

Redefinition of arhbarite, $\text{Cu}_2\text{Mg}(\text{AsO}_4)(\text{OH})_3$

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ABSTRACT

Arhbarite was described in 1982 as a new copper arsenate, $\text{Cu}_2(\text{OH})\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, from the Arhbar mine, Morocco. Due to the very small grain size no crystallographic data other than the X-ray powder diffraction data could be given. Reinvestigation of the type material and of new finds from the El Guanaco mine, Chile, is based on Rietveld refinement of X-ray powder data, electron microprobe investigations, optical studies as well as infrared and Raman spectra. The main results are: (1) arhbarite has the ideal formula $\text{Cu}_2\text{Mg}(\text{AsO}_4)(\text{OH})_3$ with magnesium oxide as an additional constituent and (2) arhbarite is isotypic with gilmarite, $\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$. Arhbarite is triclinic, space group *P1* (no. 1), unit-cell parameters (type material; refined from powder data) $a = 5.315(4)$, $b = 5.978(6)$, $c = 5.030(6)$ Å, $\alpha = 113.58(6)$, $\beta = 97.14(7)$, $\gamma = 89.30(8)^\circ$, $V = 145.2(1)$ Å³, $Z = 1$. Microprobe analyses of the type material gave MgO 10.20, CuO 47.46, NiO 0.20, CoO 0.24, As₂O₅ 33.85, SiO₂ 0.10, H₂O 7.58 (calc.), total 99.63 wt.%. The empirical formula is $\text{Cu}_{1.98}(\text{Mg}_{0.88}\text{Cu}_{0.09}\text{Ni}_{0.01}\text{Co}_{0.01})_{\Sigma 0.99}(\text{AsO}_4)_{1.02}(\text{OH})_{2.92}$, based on 7 O atoms. The Chilean arhbarite shows a slightly higher Cu content than the type material; it has the formula $\text{Cu}_{1.99}(\text{Mg}_{0.73}\text{Cu}_{0.25}\text{Zn}_{0.01})_{\Sigma 0.99}[(\text{AsO}_4)_{1.01}(\text{SiO}_4)_{0.01}]_{\Sigma 1.02}(\text{OH})_{2.92}$. The formal redefinition of arhbarite has been approved by the CNMMN of the IMA.

KEYWORDS: arhbarite, redefinition, Rietveld refinement, microprobe data, infrared spectra, Raman spectra, crystal chemistry, gilmarite.

Introduction

ARHBARITE was originally described as a new copper arsenate mineral with the formula $\text{Cu}_2(\text{OH})\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ from the Arhbar mine, Bou Azzer, Morocco (Schmetzer *et al.*, 1982), where it formed blue spherulitic aggregates (up to 0.3 mm in diameter) consisting of elongated acicular to platy crystals up to 10 µm long and 2 µm wide. The aggregates are grown on massive dolomite and associated with mcguinnessite $[(\text{Mg},\text{Cu})_2(\text{CO}_3)(\text{OH})_2]$ (sometimes closely intergrown with spherulites of the latter), hematite, löllingite, pharmacolite, erythrite and talc. The chemical formula was derived from electron microprobe analyses with H₂O calculated by

difference from 100%, since an experimental determination was not possible due to lack of suitable material. Because of the very small crystal size, no single-crystal X-ray investigations could be performed. The authors gave an unindexed X-ray powder diffraction pattern (Debye-Scherrer geometry), which showed no similarities with mineral species or synthetic compounds known at that time. Tentative indexing of the powder data revealed a possible monoclinic unit cell with $a = 16.988$, $b = 15.901$, $c = 6.100$ Å, $\beta = 97.5^\circ$ (Schmetzer *et al.*, 1982); though this was not felt to be particularly reliable. Schmetzer *et al.* (1982) suggested that arhbarite might be a 'hydrated euchroite', but they also mentioned an inconsistency regarding the refractive indices. If arhbarite $[\text{Cu}_2(\text{OH})\text{AsO}_4 \cdot 6\text{H}_2\text{O}]$ really was a hydrated euchroite $[\text{Cu}_2(\text{OH})\text{AsO}_4 \cdot 3\text{H}_2\text{O}]$, then the mean refractive index of arhbarite (mean $n = 1.73$) should be

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smaller than that of euchroite (mean $n = 1.71$). However, this is in contradiction to the experimental results.

In 1998 a second occurrence of arhbarite was discovered at the El Guanaco gold mine, near East Catalina Station, 93 km east of Taltal, Antofagasta, Chile (Färber *et al.*, 1998). The identity of the second find was confirmed by an XRD pattern and semiquantitative EDX analyses showing a good agreement with the data of the original description. Arhbarite samples of the second find were made available to the authors in 2001. A preliminary investigation by XRD methods confirmed the identity of arhbarite. However, a powder infrared (IR) spectrum (Fig. 1) showed only a very weak absorption in the range $1600\text{--}1650\text{ cm}^{-1}$ indicating very little or no molecular water, but very strong evidence for hydroxyl groups. This clearly indicated that the proposed chemical formula of Schmetzer *et al.* (1982) must be erroneous. Laser-Raman spectra of both the type and Chilean arhbarite also provided strong evidence for the presence of OH groups (see below). Unfortunately, the new material (like the original arhbarite samples) forms only dense, spherical or flattened rounded, blue aggregates composed of extremely small fibrous crystals, thus prohibiting any single-crystal investigations. Therefore, X-ray powder diffraction patterns were measured, with subsequent attempts at computer-aided indexing of the powder data (Visser, 1969). Different data sets were used because there were a few minor

differences between the new powder data and those published by Schmetzer *et al.* (1982), specifically the absence of the diffraction lines at 6.04, 4.26, 3.35 and 2.89 Å measured by Schmetzer *et al.* (1982). These might be caused by impurities like mcguinnessite, quartz and dolomite (see footnote in Table 2). The most promising unit cell found by computer indexing was a very small triclinic cell with $a = 5.31$, $b = 5.98$, $c = 5.03$ Å, $\alpha = 113.5$, $\beta = 97.3$, $\gamma = 89.3^\circ$ and $V = 145$ Å³. Subsequently, it was recognized that the unit-cell parameters and the powder data were very similar to the data of gilmarite, $\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$, a copper arsenate species recently described by Sarp and Černý (1999) as a polymorph of clinoclase. A tentative structural model for arhbarite was derived by Rietveld refinements based on the preliminary chemical composition $\text{Cu}_2(\text{OH})\text{AsO}_4 \cdot 2\text{H}_2\text{O}$ and the structural data of gilmarite, assuming one of the three Cu sites to be unoccupied.

Subsequent electron microprobe analyses of arhbarite from the El Guanaco mine surprisingly gave a Cu:As ratio of $\sim 2.3:1$. Neither the expected Cu:As ratio of 2:1 nor the absolute wt.% data given by Schmetzer *et al.* (1982) could be confirmed. Finally, a very careful and comprehensive microprobe study including new analyses of the type material (sample provided by G. Tremmel, the finder of the original material) revealed that arhbarite in fact contains an additional, previously overlooked constituent, namely magnesium. Obviously, the MgO

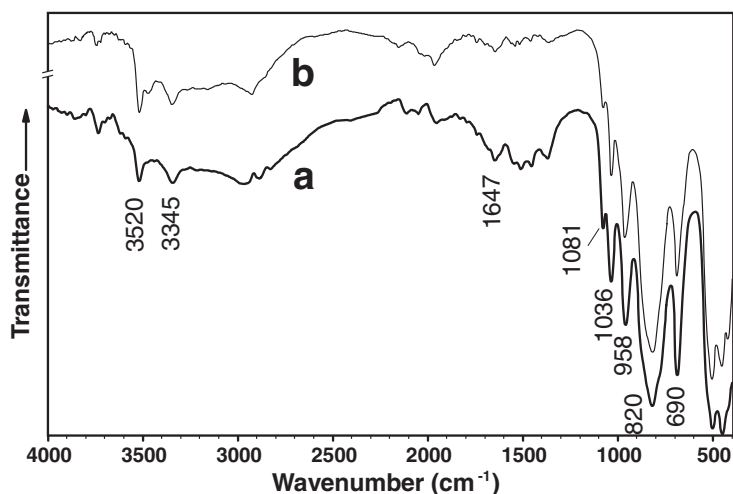


FIG. 1. FT-IR spectra of (a) the type and (b) Chilean arhbarite. See text for details and discussion.

content had not been detected in previous wavelength-dispersive electron-microprobe and energy-dispersive SEM X-ray analyses because of an almost complete overlap of the Mg- $K\alpha$ and the As- $L\alpha$ lines (for details see Chemical Data).

Paragenesis

Associated minerals at the type locality are dolomite, hematite, löllingite, pharmacolite, erythrite, talc and mcguinnessite. At the El Guanaco mine arhbarite is associated with brochantite, chrysocolla, olivenite, dolomite, baryte, iodargyrite (Färber *et al.*, 1998; this work) and a new, akrochordite-type Cu-Mg-arsenate, $\text{Cu}_2\text{Mg}_2(\text{Mg,Cu})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$ (Kolitsch *et al.*, 2000; IMA approved 2003-21). It is noteworthy that the Cu-Mg-arsenate arhbarite occurs at both localities in close association with other rare Cu-Mg-minerals, such as mcguinnessite, $(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2$, at the type locality, and the above-mentioned new Cu-Mg-arsenate at the El Guanaco mine.

Physical data

Due to the microcrystalline appearance only a portion of the physical data could be determined. The following data were given by Schmetzer *et al.* (1982): arhbarite aggregates show a blue colour, a sky-blue streak and a vitreous lustre. The refractive indices are $\alpha' = 1.720(5)$ and $\gamma' = 1.740(5)$; $2V$ is close to 90° and the optical character could not be determined. Pleochroism is distinct with $X' = \text{turquoise blue}$ and $Z' = \text{deep turquoise blue}$. The orientation is $X' = \text{parallel}$ and $Z' = \text{perpendicular}$ to the elongation of the crystals. Extinction is oblique, with an angle of $\approx 45^\circ$ to the axis of the morphological elongation.

In addition to the data given by Schmetzer *et al.* (1982) new hardness and density data could be determined. The hardness has been measured with a Vickers microhardness tester to be $\text{VHN}_{50} = 660(30) \text{ kg/mm}^2$, corresponding to 5 on the Mohs hardness scale. The density was determined by the sink-float method using Clerici solution; a mean value of $3.7(1) \text{ g/cm}^3$ was found for the Chilean

TABLE 1. Electron microprobe analyses¹ (wt.%) of arhbarite.

	Mean ²	Type material		Schmetzer <i>et al.</i> (1982)	Sample from El Guanaco mine		
		Range	Number of ions ³		Mean ⁴	Range	Number of ions ³
MgO	10.20	9.42–11.22	0.88		8.36	7.71–9.37	0.73
CuO	47.46	45.64–49.30	2.07	41.00	50.71	49.43–52.00	2.24
NiO	0.20	0.10–0.34	0.01		<0.05 ⁵		
CoO	0.24	0.03–0.54	0.01	0.03	<0.05 ⁵		
ZnO	<0.05 ⁵			0.01	0.13	0.08–0.18	0.01
FeO	<0.05 ⁵			0.04	<0.05 ⁵		
P ₂ O ₅	n.m. ⁶				0.10	0.00–0.19	<0.01
As ₂ O ₅	33.85	33.37–34.33	1.02	29.19	33.05	32.60–33.47	1.01
SiO ₂	0.10	0.07–0.15			0.24	0.19–0.35	0.01
H ₂ O ⁷	7.58				7.49		
Total	99.63				100.08		

¹ microprobe standards: mimetite (Pb, As), andradite (Fe, Ca), pyrope (Mg, Si), CaSO₄ (S), V metal (V), AlPO₄ (Al, P), CuS (Cu), ZnO (Zn), NiO (Ni) and Co metal (Co)

² means of 14 sets of electron-microprobe analyses; empirical formula: $\text{Cu}_{1.98}(\text{Mg}_{0.88}\text{Cu}_{0.09}\text{Ni}_{0.01}\text{Co}_{0.01})_{\Sigma 0.99}$

(AsO₄)_{1.02}(OH)_{2.92}

³ number of ions based on 7 oxygen atoms

⁴ means of 30 sets of electron-microprobe analyses; empirical formula: $\text{Cu}_{1.99}(\text{Mg}_{0.73}\text{Cu}_{0.25}\text{Zn}_{0.01})_{\Sigma 0.99}$

[(AsO₄)_{1.01}(SiO₄)_{0.01}]_{Σ1.02}(OH)_{2.92}

⁵ below detection limit; no contribution to analytical total

⁶ not measured

⁷ H₂O calculated to achieve 7 oxygen atoms in the idealized empirical formulae

material; a similar value was found for the type material. The density measurements were hampered by the small grain size and the fact that most of the grains tend to have small air bubbles attached to them. The calculated density according to Mandarino (1981*b*) is 4.03 g/cm^3 for the Chilean arhbarite and 3.96 g/cm^3 for the type material. Refractive indices determined on a Chilean sample, $\alpha' = 1.733(5)$ and $\gamma' = 1.754(5)$, are higher than the values given by Schmetzer *et al.* (1982) [$\alpha' = 1.720$ and $\gamma' = 1.740$], and confirm the larger Cu:Mg ratio in the Chilean material.

Chemical data

An electron microprobe (Cameca CAMEBAX, 10 nA, 20 kV, beam diameter $2 \mu\text{m}$) was used for chemical analyses; analytical results and standards are given in Table 1. The new analyses revealed Mg as one of the main elemental constituents. Obviously, the MgO content has not been detected in previous wavelength-

dispersive electron-microprobe and energy-dispersive SEM X-ray analyses because of an almost complete overlap of the Mg- $K\alpha_{1/2}$ (1.282 keV) and the As- $L\alpha_{1/2}$ (1.253 keV) lines. Small amounts of NiO, CoO, ZnO, SiO₂ and P₂O₅ were found; PbO, Al₂O₃, Fe₂O₃, V₂O₅ and SO₃ were below 0.1 wt.%. No other elements with atomic numbers >8 were detected. The Cu:As ratios of the new data and that of Schmetzer *et al.* (1982) are practically identical (2.026:1 vs. 2.029:1); however, the reason for the significantly lower CuO and As₂O₅ contents in the analyses of Schmetzer *et al.* (1982) remains unclear.

H₂O could not be determined experimentally due to lack of material; it was calculated to achieve 7 oxygen atoms in the idealized empirical formula. The presence of (OH)⁻ could be confirmed by Fourier-transform infrared (FT-IR) and laser-Raman spectra of samples from the El Guanaco mine, Chile and from the type locality. The spectra of samples from both localities are virtually identical. The IR spectra (Fig. 1) were

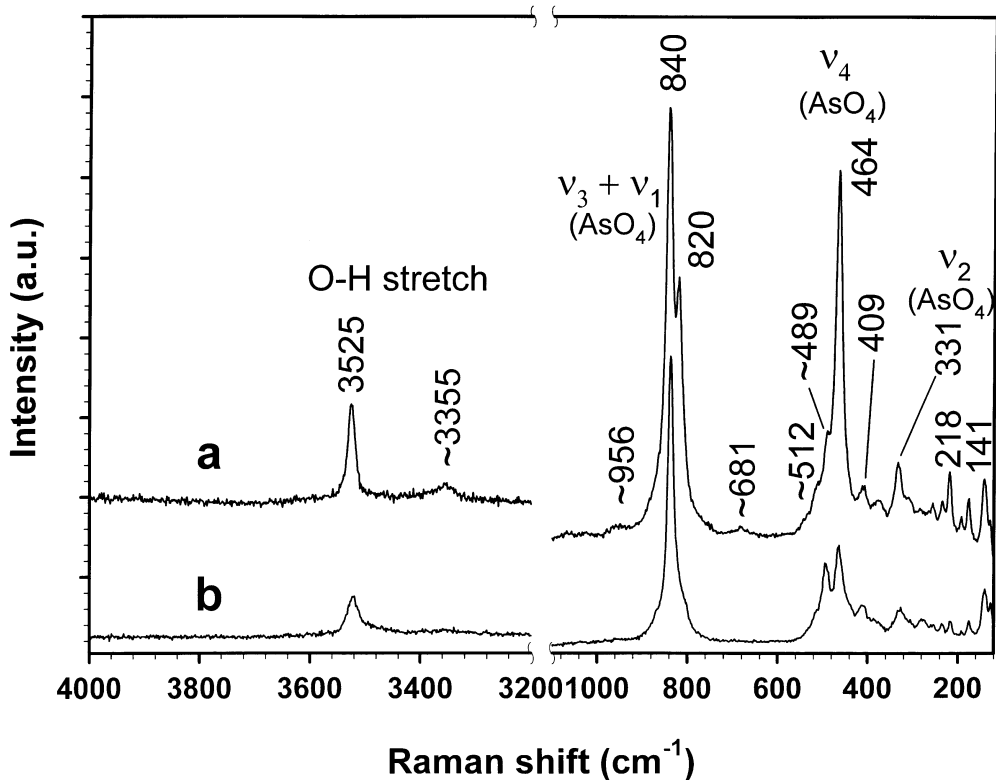


FIG. 2. Laser-Raman spectra of (a) the type and (b) Chilean arhbarite; the strong bands of the latter are at 3522, 837, 492, 464 and 411 cm^{-1} . See text for more details and discussion.

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recorded with a Nicolet 5PC FTIR using a diamond microcell (resolution $\pm 2 \text{ cm}^{-1}$, random sample orientation). The spectrum of the type material shows strong absorption bands (values for Chilean arhbarite in square brackets) at 3520 [3521] and 3345 [3346] cm^{-1} due to hydroxyl groups (O-H stretching vibrations). There is only an insignificant indication of molecular water

(feature at 1647 [1646] cm^{-1} in rough background), which might be due to absorbed moisture; no particular drying was applied prior to examination. Strong absorption bands between 400 and 1100 cm^{-1} are due to vibrations of the arsenate group: 1081 [1081], 1036 [1036], 958 [962], 820 [819], 690 [692], 504 [505], 453 [457] cm^{-1} . Schmetzer *et al.* (1982), who

 TABLE 2. X-ray powder diffraction data of arhbarite¹ and gilmarite.

Arhbarite sample from El Guanaco mine					Arhbarite type material ²			Gilmarite ³		
<i>h k l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>h k l</i>	<i>d</i> _{obs}	<i>I</i> _{obs}	
0 1 0	5.478	4	5.465	2			1 0 0	5.430	10	
1 0 0	5.263	15	5.261	15	5.26	20	0 1 0	5.321	15	
0 0 1	4.566	100	4.573	100	4.57	100	0 0 1	4.613	100	
0 1 $\bar{1}$	4.508	88	4.514	21	4.51	90	0 1 $\bar{1}$	4.580	50	
1 $\bar{1}$ 0	3.877	19	3.877	11	3.87	20	1 $\bar{1}$ 0	3.923	5	
1 1 0	3.719	56					1 1 0	3.690	10	
1 0 $\bar{1}$	3.701	39	3.703	61	3.72	60	1 0 $\bar{1}$	3.654	20	
1 1 $\bar{1}$	3.600	14	3.600	9	3.59	30	1 1 $\bar{1}$	3.535	15	
1 $\bar{1}$ 1	3.271	19	3.241	40	3.25	40	1 $\bar{1}$ 1	3.470	15	
1 0 1	3.242	47					1 0 1	3.390	60	
0 1 1	2.970	27	2.970	36	2.975	30	0 1 1	2.930	10	
0 2 $\bar{1}$	2.922	12	2.921	12	2.925	10	0 2 $\bar{1}$	2.892	<5	
0 2 0	2.739	5					2 0 0	2.713	40	
1 $\bar{1}$ $\bar{1}$	2.717	23	2.717	34	2.712	30	1 $\bar{1}$ $\bar{1}$			
2 0 0	2.632	45	2.633	65	2.632	40	0 2 0	2.663	10	
1 2 $\bar{1}$	2.600	57	2.598	16	2.603	50	1 $\bar{2}$ 1	2.579	10	
1 $\bar{2}$ 1	2.512	17	2.514	10	2.511	10	0 1 $\bar{2}$			
0 1 $\bar{2}$	2.492	17					1 2 $\bar{1}$	2.543	40	
1 1 1	2.474	16	2.472	38	2.474	50	1 1 1	2.491	5	
1 $\bar{2}$ 0	2.472	44					1 $\bar{2}$ 0	2.445	30	
2 0 $\bar{1}$	2.424	8					2 0 $\bar{1}$	2.420	5	
2 $\bar{1}$ 0	2.412	4	2.424	23	2.424	10	2 1 0			
1 2 0	2.389	6					2 1 $\bar{1}$	2.357	10	
2 1 $\bar{1}$	2.375	6	2.371	15	2.375	20	1 1 $\bar{2}$			
1 1 $\bar{2}$	2.371	19					1 2 0	2.331	<5	
0 2 $\bar{2}$	2.254	4	not observed				2 $\bar{1}$ 1			
2 $\bar{1}$ 1	2.182	11	2.190	12	2.189	20	0 0 2	2.310	10	
2 0 1	2.159	17					0 2 $\bar{2}$	2.289	10	
1 $\bar{1}$ 2	2.150	12	2.157	21	2.148	30	2 0 1			
1 2 $\bar{2}$	2.149	21					1 $\bar{1}$ 2	2.271	15	
2 $\bar{1}$ $\bar{1}$	2.086	10	2.085	19	2.088	10	1 0 $\bar{2}$	2.186	<5	
0 2 1	2.019	5	2.018	10	2.016	10	1 2 $\bar{2}$	2.124	20	

¹ X-ray powder diffractometer Philips X'pert MPD, internal standard Si, Cu-K α radiation; intensities were calculated with program LAZY PULVERIX (Yvon *et al.*, 1977); only reflections with $I_{\text{calc}} > 3$ were considered. A few broad diffraction lines [$d(\text{\AA})$ (II_0): 5.38 (4), 3.33 (9), 2.69 (15), 2.57 (9)] were attributed to impurities and are omitted in Table 2.

² Data from Schmetzer *et al.* (1982); diffraction lines at 6.04 ($II_0 = 10$), 4.23 (10), 3.35 (20) and 2.891 \AA (40) were omitted; these may be caused by impurities, such as mcguinnessite (strongest reflection at 6.039 \AA ; PDF 35-481), quartz (strongest reflections at 4.257 and 3.342 \AA ; PDF 33-1161) and dolomite (strongest reflection at 2.890 \AA ; PDF 36-426).

³ Data from Sarp and Černý (1999)

TABLE 3. Unit-cell parameters of arhbarite (refined from X-ray powder-diffraction data).

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
Type material ¹	5.315(4)	5.978(6)	5.030(6)	113.58(6)	97.14(7)	89.30(8)	145.2(2)
El Guanaco mine ²	5.318(1)	5.979(1)	5.035(1)	113.57(1)	97.13(1)	89.35(1)	145.5(1)
El Guanaco mine ³	5.311(1)	5.980(2)	5.026(1)	113.55(2)	97.31(2)	89.26(2)	145.0(1)

¹ Calculated from the data in Schmetzer *et al.* (1982)

² Philips X³pert powder diffractometer, transmission mode, horizontal capillary setting; data from Rietveld refinement

³ Philips X³pert powder diffractometer, reflection mode, internal Standard Si

recorded an IR spectrum of type arhbarite, observed O-H stretching vibrational bands at 3500 and 3325 cm⁻¹, in fairly good agreement with the bands at 3520 and 3345 cm⁻¹ observed for type arhbarite (Fig. 1). Schmetzer *et al.* (1982) also stated that the spectrum "provides qualitative evidence for the presence of water", but they did not provide a picture of the spectrum.

Laser-Raman spectra of both type and Chilean arhbarite (Fig. 2) were recorded in the range 4000–100 cm⁻¹ with a Renishaw M1000 MicroRaman Imaging System using a laser wavelength of 633 nm and excitation through a Leica DMLM optical microscope (spectral resolution ± 2 cm⁻¹, minimum lateral resolution 2 μ m, random sample orientation). The spectrum of type arhbarite shows O-H stretching vibrations at (values for Chilean arhbarite in square brackets) 3525 [3522] cm⁻¹ (sharp, slightly asymmetric band) and 3355 [3350] cm⁻¹ (small, broadened band). There was no indication of the presence of molecular water, although it must be pointed out that Raman spectroscopy is not very sensitive for the detection of water-bending modes. Vibrations of the arsenate group are responsible for the strong bands between 850 and approximately 300 cm⁻¹ (see exact values and suggested band assignments in Fig. 2); the different intensities for these vibrations are due to different orientations of the crystal aggregates measured. Most bands below ~ 400 –300 cm⁻¹ can probably be attributed to lattice modes. These bands are observed at 375 [381(sh = shoulder)], 331 [328], 307(sh) [305(sh)], 282 [278], 254 [255], 234 [234], 218 [217], 192 [191], 176 [175], 141 [140] and 128 [127] cm⁻¹ (note that most low-intensity bands are not labelled in Fig. 2).

The new empirical formula of type arhbarite based on 7 oxygen atoms per formula unit is Cu_{1.98}(Mg_{0.88}Cu_{0.09}Ni_{0.01}Co_{0.01}) $\Sigma_{0.99}$ (AsO₄)_{1.02}

(OH)_{2.92}. An exclusive occupation of the two [4+1]-coordinated Cu sites by copper was assumed; excess copper and the other cations (except As) were assigned to the [6]-coordinated Mg site. The corresponding empirical formula for the Chilean arhbarite is: Cu_{1.99}(Mg_{0.73}Cu_{0.25}Zn_{0.01}) $\Sigma_{0.99}$ [(AsO₄)_{1.01}(SiO₄)_{0.01}] $\Sigma_{1.02}$ (OH)_{2.92}. The Chilean arhbarite shows a slightly higher Cu content than the type material (Table 1). There is a distinct linear negative correlation between Cu and Mg ($R^2 = 0.95$; Fig. 3). Because Cu substitutes for the [6]-coordinated Mg, a solid solution series with gilmarite, Cu₃(AsO₄)(OH)₃, might exist. Additional incorporation of Mg on the two highly distorted [4+1]-coordinated Cu sites in gilmarite is considered improbable.

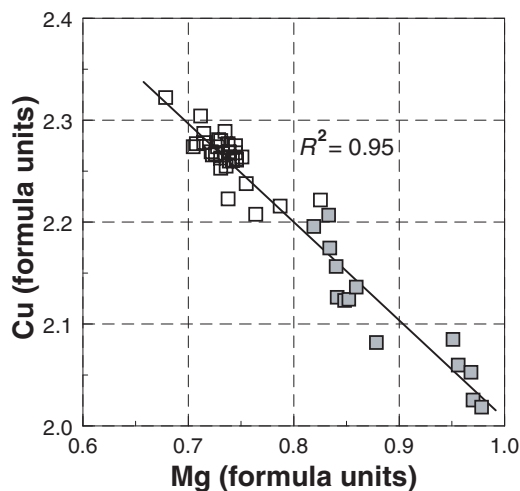


FIG. 3. Formula units of Mg vs. Cu (based on mean (Mg+Cu) = 3) derived from electron microprobe data in type (filled squares) and Chilean arhbarite (open squares). Trace amounts of Ni, Co and Zn were attributed to Cu.

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The compatibility according to the Gladstone-Dale relationship (Mandarino, 1981a) often serves as a plausibility check regarding physical and chemical data. The corresponding compatibility index based on the new chemical data of arhbarite is -0.007 for the type material and -0.011 for the Chilean material, both rated as superior, while the calculation using data from Schmetzer *et al.* (1982) (and $d = 3.96 \text{ g/cm}^3$) leads to $+0.155$ (rated as poor).

Crystallography

X-ray powder-diffraction data were obtained on samples from the El Guanaco mine, Chile. The results are compiled in Table 2 together with the data given by Schmetzer *et al.* (1982). Despite a few minor deviations, the new powder data correlate well with those given by Schmetzer *et al.* (1982). There are distinct similarities with the powder data of gilmarite (Sarp and Černý, 1999). Unit-cell parameters refined from the XRD data are compiled in Table 3. The unit-cell volume of gilmarite, $147.5(2) \text{ \AA}^3$, is slightly larger than that of type arhbarite, $145.2(2) \text{ \AA}^3$, and Chilean arhbarite, $145.0(1) \text{ \AA}^3$.

Single-crystal X-ray investigations were impossible because of the small size of the crystals available ($<10 \mu\text{m}$). Consequently, structural information was obtained by Rietveld refinement of the powder data (Rietveld, 1969). The refinement was started from the structural

TABLE 4. Fractional atomic coordinates of arhbarite from Chile¹ (first line) and gilmarite² (second line).

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu1	0.047(2)	0.599(2)	0.325(2)
Cu1	0.0492(2)	0.6036(2)	0.3224(2)
Cu2	0.548(2)	0.349(2)	0.351(2)
Cu2	0.5489(2)	0.3631(2)	0.3568(2)
Mg ³	0.566(4)	0.868(3)	0.353(4)
Cu3	0.5723(2)	0.8811(2)	0.3869(2)
As ⁴	0	0	0
As	$-0.0013(1)$	$0.0003(1)$	$0.0001(1)$

¹ Atomic parameters of the oxygen atoms were not refined

² Sarp and Černý (1999)

³ Occupation refined to Mg:Cu = 0.91(2):0.09(2)

⁴ Fixed to define the origin of the unit cell

parameters determined for gilmarite by Sarp and Černý (1999). The refinement clearly showed that the scattering power of the position Cu3 is smaller than those of the positions Cu1 and Cu2. Consequently, it was assumed that the position Cu3 in gilmarite is predominantly occupied by the Mg atoms in arhbarite as detected by the electron microprobe. This assumption is in accordance with crystal-chemical considerations: The Cu1 and Cu2 atoms exhibit a $[4+1]$ -coordination; the

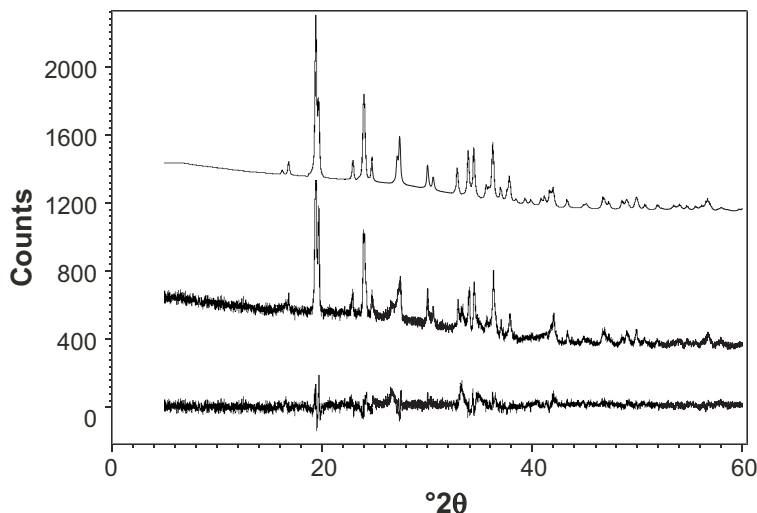


FIG. 4. Observed (middle), calculated (top) and difference (bottom) powder XRD patterns for arhbarite (sample from El Guanaco mine, Chile) refined in space group $P1$; the observed and calculated patterns have had 300 and 1100 counts added to each data point for clarity.

TABLE 5. Chemical, physical and crystallographic data of arhbarite and gilmarite.

	Arhbarite ¹	Gilmarite ²
Ideal formula	Cu ₂ Mg(AsO ₄)(OH) ₃	Cu ₃ (AsO ₄)(OH) ₃
Crystal symmetry	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>Z</i>	1	1
<i>a</i> (Å)	5.315(4)	5.445(4)
<i>b</i> (Å)	5.978(6)	5.873(3)
<i>c</i> (Å)	5.030(6)	5.104(3)
α (°)	113.58(6)	114.95(3)
β (°)	97.14(7)	93.05(5)
γ (°)	89.30(8)	91.92(4)
<i>V</i> (Å ³)	145.2(2)	147.5(2)
<i>D</i> (meas.) (g/cm ³)	3.7(1)	4.2(1)
<i>D</i> (calc.) (g/cm ³)	3.96	4.28
α	1.720(5)	1.760(5)
β	–	1.80(1)
γ	1.740(5)	1.83(1)
2 <i>V</i> (°)	near 90	77

¹ Type material; unit-cell parameters calculated from the powder diffraction data of Schmetzer *et al.* (1982). The reduced unit cell for arhbarite is $a = 5.030$, $b = 5.315$, $c = 5.978$ Å, $\alpha = 89.30$, $\beta = 66.42$, $\gamma = 82.86^\circ$. It is derived by the transformation (00 $\bar{1}$ /100/010) from the unit cell chosen to enable the comparison with gilmarite.

² Sarp and Černý (1999)

coordination figure is a tetragonal pyramid which is often found for divalent copper atoms (e.g. Eby and Hawthorne, 1990). However, the Mg atoms substitute for Cu at the [4+2]-coordinated position. Moderate shifts of the oxygen atoms allow the formation of a tetragonal bipyramid (characteristic for Cu(II) atoms) as well as a more or less regular octahedron (compatible with the stereochemistry of Mg atoms). The refined atomic coordinates of the cations (Table 4) are close to those given for gilmarite.

A refinement of the atomic coordinates of the oxygen atoms was not successful up to now. The admixture of small amounts of other phases causes a poor refinement (Fig. 4); attempts to identify the impurities were not successful. However, the correctness of the given unit cell is supported by different shapes of the peak profiles for arhbarite and the impurity phases and by different intensity ratios $I_{\text{arhbarite}}:I_{\text{admixture}}$ in individual patterns recorded from different samples.

A comparison of the essential data of arhbarite and gilmarite is given in Table 5. It demonstrates the very close relation between both species. The

formal redefinition of arhbarite was approved by the CNMMN of the IMA in September 2002.

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