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Reinvestigation of eakerite, $\text{Ca}_2\text{SnAl}_2\text{Si}_6\text{O}_{18}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$: H-atom positions by single-crystal X-ray diffraction and correlation with Raman spectroscopic data

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The crystal structure of natural eakerite [Kossiakoff & Leavens (1976). *Am. Mineral.* **61**, 956–962] has been reinvestigated, the H-atom positions determined and the hydrogen-bonding scheme elucidated. The O...O separations of the O–H...O hydrogen bonds correlate well with the frequencies of the three corresponding Raman peaks according to Libowitzky's regression curve. The Sn atom has site symmetry $\bar{1}$.

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Comment

Eakerite is a calcium tin aluminosilicate hydroxide hydrate, first reported and described by Leavens *et al.* (1970). It is of hydrothermal origin, found in a spodumene-bearing tin- and lithium-rich pegmatite. Based on X-ray precession photographs, its space group was suggested to be $P2_1/a$ (Leavens *et al.*, 1970). The full structure was described in this non-standard space group by Kossiakoff & Leavens (1976), who reported the positions of the O atoms corresponding to the water and hydroxyl groups, but the H-atom coordinates were not determined.

Here we report a redetermination of the structure of eakerite, (I), using a natural sample from the Foote Mineral Company mine, Kings Mountain, North Carolina, USA. The H-atom positions have been determined and the O–H...O hydrogen-bonding scheme elucidated. There are four hydroxyl groups and four water molecules per unit cell.

Selected geometrical data are given in Table 1. All the cations occupy general positions, except Sn, which is located at the origin ($\bar{1}$ symmetry) (Fig. 1). The refined mean bond

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{I-O}) = 0.001\text{ \AA}$

R factor = 0.027

wR factor = 0.066

Data-to-parameter ratio = 33.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

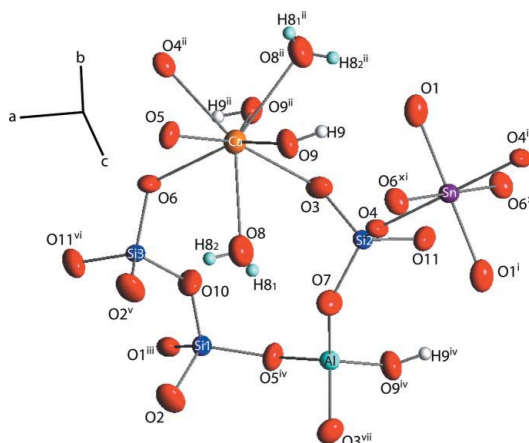


Figure 1

Fragment of (I) showing the polyhedral building units (50% displacement ellipsoids, arbitrary spheres for the H atoms). [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + 1$; (iv) $x, y, z + 1$; (v) $-x + 1, -y, -z + 1$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (vii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (x) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (xi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z$.]

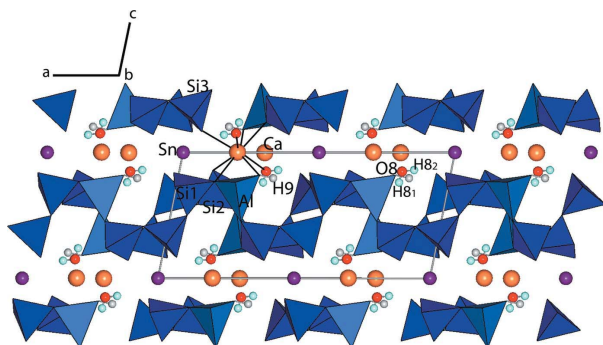


Figure 2
The packing of (I) viewed down the *b* axis.

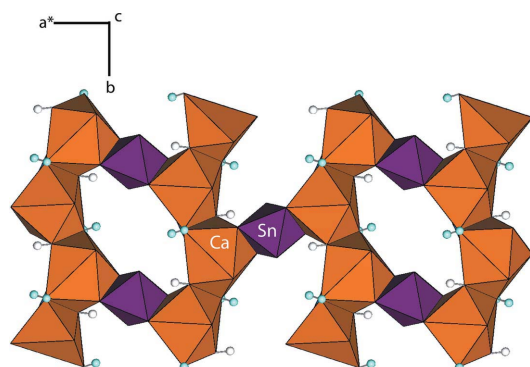


Figure 3
The Ca/Sn-centered polyhedral sheet in (I), viewed down the *c* axis.

distances for the tetrahedral sites suggest that Al is completely ordered in site *T4* (*cf.* Kroll & Ribbe, 1983): they are 1.619 (2), 1.619 (2), 1.618 (2) and 1.741 (2) Å for the mean *T1*–O, *T2*–O, *T3*–O, and *T4*–O separations, respectively. Consequently, sites *T1*–*T3* were modeled as Si and *T4* as Al. Thus, the hydroxyl group is shared by Al and Ca, while the water molecule is bonded only to Ca. The refined O–H bond lengths (Table 2) were corrected for thermal motion, using the formulation given by Downs *et al.* (1992). Since the corrected values, 0.77, 0.77 and 0.88 Å for O8–H81, O8–H82 and O9–H9, respectively, are reasonable, the refinement was performed without constraints. A TLS rigid body analysis (Downs, 2000; Schomaker & Trueblood, 1968) of the structure shows that the octahedral and tetrahedral groups all behave as rigid bodies.

The eakerite unit cell contains sixteen tetrahedra, forming layers of crankshaft-like chains parallel to the *a* axis (Fig. 2). Atoms O2, O3, O5, O7, O10 and O11 are bridging, linking the tetrahedral groups. The layers of tetrahedral chains are cross-linked by layers of eight-coordinate Ca and six-coordinate Sn atoms. These form polyhedral sheets in the *ab* plane between the tetrahedral layers; the Ca atoms form edge-sharing chains running parallel to the *b* axis, which are linked by the Sn atoms (Fig. 3). The locations of the water and hydroxyl groups are also illustrated in Figs. 1 and 2.

To further confirm the H-atom positions, Raman data for a single crystal of (I) in an unknown orientation were collected between 200 and 4000 cm^{-1} . Fig. 4 shows the resulting spectrum with three distinct peaks in the O–H hydrogen-bond

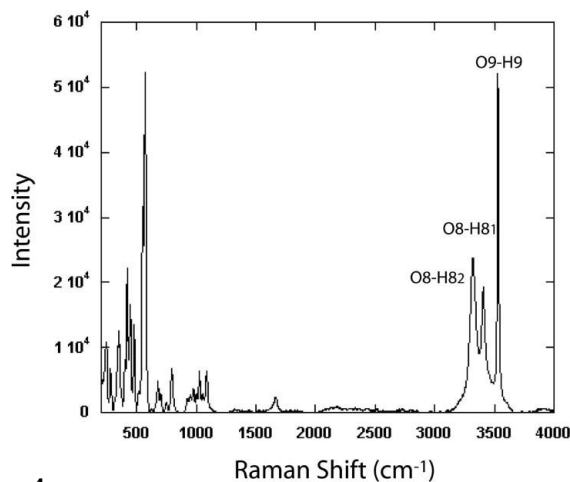


Figure 4
O–H stretching vibrational peaks in the Raman spectrum of eakerite.

stretch region at 3317, 3405 and 3528 cm^{-1} . Based on Libowitzky's (1999) regression curve, these frequencies correspond to donor–acceptor O···O separations of 2.75, 2.80 and 2.94 Å, respectively. Our refined structure shows that the separations O8···O2(1–*x*, –*y*, 1–*z*), O8···O7 and O9···O1 are 2.7415 (18), 2.7981 (18) and 3.0096 (16) Å, respectively (Table 2), in good agreement with the calculated values.

Experimental

The crystal of (I) used for data collection was a natural sample from the Foote Mineral Company mine, Kings Mountain, North Carolina, USA. A crystal of (I) from the same source was analyzed on a Cameca SX50 electron microprobe, using an acceleration voltage of 15 kV, a beam current of 20 nA, beam diameter of 2 μm and 20 s counting times. Eight points were analyzed and averaged. The analysis shows that the chemical composition is ideal within the experimental uncertainties.

Crystal data

$\text{Ca}_2\text{SnAl}_2\text{Si}_6\text{O}_{18}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 779.40$
 Monoclinic, $P2_1/a$
 $a = 15.8202$ (5) Å
 $b = 7.6963$ (3) Å
 $c = 7.4449$ (3) Å
 $\beta = 101.293$ (2)°
 $V = 888.92$ (6) Å³

$Z = 2$
 $D_x = 2.912$ Mg m^{-3}
 Mo $K\alpha$ radiation
 $\mu = 2.64$ mm^{-1}
 $T = 293$ (2) K
 Prism, colorless
 0.10 × 0.09 × 0.07 mm

Data collection

Bruker APEX2 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.776$, $T_{\max} = 0.823$

24042 measured reflections
 5432 independent reflections
 4547 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 39.8^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.066$
 $S = 1.05$
 5432 reflections
 163 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.728P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.88$ e Å⁻³
 $\Delta\rho_{\min} = -1.15$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Sn—O1	2.0096 (11)	Si1—O10	1.6361 (12)
Sn—O4	2.0281 (11)	Si2—O7	1.6080 (12)
Sn—O4 [†]	2.0281 (11)	Si2—O4	1.6096 (11)
Ca—O6	2.3997 (11)	Si2—O3	1.6220 (12)
Ca—O4 ⁱⁱ	2.4001 (11)	Si2—O11	1.6344 (12)
Ca—O3	2.4097 (11)	Si3—O6	1.6060 (11)
Ca—O9	2.4454 (12)	Si3—O10	1.6110 (12)
Ca—O8 ⁱⁱ	2.4962 (14)	Si3—O2 ^v	1.6238 (12)
Ca—O5	2.5055 (11)	Si3—O11 ^{vi}	1.6251 (12)
Ca—O8	2.6126 (14)	Al—O7	1.7195 (12)
Ca—O9 ⁱⁱ	2.6203 (13)	Al—O9 ^{iv}	1.7445 (12)
Si1—O1 ⁱⁱⁱ	1.5962 (12)	Al—O3 ^{vii}	1.7463 (12)
Si1—O5 ^{iv}	1.6106 (11)	Al—O5 ^{iv}	1.7517 (12)
Si1—O2	1.6327 (12)		
Si3 ^v —O2—Si1	148.39 (9)	Si2—O7—Al	136.77 (8)
Si2—O3—Al ^{viii}	130.99 (7)	Si3—O10—Si1	136.01 (8)
Si1 ^{ix} —O5—Al ^{ix}	134.50 (7)	Si3 ^x —O11—Si2	131.70 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + 1$; (iv) $x, y, z + 1$; (v) $-x + 1, -y, -z + 1$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (vii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (viii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (ix) $x, y, z - 1$; (x) $x - \frac{1}{2}, -y + \frac{1}{2}, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H82 ^v ···O2 ^v	0.74 (3)	2.14 (3)	2.7415 (18)	138 (3)
O8—H81···O7	0.66 (4)	2.21 (5)	2.7981 (18)	150 (5)
O9—H9···O1	0.81 (3)	2.24 (3)	3.0096 (16)	157 (3)

Symmetry code: (v) $-x + 1, -y, -z + 1$.

The non-standard space group $P2_1/a$ was chosen to give a unit cell consistent with that of Kossiakoff & Leavens (1976). The H atoms were located in difference maps and their atomic positions and U_{iso} values were refined without constraints. The deepest hole in the final difference map lies 0.40 Å from the Sn atom.

Data collection: *APEX2* (Bruker, 1997); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XTALDRAW* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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