BOLEITE: RESOLUTION OF THE FORMULA, K Pb$_{26}$ Ag$_9$ Cu$_{24}$ Cl$_{62}$ (OH)$_{48}$

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ABSTRACT

The crystal structure of boleite, K Pb$_{26}$ Ag$_9$ Cu$_{24}$ Cl$_{62}$ (OH)$_{48}$, a 15.288(2) Å, V 3574(1) Å^3, $Pm\bar{3}m$, $Z = 1$, has been refined to an *R*-index of 2.2% based on 884 observed (5σ) reflections collected with Mo$K\alpha$ X-radiation. A new site was resolved, and site-scattering refinement showed it to be occupied by a scattering species with 19 *epfu* (electrons per formula unit); this result is in accord with complete occupancy of this site by K. Potassium was detected by electron-microprobe analysis, but the amount determined is only ~50% of the amount indicated by site-scattering refinement. However, the refinement results show K to be disordered within a large cage in the structure, and the electron-beam bombardment probably induces rapid migration of K within the structure. Infrared spectroscopy shows that there is no H$_2$O present in the structure. The H-sites were determined during refinement, and a sensible H-bonding scheme results.

Keywords: boleite, crystal structure, new formula, hydrogen bonding.

SOMMAIRE

Nous avons affiné la structure cristalline de la boléite, K Pb$_{26}$ Ag$_9$ Cu$_{24}$ Cl$_{62}$ (OH)$_{48}$, a 15.288(2) Å, V 3574(1) Å^3, $Pm\bar{3}m$, $Z = 1$, jusqu'à un résidu R de 2.2% en utilisant 884 réflexions observées (5σ) prélevées avec rayonnement Mo$K\alpha$. Nous avons découvert un site nouveau, et ce site serait occupé par une espèce ayant 19 électrons par unité formulaire, selon un affinement du pouvoir de dispersion associé à ce site. D'après ce résultat, on pourrait s'attendre à l'occupation complète du site par le potassium. Nous avons confirmé la présence du potassium par analyse à la microsonde électronique, mais seulement en quantités suffisantes pour remplir la moitié du site environ. Toutefois, l'affinement montre que le K est désordonné à l'intérieur d'une cage assez volumineuse dans la structure. A notre avis, le bombardement par le faisceau d'électrons est probablement la cause d'une migration rapide des ions K. La spectroscopie dans l'infrarouge montre qu'il n'y a pas de molécules de H$_2$O dans la structure. Les sites H ont été localisés au cours de l'affinement, et un schéma raisonnable de liaisons hydrogène en résulte.

(Traduit par la Rédaction)

Mots-clés: boléite, structure cristalline, nouvelle formule, liaisons hydrogène.

INTRODUCTION

Boleite was first described by Mallard & Cumenge (1891) as a Pb–Ag–Cu oxychloride with cubic symmetry. Since then, there have been several modifications to its formula, unit cell and symmetry (Bariand *et al.* 1998). Particular interest in boleite, pseudoboleite and cumengeite arises from their curious epitactic growth, which results in spectacular bright-blue cube, cube + octahedron, and tetragonal pyramid + cube forms. The crystal structures of all three minerals have been reported [boleite: Rouse (1973); cumengeite: Hawthorne & Groat (1986); pseudoboleite: Giuseppetti *et al.* (1992)]; these results place important chemical constraints on the mineral formulae, and also provide a structural basis for the epitaxy.

The boleite formula arrived at from the structure solution (Rouse 1973) is Pb$_{26}$ Ag$_9$ Cu$_{24}$ Cl$_{62}$ (OH)$_{48}$. This formula has an excess charge of 1$^-$ as noted by Abdul-Samad *et al.* (1981), who revised the formula to Pb$_{26}$ Ag$_9$ Cu$_{24}$ Cl$_{62}$ (OH)$_{47}$ (H$_2$O), with a single additional H-atom disordered over the unit cell. The powder-diffraction file-card for boleite (PDF #27–1206) lists the formula as Pb$_{26}$ Ag$_{10}$ Cu$_{24}$ Cl$_{62}$ (OH)$_{48}$ (H$_2$O)$_3$ and gives the reference as Rouse (1975, *pers. commun.*), although Rouse (*pers. commun.,* 2000) denies any association with this latter formula; Fleischer & Mandarino (1995) also gave this formula. If the true formula for boleite were Pb$_{26}$ Ag$_9$ Cu$_{24}$ Cl$_{62}$ (OH)$_{47}$ (H$_2$O), a satisfactory crystal-chemical explanation for the H$_2$O group is needed; in addition, spectroscopic confirmation of H$_2$O is desirable. On the other hand, if the true formula

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for boleite were Pb_{26} Ag_{10} Cu_{24} Cl_{62} $(OH)_{48}$ $(H_2O)_3$, not only do the above arguments hold for the H_2O, but the structure must also possess one new site to accommodate the additional Ag, and at least one new site to accommodate the H_2O groups. We have therefore re-investigated the structure of boleite in an attempt to resolve the continuing issue of its true chemical composition.

REFINEMENT OF THE CRYSTAL STRUCTURE

The material used in this work is from the Amelia mine, Santa Rosalia, Baja California, Mexico, and was purchased from a mineral dealer.

X-ray data collection

An optically isotropic cleavage-fragment, flattened on (100), was carefully ground into a thin plate 26 μm thick. We have seen significant improvements in refinement results (in R values and light-element positions) when rigorous absorption corrections are applied to data collected from thin plates of materials with high linear-absorption coefficients (Hawthorne *et al.* 1994, Cooper & Hawthorne 1995, Finch *et al.* 1996, Cooper *et al.* 1999). The thin plate maintains a substantial diffracting volume and also constrains complete attenuation of the X-ray beam to a narrow glancing angle relative to the plate surface. We routinely prepare a thin (typically 20–30 μm) plate either by cleaving the crystal or by careful grinding. Collection of additional symmetry-equivalents is desirable so as to maintain a high proportion of unique data after removal of reflections collected within the glancing angle of rejection.

The plate was mounted on a Siemens *P*4 automated four-circle diffractometer. Cell dimensions (Table 1) were derived from the setting angles of all 48 symmetry equivalents of 3 7 11; unconstrained least-squares refinement of the cell dimensions produced correspondence to cubic metricity within the standard deviations

TABLE 1. MISCELLANEOUS INFORMATION FOR BOLEITE

a (Å)	15.288(2)	crystal size (mm)	0.34 x 0.32 x 0.026
V (Å³)	3574(1)	Radiation/monchromator	MoKα / Graphite
		No. of initial intensities	11,214
Sp. Gr.	$Pm\bar{3}m$	No. of intensities*	8,566
μm (mm⁻¹)	36.7	No. of F_o	1,108
D_c (g.cm⁻³)	5.082	No. of $|F_o| > 5\sigma|F_o|$	884
		R (azimuthal) %	25.7 → 2.2
		R (merge) %	4.7
		R (obs) %	2.2
		wR (obs) %	2.3

Cell content: K Pb^{2+}_{26} Ag^{+}_{9} Cu^{2+}_{24} Cl_{62} $(OH)_{48}$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{1/2}$, $w = 1$

* Number of intensities remaining after removal of those with a glancing angle of ≤ 12° to the plane of the crystal plate.

(0.003 Å and 0.01°). We collected intensity data from 4 to 60° 2θ over the range [$0 \le h \le 21$, $-21 \le k \le 21$, $0 \le l \le 21$], a total of 11,214 reflections. Absorption corrections were done using the psi-scan method with a plate-glancing angle of 12°, reducing R(azimuthal) from 25.7 to 2.2%. This resulted in the loss of 2648 reflections that were collected within the 12° glancing angle. However, the additional data provided by oversampling of symmetry equivalents enabled 100% recovery of all possible 1108 unique data.

The single crystal used for collection of the X-ray intensity data was later examined by long-exposure precession photography. All observed reflections are consistent with cubic symmetry ($Pm\bar{3}m$) and a cell translation of 15.29 Å.

Crystal-structure refinement

The atom positions for Pb, Ag, Cu, Cl and O atoms from Rouse (1973) were used in the initial stage of structure refinement. Scattering curves for ionized species other than H, with anomalous dispersion corrections, were taken from the International Tables of Crystallography (1992), except for that of O^{2-}, which was taken from Azavant & Lichanot (1993). Rapid convergence was achieved for isotropic- and anisotropic-displacement models ($R = 5.8$ and 3.0%, respectively). At this stage, there was a residual peak in the difference-Fourier map at the 1b position (½, ½, ½); in addition, there were two smaller peaks at 0.94 Å from O(1) and 0.88 Å from O(2), respectively. The 1b site is surrounded by twelve Cl(5) atoms at a distance of 3.663 Å. In the next cycles of refinement, the scattering factor for ionized K was assigned to the 1b site and the site-occupation factor was allowed to refine; H positions [H(1), H(2)] were also inserted, with a soft constraint that the O–H distance be close to 0.98 Å. This model refined to an R-value is 2.2%, and the site-scattering at 1b refined to 19(1) *epfu* (electrons per formula unit). Final atom coordinates and displacement factors are listed in Table 2, selected interatomic distances and angles are given in Table 3, and bond valences are given in Table 4. Structure-factor tables may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Discussion of the results of the refinement

The final refinement model shows that the *Pb*, *Cu*, *Ag*, *OH* and *Cl* sites are fully occupied by Pb, Cu, Ag, OH and Cl, respectively, and that the new (*K*) site has a refined site-scattering value of 19(1) electrons per site.

What is now required is the correct interpretation of the 19 *epfu* in terms of chemical composition. The 1b site is coordinated by twelve Cl atoms at a distance of 3.663 Å; subtracting the radius for Cl (1.81 Å) leaves a value of 1.85 Å for the radius of the cation. The only plausible chemical candidates (and their radii) for such

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT FACTORS (x 10⁴) FOR BOLEITE

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
K	1/2	1/2	1/2	478(38)	478(38)	478(38)	0	0	0	478(22)
Pb(1)	0.22633(5)	1/2	1/2	197(4)	219(2)	219(2)	0	0	0	212(2)
Pb(2)	0.30301(2)	x	x	173(1)	U_{11}	U_{11}	−23(1)	U_{23}	U_{23}	173(1)
Pb(3)	0.27356(3)	1/2	0	182(2)	345(3)	174(2)	0	0	0	234(2)
Ag(1)	0	0.1573(1)	0	308(5)	362(10)	308(5)	0	0	0	326(4)
Ag(2)	0	1/2	0	457(10)	265(13)	457(10)	0	0	0	393(6)
Cu	0.25567(5)	x	0.09458(6)	142(3)	U_{11}	97(4)	10(3)	U_{23}	30(4)	127(2)
Cl(1)	0.1222(2)	x	x	297(9)	U_{11}	U_{11}	−58(10)	U_{23}	U_{23}	297(15)
Cl(2)	0.3848(1)	x	0.1210(2)	209(6)	U_{11}	227(10)	−33(6)	U_{23}	−34(9)	215(4)
Cl(3)	0	0.3296(3)	0	243(14)	218(22)	243(14)	0	0	0	234(10)
Cl(4)	0.1316(2)	1/2	x	225(9)	143(12)	U_{11}	0	62(12)	0	198(6)
Cl(5)	0.3306(2)	1/2	x	390(13)	199(15)	U_{11}	0	195(17)	0	326(8)
O(1)	0	0.3302(4)	0.2104(4)	149(27)	146(28)	127(27)	36(22)	0	0	141(16)
O(2)	0.1880(3)	x	0.3119(4)	174(18)	U_{11}	181(30)	46(17)	46(17)	32(25)	176(13)
H(1)	0	0.339(7)	0.147(1)							272(302)
H(2)	0.162(5)	x	0.364(5)							511(401)

* U x 10⁴

an environment are Ca 1.34, Na 1.39, Sr 1.44, Pb^{2+} 1.49, Ba 1.61, Tl^{+} 1.70, K 1.64, Rb 1.72 and Cs 1.88 Å. The desired total charge at the 1b site is 1^{+} (to give electroneutrality in the formula). If the 1b site were occupied by a single species, a fully occupied K site or a half-occupied Sr site would provide the desired 1^{+} charge and meet the requirement of 19 $epfu$. There are a large number of more complicated possibilities, but we disregard these via application of Occam's razor. The

simplest interpretation of the refinement results is that the 1b site is fully occupied by K, accounting for the 19 $epfu$ and providing the additional 1^{+} charge necessary for electroneutrality. The predicted bond-length for K coordinated by twelve Cl atoms is 3.45 Å (1.64 + 1.81 Å). Considering the positional disorder at the K position in boleite, the observed bond-length, 3.66 Å, can be regarded as in adequate agreement with the bond length calculated from the sum of the cation and anion radii.

INFRARED SPECTROSCOPY

Experimental methods are identical to those reported by Roberts et $al.$ (1994). The powder infrared absorption spectrum for boleite is shown in Figure 1. There is a sharp band at ~3388 cm⁻¹ and no band at ~1630 cm⁻¹, consistent with the presence of OH and the absence of H_2O in the structure.

ELECTRON-MICROPROBE ANALYSIS

An optically isotropic cleavage fragment of boleite from the same crystal was embedded in epoxy, polished and carbon-coated. Electron-microprobe analysis was done with a Cameca SX–50 operating in wavelength-dispersion mode at 15 kV and 10 nA with a defocused (20 μm) beam. There was an immediate response of the sample surface to the electron beam: the carbon coat blistered and partially detached from the mineral surface. The time between final polishing and carbon coating of the surface was twelve hours. Boleite is a chloride and is possibly hydrophilic. As we were attempting to measure a minor element (ideally 0.36 wt% K), we

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BOLEITE

K–Cl(5)	3.663(5)	x12	Pb(1)–Cl(2)	2.966(2)	x4	
			Pb(1)–Cl(5)	3.041(1)	x4	
Ag(1)–Cl(1)	2.697(3)	x4	<Pb(1)–Cl>	3.004		
Ag(1)–Cl(3)	2.635(5)					
<Ag(1)–Cl>	2.685		Pb(2)–O(2)	2.490(6)	x3	
			Pb(2)–Cl(2)	3.298(2)	x3	
Ag(2)–Cl(3)	2.605(5)	x2	Pb(2)–Cl(5)	3.070(1)	x3	
Ag(2)–Cl(4)	2.844(3)	x4	<Pb(2)–O>	2.490		
<Ag(2)–Cl>	2.764		<Pb–Cl>	3.184		
Cu–O(1)	1.967(4)	x2	Pb(3)–O(1)	2.770(6)	x2	
Cu–O(2)	1.962(3)	x2	Pb(3)–Cl(2)	3.068(1)	x4	
Cu–Cl(1)	2.916(3)		Pb(3)–Cl(4)	2.959(1)	x2	
Cu–Cl(2)	2.821(2)		<Pb(3)–O>	2.770		
<Cu–O>	1.965		<Pb(3)–Cl>	3.032		
<Cu–Cl>	2.869					
O(1)–H(1)	0.98(2)		H(1)......Cl(3)	2.25(2)		
O(2)–H(2)	0.98(9)		H(2)......Cl(4)	2.18(8)		
O(1)–Cl(3)	3.217(6)		O(1)–H(1)–Cl(3)	169(9)		
O(2)–Cl(4)	3.124(6)		O(2)–H(2)–Cl(4)	162(8)		

TABLE 4. BOND VALENCE (*vu*) TABLE* FOR BOLEITE

	K	Pb(1)	Pb(2)	Pb(3)	Ag(1)	Ag(2)	Cu	H(1)	H(2)	Σ
Cl(1)					$0.19^{x4}\!\downarrow^{x3}\!\rightarrow$		$0.08^{x3}\!\rightarrow$			0.81
Cl(2)		$0.31^{x4}\!\downarrow$	$0.13^{x3}\!\downarrow$	$0.23^{x4}\!\downarrow^{x2}\!\rightarrow$			0.11			1.01
Cl(3)					0.23	$0.25^{x2}\!\downarrow$		$0.15^{x4}\!\rightarrow$		1.08
Cl(4)				$0.31^{x2}\!\downarrow^{x2}\!\rightarrow$		$0.13^{x4}\!\downarrow$			$0.20^{x2}\!\rightarrow$	1.15
Cl(5)	$0.05^{x12}\!\downarrow$	$0.25^{x4}\!\downarrow^{x2}\!\rightarrow$	$0.23^{x3}\!\downarrow^{x2}\!\rightarrow$							1.01
O(1)				$0.19^{x2}\!\downarrow$			$0.46^{x2}\!\downarrow^{x2}\!\rightarrow$	0.85		1.96
O(2)			$0.34^{x3}\!\downarrow$				$0.47^{x2}\!\downarrow^{x2}\!\rightarrow$		0.80	2.08
Σ	0.60	2.24	2.10	1.92	0.99	1.02	2.05	1.00	1.00	

* Bond-valence curves from Brese & O'Keeffe (1991) and Brown (1981) [Pb–O].

decided to re-prepare the mount. A fine polish was used to remove the old carbon coat. The mount was placed in a drying oven for 30 minutes, and then immediately carbon-coated. The response of the surface to the electron beam was now less dramatic, although a discoloring "burn" mark did appear within a few seconds. R.C. Rouse (*pers. commun.*, 2000) suggested that this behavior is due to the presence of numerous small fluid inclusions in boleite.

A K-bearing albite standard was cross-analyzed against a reliable orthoclase standard for the element K, and the K-bearing albite was found to be homogeneous [0.14(1) wt% K]. This albite was then used as the K standard for the boleite analysis. The Pb–Ag–Cu–Cl–O matrix components for boleite were input into the program. Counting for 50 s at the $K\alpha_1$ peak position of K (25 s background) gave an average of 0.17(2) wt% K for 10 points on boleite. As the chemical bonding of K

in albite and boleite is quite different, acquisition using peak integration was also done for comparison. Initial spectrometer (PET) scans were done for three points on both albite and boleite [64 channels, 0.41800 to 0.43375 sinθ, 30 s per channel]. The averages for the scans are shown in Figure 2. From these spectrometer scans, the sinθ range 0.425–0.430 was selected for acquisition of the peak-integration data [21 channels, 30 s per channel, backgrounds at first and last channels]. This procedure gave an average of 0.17(2) wt% K for six points on boleite. The elements (Na, Rb, Cs, Ca, Sr, Ba) were sought but are below the limits of detection.

The electron-microprobe results clearly show the presence of K [0.17(2)% K]. The K atoms are unlikely to reside at cation sites (*Pb*, *Ag*, *Cu*) other than the 1*b* position in the boleite structure. Two determinations for K in boleite by LA–ICP–MS (laser-ablation inductively coupled plasma – mass spectrometry) gave 0.166(6) wt% K, statistically identical with the results of the electron-microprobe analysis. Thus the results of structure refinement, chemical analysis and infrared-absorption spectroscopy collectively support a boleite formula with K dominant at the *K* site and no H_2O present. Attempts to measure K over shorter times and lower beam-currents were unsuccessful, as they resulted in low count-rates that gave unreliable results.

Structure Description

The boleite structure has been described by Rouse (1973) and Giuseppetti *et al.* (1992). Here, we will focus on aspects that were not dealt with previously. The structural elements are shown (Fig. 3) as two different types of complex chains consisting of cages linked along the principal axial directions.

The *Ag*(1) cage consists of six (*Ag*Cl₅) square pyramids whose square faces define a cube centered at (0,0,0); these cages are linked along [001] (and [100] and [010]) by [*Ag*(2)Cl₆] octahedra (Fig. 3a). The distance from the center of the cage at (0,0,0) to the eight Cl(1) atoms at the corners of the cube is 3.237 Å, and to the six Ag(1) atoms is 2.404 Å. The 1*a* site at (0,0,0) is vacant.
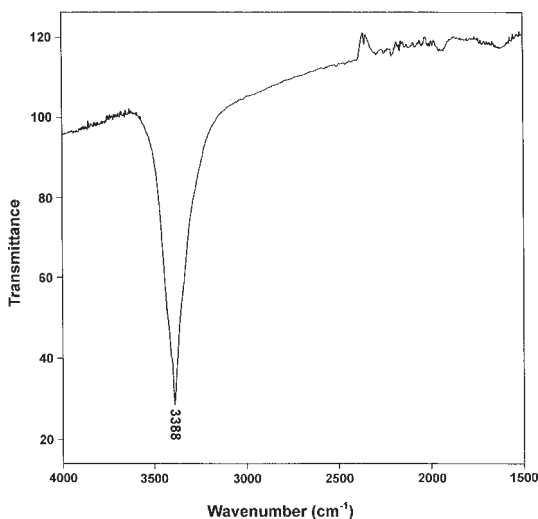

FIG. 1.   The infrared spectrum of boleite in the principal OH-stretching region.
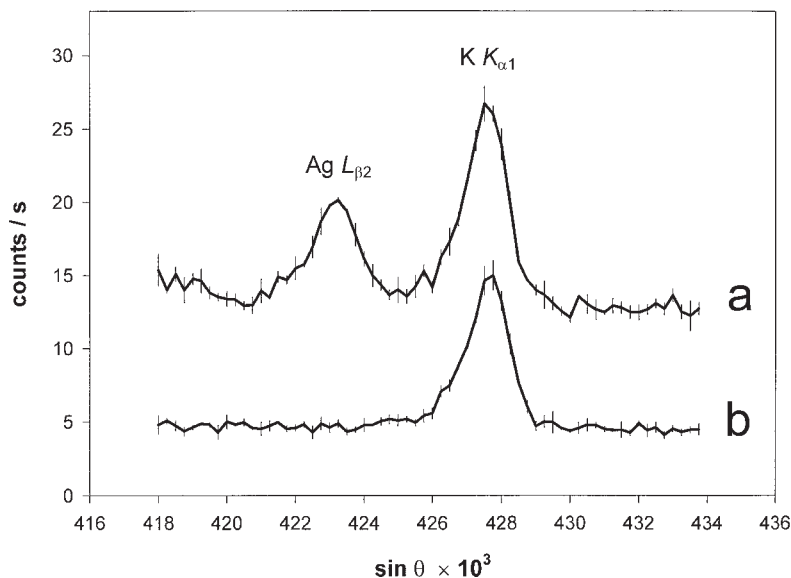
FIG. 2. Electron-microprobe wavelength scans for (a) boleite and (b) albite in the region of the K$K\alpha_1$ peak; note that the K$K\alpha_1$ peak in boleite is well resolved from the neighboring Ag$L\beta_2$ peak.

The $Pb(1)$ cage is centered at (½,½,½), and the $Pb(1,3)$ cage is centered at (½,½,0). These two cages join by sharing $Pb(1)$ vertices to form chains parallel to [100], [010] and [001] (Fig. 3b). The center of the $Pb(1)$ cage is occupied by K. The K–Cl(5) distance is 3.66 Å (× 12), which leads to a bond-valence sum of 0.60 vu at the K site (Table 4). Careful examination with the electron microprobe showed no other significant alkali or alkaline-earth cations that could occupy the K site, and we conclude that this site is fully occupied by K, as indicated by the site-scattering refinement. The <K–Cl> distance is larger than that expected for occupancy of the K site by K, as indicated by the low incident bond-valence sum (Table 4). However, the equivalent isotropic-displacement factor is very large for the K site (Table 2), indicating that the atom at the K site is disordered off the central 1b position, in accord with the low bond-valence sum at the K site. This disorder is also in accord with the idea that K easily diffuses within the structure under the influence of the electron-microprobe beam.

The $Pb(1,3)$ cage (Fig. 3) is formally vacant, but is actually occupied by the stereoactive lone-pairs of electrons of the surrounding Pb^{2+} cations.

HYDROGEN BONDING

Although not shown as such, the $Ag(2)$ site at (0,0,½) in Figure 3a can be regarded as occupying the central position of a complex cage. This cage consists of two eight-membered rings of edge-sharing Cu octahedra around the 4-fold axis at $x \approx$ ¼ and ¾. An additional four Pb(3) atoms link the two Cu rings together via bonds to the Cl(4) atoms. The lower eight-membered Cu ring is shown in Figure 4, with the $Ag(2)Cl_6$ octahedron above the ring; in this figure, the four Pb(3) atoms at the same height as the $Ag(2)$ site, and the upper Cu ring have been omitted. Hydrogen bonds from the H(1) and H(2) atoms of the OH groups of the Cu-rings are directed toward the Cl atoms of the $Ag(2)Cl_6$ octahedron. Each Cl(4) atom receives two H-bonds from H(2) atoms on opposing Cu rings, and each Cl(3) atom receives four H-bonds from the H(1) atoms at the base of a single Cu ring. All H-bonds are relatively strong, as indicated by short H...Cl distances of ~2.2 Å and O–H–Cl angles greater than 160° (Table 3).

THE USE OF ACCENTS FOR BOLEITE AND RELATED MINERALS

Boleite and the related minerals pseudoboleite, cumengeite and diaboleite have frequently been written as "...éite" rather than as "...eite", largely because French scientists did most of the early work on these species, and the situation has been somewhat confused regarding this issue. However, it was clarified, with the help of editor Bob Martin, during review of this paper. The locality Boleo in Mexico does not have an accent, and
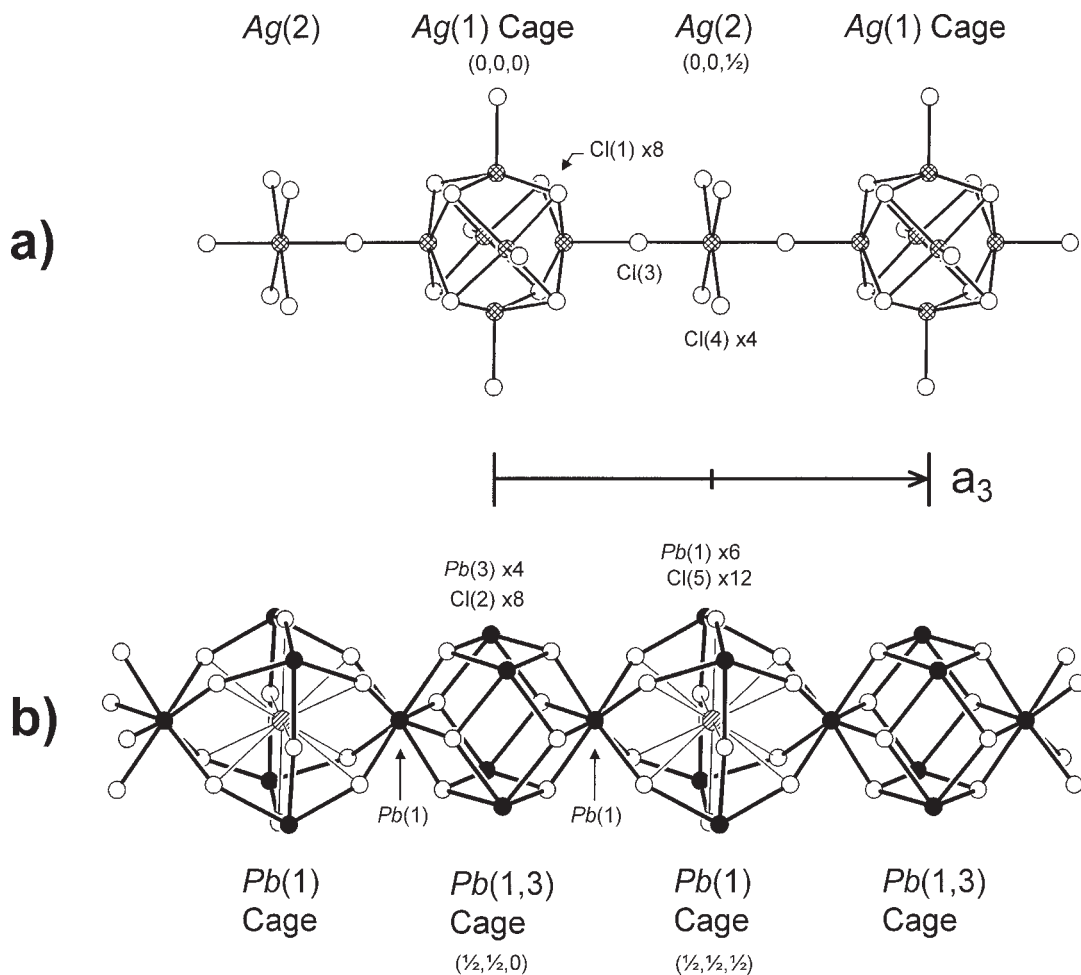
FIG. 3.   Some elements of the crystal structure of boleite: (a) the *Ag*(1) cage and the *Ag*(2) octahedron linked along [001]; (b) the *Pb*(1) and *Pb*(1,3) cages linked along [001]. *Ag* sites are shown as cross- hatched circles, Cl atoms are unshaded circles, *Pb* sites are black circles, and the *K* site is shown as a diagonally line-shaded circle.

neither does the name Cumenge, after whom the mineral cumengeite was named. Hence these minerals should be written without an accent in English. However, in order to achieve the appropriate pronunciation in French (*cf.* the Sommaire), an accent is required for all these mineral names.

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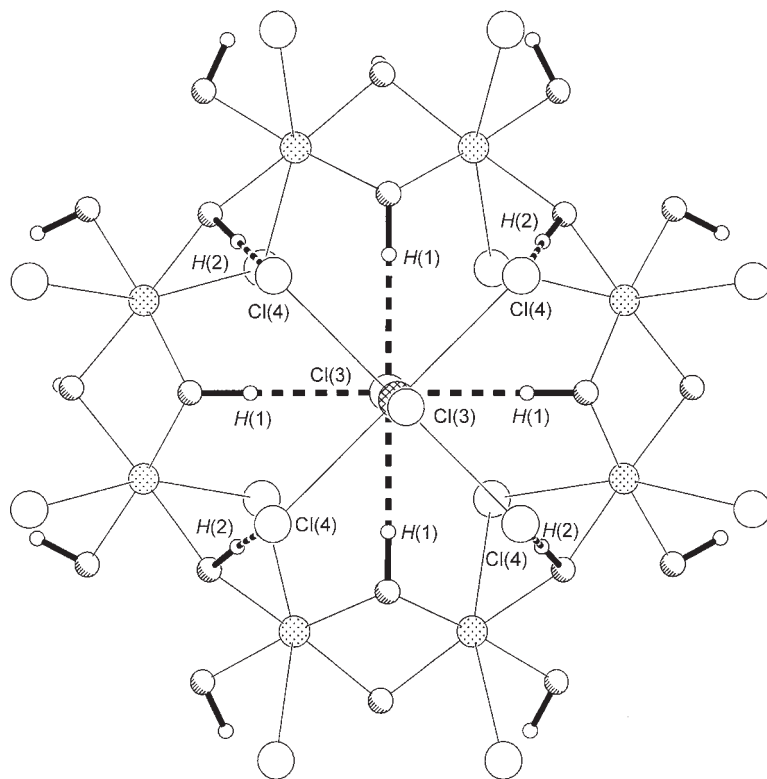
Fig. 4. The H-bonding arrangement in boleite; legend as in Figure 3. Cu atoms are dot-shaded, O atoms are highlighted circles, H atoms are small unshaded circles, and H-bonds are shown as broken lines.

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