First Italian occurrence of cumengéite from Vesuvius: crystal-structure refinement and revision of the chemical formula

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ABSTRACT

The first Italian occurrence of cumengéite, a rare Pb and Cu hydroxychloride, is described from Vesuvius (Italy). Italian cumengéite has a volcanic origin (it occurs in the fumarole), which is unique for that mineral. The mineralogy of Vesuvius' fumarole is outlined briefly. A powder X-ray diffraction (XRD) pattern of cumengéite is presented. The crystal structure of cumengéite has been refined (R = 0.036) using single-crystal XRD data. Cumengéite is tetragonal, space group $I4/mmm$, a 15.1007(2), c 24.4940(4) Å. In the structure of cumengéite there are five independent Pb atoms, which are linked to 6−9 anions in five different ways. The structural study revealed the presence of two independent and previously unobserved water molecules, and led to the revision of the accepted chemical formula for the mineral: the new formula is $Cu_{20}Pb_{21}Cl_{42}(OH)_{40} \cdot 6H_2O$. Analytical data taken from the literature for cumengéite from Boléo, Mexico (the type locality), as well as a new structural study carried out on the type material confirmed the new formula.

KEYWORDS: cumengéite, Vesuvius, Italy, crystal structure, crystal-chemical formula.

Introduction

CUMENGÉITE is a rare Pb and Cu hydroxychloride. The mineral was discovered at Boléo, near Santa Rosalia, Baja California Sur, Mexico (Mallard, 1893). After original unsuccessful attempts to define the new mineral, which had previously been misinterpreted as boléite (Mallard and Cumengé, 1891*a,b*), the first reliable chemical analysis for cumengéite (Friedel, 1906) led to the formula $4PbCl_2 \cdot 4CuO \cdot 5H_2O$. The space group symmetry ($I4/mmm$) and unit-cell parameters (a 15.14, c 24.66 Å) were determined by Gossner and Arm (1929) and Hocart (1930). Later, the chemical composition of a synthetic compound with an XRD pattern identical to that of cumengéite was reported as $5.5PbCl_2 \cdot 5Cu(OH)_2 \cdot 0.5H_2O$ (Mücke, 1969). More recently, another formula for cumengéite was given: $Cu_{24}Pb_{19}Cl_{42}(OH)_{44}$ (Winchell and

Rouse, 1974). The crystal-chemical formula accepted nowadays was eventually determined by Hawthorne and Groat (1986) on the basis of a structural study, and is $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}$ [or $20Cu(OH)_2 \cdot 21PbCl_2$].

Besides Boléo, cumengéite was reported from a few other localities: e.g. Newport Beach, Falmouth, Cornwall, England (Dean, 1982; Dean *et al.*, 1983); Abersoch, Gwynedd, Wales (Dossett and Green, 1988); and Ashburton Down, Western Australia (Nickel and Gartrell, 1993). Cumengéite occurs also as anthropogenic material within slags from Lavrio, Attiki, Greece (Kohlberger, 1976), from Val Varenna, Liguria, Italy (Palenzona *et al.*, 1998), and from the Etruscan metallurgical district (Capattoli, Baratti and nearby localities), Toscana, Italy (Bonotti, 2000). The history of the discovery of cumengéite from the type locality was outlined by Bariand *et al.* (1998).

In this paper we describe the first Italian occurrence of natural cumengéite, from Vesuvius, together with a short account of the

mineralogy of that locality. Moreover, a detailed crystal-structure refinement of cumengéite is presented, which allowed us to establish the positions of the hydrogen atoms belonging to hydroxyl groups, and to confirm the presence of additional water molecules leading to a more accurate chemical formula for the mineral.

The minerals of Vesuvius

Somma-Vesuvius is a composite central volcano comprising an ancient layer-volcano, Mount Somma, and a more recent cone, i.e. that of Vesuvius. Somma-Vesuvius has had a very variable eruptive history, with long periods of inactivity alternating with violent Plinian eruptions or with periods of semi-continuous, predominantly effusive, activity. After the sub-Plinian eruption of 1631, there was Strombolian activity (with open conduit) and effusive-explosive eruptions. Such eruptions alternated with short dormant periods. The last cycle of activity seems to have ended in the March 1944 eruption (Arnò *et al.*, 1987). This eruption marked the beginning of a quiescent phase characterized by moderate signs of both fumarolic and seismic volcanic activity.

This volcano is one of the richest areas in the world as far as mineralogical species are concerned: a total of 230 minerals is listed (after Russo, 2003); of these, more than one third (97 species) are fumarolic minerals, and for 37 of them, Vesuvius represents the type locality (Table 1).

The fumarolic activity is quite widespread on the upper rim western sector and at the bottom of the crater and is characterized by low gas flows and temperatures which at present reach ~100ºC (Russo, 1995; Chiodini *et al*, 2001).

Very little is known about the minerals formed in the fumaroles of 1944, probably because of the war ongoing at that time. The first information was given by Parascandola (1951), who listed tenorite, cotunnite, opal, sulphur, halite, gypsum and erythrosiderite at the fumaroles, sal ammoniac and hematite within the lava, and siderazot on the scoria.

At present, the crater fumaroles are of hydrothermal type with temperature rarely exceeding 100ºC.

Rock silicates are transformed into opal by the action of gases. Sassolite is another species occurring at that site. On the pre-existing tenorite, formed since the beginning of the 1960s, species that can be found are: opal, fluorite, chalcanthite and cotunnite (Russo and Langella, 1996).

Among the minerals which can be found on the fumaroles at the crater bottom are potassium

TABLE 1. Fumarolic minerals occurring on Vesuvius: 97 species and 18 doubtful species, marked with (?); those for which Vesuvius represents the type locality (37 species) are set in italic (after Russo, 2003, modified).

Native elements	selenium, siderazot, sulphur
Sulphides	chalcopyrite, *covellite*, galena, millerite, orpiment(?), pyrite, pyrrhotite, realgar
Halides	atacamite, *avogadrite*, bararite, bischofite(?), *carobbiite*, chloraluminite, *chlormanganokalite*, chlorocalcite, chloromagnesite, connellite, cotunnite, *cryptohalite*, cumengéite, *eriochalcite*, *erythrosiderite*, *ferruccite*, fluocerite(?), fluorite, halite, hieratite, hydrophilite(?), *kremersite*, lawrencite, matlockite(?), *malladrite*, *melanothallite*, *mitscherlichite*, *molysite*, paratacamite, *pseudocotunnite*, ralstonite, rinneite, *sal ammoniac*, *scacchite*, *sylvite*, villiaumite(?)
Oxides and hydroxides	cuprite, downeyite(?), gibbsite, hausmannite, hematite, *magnesioferrite*, magnetite, portlandite, sénarmontite(?), *tenorite*, valentinite(?)
Carbonates	azurite, nahcolite, natron, thermonatrite, trona
Borates	sassolite
Sulphates	aluminite, alunite, alunogen, anglesite, anhydrite, antlerite, *aphthitalite*, baryte, *bassanite*, boothite(?), chalcanthite, *chalcocyanite*, *chlorothionite*, connellite, coquimbite(?), *cyanochroite*, *dolerophanite*, epsomite(?), *euchlorine*, ferrinatrite, ferroexahydrite, glauberite, gypsum, halotrichite, jarosite, langite(?), leonite(?), linarite, mallardite(?), *manganolangbeinite*, *mascagnite*, *matteuccite*, *mercallite*, metavoltine, melanterite(?), mirabilite, misenite, *palmierite*, pickeringite, *picromerite*, piypite, polyhalite, *potassium alum*, thénardite, voltaite
Phosphates, vanadates	"mimetite", fluellite(?), volborthite
Silicates	*litidionite*, opal

alum, baryte, gypsum, halotrichite, metavoltine, opal, pickeringite and sulphur (Russo, 1997, 1998).

Description of cumengéite

Cumengéite was discovered in 1997 by one of us (MR), within small scoriae near fumaroles on the eastern part of the crater of Vesuvius. The temperature of the fumarola is at present ~70–80°C, whereas in 1954 it was close to 800°C (Parascandola, 1959).

Cumengéite occurs as small transparent indigo-blue crystals with adamantine lustre. Crystals generally display a pseudo-cubo-octahedral shape and maximum dimension of 0.1 mm (Fig. 1). The mineral is associated with tenorite, gypsum and cotunnite.

The X-ray powder pattern of cumengéite has been collected with a Gandolfi camera (diameter 114.6 mm, Cu-$K\alpha$ radiation, $\lambda = 1.54178$ Å) and is shown in Table 2. Intensities were assigned with the help of a digitized pattern profile. The following unit-cell parameters were obtained through least-squares refinement of 42 unambiguously indexed lines: a 15.109(3), c 24.48(2) Å, $V = 5588.3$ Å^3.

Crystal-structure analysis

A very small crystal fragment (dimensions $0.04 \times 0.04 \times 0.03$ mm^3) was mounted on a Nonius KappaCCD diffractometer, equipped with a Mo X-ray tube ($\lambda = 0.71073$ Å) operating at 55 kV and 30 mA. The intensity data were collected with a crystal-to-detector distance of 25 mm. As a first step, 10 φ-rotation images with
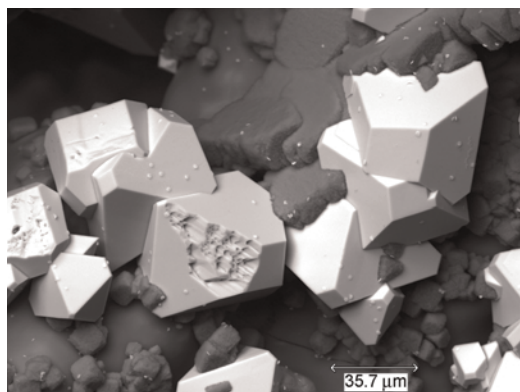

FIG. 1. SEM image of pseudo-octahedral bipyramidal crystals of cumengéite from Vesuvius.

frame widths of 1° were collected for the initial orientation matrix and cell setting. Then a total of 272 images with frame widths of 2° and 9 min of exposure per frame were collected, corresponding to 44.4% of the reciprocal space. The reflections were collected up to a resolution of 0.58 Å (θ_{max} = 37.78°) in ~41 h.

The following unit-cell parameters were refined using all measured reflections: a 15.1007(2), c 24.4940(4) Å, $V = 5585.4(1)$ Å^3. The refined mosaicity of the crystal was 0.579(1)°.

The three-dimensional data were reduced using the DENZO-SMN program from Nonius which is based on the HKL package (Otwinowski and Minor, 1997). A semi-empirical absorption correction was accomplished in DENZO-SMN using the redundancy of data measurements. 47733 reflections were extracted from the collected images. The value of R_{int}, computed on squared structure amplitudes from merging equivalent reflections in the $I4/mmm$ space group after absorption correction, was 6.87%. A set of 4177 independent reflections was obtained. Of these, 3462 were considered 'observed' having $F_o > 4\sigma(F_o)$ and were used for the least-squares refinement, which was carried out with the SHELXL-93 software package (Sheldrick, 1993).

The structural model of cumengéite was refined starting from the fractional coordinates for non-H atoms taken from Hawthorne and Groat (1986), and the R factor dropped rapidly to 4.1%. At this stage, two unexpected weak maxima were observed in the difference Fourier map. These were interpreted as water molecules, on the basis of their position and electron density, and included as such in the refinement (O5 and O6 sites). All these atoms were refined anisotropically. Some additional very weak maxima were also detected in the expected positions for hydrogen atoms. Those maxima were included in the last least-squares cycles and refined isotropically with a soft metric constraint for O4−H4 distance only. In total, four hydrogen positions were refined, linked to O1, O2, O3 and O4, respectively, each belonging to a hydroxyl group, whereas the hydrogen atoms belonging to the water molecules were not found in the difference Fourier map. The refinement converged to the following reliability indices: $R1$ (conventional R factor) = 0.036 for 3462 observed reflections, and 0.048 for all 4177 reflections; $wR2$ (weighted R on squared structure amplitudes) = 0.088; S (goodness of fit) = 1.21. There were 114 refined parameters. Maximum positive and negative peaks in the final difference

TABLE 2. X-ray powder pattern of cumengéite. Intensities were estimated by eye*. The refinement of the unit-cell parameters was carried out using 42 reflections (all those with unique indices, with the exception of those marked with an asterisk)

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
mw	12.17	12.25	002	vw	2.066	2.061	626
vw	7.53	7.55	200	m	2.037	2.036	3.0.11
mw	7.14	7.18	103	S	2.019	2.022	439
vw	6.10	6.12	004			2.016	554
w	5.20	5.20	213			1.983	730
mS	4.90	4.89	222	mw	1.982	1.983	4.2.10
mw	4.75	4.76	204			1.977	538
vw	4.48 *	4.45	312			1.966	3.2.11
vw	4.28	4.28	303	w	1.963	1.957	732
vw	4.14	4.13	321	vw	1.919	???	
m	4.02	4.02	224			1.892	716
ms	3.76	3.775	400	mS	1.888	1.892	556
		3.727	323			1.888	800
mw	3.57	3.559	330	vw	1.834	1.831	820
w	3.41	3.418	332	w	1.804	1.804	804
		3.409	107	vw	1.791	1.792	4.3.11
m	3.244	3.243	226			1.761	662
vw	3.181	3.183	325			1.755	750
m	3.107	3.107	217	m	1.756	1.755	6.0.10
vw	3.073 *	3.062	008			1.754	824
w	3.000	2.997	501	vw	1.731	1.727	833
		2.997	431	m	1.710	1.710	6.2.10
vw	2.936	2.933	415	vw	1.690	1.691	709
mw	2.839	2.837	208	vw	1.668	1.671	826
w	2.778 *	2.786	521			1.668	910
vw	2.736	???		vw	1.626	1.628	844
		2.678	109	vw	1.602	1.603	5.3.12
s	2.673	2.669	440	w	1.588	1.587	2.1.15
		2.666	514			1.549	7.0.11
w	2.603	2.608	442	mw	1.547	1.543	749
vw	2.577	2.577	318	vw	1.527	1.525	770
vw	2.518	2.517	600	vw	1.513	1.514	772
vw	2.476	2.470	611	w	1.484	1.483	927
mw	2.440	2.447	444	w	1.460	1.460	6.5.11
		2.434	525			1.444	10.3.1
vs	2.392	2.397	516	vw	1.441	1.440	6.6.10
		2.394	309			1.439	10.2.4
w	2.345	2.344	622	vw	1.430 *	1.433	7.4.11
vw	2.327	2.330	2.0.10	vw	1.411	1.411	5.2.15
		2.321	338	w	1.384 *	1.386	8.0.12
vw	2.270	2.268	428			1.365	778
		2.266	543	vw	1.364	1.364	875
vw	2.244	2.242	631			1.364	6.1.15
vw	2.227	2.226	2.2.10	w	1.335	1.335	880
ms	2.190	2.188	527	vw	1.321 *	1.323	958
mw	2.147	2.149	701			1.300	8.5.11
		2.142	606	mw	1.297	1.297	967
w	2.098	2.104	712	vw	1.281	1.282	5.2.17
		2.094	640	vw	1.271	1.271	3.3.18

Intensities were estimated by eye: vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak

TABLE 3. Final fractional coordinates and equivalent isotropic displacement parameters (Å^2) for cumengéite from Vesuvius.

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Pb1	0	0	0	0.0180(2)	0.0180(2)	0.0299(4)	0	0	0	0.0220(2)
Pb2	0	0	0.31957(4)	0.0272(2)	0.0272(2)	0.0416(4)	0	0	0	0.0320(2)
Pb3	0.27631(2)	0	0.23447(2)	0.0227(1)	0.0200(1)	0.0266(1)	0	0.0000(1)	0	0.0232(1)
Pb4	0.19781(2)	0.19781(2)	0.36442(1)	0.02182(9)	0.02182(9)	0.0248(1)	−0.00339(7)	−0.00339(7)	−0.0015(1)	0.0223(1)
Pb5 *	½	0	0.41062(4)	0.0210(4)	0.0231(4)	0.0259(4)	0	0	0	0.0235(2)
Cu1	0.26035(5)	0.09629(4)	0.09129(3)	0.0191(3)	0.0139(3)	0.0225(3)	0.0004(2)	0.0033(2)	0.0008(2)	0.0185(1)
Cu2	0.26143(7)	0.26143(7)	0	0.0186(3)	0.0186(3)	0.0156(5)	0	0	0.0036(4)	0.0176(2)
Cl1	0.1328(2)	0.1328(2)	0	0.045(1)	0.045(1)	0.036(2)	0	0	−0.026(2)	0.041(1)
Cl2	0.3812(1)	0.1267(1)	0	0.0271(7)	0.0299(7)	0.0294(6)	0.0063(6)	−0.0058(6)	−0.0074(6)	0.0290(3)
Cl3	0	0	0.1190(3)	0.026(1)	0.026(1)	0.041(2)	0	0	0	0.031(1)
Cl4	0.1687(2)	0	0.3762(1)	0.039(1)	0.023(1)	0.074(2)	0	−0.020(1)	0	0.0455(8)
Cl5	0.1274(1)	0.1274(1)	0.2461(1)	0.0326(7)	0.0326(7)	0.02577(9)	0.0027(6)	0.027(6)	0.0101(9)	0.0305(5)
Cl6	0.3694(3)	0	½	0.028(2)	0.016(1)	0.134(5)	0	0	0	0.061(2)
O1 (OH)	0.3017(3)	0.1766(3)	0.4411(2)	0.022(2)	0.016(2)	0.018(2)	0.001(1)	0.001(1)	0.004(1)	0.0189(8)
O2 (OH)	0.1865(3)	0.1865(3)	0.1270(3)	0.017(1)	0.017(1)	0.023(2)	0.004(1)	0.004(1)	0.003(2)	0.019(1)
O3 (OH)	0.2116(4)	0	0.1368(2)	0.016(2)	0.018(2)	0.020(2)	0	−0.001(2)	0	0.018(1)
O4 (OH)	0.3264(4)	0	0.0574(3)	0.019(3)	0.016(2)	0.030(3)	0	0.007(2)	0	0.022(1)
O5 (H$_2$O)	0.3799(9)	0.3799(9)	0	0.093(8)	0.093(8)	0.039(7)	0	0	−0.026(11)	0.075(5)
O6 (H$_2$O)	0	0	0.442(2)	0.13(2)	0.13(2)	0.17(4)	0	0	0	0.14(1)
H1	0.327(10)	0.121(10)	0.461(6)	0.11(5)						
H2	0.154(6)	0.154(6)	0.144(5)	0.03(3)						
H3	0.146(8)	0	0.138(4)	0.02(3)						
H4	0.378(12)	0	0.032(9)	0.27(18)						

* Pb5 site is occupied at 50%

Fourier synthesis were +5.72 and −2.58 $e/Å^3$. All residual maxima were close to Pb atoms, a common feature of Pb halides, and probably related to minor inaccuracies in the modelling of the absorption surface.

Our structural results indicate that the chemical formula of cumengéite from Vesuvius should be revised with the inclusion of six water molecules. Crystal-chemical arguments, i.e. the likelihood of having two new sites for water molecules in meaningful positions, substantiated our hypothesis. However, it was still uncertain whether the new formula could be considered valid for cumengéite for the type locality as well, and hence for the mineral in the broad sense. Since the files of the previous intensity data collection and refinement by Hawthorne and Groat (1986) on cumengéite from Boléo were not available for re-appraisal (F.C. Hawthorne, pers. comm.), we carried out a new single-crystal study using a small crystal fragment taken from the holotype specimen stored in the Museum National d'Histoire Naturelle in Paris. The new data collection was carried out in the same laboratory as for the Vesuvius sample, using the same experimental conditions. No experimental data or structural parameters for this second structural study are reported here, but the final reliability indices were: $R1$ = 0.039 for 2892 unique reflections, $wR2$ = 0.124, S = 1.049. In cumengéite from Boléo, two additional maxima, corresponding to O5 and O6, were found in the difference Fourier synthesis, although the latter is somewhat less evident. These maxima were included in the final LS refinement cycles. The only difference between the Vesuvius and Boléo refinements is that the hydrogen atoms have not been detected in the latter case.

Structure description

Final fractional coordinates and displacement parameters and the bond distances for cumengéite from Vesuvius are given in Tables 3 and 4, respectively. In Table 4, the bond distances for cumengéite from Boléo are also given for comparative purposes.

The basic structural features of cumengéite have been described previously (Hawthorne and Groat, 1986). Similarly to the previous refinement, one of the Pb positions (Pb5) is half-occupied. We did not observe any doubling of unit-cell parameters, which might have allowed us to hypothesize a possible ordering of Pb5 and vacancies within neighbouring cells. As already anticipated, the main difference with respect to the previous refinement lies in the occurrence of two new sites for water molecules, O5 and O6.

Structurally, the water molecule O5 is linked to Cu2 and represents the missing vertex in the Cu2-

TABLE 4. Selected interatomic distances (Å) for cumengéite from Vesuvius and from Boléo. The multipliers are intended as equivalent bonds for the cations; those given for hydrogen bonds are intended as equivalent bonds for the acceptor anions.

	Vesuvius	Boléo		Vesuvius	Boléo
Pb1−Cl1 (×4)	2.836(4)	2.814(4)	Cu1−Cl1	3.002(2)	2.999(1)
Pb1−Cl3 (×2)	2.915(6)	2.902(6)	Cu1−Cl2	2.853(2)	2.859(2)
Pb2−Cl4 (×4)	2.901(3)	2.901(3)	Cu1−O1	1.978(4)	1.974(4)
Pb2−Cl5 (×4)	3.262(3)	3.261(3)	Cu1−O2	1.966(3)	1.958(3)
Pb2−O6	2.99(5)	2.78(1)	Cu1−O3	1.974(4)	1.974(4)
Pb3−Cl2 (×2)	2.833(2)	2.834(2)	Cu1−O4	1.949(4)	1.955(4)
Pb3−Cl2' (×2)	3.142(2)	3.136(2)	Cu2−Cl1	2.747(4)	2.751(4)
Pb3−Cl5 (×2)	2.973(0)	2.971(0)	Cu2−O1 (×4)	1.965(4)	1.965(4)
Pb3−O3	2.585(6)	2.574(6)	Cu2−O5	2.53(2)	2.51(2)
Pb4−Cl2 (×2)	3.094(2)	3.087(2)	O1−H1	1.05(15)	
Pb4−Cl4 (×2)	3.033(1)	3.032(1)	O2−H2	0.81(13)	
Pb4−Cl5	3.266(2)	3.262(3)	O3−H3	1.00(12)	
Pb4−O1 (×2)	2.469(4)	2.469(4)	O4−H4	1.00(2)	
Pb4−O2	2.480(6)	2.489(6)	O1−H1 ⋯ Cl6 (×4)	3.198(5)	
Pb5−Cl6 (×2)	2.946(3)	2.945(3)	O2−H2 ⋯ Cl5	3.180(7)	
Pb5−Cl2 (×4)	3.418(2)	3.417(2)	O3−H3 ⋯ Cl3 (×4)	3.222(7)	
Pb5−O4 (×2)	2.736(6)	2.732(7)	O4−H4 ⋯ O4	2.81(1)	

FIG. 2. The five independent Pb-centred polyhedra in the structure of cumengéite. Pb: smaller grey circles; Cl: larger light grey circles; O: larger dark-grey circles.

centred polyhedron, lying on the opposite side with respect to the Cl1 atom in a '4+2' octahedron displaying the typical Jahn-Teller distortion for Cu^{2+}. In the previous refinement, Cu2 was five-fold coordinated by 4 O + 1 Cl in a half-octahedral configuration. The water molecule O6 is linked to Pb2. In the previous refinement Pb2 was linked to 8 Cl in a squared antiprism configuration; here the additional oxygen represents a capping anion in one of the two squared bases.

It is worth noting that the five independent Pb atoms in cumengéite display five different coordinations: Pb1 = octahedron; Pb2 = mono-capped squared antiprism; Pb3 = monocapped trigonal prism; Pb4 = irregular 10-face polyhedron; Pb5 = bicapped trigonal prism (Fig. 2).

The bond valence balance was computed according to Brese and O'Keeffe (1991), and using the parameters proposed by Krivovichev and Brown (2001) for Pb–O bonds. This is shown in Table 5. Although it is not complete, since the

TABLE 5. Bond valence balance (v.u.) for cumengéite from Vesuvius. Left and right superscripts indicate the number of equivalent bonds for cations and anions, respectively. The bond valences involving Pb5 were divided by two in the horizontal sums, in keeping with the 50% occupancy of that site.

	Pb1	Pb2	Pb3	Pb4	Pb5	Cu1	Cu2	$\Sigma_a v$
Cl1	^{4x} 0.437					0.067 ^{x4}	0.133	0.838
Cl2			^{2x} 0.441 ^{2x} 0.191	^{2x} 0.218	^{4x} 0.091	0.100		0.996
Cl3	^{2x} 0.353							0.353
Cl4		^{4x} 0.367		^{2x} 0.257 ^{x2}				0.881
Cl5		^{4x} 0.138	^{2x} 0.302 ^{x2}	0.137				0.879
Cl6					^{2x} 0.325 ^{x2}			0.325
O1				^{2x} 0.356		0.446	^{4x} 0.462	1.264
O2				0.348		0.460 ^{x2}		1.268
O3			0.281			0.451 ^{x2}		1.183
O4					^{2x} 0.206	0.482 ^{x2}		1.067
O5							0.100	0.100
O6		0.123						0.123
$\Sigma_c v$	2.454	2.143	2.149	2.147	1.426	2.006	2.081	

hydrogen atoms linked to O5 and O6 are missing, the bond valence sums over anions are acceptable, if one considers that Cl3 and Cl6, which are clearly underbonded by Pb atoms, are acceptors of four equivalent O-H$\cdots$Cl hydrogen bonds each from hydroxyls. In the hydrogen-bond scheme, O1, O2 and O3 atoms are donors (and their bond valence sum, 1.26, 1.27, 1.18, should reduce a little), whereas O4 is both donor and acceptor and its bond valence sum, 1.07, remains unchanged). As for cations, the situation is also largely acceptable, apart from the large sum for Pb1. This could be caused by the unusual coordination of Pb1, which is encapsulated in a regular and quite small octahedron by six chlorines. Moreover, the high bond-valence sum for the Pb1 atoms is probably a result of the inadequacy of the Pb$-$Cl bond-valence parameters suggested by Brese and O'Keeffe (1991). As was shown by Krivovichev and Brown (2001) for Pb$-$O bonds, the $b = 0.37$ Å parameter is inappropriate for soft bonds such as Pb$-$O or Pb$-$Cl.

Chemical composition of cumengéite

The recognition of two new atomic sites for water molecules during the structure refinement allows us to redefine the chemical formula for cumengéite from Vesuvius as $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}\cdot6H_2O$ instead of $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}$. Analytically, the difference (6 water molecules per formula unit, corresponding to ~1.30 wt.% H_2O more) is quite small. We propose that this new chemical formula be considered the correct formula for the mineral, since we have also shown that cumengéite from Boléo (the type locality) displays the same feature.

As a further test, we reconsidered the chemical composition of cumengéite, starting from a very old, but accurate chemical analysis (Friedel, 1906) of cumengéite from the type locality. The analytical data, recalculated to oxide wt.% to conform with modern presentation, are as follows: CuO 20.27, PbO 58.68, H_2O 5.90, Cl 19.03, less O=Cl -4.29, total 99.59.

The recalculation of the chemical formula on the basis of 88 total anions (in keeping with the new proposed formula) is $Cu_{20.14}Pb_{20.78}Cl_{42.41}(OH)_{39.43}\cdot6.16H_2O$, and on the basis of 82 total anions is $Cu_{18.76}Pb_{19.36}Cl_{39.52}(OH)_{36.72}\cdot5.75H_2O$.

It is evident that the former recalculation gives a formula much closer to the theoretical one, and is in close agreement with the formula resulting from our structural study, thereby confirming the new ideal formula $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}\cdot6H_2O$ for cumengéite.

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