

GOLDICHITE OF FUMAROLIC ORIGIN FROM THE SANTA BÁRBARA MINE, JUJUY, NORTHWESTERN ARGENTINA

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ABSTRACT

The first find of goldichite in Argentina and the third world-wide occurrence is described. The mineral was found in a sulfur deposit, the Santa Bárbara mine, in Jujuy province, formed by present-day activity of thermal springs. The mineral occurs with metavoltine, hexahydrate, alunogen, sideronatrite, ferrinatrite, voltaite, krausite, halotrichite, gypsum and halite. The goldichite occurs as euhedral flattened crystals 0.3 mm in length, tabular on {100}, with {100}, {110} and {011} crystallographic forms. The strongest five X-ray powder-diffraction lines [d in Å(1)(hkl)] are: 10.11(70)(100), 5.11(40)(200), 3.072(100)(202), 2.444(40)(330), and 2.283(40)(033). The refined unit-cell parameters of this monoclinic mineral are: a 10.397(7), b 10.461(8), c 9.109(4) Å, β 100.00(9)°, V 972.8(8) Å³. The crystals are transparent, brittle, and have a greenish hue in natural light and a pale pink tint under artificial light; they have a hardness of 2–3, an excellent {100} cleavage, vitreous luster and white streak. Optically, goldichite is transparent, with positive elongation, with X colorless, Y colorless to very pale yellow, and Z very pale yellow; $Z > Y > X$; biaxial (+), $2V_{\text{(calc)}}$ 75°, α 1.584(2), β 1.602(2), γ 1.634(2), $X = b$, $Y = a$, $Z \wedge c$ 9°, $v > r$, strong. The chemical composition, obtained by electron-microprobe analysis, indicates S, Fe and K as the principal components, with the following ranges in concentration of the oxides (wt.%): P₂O₅ 0.80–1.02, SO₃ 52.39–57.19, TiO₂ 0.13–0.27, Al₂O₃ 0.02–0.16, CaO 0.01–0.05, Fe₂O₃ 28.57–30.26, Na₂O 0.29–0.46, and K₂O 8.81–9.82.

Keywords: goldichite, fumarole, Santa Bárbara mine, Jujuy province, Argentina.

SOMMAIRE

Nous décrivons le premier indice de goldichite en Argentine, et seulement le troisième au monde. On trouve la goldichite dans un gisement de soufre, qu'exploite la mine de Santa Bárbara, province de Jujuy, où elle est formée actuellement à partir de sources thermales. Lui sont associées métavoltine, hexahydrate, alunogène, sidéronatrite, ferrinatrite, voltaite, krausite, halotrichite, gypse et halite. Les cristaux idiomorphes atteignent 0.3 mm; ils sont tabulaires sur {100}, aplatis, montrant les formes {100}, {110} et {011}. Les cinq raies les plus intenses du cliché de diffraction X [d en Å(1)(hkl)] sont: 10.11(70)(100), 5.11(40)(200), 3.072(100)(202), 2.444(40)(330), et 2.283(40)(033). On a affiné les paramètres réticulaires de ce minéral monoclinique: a 10.397(7), b 10.461(8), c 9.109(4) Å, β 100.00(9)°, V 972.8(8) Å³. Les cristaux sont transparents et cassants, et ont une teinte verdâtre à la lumière naturelle et une teinte rose pâle à la lumière artificielle. Les cristaux ont une dureté de 2 à 3, un clivage {100} excellent, un éclat vitreux et une rayure blanche. Les cristaux transparents ont un allongement positif, avec X incolore, Y incolore à jaune très pâle, et Z jaune très pâle; $Z > Y > X$; biaxe (+), $2V_{\text{(calc)}}$ 75°, α 1.584(2), β 1.602(2), γ 1.634(2), $X = b$, $Y = a$, $Z \wedge c$ 9°, $v > r$, intense. Sa composition chimique, obtenue par analyse à la microsonde électronique, indique la présence essentielle de S, Fe et K, et les intervalles suivants des oxydes (en pourcentages pondéraux): P₂O₅ 0.80–1.02, SO₃ 52.39–57.19, TiO₂ 0.13–0.27, Al₂O₃ 0.02–0.16, CaO 0.01–0.05, Fe₂O₃ 28.57–30.26, Na₂O 0.29–0.46, et K₂O 8.81–9.82.

(Traduit par la Rédaction)

Mots-clés: goldichite, fumarole, mine de Santa Bárbara, province de Jujuy, Argentine.

INTRODUCTION

Goldichite, ideally KFe(SO₄)₂·4H₂O, is a monoclinic mineral originally described by Rosenzweig & Gross (1955). The crystal structure was later reported by Graeber & Rosenzweig (1971). The type locality is the Dexter Number 7 mine, Calf Mesa, San Rafael Swell, Utah, where it occurs associated with coquimbite, halotrichite, roemerite, alunogen, copiapite,

melanterite, fibroferrite, voltaite, butlerite, parabutlerite, chalcantinite and diadochite. These sulfates cement a talus breccia in a uranium deposit, which has metazeunerite, chalcopyrite and pyrite as the essential minerals. To the best of our knowledge, since its discovery, no other occurrence has been described in the literature. There appears to be another occurrence of goldichite in Gansu Province, China, which crystals are illustrated in a book about minerals from that

country (A. Rosenzweig, pers. comm., 1994).

As a result of the mineralogical study of a suite of sulfate minerals of fumarolic origin found in northwestern Argentina, goldichite was identified, and we present here a brief description.

OCCURRENCE

The Santa Bárbara mine is a small sulfur prospect located at latitude $23^{\circ}50'40''$ S and longitude $64^{\circ}25'25''$ W in the El Palmar district, Santa Bárbara department, Jujuy province of northwestern Argentina (Fig. 1). It is situated near the #1 road, 131 km from San Salvador de Jujuy, the capital of the province, on the east shore of La Quinta lake. Moreno Espelta *et al.* (1981) described the geology of the area, and Reverberi (1961) evaluated the economic potential of the deposit.

The sulfur prospect is hosted by calcareous sandstone and yellow limestone of the Upper Cretaceous Yacoraite Formation, on the western fracture that defines the edge of the Santa Bárbara Range. These rocks are argillized in the mineralized zone and contain disseminated sulfur in rhombic crystals, gypsum in millimetric veinlets and lenses, and a suite of sulfates composed of voltaite, metavoltine, hexahydrite, alunogen, sideronatriite, ferrinatriite, krausite, halotrichite and goldichite. This assemblage occurs in underground works where, at the time of sampling (October, 1980), in the floor of one of these workings, two fumarolic vents 10 cm in diameter were dispersing a CO_2 -rich vapor phase at a temperature of 40° to 50°C . The fumarolic vents are surrounded by a soft mass composed of halotrichite and alunogen spotted with crystals of voltaite and krausite. The other sulfates,

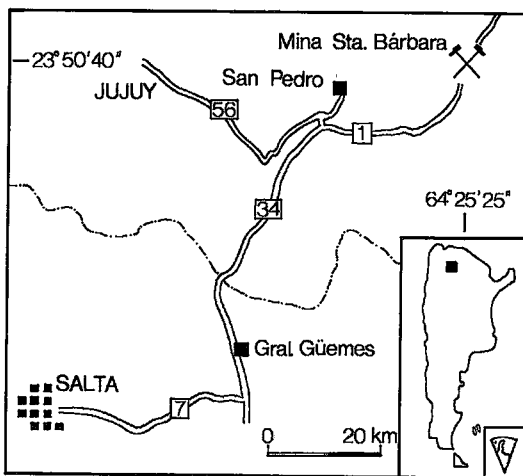


FIG. 1. Location of Santa Bárbara mine, Jujuy province, Argentina.

including goldichite, occur on the argillized rock that forms the walls of the galleries.

PHYSICAL AND OPTICAL PROPERTIES

Goldichite is found as euhedral tabular crystals, 0.3 mm in length, in parallel growth. The morphological appearance of the crystals is similar to that of the type locality, with $\{100\}$, $\{110\}$ and $\{011\}$ crystallographic forms (Fig. 2), and flattening on

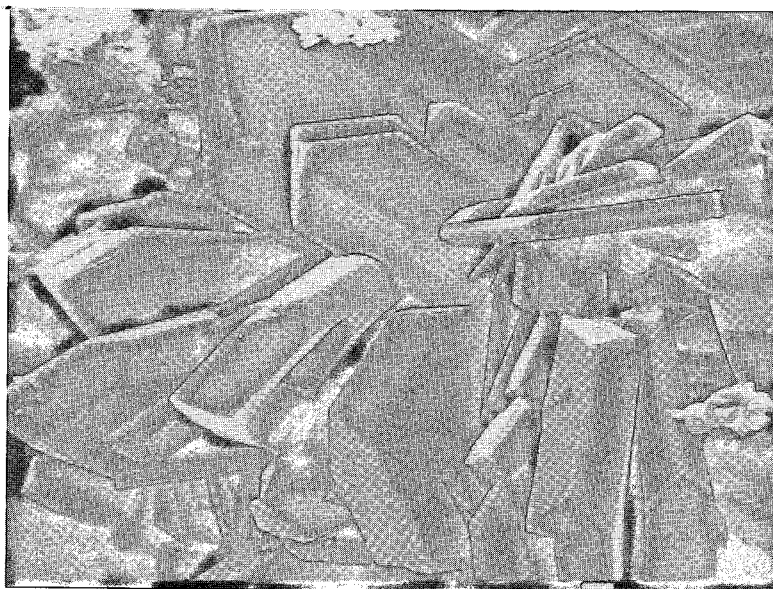


FIG. 2. SEM photomicrograph of Santa Bárbara goldichite (scale bar: 10 μm).

TABLE 1. OPTICAL PROPERTIES OF GOLDICHITE

	San Rafael (1)	Santa Bárbara (2)
α	1.582(2)	1.584(2)
β	1.602(2)	1.602(2)
γ	1.629(2)	1.634(2)
X	—	colorless
Y	—	colorless — very pale yellow
Z	—	very pale yellow
biaxial	(+)	(+)
X	b	b
Y	—	≈ a
Z	11°	9°
ZAc	82° (calc.)	75° (calc.)
2V _z	—	>7°, strong
Dispersion	—	—

(1) Rosenzweig & Gross (1955), (2) this study.

{100}. The mineral has an excellent {100} cleavage and a Mohs hardness between 2 and 3. The crystals are transparent, with a greenish hue in natural light and a pale pink hue under artificial light. They are vitreous, brittle and possess a white streak.

Optical properties were determined with Na-light using Cargille liquids at 25°C and a spindle stage. The optical properties are compared with those from the type locality in Table 1. The crystals have positive elongation and are transparent, with X colorless, Y colorless to very pale yellow, and Z very pale yellow; the pleochroic scheme is $Z > Y > X$.

X-RAY DATA

Goldichite is monoclinic, space group $P2_1/c$, $Z = 4$ (Rosenzweig & Gross 1955, Graeber & Rosenzweig 1971). Powder-diffraction data for goldichite from the

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR GOLDICHITE

<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>hkl</i>
70 *	10.11	10.13	100
20	7.47	7.47	101
20 *	6.83	6.85	011
40	5.11	5.07	200
10 *	4.32	4.33	121
15 *	4.03	4.02	121
10 *	3.381	3.378	300
10 *	3.236	3.237	221
100 *	3.072	3.072	202
30 *	2.852	2.851	320
10 *	2.660	2.659	222
5 *	2.573	2.573	401
40 *	2.444	2.444	330
40 *	2.283	2.283	033
10	1.970	1.981	341
5	1.942	1.942	431
20	1.821	1.811	342
5 *	1.781	1.784	531
<5 *	1.701	1.701	161
5	1.598	1.597	542
5	1.568	1.568	451
10	1.540	1.544	541
10	1.514	1.517	070

* Reflections used for the refinement of the unit-cell parameters.

Santa Bárbara mine were obtained utilizing $\text{CuK}\alpha$ radiation and a 114.6-mm diameter Debye-Scherrer powder camera. Intensities were visually estimated. The X-ray data obtained are shown in Table 2. The refined unit-cell parameters, calculated from readings of the Debye-Scherrer film using the Appelman & Evans (1973) computer program as adapted by Benoit (1987), are: a 10.397(7), b 10.461(8), c 9.109(4) Å, β 100.00(9)°, $a:b:c$ 0.9939:1:0.8708, V 972.8(9) Å³.

CHEMICAL COMPOSITION

The chemical analyses of the mineral were performed with a CAMECA SX-50 microprobe at the Department of Geological Sciences, Indiana University, Bloomington, Indiana. The following standards were used: fluorapatite (P), barite (S), titanite (Ti), anorthite (Al, Ca), fayalite (Fe), aegirine (Na) and orthoclase (K). The specimens were coated with carbon and analyzed on three different spots 10 µm in diameter, with a 10-nA beam. Sixteen different analyses were performed; unfortunately, goldichite is a difficult mineral to deal with, as it is invariably severely beam-damaged. The results are quite different, one outstanding feature being the low concentration of potassium, which leads to low totals. Owing to the high thermal conductivity of this element, the potassium was probably selectively evaporated; the resulting low percentage raises the proportion of the sulfur and iron when corrected to higher values than the expected ones. The composition derived reflects the same fact.

In Table 3, results of three analyses are presented, chosen for their relatively high totals and percentages of potassium, and their empirical formulas for the corrected values of the principal components.

TABLE 3. RESULTS OF CHEMICAL ANALYSIS AND EMPIRICAL FORMULA OF GOLDICHITE

Oxides	A	B	C	D
P ₂ O ₅ wt. %	1.02	0.80	0.84	—
SO ₃	57.13	52.39	57.19	55.78
TiO ₂	0.27	0.13	0.16	—
Al ₂ O ₃	0.04	0.16	0.02	—
CrO	0.01	0.02	0.05	—
Fe ₂ O ₃	30.26	28.57	28.80	27.81
Na ₂ O	0.32	0.46	0.29	—
K ₂ O	9.04	9.82	8.81	16.41
Total	98.09	92.35	96.16	100.00
Empirical formulas				
A: Fe _{1.05} (K,Nn) _{0.56} (SO ₃) _{2.03} ·4H ₂ O	B: Fe _{1.10} (K,Nn) _{0.56} (SO ₃) _{2.00} ·4H ₂ O		D: Fe(KSO ₃) ₂ ·4H ₂ O	
C: Fe _{1.04} (K,Nn) _{0.56} (SO ₃) _{2.08} ·4H ₂ O				

A, B, C: sample at different spots. D: theoretical composition on a dry basis, as water content cannot be assessed by electron-microprobe analysis.

GENESIS

Goldichite was found at the type locality, along with a large suite of accompanying sulfate-bearing minerals, as a cementing material in a near-surface deposit. This suggests that surface water was the primary agent involved in the formation of the sulfate assemblage. Surface water oxidized almost all the pyrite in the conglomerate and either formed the sulfates *in situ* or carried them in solution along impermeable layers, where crystallization later took place by evaporation (Rosenzweig & Gross 1955).

Goldichite from the Santa Bárbara mine is associated with metavoltine and occurs as soft masses developed over the irregular argillaceous wall of the galleries. These masses include a discontinuous layer less than 1 mm thick of goldichite crystals that are the base for sprays of ferrinatrite, minor sideronatrite and alunogen and scarce halite. This association and the fumarolic vents found on the floor of the galleries suggest an origin as a fumarole sublimate for the Argentinian goldichite.

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REFERENCES

- APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214; indexing and least squares refinement of powder diffraction data. *U.S. Geol. Surv., Comput. Contrib.* **20**, U.S. Nat. Tech. Inf. Serv., Doc. **PB2-16188**.
- BENOIT, P.H. (1987): Adaptation to microcomputer of Appleman – Evans program for indexing and least squares refinement of powder-diffraction data for unit-cell dimensions. *Am. Mineral.* **72**, 1018-1019.
- GRAEBER, E.J. & ROSENZWEIG, A. (1971): The crystal structures of yavapaiite $KFe(SO_4)_2$, and goldichite $KFe(SO_4)_2 \cdot 4H_2O$. *Am. Mineral.* **56**, 1917-1933.
- MORENO ESPELTA, C.H., ARIAS, J.E. & CHAVEZ, A. (1981): Geología del área termal de Santa Bárbara, Provincia de Jujuy, República Argentina. *Congr. Geol. Argentino 8°* **3**, 713-732.
- REVERBERI, O. (1961): Azufrera Santa Bárbara, Paraje La Quinta, Distrito El Palmar, Departamento Santa Bárbara, Provincia de Jujuy. *Informe Secretar a Industria y Minería, Dirección Nacional de Geología y Minería, Carpeta 484* (inérito).
- ROSENZWEIG, A. & GROSS, E.B. (1955): Goldichite, a new hydrous potassium ferric sulfate from the San Rafael Swell, Utah. *Am. Mineral.* **40**, 469-480.
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