

Lapeyreite, $\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}$, a new mineral: Its description and crystal structure

HALIL SARP,¹ RADOVAN ČERNÝ,^{2,*} HAKKI BABALIK,¹ MURAT HATIPOĞLU,³ AND GILBERT MARI⁴

¹University of Adnan Menderes, Vocational School of Memnune Inci, Karacasu-Aydın, Turkey

²Laboratory of Crystallography, University of Geneva, 24, quai Ernest-Ansermet, Geneva, Switzerland

³University of Dokuz Eylül, Vocational School of Izmir, Buca-Izmir, Turkey

⁴Les Bartavelles, Quartier le Brec, 06390 Châteauneuf-Villeveille, France

ABSTRACT

Lapeyreite, ideally $\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}$, was found in the old copper mines of Roua (Alpes-Maritimes, France). It is invariably in intimate association with trippkeite. Other associated minerals are olivenite, malachite, gilmarite, cornubite, connellite, theoparacelsite, brochantite, cuprite, native copper, algodonite, and domeykite. Lapeyreite occurs in geodes of cuprite (0.5 mm diameter) as aggregates formed by perfect elongate rectangular crystals (up to $0.2 \times 0.05 \times 0.01$ mm in size), acicular fibrous crystals or powdery masses. The mineral is translucent (transparent in thin fragments), dark pistachio-green. It has a vitreous to adamantine luster and yellowish green streak. The tenacity is brittle and the fracture conchoidal. The rectangular crystals are elongate parallel to [010], flattened on (001), and have a perfect cleavage on {001}, and good cleavage on {100}. All crystals, without exception, are twinned on the (001) plane. The recognizable crystal forms are {100}, {010}, and {001}. In transmitted light, the mineral is pistachio-green, with strong pleochroism: X = light yellow-green, Y = pistachio-green, Z = dark pistachio-green; dispersion: $r > v$, medium. Lapeyreite is biaxial (+), with $n_\alpha \sim 1.82$, $n_\beta \sim 1.85$, $n_\gamma \sim 1.90$ (for $\lambda = 589$ nm). $2V_{\text{meas}} = 76^\circ$ (universal stage), $2V_{\text{calc}} = 77^\circ$. The optical orientation is $X \wedge c \sim 12^\circ$, $Y = a$, $Z = b$. The mean chemical composition determined by electron microprobe is (wt%): CuO 46.49, As_2O_5 45.82, H_2O (from crystal structure analysis) 6.30, total 98.61. The empirical formula calculated on the basis of nine structural O atoms (excluding molecular water) is $\text{Cu}_{2.96}\text{As}_{2.01}\text{O}_{6.99}(\text{OH})_{2.01} \cdot 0.77\text{H}_2\text{O}$. Lapeyreite is monoclinic, $C2/m$, $a = 19.158(3)$, $b = 2.9361(6)$, $c = 9.193(2)$ Å, $\beta = 103.26(1)^\circ$, $V = 503.32(6)$ Å³, $Z = 8/3$. The calculated density is 4.385 g/cm³ (based on the empirical formula). The strongest X-ray powder-diffraction lines are [$d(\text{Å})$ (I) (hkl): 7.36 (30) ($\bar{2}01$), 5.842 (40) (201), 4.476 (35) (002), 3.173 (90) ($\bar{6}01$), 2.984 (100) (003), 2.883 (30) ($\bar{6}02$), 2.484 (80) (311), 2.396 (40) (112, $\bar{8}01$), and 2.337 (35) (800). The crystal structure of lapeyreite was solved by direct methods (MoK α radiation) and refined on F^2 using all 617 observed reflections to $R = 0.069$. The structure of lapeyreite is formed by a three-dimensional network of CuO_3 square pyramids and AsO_4 tetrahedra with a water molecule in structural cavities. This structure shows some similarities to that of theoparacelsite. The mineral is named in honor of Laurent Lapeyre, an eminent mineral collector and expert on Roua minerals.

Keywords: Lapeyreite, new mineral, crystal structure, copper arsenate, Roua mines, Alpes-Maritimes, France

INTRODUCTION

Lapeyreite, $\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}$, is a new mineral discovered in samples collected by Laurent Lapeyre, Danielle Mari, Pierre Rolland (mineral collectors), and Gilbert Mari (President of the Association of Naturalists of Nice and the Alpes-Maritimes) in the old copper mines of Roua (North and South group, districts of Guillaumes and Daluis, respectively), which are situated in the northwest part of the Alpes-Maritimes department (France), about 50 km from Nice.

The mineral is named in honor of Laurent Lapeyre (b. 1973), the mineral collector who found the sample containing the mineral. Both the mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classifica-

tion (CNMNC) of the International Mineralogical Association (IMA). The holotype specimens are deposited in the Laboratory of Crystallography, University of Geneva, Switzerland (registration number CR.010) and in the University of Adnan Menderes, Vocational School of Memnune Inci, Karacasu-Aydın, Turkey (registration number KMY.25). Co-type material is deposited in the University of Dokuz Eylül, Vocational School of Izmir, Buca-Izmir, Turkey (registration number BM.73).

OCCURRENCE

The new mineral described in the present work occurs in the Roua copper deposits in the upper part of the Var valley (Daluis gorge) at the western margin of the Barrot Dome in the northeastern part of the Alpes-Maritimes area (France). The Dome is characterized by the presence of numerous showings

* E-mail: Radovan.Cerny@unige.ch

of cupriferous ore and consists of a small massif formed by a folded anticline, in which the Permian series is well developed, and is separated from the Meso-Cenozoic cover by an unconformity. The geology and metallogeny of this Dome have been studied by Vinchon (1984) and Mari (1992). The cupriferous ore occurs in two distinct zones 400 m apart: a northern and a southern zone situated, respectively, in the districts of Guillaume and Daluis. The mineralization is hosted by subvertical dolomite and calcite veinlets containing accessory aragonite, and consists of native copper, cuprite, domeykite, algodonite, koutekite, and native silver. The thickness of the veinlets varies from a few millimeters to a few centimeters. Detailed mineralogical study of this ore deposit has produced several secondary, rare, and unknown mineral species (Sarp et al. 1994, 1996). The new mineral described here occurs in small geodes of cuprite (0.5 mm in diameter) in association with trippkeite (always present), olivenite, malachite, gilmarrite (Sarp and Černý 1999), cornubite, connellite, theoparacelsite (Sarp and Černý 2001), brochantite, native copper, algodonite, and domeykite. In this paragenesis, the crystallization sequence of theoparacelsite and lapeyreite is probably as follows: oxidation of native copper produced cuprite; then, reaction of copper with solutions enriched in arsenous acid produced trippkeite precipitated on the earlier-formed cuprite. Subsequent oxidation of arsenous acid produced arsenic acid that also reacted with copper, yielding crystals of lapeyreite. In the material studied, olivenite is one of the earliest secondary minerals to crystallize. Olivenite crystals are sometimes pseudomorphed by theoparacelsite (Sarp and Černý 2001), but never by lapeyreite, which is a more hydrated phase than is theoparacelsite. These paragenetic relations suggest that theoparacelsite crystallized before lapeyreite.

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Lapeyreite occurs as aggregates formed by perfect elongate rectangular crystals up to $0.2 \times 0.05 \times 0.01$ mm in size, acicular fibrous crystals, and powdery masses. The rectangular crystals are elongate parallel to [010], flattened on (001). The crystal forms are {100}, {010}, and {001} (Fig. 1). Twinning was observed neither macroscopically nor with a standard binocular microscope. However, an X-ray single-crystal study demonstrated that all crystals, without exception, are twinned by mirror reflection on (001). Macroscopically, lapeyreite is dark pistachio-green with a vitreous to adamantine luster. The mineral is translucent in aggregates and transparent in thin fragments. The streak is yellowish green. Cleavage is perfect on {001} and good on {100}. Lapeyreite is brittle and has conchoidal fracture. Mohs hardness could not be measured. The measured density is approximately 4.3 g/cm^3 , but could not be determined precisely (the mineral sinks very slowly in a pure Clerici solution with a density of 4.2 g/cm^3). The calculated density is 4.385 g/cm^3 , based on the empirical chemical formula, and 4.397 g/cm^3 based on the idealized formula. The mineral is soluble in diluted HCl and does not fluoresce.

Optically, lapeyreite is biaxial positive, with $n_\alpha \sim 1.82$, $n_\beta \sim 1.85$, $n_\gamma \sim 1.90$ (for $\lambda = 589 \text{ nm}$). These refractive indices are not precise and should be considered with caution because the mineral is very quickly attacked by Cargille liquids with refractive indices >1.80 . $2V_{\text{meas}} = 76(2)^\circ$ (universal stage), $2V_{\text{calc}} \sim 77^\circ$.

Optical orientation: $X \wedge c \sim 12^\circ$, $Y = a$, $Z = b$. In transmitted light, the mineral is pistachio-green, with a strong pleochroism: $X =$ light yellow-green, $Y =$ pistachio-green, and $Z =$ dark pistachio-green; dispersion $r > v$, medium. The Gladstone-Dale constant K_c (Mandarino 1981), calculated for the oxide proportions, determined from the electron-microprobe data and the results of crystal-structure refinement, is 0.179 and 0.175, respectively. The value of K_p , calculated using the average index of refraction, is 1.857, and the calculated density is 0.195. For the same average index of refraction and the measured density, K_p is 0.199. This low compatibility ($1 - K_p/K_c = -0.114$) is probably due to the difficulties associated with measuring the indices of refraction.

CHEMICAL COMPOSITION

Chemical analyses (10) of lapeyreite were obtained with a Cameca SX 50 electron microprobe using wavelength-dispersive spectrometry (WDS), an accelerating voltage of 15 kV, a beam current of 11 nA, and beam diameter of $10 \mu\text{m}$. Qualitative examination by energy-dispersive spectrometry (EDS) showed only Cu and As. For quantitative analysis, trippkeite (Cu, As), copper metal (Cu), and arsenic metal (As) were used as standards. Two spots were analyzed using copper metal and arsenic metal, and eight spots with the trippkeite standard. The latter gave more uniform analysis totals. The results presented in Table 1 are the average of all 10 analyses. Due to the insufficiency of material for direct water determination, the H_2O content was estimated by difference. The presence of H_2O was confirmed by infrared spectroscopy (Perkin Elmer 1330 Spectrophotometer): absorption bands at 3400 , 3260 , 2960 , 2920 , and 2845 cm^{-1} are consistent with the stretching vibrations of H_2O molecules and (OH) groups, and the band at 1630 cm^{-1} with the bending vibration of H_2O molecules (Fig. 2). The presence of H_2O in lapeyreite was also confirmed by the crystal-structure solution. With the mean chemical composition and the H_2O calculated from structure determination, the empirical formula based on nine structural O atoms (excluding molecular H_2O) is $\text{Cu}_{2.96}\text{As}_{2.01}\text{O}_{6.99}(\text{OH})_{2.01} \cdot 0.77\text{H}_2\text{O}$. The idealized formula $\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}$ requires: 47.73 wt% CuO, 45.97 wt% As_2O_5 , 6.30 wt% H_2O , total 100 wt%.

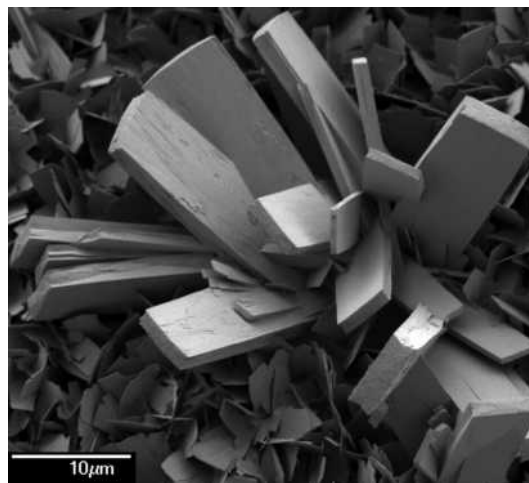


FIGURE 1. SEM photomicrograph of lapeyreite crystals, elongate along [010] and flattened on (001). The crystal forms are {100}, {010}, and {001}. A crystalline crust of small bladed crystals is also lapeyreite.

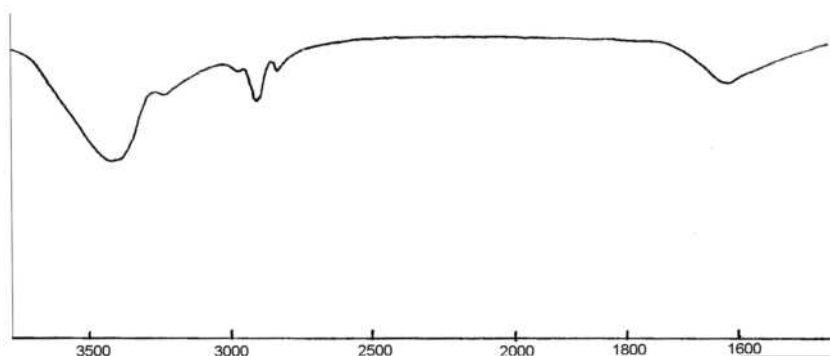


FIGURE 2. IR spectrum of lapeyreite in the 3750–1400 cm^{-1} range.

X-RAY CRYSTALLOGRAPHY

Powder X-ray diffraction data (Table 2) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered $\text{CuK}\alpha$). The relative intensities of the reflections were estimated visually. A single crystal of lapeyreite $0.085 \times 0.045 \times 0.015$ mm in size was examined by the precession method (Ni-filtered $\text{CuK}\alpha$) and the same crystal was measured on a Stoe IPDS-1 diffractometer with monochromatized $\text{MoK}\alpha$ radiation and an imaging plate detector. The lattice parameters were refined on the basis of 2000 reflections with the index ranges $-24 < h < 23$, $-3 < k < 3$, $-4 < l < 11$, and $\theta_{\text{max}} = 26.93^\circ$: $a = 19.158(3)$, $b = 2.9361(6)$, $c = 9.193(2)$ Å, $\beta = 103.26(1)^\circ$, and $V = 503.31(6)$ Å³. The crystal is twinned on the (001) plane. The twin matrix is:

$$\begin{array}{ccc} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0.229 & 0 & 1 \end{array} \quad (1)$$

The reflections belonging to two domains were identified by using the twin matrix and refined using the TWIN instruction in the SHELXL software (Sheldrick 1997). The results obtained from the data for the first domain, which occupies 75% of the crystal volume, were used in the structure solution and refinement. A total of 2277 reflections were measured, of which 1981 (617 unique) belong to the first domain; $R_{\text{int}} = 0.029$ was calculated for 1024 non-overlapping reflections (328 unique) of the first domain. The structure was solved in space group $C2/m$ by direct methods with the SHELXS program (Sheldrick 1997), and refined on F^2 (without H atoms) using all 617 observed reflections. The refinement converged to $R = 0.069$, $R_w = 0.188$, and $Goof = 1.289$ with 60 parameters. The largest residuals in the difference-Fourier map were -1.71 and 2.38 e/Å³. A CIF is on deposit¹.

Diffuse-intensity patterns were obtained at the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF). Diffraction data were taken at 15 K (controlled with a Helijet open-flow helium cooler, Oxford Diffraction) using

¹ Deposit item AM-10-002, CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy, visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

the MAR345 Image Plate detector, at a wavelength of 0.71 Å and a crystal-to-detector distance of 120 mm. Diffraction frames were collected with 1° rotation and a 40 s exposure time.

CRYSTAL STRUCTURE

The refined formula of lapeyreite is $\text{CuO}_{1/3}[\text{AsO}_3(\text{OH})]_{2/3} \cdot 1/4(\text{H}_2\text{O})$ with $Z = 8$. This formula can be converted to the quasistoichiometric formula $\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}$ by tripling the b parameter (see the discussion of diffuse intensity below). Atomic coordinates, and equivalent isotropic displacement parameters are given in Table 3, and selected interatomic distances are listed in Table 4.

The crystal structure of lapeyreite (Fig. 3) consists of two Cu and two As sites. Both Cu atoms are coordinated by 5 O atoms in a square-pyramid arrangement, which is typical for Cu^{2+} . The four O atoms in the base of the pyramid are within the bond distance range 1.93–1.96 Å. The bond distance to the apical O

TABLE 1. Electron microprobe analyses (wt%) of lapeyreite

Constituent	Mean wt%	Range of 10 analyses	Std. dev.	Idealized formula
CuO	46.49	45.23–49.26	1.2	47.73
As ₂ O ₅	45.82	42.70–47.47	1.1	45.97
H ₂ O*	7.69			6.30
Total	100			100

Note: The idealized formula is $\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}$.

* By difference.

TABLE 2. X-ray powder diffraction data for lapeyreite indexed according to the structural model from the single-crystal study

l_{obs}	d_{obs}	d_{calc}	hkl	l_{obs}	d_{obs}	d_{calc}	hkl
<5	9.35	9.324	2 0 0	5	2.054	2.052	$\bar{6}$ 0 4
30	7.36	7.353	$\bar{2}$ 0 1	10	1.930	1.930	$\bar{7}$ $\bar{1}$ 2
40	5.842	5.823	2 0 1	5	1.792	1.791	$\bar{7}$ $\bar{1}$ 3
<<5	4.658	4.662	4 0 0			1.790	0 0 5
35	4.476	4.474	0 0 2	10	1.737	1.742	1 1 4
		4.451	$\bar{2}$ 0 2			1.734	5 1 4
90	3.173	3.170	$\bar{6}$ 0 1	15	1.695	1.693	9 1 0
<5	3.114	3.108	6 0 0			1.692	9 $\bar{1}$ 2
100	2.984	2.983	0 0 3	10	1.636	1.634	3 1 4
30	2.883	2.881	$\bar{6}$ 0 2	<5	1.610	1.609	9 1 1
<5	2.729	2.731	1 1 1			1.609	8 0 5
<5	2.671	2.669	2 0 3	10	1.555	1.556	$\bar{3}$ 1 5
10	2.618	2.616	3 $\bar{1}$ 1			1.556	4 0 5
80	2.484	2.480	3 1 1	5	1.531	1.530	7 1 3
40	2.396	2.395	1 1 2	15	1.494	1.493	9 1 2
		2.394	8 0 1			1.491	0 0 6
35	2.337	2.331	8 0 0				
5	2.090	2.087	3 1 3				
		2.083	8 0 3				

Note: Intensities estimated visually.

atom is much longer, 2.45 Å for Cu1 and 2.46 Å for Cu2. The sixth O atom (OW7), which would complete the square pyramid to an octahedron, is at a distance of 2.71 Å for Cu1 and 3.07 Å for Cu2. Thus, the Cu atoms are located close to the base of the pyramid, indicating that their true coordination is possibly

TABLE 3. Atom positions and displacement parameters for lapeyreite

Atom	x	y	z	U_{eq} (Å ²)	Occ.
Cu1	0.4273(2)	0	0.1752(3)	0.0225(7)	
Cu2	0.6720(2)	0	0.4773(3)	0.0203(7)	
As1	0.0826(2)	0	0.1689(4)	0.031(1)	2/3
As2	0.2258(2)	0	0.8049(4)	0.032(1)	2/3
O1	0.2155(9)	0	0.609(2)	0.024(3)	
O2	0.123(1)	0	0.357(2)	0.036(4)	
O3	0.9937(8)	0	0.172(2)	0.026(4)	
O4	0.1388(8)	0	0.824(2)	0.030(4)	
O5	0.761(3)	0	0.873(6)	0.18(2)	
O6	0.604(3)	0	0.109(7)	0.23(3)	
OW7	0.480(3)	0	0.472(6)	0.07(2)	1/2

Note: The equivalent isotropic atomic displacement parameters are expressed as $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

TABLE 4. Selected interatomic distances (Å) in lapeyreite

Cu1-O4	1.94(1)	Cu2-O2	1.95(1)
Cu1-O4	1.94(1)	Cu2-O2	1.95(1)
Cu1-O3	1.95(1)	Cu2-O1	1.97(1)
Cu1-O3	1.95(1)	Cu2-O1	1.97(1)
Cu1-O6	2.54(1)	Cu2-O1	2.46(1)
As1-O6	1.65(3)	As2-O5	1.68(3)
As1-O6	1.65(3)	As2-O5	1.68(3)
As1-O3	1.71(1)	As2-O4	1.72(1)
As1-O2	1.72(2)	As2-O1	1.76(2)

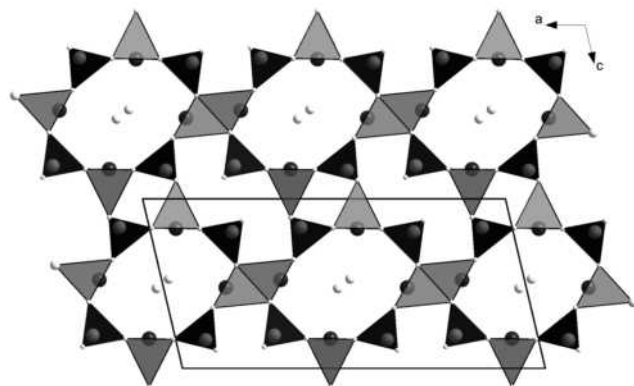


FIGURE 3. Crystal structure of lapeyreite viewed along *b*. The CuO₅ square pyramids in light gray, AsO₄ tetrahedra in dark gray, Cu in dark gray, and As in light gray. Disordered oxygen position OW7 of the water molecule shown as light spheres.

TABLE 5. Bond valence (v.u.) table for lapeyreite

	O1	O2	O3	O4	O5	O6	OW7	$\Sigma_A v$
Cu1			2 × 0.48 × 2	2 × 0.49 × 2				2.06
Cu2	2 × 0.46 × 2 0.12	2 × 0.48 × 2					0.12	2.00
2/3As1		1.14 × 0.667	1.17 × 0.667					5.05
2/3As2	1.02 × 0.667			1.14 × 0.667	2 × 1.27 × 1.334		2 × 1.37 × 1.334	4.70
$\Sigma_c v$	1.72	1.72	1.74	1.74	1.69	1.95		
1/3H					1.0 × 0.333			1
1/3H					0.1 × 0.333	0.9 × 0.333		1
H	0.1 × 0.125	0.1 × 0.125	0.1 × 0.125	0.1 × 0.125			0.9	1
H	0.1 × 0.125	0.1 × 0.125	0.1 × 0.125	0.1 × 0.125			0.9	1
Σ_{corr}	1.75	1.75	1.77	1.77	2.06	2.24	1.80	

Notes: The bond valences for H atoms were fixed to 1. Left and right multipliers refer to equivalent bonds for the cations and O atoms, respectively.

square planar. Both As atoms are coordinated by four O atoms in a tetrahedral configuration with As-O distances within the range 1.65–1.76 Å.

The structure of lapeyreite belongs to the group of $M = M - T$ framework structures according to the classification of Eby and Hawthorne (1993). The structure is formed by a three-dimensional network of CuO₅ square pyramids and AsO₄ tetrahedra with a water molecule in a structural cavity (Fig. 3). This structure is similar to the structure of theoparacelsite, in that it contains chains of CuO₅ square pyramids and AsO₄ tetrahedra running along the shortest cell axis (the *b* axis whose length is similar in both minerals). However, interconnectivity between the chains is different in the two minerals. The *c* axis of lapeyreite is approximately two times longer than the *c* axis of theoparacelsite. It displays a similar stacking pattern of the chains in one direction perpendicular to *c* with a double periodicity in lapeyreite. There are two symmetrically independent chains of CuO₅ polyhedra in lapeyreite, and there is only one type of chain in theoparacelsite. The reason for this is probably the presence of the H₂O molecule in the structure of lapeyreite, which results in completely different patterns of chain stacking along *a* in the two minerals.

The water molecule is the only difference in the chemical compositions of lapeyreite and theoparacelsite. This resembles the relationship between the Cu polysilicate CuSiO₃ and its hydrated counterpart, the mineral diopside, Cu₆Si₆O₁₈·6H₂O, or between the Cu polygermanate CuGeO₃ and synthetic germanate diopside, Cu₆Ge₆O₁₈·6H₂O. The compounds CuSiO₃ and CuGeO₃, known as spin-Peierls phases, have been recently identified as isostructural with theoparacelsite (Otto and Wolfram 2002), whose formula can be written also as CuAs_{2/3}H_{2/3}O₃, where Si⁴⁺ and Ge⁴⁺ are nominally replaced by {As_{2/3}H_{2/3}}⁴⁺ to maintain charge balance. The crystal structures of diopside (Heide et al. 1955) and diopside-type Cu₆Ge₆O₁₈·6H₂O (Brandt and Otto 1997) are, however, completely different from that of lapeyreite, the hydrated counterpart of theoparacelsite.

Because H atoms were not detected in the difference-Fourier map, the concept of bond valences (Brown and Kang Kun Wu 1976) was used to locate hydrogen bonds. The data of Brese and O'Keeffe (1991) were used to calculate the bond valences for all non-H atoms (Table 5). The bond-valence sum for O7 is zero, indicating an isolated H₂O molecule. The sums for all other O atoms range from 1.69 to 1.95, thus indicating that some of them may act as proton acceptors in H···O bonds. The bond-valence sums for the cations are in good agreement with their corresponding ionic charges. Based on the charge-balance considerations and on the dependence of H···O bond valence on O···O distance

(assuming stretched O-H...O bond angles) according to Brown and Altermatt (1985), we propose possible hydrogen bonds. The results are given in Table 5. Two H atoms compensate for the observed charge deficiency in the partly occupied As sites as in theoparacelsite, and transform one third of O atoms O5 and O6 in AsO_4 tetrahedra to OH groups. Two other H atoms interconnect water molecules in the cavity with O atoms O1, O2, O3, and O4. The presence of the OH groups and water molecule in the crystal structure is consistent with the infrared spectroscopy data. A possible local configuration of the hydrogen bonds is shown in Figure 4. However, as the H atoms of two OH groups compensate for the missing positive charge at the partially occupied As sites, it is possible that the protons are located inside the empty oxygen tetrahedra. The exact location of the H atoms in the structure remains to be ascertained.

The crystal structure of lapeyreite is disordered with respect to the occupancy of the As sites, as is the structure of theoparacelsite. The occupational disorder induces positional disorder in other atomic sites as reflected in relatively high values of displacement parameters for most of the atoms, which decreases the precision of the bond-valence calculations. The X-ray diffraction pattern of theoparacelsite shows a weak diffuse intensity in planes perpendicular to the b axis, and repeating with a periodicity of $1/3 b^*$. Lapeyreite shows exactly the same type of diffuse intensity. These planes can be recognized as weak lines in the reciprocal space plane ($hk0$) shown in Figures 5 and 6, and one such plane ($h 5/3 l$) is shown in Figure 7. The observed diffuse intensity probably stems from a local order in the chains of AsO_4 tetrahedra in both minerals. A fully ordered threefold superstructure would give a stoichiometric formula

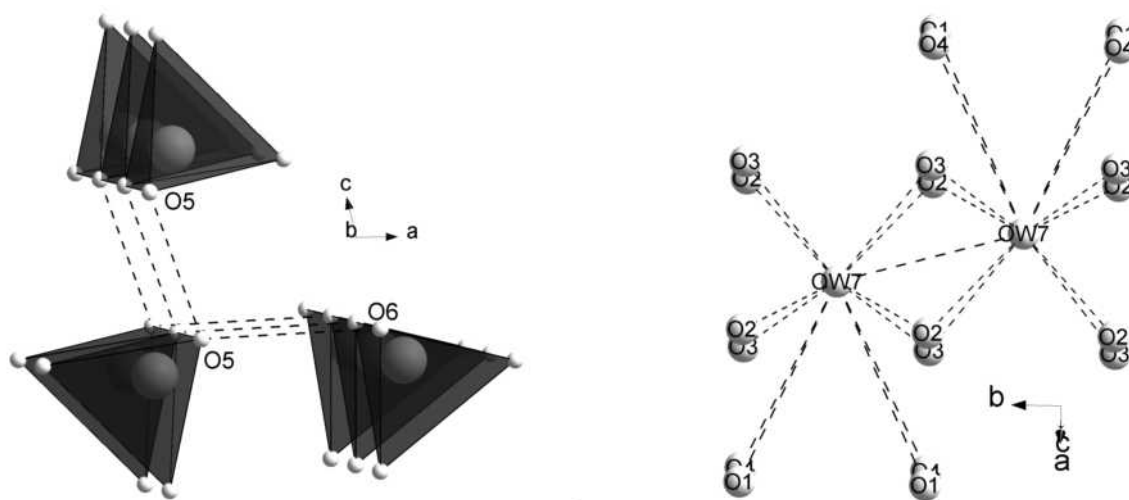


FIGURE 4. Possible hydrogen bonds in lapeyreite: (a) two hydrogen bonds between OH groups in AsO_4 tetrahedra, and (b) two hydrogen bonds between water molecules in the cavity and neighboring O atoms.

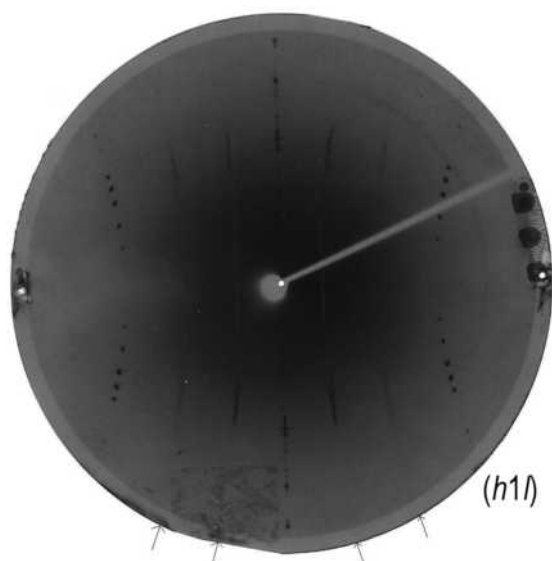


FIGURE 5. Rotation photograph around b showing two planes of diffuse intensity (marked by arrows) as continuous lines between the center of the film and the plane ($h1l$).

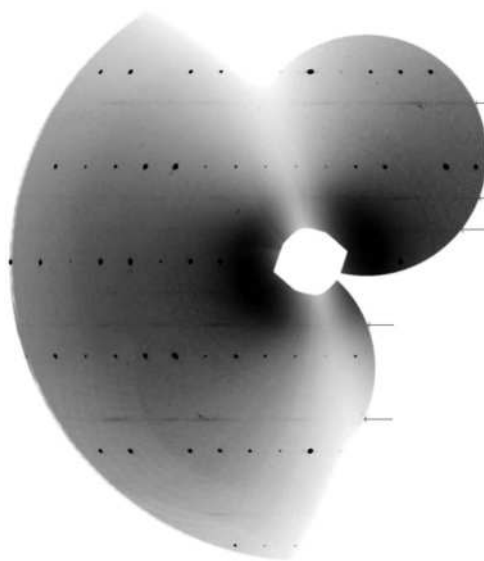


FIGURE 6. Planes of diffuse intensity (marked by arrows) perpendicular to the b axis, repeating with a periodicity of $1/3 b^*$ in lapeyreite.

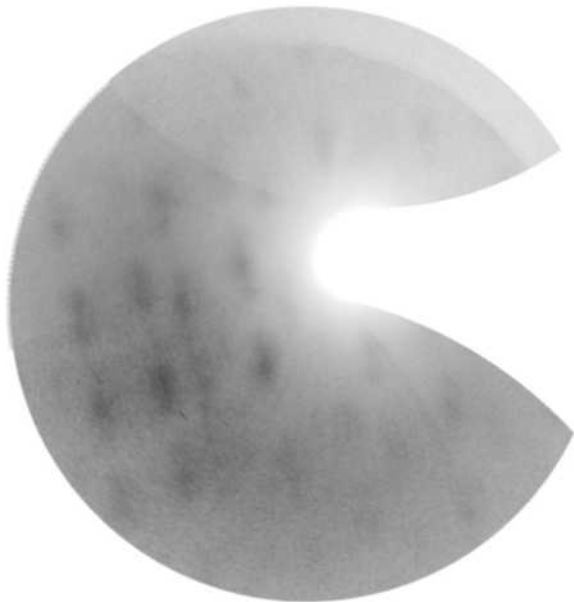


FIGURE 7. The most intense diffuse plane ($h\ 5/3\ l$) showing the arrangement of the diffuse intensity within the plane.

with $Z = 8$ for lapeyreite. The diffuse intensity is currently being modeled in both minerals.

ACKNOWLEDGMENTS

The authors thank Jean-Pierre Laugier, from Centre Commun de Microscopie Appliquée de l'Université de Nice-Sophia Antipolis, for assistance with the SEM photomicrographs. The help of Dmitry Chernyshov (SNBL, ESRF Grenoble) with the collection of diffuse intensity images is highly appreciated. The help of referees to improve the readability of manuscript is highly appreciated.

REFERENCES CITED

Brandt, H.-J. and Otto, H.H. (1997) Synthesis and crystal structure of $\text{Cu}_6[\text{Ge}_6\text{O}_{18}]\cdot 6\text{H}_2\text{O}$, a diopside-type cyclo-germanate. *Zeitschrift für Kristallographie*, 212, 34–40.

- Breese, N.E. and O'Keeffe, M. (1991) Bond valence parameters for solids. *Acta Crystallographica*, B47, 192–197.
- Brown, I.D. and Altermatt, D. (1985) Bond valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, B41, 244–247.
- Brown, I.D. and Wu, K.K. (1976) Empirical parameters for calculating cation-oxygen bond valences. *Acta Crystallographica*, B32, 1957–1959.
- Eby, R.K. and Hawthorne, F.C. (1993) Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallographica*, B49, 28–56.
- Heide, H.G., Boll-Dornberger, K., Thilo, E., and Thilo, E.M. (1955) Die struktur des diopside, $\text{Cu}_6\text{Si}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$. *Acta Crystallographica*, 8, 425–430.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV: The compatibility concept and its application. *Canadian Mineralogist*, 19, 441–450.
- Mari, G. (1992) *Les Anciennes Mines de Cuivre du Dôme de Barrot (Alpes-Maritimes)*, 112 p. Edition Serre, Nice.
- Otto, H.H. and Wolfram, H. (2002) Isotypism and low-dimensional physical properties of $\text{CuAs}_{2/3}\text{H}_{1/3}\text{O}_3$ (theoparacelsite), the spin-Peierls phase CuGeO_3 and CuSiO_3 . *Zeitschrift für Kristallographie*, 217, 431–434.
- Sarp, H. and Černý, R. (1999) Gilmarite, $\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$, a new mineral: Its description and crystal structure. *European Journal of Mineralogy*, 11, 549–555.
- (2001) Theoparacelsite, $\text{Cu}_3(\text{OH})_2\text{As}_2\text{O}_7$, a new mineral: Its description and crystal structure. *Archives des Sciences*, Genève, 54, 7–14.
- Sarp, H., Mari, G., Mari, D., and Rolland, P. (1994) Contribution à l'étude minéralogique des indices cuprifères de Roua (Daluis, Alpes-Maritimes, France). *Riviera Scientifique*, Nice, 47–56.
- (1996) Données nouvelles sur la minéralogie des indices cuprifères de Roua (Daluis et Guillaumes, Alpes-Maritimes, France). *Riviera Scientifique*, Nice, 27–36.
- Sheldrick, G.M. (1997) SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Vinchon, C. (1984) *Sédimentogenèse et métallogenèse du Permien du Dôme de Barrot (Alpes-Maritimes)*. Thèse d'Etat, University of Orléans, Document B.R.G.M., no. 70, 445 p.

MANUSCRIPT RECEIVED FEBRUARY 23, 2009

MANUSCRIPT ACCEPTED AUGUST 20, 2009

MANUSCRIPT HANDLED BY ANTON CHAKHMOURADIAN