

Barquillite, $\text{Cu}_2(\text{Cd}, \text{Fe})\text{GeS}_4$, a new mineral from the Barquilla deposit, Salamanca, Spain

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Abstract: Barquillite, ideally $\text{Cu}_2(\text{Cd}, \text{Fe})\text{GeS}_4$, is a new mineral species found in the Barquilla Sn-Ge-Cd-Cu-Fe vein-type deposit, Salamanca, Spain. This mineral occurs as plates and rosette-like aggregates of thin platy crystals, less than 50 μm in size. It is commonly in contact with tetrahedrite and chalcopyrite, less so with bornite, mawsonite, stannite and stannoidite. Barquillite is opaque, with a metallic luster. In reflected light, it has a grey colour with a violet tint, very weak pleochroism, very weak birefractance, and is very weakly anisotropic. Reflectance spectra are given. The micro-indentation hardness ranges between 180 and 300 kg/mm^2 . The mean of thirty four analyses gives: Cu 30.67, Ag 0.26, Cd 20.38, Fe 2.20, Mn 0.43, Zn 0.09, Ge 14.99, Sn 0.17, Sb 0.09, Bi 0.16, Ga 0.05, S 29.42, a total of 98.91 wt.%, corresponding to: $(\text{Cu}_{2.10}\text{Ag}_{0.01})_{\Sigma 2.11}(\text{Cd}_{0.79}\text{Fe}_{0.17}\text{Mn}_{0.03}\text{Zn}_{0.01})_{\Sigma 1.00}(\text{Ge}_{0.90}\text{Sn}_{0.01})_{\Sigma 0.91}\text{S}_{3.98}$ (on the basis of 8 atoms) or simply $\text{Cu}_2(\text{Cd}, \text{Fe})\text{GeS}_4$. Based on the empirical formula and $Z = 2$, $D_{\text{calc}} = 4.53 \text{ g}/\text{cm}^3$. The X-ray powder diffraction pattern obtained is analogous to that of briartite (JCPDS 25-282). The strongest X-ray powder diffraction lines are (d in $\text{\AA}(1)(hkl)$): 3.10(100)(112), 1.92(80)(220), 1.89(70)(204), 1.64(60)(312), 1.60(20)(303, 116) and 2.73(10)(200). The refinement of the lattice parameters leads to $a = 5.45(4) \text{ \AA}$ and $c = 10.6(1) \text{ \AA}$, indexed by analogy to briartite. Barquillite is therefore a member of the stannite group, the Cd-dominant analogue of briartite. The name is given after the village of Barquilla, very near the type locality.

Key-words: barquillite, new mineral, sulphides, cadmium, germanium, stannite group.

Introduction

A new mineral of the stannite group was discovered during the investigations of a series of samples taken from the Barquilla Sn-Ge-Cd-Cu-Fe deposit (Murciego, 1990; Babkine *et al.*, 1990;

Murciego *et al.*, 1992a; Pascua *et al.*, 1997). It is the Cd-analogue of briartite, $\text{Cu}_2(\text{Fe}, \text{Zn})\text{GeS}_4$, produced by the substitution of Fe and Zn by Cd (Francotte *et al.*, 1965; Viaene & Moreau, 1968; Springer, 1969; Geier & Ottemann, 1972; Ottenburgs & Goethals, 1972). The mineral phas-

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es with stannite-type structures can be represented by the general composition A_2BCS_4 with $A = Cu$ or Ag ; $B = Fe, Zn$ or Cd , and $C = Sn, In$ or Ge . The corresponding minerals are stannite (Klaproth, 1797), kesterite (Orlova, 1956), sakuraiite (Kato, 1965), hocrartite (Caye *et al.*, 1968), černýite (Kissin *et al.*, 1978), briartite (Francotte *et al.*, 1965) and the new mineral, barquillite.

The name of the new mineral is after the village of Barquilla, locality very close to the deposit where it has been found. The mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (ref. 96-050). Type material, consisting of polished sections and slides, is deposited at the Museo Geominero, Madrid, Spain under the catalogue number MGM-3000; it is also stored at the Institut für Mineralogie, Bochum, Germany; at the Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, Nancy, France; at the Departamento de Geología, Salamanca, Spain, and at the Area de Cristalografía y Mineralogía, Badajoz, Spain.

Occurrence

Barquillite occurs in the Barquilla deposit, located in the southwest of Salamanca, Spain. This vein-type deposit has been worked in three mines, Aurora, La Inesperada and Fuentes Villanas, since 1930 for lithium and tin.

The veins trend N-S to $N70^\circ E$, dip $5-80^\circ SE$, and their width ranges from a few centimetres to one metre (Murciego, 1990). The host rocks are low-grade metamorphic rocks of pre-Ordovician

age (Schist Greywacke Complex; Corretgé & López Plaza, 1976): greywackes, conglomerates and schists in the Aurora and La Inesperada Mines; and impure limestones in Fuentes Villanas Mine. Sericitic alteration, developed along the borders of the veins, rarely extends more than one metre into the host rocks.

The mineral assemblage in veins at Aurora and La Inesperada Mines is cassiterite, apatite, albite, montebrasite, quartz and sericite with minor proportions of a columbite-tantalite-group mineral and microlite (Murciego, 1990). Murciego *et al.* (1992b) have recognised two generations of cassiterites, one related to an early stage of mineralization, the second to sericitization. Sericite-(apatite-fluorite)-cassiterite II is the mineral association recognised in the altered host-rocks.

In the Fuentes Villanas Mine sulphides and sulphosalts are minor or even rare constituents that appear locally. Two different sulphides and sulphosalts assemblages, in the veins and in the altered host rocks, have been defined (Murciego *et al.*, 1992c; Pascua *et al.*, 1997). 1) In the cassiterite-montebrasite-apatite-albite-quartz-mica veins: černýite (Murciego *et al.*, 1992a), greenockite, tetrahedrite, herzenbergite and, in subordinate amounts, chalcopyrite, galena, native bismuth, covellite and Ag-Bi-Pb-Cu-bearing sulphosalts. 2) In the altered host rocks close to the veins that consist of fluorite, sericite and apatite, a banded zonal distribution of sulphides and sulphosalts has been recognised. From the vein toward the unaltered host-rocks three bands with a variable width (millimetre scale) and gradual limits have been defined as follows:

- Band A consists of černýite, stannoidite and tetrahedrite.

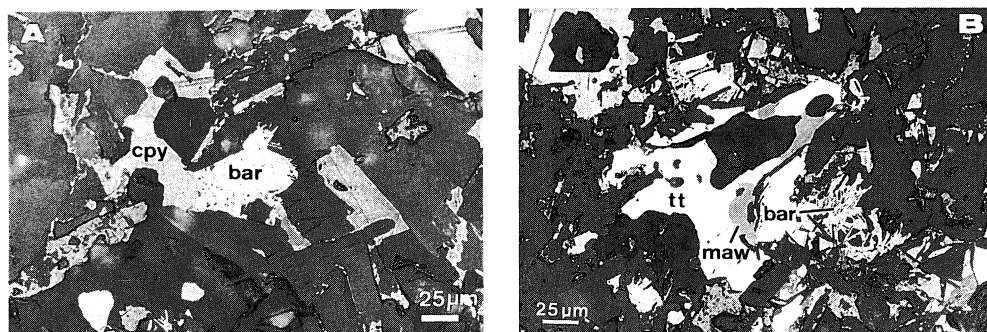


Fig. 1. Plates (A) and rosette-like aggregates of thin platy crystals (B) of barquillite. maw, mawsonite; bar, barquillite; cpy, chalcopyrite; tt, tetrahedrite.

- Band B consists of chalcopyrite, tetrahedrite, mawsonite, barquillite, mohite, antimonpearceite, bornite, stannoidite, native Bi and bismuthinite. These phases surround flakes of mica and fill interstices among them.

- Band C involves chalcopyrite and digenite.

Appearance and physical properties

Barquillite exhibits a tabular habit. No crystal forms, cleavages or twinning were optically discernible. It is a rare mineral that occurs as plates, ranging in size from 20 to 50 μm , and rosette-like aggregates of thin (< 20 μm) platy crystals (Fig. 1A,B). Barquillite appears with an irregular distribution, as isolated grains within sericite and, more commonly, in contact with tetrahedrite and chalcopyrite, even though it has also been found in association with bornite, mawsonite, stannite, stannoidite, mohite and digenite. It commonly contains tetrahedrite and greenockite inclusions. Due to the small size of this material we cannot supply information about physical properties such as megascopic colour, streak and density. Barquillite is opaque with a metallic lustre and takes a very good polish. This mineral has a micro-indentation hardness of 180-300 kg/mm^2 , corresponding to a calculated Mohs' hardness of 4 to 4.5. Assuming the empirical formula derived from the electron-microprobe analyses and $Z = 2$, the calculated density for barquillite is $D_{\text{calc}} = 4.53 \text{ g}/\text{cm}^3$. In reflected light, in air, it is grey with pale violet tint, with very weak pleochroism, very weak bireflectance and very weak anisotropy. The spectral reflectances in the wavelength range 400 to

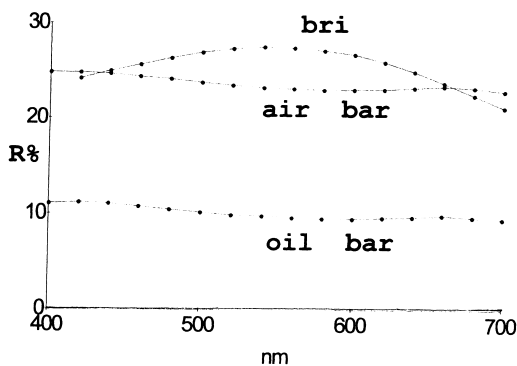


Fig. 2. Reflectance dispersion curves of barquillite (bar), measured in air and in oil, and briartite (bri) (Picot & Johan, 1982).

700 nm were measured in steps of 20 nm in air and immersion oil (DIN 58.884) using an automatic microscope photometer similar to that described by Bernhardt (1987) (Leitz-Orthoplan microscope; monochromator: 16 homogeneous interference filters, $\lambda = 10 \text{ nm}$; plane glass reflector; 20x objective (air and oil); Hamamatsu 3896 photomultiplier; SiC reflectance standard, Leitz no. 462). The mineral surface was freshly repolished with diamond paste (1/4 μm) on cloth. Reflectance values and the respective colour values relative to CIE illuminant C are tabulated in Table 1; the spectra are plotted together with that of briartite in Fig. 2. The lowest reflectance values of barquillite are observed at 700 nm, both in air and in oil. The highest R% values appear in oil at 420 nm and in air at 400-420 nm.

Table 1. Reflectance data for barquillite in air and oil.

λ (nm)	R%oil	R%air
400	11.09	24.84
420	11.21	24.83
440	11.1	24.71
460	10.79	24.42
480	10.49	24.18
500	10.02	23.8
520	9.93	23.52
540	9.85	23.29
560	9.69	23.19
580	9.59	23.04
600	9.54	23.07
620	9.65	23.10
640	9.72	23.28
660	9.91	23.46
680	9.71	23.30
700	9.52	22.94

Chemical composition

Chemical analyses were performed at the Service de Microanalyse, Université de Nancy I (France), on a CAMECA SX-50 electron microprobe operated at 20 kV, 20 nA and 10 to 20 s counting time for the peaks and 5 to 10 s for the background. The following standards and X-ray lines were used: PbS (PbM α), FeAsS (AsL α), ZnS(ZnK α), CuFeS₂ (SK α , CuK α), SnO₂ (SnL α), FeS₂(FeK α), Sb₂S₃ (SbL α), CdS (CdL α), MnS (MnK α), GaAs(GaK α) and pure metals (AgL α , BiM α , GeK α). Raw data were reduced with the PAP procedure (Pouchou & Pichoir, 1984).

Thirty-four analyses of nine grains of barquillite have been performed. The mean chemical composition of each grain and their atomic pro-

SAMPLES No. analyses	I 2	II 3	III 4	IV 9	V 2	VI 2	VII 3	VIII 3	IX 6	X 1
WEIGHT PERCENT										
S	29.31	29.03	29.17	29.24	28.81	29.36	29.5	29.13	31.22	31.62
Ge	15.44	15.61	15.53	15.21	14.06	14.61	14.62	14.47	15.38	15.35
Sn	0.00	0.00	0.00	0.13	0.00	0.30	0.00	0.61	0.51	0.00
Ga	0.11	0.04	0.05	0.05	0.06	0.02	0.00	0.02	0.07	0.00
Cu	29.64	29.34	29.92	30.82	31.63	30.82	30.81	31.07	31.94	31.74
Ag	0.24	0.03	0.23	0.10	0.72	0.15	0.44	0.43	0.00	0.00
Cd	23.93	24.14	23.14	21.21	20.33	19.75	20.03	19.50	11.42	9.65
Fe	0.10	0.66	0.98	1.55	2.37	2.51	2.98	3.03	5.66	7.70
Mn	0.25	0.15	0.46	0.26	0.00	0.43	0.12	0.02	2.15	2.02
Zn	0.14	0.00	0.16	0.09	0.04	0.20	0.11	0.04	0.03	0.17
Sb	0.05	0.01	0.00	0.27	0.02	0.29	0.01	0.09	0.09	0.00
Bi	0.03	0.29	0.08	0.15	0.21	0.21	0.07	0.13	0.23	0.24
Total	99.24	99.30	99.72	99.08	98.25	98.65	98.69	98.54	98.70	98.49
ATOMIC PROPORTIONS										
S	4.02	3.99	3.97	3.98	3.94	3.98	3.99	3.96	4.02	4.02
Ge	0.94	0.95	0.93	0.91	0.85	0.88	0.87	0.87	0.88	0.86
Sn	-	-	-	0.01	-	0.01	-	0.02	0.02	-
Ga	0.01	-	-	-	-	-	-	-	-	-
Cu	2.05	2.04	2.06	2.12	2.19	2.11	2.10	2.13	2.07	2.04
Ag	0.01	-	0.01	0.01	0.03	0.01	0.02	0.02	-	-
Cd	0.93	0.95	0.90	0.82	0.79	0.76	0.77	0.76	0.42	0.35
Fe	0.01	0.05	0.08	0.12	0.19	0.20	0.23	0.24	0.42	0.56
Mn	0.02	0.01	0.04	0.02	-	0.03	0.01	-	0.16	0.15
Zn	0.01	-	0.01	0.01	-	0.01	0.01	-	-	0.01
Sb	-	-	-	-	-	0.01	-	-	-	-
Bi	-	0.01	-	-	0.01	-	-	-	0.01	0.01
Cd/(Cd+Fe)	0.99	0.95	0.92	0.87	0.81	0.79	0.77	0.76	0.50	0.38

Table 2. Electron-microprobe analyses of barquillite (I-IX) and briartite (?) (X).

portions are given in Table 2. All the grains examined are compositionally homogeneous. Barquillite is characterized by a complex composition, with S, Cu, Cd and Ge as major constituents. Other elements as Fe, Mn, Zn, Bi, Ag, Sn, Ga and Sb are present in minor and/or trace amounts, and in some analyses below the detection limit. Pb and As have been analysed but not detected. The mean (and ranges) of the analyses shown in Table 2 give (wt.%): Cu 30.67 (29.34-31.94), Ag 0.26 (bdl.-0.72), Cd 20.38 (11.42-24.14), Fe 2.20 (0.1-5.66), Mn 0.43 (bdl.-2.15), Zn 0.09 (bdl.-0.20), Ge 14.99 (14.06-15.61), Sn 0.17 (bdl.-0.61), Ga 0.05 (bdl.-0.11), Bi 0.16 (0.03-0.29), Sb 0.09 (bdl.-0.29), S 29.42 (28.81-31.22), total 98.91 (98.25-99.72). The average empirical formula, calculated on the basis of 8 atoms, is $(\text{Cu}_{2.10}\text{Ag}_{0.01})_{\Sigma 2.11}(\text{Cd}_{0.79}\text{Fe}_{0.17}\text{Mn}_{0.03}\text{Zn}_{0.01})_{\Sigma 1.00}(\text{Ge}_{0.90}\text{Sn}_{0.01})_{\Sigma 0.91}\text{S}_{3.98}$. The simplified formula is $\text{Cu}_2(\text{Cd,Fe})\text{GeS}_4$, and barquillite is defined as the Cd-dominant member.

Minor amounts of Mn and Zn may substitute for Cd, but there is actually a considerable range of Cd-Fe substitution found in samples from the Barquilla deposit, which leads to Fe-dominant members (briartite?) for some crystals (see Table 2 and Fig. 3).

X-ray powder diffraction

Due to the scarcity of the mineral and its minute grain size, standard preparation and X-ray methods were not applicable. After careful microscopic studies, barquillite-rich areas were separated under microscopic control by means of a microdrill as described in detail by Förtsch *et al.* (1992). Even for single-crystal areas of suitable size in the polished surface, pure single-phase separates could not be obtained. This is due to the platy habit of the crystals (which are less than 20 μm thick) and thus contamination of the sample by other underlying minerals. Subsequently, these separates have been investigated using Gandolphi-cameras both with 57.3 and 114.7 mm diameter and Ni-filtered $\text{CuK}\alpha$ radiation. Attempts to achieve a better precision (using the large-diameter camera) failed; the exposure time increased drastically and the lines became more diffuse. Table 3 compares X-ray data of the new mineral with those of briartite (JCPDS 25-282); the additional lines at $d = 3.44, 3.13$ and 2.79 \AA might be due to contamination. The analogy of both sets is evident. Therefore we assume that barquillite is a member of the stannite group (space group $I\bar{4}2m$).

Discussion

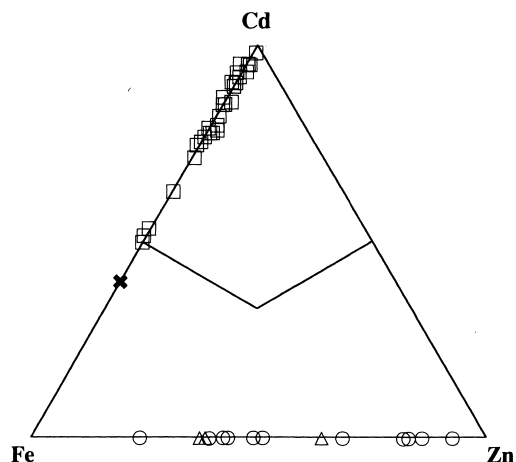


Fig. 3. Analyses of barquillite (□) and briartite (?) (×) from Barquilla and of briartite from Kipushi (Δ) and Tsumeb (○) (Francotte *et al.*, 1965; Geier & Ottemann, 1972; Mozgova *et al.*, 1994) projected onto the Cd-Fe-Zn plane (at. proportions).

and can be described as the Cd-analogue of briartite. The refinement of the lattice parameters leads to $a = 5.45(4)$ and $c = 10.6(1)$ Å for barquillite, on the basis of the 6 lines between $d = 3.10$ and 1.60 Å, indexed in analogy to briartite.

Although the unit cell proposed for barquillite provides satisfactory indexing for the X-ray powder diffraction pattern and gives a reasonable calculated density, a single-crystal study is required to confirm the crystallographic parameters.

Barquillite is the first Cu-Cd-Ge sulphide found in nature. The crystallization of this unusual mineral in the Barquilla deposit must be attributed to the extremely high concentrations of Ge (16 ppm) found in calc-silicate host-rocks. This enrichment in Ge is also reflected in coexisting tetrahedrite (up to 0.72 wt.% Ge) and stannite (0.69 wt.% Ge). The presence of Ge in the altered host rocks and its absence in the veins may be explained by the leaching of Ge from the host rocks (Pascua *et al.*, 1997).

The new mineralogical species pertains to the $\text{Cu}_2\text{CdGeS}_4$ - $\text{Cu}_2\text{FeGeS}_4$ - $\text{Cu}_2\text{ZnGeS}_4$ pseudoternary system in which briartite ($\text{Cu}_2(\text{Fe,Zn})\text{GeS}_4$) has previously been discovered (Francotte *et al.*, 1965). Barquillite is defined as the Cd-dominant member (*i.e.* $\text{Cd} > \text{Zn}$ and $\text{Cd} > \text{Fe}$ in the relevant crystallographic site). However, compositional variations in the barquillite-type phase in the Barquilla deposit extend to Fe-dominant compositions (briartite? Fig. 3), covering the whole Cd-Fe binary. The definition of briartite at this moment is not clear. This mineral was accepted by the IMA as a solid-solution series between the Zn and Fe end-members; for this reason, the 50-50 principle of nomenclature rules for each atomic site is difficult to apply to this mineral. On the basis of the analyses of barquillite and of briartite from Tsumeb and Kipushi, the idea of a series with Cd-dominant, Fe-dominant and Zn-dominant members should be introduced (see Fig. 3). According to the 50-50 principle of nomenclature rules, the briartite name should apply to the Fe-dominant

Table 3. X-ray powder diffraction patterns of barquillite (57.3 and 114.7 mm Gandolfi cameras) and briartite (JCPDS 25-282).

barquillite			briartite		
d_{meas}	d_{cal}	I/I_1	d_{meas}	I/I_1	hkl
3.44		10	4.76	20	101
3.13		10			
3.10	3.104	100	3.06	100	112
2.79		10	2.966	10	n.i.
2.73	2.716	10	2.663	80	200
			2.633	40	004
			2.323	10	211
			1.970	10	213
1.92	1.921	80	1.883	100	220
1.89	1.891	70	1.870	100	204
1.64	1.633	60	1.603	100	312
1.60	1.610/1.598	20	1.590	50	303/116
			1.527	40	224
1.35		5			
1.23		5			

member and the Zn-dominant analyses from Kipushi and Tsumeb may justify a new mineral name, provided it is clear that all these atoms occupy the same position. A revision of briartite may be necessary, therefore.

Otherwise, Ottenburgs & Goethals (1972) synthesized the Fe end-member and reported the existence of a Fe-Zn solid-solution series. However, the natural Fe end-member has not been reported in literature; a Fe-Zn and a Cd-Fe solid solution series in nature could only be suggested (Fig. 3). Also experimental studies (Moh, 1975) have shown the possible existence of a solid-solution series between Sn and Ge end-members ($\text{Cu}_2\text{CdSnS}_4$ and $\text{Cu}_2\text{CdGeS}_4$, respectively); evidence for it has not been found in the Barquilla deposit between černýite ($\text{Cu}_2\text{CdSnS}_4$) and barquillite. The concentration of Ge in černýite is below the detection limit.

Like briartite, barquillite shows Ge deficiencies and Cu excess with respect to the ideal formula Cu_2MGeS_4 (M: Cd, Fe, Zn). This may be explained by a structural disorder of tetrahedral site occupancy by the different metals, observed in the synthetic compounds (Parthé *et al.*, 1969).

Single-crystal X-ray diffraction of $\text{Cu}_2\text{FeGeS}_4$ synthesised at 700°C shows that the compound belongs to the space group *I42m* (Wintenberger, 1979) with a structure type related to stannite or ZnS sphalerite. No polymorph has been observed at high temperature (Ottenburgs & Goethals, 1972). In contrast the Zn-varieties exhibit a polymorphism with increasing temperature, the tetragonal structure derived from stannite, as for the Fe-variety, is transformed (815°C) into an orthorhombic structure with space group *Pmn2*₁, related to that of enargite or ZnS wurzite.

The structure of $\text{Cu}_2\text{CdGeS}_4$ synthesized at high temperature (Parthé *et al.*, 1969) is also the same superstructure of wurzite, space group *Pmn2*₁. No low-temperature synthetic variety has been studied, but, by analogy with the polymorphism of $\text{Cu}_2\text{ZnGeS}_4$, the Cd compounds probably exhibit the same polymorphism, with a high-temperature synthetic orthorhombic variety and the natural low-temperature (?) tetragonal variety (barquillite).

By comparison, the structure of the stannite $\text{Cu}_2\text{MnSnS}_4$ exhibits the tetragonal superstructure of ZnS sphalerite (Allemand & Wintenberger, 1970). In contrast the structure of synthetic $\text{Cu}_2\text{MnGeS}_4$ is *Pmn2*₁ but, concerning the latter compound, no information related to the temperature of synthesis is given. The structure of černýite,

$\text{Cu}_2\text{CdSnS}_4$, is analogous to that of stannite, (Szymanski, 1978).

In summary the low-temperature and high-temperature varieties of these compounds are, respectively, tetragonal and orthorhombic. Barquillite should be the low-temperature variety.

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