like structures of Br–C≡N (Geller & Schawlow, 1955) with Br···N = 2·87 Å and Br–C≡C–C≡N (Bjorvatten, 1968) with Br···N = 2·96 Å. Other examples of such weak Br···N interactions are found in: 2,4-dibromodiazoaminobenzene (Omel'Chanko & Kondrashev, 1966), Br···N = 3·22 Å, C–Br···N = 163°; bromotricyanomethane (Witt, Britton & Mahon, 1972) Br···N = 3·03 Å, C–Br···N = 163°; and 2,4,6-tribromobenzonitrile (Carter & Britton, 1972), Br···N = 3·06 Å, C–Br···N = 170° (angles computed from published coordinates).

References

BJORVATTEN, T. (1968). *Acta Chem. Scand.* **22**, 410–420.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CARTER, V. B. & BRITTON, D. (1972). *Acta Cryst.* B**28**, 945–950.

GELLER, S. & SCHAWLOW, A. C. (1955). *J. Chem. Phys.* **23**, 779–783.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.

International Tables for X-ray Crystallography (1959). Vol. II. p. 295. Birmingham: Kynoch Press.

MUKHERJEE, T. K. (1969). *J. Phys. Chem.* **73**, 4381–4382.

OMEL'CHANKO, YU. A. & KONDRASHEV, YU. D. (1966). *Sov. Phys. Crystallogr.* **10**, 690–693.

PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746–751.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

SILVERMAN, J., KRUKONIS, A. P. & YANNONI, N. F. (1967). *Acta Cryst.* **23**, 1057–1063.

SILVERMAN, J., KRUKONIS, A. P. & YANNONI, N. F. (1968). *Acta Cryst.* B**24**, 1481–1488.

WITT, J. R., BRITTON, D. & MAHON, C. (1972). *Acta Cryst.* B**28**, 950–955.

Acta Cryst. (1973). B**29**, 2024

The Crystal Structure of Meionite

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

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

(*Received* 17 *April* 1973; *accepted* 9 *May* 1973)

Abstract. Meionite with cell formula $(Ca_{7\cdot32}Na_{0\cdot39}K_{0\cdot19}Fe_{0\cdot038}Mg_{0\cdot004}Sr_{0\cdot015})(Si_{12\cdot41}Al_{11\cdot33})O_{48\cdot51}[Cl_{0\cdot053}(SO_4)_{0\cdot053}(CO_3)_{1\cdot895}]$ is tetragonal, $P4_2/n$ rather than $I4/m$, $a = 12\cdot194$ (4), $c = 7\cdot557$ (4) Å, $D_x = 2\cdot78$ g cm^{-3}. This mineral is from Monte Somma, Italy. The structure is similar to that of marialite but with significant differences in atomic coordinates and Al site occupancies. The CO_3 groups are essentially disordered on the (001) plane and displaced from the site 0,0,0. The Ca ion is 8-coordinated rather than 6-coordinated.

Introduction. The intensities and cell dimensions were measured from a transparent, colourless crystal about 0·4 mm wide, using the integrating precession camera (Zr-filtered Mo $K\alpha$ radiation). 688 reflexions were collected, of which 166 had an intensity less than the minimum observable value and were assigned a value of $I_{\min}/3$ (Hamilton, 1955). Lorentz and polarization corrections were applied. The systematic absences were hkl with $h+k+l$ odd, $hk0$ with $h+k$ odd and $00l$ with l odd. The apparent space groups is $I4/m$ but the most probable space group of this impure meionite should be $P4_2/n$ (Lin, 1971; Lin & Burley, 1971, 1973*b*). The trial-structure atomic parameters correspond to those of marialite (Lin & Burley, 1973*a*). Full-matrix least-square refinement with isotropic temperature factors and Cruickshank's weighting scheme gave a residual $[R = \sum(|F_o| - |F_c|)/\sum|F_o|]$ of 0·079 first based on $I4/m$ and 0·072 subsequently based on $P4_2/n$. Those unobserved reflexions consistent with $P4_2/n$ were given a much smaller weight inferred from the relationship between the intensity of $h+k+l$ odd reflexions and composition of scapolites (Lin & Burley 1971, 1973*b*). The refined parameters are listed in Table 1. A table of $F_{\rm cal}$ and $F_{\rm obs}$ values is obtainable.* The bond lengths and angles are in Tables 2 and 3.

Discussion. The structure is similar to that of marialite (Lin & Burley, 1973*a*) but some significant differences mainly arising from the chemical difference are observed. Ignoring the difference in z coordinates, the structure can be considered as being derived from the marialite structure by rotating (type 1) tetrahedra rings counter-clockwise while rotating (type 2) tetrahedra rings clockwise. Thus the oval-shaped cation channels relatively increase their long diameter and decrease the short one. This meionite is the most Ca, CO_3-rich scapolite found in nature. The role of the CO_3 group in this meionite is similar to that described in mizzonite (Papike & Stephenson, 1966). The CO_3 group is positionally disordered maily on the xy plane, though it could tilt slightly from this plane, as indicated by the very high thermal factor and z coordinates of O(7).

This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30133 (11 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

This hypothesis is also favoured by the high thermal factor of the C atom, the square plateau of electron density around the 0,0,0 site, and the slightly shorter C–O bond. The Ca ion is 8-coordinated rather than 6-coordinated as reported by Papike & Stephenson (1966). The main difference between the coordination of Ca in meionite and Na in marialite is that in meionite O(7) of the CO_3 group is coordinated to Ca while in marialite Cl(1) at 0,0,0 is coordinated to Na. This further gives rise to the differences between the *x*, and *y* coordinates of Na in marialite and those of Ca in meionite.

The assumption of $P4_2/n$ for the space group of this impure meionite has developed from a consideration of the crystallography of the scapolite family as a whole (Lin & Burley, 1971; 1973*b*). The structure was successfully refined in $P4_2/n$ to give an *R* of 7·2%, which is lower than the *R* of 7·9% obtained in space group $I4/m$. Though a lower *R* is by no means an absolute measure of the correctness of a structure model, nevertheless, a satisfactory refinement with a lower *R* does tend to favour the possibility of $P4_2/n$ being the real space group. The temperature factors refined in $P4_2/n$ are more similar to those of other scapolites (Lin,

Table 1. *Atomic coordinates and temperature factors of meionite* (93% Me, *Mt. Somma, Italy*)

Standard deviations, σ, given in parentheses. The comparison for marialite is also given.

Atom		Specimen 1 Meionite ($P4_2/n$)	 2 Meionite ($I4/m$)	 3 Marialite* ($P4_2/n$)
	x	0·3565 (2)	0·3565 (2)	0·3659 (2)
(Ca, Na, K) (1)	*y*	0·2807 (2)	0·2809 (2)	0·2884 (3)
	z	0·5001 (3)	$\frac{1}{2}$	0·5064 (4)
	B	1·79 (4)	1·54 (5)	2·68 (6)
	x	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
(C, Cl S) (1)	*y*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	z	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	B	1·97 (29)	1·36 (40)	3·85 (12)
	x	0·3395 (2)	0·3395 (3)	0·3390 (1)
(Si, Al) (1)	*y*	0·4074 (2)	0·4071 (3)	0·4100 (1)
	z	1·0000 (3)	1	0·9989 (3)
	B	0·47 (4)	0·29 (5)	0·69 (3)
	x	0·6599 (2)	0·6598 (2)	0·6621 (2)
(Si, Al) (2)	*y*	0·9129 (2)	0·9134 (2)	0·9152 (2)
	z	0·7930 (3)	0·7934 (2)	0·7956 (2)
	B	0·51 (5)	0·32 (3)	0·79 (4)
	x	0·4130 (2)		0·4145 (2)
(Si, Al) (3)	*y*	0·8401 (2)		0·8368 (2)
	z	0·7072 (3)		0·7085 (2)
	B	0·51 (5)		0·63 (4)
	x	0·4593 (5)	0·4591 (7)	0·4574 (4)
O(1)	*y*	0·3475 (5)	0·3484 (7)	0·3511 (4)
	z	0·9999 (10)	1	1·0011 (7)
	B	1·33 (9)	1·13(14)	1·39 (8)
	x	0·6871 (4)	0·6873 (6)	0·6939 (4)
O(2)	*y*	0·8732 (5)	0·8726 (7)	0·8797 (4)
	z	0·9999 (9)	1	1·0048 (7)
	B	0·98 (8)	0·57 (12)	1·25 (7)
	x	0·3491 (5)	0·3482 (4)	0·3486 (6)
O(3)	*y*	0·9495 (5)	0·9510 (4)	0·9448 (5)
	z	0·7941 (9)	0·7965 (6)	0·7898 (6)
	B	1·09 (10)	0·84 (9)	1·48 (10)
	x	0·5504 (5)		0·5499 (5)
O(4)	*y*	0·8491 (5)		0·8475 (6)
	z	0·7055 (9)		0·7163 (6)
	B	1·11 (10)		1·49 (10)
	x	0·2674 (5)	0·2669 (4)	0·2706 (5)
O(5)	*y*	0·3645 (6)	0·3647 (4)	0·3699 (5)
	z	0·8245 (7)	0·8293 (7)	0·8277 (6)
	B	1·42 (12)	1·10 (9)	1·30 (9)
	x	0·3643 (6)		0·3710 (6)
O(6)	*y*	0·7345 (5)		0·7282 (6)
	z	0·8269 (7)		0·8270 (7)
	B	1·48 (12)		1·47 (10)
	x	0·3995 (16)	0·3961 (16)	0·3833 (62)
O(7)	*y*	0·4865 (16)	0·4822 (19)	0·4817 (64)
	z	0·5001 (25)	$\frac{1}{2}$	0·5012 (101)
	B	6·42 (41)	6·27 (52)	4·01 (1·28)
R		7·2%	7·9%	7·4%

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

Table 2. *Interatomic distances in meionite* (93% Me, *Monte Somma, Italy*)

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

(Si, Al) tetrahedron	T–O distances (Å) Atoms	 Distance	O–O distances (Å) Atoms	 Distance
T(1)	O(1)	1·634 (6)	O(1)–O(5)	2·697 (9)
	O(5)	1·674 (6)	O(1)–O(1′)	2·721 (9)
	O(1′)	1·628 (6)	O(1)–O(6′)	2·709 (10)
	O(6′)	1·674 (6)	O(1′)–O(5)	2·707 (10)
			O(1′)–O(6′)	2·709 (9)
			O(5)–O(6′)	2·635 (8)
Average		1·653 (6)		2·696 (9)
T(2)	O(2)	1·670 (7)	O(2)–O(4)	2·796 (9)
	O(4)	1·681 (7)	O(2)–O(3′)	2·699 (9)
	O(3′)	1·681 (7)	O(2)–O(5′)	2·642 (8)
	O(5′)	1·690 (7)	O(4)–O(5′)	2·663 (9)
			O(4)–O(3′)	2·825 (9)
			O(3′)–O(5′)	2·822 (10)
Average		1·681 (7)		2·741 (9)
T(3)	O(3)	1·679 (7)	O(3)–O(4)	2·824 (9)
	O(4)	1·680 (7)	O(3)–O(6)	2·640 (9)
	O(6)	1·682 (6)	O(3)–O(2′)	2·699 (9)
	O(2′)	1·673 (7)	O(4)–O(6)	2·819 (10)
			O(4)–O(2′)	2·698 (9)
			O(6)–O(2′)	2·652 (8)
Average		1·679 (7)		2·722 (9)

(*b*) Selected interatomic distances

Type	From	To	Multiplicity	Distance (Å)
Cation Coordination polyhedron	(Ca, Na, K)	O(2′)	1	2·353 (6)
		O(3′)	1	2·493 (7)
		O(4′)	1	2·490 (7)
		O(5)	1	2·870 (6)
		O(5′)	1	2·679 (7)
		O(6′)	1	2·655 (7)
		O(6″)	1	2·893 (6)
		O(7′)	1	2·402 (20)
Anion cage diagonals	O(1)	O(1′)	4	8·480 (10)
	O(5)	O(6′)	4	8·223 (8)
	O(2)	O(2′)	2	8·234 (8)
Carbonate group	C	O(7)	3	1·236 (20)

Table 3. *Interatomic angles in meionite* (93 % Me, *Monte Somma, Italy*

Type	Atoms	Angle ± σ(°)
O–T(1)–O angles [T(1) tetrahedron]	O(1)–T(1)–O(5)	109·22 ± 0·37
	O(1)–T(1)–O(1′)	113·09 ± 0·34
	O(1)–T(1)–O(6′)	109·98 ± 0·37
	O(5)–T(1)–O(1′)	110·12 ± 0·39
	O(5)–T(1)–O(6′)	103·79 ± 0·31
	O(1′)–T(1)–O(6′)	110·23 ± 0·39
O–T(2)–O angles [T(2) tetrahedron]	O(2)–T(2)–O(4)	113·06 ± 0·34
	O(2)–T(2)–O(3′)	107·32 ± 0·33
	O(2)–T(2)–O(5′)	103·66 ± 0·32
	O(4)–T(2)–O(3′)	114·36 ± 0·34
	O(4)–T(2)–O(5′)	104·33 ± 0·34
	O(3′)–T(2)–O(5′)	113·70 ± 0·36
O–T(3)–O angles [T(3) tetrahedron]	O(3)–T(3)–O(4)	114·44 ± 0·34
	O(3)–T(3)–O(6)	103·54 ± 0·34
	O(3)–T(3)–O(2′)	112·93 ± 0·34
	O(4)–T(3)–O(6)	113·98 ± 0·36
	O(4)–T(3)–O(2′)	107·16 ± 0·33
	O(6)–T(3)–O(2′)	104·44 ± 0·32
T–O–T angles	T(1)–O(1)–T(1′)	156·91 ± 0·45
	T(2)–O(2)–T(3′)	138·85 ± 0·40
	T(3)–O(3)–T(2′)	145·23 ± 0·44
	T(2)–O(4)–T(3)	145·05 ± 0·44
	T(1)–O(5)–T(2′)	135·56 ± 0·46
	T(3)–O(6)–T(1′)	136·19 ± 0·47

1971; Burley, 1973*a*) than those refined in *I*4/*m*. The Al occupancy of each (Si, Al) tetrahedral site was estimated as follows (Smith & Bailey, 1963).

(*a*) Based on space group *I*4/*m*.

Tetrahedral ring	Tetrahedral sites	Mean (Si, Al)–O distance (Å)	Aluminum occupancy (%)
Type 1	(Si, Al) (1) = T(1)	1·639	21
Type 2	(Si, Al) (2) = T(2)	1·687	55

(*b*) Based on space group $P4_2/n$.

Tetrahedral ring	Tetrahedral sites	Mean (Si, Al)–O distance (Å)	Aluminum occupancy (%)
Type 1	(Si, Al) (1) = T(1)	1·653	30·7
Type 2	(Si, Al) (2) = T(2)	1·681	50·7
	(Si, Al) (3) = T(3)	1·679	49·3

In contrast to the situation in the Na Cl-rich scapolite (Lin & Burley, 1973*a*) in which Al only enters T(2) and T(3) sites, Al in this $CaCO_3$-rich scapolite is located on all three tetrahedral sites. This may be explained by the fact that the $CaCO_3$-rich scapolite has a higher ratio of Al/Si (Deer, Howie & Zussman, 1963), and requires the average value of Al occupancies of T(2) and T(3) sites in the (type 2) ring to be greater than 50 %, thus inevitably forming a larger number of unstable Al–O–Al linkages (Loewenstein, 1954) than if T(1) are partially occupied by Al to restrict the Al occupancy of (type 2) ring to not more than 50 %. Of course Al–O–Al linkages will still form in the 5-membered (Si, Al)-tetrahedra rings in the structure, but the total number of such linkages will be fewer in the whole structure (*cf.* figure in Lin & Burley, 1973*a*). In other words, after the Al % of (type 2) ring reaches 50 % as the meionite content increases, the rate of increase of Al–O–Al linkages will be greater when every additional Al atom enters the (type 2) ring to replace Si, than when the additional Al enters the (type 1) ring [*i.e.*, T(1) sites]. Therefore, the structure based on $P4_2/n$ is preferred as far as the number of Al–O–Al linkages in the whole structure and the refinement results are concerned

A Hamilton statistical test is not applicable in this special case to determine the better structure, since it is well known that every statistical test is only based on the assumption of random errors in the data (Hamilton, 1965). Further, the authors have failed to refine the structure in $P4_2/n$ by ignoring those unobserved ($h+k+l=$odd) reflexions. On the other hand, to exclude the likely systematic presence of the ($h+k+l=$ odd) reflexions and refine in *I*4/*m* (or $P4_2/n$) is likely to constitute a systematic error. The least-squares refinement based on *I*4/*m* by ignoring the unobserved ($h+k+l$ odd) reflexions also tends to give lower temperature factors for the (Si, Al) sites and some oxygen atoms, a higher *R* value and a (type 2) ring with more than 50 % Al occupancy when compared with those refined in $P4_2/n$. It is thought that the abnormally low and negative temperature factors, a higher *R* value (15·7 %) and a (type 2) ring having 52 % Al occupancy, present in the model of Papike & Stephenson (1966) have partly resulted from a refinement in the space group *I*4/*m*.

This research was supported by the National Research Council and the Geological Survey of Canada.

References

Deer, W. A., Howie, R. A. & Zussman, J. (1963). *Rock Forming Minerals*, **4**, 321–337. London: Longmans.

Hamilton, W. C. (1955). *Acta Cryst.* **8**, 185–186.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Lin, S. B. (1971). Ph. D. thesis, McMaster Univ. Canada.

Lin, S. B. & Burley, B. J. (1971). *Geol. Soc. Amer. Abstr.* with Programs, 3, 634.

Lin, S. B. & Burley, B. J. (1973*a*). *Acta Cryst.* B**29**, 000–000.

Lin, S. B. & Burley, B. J. (1973*b*). *Tschermaks Mineral. Petrogr. Mitt.* To be published.

Loewenstein, W. (1954). *Amer. Min.* **39**, 92–96.

Papike, J. J. & Stephenson, N. C. (1966). *Amer. Min.* **51**, 1014–1027.

Smith, J. V. & Bailey, S. W. (1963). *Acta Cryst.* **16**, 801–811.