A Re-investigation of the Structure of Afwillite*

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The crystal structure of afwillite, $Ca_3(SiO_3OH)_2.2H_2O$, [monoclinic, Cc, $a=16\cdot278$ (1), $b=5\cdot6321$ (4), $c=13\cdot236$ (1) Å, $\beta=134\cdot898$ (3)°, $Z=4$] has been re-investigated and refined to a conventional R value of $3\cdot7\%$ for 3289 independent intensities. The present results confirm the overall conclusion reached by Megaw [*Acta Cryst.* (1952). **5**, 477–491] that the Si tetrahedra are linked together through edges and corners by rather irregular Ca polyhedra to form a fairly close-packed arrangement. The positions of the H atoms, having been experimentally determined for the first time, show the true nature of hydrogen bonding in this mineral. One O atom, O(9), in Megaw's structure shows a significantly large shift (0·63 Å) from its original position, altering the nature of the Ca(1)–O(9) bond but not the general environment of any atom. The interatomic distances and angles have been determined with a high degree of accuracy.

Introduction

Afwillite was first discovered in the Dutoitspan mine (Kimberly, South Africa) in 1923. On the basis of physicochemical measurements, Parry & Wright (1925) suggested a formula of $3CaO.2SiO_2.3H_2O$ or $2H_2CaSiO_4.Ca(OH)_2$ for this mineral. Tilley (1930) suggested from a microscopic study that afwillite was a derivative of spurrite, $2CaCaSiO_4.CaCO_3$. Megaw (1952) determined the crystal structure of this mineral by X-ray diffraction and found that the structure can be best represented by the formula $Ca_3(SiO_3OH)_2.2H_2O$. This work showed the presence of O^{2-} and OH^- ions and neutral H_2O molecules in the structure. It also suggested a hydrogen-bonding scheme based on structural grounds which was in moderate agreement with the observed polarized infrared spectrum (Petch, Sheppard & Megaw, 1956) and with measured thermal expansion coefficients (Shaw, 1953). However, the positions of the H atoms could not be determined from electron density maps, possibly because of the lack of sufficiently accurate data and/or incomplete refinement ($R=24\cdot51\%$). At a later stage McIver (1960) used the same data (1600 reflexions) to refine Megaw's model to an R value of 19% and raised some questions about some of Megaw's conclusions. Both these studies, however, were inadequate because the positions of the H atoms were merely postulated and not actually determined from diffraction analysis. It was therefore decided to re-study the structure of this interesting mineral by using accurate intensity data. Resolution of the problem of hydrogen bonding has been the principal aim of the present study.

Experimental

The specimens were selected from the Dutoitspan sample kindly made available by Dr H. D. Megaw. A needle-shaped crystal mounted about the b axis was used to take oscillation and Weissenberg photographs which confirmed the identity of the mineral. The accurate cell parameters given in Table 1 (along with other physical data) were obtained by the least-squares refinement of 20 θ values measured at the beginning of diffractometer data collection, and agree with those published by Megaw (1952). The systematic absences are compatible with the space group Cc.

Table 1. *Crystal data*

Afwillite, $Ca_3(SiO_3OH)_2.2H_2O$
F.W. 342·45
Monoclinic
$a=16\cdot278$ (1), $b=5\cdot6321$ (4), $c=13\cdot236$ (1) Å, $\beta=134\cdot898$ (3)°
$V=859\cdot59$ Å^3
$D_m=2\cdot630$ g cm^{-3} (Parry & Wright, 1925)
$D_c=2\cdot646$ g cm^{-3}
$Z=4$
$F(000)=688$
Linear absorption coefficient $=21\cdot3$ cm^{-1} (Mo $K\alpha$)
Absent spectra: hkl for $h+k=2n+1$
$\qquad\qquad\quad h0l$ for $\quad l=2n+1$
Pyro- and piezo-electric test, positive (Megaw, 1952)
Space group: Cc

For data collection a separate crystal was taken from the same sample, ground to a sphere of diameter 0·352 (4) mm ($\mu R=0\cdot37$) and mounted approximately about the b axis. The intensities were measured on a relative scale by using a Hilger and Watts Y290 four-circle automatic diffractometer equipped with a moving scintillation counter. The θ–2θ scanning technique was used with a scan rate of $0\cdot01°$ s^{-1}, base width of $1°$ in θ and $0\cdot1°$ background on both sides of the peak. More than a quarter of the reflexion sphere

$(h \geq 0, \theta \leq 45°)$was scanned, with Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å). Three standard reflexions were checked after every 50 measurements to detect and allow for any slow fluctuation in the primary beam. It was found that the intensities did not vary to any appreciable extent during the data collection. Equivalent reflexions were corrected for Lorentz and polarization factors and averaged. 3289 unique reflexions were thus processed of which 512 had amplitudes smaller than the corresponding 3σ values. No correction was made for absorption or anomalous dispersion.

Structure analysis

A Patterson synthesis suggested that the non-hydrogen atomic positions found by Megaw (1952) were correct within experimental error. Several cycles of full-matrix least-squares refinement of this model together with individual isotropic temperature factors improved the agreement between $|F_o|$ and $|F_c|$ but raised doubts about the position of O(9). This atom was shifted to a new position as indicated in a difference Fourier map and the refinement continued. Isotropic refinement of all the Ca, Si and O atoms reduced $R\{=[\sum(|F_o| - G|F_c|)]/\sum|F_o|\}$ from an initial value of 21% to 7.1%. The positions of the H atoms were determined from a difference map but showed unacceptably large shifts when refined. It has been suggested that O–H distances based on Fourier H coordinates are more reliable than those derived from refined coordinates (Catti & Ferraris, 1973), and so the H atoms were treated as 'fixed atom contributors', with temperature factors equal to those of their parent O atoms (obtained in the last cycle of isotropic refinement), and included in the calculation of structure factors. Further refinement with anisotropic factors for the Ca, Si and O atoms, one overall scale factor and a parameter for secondary extinction gave a final R value of 3.7% [2.8% with the 2777 reflexions having $I \geq 3\sigma(I)$]. The refinement was terminated when the parameter shift was less than one

tenth of the corresponding e.s.d. During refinement, space-group symmetry required the x and z coordinates of Ca(1) to be fixed and not refined along with the other parameters. These two parameters were varied, however, in the last cycle of refinement together with all other parameters except the corresponding values of Ca(2). Thus e.s.d.'s were obtained for all the parameters.

The function minimized in the least-squares refinement was: $M = \sum w[|F_o| - G(1 + g|F_c|^2)^{1/2}|F_c|]^2$ where G is a scale parameter and g is a coefficient of secondary extinction. The weight, w, assigned to an unscaled $|F_o|$ was calculated, at the final stage of refinement, from the relations: $w = 0.0012$ for $|F_o| \leq 25$, and $w = (1 - \exp\{-20[(\sin \theta)/\lambda]^2\})/(90 + |F_o| + 0.0055|F_o|^2)$ for $|F_o| > 25$.

This gave reasonably constant averages of M over different $|F_o|$ and $(\sin \theta)/\lambda$ ranges. The parameter g was refined because the strongest $|F_o|$ values were systematically smaller than the corresponding $|F_c|$'s. Refinement of g [final value $= 0.0000143(5)$] considerably improved the agreement between $|F_o|$ and $|F_c|$. The final value of G was $1.780(4)$. The scattering factors for neutral Ca, Si, O and H were taken from Hanson, Herman, Lea & Skillman (1964) and used without correction for the possible ionic states. The refined parameters of the non-hydrogen atoms are listed in Table 2. The positional and isotropic thermal parameters of the H atoms are given in Table 3.* The computations were made on the University of London CDC6600 computer with the *DIFF4C*, *SFFP* and *SFLS* programs of Birkbeck College Crystallographic Program Library.

Table 2. *Fractional coordinates* ($\times 10^5$) *and thermal parameters* ($\times 10^4$) *of the non-hydrogen atoms*

The e.s.d.'s are given in parentheses. The anisotropic temperature factor has the form
$$T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31})].$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{21}$
Ca(1)	19680 (5)	3703 (6)	29200 (5)	61 (1)	66 (1)	63 (1)	13 (2)	84 (2)	8 (2)
Ca(2)	80171 (4)	4990 (7)	21213 (5)	67 (1)	110 (1)	78 (1)	−51 (2)	103 (2)	−2 (2)
Ca(3)	50392 (4)	2829 (7)	3131 (6)	60 (1)	71 (1)	128 (1)	34 (2)	114 (2)	12 (2)
Si(1)	11768 (6)	5129 (10)	184 (7)	63 (2)	63 (2)	57 (2)	−3 (3)	84 (3)	−12 (3)
Si(2)	86923 (6)	98073 (10)	188 (7)	60 (2)	54 (2)	60 (2)	2 (3)	87 (3)	−2 (3)
O(1)	99020 (15)	90943 (34)	34297 (18)	72 (5)	180 (6)	73 (5)	−17 (9)	78 (9)	20 (9)
O(2)	197 (15)	90887 (33)	15827 (18)	67 (5)	171 (6)	69 (5)	38 (9)	83 (9)	28 (9)
O(3)	78272 (14)	97821 (29)	2343 (18)	89 (5)	123 (5)	100 (5)	−5 (8)	155 (9)	−12 (8)
O(4)	21228 (15)	5467 (27)	98665 (19)	113 (5)	95 (5)	135 (6)	−35 (8)	206 (8)	−42 (8)
O(5)	33680 (15)	73414 (27)	39691 (17)	93 (5)	72 (5)	75 (5)	73 (7)	117 (9)	20 (7)
O(6)	36651 (16)	26997 (30)	44054 (21)	100 (5)	91 (5)	139 (6)	−60 (9)	159 (10)	−17 (8)
O(7)	15230 (15)	27093 (26)	10640 (18)	102 (5)	73 (4)	99 (6)	−33 (7)	155 (9)	−3 (8)
O(8)	13667 (15)	80824 (26)	8125 (19)	108 (5)	76 (4)	110 (5)	34 (8)	165 (9)	−4 (8)
O(9)	59284 (16)	89321 (35)	26963 (20)	124 (6)	159 (6)	128 (6)	−43 (10)	165 (10)	11 (10)
O(10)	41837 (20)	96957 (40)	26654 (26)	194 (8)	186 (8)	226 (9)	147 (13)	279 (14)	64 (13)

Table 3. *Fractional coordinates* ($\times 10^3$) *of the hydrogen atoms determined from difference map*

The atomic numbering indicates the two O atoms involved in H bonding. The U_{Iso}'s ($\times 10^4$) are those of the parent O atoms, prior to anisotropic refinement.

	x	y	z	U_{Iso} (Å²)
H(21)	496	415	243	102
H(43)	228	240	000	101
H(93)	150	450	375	140
H(910)	30	360	270	140
H(101)	430	105	312	197
H(104)	346	975	164	197

Description and discussion of the structure

The crystal structure of afwillite, illustrated in Fig. 1, consists of double chains of Ca and Si polyhedra, linked by sharing edges and corners to form continuous sheets parallel to ($\bar{1}01$). These sheets of composition $|Ca_3Si_2O_4|^{6+}$ are linked by Ca–O–Si bonds and H bonds, which explains the presence of a dominant cleavage plane in the structure parallel to ($\bar{1}01$). Some similarity with the structure of bultfonteinite was first noticed by Parry, Williams & Wright (1932) and fully discussed by Megaw & Kelsey (1955) and McIver (1963). The important interatomic distances and angles in afwillite are given in Table 4 (cation polyhedra), Table 5 (H bonds) and Fig. 3 (H_2O coordination).

Calcium coordination

The Ca–O distances in afwillite vary from 2·325(2) to 2·870(1) Å. While most of these distances lie in the

Table 5. *Interatomic distances* (Å) *and angles* (°) *in the* H *bonds*

B	C	D	BD	BC	CD	∠BCD
O(2)—H(21)····O(1)			2·583 (2)	1·19	1·39	177
O(4)—H(43)····O(3)			2·540 (2)	1·06	1·52	161
O(9)—H(93)····O(3)			2·590 (3)	1·04	1·64	149
O(9)—H(910)···O(10)			2·844 (3)	1·04	1·89	151
O(10)-H(101)···O(1)			2·619 (3)	0·90	1·87	139
O(10)-H(104)···O(4)			2·768 (3)	0·99	1·80	167

range 2·325(2)–2·558(2) Å, there are four bonds having values 2·708(2) to 2·870(2) Å. The corresponding values observed in some other minerals are 2·289(3)–2·912(3) Å in rosenhahnite (Lindley, 1974), 2·35–2·78 Å in ettringite (Moore & Taylor, 1970), 2·263(3)–2·641(3) Å in wollastonite (Vincent, 1974), 2·41(5)–2·54(3) Å in jouravskite (Granger & Protas, 1969), 2·31(2)–2·59(2) Å in bultfonteinite (McIver, 1963) and 2·40(1)–2·50(2) Å in thaumasite (Edge & Taylor, 1971). Of all the Ca–O distances, Ca(1)–O(9) [2·504(2) Å] shows the largest variation from the previously reported values, 3·14 Å (Megaw, 1952) and 2·99 Å (McIver, 1960) showing that the Ca(1)–O(9) bond is quite strong. It is found that the shortest unshared edge of a calcium polyhedron in the whole structure is the O(2)–O(9) distance in the Ca(1) polyhedron, which has a value of 2·954(3) Å, not 2·59 Å as reported by Megaw (1952). All three Ca atoms are seven coordinated, and the coordination polyhedra may be considered as derived from an octahedron or more suitably from a trigonal prism with the seventh atom intruding on a rectangular face of the prism.

Table 4. *Geometry of the cation polyhedra*

All distances are expressed in Å.

(*a*) Cation–oxygen distances (e.s.d.'s are less than 0·002 Å)

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)
Ca(1)	–	2·406	–	2·460	2·359	2·356	2·405	2·558	2·504	–
Ca(2)	2·353	–	2·325	–	2·326	2·870	2·353	2·401	–	2·789
Ca(3)	–	2·738	–	–	2·350	2·340	2·352	2·361	2·486	2·708
Si(1)	1·618	–	–	1·688	–	–	1·632	1·617	–	–
Si(2)	–	1·674	1·622	–	1·624	1·607	–	–	–	–

(*b*) Oxygen–oxygen (coordinated round same cation) distances (e.s.d.'s are 0·002–0·003 Å)

Shared edges, Ca–Si and Ca–Ca polyhedra			Unshared edges, Si tetrahedra			Unshared edges, Ca polyhedra			Unshared edges, Ca polyhedra		
Cations	O–O		Cation	O–O		Cation	O–O		Cation	O–O	
Ca(1)–Si(1)	7–8	2·617	Si(1)	1–4	2·650	Ca(1)	2–4	3·106	Ca(2)	3–7	3·220
Ca(2)–Si(2)	5–6	2·647	Si(1)	1–7	2·677	Ca(1)	2–7	3·604	Ca(2)	3–8	3·502
Ca(3)–Si(2)	2–5	2·591	Si(1)	1–8	2·744	Ca(1)	2–9	2·954	Ca(2)	3–10	3·661
Ca(1)–Ca(2)	5–8	3·005	Si(1)	4–7	2·671	Ca(1)	4–5	3·214	Ca(2)	8–10	3·463
Ca(1)–Ca(2)	6–7	3·154	Si(1)	4–8	2·680	Ca(1)	4–6	3·490	Ca(3)	2–9	3·117
Ca(1)–Ca(3)	2–8	3·053	Si(2)	2–3	2·611	Ca(1)	4–9	3·242	Ca(3)	6–7	3·478
Ca(1)–Ca(3)	5–6	3·046	Si(2)	2–6	2·733	Ca(1)	5–7	3·783	Ca(3)	6–9	3·277
Ca(1)–Ca(3)	7–9	3·005	Si(2)	3–5	2·663	Ca(2)	1–3	3·046	Ca(3)	6–10	3·410
Ca(2)–Ca(3)	7–8	3·035	Si(2)	5–6	2·681	Ca(2)	1–5	3·551	Ca(3)	7–10	3·562
Ca(2)–Ca(3)	5–10	3·120				Ca(2)	1–6	3·164	Ca(3)	8–10	3·396
						Ca(2)	1–10	3·267			

(*c*) Angles (°) of Si tetrahedra (e.s.d.'s are 0·1°)

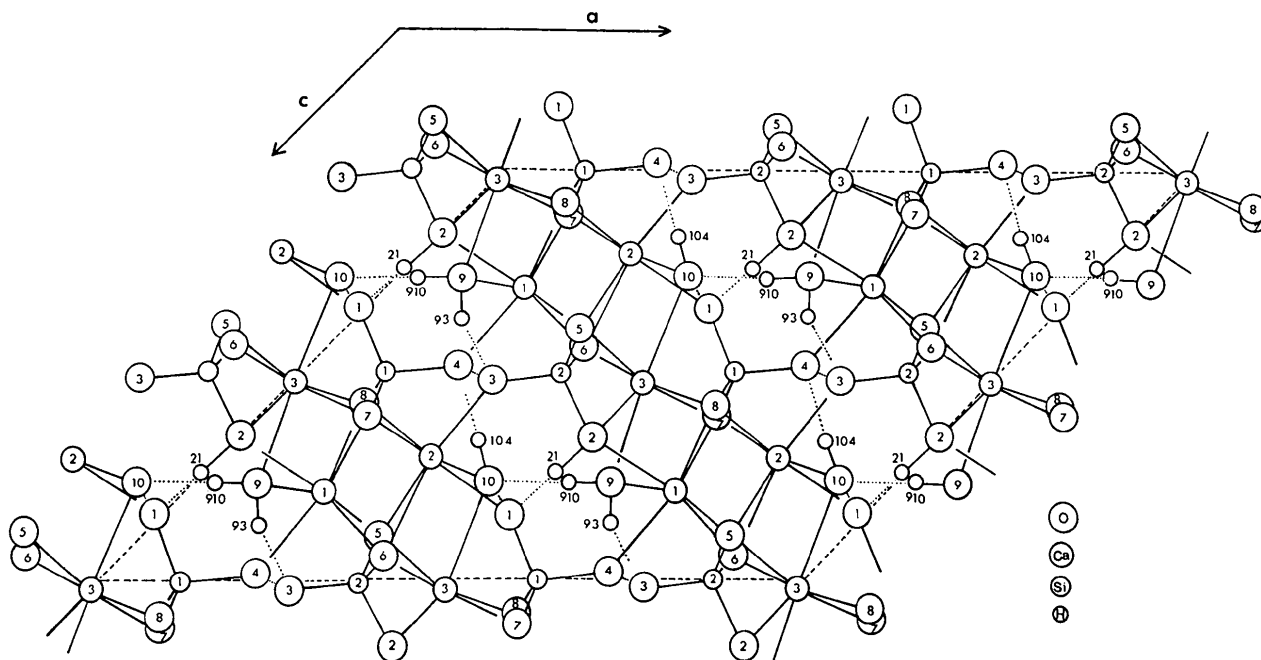|									
O(1)–Si(1)–O(4)	106·5	O(4)–Si(1)–O(7)	107·1	O(2)–Si(2)–O(3)	107·7	O(3)–Si(2)–O(5)	110·2
O(1)–Si(1)–O(7)	110·9	O(4)–Si(1)–O(8)	108·4	O(2)–Si(2)–O(5)	103·5	O(3)–Si(2)–O(6)	112·2
O(1)–Si(1)–O(8)	116·2	O(7)–Si(1)–O(8)	107·3	O(2)–Si(2)–O(6)	112·8	O(5)–Si(2)–O(6)	110·0

Fig. 1. The crystal structure of afwillite projected on (010). For the sake of clarity H(43) and H(101) are not shown.
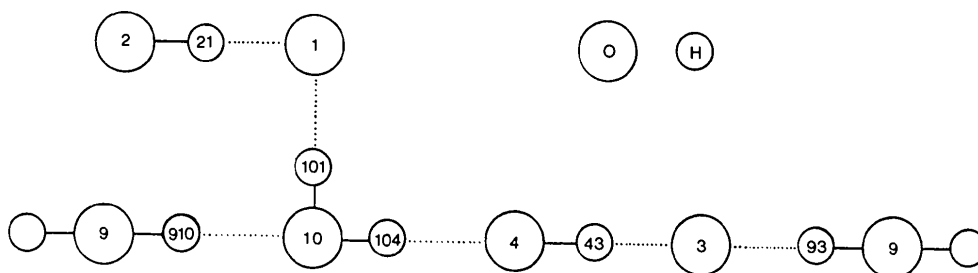

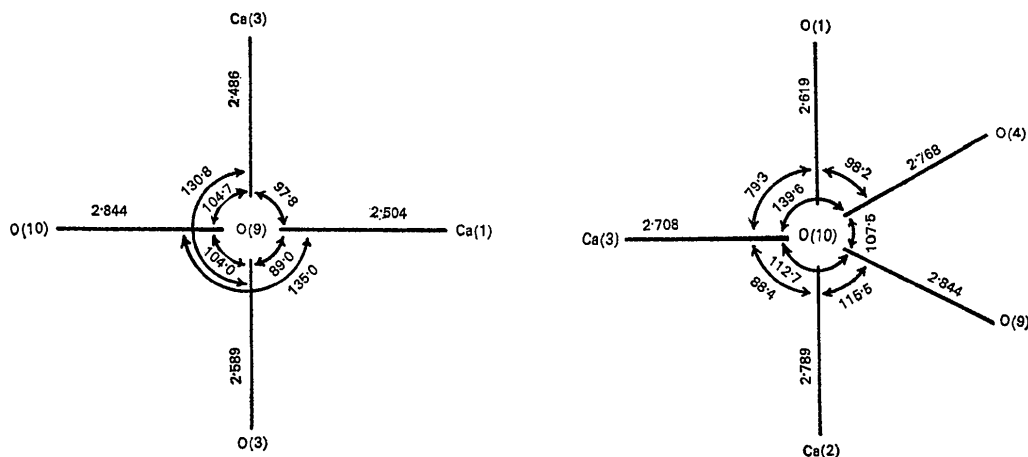Fig. 2. Schematic diagram of hydrogen bonds in afwillite.

Fig. 3. Schematic diagram illustrating the environments of water molecules in afwillite, (a) $H_2O(9)$, and (b) $H_2O(10)$. All distances are shown in Å, angles in degrees. In (a), Ca(1) and O(10) are up, Ca(3) and O(3) down. In (b), Ca(3), O(4) and O(9) are nearly in the plane of the paper, O(1) and Ca(2) above and below. Angles not shown in (b): O(1)-O(10)-Ca(2) = 159·8, O(1)-O(10)-O(9) = 88·2, Ca(2)-O(10)-O(4) = 80·8°.

Silicon coordination

Each of the Si atoms has one OH^- and three O^{2-} immediate neighbours and sits at the centre of a nearly regular tetrahedron. The Si–O distances vary from 1·607 (2) to 1·688 (2) Å and the tetrahedral O–Si–O angles from 103·5 (1) to 116·2 (1)° (mean = 109·4°). These values compare well with those observed in feldspar (Cole, Sørum & Kennard, 1949), wollastonite (Vincent, 1974) and rosenhahnite (Lindley, 1974). It is also observed that the Si–OH distances, 1·688 (2) and 1·674 (2) Å, are significantly longer than the Si–O^{2-} distances, 1·607 (2)–1·624 (2) Å. The Si(1) tetrahedron shares an edge with Ca(1) polyhedron, while Si(2) tetrahedron shares two edges with Ca(2) and Ca(3) polyhedra. The average length of these shared edges of Si tetrahedra, 2·618 Å, is noticeably smaller than the average length of their unshared edges, 2·679 Å, and this is a general trend which is also observed in the Ca polyhedra. The two Si tetrahedra do not share any edges or corners but are linked together by strong hydrogen bonds.

Hydrogen bonding

The positions of the H atoms determined from a difference map established the H bonding system shown in Fig. 2. The difference map showed that the H peaks for the O(2)–O(1), O(4)–O(3) and O(9)–O(3) bonds were elongated approximately along the O–O axis whereas those for the O(9)–O(10) and O(10)–O(4) were spread in an 'elongated disc' nearly perpendicular to this axis. The peak for H(101) was severely distorted with a considerable kinking of the O(10)–H(101)–O(1) angle. The shapes of the H peaks in the electron density map, considered together with the O–O distances, suggest some interesting conclusions. Thus, if it is assumed that the elongation of the peak is mainly due to the vibration of the H atom, it may be concluded that the H atoms in the three short bonds (O–O ≤ 2·59 Å) vibrate mainly along the O–H bond while those on the two long bonds (O–O ≥ 2·77 Å) vibrate in an 'elongated disc' nearly perpendicular to the O–H direction.

This seems quite reasonable because the proton in a short H bond is more evenly shared between the two atoms than that in a long H bond. In a short H bond, the strong interaction of the H atom with the acceptor O atom restricts its vibration in the perpendicular direction. It has also the effect of 'lengthening' the O–H bond, and in the most favourable cases a symmetrical H bond with a single minimum in the potential energy curve results. One such example is potassium hydrogen chloromaleate where the H atom is equidistant from two O atoms (O–O distance = 2·403 (3) Å and O–H–O angle = 180°) (Ellison & Levy, 1965).

In afwillite, it is possible that such lengthening occurs in the O(2)–H(21) bond (1·19 Å) which, however, cannot be confirmed without neutron diffraction data. Assuming the electron density to be inversely proportional to the energy at a point in the O–O line, there are indications in the difference map that the O(2)–O(1) H bond is asymmetric with double minima, the minimum near O(2) predominating. In this respect, the O(2)–O(1) H bond seems to be significantly different from the rest of the structure. It is also noticed that the O(10)–O(1) distance is moderate (2·62 Å) but the O(10)–H(101) distance is short (0·90 Å) which indicates a very weak H bond. This is probably due to an unfavourable O–H–O angle (139°). Other H bonds in the structure seem normal.

From interatomic distances, electrostatic valency requirements, etc., Megaw (1952) identified O(9) and O(10) as H_2O, O(2) and O(4) as OH^- and O(1), O(3), O(5), O(6), O(7), O(8) as O^{2-} groups. Our results show that this is essentially correct. Furthermore, we calculated the bond valencies of the cations and anions (Table 6) following a method proposed by Donnay & Allmann (1970) and found that the sum of the valencies contributed to an O atom by its neighbouring cations $(\sum_c v)$ agrees well with the theoretical value. Ideally these sums should be equal to 2·0, 1·0 and 0·0 for O^{2-}, OH^- and H_2O respectively. It is interesting that the $\sum_c v$ values immediately identify O(5), O(6), O(7) and O(8) as O^{2-}, O(4) as OH^- and, to a lesser extent, O(10) as H_2O. But the true nature of O(1), O(2) and O(9) is correctly revealed only when allowances are made for the H bonds. This confirms Donnay & Allmann's method of recognizing O^{2-}, OH^- and H_2O groups in crystal structures. It also suggests, as would be expected, that the H atoms in the O–H–O bonds in

Table 6. *Estimated bond valencies (v.u.) in afwillite*

	Ca(1)	Ca(2)	Ca(3)	Si(1)	Si(2)	$\sum_c v$	$\sum_c v$ corrected for H bond	Anion chemistry
O(1)	–	0·34	–	1·05	–	1·39	1·90	O^{2-}
O(2)	0·29	–	0·19	–	0·91	1·39	1·13	OH^-
O(3)	–	0·36	–	–	1·02	1·38	1·93	O^{2-}
O(4)	0·28	–	–	0·88	–	1·16	1·05	OH^-
O(5)	0·31	0·36	0·34	–	1·02	2·03	2·03	O^{2-}
O(6)	0·31	0·15	0·34	–	1·04	1·84	1·84	O^{2-}
O(7)	0·29	0·34	0·34	1·02	–	1·99	1·99	O^{2-}
O(8)	0·24	0·32	0·33	1·04	–	1·93	1·93	O^{2-}
O(9)	0·26	–	0·28	–	–	0·54	0·13	H_2O
O(10)	–	0·17	0·20	–	–	0·37	0·09	H_2O
$\sum_a v$	1·98	2·04	2·02	3·99	3·99			

afwillite play an important role in affecting the charge distribution of the anions.

Environment of the water molecules

The environment of the two water molecules, $H_2O(9)$ and $H_2O(10)$ is illustrated in Fig. 3. There are significant differences in the nature of their bonds and environments. O(9) and O(10) are each linked to two Ca atoms but the Ca–O(9) distances, 2·504(2) and 2·486(2) Å, are significantly shorter than the Ca–O(10) distances, 2·789(2) and 2·708(2) Å. This suggests that the Ca–O(9) bonds are much stronger and more electrostatic in character than the Ca–O(10) bonds. In this regard one of Megaw's (1952) conclusions that the Ca(1)–O(9) contact is of van der Waals type is obviously incorrect.

Another marked difference between the water molecules lies in their environments. The $H_2O(9)$ molecule, surrounded by Ca(1), Ca(3), O(3) and O(10), may be considered as situated at the middle of a seriously distorted tetrahedron. The sum of the Ca(3)–O(9)–O(3), Ca(3)–O(9)–O(10) and O(3)–O(9)–O(10) angles is 339·5°, which shows that the O(9)–Ca(3), O(9)–O(3) and O(9)–O(10) bonds are not 'almost planar' as suggested by Megaw (1952). The other water molecule, $H_2O(10)$, has five immediate neighbours, Ca(2), Ca(3), O(1), O(4) and O(9), situated at the corners of an irregular trigonal bipyramid. The sum of the Ca(3)–O(10)–O(4), Ca(3)–O(10)–O(9) and O(4)–O(10)–O(9) angles is 359·8° which shows that the O(10)–Ca(3), O(10)–O(4) and O(10)–O(9) bonds are planar. Ca(2) and O(1) are disposed on either side of the equatorial plane, with a Ca(2)–O(10)–O(1) angle of 159·8°.

The two water molecules are also different in their hydrogen-bonding systems. O(9) is involved in two H bonds whereas O(10) is involved in three. The former always acts as a donor atom while the latter acts as both donor and acceptor. It is also important to note that the H bond between O(9) and O(10) is not short (2·52 Å) as suggested by Megaw (1952). It is in fact a long H bond with O(9)–O(10) distance of 2·844(3) Å.

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