STEPHENSON (1966). Oxygen: large circles; carbon: small circles.

Ca- and Na-atoms. The unusually large temperature factor and root-mean-square amplitudes of (Ca, M) are nevertheless strong indications of a slight positional disorder between Na and Ca (tables 1 and 2). K, Sr, Mg and Fe (here collectively designated, together with Na, as M) are presumably also

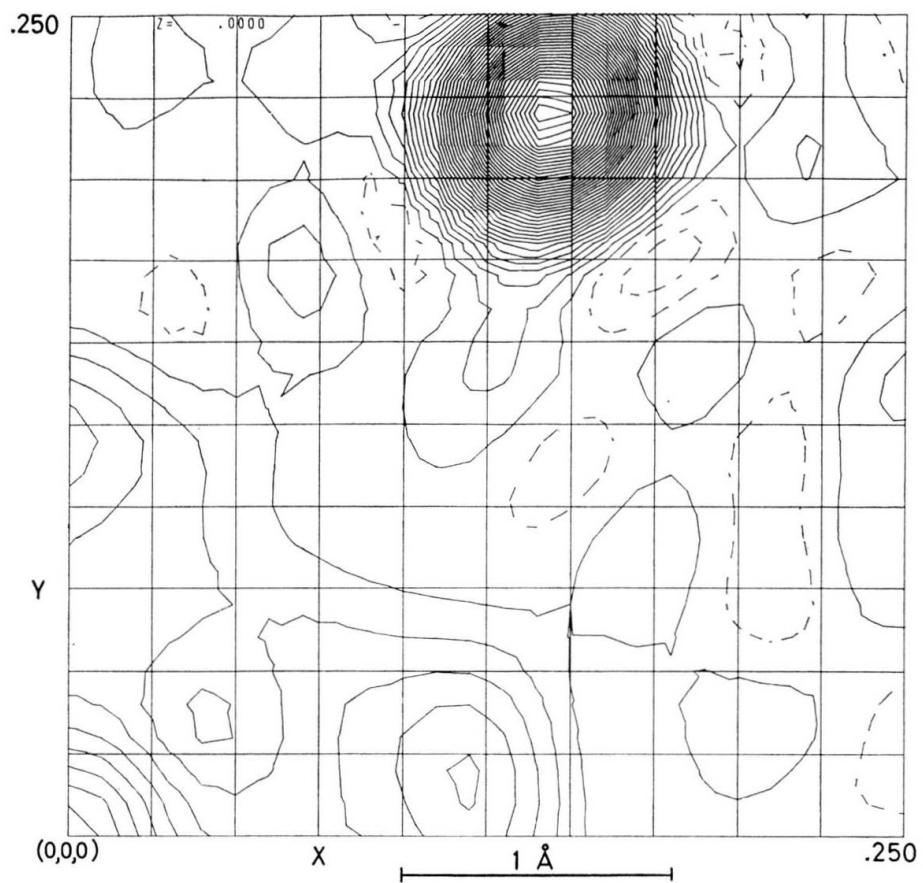


Fig. 3 a.

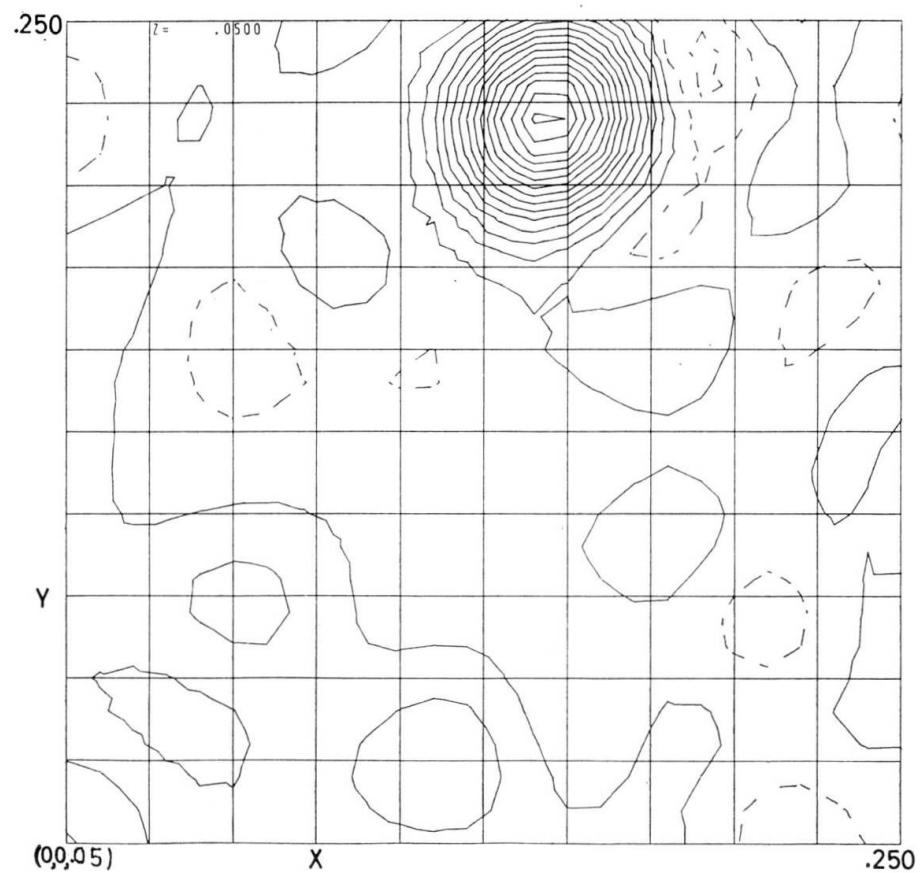


Fig. 3 b.

located at the same equivalent position as Ca, but slightly displaced from the Ca-coordinates, and should add their disturbing effect to that of Na. A Fourier summation computed after the last least square cycle – from F^2 (observed) and signs from F^2 (calculated) – shows the environment of Ca, C and O_5 (fig. 3a). The fact that the C atom is not at the origin but dispersed as suggested by PAPIKE's model (fig. 2) explains the low peak height at the origin; a similar reasoning applies to O_5 . (Ca, M) is here the "heavy" atom and shows a central peak with a ring of disturbances. As expected, the O_5 clusters yield a non-uniform band with a marked maximum (the refined position of O_5). The cluster of C atoms at the origin develops an electron density with the shape of a distorted spheroid (shortest dimension along the a-axes, fig. 3a/b).

Fractional tetrahedral occupancies were estimated according to the usual procedure (SMITH and BAILEY, 1963), using cell parameters from PAPIKE et al. (1965, 1966) and table 3, and compositional data from EVANS et al. (1969). Four points are available for drawing a tetrahedral occupancy line, as represented in fig. 4. From there, the Al-distribution in the meionite is as follows:

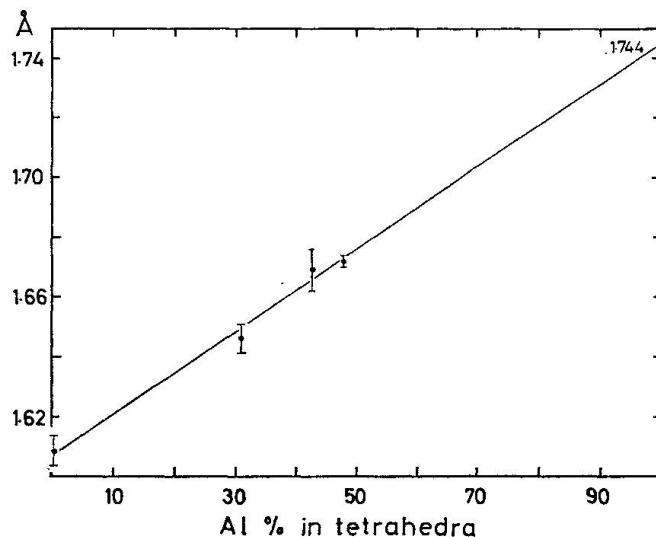


Fig. 4. Mean tetrahedral distances vs. tetrahedral aluminum occupancy in scapolites. Data from PAPIKE et al. (1965, 1966), EVANS et al. (1969) and table 3. The value 1.744 Å is the extrapolated mean distance for Al-0 tetrahedra in scapolites.

Fig. 3. Fourier synthesis on and near the plane (xy0). Origin is at the lower left corner. Electron densities in arbitrary units. Broken lines: negative areas. Cluster at the origin, due to carbon atom. Clusters alongside a_1 and a_2 , oxygen atoms (cf. fig. 2). The heavy peak defines the (Ca, M) atom.

a: section at $z = 0$. b: section at $z = 0.05$.

34.0% Al, 66.0% Si in position T-1; 53.0% Al, 47.0% Si in position T-2. The Monte Somma scapolite is therefore partially ordered, with a Si-Al ratio of approximately one in T-2³).

The C-O distances in the CO₃-groups of carbonates are as follows: in aragonite, 1.283 (4) Å (DAL NEGRO and UNGARETTI, 1971) and 1.282 (4) Å (DE VILLIERS, 1971); in strontianite, 1.285 (8) Å and witherite, 1.287 (9) Å (DE VILLIERS, 1971); and in calcite, 1.283 (2) Å (CHESSIN et al., 1965). The C-O average distance is 1.291 (6) Å in the Monte Somma meionite, and the discrepancy with the former values probably does not reflect a real difference but is only a result of the positional clustering of O₅ in the scapolite structure.

Acknowledgments

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³) The equation of the regression line in fig. 4 is $y = 1.6487 + 0.001371 (x - \bar{x})$, where $\bar{x} = 30.2875$ (cf. HOEL, 1966), close to the one represented by PAPIKE and STEPHENSON (1966).

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