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Structure of $Na_4Ca_4[Si_6O_{18}]$

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Abstract. $Na_4Ca_4[Si_6O_{18}]$, $M_r = 708{\cdot}8$, trigonal, $P3_121$ (or $P3_221$), $a = 10{\cdot}464\,(2)$, $c = 13{\cdot}168\,(2)$ Å, $V = 1248{\cdot}7\,(3)$ Å^3, $Z = 3$, $D_m = 2{\cdot}817$, $D_x = 2{\cdot}829$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}89$ mm^{-1}, $F(000) = 1056{\cdot}0$, $T = 293$ K, final $R = 0{\cdot}031$ for 2764 reflections. $Na_4Ca_4[Si_6O_{18}]$ is a terminal composition enriched with Ca in the $Na_{6-2x}Ca_{3+x}Si_6O_{18}$ ($0 \le x \le 1$) solid-solution series. The structure is built up of stacked six-membered $[Si_6O_{18}]^{12-}$ rings (point symmetry 2) of silicate tetrahedra and is a distortion derivative of the one (point symmetry $\bar{3}m$) found in $Na_6Ca_3[Si_6O_{18}]$. Each of the cations just above and below the ring is split into two. Vacant sites caused by the replacement of 2Na by Ca in the solid-solution series are located around the 3_1 axis which intersects with the twofold axes.

Introduction. Wyckoff & Morey (1926) first found $Na_4Ca_4[Si_6O_{18}]$† as a distinct phase (pseudocubic, $a = 7{\cdot}65$ Å) in the ternary system Na_2O–CaO–SiO_2. Based on X-ray powder diffraction, Köppen & Padurow (1958) gave the rhombohedral lattice parameters $a = 7{\cdot}41$ Å, $\alpha = 89{\cdot}7°$ for this compound. Later, this compound was shown to have a trigonal lattice with $a = 10{\cdot}48$, $c = 13{\cdot}19$ Å and the space group $P3_121$ or $P3_221$ (Glasser & Mileson, 1968). Maki & Sugimura (1968) showed that $Na_4Ca_4[Si_6O_{18}]$ forms solid solutions with $Na_6Ca_3[Si_6O_{18}]$ accompanying a phase change at an intermediate composition. The existence of the solid solutions was confirmed by Moir & Glasser (1974). The X-ray diffraction pattern of $Na_4Ca_4[Si_6O_{18}]$ is very similar to that of $Na_6Ca_3[Si_6O_{18}]$, but does not show systematic absence $-h + k + l \ne 3n$. The structure of $Na_4Ca_4[Si_6O_{18}]$ is therefore very likely to be a derivative of $Na_6Ca_3[Si_6O_{18}]$ (Ohsato, Maki & Takéuchi, 1985). On the other hand, Sahama & Hytönen (1957) described a rhombohedral mineral combeite, which has a composition near to $Na_4Ca_4[Si_6O_{18}]$. Recently, Fischer & Tillmanns (1983) found a trigonal modification of combeite and studied the crystal structure. According to them, the refinement of the structure was unsuccessful with the space group $P3_221$ but successful with $P3_2$. The present paper shows that we have been successful in determining the structure of synthetic $Na_4Ca_4[Si_6O_{18}]$ with $P3_121$. The result is compared with the structure of $Na_6Ca_3[Si_6O_{18}]$ (Ohsato *et al.*, 1985) and that of trigonal-type combeite proposed by Fischer & Tillmanns (1983).

Experimental. Single crystals of $Na_4Ca_4[Si_6O_{18}]$ were prepared by slowly cooling a melt of the same composition. D_m measured by flotation in methylene iodide diluted with acetone. The crystal obtained was ground to the shape of a sphere of radius 0·138 mm by the method of Bond (1951). Rigaku AFC-5 four-circle single-crystal diffractometer, ω–2θ scan, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters refined by the least-squares procedure using 25 reflections in the range $79 < 2\theta < 85°$. 2994 reflections collected, 2852 unique, 2764 with $F_o > 3\sigma(|F_o|)$. $2\theta < 80°$. $0 < h < 16$, $0 < k < 16$, $0 < l < 23$. Three standard reflections with no significant variations. Intensity data corrected for Lorentz and polarization factors but not for absorption because of the small μr, 0·236. Initial atomic parameters were derived from those of $Na_6Ca_3[Si_6O_{18}]$ (Ohsato, Maki & Takéuchi, 1985) by taking into account the change in both the space group and the composition. Anisotropic refinement on F of these atomic parameters was carried out with the full-matrix least-squares program *RADY* (Martin & Levy, 1962). Successive difference Fourier syntheses revealed the distribution of alkali and alkaline-earth ions and the splitting of the $M(1)$ site. The Na/Ca ratio was varied assuming full occupancies for O and Si sites and neutrality of the crystal. The refinement indicated that the ratio coincided with the

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† The compound is in general denoted by $Na_2Ca_2Si_3O_9$. A structural formula is used here to allow discussion of the relationship between this compound and $Na_2CaSi_2O_6$ whose structural formula is $Na_6Ca_3[Si_6O_{18}]$.

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ideal ratio of $Na_4Ca_4[Si_6O_{18}]$. Final occupancies for Na and Ca atoms at $M(1)$ and $M(31)$ were refined constraining the composition to be $Na_4Ca_4[Si_6O_{18}]$. Subsequently, $M(1)$ was split into two sites, here denoted $M(1)$ and $M(1')$. Final refinement with atomic parameters, anisotropic thermal parameters, a ratio containing atoms in $M(1')$ and isotropic extinction parameter. Unit weights. Final $R = 0{\cdot}0306$, $wR = 0{\cdot}0321$, for 158 variables and 2764 reflections. Isotropic extinction correction applied ($G_{\rm iso} = 0{\cdot}399 \times 10^{-4}$), $\Delta\rho = \pm 0{\cdot}7$ e Å^{-3}. $(\Delta/\sigma)_{\max} = 0{\cdot}14$ [$M(1)$ and $M(1')$], otherwise $\Delta/\sigma < 0{\cdot}01$. Atomic scattering factors for O^{2-} provided by Tokonami (1965) and for other ionized atoms, and f', f'' values from *International Tables for X-ray Crystallography* (1974). Calculations were carried out on the HITAC M-280H computer of the University of Tokyo.

Discussion. The final atomic parameters and $B_{\rm eq}$'s are listed in Table 1;* the origin is at 3_121. The structure is basically similar to that of $Na_6Ca_3[Si_6O_{18}]$ (Ohsato *et al.*, 1985) and the trigonal unit cell consists of 24 pseudocubic subcells with the edge length of 3·73 Å. The arrangement of the puckered six-membered silicate rings (Fig. 1) and the cations with respect to the subcells shares features with that of $Na_6Ca_3[Si_6O_{18}]$. The rings are arranged in a cubic-close-packed fashion as shown in Fig. 2. One marked feature of the present structure is the configuration of the silicate ring. While the ring in $Na_6Ca_3[Si_6O_{18}]$ has a symmetrical form with point symmetry $\bar{3}m$, that in the present structure is highly distorted and has point symmetry 2. The distortion may be best expressed in terms of the angles subtended by bridge bonds at the bridging O atoms: the angle subtended at O(11) is 146·6° in contrast to 175·9° at the opposite bridging O(12) atom. In agreement with this situation the mean Si—O bond lengths of the tetrahedra that share O(11) have a maximum value of 1·626 Å and those of the tetrahedra sharing O(12) a minimum value of 1·615 Å (Table 2).

A notable feature is the contents of the cation site corresponding to $M(2)$ of $Na_6Ca_3[Si_6O_{18}]$ at which a small amount of vacancy in the structure is preferably concentrated (Ohsato *et al.*, 1985). This site is differentiated into two distinct sites in the present structure, here denoted $M(21)$ and $M(22)$. $M(21)$ is located around the 3_1 axes at $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}z$, and fully occupied by Na (Table 1), whereas $M(22)$ is located around 3_1 passing through the origin and is entirely vacant. Thus in general the deficiency in atomic contents resulting from the replacement of 2Na by Ca in the $Na_{6-2x}Ca_{3+x}Si_6O_{18}$ $(0 \le x \le 1)$ solid-solution series is structurally adjusted by preferentially allocating a vacancy at $M(22)$. Hence this site is important in the structural characterization of the solid-solution series. The preferential location of vacancy in fact plays a significant role in the phase transition in $Na_4Ca_4[Si_6O_{18}]$ (Ohsato, Takéuchi & Maki, 1986).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (*origin at* 3_121)

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Position	Occupancy	x	y	z	$B_{\rm eq}$(Å^2)
O(11)	3(*b*)		0·1671 (3)	0	$\frac{5}{6}$	1·4 (1)
O(12)	3(*b*)		0·5555 (3)	0	$\frac{5}{6}$	1·6 (1)
O(13)	6(*c*)		0·3442 (2)	0·2842 (2)	0·8382 (1)	0·90 (4)
O(14)	6(*c*)		0·5849 (2)	0·2643 (2)	0·8199 (2)	1·05 (5)
O(21)	6(*c*)		0·2468 (2)	0·1535 (2)	0·6622 (1)	1·09 (5)
O(22)	6(*c*)		0·4782 (2)	0·2472 (2)	0·0032 (1)	1·22 (5)
O(23)	6(*c*)		0·5513 (2)	0·1104 (3)	0·6540 (1)	1·38 (5)
O(31)	6(*c*)		0·0652 (2)	0·1853 (2)	0·7949 (1)	0·79 (4)
O(32)	6(*c*)		0·5965 (3)	0·4991 (2)	0·8880 (1)	1·38 (5)
O(33)	6(*c*)		0·7990 (2)	0·2184 (2)	0·7763 (1)	1·07 (5)
Si(1)	6(*c*)		0·1986 (1)	0·1526 (1)	0·7780 (1)	0·46 (1)
Si(2)	6(*c*)		0·4996 (1)	0·3234 (1)	0·8958 (1)	0·54 (1)
Si(3)	6(*c*)		0·6243 (1)	0·1485 (1)	0·7635 (1)	0·50 (1)
M(1)	6(*c*)	0·59 (1) Na	0·3086 (1)	0·9830 (1)	0·5892 (1)	0·59 (2)
M(1')†	6(*c*)	0·41 (1) Ca	0·2821 (7)	0·9704 (5)	0·6151 (5)	2·6 (2)
M(21)	6(*c*)	1·00 Na	0·5041 (2)	0·3380 (2)	0·6642 (1)	1·69 (3)
M(22)‡	3(*a*)		0·165	0·165	0	
M(31)	6(*c*)	0·41 (1) Na 0·59 (1) Ca	0·5262 (1)	0·3704 (1)	0·1558 (1)	1·56 (2)
M(32)	3(*b*)	1·00 Ca	0·8203 (1)	0	$\frac{5}{6}$	0·76 (2)
M(4)	6(*c*)	1·00 Ca	0·3039 (1)	0	$\frac{1}{3}$	0·59 (2)

† The ratio $M(1')/[M(1) + M(1')]$ is 0·286 (4).

‡ $M(22)$ is vacant and the coordinates are only approximate.

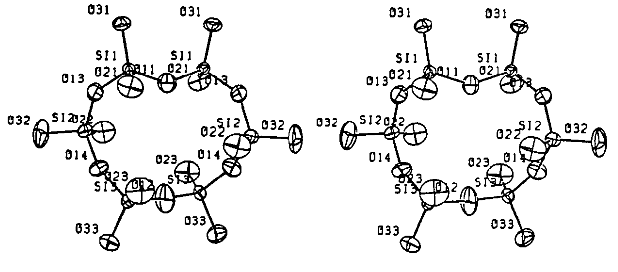

Fig. 1. Stereoscopic drawing of the distorted $[Si_6O_{18}]^{12-}$ six-membered ring with the *ORTEP* program (Johnson, 1965).

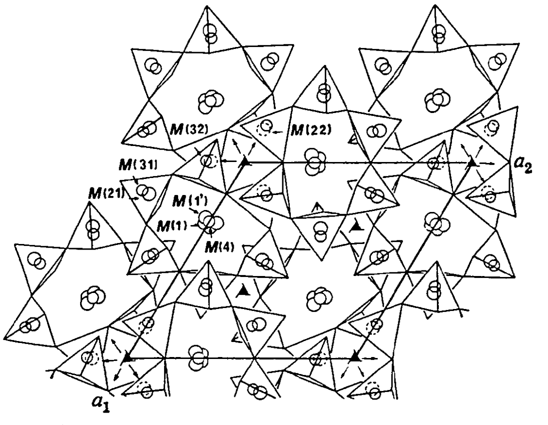

Fig. 2. Projection of the structure along the *c* axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42910 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The site corresponding to *M*(1) of $Na_6Ca_3[Si_6O_{18}]$ is slightly split into two sites [*M*(1) and *M*(1′)] in the present structure. *M*(1) is octahedrally coordinated by six O atoms, whereas *M*(1′) is shifted from *M*(1) towards the centre of the ring by about 0·5 Å, thus having an additional O(11) atom at a distance 3·189 Å. The splitting of the site is therefore related to the distortion of the ring which is characterized by a large shift of O(11) towards the ring relative to its position in the symmetrical $Na_6Ca_3[Si_6O_{18}]$ ring (Ohsato *et al.*, 1985). The large difference in B_{eq} (Table 1) between the two sites would then probably be related to the difference in the Ca/Na ratio. It was however difficult to differentiate the atomic contents at these sites with accuracy.

The trigonal-type structure proposed for combeite by Fischer & Tillmanns (1983) is basically the same as that described here. There is, however, a marked difference in the distribution of cations. In particular, Fischer & Tillmanns fully located Na at their Na(4) site, whereas the corresponding *M*(22) site of our structure is vacant as mentioned above. Although the

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Si(1) site		
Si(1)–O(11)	1·631 (1)	
Si(1)–O(13)	1·657 (2)	
Si(1)–O(21)	1·604 (2)	
Si(1)–O(31)	1·610 (3)	
Average	1·626 (2)	
O(11)–O(13)	2·602 (2)	104·6 (1)
O(11)–O(21)	2·648 (2)	109·8 (1)
O(11)–O(31)	2·686 (3)	112·0 (1)
O(13)–O(21)	2·624 (3)	107·1 (1)
O(13)–O(31)	2·626 (3)	107·0 (1)
O(21)–O(31)	2·720 (3)	115·6 (1)
Average	2·651 (3)	109·4 (1)
Si(2) site		
Si(2)–O(13)	1·649 (2)	
Si(2)–O(14)	1·652 (3)	
Si(2)–O(22)	1·583 (2)	
Si(2)–O(32)	1·599 (2)	
Average	1·621 (2)	
O(13)–O(14)	2·640 (4)	106·2 (1)
O(13)–O(22)	2·716 (3)	114·3 (1)
O(13)–O(32)	2·554 (3)	103·7 (1)
O(14)–O(22)	2·627 (3)	108·6 (1)
O(14)–O(32)	2·561 (4)	104·0 (1)
O(22)–O(32)	2·741 (3)	119·0 (1)
Average	2·640 (3)	109·3 (1)
Si(3) site		
Si(3)–O(12)	1·631 (1)	
Si(3)–O(14)	1·640 (3)	
Si(3)–O(23)	1·586 (2)	
Si(3)–O(33)	1·603 (2)	
Average	1·615 (2)	
O(12)–O(14)	2·631 (3)	107·1 (1)
O(12)–O(23)	2·639 (2)	110·2 (1)
O(12)–O(33)	2·541 (3)	103·5 (1)
O(14)–O(23)	2·631 (3)	109·3 (1)
O(14)–O(33)	2·580 (4)	105·4 (1)
O(23)–O(33)	2·768 (3)	120·4 (1)
Average	2·632 (3)	109·3 (1)
M(1) site		
M(1)–O(21)	2·383 (3)	
M(1)–O(22$^{\mathrm{v}}$)	2·338 (3)	
M(1)–O(23)	2·360 (2)	
M(1)–O(31$^{\mathrm{iii}}$)	2·445 (2)	
M(1)–O(32$^{\mathrm{iv}}$)	2·474 (2)	
M(1)–O(33$^{\mathrm{iii}}$)	2·758 (2)	
Average	2·460 (2)	
O(21)–O(22$^{\mathrm{v}}$)	4·113 (4)	121·2 (1)
O(21)–O(23)	3·435 (4)	92·8 (1)
O(21)–O(31$^{\mathrm{iii}}$)	3·309 (3)	86·5 (1)
O(21)–O(33$^{\mathrm{iii}}$)	3·309 (3)	79·7 (1)
O(22$^{\mathrm{v}}$)–O(23)	3·566 (3)	98·7 (1)
O(22$^{\mathrm{v}}$)–O(31$^{\mathrm{iii}}$)	3·776 (3)	104·3 (1)
O(22$^{\mathrm{v}}$)–O(32$^{\mathrm{iv}}$)	3·338 (2)	87·8 (1)
O(23)–O(32$^{\mathrm{iv}}$)	3·363 (3)	88·1 (1)
O(23)–O(33$^{\mathrm{iii}}$)	3·440 (3)	84·1 (1)
O(31$^{\mathrm{iii}}$)–O(32$^{\mathrm{iv}}$)	3·155 (3)	79·8 (1)
O(31$^{\mathrm{iii}}$)–O(33$^{\mathrm{iii}}$)	2·984 (1)	69·7 (1)
O(32$^{\mathrm{iv}}$)–O(33$^{\mathrm{iii}}$)	3·042 (3)	70·9 (1)
Average	3·403 (3)	88·6 (1)
M(1′) site		
M(1′)–O(11)	3·189 (7)	
M(1′)–O(21)	2·213 (7)	
M(1′)–O(22$^{\mathrm{v}}$)	2·159 (6)	
M(1′)–O(23)	2·493 (6)	
M(1′)–O(31$^{\mathrm{iii}}$)	2·544 (7)	
M(1′)–O(32$^{\mathrm{iv}}$)	2·832 (8)	
M(1′)–O(33$^{\mathrm{iii}}$)	3·092 (6)	
Average	2·646 (7)	
O(11)–O(21)	2·648 (2)	55·2 (3)
O(11)–O(22)	3·724 (3)	86·0 (2)
O(11)–O(31$^{\mathrm{iii}}$)	4·934 (2)	118·3 (2)
O(21)–O(22$^{\mathrm{v}}$)	4·113 (4)	140·3 (4)
O(21)–O(23)	3·435 (4)	93·6 (2)
O(21)–O(31$^{\mathrm{iii}}$)	3·309 (3)	87·8 (3)
O(21)–O(33$^{\mathrm{iii}}$)	3·309 (3)	75·1 (2)
O(22$^{\mathrm{v}}$)–O(23)	3·566 (3)	99·8 (3)
O(22$^{\mathrm{v}}$)–O(31$^{\mathrm{iii}}$)	3·776 (3)	106·5 (2)
O(22$^{\mathrm{v}}$)–O(32$^{\mathrm{iv}}$)	3·338 (2)	82·8 (2)
O(23)–O(32$^{\mathrm{iv}}$)	3·363 (3)	78·0 (2)
O(23)–O(33$^{\mathrm{iii}}$)	3·440 (3)	75·2 (2)
O(31$^{\mathrm{iii}}$)–O(32$^{\mathrm{iv}}$)	3·155 (3)	71·6 (2)
O(31$^{\mathrm{iii}}$)–O(33$^{\mathrm{iii}}$)	2·984 (1)	63·1 (2)
O(32$^{\mathrm{iv}}$)–O(33$^{\mathrm{iii}}$)	3·042 (3)	61·6 (2)
Average	3·476 (3)	86·3 (2)
M(21) site		
M(21–O(12$^{\mathrm{iii}}$)	2·646 (3)	
M(21)–O(13)	2·724 (2)	
M(21)–O(14)	2·483 (3)	
M(21)–O(14$^{\mathrm{iii}}$)	2·830 (2)	
M(21)–O(21)	2·404 (2)	
M(21)–O(22$^{\mathrm{iii}}$)	2·462 (2)	
M(21)–O(23)	2·667 (4)	
M(21)–O(23$^{\mathrm{iv}}$)	2·658 (3)	
M(21)–O(32)	3·291 (2)	
M(21)–O(33$^{\mathrm{iii}}$)	3·172 (2)	
Average	2·734 (3)	
O(12$^{\mathrm{iii}}$)–O(14$^{\mathrm{iii}}$)	2·631 (4)	57·3 (1)
O(12$^{\mathrm{iii}}$)–O(21)	3·437 (3)	85·7 (1)
O(12$^{\mathrm{iii}}$)–O(23$^{\mathrm{iv}}$)	2·639 (2)	59·7 (1)
O(12$^{\mathrm{iii}}$)–O(33$^{\mathrm{iii}}$)	2·541 (4)	50·8 (1)
O(13)–O(14)	2·640 (4)	60·7 (1)
O(13)–O(21)	2·624 (3)	61·2 (1)
O(13)–O(23)	4·222 (4)	103·1 (1)
O(13)–O(23$^{\mathrm{iv}}$)	3·272 (2)	74·9 (1)
O(13)–O(32)	2·554 (3)	49·1 (1)
O(14)–O(22$^{\mathrm{iii}}$)	3·113 (3)	78·0 (1)
O(14)–O(23)	2·631 (3)	61·3 (1)
O(14)–O(32)	2·561 (4)	50·3 (1)
O(14$^{\mathrm{iii}}$)–O(22$^{\mathrm{iii}}$)	2·627 (3)	59·0 (1)
O(14$^{\mathrm{iii}}$)–O(23)	3·542 (3)	80·2 (1)
O(14$^{\mathrm{iii}}$)–O(23$^{\mathrm{iv}}$)	4·263 (3)	101·9 (1)
O(14$^{\mathrm{iii}}$)–O(33$^{\mathrm{iii}}$)	2·580 (1)	50·5 (1)
O(21)–O(23)	3·435 (4)	85·1 (1)
O(21)–O(23$^{\mathrm{iv}}$)	3·683 (2)	93·2 (1)
O(21)–O(33$^{\mathrm{iii}}$)	3·309 (3)	71·3 (1)
O(22$^{\mathrm{iii}}$)–O(23)	3·736 (3)	93·4 (1)
O(22$^{\mathrm{iii}}$)–O(23$^{\mathrm{iv}}$)	3·566 (3)	88·2 (1)
O(22$^{\mathrm{iii}}$)–O(32)	3·338 (3)	69·2 (1)
O(23)–O(33$^{\mathrm{iii}}$)	3·440 (3)	71·6 (1)
O(23$^{\mathrm{iv}}$)–O(32)	3·363 (3)	67·9 (1)
Average	3·156 (3)	71·8 (1)
M(31) site		
M(31)–O(13$^{\mathrm{i}}$)	2·409 (3)	
M(31)–O(14$^{\mathrm{ii}}$)	2·494 (3)	
M(31)–O(22)	2·303 (2)	
M(31)–O(23$^{\mathrm{iii}}$)	2·286 (2)	
M(31)–O(31$^{\mathrm{i}}$)	3·458 (2)	
M(31)–O(32$^{\mathrm{ii}}$)	2·867 (2)	
M(31)–O(32$^{\mathrm{i}}$)	2·585 (3)	
M(31)–O(33$^{\mathrm{ii}}$)	2·544 (2)	
Average	2·618 (2)	
O(13$^{\mathrm{i}}$)–O(22)	3·402 (4)	92·4 (1)
O(13$^{\mathrm{i}}$)–O(23$^{\mathrm{iii}}$)	3·272 (2)	88·3 (1)
O(13$^{\mathrm{i}}$)–O(31$^{\mathrm{i}}$)	2·626 (3)	49·3 (1)
O(13$^{\mathrm{i}}$)–O(32$^{\mathrm{i}}$)	2·554 (3)	61·4 (1)
O(14$^{\mathrm{ii}}$)–O(22)	3·113 (3)	80·8 (1)
O(14$^{\mathrm{ii}}$)–O(23$^{\mathrm{iii}}$)	3·542 (3)	95·6 (1)
O(14$^{\mathrm{ii}}$)–O(32$^{\mathrm{ii}}$)	2·561 (2)	56·6 (1)
O(14$^{\mathrm{ii}}$)–O(33$^{\mathrm{ii}}$)	2·580 (1)	61·6 (1)
O(22)–O(31$^{\mathrm{i}}$)	3·776 (3)	79·1 (1)
O(22)–O(32$^{\mathrm{ii}}$)	3·338 (3)	79·6 (1)
O(22)–O(32$^{\mathrm{i}}$)	3·828 (4)	103·0 (1)
O(22)–O(33$^{\mathrm{ii}}$)	3·625 (2)	96·7 (1)
O(23$^{\mathrm{iii}}$)–O(31$^{\mathrm{i}}$)	4·246 (2)	93·1 (1)
O(23$^{\mathrm{iii}}$)–O(32$^{\mathrm{ii}}$)	3·655 (3)	89·6 (1)
O(23$^{\mathrm{iii}}$)–O(32$^{\mathrm{i}}$)	3·363 (3)	87·1 (1)
O(23$^{\mathrm{iii}}$)–O(33$^{\mathrm{ii}}$)	3·440 (2)	90·7 (1)
O(31$^{\mathrm{i}}$)–O(32$^{\mathrm{ii}}$)	3·155 (3)	59·0 (1)
O(32$^{\mathrm{i}}$)–O(33$^{\mathrm{ii}}$)	3·042 (4)	72·8 (1)
Average	3·284 (3)	79·8 (1)
M(32) site		
M(32)–O(12)	2·770 (4)	
M(32)–O(21$^{\mathrm{ii}}$)	2·307 (2) ×2	
M(32)–O(31)	2·370 (2) ×2	
M(32)–O(33)	2·519 (3) ×2	
Average	2·452 (2)	
O(12)–O(21$^{\mathrm{ii}}$)	3·437 (4)	84·7 (1) ×2
O(12)–O(33)	2·541 (3)	57·2 (1) ×2
O(21$^{\mathrm{ii}}$)–O(31)	3·309 (3)	90·0 (1) ×2
O(21$^{\mathrm{iv}}$)–O(31)	3·506 (3)	97·1 (1) ×2
O(21$^{\mathrm{ii}}$)–O(33)	3·309 (3)	86·4 (1) ×2
O(21$^{\mathrm{iv}}$)–O(33)	3·350 (2)	87·8 (1) ×2
O(31)–O(31$^{\mathrm{v}}$)	3·507 (3)	95·5 (1)
O(31)–O(33)	2·984 (3)	75·2 (1) ×2
Average	3·225 (3)	83·5 (1)
M(4) site		
M(4)–O(31$^{\mathrm{iii}}$)	2·388 (1) ×2	
M(4)–O(32$^{\mathrm{ii}}$)	2·315 (2) ×2	
M(4)–O(33$^{\mathrm{iii}}$)	2·330 (2) ×2	
Average	2·344 (2)	
O(31$^{\mathrm{iii}}$)–O(31$^{\mathrm{i}}$)	3·577 (2)	97·0 (1)
O(31$^{\mathrm{iii}}$)–O(32$^{\mathrm{v}}$)	3·155 (3)	84·2 (1) ×2
O(31$^{\mathrm{iii}}$)–O(33$^{\mathrm{iii}}$)	2·984 (1)	78·5 (1) ×2
O(31$^{\mathrm{iii}}$)–O(33$^{\mathrm{i}}$)	3·788 (3)	106·8 (1) ×2
O(32$^{\mathrm{ii}}$)–O(32$^{\mathrm{v}}$)	3·436 (2)	95·8 (1)
O(32$^{\mathrm{ii}}$)–O(33$^{\mathrm{iii}}$)	3·368 (3)	93·0 (1) ×2
O(32$^{\mathrm{ii}}$)–O(33$^{\mathrm{i}}$)	3·042 (2)	81·8 (1) ×2
Average	3·307 (2)	90·1 (1)
Si(1)–O(11)–Si(1$^{\mathrm{v}}$)	146·6 (2)	
Si(3)–O(12)–Si(3$^{\mathrm{v}}$)	175·9 (4)	
Si(1)–O(13)–Si(2)	144·0 (1)	
Si(2)–O(14)–Si(3)	158·9 (3)	

Symmetry operations: (i) $y,x,-z$; (ii) $-y,x-y,z+\frac{1}{3}$; (iii) $-x+y,\ -x,z+\frac{2}{3}$; (iv) $-x,-x+y,\ -z+\frac{1}{3}$; (v) $x-y,-y,-z+\frac{2}{3}$.

chemical composition of the mineral is slightly richer in Na compared with our structure, their Na(4) site is expected to be substantially vacant by analogy with the structures of the present material and $Na_6Ca_3[Si_6O_{18}]$ (Ohsato *et al.*, 1985). The fact that they ignored this possibility and did not carry out site-occupancy refinement would presumably explain why they failed to refine the structure in $P3_121$ (or $P3_221$).

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X-ray Structure Refinement of Mesolite

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Abstract. $Na_2Ca_2Al_6Si_9O_{30}.8H_2O$, $M_r = 1164\cdot9$, orthorhombic, $Fdd2$, $a = 18\cdot4049$ (8), $b = 56\cdot655$ (6), $c = 6\cdot5443$ (4) Å, $V = 6823\cdot94$ Å^3, $Z = 8$, $D_x = 2\cdot27$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, $\mu = 9\cdot4$ cm^{-1}, spherical crystal, $T = 294$ K, $F(000) = 4688$, $R(F^2) = 0\cdot032$, 5267 reflections. The mesolite structure has complete Si/Al order and the same framework topology as natrolite and scolecite. The Na atom coordinates four O atoms and two water O atoms in a distorted trigonal prism (Na—O 2·40–2·74, Na—OW 2·34 Å) and the Ca atom coordinates four framework O atoms and three water O atoms in a distorted pentagonal bipyramid (Ca—O 2·50–2·54, Ca—OW 2·31–2·36 Å). H atoms were located for each of the four independent water molecules. The hydrogen-bonding system is generally similar to the arrangements found in natrolite and scolecite. The local geometry of the water molecules adapts to the framework distortions.

Introduction. A series of neutron diffraction studies of fibrous zeolites recently produced accurate positions for O and H atoms of the water molecules, as well as for the framework atoms and the extraframework cations [natrolite: Artioli, Smith & Kvick (1984); scolecite: Kvick, Stahl & Smith (1985); edingtonite: Kvick & Smith (1983); thomsonite: Pluth, Smith & Kvick (1985)]. Mesolite has the same framework topology as natrolite and scolecite, and has an intermediate composition near $Na_2Ca_2Al_6Si_9O_{30}.8H_2O$ (Alberti, Pongiluppi & Vezzalini, 1982). The similarity of the framework topology and Si/Al order between natrolite, mesolite and scolecite was aready postulated by Taylor, Meek & Jackson (1933). The proposed mesolite structure was confirmed by Adiwidjaja (1972) and refined by Pechar (1982) with low-accuracy data. The present X-ray refinement aims to obtain precise coordinates for mesolite, comparable to those of the

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