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Crystal structures of natural and synthetic α-eucryptite, $LiAlSiO_4$

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Crystal structure / $LiAlSiO_4$

Abstract. The structures of natural and synthetic* α-eucryptites, $LiAlSiO_4$, are trigonal with space group $R\bar{3}$, a = 13.471(3) [13.473(3)] Å, c = 8.998(2) [9.001(2)] Å, Z = 18, D_x = 2.66 [2.66] gcm^{-3}. They were refined to R (unweighted) = 0.055 [0.054] and R (weighted) = 0.043 [0.041] using 1721 [1710] non-equivalent reflections. The structures consist of $[LiO_4]$ tetrahedra (mean Li–O distance 1.982 [1.983] Å) and $[TO_4]$ tetrahedra with T = Al/Si (mean T–O distance 1.688 [1.688] Å). It is confirmed that α-eucryptite, natural and synthetic, is isostructural with phenakite and willemite, and has a three-dimensional tetrahedral framework. The Li atoms of eucryptite occupy the sites equivalent to the Si positions in phenakite and willemite. The Al and Si atoms of eucryptite are disordered in the sites equivalent to the Be and Zn positions in phenakite and willemite.

Introduction

According to Winkler (1953) the low-temperature polymorph of $LiAlSiO_4$, α-eucryptite, is isostructural with phenakite, Be_2SiO_4, and willemite, Zn_2SiO_4, and has an ordered Al/Si distribution. However, no structure determination has been published.

Experimental

Natural α-eucryptite crystals investigated in the present study were colourless, transparent fragments of crystals from Zimbabwe. Synthetic α-eucryptite used for this study was synthesized hydrothermally by K. H.

* Data for synthetic material are given in square brackets

Table 1. Positional and thermal parameters for natural and synthetic α-eucryptite with standard deviations. The anisotropic temperature factors have the form exp $[-2\pi^2 (U_{11} h^2 a^{*2} + \ldots + 2 U_{23} klb^* c^*)]$. The standard deviations in parentheses refer to the last digit

Natural	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li	0.0198(4)	0.8125(4)	0.7513(6)	0.0153(21)	0.0107(20)	0.0206(22)	0.0044(18)	−0.0017(18)	0.0024(17)
T(1)	0.5302(1)	0.8807(1)	0.7495(1)	0.0065(2)	0.0063(2)	0.0055(2)	0.0000(2)	−0.0001(2)	0.0035(2)
T(2)	0.8753(1)	0.3444(1)	0.9160(1)	0.0062(2)	0.0051(2)	0.0056(2)	0.0000(2)	−0.0003(2)	0.0026(2)
O(1)	0.7594(1)	0.2133(1)	0.8940(2)	0.0129(7)	0.0069(6)	0.0058(6)	0.0010(5)	0.0022(5)	0.0043(6)
O(2)	0.7325(1)	0.1990(1)	0.5844(2)	0.0048(6)	0.0044(6)	0.0124(7)	0.0002(5)	0.0007(5)	0.0007(5)
O(3)	0.1005(1)	0.8844(1)	0.9415(1)	0.0077(6)	0.0081(6)	0.0062(6)	−0.0015(5)	−0.0022(5)	0.0029(5)
O(4)	0.6590(1)	0.0026(1)	0.7496(1)	0.0066(6)	0.0114(7)	0.0085(6)	−0.0008(5)	−0.0009(5)	0.0072(5)
Synthetic	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li	0.0198(4)	0.8122(4)	0.7511(5)	0.0167(21)	0.0115(19)	0.0195(20)	0.0037(17)	−0.0011(17)	0.0031(16)
T(1)	0.5303(1)	0.8807(1)	0.7496(1)	0.0070(2)	0.0067(2)	0.0057(2)	0.0000(2)	−0.0001(2)	0.0036(2)
T(2)	0.8752(1)	0.3443(1)	0.9161(1)	0.0068(2)	0.0058(2)	0.0057(2)	0.0000(2)	−0.0004(2)	0.0031(2)
O(1)	0.7593(1)	0.2132(1)	0.8938(2)	0.0132(7)	0.0070(6)	0.0061(6)	0.0009(5)	0.0019(5)	0.0040(5)
O(2)	0.7322(1)	0.1989(1)	0.5844(2)	0.0059(6)	0.0052(6)	0.0129(7)	0.0000(5)	0.0002(5)	0.0012(5)
O(3)	0.1006(1)	0.8844(1)	0.9417(2)	0.0089(6)	0.0086(6)	0.0068(6)	−0.0014(5)	−0.0020(5)	0.0036(5)
O(4)	0.6590(1)	0.0026(1)	0.7495(2)	0.0073(6)	0.0117(6)	0.0086(6)	−0.0006(5)	−0.0007(5)	0.0074(5)

Table 2. Microprobe analyses of the α-eucryptites

	Microprobe analysis (wt – %)		Theoretical (wt – %)
	nat.	synth.	
SiO_2	48.00	46.28	47.69
Al_2O_3	40.78	38.86	40.45
Li_2O	–	–	11.86
Total	88.78	85.14	100.00

Klaska, Hamburg. Mixtures of Li(OH), $Al(OH)_3$ and SiO_2 were heated up to 723 K and 600 bar and kept for 3 days yielding colourless transparent hexagonal prisms of α-eucryptite. Crystals measuring 0.150 × 0.150 × 0.300 [0.150 × 0.150 × 0.300] mm were used for data collection on an automatic Philips PW 1100 four circle diffractometer with graphite-monochromatized Mo*Kα* radiation (λ = 0.7107 Å) and ω-2 θ scan (θ_{max} = 40°). The intensities of 5863 [5863] reflections were measured. Symmetry equivalent intensities were averaged to give 1950 [1957] non-equivalent reflections; 1721 [1710] of them had $I \geq 3\,\sigma(I)$ and were used for the subsequent refinement. The standard deviations, $\sigma(I)$, were estimated using the formula cited by Stout and Jensen (1968). Refined cell dimensions were determined with the program LAT written by Hornstra and Vossers (1973/74). Lorentz, polarization, and absorption corrections (Busing and Levi, 1957) were applied [μ(Mo*Kα*) = 8.54 cm^{-1}]. The structures were determined and refined by full-matrix least-squares analysis with the program SHELX-76 (Sheldrick, 1976), starting with the atomic coordinates given by Zachariasen (1972) for phenakite. Difficulties that arose during refinement and a difference in the Fourier synthesis indicated that the Li atoms had to be located at the Si positions of the phenakite structure. The atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, Vol. IV, 1974, for neutral atoms. Anisotropic refinements of the crystal structures converged at R(unweighted = 0.055 [0.054] and R(weighted) = 0.043 [0.041]. {R(weighted) = $[\Sigma w(|F_o|-|F_c|)^2]^{1/2}/(\Sigma w F_o^2)^{1/2}$, $w = 1/\sigma^2$}. Final atomic parameters are given in Table 1. Lists of bond lengths and angles and of observed and calculated structure factors have been deposited[1]. The results of the microprobe analyses are given in Table 2.

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51325, the names of the authors and the title of the paper

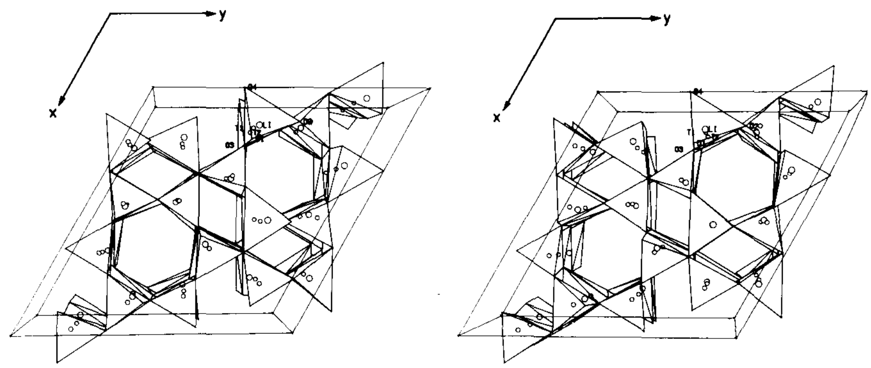

Fig. 1. Stereoscopic view of the unit cell as seen down the *c* axis

Description of the structures and results

The natural and synthetic low temperature polymorph of $LiAlSiO_4$, α-eucryptite, is isostructural with phenakite, Be_2SiO_4 (Zachariasen, 1972), and willemite, Zn_2SiO_4 (Klaska et al., 1978). However, in α-eucryptite Li occupies the Si position and the T atoms occupy the Be and Zn positions of phenakite and willemite. The structure consists of $[LiO_4]$ tetrahedra and $[TO_4]$ tetrahedra. Li – O distances vary between 1.960 Å and 1.999 Å [1.961 Å and 2.004 Å], mean 1.982 [1.983] Å, and T – O distances between 1.678 Å and 1.697 Å [1.678 Å and 1.696 Å], mean 1.688 [1.688] Å. According to Liebau's classification of silicates (Liebau, 1985) the connection of the $[TO_4]$ tetrahedra forms an example of the unbranched vierer framework.

The T – O distances suggest that within the limits of error there is either a completely random distribution of the Al and Si atoms in the T positions or a microtwinning with very small ordered domains in both natural and synthetic α-eucryptite. High-resolution electron microscopy and electron diffraction experiments strongly favour statistical Al/Si distribution, since no micro-domains were visible.

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The crystal structure of *parthéite*

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Calcium alumino-silicate / Interrupted framework / Zeolite-like

Abstract. *Parthéite* is a zeolite-like mineral of composition $Ca_2Al_4Si_4O_{15}(OH)_2 \cdot 4H_2O$. It crystallizes with monoclinic symmetry, space group $C2/c$, $a = 21.555(3)$, $b = 8.761(1)$, $c = 9.304(2)$ Å, $\beta = 91.55(2)$, $Z = 4$, $D_m = 2.39$ g/cm^3, $D_x = 2.41$ g/cm^3. Its structure consists of T-centered TO_4 tetrahedra (T = Al, Si) which are connected *via* corners to a 3-dimensional framework. Due to the presence of hydroxyl groups the framework is interrupted at every second AlO_4 tetrahedron. Water molecules and Ca atoms are situated in large channels which cross the structure parallel to c. The channels are delimited by *zig-zag* chains of nearly flat 10-membered rings. The framework also contains 8-membered rings and two types of 4- and 6-membered rings of oxygen tetrahedra.

Introduction

Parthéite was discovered by H. Sarp in rodingitic dykes from an ophiolitic zone in the Taurus Mountains, Southwest Turkey (Sarp et al., 1979). The mineral was originally described as a hydrated silicate of composition $CaAl_2Si_2O_8 \cdot 2H_2O$, $Z = 8$. In this paper we report its crystal structure and revised chemical composition. It will be shown that *parthéite* has a zeolite-like structure which contains both water *and* hydroxyl groups. As a consequence its oxygen tetrahedra framework is interrupted, and its correct formula is $Ca_2Al_4Si_4O_{15}(OH)_2 \cdot 4H_2O$, $Z = 4$. A preliminary report on its structure has been given previously (Engel and Yvon, 1983).

Experimental

A plate-like crystal of dimensions 20 × 50 × 160 µm was isolated by H. Sarp from a holotype sample deposited in the Muséum d'Histoire Naturelle,

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Geneva. It was measured on a computer controlled 4-circle diffractometer using graphite monochromated Mo$K\alpha$ radiation. The cell parameters (see Abstract) were consistent with those reported previously (Sarp et al., 1979), and the systematically absent reflections (hkl: $h+k=2n+1$, $h0l$: $l=2n+1$) confirmed the space group assignment $C2/c$ or Cc (International Tables for Crystallography, Vol. A, 1983). The intensities of 2863 reflections, included in a quarter sphere of reciprocal space were measured in the ω-2θ scan mode out to a limit of $\sin\theta/\lambda = 0.71$ Å^{-1}, yielding 693 unique observed reflections with $I > 3\sigma(I)$. In view of the low absorption coefficient ($\mu_{MoK\alpha} = 12.1$ cm^{-1}) no correction for absorption was made. The structure was solved by MULTAN (Main et al., 1980) in space group $C2/c$, and refined with CRYLSQ (Stewart et al., 1976) to a consistency index of $R[=\Sigma(||F_o| - |F_c||)/\Sigma|F_o|] = 0.07$ (2012 reflections[1], 142 variables, weights $w = 1/\sigma^2$). Scattering factors were taken from the International Tables, Vol. IV (1974). The refinement did not include the intense 200, 400 and 600 reflections which had ill-shaped profiles and were not correctly measured. A final electron density difference map showed no peaks higher than 1.1 eÅ^{-3}. The strongest peaks were all situated in the vicinity (< 0.6 Å) of metal and oxygen atom sites. The atomic coordinates and anisotropic temperature factors are listed in Table 1, and lists of bond distances and angles are given in Tables 2, 3 and 4. Stereographic projections of the structure as drawn by ORTEP (Stewart et al., 1976) are represented in Figures 1, 2 and 3.

Discussion

Parthéite shows structural features typical for zeolites (for stereo drawings and descriptions of the latter, see Meier and Olson, 1978). It consists of a three-dimensional framework of T-centered TO_4 tetrahedra (T = Al, Si) which share corners, and a system of interconnected cavities which are filled by Ca^{2+} ions and water molecules. The framework density is low, 18.2 T atoms/1000 Å^3. However, in contrast to the known zeolites, not all oxygen tetrahedra share their four corners but some (those centered by Al(1), see Fig. 1) share only three, thus leading to an *interrupted framework* (see, for instance, *bavenite*, Cannillo et al., 1966). As will be shown below, the framework of *parthéite* is interrupted due to the presence of hydroxyl groups (OH) in the coordination sphere of Al(1). The sharing coefficients of the tetrahedra framework are 1.94 (Zoltaï, 1960) or 3.75 (Coda, 1969).

The oxygen tetrahedra are linked *via* T – O – T bonds to rings of different size and shape (Fig. 1 and 2). There are two types of 4-membered rings, which connect respectively two Si(2) and two Al(2) sites (type I), and one Si(1), one

[1] Additional material to this paper can be ordered referring to the No. CSD 51076, Engel and Yvon: The Crystal Structure of *parthéite*, at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 1. Atom positions for *parthéite*, space group $C2/c$, all atoms are in equipoint (8f) except O(8), which are in (4e). The anisotropic temperature factors are expressed as $T = \exp\left(-2\pi^2 \times 10^{-2} \sum_{ij} U_{ij} a_i a_j\right)$ where $a_1 = ha^*$, $a_2 = kb^*$ etc. (e.s.d's are given in parentheses)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	0.06729(9)	0.1832(3)	0.2896(2)	0.46(9)	0.90(10)	0.65(10)	0.08(8)	−0.07(7)	0.04(9)
Si(2)	0.23983(9)	0.0077(3)	0.4621(2)	0.46(8)	0.62(9)	0.69(10)	0.17(8)	0.12(7)	−0.01(9)
Al(1)	0.1161(1)	0.0844(3)	0.6006(3)	0.73(10)	0.77(11)	0.63(11)	−0.06(9)	0.13(9)	−0.03(10)
Al(2)	0.1999(1)	0.3162(3)	0.2858(2)	0.90(10)	0.55(11)	0.49(10)	0.08(9)	−0.01(8)	0.09(10)
Ca	0.35586(7)	0.1991(2)	0.0444(2)	1.22(7)	1.30(8)	0.99(8)	−0.48(7)	−0.23(6)	0.10(7)
O(1)	0.0695(2)	0.0181(7)	0.2162(6)	0.6(2)	1.3(3)	0.9(3)	0.2(2)	0.3(2)	−0.1(2)
O(2)	0.0725(2)	0.1719(7)	0.4626(6)	0.8(2)	1.7(3)	0.7(3)	0.4(2)	0.0(2)	0.1(2)
O(3)	0.1222(2)	0.2883(7)	0.2295(6)	1.1(3)	1.7(3)	0.6(2)	−0.4(2)	0.0(2)	−0.1(2)
O(4)	0.1722(2)	0.0363(6)	0.0250(6)	1.1(2)	0.9(3)	1.3(3)	0.0(2)	0.7(2)	−0.2(2)
O(5)	0.2081(2)	0.4669(6)	0.4096(6)	1.0(2)	0.6(3)	1.1(3)	−0.4(2)	−0.2(2)	0.1(2)
O(6)	0.2345(3)	0.1550(6)	0.3605(6)	1.4(3)	0.7(3)	1.1(3)	0.3(2)	0.1(2)	0.5(2)
O(7)	0.2340(2)	0.3599(6)	0.1221(6)	1.3(3)	0.9(3)	0.7(3)	−0.5(2)	0.1(2)	0.2(2)
O(8)	0	0.2632(9)	$\frac{1}{4}$	0.6(3)	0.7(4)	1.1(4)	0	−0.2(3)	0
OH	0.3523(3)	0.2673(7)	0.2918(6)	1.7(3)	1.6(3)	0.9(3)	−0.6(2)	−0.2(2)	−0.6(2)
$H_2O(1)$	0.0712(3)	0.5050(8)	0.0159(9)	2.8(3)	0.4(3)	6.8(6)	−0.2(3)	0.6(4)	0.1(4)
$H_2O(2)$	0.4541(3)	0.3070(8)	0.0800(7)	0.9(3)	2.5(3)	3.2(4)	−0.9(3)	1.2(3)	−0.7(3)

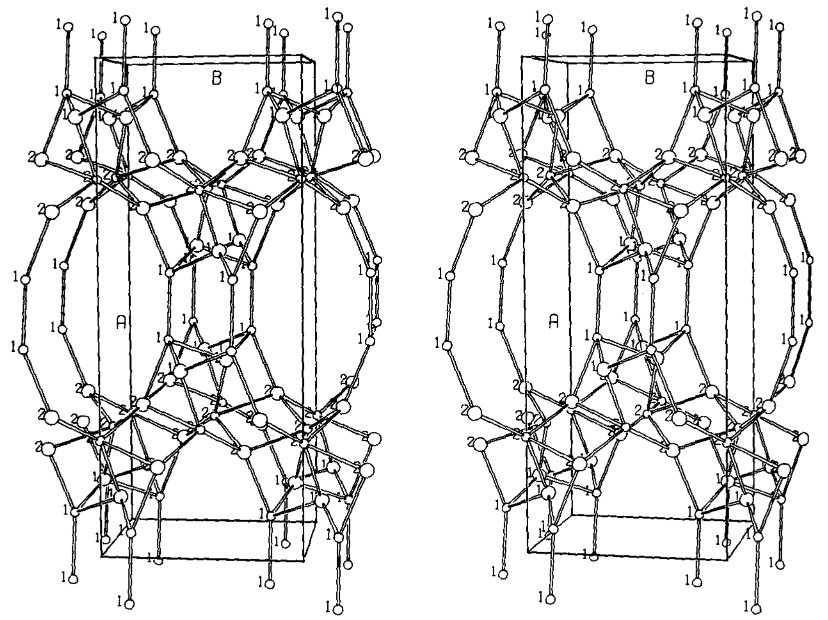

Fig. 1. Stereoscopic pair of the T atom framework (T = Al, Si) of *parthéite*, viewed approximately parallel to *c*. Large circles: Al, small circles: Si, atom numbering as in Table 1. The straight lines connecting the T atoms represent idealized (non-linear) T – O – T bonds

Si(2), one Al(1) and one Al(2) site (type II). The type I ring has nearly square-planar cross-section, whereas the type II ring is distorted. The latter carries the hydroxyl group and could be considered as a *secondary building unit* of *parthéite* as defined for zeolite frameworks (Meier, 1968). Two rings of type II are joined by a ring of type I such that these three form a finite ladder-like chain directed approximately along [110]. There also exist two types of 6-membered rings, of which one has the shape of a nearly planar hexagon and connects four Si(1) and two Al(1) sites (type I) and the other has the shape of a bent hexagon which connects one Si(1), two Si(2), one Al(1), one Al(2) and alternatively one Al(1) or one Al(2) site (type II). There occur pairs of squeezed, doubly bent 8-membered rings, which are fused together at their centres, of which each connects one Si(1), three Si(2), one Al(1) and three Al(2) sites. Finally there exist nearly circular and flat 10-membered rings, which are oriented approximately parallel to (011) and ($0\bar{1}1$) and connect four Si(1), two Si(2) and four Al(2) sites. Both, the 6-membered rings of type I and the 10-membered rings are fused side by side (mainly *via* Si(1) – O – Si(1) bonds) such that they form a system of interconnected *zig-zag* chains which cross the structure parallel to *c*. These chains partially delimit large cavities which are interconnected to wide *zig-zag* channels of elliptical cross-section

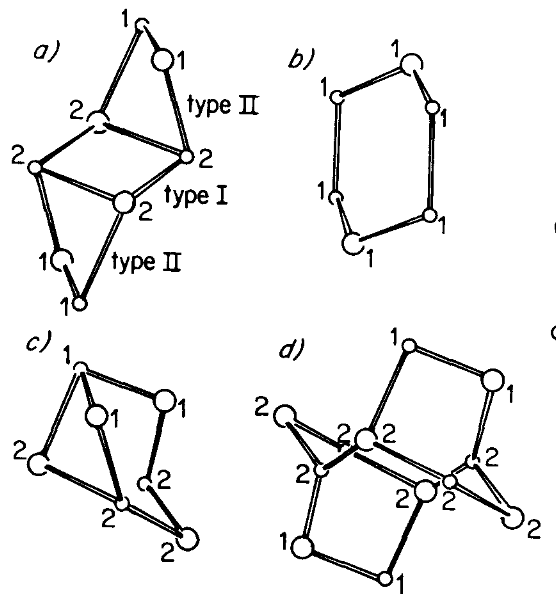

Fig. 2. Isolated T-rings taken from Fig. 1. *a)* a finite ladder-like chain built of two types of 4-membered rings; *b)* a 6-membered ring of type I; *c)* a 6-membered ring of type II; *d)* a doubly bent 8-membered ring; *e)* a 10-membered ring. Large circles: Al, small circles: Si

running parallel to *c* through the 10-membered rings. As a consequence the concentration of T–O–T bonds across the plane bisecting those channels perpendicular to *a* is lower by a factor of at least two compared to the concentration of T–O–T bonds across any other plane in the structure. This conveys to the framework some two-dimensional character, and could be related to the observed cleavage of the crystals parallel to (100).

The elliptical *zig-zag* channels have free apertures[2] of 6.0 Å (parallel to [100]) and 3.5 Å (parallel to [011]). They are filled by Ca^{2+} ions and water molecules (Fig. 3). The former are situated in cavities which are delimited by six oxygen atoms belonging to the framework (of which one is the OH^- group) and by two water molecules, which together form a distorted cube-like configuration. The latter are fixed on two crystallographic sites. One is located near the channel axis and close to the plane defined by the 10-membered ring [$H_2O(1)$], whereas the other is located off-center and lies above the 6-membered ring of type II [$H_2O(2)$]. Both sites occur at about the same heights in the channels (around $z = 0, \frac{1}{2}$, etc), and they are clustered in groups of four in a nearly planar configuration. Within each group

[2] Calculated with an oxygen radius of 1.35 Å.

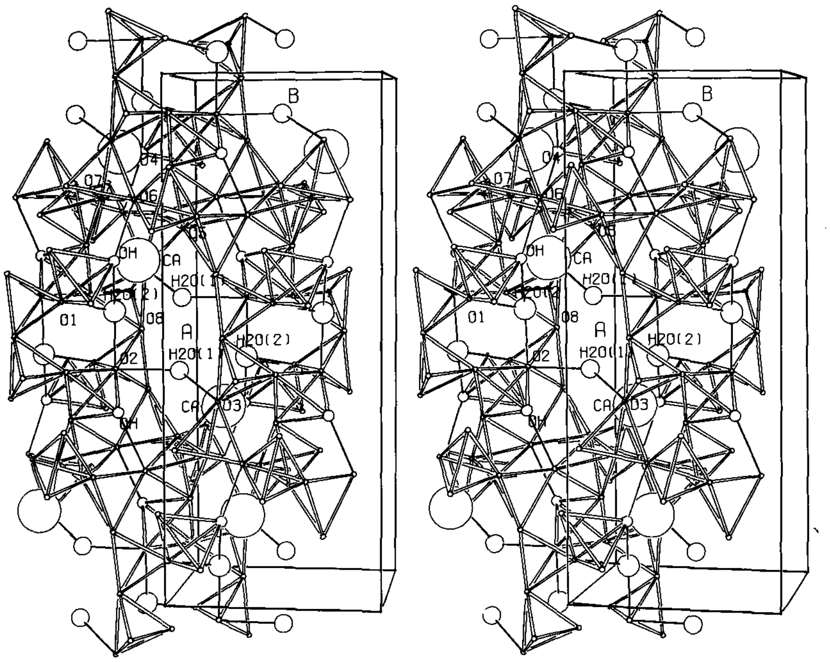

Fig. 3. Stereoscopic pair of the oxygen tetrahedra (double lines), Ca^{2+} ion (large circles) and water molecules (medium circles) in *parthéite*, viewed approximately parallel to *c*. The tetrahedra corners marked by small circles designate hydroxyl groups. The single lines indicate short O–H...O distances (less than 3.1 Å) of relevance for the possible location of hydrogen bonds

their shortest separations are 2.92 Å [$H_2O(1)-H_2O(2)$] and 3.08 Å [$H_2O(1)-H_2O(1)$]. The shortest separations of both sites from the oxygen atom sites of the framework are, respectively, d[$H_2O(1)-O$] = 2.87 Å (O(2)) and 3.32 Å (OH), and d[$H_2O(2)-O$] = 2.71 Å (O(1)) and 3.01 Å (OH) (see single lines in Fig. 2). Their distances from the Ca atom sites (d[Ca–O] = 2.46 Å [$H_2O(1)$], 2.34 Å [$H_2O(2)$] suggest that both water molecules are in close contact with the Ca^{2+} ions.

The other oxygen atoms in the structure all belong to the framework. They have two metal ligands (O(1), O(2),... O(8)), except for (OH) which has only one (Al(1)). The former are linked either to one Al and one Si atom (O(1), O(2),... O(7), or to two symmetry equivalent Si atoms (O(8)). None is linked to two Al atoms, in agreement with the Al–O–Al *avoidance rule* (Loewenstein, 1954). The average T–O bond distances within the TO_4 tetrahedra are 1.62 Å (T = Si(1), Si(2)), 1.75 Å (T = Al(2)) and 1.76 Å (T = Al(1)) (Table 2). These values are indicative for an *ordered* Si/Al atom arrangement ($\bar{d}$[Si–O] = 1.60 Å, $\bar{d}$[Al–O] = 1.76 Å; Jones, 1968). The O–T–O bond angles are all close to 109.4°. Their greatest spread

Table 2. Interatomic distances (Å) and angles (°) within the $[TO_4]$ tetrahedra of *parthéite*. (E.s.d's are given in parentheses)

T-atoms	O(a)	Distances Si–O(a)	O(b)	Angles O(a)–Si–O(b)	T-atoms	O(a)	Distances Al–O(a)	O(b)	Angles O(a)–Al–O(b)
Si(1)	–O(1)	1.601(6)	–O(2)	111.6(3)	Al(1)	–OH	1.766(6)	–O(1)	104.5(3)
			–O(3)	109.7(3)				–O(2)	106.6(3)
			–O(8)	109.0(3)				–O(4)	114.1(3)
	–O(2)	1.613(6)	–O(3)	110.4(3)		–O(1)	1.741(6)	–O(2)	111.9(3)
			–O(8)	106.7(2)				–O(4)	110.5(3)
	–O(3)	1.612(6)	–O(8)	109.3(3)		–O(2)	1.748(6)	–O(4)	109.3(3)
	–O(8)	1.644(4)				–O(4)	1.767(6)		
	ave	*1.618*				*ave*	*1.756*		
Si(2)	–O(4)	1.632(6)	–O(5)	111.9(3)	Al(2)	–O(3)	1.757(6)	–O(5)	112.2(3)
			–O(6)	110.6(3)				–O(6)	113.8(3)
			–O(7)	108.1(3)				–O(7)	101.0(3)
	–O(5)	1.631(6)	–O(6)	111.0(3)		–O(5)	1.758(6)	–O(6)	108.3(3)
			–O(7)	102.8(3)				–O(7)	111.6(3)
	–O(6)	1.602(6)	–O(7)	112.2(3)		–O(6)	1.734(6)	–O(7)	109.9(3)
	–O(7)	1.622(6)				–O(7)	1.752(6)		
	ave	*1.622*				*ave*	*1.750*		

Table 3. Angles (°) between tetrahedra (E.s.d's are given in parentheses)

Angles			
T	O	T	
Si(1)	O(1)	Al(1)	138.9(4)
Si(1)	O(2)	Al(1)	141.4(4)
Si(1)	O(3)	Al(2)	132.7(4)
Si(2)	O(4)	Al(1)	129.0(4)
Si(2)	O(5)	Al(2)	129.6(3)
Si(2)	O(6)	Al(2)	156.3(4)
Si(2)	O(7)	Al(2)	138.9(4)
Si(1)	O(8)	Si(1)	129.5(5)

(101.0° – 113.8°) occurs for the tetrahedra which are centered by Al(2). The T–O–T bond angle between Si-centered tetrahedra is 129.5°, whereas those between Si- and Al-centered tetrahedra range between 129.0° and 156.3° (Table 3). The correlations between the T–O distances and T–O–T angles are consistent with those in *anorthite* as discussed by Brown et al. (1969). The shortest oxygen-oxygen contact in the structure occurs within the Si(2) centered tetrahedron (d[O(5)–O(7)] = 2.54 Å). The distance between the OH^- group and the oxygen atom (O(6)) which could possibly participate in hydrogen bonding is d[OH...O(6)] = 2.81 Å (see single line in Fig. 3).

Although none of the five hydrogen atoms and in particular that of the OH^- group could be located with certainty on the electron density difference map, their presence was established from a bond-valence calculation (Donnay and Allmann, 1970). The valence sums (not corrected for H-bonding) are 1.05, 0.28 and 0.34 valence units for the O atoms which belong respectively to the OH^- group and the water molecules $H_2O(1)$ and $H_2O(2)$, and they range between 1.77 and 2.07 valence units for the other O atoms (Table 4). The lowest value occurs for those oxygen atoms of the framework which are closest to the OH^- group (O(6)) or one of the water molecules (O(2)... $H_2O(2)$), thus indicating that both O(6) and O(2) may participate in the formation of hydrogen bonds.

According to these structural results the chemical formula of *parthéite* needs to be rewritten as $Ca_2Al_4Si_4O_{15}(OH)_2 \cdot 4H_2O$, $Z = 4$. This composition is close to the previously proposed formula $CaAl_2Si_2O_8 \cdot 2H_2O$, $Z = 8$ (Sarp et al., 1979), and falls within the error limits of the microprobe analysis. The theoretical density calculated according to this new formula is $D_x = 2.41$ gcm^{-3} which compares well with the experimental density $D_m = 2.39$ gcm^{-3}, measured by Sarp et al. (1979).

In conclusion we note that, due to the presence of hydroxyl groups in its structure, *parthéite* shows only little resemblance with other alumino-silicates of similar composition, such as the feldspar *anorthite*, $CaAl_2Si_2O_8$ (Megaw et

Table 4. Donnay-Allmann bond valence (v) calculation for Parthéite. The interatomic distances [d(Å)] between heavy cations and oxygen atoms are given up to their corresponding d_{max}-value (e.s.d.'s are given in parentheses)

	Ca(1)	v	Al(1)	v	Al(2)	v	Si(1)	v	Si(2)	v	$\Sigma v_{cations}$
O(1)			1.741(6)	0.77			1.601(6)	1.03			1.80
O(2)			1.748(6)	0.76			1.613(6)	1.01			1.77
O(3)	2.607(6)	0.23			1.757(6)	0.74	1.612(6)	1.02			1.99
O(4)	2.476(6)	0.28	1.767(6)	0.73					1.632(6)	0.98	1.99
O(5)	2.501(6)	0.27			1.758(6)	0.74			1.631(6)	0.98	1.99
O(6)					1.734(6)	0.77			1.602(6)	1.03	1.80
O(7)	2.502(6) 3.083(6)	0.26 0.06			1.752(6)	0.75			1.622(6)	1.00	2.07
O(8)							2 × 1.644(4)	0.95			1.90
OH	2.381(6)	0.32	1.766(6)	0.73							1.05
$H_2O(1)$	2.456(7)	0.28									0.28
$H_2O(2)$	2.335(6)	0.34									0.34
Σv_{anions}		2.04		2.99		3.00		4.01		3.99	
d_{ave}	2.543		1.756		1.750		1.618		1.622		
d_{max}[a]	3.25		2.26		2.26		2.13		2.13		
$p = \frac{d_{ave}}{d_{max} - d_{ave}}$	3.60		3.48		3.48		3.16		3.16		

[a] taken from Donnay and Allmann, 1970

al., 1962), and the zeolite *gismondite*, $CaAl_2Si_2O_8 \cdot 4H_2O$ (Fischer, 1963) which are both framework silicates *without* hydroxyl groups. Its structure also differs significantly from that of *lawsonite*, $CaAl_2(OH)_2Si_2O_7 \cdot H_2O$, which is a mineral of similar composition containing both water and hydroxyl groups (Baur, 1978). In contrast to *parthéite*, it is a *soro*silicate, which displays *octahedrally* coordinated Al atoms. For framework alumino-silicates the observation of an *interrupted framework* is rare but not unique. Other known examples are *roggianite* $Ca_{16}Al_{16}Si_{32}O_{88}(OH)_{16} \cdot \sim 26H_2O$ (Galli, 1980; modified sharing coefficient after Coda, 3.67) and *wenkite* $Ba_4(Ca_{0.9}\square_{0.1})_6(Al, Si)_{20}O_{39}(OH)_2(SO_4)_3 \cdot nH_2O$ (Wenk, 1973; modified sharing coefficient 3.90; Merlino, 1974). Both minerals contain hydroxyl groups.

The structural features of *parthéite* suggest that this mineral may have zeolite-like properties. In particular, the shape and size of its channels could allow for easy dehydration and cation exchange. As to the former no major structural change was observed after heating crystals to 150 °C for 64 h, whereas a structural transformation to *anorthite* was observed after a heat treatment at 400 °C for 40 h (Sarp et al., 1979). In this context it is worth noting that *parthéite* was found to be closely associated in nature to *thomsonite* (Sarp et al., 1979), which is a Ca- and Na-bearing zeolite.

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