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SERPIERITE $Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$ - THE FIRST OCCURENCE IN ROMANIA

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ABSTRACT. Serpierite $Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$ occurs as small blue crusts covering millimeter-size gypsum crystals on the ceiling of a small mining gallery in Trestia-Băița area, Metaliferi Mountains. X-ray diffraction, optical, and scanning electron microscope with EDX and Raman spectroscopy have been used to identify the mineral. Genetically, serpierite derived from weathering of primary hydrothermal cooper and lead deposits. This is the first reported occurrence of serpierite in Romania.

Keywords: Serpierite, hydrothermal, Trestia-Băița, Metaliferi Mountains, Romania.

INTRODUCTION

Serpierite is a hydrated copper calcium sulfate first described in the mines of Laurion (Greece) by Bertrand (1881) (in Sabelli & Zanazzi, 1968). Its first description, including optical properties and crystal morphology, was given by Des Cloizeaux (1881) (in Sabelli & Zanazzi, 1968). Faraone et al. (1967) determined the cell parameters and space group, showing that the mineral belongs to the monoclinic system. They carried out investigation on chemical properties, which leads them to the formula of the serpierite. The crystal analysis of the mineral, presenting its structural features was made by Sabelli & Zanazzi (1968).

In Romania, serpierite has been found in a mining gallery that intersects the Cave No. 4 from Runcului Hill. The cave is located in the southeastern part of Trestia-Băița metalogenic district, Metaliferi Mountains (Romania), at 455 asl. It is the largest cave in the respective karst area and consists of several rooms linked by small pits and narrow passages. The mining gallery, which is no longer connected to the surface, was discovered during the exploration of the cave and was probably dug for prospecting a hydrothermal vein. Serpierite was found as small blue crusts on tiny gypsum crystals on the ceiling, within the hydrothermal vein excavation (Fig.1).

GEOLOGICAL SETTING

The basement in the cave area consists of Early Jurassic ophiolites, represented by pyroclastic basalts, covered by Tithonic-Berriasian limestone blocks. Both ophiolites and limestones are part of the Căpâlnaş-Techereu Nappe (Balintoni, 1997). Starting with the Sarmatian, quartiferous amphibolitic andesites (known as Barza Andesites) were placed in the entire area as lava flows and intrusive bodies (Bordea & Borcoş, 1972) (Fig. 2). The hydrothermal activity associated to the Neogene volcanism (2nd Cycle) resulted in the formation of several sulfide veins, emplaced both within limestones and basalts (Ianovici et al., 1969).

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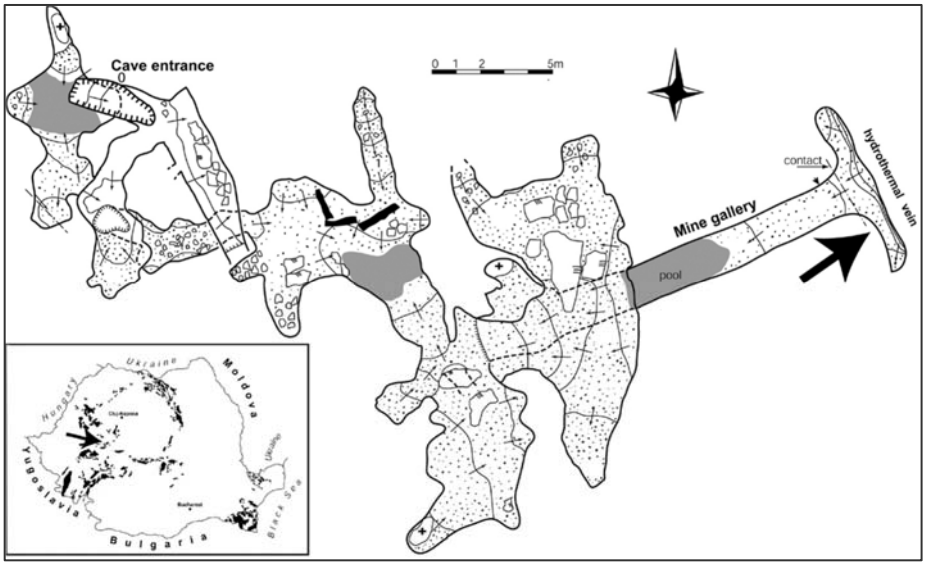


Fig. 1. *The location of Cave No. 4 in Romania and the sampling point of serpierite.*

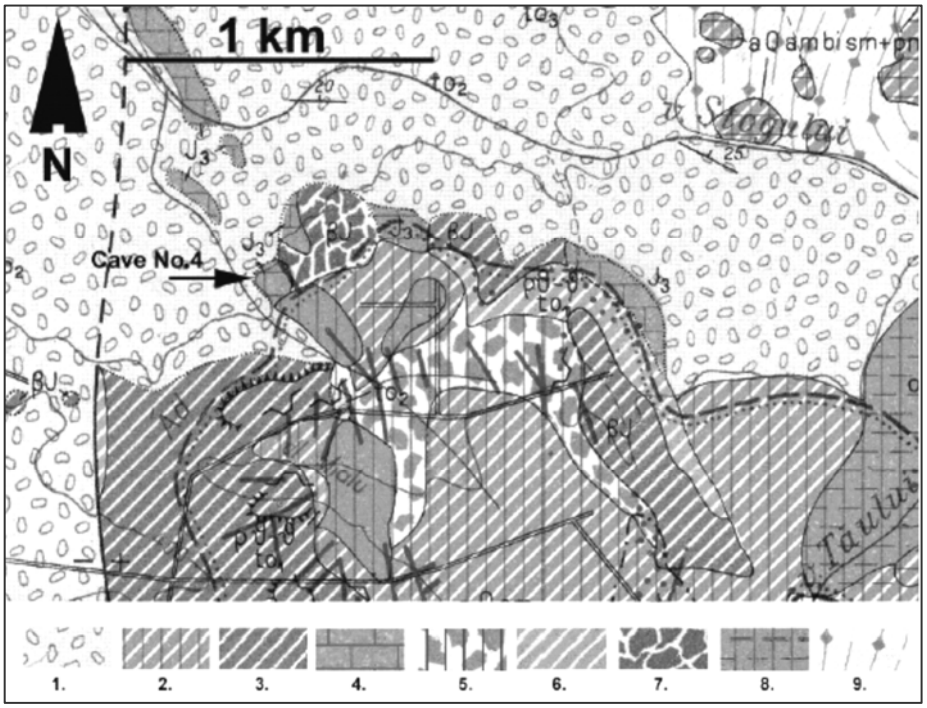


Fig. 2. *Geological map of the investigated area (after Bordea & Borcoş, 1972).*
1,9 Miocene sedimentary complexes; 2,5,8 Barza Andesites;
3,7 Ophiolites; 4 Reefal limestone; 6 Băița Dacites.

ANALYTICAL METHODS

X-ray diffraction analysis

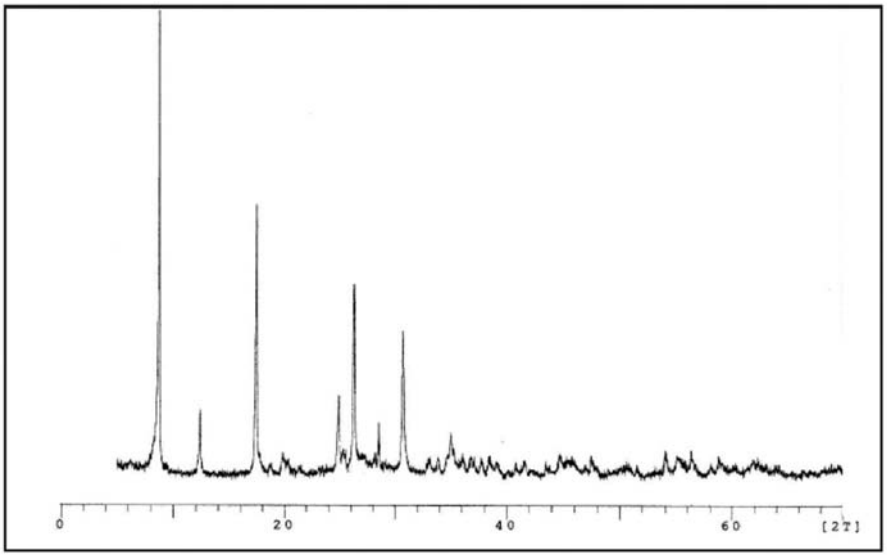
The X-ray powder diffraction obtained on a Phillips diffractometer (Cu-Kα, $\lambda\alpha_1$ = 1.54060) was used for the identification of the mineral. The lines of the pattern are well marked and sharp (Fig 3). The cell parameters obtained by least-squares refinement of XRD data, using the UnitCell Program (Holland & Redfern, 1997) are given in Table 1. The refinement was carried out using 18 powder reflections in the 2θ range 5 -70°, with a step interval of 0.01° 2θ. As shown in Table 1, the cell parameters of the Runcului Hill serpierite have close values with the ones reported in ICDD catalog.

Table 1.

Comparison of cell parameters for serpierite from Runcului and ICDD catalog.

Serpierite from Runcului Hill	ICDD 22-148
a = 22.1935 *b* = 6.2431 *c* = 21.8480 β =113.252	*a* = 22.186 *b* = 6.250 *c* = 21.853 β= 113.37

Fig. 3. *The diffraction pattern of serpierite.*



Optical and scanning electron microscope analyses

A Nikon Optiphot 2-POL binocular at 50x magnification was used to observe serpierite habitus. The observations revealed that thin sky-blue crusts coat millimeter-size, transparent to translucent, colorless gypsum crystals. Minor amounts of clay may occur on top of gypsum, together with serpierite.

The SEM investigations were conducted on a Jeol Scanning Electron Microscope. They revealed lamellar to tabular crystals, scattered or packed as the pages of a book (Plate I, Fig. 1 & 2). Four crystals of serpierite were examined by means of electron microanalysis, using an EDX detector attached to the SEM. The semi-quantitative elemental analysis accounts the participation of Ca (5.906 %), Cu (31.5 %), Zn (11.39 %), S (9.086 %) and O (42.118 %). Copper shows the highest concentration of all the metallic ions.

Raman spectroscopy analysis

The Raman spectrum recorded from the almost pure serpierite sample was in the measured range of 0-3700 cm^{-1}. The wave number, characters and intensities of the bands are reported in Table 2, while the spectrum between 0-1300 cm^{-1} is presented in the Fig. 4. As the Raman spectrum deals mostly with IR one, for the same mineral, the interpretation of the peak position was made according with Farmer (1974).

The spectrum shows two distinctive absorption bands in the region of the O-H stretching vibration. These are characteristic for the hydrogen-bound O-H stretching and correspond to the weakly bounded OH or to molecular water.

The vibrational bands at 1133, 1074, 987, 646, 609, 482 and 445 cm^{-1} may be assigned to the vibrational modes of the SO_4 structural group.

Table 2.

Position and assumptions concerning the Raman bands recorded for the serpierite from Runcului Hill.

Raman shift (cm^{-1})	Structural group	Vibrational mode	Intensity, character[1]
3611	$(OH)^-$, H_2O	O-H stretching	m, br
3558	$(OH)^-$, H_2O	O-H stretching	m, br
1133	SO_4	antisymmetric stretching	s, sh
1074	SO_4	antisymmetric stretching	m, sh
987	SO_4	symmetric stretching	vs, sh
646	SO_4	antisymmetric bending	w, sh
609	SO_4	antisymmetric bending	m, sh
482	SO_4	symmetric bending	m, br
445	SO_4	symmetric bending	s, sh
332, 252	-	lattice modes	w, br

[1] s=strong; m=medium; w=weak; vs= very strong; sh=sharp; b=broad;

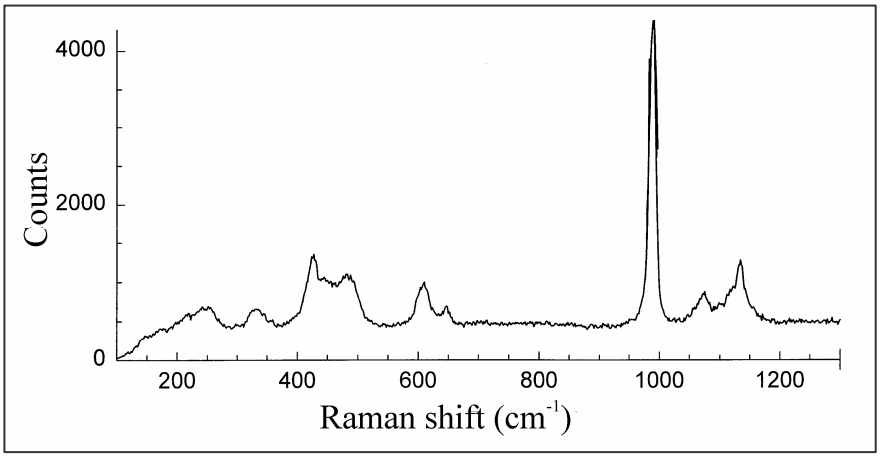


Fig. 4. *Raman spectrum of serpierite.*

DISCUSSION AND CONCLUSION

The Cave no 4 from Runcului Hill has a vadose origin, but some features indicating hydrothermal influences were recognized. These are the close vicinity with the hydrothermal veins and „exotic" hydrothermally-deposited minerals (barite, galena, cerusite, quartz) occurring in the cave (Zaharia et al., unpubl. data). The degree of hydrothermal influence is difficult to establish due to the thick clay layer covering the floor, and the walls and ceiling of the cave at several locations which did not allow a good observation of the morphology. The excavated part has a high grade of alteration, resulted in the earth masses and crusts occurring on the walls.

All the analyses implied confirm the presence of serpierite. Macroscopically it looks like sky-blue crusts, coating gypsum crystals, whereas microscopically, under SEM, serpierite shows thin elongated plates, scattered or packed. Both the X-ray diffraction and Raman spectral analyse showed an almost pure sample.

Serpierite is associated with gypsum. We assume that the crystallization sequence starts with precipitation of gypsum. The Ca-depleted solution suffered a change of the relative Cu:Zn:Ca ratio, which allowed a precipitation of serpierite. Primary metallic mineral formed within the hydrothermal vein, provide the ions of copper and zinc.

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REFERENCES

Balintoni, I. 1997, *Geologia terenurilor metamorfice din România.* Ed. Carpatica, Cluj-Napoca, 174 pp.

Bordea, S. & Borcoş, M. 1972, *The Geological Map of Romania,* 1:50.000, 73d, Brad sheet.

Faraone, D., Sabelli, C. & Zanazzi, P. F. 1967, Su di solfatibasici idrati : serpierite e devillite. *Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali* 43, pp. 369-382.

Farmer, V. C. 1974, *The Infrared Spectra of Minerals*, Mineralogical Society, London, 534 pp.

Holland, T. J .B. & Redfern, S. A.T. 1997, Unit cell refinement: from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine* 61, pp. 65-77.

Ianovici, V., Giuşcă, D., Ghițulescu, T. P., Borcoş, M., Lupu, M., Bleahu, M. & Savu, H. 1969, *Evoluția geologică a Munților Metaliferi*. Editura Academiei RSR, Bucureşti, 741 pp.

Sabelli, C. & Zanazzi, P. F. 1968, The Crystal Structure of Serpierite, *Acta Crystalographica* 24, pp. 1214-1221.

Plate I

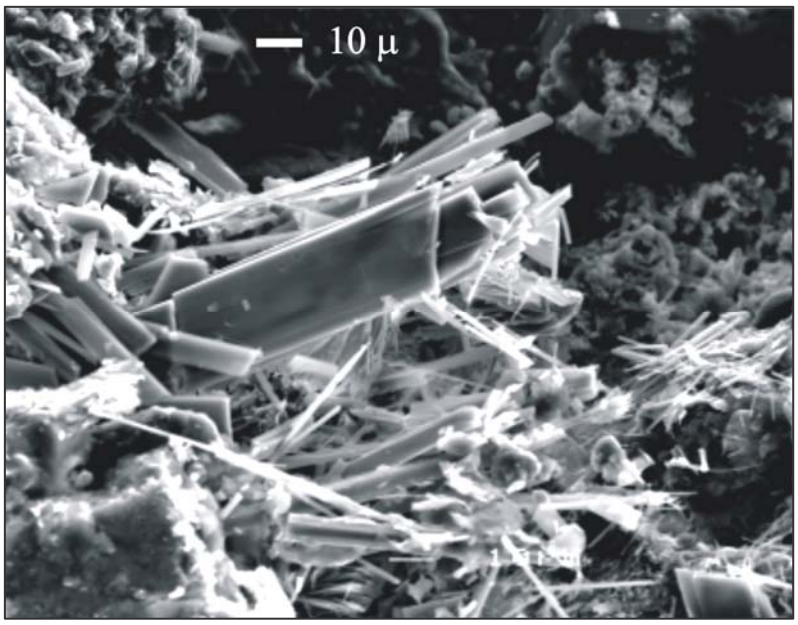

Fig. 1. *Scattered serpierite crystals (SEM image).*

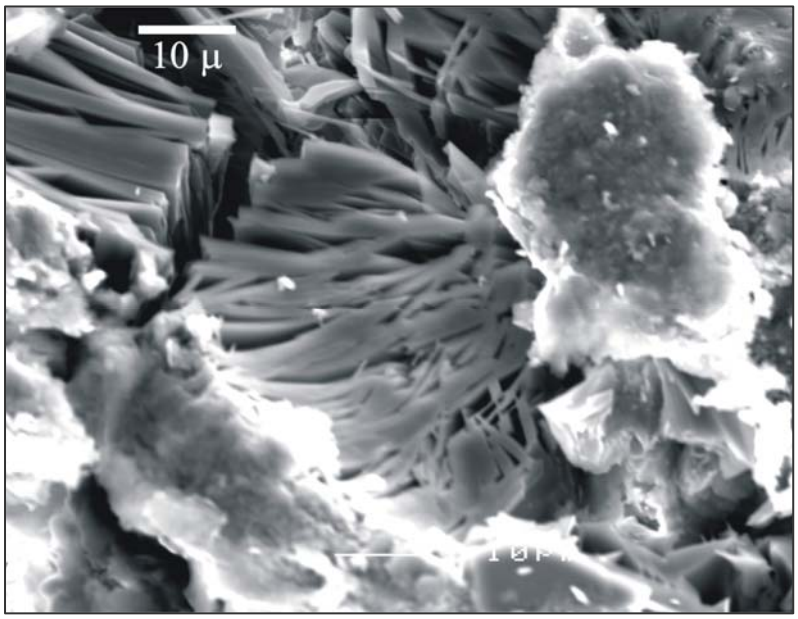

Fig. 2. *Packed serpierite crystals (SEM image).*