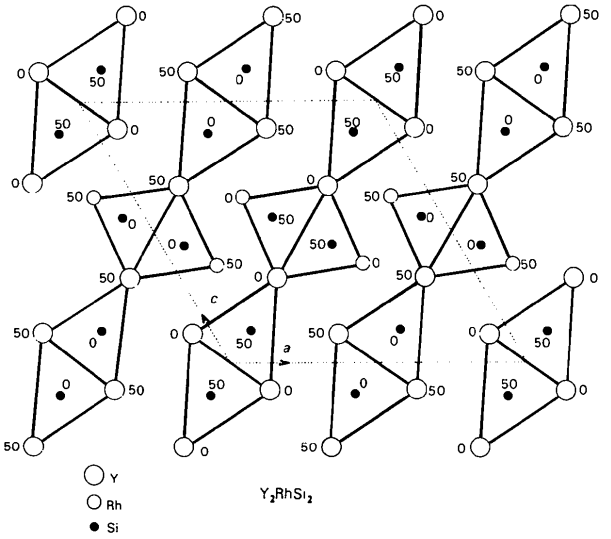

Fig. 1. Projection along the b axis for Y_2RhSi_2. Numbers correspond to y parameters multiplied by 100. All Si atoms are at the centres of trigonal prisms with Y or Rh atoms at the six vertices.

The structure of Y_2RhSi_2 is shown (Fig. 1) in projection along the b axis. All Y and Rh atoms participate in the formation of trigonal prisms centred by Si atoms. The atomic model is isotypic with Sc_2CoSi_2 (Gladyshevskii & Kotur, 1978). Two columns of Y prisms with formula Y_3Si_2 are connected with two columns of Y and Rh prisms with formula $Y_3Rh_2Si_2$ to form the whole structure with formula $Y_3Si_2+YRh_2Si_2 = Y_4Rh_2Si_4$ or Y_2RhSi_2. If the columns of Y prisms only are considered, it is possible to join n prisms together to form a band with formula $Y_{n+1}Si_n$ and thus compounds with formula $Y_{n+1}Si_n+YRh_2Si_2 = Y_{n+2}Rh_2Si_{n+2}$. Some structures have already been identified with this composition. YRhSi with $n=0$ (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982), $Y_3Rh_2Si_3$ with $n=1$ (Paccard, Le Roy & Moreau, 1982), and Y_3RhSi_3 with $n=4$ (Paccard, Paccard & Moreau, 1985). Similar structures have been recognized in the Sc–Fe–Si system (Chabot, Engel & Parthé, 1984): ScFeSi, $Sc_3Fe_2Si_3$ and Sc_2FeSi_2.

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Multiple Hydrogen Positions in the Zeolite Brewsterite, $(Sr_{0.95}, Ba_{0.05})Al_2Si_6O_{16}.5H_2O$

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Abstract. $M_r = 658{\cdot}64$, monoclinic, $P2_1/m$, $a = 6{\cdot}767$ (2), $b = 17{\cdot}455$ (2), $c = 7{\cdot}729$ (1) Å, $\beta = 94{\cdot}40$ (2)°, $V = 910{\cdot}2$ Å^3, $Z = 2$, $D_x = 2{\cdot}40$ g cm^{-3}, Be-monochromatized neutrons, $\lambda = 1{\cdot}05097$ (6) Å, $\mu = 0{\cdot}616$ cm^{-1}, $T \sim 295$ K, $R(F^2) = 0{\cdot}098$ (1880 reflections). Multiple proton positions occur for three out of the four types of water molecules, and they cannot be related to models of short-range Al,Si order. There is greater freedom of proton positions for water molecules lying well inside the cavity. The T—O distances correlate with T—O—T angle, and inferred Al contents are $T(1)$ 0, $T(2)$ 25, $T(3)$ and $T(4)$ 37%. Sr is coordinated to five water oxygens at 2·56–2·74 Å and five framework oxygens at 2·77–3·14 Å.

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Introduction. Accurate positions of the H atoms are needed for an understanding of the interaction of water molecules with the framework atoms and exchangeable cations of zeolite molecular sieves and ion-exchangers. Crystals large enough for single-crystal neutron diffraction are rare and we began with the fibrous zeolites edingtonite (Kvick & Smith, 1983), scolecite (Smith, Pluth, Artioli & Ross, 1984) and natrolite (Torrie, Brown & Petch, 1964; Pechar, Schafer & Will, 1983; Artioli, Smith & Kvick, 1984) for which unique positions were found for water molecules. This was expected because each zeolite has essentially complete Al,Si order and only trivial substitution of exchangeable cations. A well defined set of water molecules was also found (Bartl, 1970) in leonhardite, the partly dehydrated variety of laumontite. Although thomsonite (Pluth, Smith & Kvick, 1985) has substitutional disorder of Na and Ca in one site, the O and H atoms of all water molecules are well defined. Moving on from these five zeolites with ordered Al and Si atoms, we chose brewsterite (Perrotta & Smith, 1964; Schlenker, Pluth & Smith, 1977) whose Al,Si disorder should provide a range of chemical forces around each type of water molecule. In any one unit cell, there must be a particular Al,Si distribution which cannot be equal to the average distribution, and it is important to determine whether the water molecules respond to this irregular variation. Although long-range order does not occur in three out of the four tetrahedral sites of brewsterite (Schlenker *et al.*, 1977), some type of short-range order is needed to inhibit occupancy of adjacent tetrahedral nodes by Al atoms.

The structure of brewsterite, $(K_{0.01}Sr_{0.71}Ba_{0.24})$-$Al_{2.06}Si_{5.97}O_{16}.5H_2O$, from the type locality, Strontian, was determined (Perrotta & Smith, 1964) and refined (Schlenker *et al.*, 1977) with X-ray diffraction intensities. The tetrahedral nodes of the framework can be described in terms of a 4–4–1 secondary building unit (Meier, 1968; Breck, 1974), which can be obtained from a cube by converting each of two opposing edges into a pair of edges (Schlenker *et al.*, 1977; Fig. 1). One of each pair of edges is shared with an adjacent 4–4–1 unit to generate a chain which lies parallel to the *a* axis. Chains are connected by single 4-rings to form sheets in the *ac* plane, and the sheets are bridged by O atoms lying in (010) mirror planes to form a framework (Alberti, 1979) with topological symmetry $P2_1/m$. Although there are 2 Al and 6 Si atoms in the chemical formula, the mean Si,Al—O distances (Schlenker *et al.*, 1977) indicated that only one tetrahedral site is ordered [$T(1)$ with only Si] while the other three sites [$T(2)$–$T(4)$] contain approximately $Al_{1/3}Si_{2/3}$. Reduction of the space-group symmetry to $P2_1$ or Pm does not allow an ordered arrangement. In spite of the Al,Si disorder, the refinement of the X-ray diffraction intensities yielded only one site for the exchangeable cations and one position for each O atom of the five water molecules.

Single crystals from the type locality are too small for neutron diffraction, and a larger crystal from Yellow Lake near Olalla, British Columbia, Canada, was selected. Because the crystal was milky at one end, it was split into two major parts. A small clear fragment yielded an electron microprobe analysis of $(Sr_{0.95}$-$Ba_{0.04})Al_{2.10}Si_{5.93}O_{16}.nH_2O$ using feldspar standards. A small systematic error is likely because of uncertainty in correction factors, and the composition is assumed to be $(Sr_{0.95}Ba_{0.05})Al_2Si_6O_{16}.nH_2O$. Because Sr has a smaller ionic radius than Ba, the Yellow Lake crystal should have smaller cell dimensions than the Strontian one, as indeed was found (see *Experimental*).

Experimental. The largest clear fragment (volume 4·4 mm^3) was mounted on an aluminum pin so that its axis of elongation (a) was slightly off the φ axis of a four-circle diffractometer at the Brookhaven High-Flux Beam Reactor. Unit-cell dimensions obtained through least-squares fitting of observed 2θ for 32 reflections with $43° < 2\theta < 60°$. Intensities measured with the θ–2θ scan technique, with fixed scan width $2\theta = 3{\cdot}0°$ for $2\theta < 60°$ and variable $2\theta = (1{\cdot}25 + 3{\cdot}25\tan\theta)°$ for $2\theta > 60°$. Between 60 and 100 steps adjusted per scan, with 6–10 steps of each side representing background. Each step counted for about 2 s until a preset number of counts was accumulated in the direct-beam monitor. Intensities of two standard reflections measured at regular intervals did not vary systematically during data collection. Reciprocal space explored for $+h +k +l$ to $(\sin\theta)/\lambda = 0{\cdot}77$ Å^{-1}. Gaussian integration for a $6 \times 6 \times 6$ grid with a calculated absorption coefficient of 0·616 cm^{-1} gave transmission factors between 0·88 and 0·93 for the absorption correction. A total of 3260 averaged intensities gave 1880 F_o^2 values above the 2σ level for the structure refinement. $R_{\rm int} = 0{\cdot}014$. Initial positions of non-hydrogen atoms were taken from Schlenker *et al.* (1977). Scattering lengths (Koester, Rauch, Herkens & Schroder, 1981) were averaged according to the Si,Al occupancies derived from the X-ray refinement for the tetrahedral sites and according to the microprobe analysis for the Sr,Ba site. Space group $P2_1/m$ was assumed. A difference-Fourier synthesis following the first cycle of least squares yielded five positions for H atoms. Introduction of these H atoms into the model improved the fit [$R(F^2) = 0{\cdot}17$], but the presence of four intense negative peaks near the O atoms of the water molecules indicated that there are nine principal H positions instead of the five expected for the four crystallographic types of water molecules. Although the O of each water molecule was well defined, the H atoms of two water molecules [$OW(3)$ and $OW(4)$] were represented by two sets of sites, and of the fourth water molecule [$OW(2)$] by four sets of sites (Table 1). Refinement in $P2_1$ was unsuccessful.

Table 1. *Atomic coordinates* ($\times 10^4$), *fractional occupancy factors, and isotropic root-mean-square amplitudes of displacement*

	x	y	z	G	$\bar{U}$(Å)
$T(1)$	9081 (4)	527 (2)	6415 (3)	1·0	0·114
$T(2)$	3218 (4)	810 (2)	8214 (3)	1·0	0·109
$T(3)$	4063 (4)	574 (2)	2097 (3)	1·0	0·113
$T(4)$	5555 (4)	1580 (2)	5326 (3)	1·0	0·107
O(1)	3506 (4)	1064 (1)	271 (3)	1·0	0·144
O(2)	4227 (4)	1254 (2)	3593 (3)	1·0	0·172
O(3)	7819 (4)	1209 (1)	5444 (3)	1·0	0·155
O(4)	4499 (4)	1409 (1)	7127 (3)	1·0	0·159
O(5)	843 (4)	921 (2)	7625 (4)	1·0	0·171
O(6)	2233 (4)	9972 (2)	2374 (4)	1·0	0·192
O(7)	3852 (3)	9917 (1)	7960 (3)	1·0	0·148
O(8)	0	0	5000	0·5	0·216
O(9)	5724 (8)	2500	4989 (6)	0·5	0·202
Sr,Ba	2543 (4)	2500	1804 (4)	0·5	0·152
$OW(1)$	730 (9)	2500	4687 (7)	0·5	0·218
H(1)	9868 (17)	2096 (5)	4825 (13)	1·0	0·302
$OW(2)$	9404 (9)	1506 (4)	1587 (10)	1·0	0·258
H(2*A*)	8923 (59)	1063 (18)	1898 (86)	0·574 (31)	0·332
H(2*B*)	9634 (23)	1140 (13)	618 (56)	0·669 (18)	0·348
H(2*C*)	8232 (29)	1799 (14)	1221 (26)	0·369 (11)	0·253
H(2*D*)	8943 (46)	1358 (39)	2792 (73)	0·382 (28)	0·287
$OW(3)$	5937 (9)	2500	327 (12)	0·5	0·235
H(3*A*)	5587 (22)	2163 (9)	9249 (19)	0·623 (31)*	0·278
H(3*B*)	6910 (46)	2125 (13)	453 (51)	0·377 (31)*	0·326
$OW(4)$	818 (11)	2500	8737 (7)	0·5	0·230
H(4*A*)	9541 (17)	7041 (7)	1819 (16)	0·698 (47)*	0·239
H(4*B*)	8675 (128)	7500	2265 (54)	0·302 (47)*	0·452

* Constrained to unit sum.

Refinement of the scattering lengths was puzzling. The consistently observed scattering length of 6·70 (5) fm for the Sr, *etc.* site of brewsterite is less than the expected scattering length of 6·93 fm (0·95 × 7·02 + 0·05 × 5·25) for $Sr_{0.95}Ba_{0.05}$, and some kind of positional disorder related to the multiple occupancy of water molecules may be responsible. Schlenker *et al.* (1977) estimated the Al,Si substitution of the four tetrahedral sites of the Strontian brewsterite from the mean Si,Al—O distances: $T(1)$—O, 1·607, ~0·0 Al; $T(2)$—O, 1·645, ~0·3 Al; $T(3)$—O, 1·664, ~0·4 Al; $T(4)$—O, 1·660 Å, ~0·4 Al. Similar mean distances were found for the Yellow Lake brewsterite (1·605, 1·640, 1·657, 1·647 Å), and it is presumed that there is ~0·0 Al in $T(1)$, and ~0·3–0·4 in the other three sites. The scattering lengths for the Yellow Lake brewsterite were strongly correlated with the displacement parameters (correlation factors between 0·85 and 0·95), and linear interpolation between the reference values of 4·15 fm for Si and 3·45 fm for Al indicated the following Al contents for refinement in $P2_1/m$: $T(1)$, 0·13; $T(2)$, 0·00; $T(3)$, 0·37; $T(4)$, 0·35. Refinement in $P2_1$ did not reduce the discrepancy between the estimates of Al content in $T(1)$ and $T(2)$. However, in the final refinement in $P2_1/m$ for which the scattering lengths were fixed at $T(1)$ 4·15, $T(2)$ 3·96, $T(3)$ 3·88, $T(4)$ 3·90 fm the mean-square amplitudes of displacement (Table 1) were found to be equal within experimental error. The Hamilton (1965) $\mathscr{R}$ ratio at the 0·005 significance level was 1·03 for the final anisotropic refinements in the two space groups: $P2_1/m$, $R = 0{\cdot}098$, 232 parameters refined; $P2_1$, $R = 0{\cdot}086$, 323 parameters refined. In both refinements isotropic extinction correction type I was applied. {In $P2_1/m$: $wR = 0{\cdot}107$, $S = 1{\cdot}476$; $w^{-1} = [\sigma_c(F^2)]^2 + (0{\cdot}02F^2)^2$ where σ_c is based on counting statistics and the term 0·02 is based on the fluctuations of the standards.}

Table 1* lists the results of the final least-squares refinement in $P2_1/m$ for one scale factor, one isotropic type I extinction parameter, 72 positional parameters, and 150 anisotropic displacement parameters. The framework atoms, the exchangeable cation, the water oxygens, and H(1) were assigned full occupancy. Occupancies of the four H attached to $OW(2)$ were refined separately, and the total of 1·994 is closer to 2 than the combined standard error of 0·09. Although the combined populations of H(3*A*) and H(3*B*) were constrained to unity, the mean-square displacement amplitudes are similar, and within the range for the four H attached to $OW(2)$. The combined occupancies of H(4*A*) and H(4*B*) were also constrained to unity, and the large anisotropic displacement for H(4*B*) may result merely from enforced averaging of a general symmetry position onto a mirror plane. $(\Delta/\sigma)_{max} = 0{\cdot}8$ for occupancy factor of H(2*B*); $\Delta/\sigma < 0{\cdot}15$ for positional and thermal parameters. The final difference-Fourier synthesis showed random positive and negative regions around the framework oxygens and water molecules, whose peaks correspond to less than 10% of an O atom. Expansion of the harmonic temperature factors to include anharmonic contributions to the thermal motions (Gram–Charlier formalism; Johnson & Levy, 1974) of the framework oxygens and water molecules reduced $R(F^2)$ from 0·098 to 0·090, and gave an essentially featureless difference-Fourier map. However, this improvement probably represents numerical fitting of positional and substitutional disorder rather than curvilinear atomic motion, and all further discussion is based on the conventional refinement. All calculations were based on a crystallographic program package from the University of Uppsala, Sweden.

Discussion. The interatomic distances and angles are given in Table 2. Tetrahedral sites *A*, *B*, *C* and *D* of Schlenker *et al.* (1977) were relabeled as 2, 3, 4, and 1. All atomic coordinates are similar to those in the X-ray refinement of the Strontian specimen, and the only major difference is the closer approach of the Sr,Ba site to the framework and water oxygens in the Yellow Lake specimen. The decrease of 0·07 Å in the mean of the six independent Sr,Ba—O distances is actually greater than the value of ~0·03 Å expected from the microprobe analyses and the ionic radii (Shannon & Prewitt, 1969), and provides further support to the conclusion that there is little Ba in the Yellow Lake brewsterite.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39919 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Tetrahedra			
$T(1)$–O(3)	1·615 (4)	O(3)–$T(1)$–O(5)	107·2 (2)
O(5)	1·612 (4)	O(6)	122·1 (2)
O(6)	1·599 (4)	O(8)	109·1 (2)
O(8)	1·592 (3)	O(5)–$T(1)$–O(6)	108·2 (2)
Mean	1·605	O(8)	109·6 (2)
$T(2)$–O(1)	1·647 (3)	O(6)–$T(1)$–O(8)	110·6 (2)
O(4)	1·632 (4)	O(1)–$T(2)$–O(4)	107·2 (2)
O(5)	1·648 (4)	O(5)	106·0 (2)
O(7)	1·632 (4)	O(7)	111·1 (2)
Mean	1·640	O(4)–$T(2)$–O(5)	109·1 (2)
$T(3)$–O(1)	1·668 (3)	O(7)	113·3 (2)
O(2)	1·654 (4)	O(5)–$T(2)$–O(7)	109·8 (2)
O(6)	1·650 (4)	O(1)–$T(3)$–O(2)	102·8 (2)[a]
O(7)	1·654 (4)	O(6)	108·2 (2)
Mean	1·657	O(7)	112·4 (2)
$T(4)$–O(2)	1·656 (4)	O(2)–$T(3)$–O(6)	112·1 (2)
O(3)	1·660 (4)	O(7)	112·2 (2)
O(4)	1·640 (4)	O(6)–$T(3)$–O(7)	108·9 (2)
O(9)	1·633 (3)	O(2)–$T(4)$–O(3)	110·6 (2)
Mean	1·647	O(4)	112·3 (2)
		O(9)	104·5 (2)[a]
		O(3)–$T(4)$–O(4)	110·1 (2)
		O(9)	108·5 (3)
		O(4)–$T(4)$–O(9)	110·8 (2)

Framework		Strontium	
$T(2)$–O(1)–$T(3)$	132·9 (2)	Sr–O$W(4)$	2·561 (7)
$T(3)$–O(2)–$T(4)$	144·6 (2)	Sr–O$W(1)$	2·624 (6)
$T(1)$–O(3)–$T(4)$	140·0 (2)	Sr–O$W(3)$	2·643 (8)
$T(2)$–O(4)–$T(4)$	146·8 (2)	2 Sr–O$W(2)$	2·738 (7)
$T(2)$–O(5)–$T(2)$	140·6 (2)	2 Sr–O(2)	2·775 (3)
$T(1)$–O(6)–$T(3)$	151·6 (3)	2 Sr–O(1)	2·869 (3)
$T(2)$–O(7)–$T(3)$	136·9 (2)	Sr–O(9)	3·144 (6)
$T(1)$–O(8)–$T(1)$	180		
$T(4)$–O(9)–$T(4)$	159·4 (4)		

Water molecules and hydrogen bonding

A–H···B	A···B	A–H	H···B	∠A–H···B
O$W(1)$–H(1)···O(3)	3·079 (5)	0·93 (1)	2·16 (1)	173·3 (9)
O$W(2)$–H(2A)···O(7)	3·357 (7)	0·88 (4)	2·55 (4)[b]	153·0 (3·9)
–H(2B)···O(5)	3·438 (8)	1·01 (4)	2·54 (4)[b]	148·5 (2·1)
–H(2C)···O$W(3)$	3·019 (9)	0·97 (2)	2·05 (2)	174·0 (1·9)
–H(2D)···O(3)	3·287 (8)	1·04 (6)	2·26 (5)	172·1 (5·3)
O$W(3)$–H(3A)···O(4)	3·213 (7)	1·03 (2)	2·19 (2)	172·6 (1·3)
–H(3B)···O$W(2)$	3·019 (9)	0·93 (3)	2·14 (3)	158·7 (3·1)
O$W(4)$–H(4A)···O(5)	2·887 (3)	0·93 (1)	2·02 (1)	153·5 (1·1)
–H(4B)···O$W(1)$	3·126 (8)	0·87 (5)	2·36 (4)	147·1 (7·3)

H(1)–O$W(1)$–H(1)	99·2 (1·4)	H(3A)–O$W(3)$–H(3A)	69·5 (1·8)[c]
H(2A)–O$W(2)$–H(2C)	103·4 (3·0)	H(3A)–O$W(3)$–H(3B)	78·4 (2·4)[c]
H(2A)–O$W(2)$–H(2B)	74·2 (4·3)[c]	H(3A)–O$W(3)$–H(3B)	127·1 (2·6)[c]
H(2A)–O$W(2)$–H(2D)	52·6 (5·4)[c]	H(3B)–O$W(3)$–H(3B)	89·7 (3·4)
H(2B)–O$W(2)$–H(2C)	103·4 (3·0)	H(4A)–O$W(4)$–H(4A)	118·5 (1·6)[c]
H(2B)–O$W(2)$–H(2D)	125·8 (4·1)[c]	H(4A)–O$W(4)$–H(4B)	72·4 (2·4)[c]
H(2C)–O$W(2)$–H(2D)	95·6 (2·8)		

Notes: (*a*) shared edge; (*b*) too long for hydrogen bond; (*c*) outside expected range for water molecules in crystalline hydrates.

Although it is easy to make a general interpretation of the bonding and framework geometry of brewsterite, it is difficult to develop a detailed quantitative analysis. There is no simple relation between the Al,Si distribution and the multiple positions for the protons (Fig. 1); in particular, brewsterite is not a simple mixture of domains with short-range Al,Si order and associated water positions. Instead, there is one set of water oxygens, and several sets of protons which are not uniquely coupled to the local arrangement of Al and Si atoms. Presumably these sets of positions for the protons correspond to similar energies, and are largely controlled by the geometrical arrangement of framework oxygens and Sr atoms. Local deviations from balance of ionic charges will be compensated by adjustments of bond distances and angles. The following detailed discussion assumes knowledge of the conclusions in Schlenker *et al.* (1977).

Strontium coordination. The channel system in brewsterite is too wide to allow the Sr atom to become bonded *closely* to more than four framework oxygens. A 1 Å displacement from the center of a boat-shaped 8-ring (Schlenker *et al.*, 1977, Fig. 1) allows bonding to two O(2) at 2·78 Å and two O(1) at 2·87 Å, plus five water molecules [O$W(4)$ 2·56; O$W(1)$ 2·62; O$W(3)$ 2·64; two O$W(2)$ 2·74 Å]. These nine oxygens generate a distorted tricapped trigonal prism. The distortion of the prism can be described by the following dihedral angles (Muetterties & Guggenberger, 1974): $\delta(b_1) = 3{\cdot}3,\ 31{\cdot}9,\ 71{\cdot}5$; $\delta(b_2) = 102{\cdot}3,\ 130{\cdot}1,\ 163{\cdot}1°$; torsional angles are close to zero. However, a fifth framework oxygen O(9) is now arbitrarily considered to be bonded to Sr even though it lies at 3·14 Å. Addition of this tenth O yields a triangulated polyhedron with all O–O edges in the range 2·6–3·6 Å, and eliminates the long O(2)–O(2) edge (4·35 Å) found in the tricapped trigonal prism when O(9) is omitted. Furthermore, the charge balance is improved by addition of an Sr–O(9) bond (see later).

As in fibrous zeolites, the extraframework cation is closer to the water oxygens than to the framework oxygens. Substitution of Ba for Sr in the Strontian specimen moves the cation site away from the framework oxygens. All the H positions are directed away from the Sr site (Fig. 1).

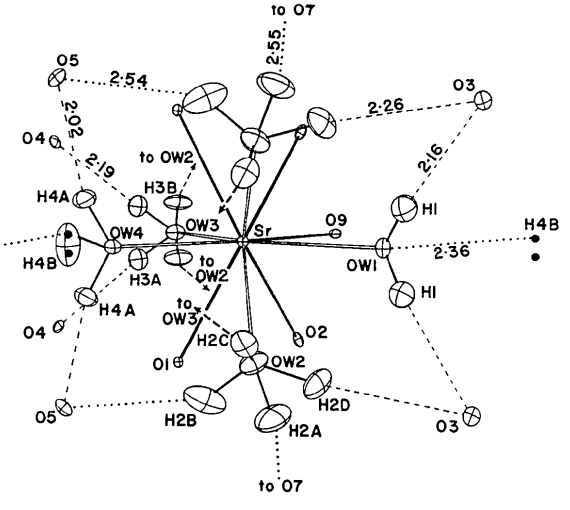

Fig. 1. Bonding around Sr and H_2O molecules in brewsterite. The orientation is similar to that in Fig. 1 of Schlenker *et al.* (1977). There is a mirror plane east–west through Sr. See Table 1 and text for discussion of occupancy of multiple proton positions. The ellipsoid for H(4B) probably represents a pair of positions (dots) related by a mirror plane, and bonding is shown to one position from O$W(1)$. Distances between H and O are distinguished by dashes (<2·3 Å) and dots (>2·2 Å), respectively, in the coordination spheres of Sr above or below the depicted Sr.

Water molecules. The hydrogen-bond system is different for each molecule, and three out of the four water molecules have multiple choices of proton positions. Nevertheless, all four water oxygens have full occupancy and small displacement parameters (Table 1).

O*W*(1) lies on a mirror plane in a near-tetrahedral arrangement (tetrahedral angles 87·0, 99·3, 115·9, 115·9°) between a single set of H(1), the Sr cation, and H(4*B*) with 30% occupancy. Each H(1) is also linked to O(3) at 2·16 Å by a hydrogen bond, even weaker than the hydrogen bonds (2·10 Å) to O bridges between two Si in edingtonite (Kvick & Smith, 1983) and natrolite (Artioli *et al.*, 1984). Although O(3) is not fully satisfied by the adjacent tetrahedral atoms (1·63 Si and 0·37 Al, Table 3), any shortening of the O*W*(1)—O(3) distance would require even greater distortion of a boat-shaped 8-ring (Schlenker *et al.*, 1977, Fig. 1). Hydrogen bonding to the next-nearest framework oxygens would require even greater crumpling because the two O(9) are separated by $a = 6{\cdot}77$ Å. Hence, the position of this water molecule is the best geometrical solution for a near-tetrahedral arrangement around the water O.

The hydrogen-bonding situation around *W*(4) is complicated by the fact that the closest O hydrogen-bond acceptor O(5) is bonded to *T*(1) with 0% Al and *T*(2) with approximately 25% Al and 75% Si giving rise to three different hydrogen-bonding environments for this water molecule. *W*(4) may straddle a pair of O(5) atoms completely attached either to Si atoms or to three possible combinations of either 25 or 50% contribution of Al atoms in the *T*(2) position. One may also expect an Si—O—Al oxygen atom to be a somewhat better hydrogen-bond acceptor than an Si—O—Si oxygen because of the larger negative charge on the accepting atom. It is plausible that this gives rise to three water configurations H(4*A*)—O*W*(4)—H(4*A*), H(4*A*)—O*W*(4)—H(4*B**) and H(4*B***)—O*W*(4)—H(4*A*). A superposition of these water molecules is observed in the diffraction experiment since there is no long-range ordering of these different situations. The refined position H(4*B*) may for instance result from the symmetry constraint on two half-positions H(4*B**) and H(4*B***) displaced about 0·2 Å from the statistical mirror plane (see dots in Fig. 1). The observed thermal ellipsoids support such a conclusion. The complications caused by the disorder may thus give large errors in the observed occupancies for the H atoms as well as unrealistic water geometries based on the averaged H-atom positions. It is well known that the water angle H—O—H varies between 100–114° (Chiari & Ferraris, 1982), and our values computed from the averaged positions given by the refinement are clearly outside this acceptable range (Table 2). It is interesting to note that the H(4*B*) positions are stabilized by a rather weak bonding interaction to oxygen O*W*(1) with an approximate O*W*(1)···H(4*B*) distance of 2·36 Å. This bond completes a weak chain Sr—*W*(4)—*W*(1)—Sr in the channel parallel to the *c* axis (Schlenker *et al.*, 1977). The O*W*(1) oxygen atom lies near the bottom of a boat-shaped 8-ring whereas the O*W*(4) atom lies about half-way between the two O(5) atoms at the prow and the stern.

W(2) is the only water molecule in a general position. Three proton positions [57% H(2*A*), 67% H(2*B*) and 38% H(2*D*)] are close to a framework oxygen [O(7), 2·55; O(5), 2·54; O(3), 2·26 Å], but only the third distance is short enough for a well established hydrogen bond. The fourth proton [37% H(2*C*)] is hydrogen-bonded to O*W*(3) at 2·05 Å. Three out of the six choices of H—O—H angles in Table 2 (95·4, 103·3, 106·9°) are within the range for water molecules in crystalline hydrates (Chiari & Ferraris, 1982), and the others might enter the range when overlap is considered. *W*(2) lies well inside the cavity at the channel intersection in brewsterite, and the multiple choice of proton positions is consistent with the lack of geometrical restrictions.

W(3) apparently has two pairs of protons related by a mirror plane [62% H(3*A*); 38% H(3*B*)] and hydrogen-bonded respectively to O(4) at 2·19 Å and O*W*(2) at 2·14 Å. However, these two positions are probably averages of several positions because of the unusual angles listed in Table 2. Like *W*(2), *W*(3) is well inside the cavity and subject to little geometrical restraint.

Aluminosilicate framework. Because of uncertainty in the interpretation of the scattering lengths for the *T* atoms, the Al substitution is estimated from the *T*—O distances. Fig. 2 shows that to a first approximation the *T*—O distances can be related linearly to secant(*T*—O—*T*) and inferred Al substitution. For an overall mean Al content of 25%, a reasonable fit is obtained for 0, 25,

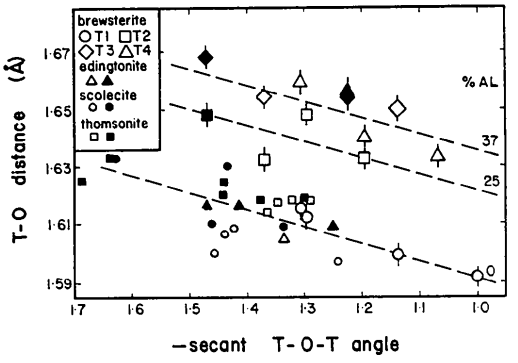

Fig. 2. Relation between *T*—O distance and secant(*T*—O—*T*) for brewsterite (large symbols). The small symbols are for the fibrous zeolites containing divalent cations (see *Introduction*). A filled symbol denotes a framework oxygen linked to an extra-framework cation. Eye-estimated isopleths of Al content have no statistical significance.

Table 3. *Nearest neighbors of framework* O *atoms*

	% Al occupancy				Total	Strontium	Hydrogen
	$T(1)$	$T(2)$	$T(3)$	$T(4)$	Al	bonding	neighbors
O(1)		25	37		62	2·87 Å	
O(2)			37	37	74	2·78	
O(3)	0			37	37		100% H(1); 38% H(2*D*)
O(4)		25		37	62		62% H(3*A*)
O(5)	0	25			25		67% H(2*B*);* 35% H(4*A*)
O(6)	0		37		37		
O(7)		25	37		62		57% H(2*A*)*
O(8)	2 × 0				0		
O(9)				2 × 37	74	3·14	

* Too distant (2·5 Å) for hydrogen bonding.

37 and 37% Al respectively in $T(1)$, $T(2)$, $T(3)$ and $T(4)$. Most distances are within 2σ of the dashed lines, and some of the displacements can be attributed plausibly to misbalance of charge (Table 3). The dashed line for 0% Al passes through the middle of the data for Al-free tetrahedra in the fibrous zeolites. It is desirable to emphasize that the distances are uncorrected for the swinging-arm effect resulting from thermal motion. Because the r.m.s. displacement correlates negatively with secant(T—O—T), the slope of the dashed lines in Fig. 2 would be reduced by a correction for riding motion [*cf.* Tables 1 and 2: O(8), $\bar{U}$ 0·22 Å, sec(T—O—T) −1; O(1), 0·14 Å, −1·47].

The above assignment of Al atoms corresponds to occupancy only of the T sites in the $(4.6.8)_2(6.8^2)$ two-dimensional (2D) net shown by open ellipsoids in Fig. 1 of Schlenker *et al.* (1977). Pairs of bridging nodes $T(1)$ are free of Al, and it is these nodes which are most distant from the Sr atoms.

Overall consideration of bonding. Because the Al/Si ratio is a simple fraction, it is tempting to invent models for short-range order, and to search for a match with the proton positions. However, the Al/Si ratio of 1/2 for the $T(2)$, $T(3)$ and $T(4)$ sites of the 2D net is too small to provide a useful constraint on the number of simple models, even when the Al-avoidance rule is employed. Even if Al atoms are placed only in the two *para* positions of each 6-ring, there are multiple choices. Furthermore, the data presented in *Water molecules* makes it necessary for some hydrogen bonds to be attached to O atoms bonded to two Si. Hence, it is concluded that the bonding schemes in brewsterite are tolerant of a variety of Al distributions, and that each bond distance or angle is subject to a minor perturbation in response to the actual distribution of nearby atoms. Table 3 summarizes the average number of Al and H neighbors for each framework O, together with the presence or not of a bond to Sr. In general, there is a moderate degree of charge compensation, but O(6) is not compensated for the 37% Al substitution, and O(7) is too far from H(2*A*) for compensation of its 62% Al substitution. An electrostatic interaction between framework oxygens and water protons always exists, although a formal cut-off of 2·40 Å was considered for the hydrogen bonding. There is overcompensation for O(3), especially for the 38% O(3) bonded to both H(1) and H(2*D*).

To conclude, it is obvious that there is no simple quantitative explanation of the multiple proton positions in brewsterite at room temperature. Further study at low temperature and high temperature is desirable to test whether thermal energy is important for establishing the distribution between sites with similar lattice energy. The tentative conclusion that there is greater freedom of proton positions for water molecules displaced further into a cavity than those close to the framework is quite plausible, and will be tested by neutron diffraction study of zeolites with larger cavities such as chabazite and faujasite. However, the position in a cavity cannot be the only factor, and the ionic potential of the exchangeable cation and the Al/Si ratio must also be considered. Magic-angle-spinning nuclear magnetic resonance of ^{29}Si and ^{27}Al may provide information on short-range order, but peak overlap may preclude a unique interpretation.

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