

## The crystal structure of perhamite

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### ABSTRACT

The crystal structure of perhamite,  $(\text{Ca,Sr})_3\text{Al}_{7.7}\text{Si}_3\text{P}_4\text{O}_{23.5}(\text{OH})_{14.1}\cdot 8\text{H}_2\text{O}$ , from the Emmons mine, Maine, USA, has been determined using single crystal X-ray data. The average structure has trigonal symmetry,  $P\bar{3}m1$ , with cell parameters  $a = 7.021(1)$  Å and  $c = 20.218(1)$  Å. It was refined to  $R_1 = 0.044$  for 618 observed reflections. The structure comprises ordered blocks of crandallite-type structure, centred at  $z = 0$ , intergrown parallel to (001) with disordered aluminosilicate structure blocks centred at  $z = 1/2$  to form a microporous structure containing large channels along [100]. These channels are bounded by 8-member rings of 6 tetrahedra (2  $\text{SiO}_4$ , 2  $\text{AlO}_4$  and 2  $\text{PO}_4$ ) and 2  $\text{AlO}_6$  octahedra. Calcium atoms and water molecules are distributed in the [100] channels. A model was developed for the local ordering of silicon into the fractionally occupied sites in the (001) layer at  $z = 1/2$  and this model was refined in space group  $P321$  to  $R_1 = 0.041$  for 933 observed reflections. The dominant contributors to the local order are  $\text{Si}_3\text{O}_9$  rings of corner-shared tetrahedra, together with  $\text{Si}_2\text{O}_7$  pairs of tetrahedra. These units corner-link to  $(\text{Al,Si})\text{O}_4$  tetrahedra above and below the plane at  $z = 1/2$  to form 4-member rings, which in turn corner-share to  $\text{PO}_4$  tetrahedra in the crandallite blocks to give the 8-member rings. The analysis suggests that 5-coordinated Si may also be present in the (001) plane at  $z = 1/2$ .

**KEYWORDS:** crystal structure, perhamite, Maine, USA, XRD.

### Introduction

PERHAMITE was first described in 1977 by Dunn and Appleman (1977). They gave the composition as  $3\text{CaO}\cdot 3.5\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2\cdot 2\text{P}_2\text{O}_5\cdot 18\text{H}_2\text{O}$  and reported the powder X-ray pattern but no structure analysis was undertaken. We have recently identified this rare mineral in the Moculta phosphate quarry in the Mount Lofty Ranges, South Australia, where it occurs as rosettes of thin blade-like crystals, strongly resembling crandallite, on an apatite-quartz matrix (Mills, 2003). The crystals from the Moculta quarry proved to be unsuitable for a single crystal structure analysis. We subsequently obtained a sample of one of the previously described specimens (Dunn and Appleman, 1977) for a structure determination. The analysis showed that the structure of

perhamite is made up of blocks of ordered crandallite-type structure (Blount, 1974), intergrown at the unit-cell scale with blocks containing disordered chains and rings of aluminosilicate tetrahedra. We describe here the determination and refinement of the average structure, containing fractionally occupied atom sites in the disordered region, as well as the development and refinement of models for local ordering.

### Experimental

A perhamite specimen from the Emmons mine, Greenwood, Maine (Smithsonian Institution #143393), was used in this investigation. It was in the form of a small blocky mass of platy colourless crystals. Electron microprobe analyses were made on the sample using a JEOL Superprobe Model JXA-8900R, at a beam current of 19 nA. Standards used were wollastonite (Ca, Si), hematite (Fe), apatite (P),  $\text{MgAl}_2\text{O}_4$

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(Al) and NaCl (Na). In order to minimize the effect of varying analysis totals from loss of water due to beam heating, a low accelerating voltage of 10 kV was used and the sample stage was moved continuously during the analyses. The average of four analyses gave 21.34 wt.% P<sub>2</sub>O<sub>5</sub>, 11.66 wt.% CaO, 13.47 wt.% SiO<sub>2</sub>, 29.33 wt.% Al<sub>2</sub>O<sub>3</sub>, with an analysis total of 75.8%. The difference of 24.2% is approximately equal to the water content.

The analyses are close to those reported by Dunn and Appleman (1977) for the type specimen of perhamite from the Bell Pit mine, Maine, i.e. 21.90 wt.% P<sub>2</sub>O<sub>5</sub>, 12.26 wt.% CaO, 13.64 wt.% SiO<sub>2</sub>, and 27.09 wt.% Al<sub>2</sub>O<sub>3</sub>. Dunn and Appleman (1977) also reported low levels (<0.3%) of F, FeO, TiO<sub>2</sub>, MgO and Na<sub>2</sub>O and a water content by difference of 24.62%. An inspection of our perhamite sample in a scanning electron microscope using a back-scattered electron detector showed some very thin (1–2 μm) bands of a high atomic contrast

phase. Although the bands were too thin to analyse quantitatively, energy dispersive X-ray analysis showed that the elemental distribution was similar to that for perhamite but containing Sr partially substituting for Ca.

For X-ray diffraction (XRD) studies, a thin platelet was cleaved from the sample and further dissected with a scalpel into a rhomb-shaped lath measuring 0.1 mm long and 0.035 mm thick. Precession photographs of the crystal showed sharp spots with no sign of twinning or of streaks due to stacking disorder. Upper-level precession photographs along *c*\* displayed trigonal symmetry, whereas hexagonal symmetry was reported by Dunn and Appleman (1977). Approximate unit-cell parameters from the precession photographs were *a* = 7.00 Å and *c* = 20.20 Å.

An X-ray intensity data collection was obtained using a Nonius Kappa diffractometer employing a CCD area detector. The data collection and processing parameters are given in Table 1. The

TABLE 1. Crystal data, data collection conditions and refinement parameters for perhamite.

Crystal data	
Unit-cell composition	(Ca,Sr) <sub>3</sub> Al <sub>7.7</sub> Si <sub>3</sub> P <sub>4</sub> O <sub>23.5</sub> (OH) <sub>14.1</sub> ·8H <sub>2</sub> O
Cell parameters	<i>a</i> = 7.021 (1) Å <i>c</i> = 20.218 (1) Å
Space group	<i>P</i> $\bar{3}$ <i>m</i> 1 (average structure) <i>P</i> 321 (local order)
Calculated density	2.49 g/cm <sup>3</sup>
Data collection conditions	
Temperature (K)	295
λ (Mo-Kα)	0.71073
Crystal size (mm)	0.10 × 0.10 × 0.035 mm
Collection mode	φ scan 0–360°, 0.5° steps
Count time per frame	15 s
2θ max	55.7°
Reflection range	–9 ≤ <i>h</i> , <i>k</i> ≤ 9, –26 ≤ <i>l</i> ≤ 26
Total no. reflections	9368
No. unique reflections	847 in <i>P</i> $\bar{3}$ <i>m</i> 1, 1380 in <i>P</i> 321
No. reflections, <i>F</i> > 4σ( <i>F</i> )	618 in <i>P</i> $\bar{3}$ <i>m</i> 1, 933 in <i>P</i> 321
Absorption correction	Empirical, SORTAV, μ = 1.1 mm <sup>–1</sup> <i>T</i> <sub>min</sub> = 0.88, <i>T</i> <sub>max</sub> = 0.91
R(merge)	0.064 in <i>P</i> $\bar{3}$ <i>m</i> 1, 0.063 in <i>P</i> 321
Refinement	Anisotropic <i>U</i> <sub>ij</sub> refinements
No. parameters refined	94 in <i>P</i> $\bar{3}$ <i>m</i> 1, 132 in <i>P</i> 321
<i>R</i> <sub>1</sub> , <i>F</i> > 4σ( <i>F</i> )	0.044 in <i>P</i> $\bar{3}$ <i>m</i> 1, 0.041 in <i>P</i> 321
<i>R</i> <sub>1</sub> , all data	0.070 in <i>P</i> $\bar{3}$ <i>m</i> 1, 0.077 in <i>P</i> 321
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), all data	0.157 in <i>P</i> $\bar{3}$ <i>m</i> 1, 0.162 in <i>P</i> 321
Δσ <sub>min</sub> , Δσ <sub>max</sub> (e/Å <sup>3</sup> )	0.7, –0.7 ( <i>P</i> $\bar{3}$ <i>m</i> 1), 0.7, –0.8 ( <i>P</i> 321)

## THE CRYSTAL STRUCTURE OF PERHAMITE

intensity statistics indicated trigonal symmetry, with possible space groups  $P3$ ,  $P\bar{3}$ ,  $P321$ ,  $P3m1$  or  $P\bar{3}m1$ . A starting structural model was obtained using the direct methods program SIR97 (Altomare *et al.*, 1999) and refined using SHELX-97 (Sheldrick, 1997) to  $R_1 = 0.09$ . An inspection of the model in ATOMS showed that the structure comprised blocks of crandallite-type structure (Blount, 1974), centred at  $z = 0$ , separated by regions centred at  $z = 1/2$  that were highly disordered with fractionally occupied sites. The disposition of atomic positions in the disordered region corresponded to fractional occupancy of tetrahedrally coordinated metal atom sites.

The average structure for perhamite, involving fractional occupancy in the disordered region, was refined in the highest-symmetry trigonal space

group consistent with the intensity statistics and extinctions,  $P\bar{3}m1$ . The refinement using isotropic displacement parameters converged at  $R_1 = 0.065$ . Conversion to anisotropic displacement parameters gave convergence at  $R_1 = 0.044$  for reflections with  $F > 4\sigma(F)$  and  $R_1 = 0.070$  for all reflections. A list of the refined parameters is given in Table 2. Polyhedral bond lengths are reported for the average structure in Table 3, together with calculated valence sums at the cation sites (Brese and O'Keeffe, 1991).

**Results and discussion**
*The average structure for perhamite*

A polyhedral representation of the average perhamite structure is shown in Fig. 1. The crandallite part of the structure is well defined.

 TABLE 2. Parameters from isotropic refinements in  $P\bar{3}m1$  and  $P321$ .

	<i>x</i>	<i>y</i>	<i>z</i>	SOF	<i>U</i> (Å <sup>2</sup> )
<i>P<math>\bar{3}m1</math> refinement</i>					
Ca(1)	0	0	0	0.101(2)	0.015(1)
Ca(2)	1/3	2/3	0.7446(1)	1/6	0.0193(7)
P(1)	1/3	2/3	0.9829(1)	1/6	0.0085(7)
P(2)	0	0	0.2470(1)	1/6	0.0088(7)
Al(1)	0.1657(2)	0.3314(3)	0.8693(1)	1/2	0.0082(6)
Al(2)	0	0	0.4071(2)	1/6	0.0196(9)
Si(1)	0.1573(9)	0.7508(9)	0.4991(3)	0.23(1)	0.020(2)
O(1)	0.4288(8)	0.2144(4)	0.0435(2)	1/2	0.011(1)
O(2)	1/3	2/3	0.0580(4)	1/6	0.012(2)
O(3)	0.1262(4)	0.2524(8)	0.1085(2)	1/2	0.009(1)
O(4)	0.9137(8)	0.4569(4)	0.1591(2)	1/2	0.010(1)
O(5)	0.2394(8)	0.1197(4)	0.2231(2)	1/2	0.011(1)
O(6)	0	0	0.3231(5)	1/6	0.021(2)
O(7)	0.269(3)	0.135(1)	0.4357(7)	1/4	0.047(4)
O(8)	0.134(2)	0.268(3)	0.4339(9)	1/4	0.060(4)
O(9)	1/2	0	1/2	0.234(7)	0.22(2)
O(10)	1/3	2/3	0.496(2)	0.08(1)	0.08(1)
O <sub>w</sub> (1)	1/3	2/3	0.2366(8)	1/6	0.056(4)
O <sub>w</sub> (2)	0.969(1)	0.4847(6)	0.3351(3)	1/2	0.037(2)
<i>P321 refinement*</i>					
Si(1A)	0.128(2)	0.726(2)	0.499(1)	0.226(9)	0.014(2)
Si(1B)	0.227(2)	0.817(2)	0.500(1)	0.247(10)	0.014(2)
O(7)	0.267(2)	0.164(2)	0.4352(5)	1/2	0.033(3)
O(8)	0.106(3)	0.268(2)	0.4333(6)	1/2	0.042(3)
O(9A)	0.048(21)	0.532(12)	0.5**	0.19(7)	0.06(2)
O(9B)	0.129(17)	0.536(15)	0.5**	0.21(7)	0.06(2)
O(10)	1/3	2/3	0.498(1)	0.12(2)	0.05(1)

\*Parameters for other atoms within 1 esd of values from  $P\bar{3}m1$  refinement.

\*\*Held constant during refinement.

TABLE 3. Polyhedral bond lengths (Å) in perhamite from the  $P\bar{3}m1$  refinement and calculated\* valence sums.

<i>M</i> –O	Distance (Å)	Bond valence	<i>M</i> –O	1.70(1)	Bond valence
Al(1)–O(1)	1.859(5)	0.57	Al(2)–O(6)	1.70(1)	0.876
–O(3) × 2	1.877(3)	0.543 × 2	–O(7) × 3	1.74(2)	0.786 × 3
–O(4) × 2	1.918(3)	0.486 × 2	or		Σ3.23
–O(5)	1.951(5)	0.444	–O(8) × 3	1.72(2)	0.830 × 3
		Σ3.07			Σ3.37
P(1)–O(2)	1.518(8)	1.262	P(2)–O(6)	1.538(9)	1.195
–O(1) × 3	1.542(5)	1.182 × 3	–O(5) × 3	1.534(5)	1.208 × 3
		Σ4.81			Σ4.82
Ca(1)–O(3) × 6	2.677(5)	0.147 × 6	Si(1)–O(7)	1.59(2)	**
–O(1) × 6	2.752(6)	0.120 × 6	–O(8)	1.60(2)	
		Σ1.60	–O(10)	1.616(7)	
Ca(2)–O <sub>w</sub> (2) × 3	2.446(7)	0.274 × 3	–O(9)	1.541(6)	
–O(4) × 3	2.460(5)	0.264 × 3	–O(9)'	2.154(6)	
–O(5) × 3	2.679(6)	0.146 × 3			
		Σ2.05			

\* Calculated bond valence sums using parameters of Brese and O'Keeffe (1991).

\*\* Si bond valences reported in Table 4.

The polyhedral bond lengths and calculated valence sums given in Table 3 are consistent with ordering of Al in the octahedra and P in the tetrahedra in this part of the structure. The crandallite blocks are connected to the disordered region via corner linking of the PO<sub>4</sub> units with tetrahedra containing predominantly Al, as proven by the bond lengths for the latter, 1.70–1.72 Å. These Al(2)O<sub>4</sub> tetrahedra have two orientations, corresponding to rotation by 60° about [001]. The site occupancies of the fractionally occupied basal oxygen atoms, O(7) and O(8), correspond to equal probabilities of both orientations.

The Al(2)O<sub>4</sub> tetrahedra corner-link via the basal oxygen atoms with tetrahedra located in the (001) plane at  $z = 1/2$ . The *M*–O distances for these latter tetrahedra, 1.54–1.62 Å, correspond to occupation by Si atoms. The Si atoms are disordered over 12 positions corresponding to the general site in  $P\bar{3}m1$ . The refined fractional occupancy at each of the 12 positions is 0.23(1), giving 2.7 Si atoms per unit cell in the planes at  $z = 1/2$ . The corner-linking of the SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra results in 4-member rings that are interconnected within the (001) planes via corner-linking of SiO<sub>4</sub> tetrahedra to form chains. The framework connectivity between the crandallite

blocks and the alumino-silicate chains, shown in Fig. 1, produces large zeolitic-type cavities centred at  $z = 1/4$  and  $3/4$ . These cavities are occupied by Ca atoms and by the water molecules, O<sub>w</sub>(1) and O<sub>w</sub>(2). The Ca(1) site in the crandallite block at the origin had a refined occupancy >1, probably because of partial occupancy of this site by Sr. The Sr analogue of crandallite occurs naturally as the mineral goyazite (Kato, 1971).

The microprobe analyses for perhamite, when converted to atoms and normalized to 4 P atoms per unit cell, gives the metal atom proportions Ca<sub>2.7</sub>Al<sub>7.7</sub>Si<sub>3</sub>P<sub>4</sub>. The total number of framework metal atoms, 14.7, agrees with the value obtained from the structure analysis. If Si is fully ordered into the tetrahedra at  $z = 1/2$ , this gives the occupancy of the Al(2) tetrahedra as Al<sub>0.85</sub>Si<sub>0.15</sub>. The analysed 2.7 Ca per unit cell is lower than the 3 Ca atoms obtained from the structure analysis based on full occupation of the Ca(1) and Ca(2) sites. This may be due to Ca migration during the microprobe analysis, as well as partial Sr substitution for Ca at the Ca(1) site as mentioned above. Combining the metal atoms in the unit cell with the number of framework anions found from the structure analysis and adjusting the O<sup>2-</sup>/OH<sup>-</sup> ratio for charge balance, gives the unit-cell

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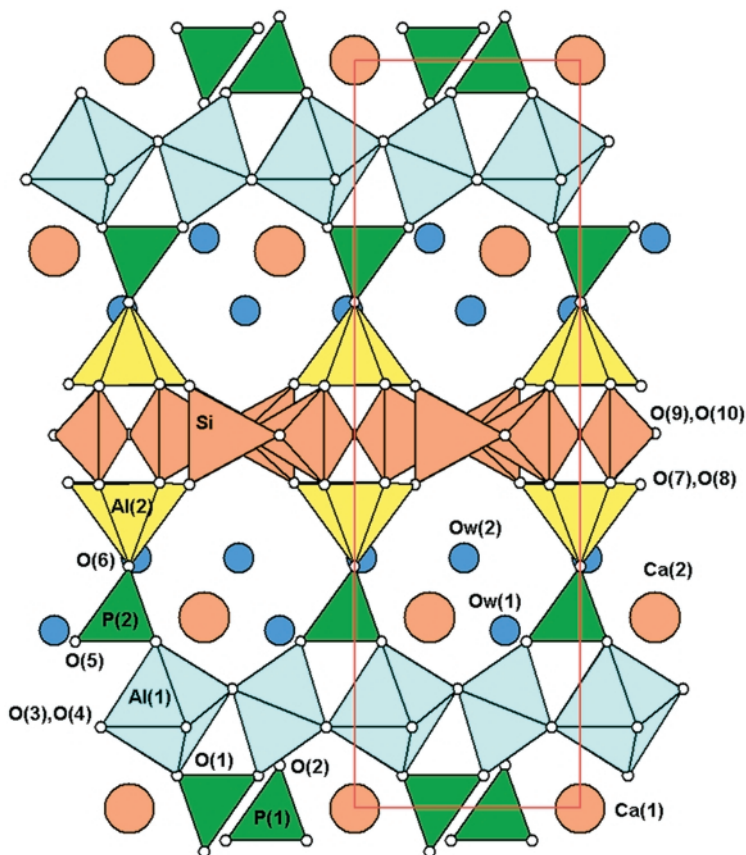


FIG. 1. Polyhedral representation of the average structure of perhamite, in projection along [100]. Unit cell outline shown, *c* axis vertical.

composition for perhamite as:  $(\text{Ca},\text{Sr})_3\text{Al}_{7.7}\text{Si}_3\text{P}_4\text{O}_{23.5}(\text{OH})_{14.1}\cdot 8\text{H}_2\text{O}$ . Expressed as oxides, the composition is  $3(\text{Ca},\text{Sr})\text{O}\cdot 3.85\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2\cdot 2\text{P}_2\text{O}_5\cdot 15\text{H}_2\text{O}$ , compared with Dunn and Appleman's (1977) formula of  $3\text{CaO}\cdot 3.5\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2\cdot 2\text{P}_2\text{O}_5\cdot 18\text{H}_2\text{O}$ .

By analogy with crandallite (Blount, 1974), 13 of the  $\text{OH}^-$  anions are associated with the crandallite blocks in perhamite. The unit-cell composition can be divided into crandallite and aluminosilicate parts:

crandallite block composition:



aluminosilicate composition:



where the  $\text{O}_{2/2}$  corresponds to the O(6) bridging anion that is shared between the  $\text{PO}_4$  and  $\text{Al}(2)\text{O}_4$  tetrahedra in the two structural blocks.

*Models for the local structures in the disordered region*

A plot of the atoms in the disordered region at  $z = 1/2$ , is given in Fig. 2, showing the anisotropic displacement ellipsoids and the Si–O tetrahedral bonds obtained from the refinement of the average structure in  $P\bar{3}m1$  (the centrosymmetrically related atoms are removed for ease of interpretation). This diagram provides some important clues to the locally ordered atomic arrangements. It is seen that the ellipsoid for O(9) is very anisotropic, suggesting that O(9) is split over a number of different positions. Location of O(9) at different points along the extended ellipses could provide alternative tetrahedral coordination for the Si atoms, involving 2 Si–O(9) bonds in the (001) plane rather than one Si–O(9) and one Si–O(10) as shown. Polyhedral representations of these two possibilities are shown in Fig. 3*a,b*. The  $\text{SiO}_4$

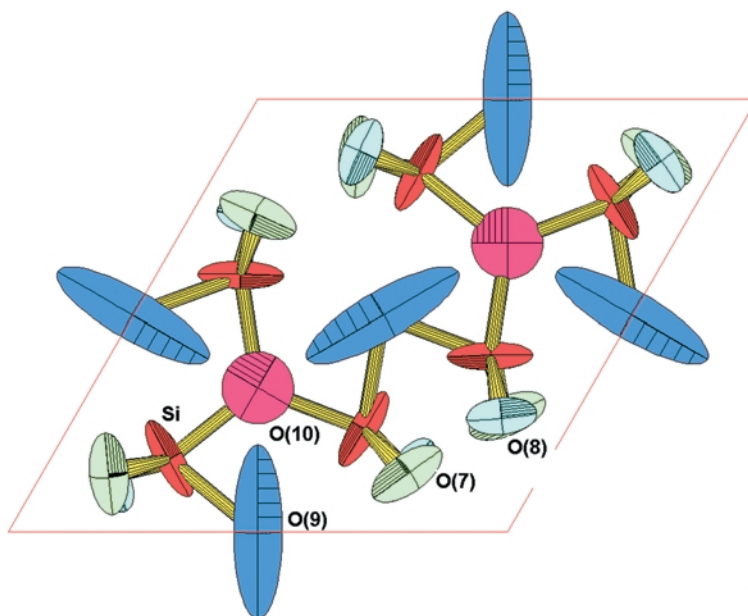


FIG. 2. Coordination of Si in the (001) plane at  $z = 1/2$ . Anisotropic displacement ellipsoids from the refinement in  $P\bar{3}m1$  are shown.

tetrahedra in both cases involve one O(7) and one O(8) lying above and below the plane at  $z = 1/2$ . These two O atoms are basal plane anions for the  $\text{Al}(2)\text{O}_4$  tetrahedra as shown in Fig. 1. The two opposing  $\text{Al}(2)\text{O}_4$  tetrahedra have to be in the eclipsed position to provide the tetrahedral coordination around the Si atoms shown in Fig. 2. This means that the local structure has to be non-centrosymmetric, because a centrosymmetric structure gives a staggered arrangement of  $\text{Al}(2)\text{O}_4$  tetrahedra across  $z = 1/2$ .

A third possibility for Si coordination within the (001) plane at  $z = 1/2$  is the in-plane bonding of Si to O(10) plus two O(9) anions, giving 5-fold coordination. This possibility is illustrated in Fig. 3c. The trigonally equivalent  $\text{SiO}_5$  units are shaded differently, to help identify them.

The layer shown in Fig. 2 contains, on average, 2.7 atoms of Si. If the local symmetry remains trigonal, then only one grouping of three tetrahedra can be occupied. The local ordering would then conform to space group  $P3$ , and the average structure is obtained by having equal weights of two different microdomains with the three tetrahedra located around  $(1/3, 2/3, 1/2)$  or  $(2/3, 1/3, 1/2)$ , respectively. When the three tetrahedral sites share a common anion, O(10), as shown in Fig. 3a, only two of the sites are

likely to be occupied, otherwise the O(10) site is severely oversaturated (formal valence of 3). This corresponds to the presence of  $\text{Si}_2\text{O}_7$  units. However, when the  $\text{SiO}_4$  tetrahedra involve in-plane bonds to  $2 \times \text{O}(9)$  rather than to  $\text{O}(9) + \text{O}(10)$ , as in Fig. 3b, this constraint does not apply and all three sites may be occupied, giving  $\text{Si}_3\text{O}_9$  rings. The 2.7 Si atoms found from the structure analysis could be explained by a mixture of the different types of coordinations that allow for either two or three Si atoms per layer. In the former case, Fig. 3a, the trigonal symmetry is locally broken. To obtain the average of 2.7 Si atoms per layer at  $z = 1/2$  the ratio of  $\text{Si}_3\text{O}_9$  rings to  $\text{Si}_2\text{O}_7$  groups (or to pairs of trigonal bipyramids) is  $\sim 2:1$ .

Attempts were made to refine ordered local structures in space group  $P3$ , with only one set of three Si sites occupied and only one orientation of the  $\text{Al}(2)\text{O}_4$  tetrahedra. However, high  $R$  factors were obtained and difference Fourier maps always gave strong peaks due to the second set of three Si sites and the alternative orientation of the  $\text{Al}(2)\text{O}_4$  tetrahedra. It thus appears that domains containing the different possible groupings of tetrahedra are intergrown on a very fine scale so that the signs of the structure factors from the different domains have to be taken into



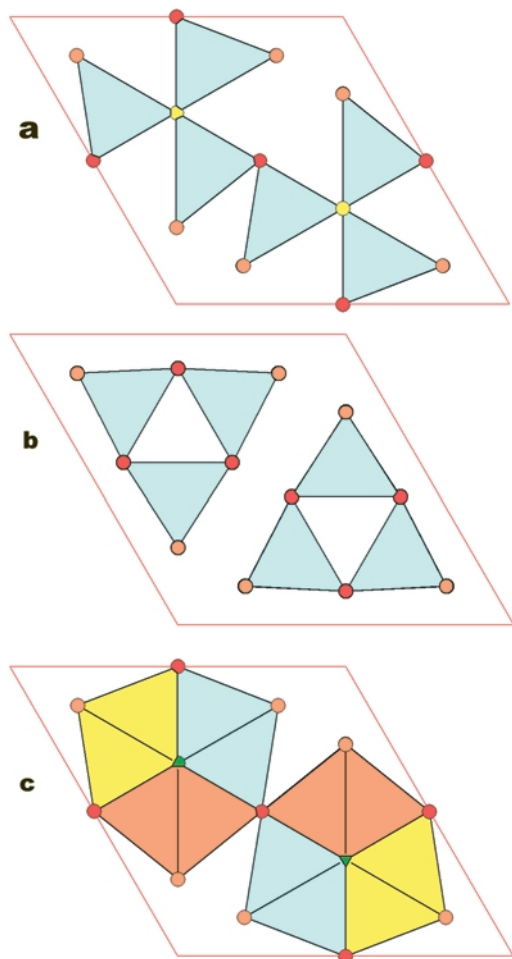


FIG. 3. Different possible modes of coordination of Si in the (001) plane at  $z = 1/2$ . (a) tetrahedral coordination to O(7), O(8), O(9) and O(10); (b) tetrahedral coordination to O(7), O(8),  $2 \times$  O(9); (c) trigonal bipyramidal coordination to O(7), O(8),  $2 \times$  O(9), O(10).

account. This was supported by the failure of attempts to model the contributions from the different domains during refinement by including twinning. A satisfactory refinement was achieved by increasing the space group symmetry from  $P3$  to  $P321$  to include tetrahedral groupings related by a 2-fold axis along [110]. The  $P321$  model involved splitting both the Si and the O(9) sites. The refined parameters associated with the crandallite part of the structure remained within one end of the values obtained from the  $P\bar{3}m1$  refinement. The refinement in  $P321$  converged to

$R_1 = 0.055$  for isotropic displacement parameters and to  $R_1 = 0.041$  for anisotropic displacement parameters. The refined parameters for the atoms in the aluminosilicate block are given in Table 2. The splitting of the O(9) position at  $(1/2, 0, 1/2)$  into two general positions resulted in a marked lowering of the displacement parameters for these atoms. The displacement parameters, however, remain high and are typical of those in microporous framework structures where there is considerable flexibility of the framework tetrahedra about the corner-linkages.

The Si–O distances corresponding to the alternative local models for the  $\text{SiO}_4$  tetrahedra, based on the refined coordinates in  $P321$  are given in Table 4. The spread of Si–O distances is large, but not significantly different from the expected Si–O distance of 1.62 based on ionic radii, when the associated large errors are considered. Calculated valence sums (Bresé and O’Keeffe, 1991) at the Si atoms for the different possible co-ordinations are given in Table 4. In each case they are close to the expected formal valency of 4. Some of the local co-ordinations given in Table 4 give unrealistic O–Si–O angles, in particular O(10)–Si(1B)–O(9A) is  $63^\circ$  and O(10)–Si(1B)–O(9B) is only  $44^\circ$ . The tetrahedra involving O(7), O(8) and  $2 \times$  O(9) have reasonable tetrahedral angles, consistent with  $\text{Si}_3\text{O}_9$  rings being the dominant contributors to give the 2.7 Si per layer.

A [100] projection of a local ordering for the perhamite structure is shown in Fig. 4, based on the  $\text{Si}_3\text{O}_9$  rings shown in Fig. 3b. As seen in Fig. 4, these rings of tetrahedra corner-share with  $\text{Al}(2)\text{O}_4$  tetrahedra to form 4-member rings, which in turn connect to the crandallite-type structure to create large channels along [100], bounded by six tetrahedra and two octahedra. The channels are occupied by water molecules and Ca atoms. There is a strong resemblance of the topology of the 4- and 8-membered rings to that which occurs in zeolites and other microporous structures.

#### Five-coordinated Si in perhamite?

An inspection of the anisotropic displacement ellipsoids in Fig. 2 shows that five-fold coordination of Si in perhamite cannot be discounted. An anisotropic refinement in  $P\bar{3}m1$  of a model with O(9) at the special site  $(1/2, 0, 1/2)$  and Si at the special site  $(x, -x, z)$  with  $x = 0.2$  and  $z = 0.5$  converged at the low  $R_1$  factor of

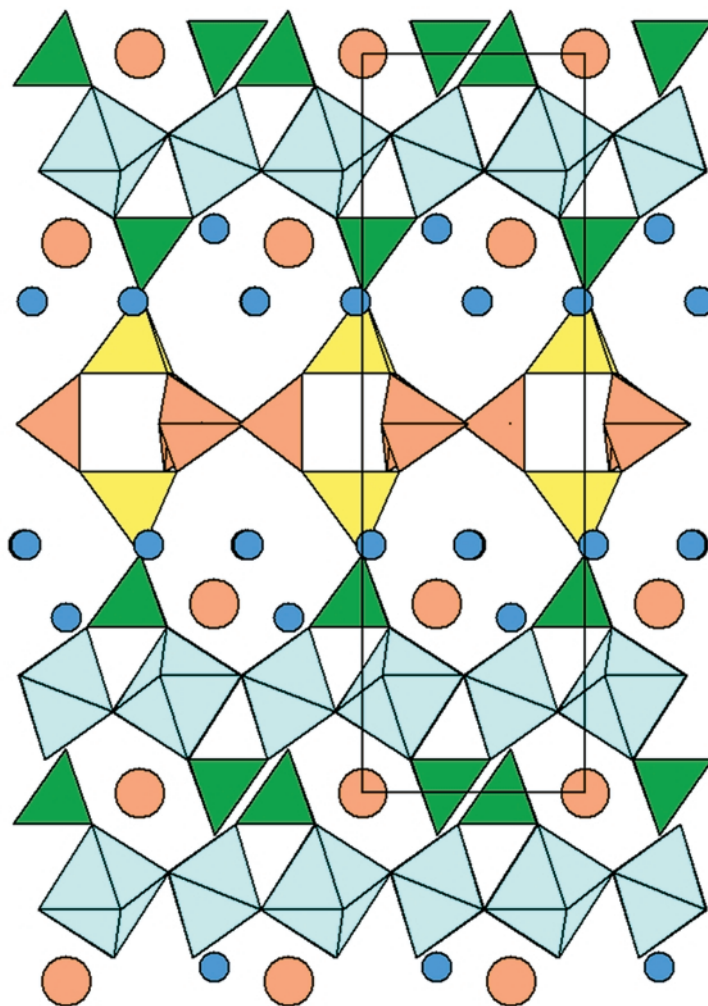


FIG. 4. Polyhedral representation of the locally ordered structure in perhamite, based on the formation of  $\text{Si}_3\text{O}_9$  rings of tetrahedra at  $z = 1/2$  as shown in Fig. 3*b*.

0.046 and gave Si–O distances of 1.56, 1.58, 1.59 and  $2 \times 1.86$  Å. The  $P321$  refinement, with split Si and O(9) atom sites, gave four Si–O distances to Si(1A) in the range 1.59 to 1.71 Å and a fifth distance at 2.05 Å. The average of the five Si(1A)–O distances is 1.75 Å, which is comparable with the average Si–O distance of 1.73 Å found for 5-coordinated silicon in  $\text{CaSi}_2\text{O}_5$  (Angel *et al.*, 1996). Recently Alberti *et al.* (1999) reported the presence of 5-coordinated (Si,Al) sites in the zeolite, brewsterite, after heating *in vacuo* at 550 K. The 5-coordinated sites were associated with 4-member rings, as in perhamite.

An EXAFS study of perhamite at the silicon absorption edge is warranted to establish unambiguously whether a portion of the silicon is 5-coordinated.

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TABLE 4. Si–O distances (Å) for different possible local co-ordinations from *P321* refinement, and calculated bond valences.

Si–O	Distance	Valence sum	Si–O	Distance	Valence sum
Si(1A)–O(7)	1.59(1)	1.09	Si(1B)–O(7)	1.61(1)	1.04
–O(8)	1.71(2)	0.79	–O(8)	1.60(1)	1.07
–O(9A)	1.52(14)	1.32	–O(9A)	1.75(3)	0.71
–O(10)	1.69(1)	0.84	–O(10)	1.568(8)	1.16
see Fig. 3a		Σ4.04	Fig. 3a		Σ3.98
Si(1A)–O(7)	1.59(1)	1.09	Si(1B)–O(7)	1.61(1)	1.04
–O(8)	1.71(2)	0.79	–O(8)	1.60(1)	1.07
–O(9A)	1.52(14)	1.32	–O(9B)	1.73(2)	0.75
–O(9B)	1.70(11)	0.81	–O(10)	1.568(8)	1.16
see Fig. 3b		Σ4.01	Fig. 3a		Σ4.02
Si(1A)–O(7)	1.59(1)	1.09	Si(1B)–O(7)	1.61(1)	1.04
–O(8)	1.71(2)	0.79	–O(8)	1.60(1)	1.07
–O(10)	1.69(1)	0.84	–O(9A)	1.56(13)	1.19
–O(9B)	1.70(11)	0.81	–O(9A)′	1.75(3)	0.71
–O(9B)′	2.05(12)	0.32	Fig. 3b		Σ4.01
see Fig. 3c		Σ3.85	Si(1B)–O(7)	1.61(1)	1.04
			–O(8)	1.60(1)	1.07
			–O(9A)	1.56(13)	1.19
			–O(9B)	1.73(2)	0.75
			Fig. 3b		Σ4.05

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