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PROTON LOCATION AND HYDROGEN BONDING IN THE HYDROUS LEAD COPPER SULFATES LINARITE, $\text{PbCu}(\text{SO}_4)(\text{OH})_2$, AND CALEDONITE, $\text{Pb}_5\text{Cu}_2(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$

PAUL F. SCHOFIELD[§]

Department of Mineralogy, Natural History Museum, Cromwell Road, London, SW7 5BD, United Kingdom

CHICK C. WILSON

Department of Chemistry, Joseph Black Building, University of Glasgow, University Avenue, Glasgow, G12 8QQ, and ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, United Kingdom

KEVIN S. KNIGHT

ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, and Department of Mineralogy, Natural History Museum, Cromwell Road, London, SW7 5BD, United Kingdom

CAROLINE A. KIRK

Chemistry Department, Loughborough University, Loughborough, LE11 3TU, and Department of Mineralogy, Natural History Museum, Cromwell Road, London, SW7 5BD, United Kingdom

ABSTRACT

Neutron, time-of-flight, Laue diffraction has been carried out on natural single crystals of linarite, $\text{PbCu}(\text{SO}_4)(\text{OH})_2$, and caledonite, $\text{Pb}_5\text{Cu}_2(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$, at 293 K. The structural refinements converged to $R_w(F) = 0.085$ on the basis of 869 observed reflections for linarite and $R_w(F) = 0.066$ from 1605 observed reflections for caledonite. The locations of all the hydrogen atoms within these structures were extracted from the refinements, enabling calculation of the hydrogen bonding. Linarite is monoclinic, space group $P2_1/m$, with a 9.682(2), b 5.646(1), c 4.683(6) Å, and β 102.66(1)°. It comprises chains of edge-sharing Jahn–Teller-elongated CuO_6 square bipyramids running parallel to the [010] direction, bound together by hydrogen bonds. Between these layers are double PbO_8 and SO_4 layers. The two independent hydrogen atoms have been located and are bound as hydroxyl groups to the oxygen atoms at the corners of the CuO_4 square plane. The H(4) atom has conventional hydrogen bonding. The donor–acceptor distance is 2.924(5) Å, and the hydrogen bond is nearly linear, with an angle of 176.1(6)°. The O(4)–H(4) hydroxyl bond distance is 0.952(7) Å, and the H(4) ... O(2) hydrogen bond has a length of 1.973(9) Å. The H(5) hydrogen atom, however, forms a stronger hydrogen bond, with a donor–acceptor distance of 2.706(5) Å and an angle of 171.8(6)°. The O(5)–H(5) hydroxyl bond is lengthened to 1.025(8) Å, and the H(5) ... O(4) hydrogen bond is a short 1.687(8) Å. Caledonite is orthorhombic, space group $Pmn2_1$ with a 20.085(3) Å, b 7.141(1) and c 6.563(1) Å; like linarite, it comprises chains of edge-sharing Jahn–Teller-elongated CuO_6 square bipyramids, although these chains run parallel to the [001] direction. There are three independent Pb sites, in which Pb is coordinated to nine oxygen ligands, with a range of Pb–O distances of 2.352(4) to 3.571(6) Å. Caledonite has three independent hydrogen atoms that similar to those in the linarite structure: they are bound as hydroxyl groups to the oxygen atoms at the corners of the square plane of the axially elongate CuO_6 square bipyramids. The hydrogen bonds in caledonite are all significantly bent, with angles between 160 and 170°; otherwise, the H(1) and H(2) atoms have fairly conventional hydrogen bonding. The donor–acceptor distance for O(1) ... O(4) and O(2) ... O(4) are 2.887(7) and 2.776(6) Å, respectively; although the O(1)–H(1) hydroxyl bond at 0.95(1) Å is shorter than the O(2)–H(2) hydroxyl bond at 0.98(1) Å, the H(1) ... O(4) hydrogen bond, 1.97(1) Å in length, is slightly longer than the H(2) ... O(4) hydrogen bond at 1.84(1) Å. The O(3)–H(3) hydroxyl bond is 0.946(8) Å in length, and the H(3) ... O(8) hydrogen bond is slightly shorter than expected at 1.777(9) Å. With the O(3) ... O(8) donor–acceptor distance of 2.711(5) Å and the 20° deviation from linearity, this hydrogen bond may be strained.

Keywords: linarite, caledonite, neutron diffraction, hydrogen bonding, crystal structure.

[§] E-mail address: pfs@nhm.ac.uk

SOMMAIRE

Nous avons utilisé la diffraction Laue de neutrons à temps de vol pour caractériser la structure de minocristaux naturels de linarite, $\text{PbCu}(\text{SO}_4)(\text{OH})_2$, et de calédonite, $\text{Pb}_5\text{Cu}_2(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$, à 293 K. Les affinements structuraux ont convergé à un résidu $R_w(F) = 0.085$ en utilisant 869 réflexions observées pour la linarite, et $R_w(F) = 0.066$ en utilisant 1605 réflexions observées pour la calédonite. Les coordonnées de tous les atomes d'hydrogène dans ces structures ont été extraites des affinements, ce qui nous a permis de calculer les liaisons hydrogène. La linarite est monoclinique, groupe spatial $P2_1/m$, avec a 9.682(2), b 5.646(1), c 4.683(6) Å, et β 102.66(1)°. Elle est faite de chaînes de pyramides carrées CuO_6 allongées par l'effet de Jahn et Teller et partageant les arêtes, alignées parallèles à la direction [010], et liées entre elles par des liaisons hydrogène. Entre ces niveaux se trouvent des couches doubles de PbO_8 et SO_4 . Les deux atomes d'hydrogène indépendants ont été localisés; ils font partie de groupes hydroxyle avec les atomes d'oxygène situés aux coins des agencements CuO_4 en plans carrés. L'atome H(4) participe à une liaison hydrogène conventionnelle. La distance donneur-accepteur est 2.924(5) Å, et la liaison hydrogène est presque linéaire, avec un angle de 176.1(6)°. La distance O(4)–H(4) est 0.952(7) Å, et la liaison hydrogène impliquant H(4) ... O(2) a une longueur de 1.973(9) Å. L'atome H(5), en revanche, forme une liaison hydrogène plus forte, avec une séparation entre donneur et accepteur de 2.706(5) Å et un angle de 171.8(6)°. La liaison hydrogène O(5)–H(5) est allongée jusqu'à 1.025(8) Å, et la liaison H(5) ... O(4) est courte, 1.687(8) Å. La calédonite est orthorhombique, groupe spatial $Pmn2_1$, avec a 20.085(3), b 7.141(1), et c 6.563(1) Å. Tout comme la linarite, elle est faite de chaînes de pyramides carrées CuO_6 à arêtes partagées, allongées à cause de l'effet de Jahn et Teller, quoique ces chaînes sont alignées de long de la direction [001]. Il y a trois sites Pb indépendants à coordinence neuf avec des atomes d'oxygène, les distances Pb–O étant comprises entre 2.352(4) et 3.571(6) Å. La calédonite possède trois atomes d'hydrogène indépendants qui ressemblent à ceux dans la linarite, faisant partie de groupes d'hydroxyle impliquant les atomes d'oxygène aux coins du plan carré des pyramides CuO_6 allongées. Les liaisons hydrogène dans la calédonite sont toutes articulées, ayant des angles allant de 160 à 170°; autrement, les liaisons impliquant H(1) et H(2) sont relativement conventionnelles. Les distances donneur-accepteur pour O(1) ... O(4) et O(2) ... O(4) sont 2.887(7) et 2.776(6) Å, respectivement. Quoique la liaison O(1)–H(1), d'une longueur de 0.95(1) Å, est plus courte que la liaison O(2)–H(2), 0.98(1) Å, la liaison H(1) ... O(4), 1.97(1) Å, est légèrement plus longue que la liaison H(2) ... O(4), 1.84(1) Å. La liaison O(3)–H(3) a une longueur de 0.946(8) Å, et la liaison H(3) ... O(8) est légèrement plus courte que la normale, 1.777(9) Å. Compte tenu de la distance donneur-accepteur O(3) ... O(8) de 2.711(5) Å et un écart de 20° de la linéarité, cette liaison hydrogène pourrait bien être étirée.

(Traduit par la Rédaction)

Mots-clés: linarite, calédonite, diffraction de neutrons, liaisons hydrogène, structure cristalline.

INTRODUCTION

Linarite, $\text{PbCu}(\text{SO}_4)(\text{OH})_2$, and calcedonite, $\text{Pb}_5\text{Cu}_2(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$, are hydrous sulfates that generally form in oxidized zones around Pb–Cu ore deposits. Environmental awareness associated with the mining and processing of these potentially toxic metals has recently reactivated interest in hydrous heavy-metal minerals. Traditionally classed as secondary weathering-induced minerals, it has become clear that the low-temperature processes involved in the formation of such minerals involve the cycling of toxic metals from the meteoric system. The stability of these minerals is poorly known, yet may be significant if we are to prevent the remobilization of the toxic metals. Furthermore, a lack of accurate structural information hinders significantly attempts at identification of ultrafine-grained materials in soils and muds (*e.g.*, Lanfranco *et al.* 2003), as well as an understanding of the structural controls on mineral stability. In this contribution, we have used neutron, time-of-flight, Laue diffraction on single crystals of linarite and calcedonite in order to locate the positions of the hydrogen atoms and to accurately refine their complete crystal structures.

BACKGROUND INFORMATION

Bachmann & Zemann (1961) and Araki (1962) examined the structure of linarite; they located the positions of the heavy atoms and their coordinating oxygen atoms. Effenberger (1987) refined this structure using four-circle diffractometer X-ray data with a monoclinic cell related to the least oblique cell of Berry (1951), space group $P2_1/m$ a 9.701, b 5.650 c 4.69 Å, β 102.65° and $Z = 2$, showing that it is the sulfate analogue of the selenate mineral schmiederite. The structure is characterized by chains of edge-sharing CuO_4 squares running parallel to the [010] direction, bound together by hydrogen bonds to form layers in the (100) plane. The CuO_6 square bipyramids are strongly Jahn–Teller-elongated such that the Cu–O axial bonds are 2.54 Å, whereas the square planar Cu–(OH) bonds are only 1.93–1.98 Å. The layers of hydrogen-bonded chains of CuO_6 square bipyramids are bound together by double layers of PbO_8 and SO_4 polyhedra. The Pb atoms occur off-center in one-sided PbO_8 polyhedra that contain only one (OH) oxygen. None of the investigators named has been able to locate the protons despite their importance to the structural topology; indeed, Effenberger (1987) could only postulate that the hydrogen bonds will range between 2.6 Å and 2.9 Å.

It was initially thought that caledonite, $\text{Pb}_5\text{Cu}_2(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$, is monoclinic, but Palache & Richmond (1939) and Giacobozzo *et al.* (1973) stated that caledonite is orthorhombic. Whereas Palache & Richmond (1939) argued for space group $Pnmm$, Giacobozzo *et al.* (1973) assigned the space group $Pmn2_1$. The structural topology was solved by Giacobozzo *et al.* (1973) using single-crystal X-ray diffraction and the orthorhombic cell a 20.089, b 7.146, c 6.56 Å with $Z = 2$ and space group $Pmn2_1$. The topology is based on the $[\text{Cu}(\text{OH})_3\text{O}]^{3-}$ repeat unit, which forms a chain around the screw axis. The Cu atoms are strongly Jahn–Teller-distorted with four Cu–(OH) square planar bonds and two elongate axial Cu–O bonds. The chains of CuO_6 square bipyramids are linked by $\text{S}(1)\text{O}_4$ sulfate tetrahedra to form layers in the (100) plane. Binding these planes together is a unit in which layers of Pb atoms parallel to [010] are stacked in an alternate fashion Pb(1):Pb(2):Pb(3). The $\text{S}(2)\text{O}_4$ tetrahedra and the carbonate groups reside between the Pb(2) and Pb(3) layers. Giacobozzo *et al.* (1973) reported the presence of very distorted PbO_9 polyhedra with Pb–O bonds ranging from 2.33 to 3.55 Å, and two of the three crystallographically independent Pb atoms located strongly off-center in one-sided polyhedra. No attempt was made by Giacobozzo *et al.* (1973) to locate the hydrogen atoms, and the hydrogen bonds were postulated to have distances up to 2.9 Å.

a spot size of 5 μm . Three points were analyzed on each crystal with a count time of 100 seconds using an Oxford Instruments Inca system. No impurity cations were detected. The resulting compositions and formulae are given in Table 1.

X-ray powder diffraction

The unit-cell dimensions for linarite and caledonite were determined using X-ray powder-diffraction data collected on a Nonius PDS 120 powder-diffraction system consisting of an Inel curved position-sensitive detector (PSD). Copper $K\alpha_1$ radiation was selected from the primary beam by a germanium 111 crystal monochromator, with the X-ray tube operating conditions at 45 kV and 32 mA. Horizontal and vertical slits were used to restrict the beam to a height of 50 μm and a length of 2.0 mm (Schofield *et al.* 2002). Measurements were made in reflection geometry with the sample surface at an angle of 7.5° to the incident beam and for 1310 and 1880 minutes for linarite and caledonite, respectively. Calculation of the unit-cell dimensions was performed using the Stoe WINXPOW software package on the basis of 68 and 57 indexed reflections for linarite and caledonite, respectively.

Neutron, time-of-flight, Laue diffraction

The crystals were mounted on a (φ, χ) orienter and maintained at 293 K throughout the duration of the data collection. Data were collected on the SXD instrument at the ISIS spallation neutron source (Wilson 1995) using the time-of-flight Laue diffraction method described elsewhere (Wilson 1997). The data-collection parameters are summarized in Table 2. The intensities

METHODOLOGY

The single crystals of linarite and caledonite used in this experiment were from specimen BM1947,271 from the mineral collection of the Natural History Museum, London. This specimen originates from Leadhills, Lanarkshire, Scotland, and the dark blue linarite and blue-green caledonite crystals occur with cerussite.

Electron-microprobe analyses

Samples of linarite and caledonite were set in an araldite block, polished and carbon-coated. These samples were analyzed in a low-vacuum JEOL 5900 electron microprobe operating at 20 kV with beam current of 1 nA, a working distance of 10 mm and

TABLE 1. CHEMICAL COMPOSITIONS AND CHEMICAL FORMULAE[†] OF LINARITE AND CALEDONITE

	linarite	caledonite		linarite	caledonite
PbO wt%	56.47	66.57	Pb <i>apfu</i>	0.98	5.11
CuO	21.50	10.39	Cu	1.09	2.23
SO ₃	19.43	13.51	S	0.98	2.89
CO ₃ [*]		2.58	C		1
H ₂ O [*]	4.47	3.16	OH	2	6
Σ	101.87	96.21			

[†] Calculated on the basis of 5 and 18 anions per formula unit for linarite and caledonite, respectively. ^{*} Calculated according to stoichiometry.

TABLE 2. DATA COLLECTION AND REFINEMENT PARAMETERS

	Linarite	Caledonite
Diffractometer	SXD neutron time-of-flight Laue diffractometer	
Detector	64 × 64, 3 mm pixel, scintillator PSD	
Detector position	2 θ_c = 123°, L ₂ = 151 mm	
Wavelength range	0.48–4.8 Å	
Crystal size mm	1.5 × 0.25 × 0.25	2 × 0.5 × 0.5
Space group	$P2_1/m$, $Z = 2$	$Pmn2_1$, $Z = 2$
Unit-cell parameters		
a (Å)	9.682 (2)	20.085 (3)
b (Å)	5.646 (1)	7.141 (1)
c (Å)	4.683 (6)	6.563 (1)
β (°)	102.66 (1)	
Volume (Å ³)	249.80 (6)	941.2 (2)
Measured reflections	2064	3018
Unique reflections	896	1605
[of which I > 3 σ (I)]	869	1605
R _{int}	0.065	0.082
Index limits h , k , l	14, 10, 8	35, 13, 12
Maximum sin θ/λ (Å ⁻¹)	ca. 0.8	ca. 0.8
Refined parameters	64	180
Thermal parameters	all atoms (including hydrogen) anisotropic	
R(F)	0.082	0.081
R _w (F)	0.085	0.066
R _w (F ²)	0.160	0.129
$w = 1/[\sigma(F_o)]^2$		

were extracted and reduced to structure factors using standard SXD procedures (Wilson 1997). The resulting structure-factors were used in the CCSL (Brown & Matthewman 1993) least-squares refinement program SFLSQ, to apply a variable wavelength-extinction correction based on the Becker-Coppens formalism (Becker & Coppens 1974) using a Gaussian model.

Crystal-structure refinement

Structural refinement (GSAS; Larsen & Von Dreele 1988) was carried out on F^2 , using the data of Araki (1962) and Giacobozzo *et al.* (1973) as starting models for linarite and caledonite, respectively. In the final refinement, positional and anisotropic thermal parameters were refined for all atoms, including the hydrogen atoms. The refinements converged satisfactorily to $R_w(F) = 0.085$ and 0.066 , the final refinements comprising 64 and 180 parameters for linarite and caledonite, respectively. The final refined coordinates and atomic displacement parameters are summarized in Tables 3 (linarite) and 4 (caledonite). Bond lengths and bond angles for linarite and caledonite are reported in Tables 5 and 6, respectively.

One of the advantages of neutron diffraction over X-ray diffraction is the ability of neutron diffraction to locate accurately the positions of the light atoms such as H in systems that contain heavy atoms such as Pb. Consequently, the refinements do not require any constraints on the hydrogen atom positions or the lengths of hydrogen bonds. These bond lengths, however, may be susceptible to influences such as librational shortening. In order to test the veracity of the apparent changes in bond lengths associated with the hydrous components, we have performed a TLS analysis (Schomaker & Trueblood 1968, Trueblood & Huber-Buser 1987). These analyses have been performed within the limitations of precision of our data. The calculated bond-length corrections were found not to be significant.

Throughout this manuscript, values quoted for polyhedron volumes and distortions were calculated using the program VOLCAL (Finger 1996). The crystallographic files in cif format have been deposited with FIZ Karlsruhe as CDS numbers 420744 for linarite and 420745 for caledonite.

THE STRUCTURE OF LINARITE

Cation polyhedra

The only Pb site in linarite (Fig. 1a) is surrounded by eight oxygen atoms, one of which is associated with a proton as a hydroxyl group. The mean Pb–O distance is 2.770 \AA , and the volume of this polyhedron is a relatively modest 34.7 \AA^3 . The bonds within the PbO_8 polyhedron are split into two groups, three shorter Pb–O bonds, one of which is with the oxygen atom of a hydroxyl group, with an average distance of 2.398 \AA , and five longer Pb–O bonds, with an average distance of 2.993 \AA . The three shorter bonds are all clustered together within the PbO_8 polyhedron, and all link the Pb atom with the Cu atoms, with two Pb–O(3) bonds linking to the axis of the axially elongate CuO_6 square bipyramids and the Pb–O(5) bond linking to the square plane of the CuO_6 square bipyramids. If viewed along the $[001]$ direction (Fig. 1b), channels in which Pb and O(2) form nominal corners (although their z positions differ) are evident. It is probable that the Pb lone pairs are located within these channels.

The CuO_6 square bipyramids (Fig. 2), which form chains running along $[010]$, are Jahn–Teller-elongated, with a quadratic elongation of 1.05 and a volume of 12.7 \AA^3 . The two axial Cu–O(3) bonds have a length of $2.567(3) \text{ \AA}$, whereas the shorter Cu–O bonds within the square plane average to 1.938 \AA . The bonds within the square plane of the CuO_6 square bipyramids involve either the O(4) or the O(5) atoms, both of which are the O atoms of the hydroxyl groups. The S atoms are surrounded by four O atoms and are placed near the center of a regular tetrahedron, with a minimal angular

TABLE 3. COORDINATES AND ANISOTROPIC THERMAL PARAMETERS (\AA^2) OF ATOMS IN LINARITE BM1947,271 AT 293 K

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.3420(3)	0.25	0.0123(6)	0.014(1)	0.0220(8)	0.021(1)	0	0.007(1)	0
Cu	0	0	0	0.014(1)	0.0092(6)	0.009(1)	0.0016(5)	0.004(1)	-0.0005(7)
S	0.6687(6)	0.25	0.556(2)	0.007(3)	0.008(2)	0.011(3)	0	0.001(2)	0
O(1)	0.5254(4)	0.25	0.590(1)	0.012(2)	0.022(1)	0.024(2)	0	0.006(2)	0
O(2)	0.6624(5)	0.25	0.234(1)	0.024(3)	0.038(2)	0.013(2)	0	0.006(2)	0
O(3)	0.2527(3)	0.5372(3)	0.3107(7)	0.015(1)	0.0145(7)	0.023(1)	-0.0004(6)	0.004(1)	-0.0024(8)
O(4)	0.9662(4)	0.25	0.2526(8)	0.012(2)	0.0107(8)	0.009(1)	0	0.003(3)	0
O(5)	0.0959(4)	0.25	0.8265(8)	0.010(1)	0.0118(9)	0.010(1)	0	0.003(1)	0
H(5)	0.0555(7)	0.25	0.605(2)	0.021(3)	0.024(2)	0.018(3)	0	0.004(3)	0
H(4)	0.8682(8)	0.25	0.256(2)	0.021(4)	0.029(2)	0.036(4)	0	0.014(3)	0

TABLE 4. COORDINATES AND ANISOTROPIC THERMAL PARAMETERS (\AA^2) OF ATOMS IN CALEDONITE BM1917,736 AT 293 K

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	0.5	0.0933(5)	0.5*	0.009(1)	0.016(2)	0.012(1)	0	0	-0.001(1)
Pb(2)	0.3995(1)	0.4147(3)	0.0401(4)	0.0113(8)	0.0107(8)	0.0104(9)	0.0023(7)	-0.001(1)	-0.001(1)
Pb(3)	0.3387(1)	0.8873(3)	0.0698(4)	0.0114(9)	0.0071(8)	0.012(1)	-0.0007(7)	0.001(1)	0.002(1)
Cu	0.2510(2)	0.4920(5)	0.3007(5)	0.0081(8)	0.007(1)	0.0038(7)	-0.0008(8)	0.0014(8)	-0.0010(7)
S(1)	0.3370(3)	0.1236(8)	0.551(2)	0.006(2)	0.008(2)	0.007(2)	0.002(2)	0.001(4)	-0.001(4)
S(2)	0.5	0.560(1)	0.542(2)	0.010(4)	0.004(3)	0.007(3)	0	0	-0.004(4)
O(1)	0.1634(3)	0.3702(7)	0.3360(6)	0.008(2)	0.013(2)	0.008(2)	-0.006(2)	0.003(1)	0.001(1)
O(2)	0.3386(2)	0.6065(6)	0.2651(6)	0.007(2)	0.006(2)	0.007(1)	-0.001(1)	0.001(1)	-0.001(1)
O(3)	0.2732(2)	0.3618(4)	0.0467(6)	0.006(1)	0.008(1)	0.002(1)	-0.0012(9)	-0.001(2)	0.001(2)
O(4)	0.4409(2)	0.6796(6)	0.5381(7)	0.015(2)	0.019(2)	0.019(2)	0.007(1)	-0.002(2)	-0.007(2)
O(5)	0.5	0.435(1)	0.7230(9)	0.033(5)	0.019(4)	0.010(3)	0	0	0.008(2)
O(6)	0.5	0.432(1)	0.3589(9)	0.012(3)	0.014(3)	0.016(3)	0	0	-0.006(2)
O(7)	0.2871(2)	0.2732(5)	0.5665(7)	0.018(2)	0.013(2)	0.015(2)	0.007(1)	0.003(2)	-0.001(2)
O(8)	0.3037(3)	0.9475(6)	0.5028(9)	0.027(3)	0.014(2)	0.050(3)	-0.009(2)	0.0100(2)	-0.010(2)
O(9)	0.3752(3)	0.1093(9)	0.7361(7)	0.025(3)	0.039(3)	0.016(2)	0.010(2)	-0.003(2)	0.007(2)
O(10)	0.3833(3)	0.1691(8)	0.3791(7)	0.015(2)	0.027(3)	0.017(2)	0.003(2)	0.005(2)	0.004(2)
O(11)	0.4459(2)	0.7555(5)	0.0529(9)	0.006(1)	0.014(2)	0.026(2)	-0.002(1)	-0.004(2)	-0.001(2)
O(12)	0.5	0.013(1)	0.143(1)	0.032(4)	0.015(3)	0.026(3)	0	0	-0.008(3)
C	0.5	0.8428(6)	0.0815(6)	0.007(2)	0.012(2)	0.007(2)	0	0	-0.002(2)
H(1)	0.1365(7)	0.341(2)	0.222(2)	0.051(8)	0.041(6)	0.043(5)	-0.012(6)	-0.031(5)	0.002(5)
H(2)	0.3666(6)	0.630(2)	0.385(1)	0.038(6)	0.036(5)	0.025(4)	-0.004(4)	0.000(4)	-0.009(4)
H(3)	0.2512(4)	0.245(1)	0.038(2)	0.039(4)	0.016(3)	0.037(4)	-0.004(3)	-0.007(5)	0.001(4)

* the z parameter of Pb(1) was fixed at 0.5 in order to define the origin.

TABLE 5. SELECTED BOND-LENGTHS (\AA) AND BOND-ANGLES ($^\circ$) FOR LINARITE AT 293 K

Pb–O(1)i	2.933(4)	S–O(1)	1.431(7)
Pb–O(1)	2.893(5)	S–O(2)	1.496(8)
Pb–O(3)	2.421(3)	S–O(3)ix	1.485(5)
Pb–O(3)iv	2.421(3)	S–O(3)x	1.485(5)
Pb–O(2)	3.048(6)	<S–O>	1.474
Pb–O(2)ii	3.046(2)		
Pb–O(2)iii	3.046(2)	O(4)–H(4)	0.952(7)
Pb–O(5)v	2.351(4)	O(5)–H(5)	1.025(8)
<Pb–O>	2.770	O(2)...H(4)	1.973(9)
		O(4)...H(5)xi	1.687(8)
		O(4)...O(2)	2.924(5)
Cu–O(3)iv	2.567(3)	O(5)...O(4)vii	2.706(5)
Cu–O(3)vi	2.567(3)		
Cu–O(4)vii	1.915(2)		
Cu–O(4)ii	1.915(2)	O(4)–H(4)...O(2)	176.1(6)
Cu–O(5)j	1.961(2)	O(5)–H(5)...O(4)vii	171.8(6)
Cu–O(5)viii	1.961(2)		
<Cu–O>	2.148		

The relevant symmetry codes are (i) x, y, z–1; (ii) 1–x, –y, –z; (iii) 1–x, ½+y, –z; (iv) x, ½–y, z; (v) x, y, z–1; (vi) –x, ½–y, –z; (vii) x–1, y, z; (viii) –x, –y, 1–z; (ix) 1–x, y–½, 1–z; (x) 1–x, 1–y, 1–z; (xi) 1+x, y, z.

variance ($\sim 2.8^\circ$ squared) and a quadratic elongation very close to unity. The mean S–O distance is 1.474 \AA , very close to the grand <S–O> distance, 1.473 \AA (Hawthorne *et al.* 2000), making a sulfate tetrahedron with a volume of 1.7 \AA^3 .

Hydrogen bonding

Table 7 shows the calculated bond-valence sums for all the atoms in the linarite structure as refined in

this study. Excluding the hydrogen atoms from the bond-valence calculations gives incident bond-valence sums for O(4) and O(5) of 1.06 and 1.39 *vu* (valence units), respectively, falling significantly below the ideal value of 2 *vu*. With the hydrogen atoms included in these calculations, the bond valence on O(4) and O(5) becomes much more acceptable, and furthermore, the calculated bond-valence for both of the two hydrogen atoms is very close to unity [1.04 and 0.96 *vu* for H(4) and H(5), respectively]. These calculations confirm that O(4) and O(5) are indeed the donor atoms for the hydrogen atoms, and also that H(4) and H(5) have been well located in the refinements. Figure 3 shows the hydrogen atoms and their bonding within the context of the rest of the linarite structure.

The bonding associated with the H(4) hydrogen atom (Table 5) and the bond-valence calculations (Table 7) are all indicative of normal hydrogen bonding (Brown 1976, 2002). The O(4)–H(4) bond distance is 0.952(7) \AA , and the H(4) ... O(2) hydrogen bond has a distance of 1.973(9) \AA . In addition, the O(4) ... O(2) donor–acceptor distance is 2.924(5) \AA , and the hydrogen bond is almost linear, with a O(4)–H(4) ... O(2) angle equal to 176.1(6) $^\circ$. The bonding associated with the H(5) hydrogen atom, however, is non-standard, and strongly suggestive of the presence of strong hydrogen bonding. Although bent, the O(5)–H(5) ... O(4) angle is still fairly linear at 171.8(6) $^\circ$, and the O(4) ... O(5) donor–acceptor distance is 2.706(5) \AA . Moreover, the

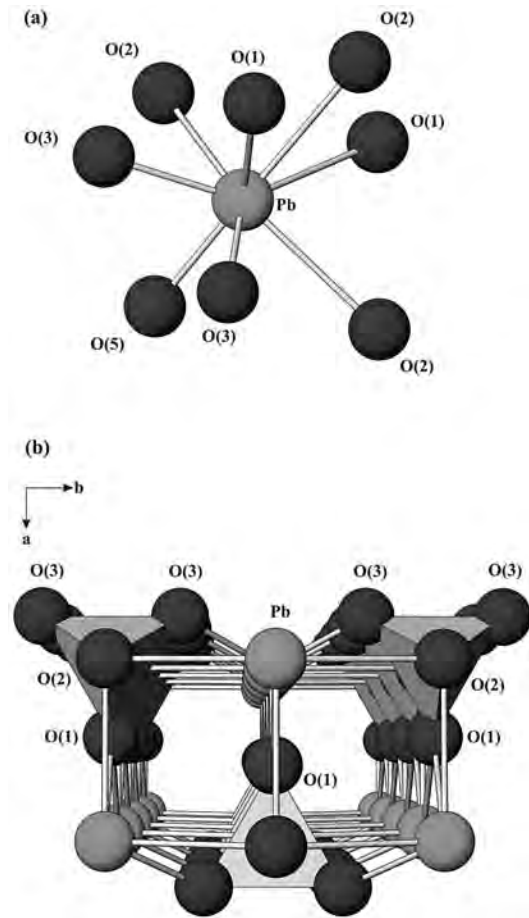


FIG. 1. (a) Coordination polyhedron around the Pb atom in linarite. (b) Channels parallel to [001] with Pb and O(2) atoms at the corners showing possible locations of the Pb lone pair; Pb are represented by light grey spheres, O, by dark grey spheres, and sulfate tetrahedra are in grey.

O(5)–H(5) molecular hydroxyl bond has become elongated to 1.025(8) Å, with a concomitant shortening of the hydrogen bond H(5) ... O(4) to 1.687(8) Å.

THE STRUCTURE OF CALEDONITE

Cation polyhedra

Caledonite has three Pb sites (Fig. 4), all of which are bonded to nine oxygen atoms, rather than the eight oxygen atoms for the Pb site in linarite. The range of Pb–O distances in the first Pb site is 2.415 to 3.194 Å, with a mean value of 2.800 Å and a polyhedron volume of 38.0 Å³, although the bond-distance distribu-

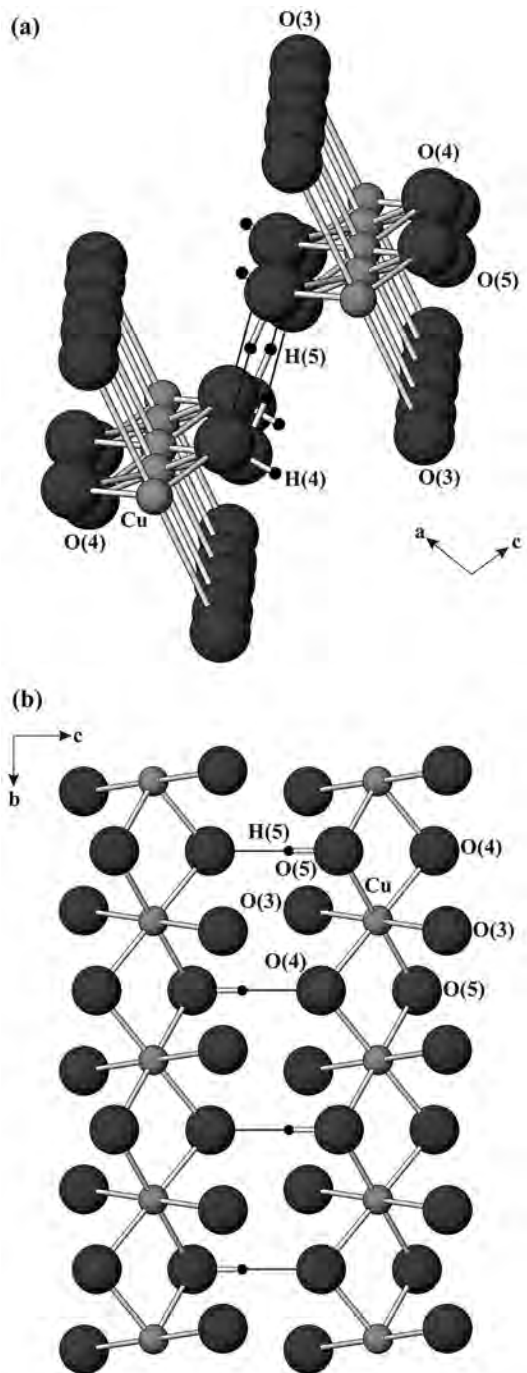


FIG. 2. Chains of Jahn–Teller-elongated CuO₆ square bipyramids bound together by hydrogen bonding in linarite (a) viewed along [010], and (b) viewed along [100]. The Cu atoms are represented by small light grey spheres, O, by dark grey spheres, and H, by small black spheres; hydrogen bond are shown by a black line.

TABLE 6. SELECTED BOND-LENGTHS (Å) AND BOND-ANGLES (°) FOR CALEDONITE AT 293 K

Pb(1)–O(4)j	3.194(5)	Pb(2)–O(1)iv	2.398(5)	Pb(3)–O(1)vi	2.395(5)
Pb(1)–O(4)jii	3.194(5)	Pb(2)–O(2)	2.356(5)	Pb(3)–O(2)	2.380(5)
Pb(1)–O(5)	2.845(9)	Pb(2)–O(3)	2.565(4)	Pb(3)–O(7)vii	2.775(5)
Pb(1)–O(6)	2.590(8)	Pb(2)–O(5)v	2.903(5)	Pb(3)–O(8)	2.959(6)
Pb(1)–O(9)	2.949(6)	Pb(2)–O(6)	2.910(5)	Pb(3)–O(8)viii	3.125(6)
Pb(1)–O(9)jiii	2.949(6)	Pb(2)–O(9)v	2.996(7)	Pb(3)–O(9)ix	2.801(6)
Pb(1)–O(10)	2.533(5)	Pb(2)–O(10)	2.852(5)	Pb(3)–O(10)	2.995(6)
Pb(1)–O(10)jiii	2.533(5)	Pb(2)–O(11)	2.607(4)	Pb(3)–O(11)	2.352(4)
Pb(1)–O(12)	2.415(7)	Pb(2)–O(12)	3.571(6)	Pb(3)–O(12)x	3.395(3)
<Pb(1)–O>	2.800	<Pb(2)–O>	2.795	<Pb(3)–O>	2.797
Cu–O(1)	1.976(7)	S(1)–O(7)	1.469(7)	S(2)–O(4)	1.463(6)
Cu–O(2)	1.954(7)	S(1)–O(8)j	1.458(8)	S(2)–O(4)xi	1.463(6)
Cu–O(3)	1.960(5)	S(1)–O(9)	1.44(1)	S(2)–O(5)	1.49(1)
Cu–O(3)vii	1.983(5)	S(1)–O(10)	1.50(1)	S(2)–O(6)	1.51(1)
Cu–O(7)	2.452(6)	<S(1)–O>	1.467	<S(2)–O>	1.482
Cu–O(7)iv	2.400(6)	O(1)–H(1)	0.95(1)	O(1)...O(4)iv	2.887(7)
<Cu–O>	2.121	O(2)–H(2)	0.98(1)	O(2)...O(4)	2.776(6)
C–O(11)	1.267(4)	O(3)–H(3)	0.946(8)	O(3)...O(8)iv	2.711(5)
C–O(11)xi	1.267(4)	O(4)...H(1)xii	1.97(1)	O(1)–H(1)...O(4)iv	161.6(1)
C–O(12)x	1.280(8)	O(4)...H(2)	1.84(1)	O(2)–H(2)...O(4)	160.0(1)
<C–O>	1.271	O(8)...H(3)vii	1.777(9)	O(3)–H(3)...O(8)iv	168.6(1)
O(11)–C–O(11)xi	118.14(1)				
O(11)–C–O(12)x	120.92(2)				
O(11)xi–C–O(12)x	120.92(2)				

The relevant symmetry-codes are (i) $x, y-1, z$; (ii) $1-x, y-1, z$; (iii) $1-x, y, -z$; (iv) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (v) $x, y, 1-z$; (vi) $\frac{1}{2}-x, 1-y, \frac{1}{2}-z$; (vii) $\frac{1}{2}-x, 1-y, z+\frac{1}{2}$; (viii) $\frac{1}{2}-x, 2-y, z-\frac{1}{2}$; (ix) $x, 1+y, 1-z$; (x) $x, 1+y, z$; (xi) $1-x, y, z$; (xii) $\frac{1}{2}-x, 1-y, 1-z$.

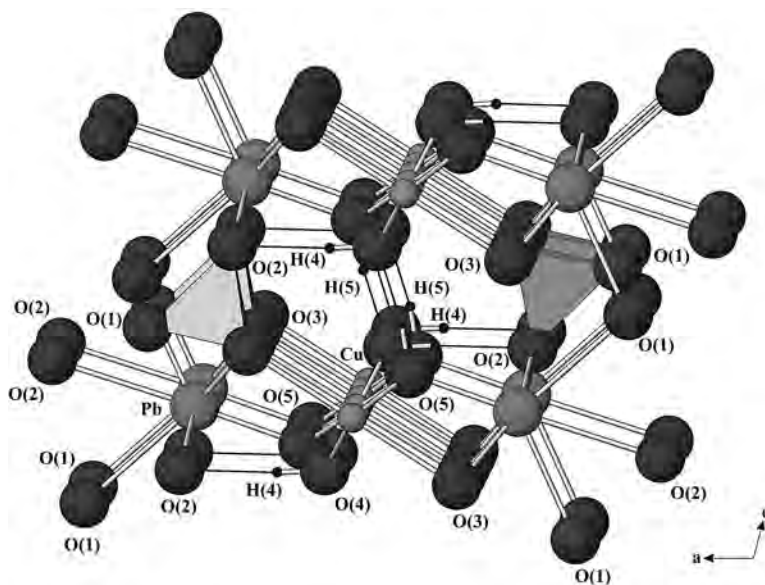


FIG. 3. The hydrogen atoms and their bonding within the context of the linarite structure viewed along [010]. The Pb atoms are represented by light grey spheres, O, by dark grey spheres, Cu, by small light grey spheres, and H, by small black spheres; the sulfate tetrahedra are shown in grey, and hydrogen bond, by a black line.

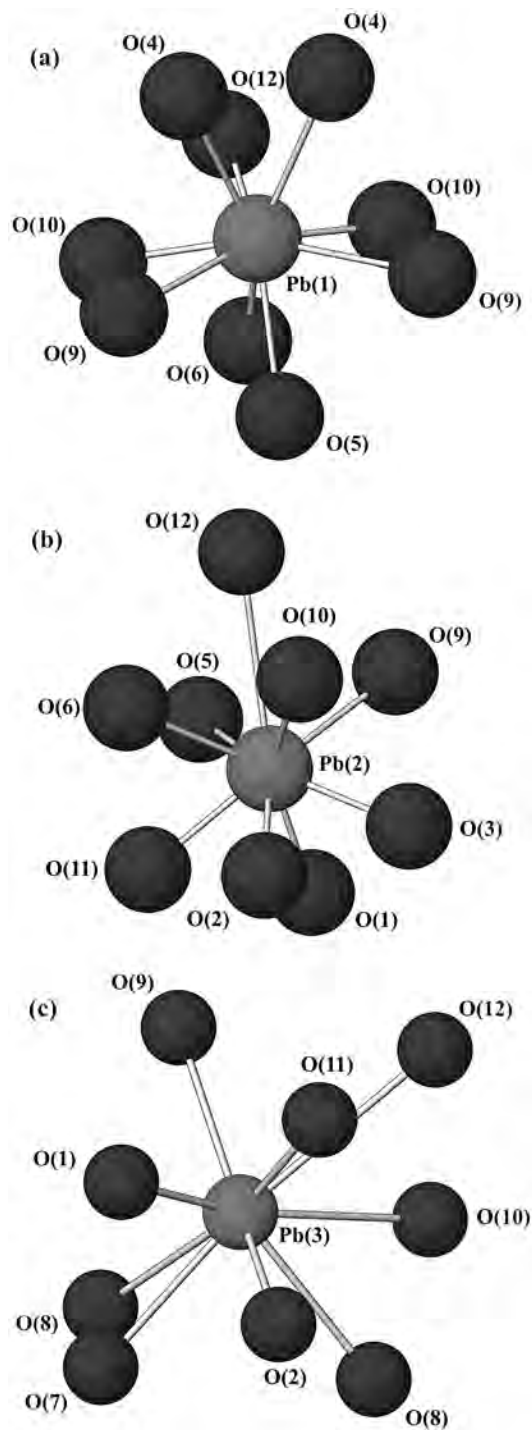


FIG. 4. Coordination polyhedra around the Pb atoms in calcedonite; the Pb atoms are represented by light grey spheres, and O, by dark grey spheres.

tion is clustered into two groups. There are four short Pb(1)–O bonds with an average distance of 2.518 Å that are all one side of the Pb(1)O₉ polyhedron, one of which is with the O(12) oxygen atom. The remaining five Pb(1)–O distances are all longer than that of the overall mean value for this polyhedron, with an average of 3.026 Å.

Whereas the Pb(2) site has a similar mean Pb–O distance (2.795 Å) to those of the other two Pb sites, the Pb(2)O₉ polyhedron volume at 43.1 Å³ is almost 15% larger than that of the other two PbO₉ polyhedra. This reflects distortions due to the very large Pb(2)–O(12) distance, 3.571(6) Å, that is over half an ångström larger than the next longest Pb(2)–O distance. The Pb(2)–O bond distances fall into three groups, with four short bonds, Pb(2) bonded to O(1), O(2), O(3) and O(11), four longer bonds in which Pb(2) is bonded to O(5), O(6), O(9) and O(10), and finally the very long Pb(2)–O(12) bond. The four shorter bonds are all on the same side of the Pb(2)O₉ polyhedron, and three of these bonds involve the hydroxyl oxygen atoms O(1), O(2) and O(3).

The average Pb–O distance for the third Pb site is 2.797 Å, similar to the other two Pb sites, and the polyhedron volume, 38.7 Å³, is similar to that of the Pb(1) site. Again, there is a clustering of the Pb(3)–O bond distances, with three short distances, with an average distance of 2.376 Å, and six Pb(3)–O distances, with an average of 3.008 Å that is longer than the overall Pb–O(3) mean distance. The shorter Pb(3)–O bonds are all on one side of the Pb(3)O₉ polyhedron, two of these bonds are with hydroxyl oxygen atoms, and one is with the O(11) oxygen atom.

The potential location of the Pb atom lone pairs is less obvious for calcedonite than for linarite. Figure 5 shows structural units comprising all three Pb atoms, O(9), O(10) and O(12) extracted from the entire structure. These units form a structural layer within the (010) plane and are likely to contain the lone pairs from the Pb atoms, with those for Pb(1) located between the O(9) atoms, whereas those for the Pb(2) and Pb(3) atoms are positioned between O(9), O(10) and O(12).

TABLE 7. EMPIRICAL BOND-VALENCES (*ν_i*) FOR LINARITE

	Pb	Cu	S	H4	H5	Total
O1	0.15 0.14		1.68			1.97
O2	0.11 0.111 × 2		1.41	0.19		1.93
O3	0.391 × 2	0.09 × 2	1.461 × 2			1.94
O4		0.53 × 2		0.85	0.30	2.21
O5	0.45	0.47 × 2			0.66	2.05
Total	1.85	2.09	6.01	1.04	0.96	

The bond-valence sums have been calculated using the parameters of Brown & Altermatt (1985), Krivovichev & Brown (2001) and Brown (2006).

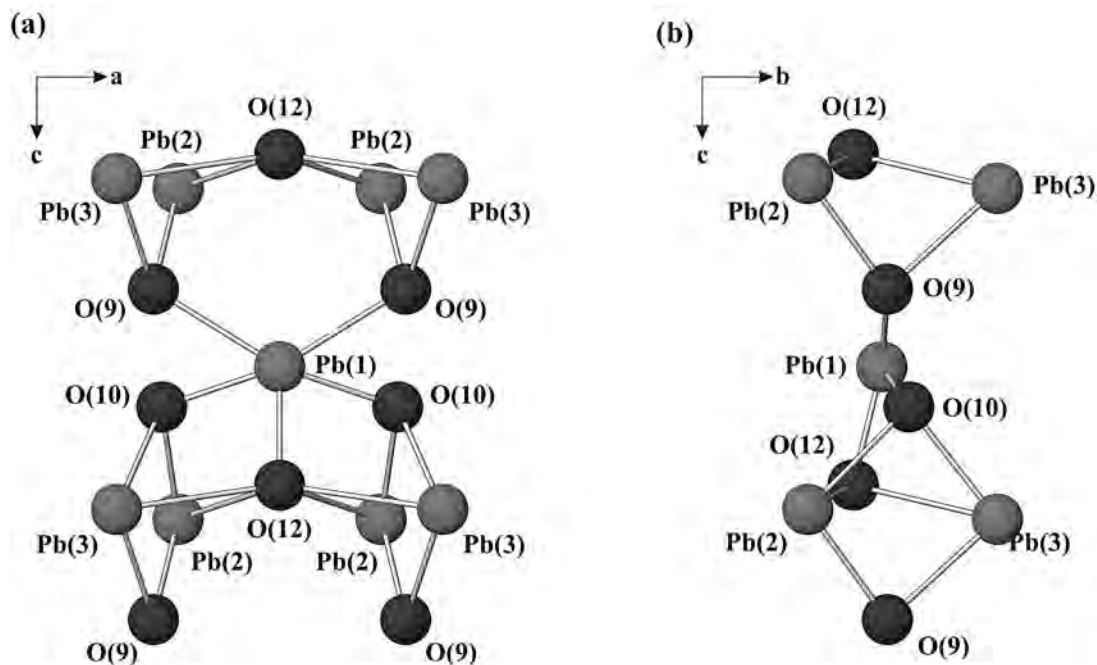


FIG. 5. Structural units involving the Pb atoms, O(9), O(10) and O(12) that form layers parallel to the (010) plane and that contain cavities that may contain the Pb lone pairs. (a) viewed along [010] and (b) viewed along [100]. The Pb atoms are represented by light grey spheres, and O, by dark grey spheres.

The nature and structural role of the CuO_6 square bipyramids within caledonite (Fig. 6) appear at first to be the same as that in linarite in that they form chains running along [010], are Jahn–Teller-elongated, have similar dimensions of the polyhedra, and the bonds within the CuO_4 square plane involve oxygen atoms of the hydroxyl groups. The two axial $\text{Cu–O}(3)$ bonds have lengths of 2.452(6) and 2.400(6) Å, and the shorter Cu–O bonds within the square plane average to 1.969 Å, resulting in a quadratic elongation for the CuO_6 square bipyramid in caledonite of 1.04 and a volume of 12.3 Å³. The similarity of the structural role of the Cu atoms in linarite and caledonite ends there. The bond lengths of the two axial $\text{Cu–O}(7)$ in caledonite differ by 0.052 Å, with the Cu atom being on a general position, rather than on the center of symmetry as in linarite. More significantly, the CuO_6 square bipyramids that form the chains are not linked by edge-sharing on the square plane as they are in linarite. Rather, the CuO_6 square bipyramids are linked through the axial O(7) oxygen atoms as well as the square-planar O(3) oxygen atoms.

In caledonite, there are two S sites, both of which are SO_4 tetrahedra. The S(1) site is the more symmetrical, with an angular variance of 1.7° squared and a quadratic elongation very close to unity (1.0005), whereas the

S(2) site has an angular variance of 4.2° squared and a larger quadratic elongation (1.0012). The S(2) site has a larger mean S–O distance of 1.482 Å compared with 1.467 Å for the S(1) site, and the polyhedron volumes are 1.6 Å³ and 1.7 Å³ for the S(1) and S(2) sites, respectively. The mean S–O distance for the S1 site is lower than the grand $\langle \text{S–O} \rangle$ distance, 1.473 Å (Hawthorne *et al.* 2000), whereas that of the more distorted S2 site is larger. The mean C–O bond distance is 1.271 Å, slightly lower than the grand value of 1.284 Å (Zemann 1981), but the mean O–C–O angle is 119.99°, just below that of the ideal 120° (Zemann 1981). The reduced symmetry of the CO_3 molecule may be related to the involvement of the O(12) oxygen atoms, which are bonded to each of the three independent Pb sites with somewhat erratic bond-distances. Giacobizzo *et al.* (1973) suggested that the C is off the plane of the oxygen atoms, but the uncertainty in their data prevented a definitive description of the distortion of this unit. Our data confirm that the C atom is indeed off the plane of the oxygen atoms, by 0.012(3) Å.

Hydrogen bonding

The calculated bond-valence sums incident at the atoms in the structure of caledonite refined in this

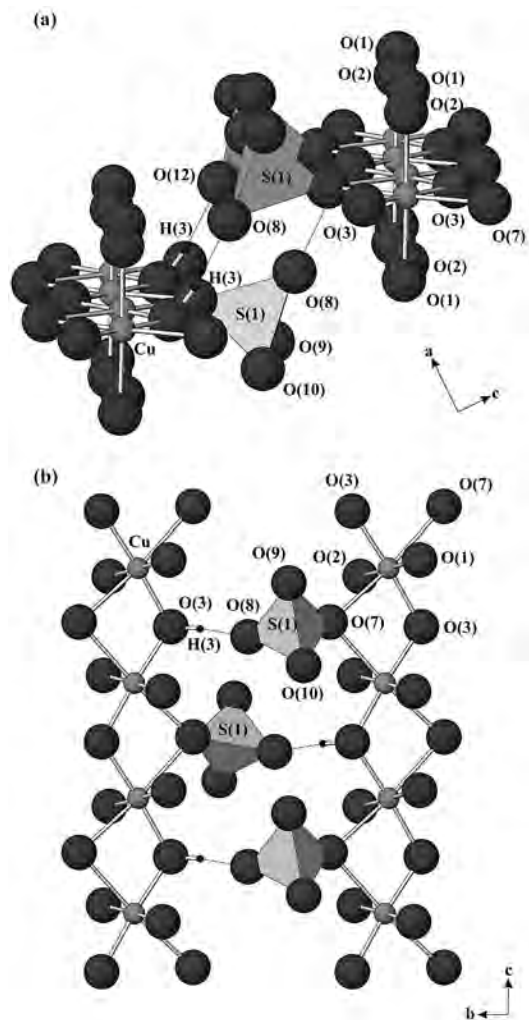


FIG. 6. Chains of Jahn–Teller-elongated CuO_6 square bipyramids bound together by $\text{S}(1)$ tetrahedra in caledonite, (a) viewed along 001 and (b) viewed along [100]. The atoms of Cu are represented by small light grey spheres, O, by dark grey spheres, and H, by small black spheres; the sulfate tetrahedra are shown in grey, and the hydrogen bonds, by black lines.

study are presented in Table 8. The hydrogen atoms are bonded to the oxygen atoms O(1), O(2) and O(3) as hydroxyl groups, and without this hydroxyl bond, these oxygen atoms are strongly underbonded, with incident bond-valence sums of 1.27, 1.36 and 1.20 *vu*, respectively. Two other oxygen atoms would have noticeably low incident bond-valence sums without the inclusion of any hydrogen atoms in the calculations, O(4) and O(8) having values of 1.63 and 1.79 *vu*, respectively.

With O(8) acting as an acceptor to hydrogen-bond interactions with H(3) and O(4) becoming involved in hydrogen bonding with the two remaining H atoms, the structural bond-valence requirements become satisfied. Figure 7 shows the structure of caledonite including the hydrogen atoms and the hydrogen bonding.

The bonding associated with the H(1) and H(2) (Table 6) and the bond-valence calculations (Table 8) are indicative of fairly normal hydrogen bonding (Brown 1976, 2002). Although these hydrogen bonds are significantly bent, with angles of $\sim 160^\circ$, the O(1) ... O(4) and O(2) ... O(4) donor–acceptor distances are 2.887(7) and 2.776(6) Å, respectively, and the slightly longer O(2)–H(2) hydroxyl bond is counterbalanced by a correspondingly shorter H(2) ... O(4) hydrogen bond. The H(3) ... O(8) bond is slightly shorter than expected, and coupled with the O(3) ... O(8) donor–acceptor distance of 2.711(5) Å and the 20° deviation from linearity, all suggest that this hydrogen bond may be slightly strained. Such a strained hydrogen bond may account for the higher than expected incident bond-valence to the H(3) atom (Table 8).

On the basis of the work of Libowitzky (1999), Frost *et al.* (2003) used Raman spectroscopy in an attempt to predict the lengths of the hydrogen bonds within the caledonite structure, but they were not able to compare their results with structural information measured from diffraction experiments. The estimated hydrogen-bond distances from Frost *et al.* (2003) are 2.823, 2.810 and 2.785 Å for OH1, OH2 and OH3 (using their nomenclature), respectively. Whereas these differ from our measurements of the hydrogen bonding (Table 6), their identification of the relative order in terms of the length of the hydrogen bonds does match our results. Our data for O(1) ... O(4) lies 0.017 Å above the estimated hydrogen-bond distance of Frost *et al.* (2003), whereas we find that O(2) ... O(4) and O(3) ... O(8) both lie below the estimated hydrogen-bond distance of Frost *et al.* (2003), by 0.027 Å and 0.064 Å, respectively.

DISCUSSION

A comparison of the bond-valence sums (Table 7) with simplistically calculated values of formal valence might provide some insight into the specifics of the topology of the linarite structure. The formal valences for the two oxygen atoms O(1) and O(3), both of which are three-coordinated, are close to the ideal value at 2.00 and 2.08 *vu*, respectively. The remaining three oxygen atoms, however, have formal valences that differ significantly from the ideal values. If the O–H bond is assigned a formal valence of 0.8 *vu*, whereas the hydrogen bonds are assigned a formal valence of 0.2 *vu*, values of 2.45, 1.66 and 1.77 *vu* are calculated for the O(2), O(4) and O(5), respectively.

Atom O(2) is five-coordinated, with three bonds to the Pb cation, one to the S cation and also participating in hydrogen bonding with H(4). In order to accom-

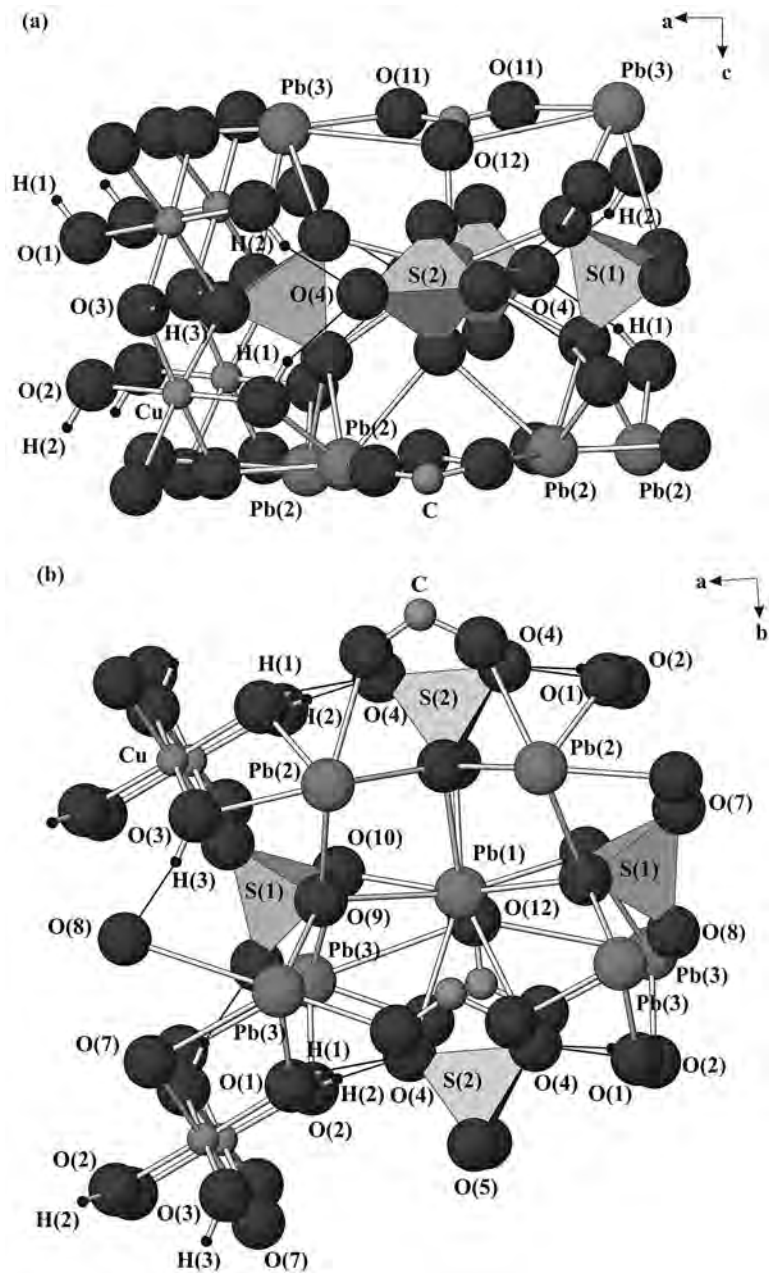


FIG. 7. The caledonite structure incorporating the hydrogen atoms and the hydrogen bonding, (a) viewed along [010], and (b) viewed along [001]. The Pb atoms are represented by light grey spheres, O, by dark grey spheres, Cu, by small light grey spheres, and H, by small black spheres; the sulfate tetrahedra are shown in grey, and the hydrogen bonds, by black lines.

TABLE 8. EMPIRICAL BOND-VALENCES (*vu*) FOR CALEDONITE

	Pb1	Pb2	Pb3	Cu	S1	S2	C	H1	H2	H3	Total
O1		0.41	0.41	0.45				0.86			2.13
O2		0.45	0.43	0.48					0.77		2.13
O3		0.29		0.47						0.87	2.07
				0.44							
O4	0.081×2					1.551×2		0.19	0.24		2.06
O5	0.17	0.15→2				1.44					1.91
O6	0.28	0.15→2				1.36					1.94
O7			0.19	0.12	1.52						1.97
				0.14							
O8			0.13		1.57					0.26	2.05
			0.09								
O9	0.131×2	0.12	0.18		1.64						2.07
O10	0.311×2	0.16	0.12		1.40						1.99
O11		0.27	0.45				1.391×2				2.11
O12	0.40	0.04→2	0.05→2				1.35				1.92
Total	1.89	2.04	2.05	2.10	6.13	5.90	4.13	1.05	1.01	1.14	

The bond-valence sums have been calculated using the parameters of Brown & Altermatt (1985), Krivovichev & Brown (2001) and Brown (2006).

modate this high coordination, all the bonds involving O(2) are lengthened, with the three Pb–O(2) bonds all being in excess of 3 Å and also being the three longest bonds of the PbO₈ polyhedron. Moreover, the O(2) ... H(4) hydrogen bond is stretched to almost 2 Å, and the S–O(2) bond is the longest of those within the sulfate tetrahedron. The overall effect of the increases in length of the bonds involving O(2) is an actual bond-valence for O(2) of 1.93 *vu* (Table 7).

Atom O(4) and O(5) are both four-coordinated, formally underbonded, and also have two bonds within the equatorial square plane of the Jahn–Teller-elongated CuO₆ square bipyramids. In order to maintain a bond valence of 2 *vu* for the Cu atom within a Jahn–Teller-elongated CuO₆ polyhedron, there must be a shortening of the square planar bonds to account for the inherent lengthening of the axial Cu–O(3) bonds. This is indeed the case within the linarite structure, with a final bond-valence of 2.09 *vu* on the Cu atom. In addition to the Pb–O(5) bond becoming the shortest of all the Pb–O bonds at 2.351 Å, the O(5)–H(5) bond is unusually long at 1.025 Å, and the O(4) ... H(5) hydrogen bond is shortened to 1.687 Å. The net result is a structure with incident bond-valence sums that satisfy the valence-sum rule.

The same approach can be applied toward the much larger structure of caledonite. The oxygen atoms O(5), O(6), O(9) and O(10) are four-coordinated, being bonded to three Pb atoms and one S atom, and all have a formal valence of 2.16 *vu*. If again the molecular O–H bond is assigned a formal valence of 0.8 *vu* and that of the hydrogen bond is assigned a formal valence of 0.2 *vu*, the four-coordinated oxygen atoms O(4) and O(8) have formal valence values of 2.12 and 2.14 *vu*, respectively. The three hydroxyl oxygen atoms O(1),

O(2) and O(3) are all four-coordinated, but in formal terms they are all significantly underbonded, as is the three-coordinate O(11) oxygen atom. On the other hand, the oxygen atoms O(7) and O(12) are formally overbonded at 2.38 and 2.43 *vu*, respectively.

All of the bonds between the Pb(2) and Pb(3) and hydroxyl oxygen atoms O(1) and O(2) are shorter than the mean Pb–O bonds, and with the relatively short Cu–O(1) and Cu–O(2) bonds that are involved in the equatorial square plane of the Jahn–Teller-elongated CuO₆ square bipyramids, sensible incident bond-valence sums for these two oxygen atoms can be achieved through normal hydrogen bonding for the H(1) and H(2) atoms. The bonding environment of O(3) differs slightly from that of O(1) and O(2) in that it is bonded to only one Pb atom and two Cu atoms. As the Cu–O(3) bonds are both involved in the CuO₄ square plane, their incident bond-valence increases with respect to the nominal formal valence. Although the Pb(2)–O(3) bond is shorter than the mean value for the Pb(3) site, it is slightly longer than the Pb bonds to the other hydroxyl oxygen atoms O(1) and O(2), which may enable a slightly shorter O(3)–H(3) bond. As the Pb(3)–O(8) bonds are longer than the mean value within the Pb(3)O₉ polyhedron, the O(8) requires a shorter hydrogen bond to satisfy its bond-valence requirements, resulting in a slightly stronger hydrogen bond for H(3).

The formally overbonded oxygen atom O(7) attains an incident bond-valence close to 2 *vu*, through the axial bonds of the Jahn–Teller-elongated CuO₆ square bipyramid, whereas the formally underbonded, three-coordinated O(11) oxygen atom increases its incident bond-valence through a shortened bond with Pb(3). One of the more unusual aspects of the caledonite structure

is the bonding environment of the oxygen atom O(12). The O(12) oxygen is six-coordinated, linking a Pb(1), two Pb(2) and two Pb(3) polyhedra with a carbonate group, and has a formal valence of 2.43 *vu*. In order to maintain a sensible incident bond-valence, however, four of the Pb–O(12) bonds are extremely long and the remaining Pb–O(12) bond is correspondingly short. Indeed, the Pb(2)–O(12) and Pb(3)–O(12) bonds are 3.571(6) and 3.395(3) Å, respectively, which reduces the valence of these bonds to 0.04 and 0.05 *vu*, respectively. The remaining bond that involves the O(12) oxygen atom is with the C atom of the carbonate group, and this C–O(12) bond is slightly longer than the two symmetry-related C–O(11) bonds.

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