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CAVES FORMED WITHIN UPPER CRETACEOUS SKARNS AT BĂIŢA, BIHOR COUNTY, ROMANIA: MINERAL DEPOSITION AND SPELEOGENESIS

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Abstract

The Băiţa metallogenic district, in Bihor County, Romania, is genetically connected to a deep-seated Upper Cretaceous granitic pluton. Within this district, several bodies of skarn host economic concentrations of Mo, W, Bi, Cu, Pb, Zn, B, wollastonite, and marble. During mining, numerous karst cavities were encountered. Minerals such as wittichenite, antimonian luzonite, natrolite, quartz, chalcanthite, rosasite, glaukosphaerite, aurichalcite, azurite, malachite, norsethite and, more commonly, calcite, aragonite, hydromagnesite, and goethite were found within these skarn-hosted caves as crusts, coralloids, minute crystals, aggregates, and earthy masses. Some of the minerals are of hydrothermal origin, whereas others are interpreted to have formed during episodes of hydrothermal or vadose alteration. A third group consists of minerals that were precipitated from low-temperature karstic waters. Although most skarn-hosted cavities exhibit the classical features of meteoric-water-induced cave, their mineralization, morphology, and position within the skarn support a hydrothermal or a mixed hydrothermal-vadose origin.

Keywords: skarn, hydrothermal karst, cave, mineralogy, speleogenesis, Băiţa, Bihor County, Romania.

Sommaire

Le district métallogénique de Băiţa, comté de Bihor, en Roumanie, est génétiquement associé à un pluton crétacé supérieur profond de composition granitique. Dans ce district, plusieurs masses de skarn contiennent des concentrations économiques de Mo, W, Bi, Cu, Pb, Zn, B, wollastonite, et marbre. Au cours de l'activité minière, de nombreuses cavités karstiques y ont été trouvées. La présence de minéraux tels que wittichénite, luzonite stibifère, natrolite, quartz, chalcanthite, rosasite, glaukosphaerite, aurichalcite, azurite, malachite, norséthite et, plus couramment, calcite, aragonite, hydromagnésite et goethite, a été notée dans les grottes développées à l'intérieur des skarns. Ces minéraux se présentent sous forme de croûtes, de coralloïdes, de petits cristaux et d'aggrégats. Un sous-groupe de ces minéraux a une origine hydrothermale ou vadose. Par contre, les minéraux d'un troisième groupe ont été précipité à partir des eaux karstiques à basse température. Bien que la plupart des cavités des skarns montrent des traits classiques d'une grotte due à des eaux météoriques, leur minéralisation, leur morphologie et leur position à l'intérieur des massifs skarnifiés étayent une origine hydrothermale ou hydrothermale-vadose.

Mots-clés: skarns, karst hydrothermal, grottes, minéralogie, spéléogenèse, Băiţa, comté de Bihor, Roumanie.

Introduction

Hypogene caves are formed by dissolution by deep CO_2- or H_2S-enriched hot fluids as they approach the surface (Egemeier 1981, Palmer 1991, Ford 1995). Such caves develop at the expense of sedimentary or metamorphic carbonate rocks. According to Ford & Williams (1989), caves referred to as "hydrothermal" develop when hot fluids rise through pores or along fissures, faults, brecciated zones or bedding planes and cool in carbonate rocks with or without mixing with shallow meteoric waters. As discussed in this paper, a particular type of hydrothermal cave occurs where volcanogenic fluids trigger the dissolution process. In such cases, economic ore deposits, mainly of Pb–Zn, may be associated with the host rock (Mozgova 1963, Dżułyński & Sass-Gustkiewicz 1989, Sass-Gustkiewicz & Dżułyński 1998). This type of hydrothermal cave has received much less attention than the classical dissolution-induced cave.

Several Romanian caves show evidence of hydrothermal mineralization (Nedopaca & Grama 1987, Onac *et al.* 1995); however, only a few were documented to be dissolved or mineralized by postmagmatic solutions (Mârza & Silvestru 1988, Mârza *et al.* 1995, Ghergari *et al.* 1997, Damm 2000, Onac *et al.* 1995, 2000).

In this paper, I focus on the origin of the minerals found within the skarn-hosted caves at Băiţa, in Bihor

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County. Knowledge of their mineralogy may help to answer the question of whether hypogene or supergene processes triggered the mineral deposition, which would provide an interpretation of the speleogenesis of these cavities.

GEOLOGICAL SETTING

The Băiţa metallogenic district is located in the western part of the Bihor Mountains, in the upper reaches of the Crişul Băiţei River (Fig. 1, inset). Old mining documents provide evidence of continuous mining activity from the Middle Ages up to the present (Stoici 1983). More than 100 mineral species have been identified in the skarn deposits of the district. Hemimorphite, kotoite, makovickyite, padĕraite, and szaibelyite have their type localities in the district (Udubaşa *et al.* 1992, Udubaşa 1999).

The major structural units of the region are the Bihor Unit, in para-autochthonous position, consisting of Upper Jurassic and Lower Cretaceous limestones, and the Apusenides (Balintoni 2001). The latter include the Codru and Biharia Nappe systems, represented in the area by the Vetre and Arieşeni nappes, respectively (Bordea *et al.* 1975). The Vetre Nappe is the lowermost unit of the Codru Nappe system in the Crişul Băiţei region and comprises a complete Triassic sequence. The assemblage consists of quartzite and hornfels (Ladinian to Lower Carnian), the Frăsinel dolomite marble (Carnian), and the Băiţa marble (Norian) (Bleahu *et al.* 1994). Within the upper part of the Crişul Băiţei area, the metamorphosed Triassic carbonate rocks of the Vetre Nappe are in tectonic contact with quartzite and hornfels belonging to the Coşuri Beds (Vălani Nappe) (Matyaşi *et al.* 2001). The Arieşeni Nappe covers the Vetre unit unit and consists of Permo-Triassic detrital rocks (Fig. 1).

Intrusive rocks are represented by Upper Cretaceous (Balintoni 2001) (Alpine) calc-alkaline granitic rocks ("banatites": Codarcea 1931). The skarn-type mineralization consists of economic concentrations of Mo, Bi, W, Pb, Zn, Cu, B ± Au, Ag, Te, and Fe. The rich magnesian and calcic skarns of Băiţa and their associated ore deposits are connected to a deep-seated pluton of granitic to dioritic composition. Several dykes, ranging in composition from rhyolite to basalt, are related to the Cu–Pb–W–Bi–B ores (Stoici 1983). The ore deposits occur as metasomatic columns or irregular bodies and impregnations in marbles. The geology of the deposits was the subject of many detailed studies, carried out among others by Stoicovici & Stoici (1972), Cioflica *et al.* (1974, 1977, 1995), Cioflica & Vlad (1979), Stoici (1983), and Matyaşi *et al.* (2001).

DESCRIPTION OF CAVES IN SKARNS

Most of the cavities discussed here were intercepted by mine adits and shafts. As listed in Table 1 and shown in Figure 1, two mining sectors contain these caves, Coşuri and Frăsinel–Antoniu. The most important category concerns caves developed within the skarns (the main subject of this paper), but also included are classi-

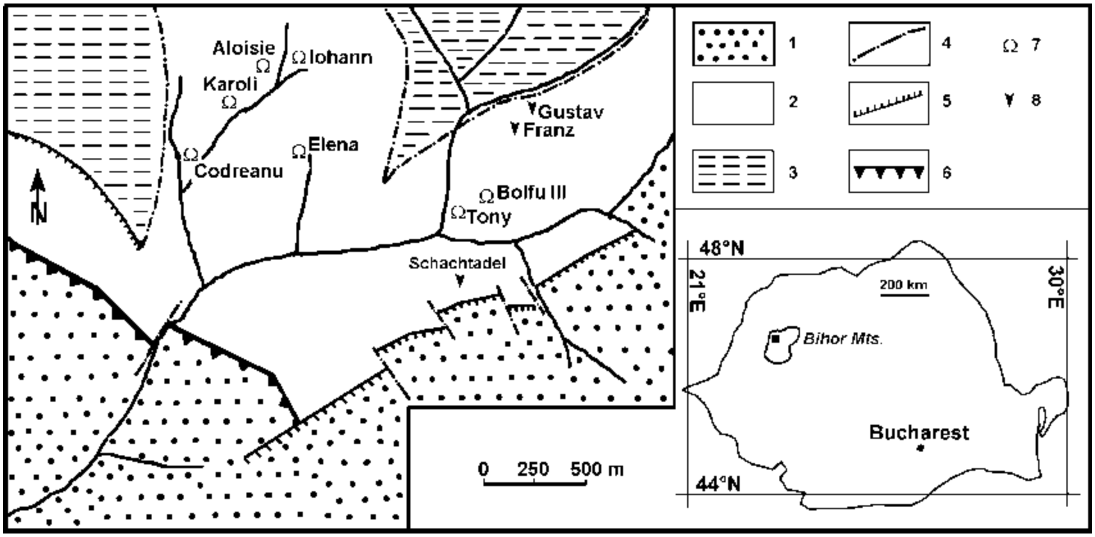

FIG. 1. Simplified geological map of the Băiţa metallogenic district, in Bihor County, Romania, showing the location of the mining galleries in which the caves were intercepted. 1: Arieşeni Nappe, 2: Codru Nappe, 3: Bihor Unit, 4: Geological boundaries, 5: Fault, 6: Thrust fault, 7: Adits, and 8: Shaft (modified from Stoici 1983).

cal dissolution-induced caves. The size of the caves varies between 8 and 550 m in length. The cavities consist of medium-size passageways (or rooms), from which small irregular side passages may develop. The cave walls are lined with thick crusts of calcite and display exotic minerals. No other dissolution or erosion features are present in these caves, except for some cupolas and corrosion notches located in the ceiling of the caves. The most common speleothems found in the skarn-hosted caves are coatings, coralloids, crusts, flowstones, moonmilk, powder, minute crystals and, less commonly, stalactites and stalagmites. This morphology and mineralogy are indicative of cavities whose origins where either partially or completely hydrothermal in nature (Ford & Williams 1989).

The host rock of the investigated caves is represented by either calcic (Coşuri sector) or magnesian and calcic-magnesian skarn bodies (Frăsinel–Antoniu sector). These skarns formed at the expense of Mesozoic carbonate paleosome belonging to the Codru Nappe system (Stoici 1983). On the basis of their spatial development, the caves closely follow the metasomatic contact between Coşuri Beds and the skarn bodies. Since this contact is inclined at about 45–70°, the caves show subvertical, irregularly domed passages. A single cave was found to develop within a copper-rich breccia pipe orebody. After being intercepted, the mineralization of this cave was mined to a depth of 36 m through the Schachtadel vertical shaft (Pošepny 1874, cited by Stoici 1983).

ANALYTICAL METHODS

Chemical and mineralogical characterization of the samples was undertaken by X-ray powder diffraction (XRD), energy-dispersion spectrometry (EDS), electron-microprobe analyses (EMPA), atomic absorption spectrometry (AAS), infrared spectrometry (IR), as well as carbon and oxygen stable isotope analyses. Textural and morphological observations were undertaken using both optical microscopy. X-ray data were obtained by means of Philips PW1800 and DRON–3 diffractometers. Operating conditions were 45 kV at 40 mA and 20 kV at 20 mA, respectively, using Cu$K\alpha$ radiation, and quartz as internal standard. All samples were continuously scanned from 6 to 70° 2θ with a step size of 0.025° 2θ. The characterization of the mineral species relied solely on the XRD patterns in cases where the spectrum was complete and well resolved. In this case, unit-cell parameters for the analyzed minerals were also calculated. Where the spectra obtained showed evidence of multiple phases, additional investigations (*i.e.,* EDS, EMPA, AAS, IR and, where possible, thin section observations) were made.

TABLE 1. LIST OF SKARN-HOSTED CAVES OF THE BĂIŢA MINING DISTRICT, ROMANIA

Name of cave and hosting mining galleries	Type of skarn
Coşuri mining sector	
The cave in the Aloisie mine	calcic
Water Cave in the Codreanu mine	calcic
Crystal's Cave in Codreanu mine	calcic
The cave in the Elena mine	calcic
Water Cave in the Karoli mine	calcic
The cave in the Iohann mine	calcic
Frăsinel – Antoniu mining sector	
The cave in the Gustav mine	calcic-magnesian
The cave in the Franz mine	magnesian
Small cave in the Bolfu III mine	calcic-magnesian and magnesian
Big cave in the Bolfu III mine	calcic-magnesian and magnesian
Surprise cave in the Tony mine	calcic-magnesian and magnesian
The cave from the Schachtadel shaft	calcic-magnesian and magnesian

The caves that were sampled are shown in italics; for location, see Figure 1.

A JEOL JXA–8600 Superprobe (Department of Earth Sciences, University of Bristol) was used in the wavelength-dispersion mode, under the following conditions: excitation voltage 20 kV, specimen current 5 nA, peak count-time 20 s, background count-time 10 s.

Twenty-nine samples were collected from eight caves located in various skarn-hosted mines in the Băiţa metallogenic district. Data available from published sources (Stoici 1983) and unpublished reports were also incorporated, in order to provide a complete mineralogical inventory of these caves. The specimens are deposited in the Mineralogical Museum of the University of Cluj and at the Speleological Institute in Cluj, Romania.

RESULTS

Wittichenite, Cu_3BiS_3

Wittichenite was found in the upper part of the Big Cave in the Bolfu III mine (Fig. 1), appearing as white to lead-grey granular aggregates of submillimetric size crystals. The chemical composition of wittichenite, obtained by AAS, is 37.54 wt.% Cu, 41.72% Bi, 19.22% S, and 1.14% Pb, corresponding to the formula $Cu_{2.95}Bi_{0.99}S_{2.99}$. In the X-ray powder-diffraction pattern, the strongest 14 XRD lines are identical or close to those reported by Nuffield (1947).

Antimonian luzonite, $Cu_3(As_{0.64}Sb_{0.36})S_4$

Luzonite and enargite are polymorphs, luzonite being stable at low temperatures. According to the chemical composition resulting from AAS analyses (47.52 wt.% Cu, 11.15% As, 10.12% Sb, and 31.98% S), the luzonite from Crystal's Cave (Codreanu mine) is antimony-rich and forms thin greyish black crusts (3–4 mm thick) on the walls. In some parts of this cavity, transparent coatings of calcite and clusterites cover the dark crusts. Except for a few lines assigned to calcite, the strongest reflections on the X-ray spectra belong to antimonian luzonite.

Under present-day oxidizing conditions (the pH of the seeping waters in the cave range between 7.1 and 8.3, whereas the Eh is around 0.72 V), this mineral quickly alters to form malachite, azurite, or other rare hydrous carbonates (*e.g.*, rosasite, glaukosphaerite).

Goethite, α-Fe^{3+}O(OH)

Goethite was noted in most of the caves investigated, coating and staining various speleothems in shades of yellow, orange-red or brown. The IR spectrum of crystalline goethite is sharp and well resolved; it shows characteristic bands at 405, 460, 575, 802, and 898 cm^{-1} respectively. The presence of goethite in these caves is related to oxidation of iron-bearing minerals (*i.e.*, pyrite, chalcopyrite) in the wallrock.

Aragonite, CaCO$_3$

Speleothems of aragonite were found in the two caves from the Bolfu III mine. The aragonite is present as white or cream-colored globular and botryoidal coralloids. They range from 4 to 10 mm in diameter and can protrude from the cave wall as much as 30 mm. The aragonite globules and botryoids are the most common speleothems in these caves. In thin section, they exhibit concentric growth-layers composed of length-fast calcite (Folk & Assereto 1976) and layers of aragonite fibers. The crystals grow perpendicular to the layers and are radial around the botryoid. Parts of the aragonite fibers are now inverted to a mosaic of sparry calcite. The probable sequence of deposition was as follows: (i) calcite was deposited as length-fast columnar crystals, (ii) aragonite was deposited as layers of fibers or parallel needles bounded in rays, and (iii) some of the aragonite layers later inverted to a mosaic of sparry calcite crystals. Chemically, these changes probably reflect changes in the composition of cave water from more calcium-rich to alkaline solutions, with a relatively high Mg:Ca ratio when aragonite was precipitated.

Both aragonite and calcite were identified by X-ray powder diffraction and by etching and staining an uncovered thin section with Feigl's solution. The stained fibers of aragonite are bright, and the unstained parts (calcite) remain dark in a back-scattered electron image.

Norsethite, BaMg(CO$_3$)$_2$

Well-crystallized, submillimetric milky white nodules of norsethite are present on the walls of Crystal's Cave at the Codreanu mine and in the Surprise Cave at the Tony mine. X-ray powder-diffraction analyses confirm that the nodules are composed of norsethite, a rare rhombohedral double carbonate. The values for the X-ray reflections of norsethite are much closer to dolomite than to calcite (Table 2). More precisely, when comparing the *d* values for the characteristic lines of norsethite, one can easily note that it shows three distinct lines (values shown in bold in Table 2) in addition to those present in a calcite spectrum. According to Lippmann (1973), the presence of superstructure reflections having *d* values of 4.22, 2.67 and 2.15 Å, which are characteristic for (10$\overline{1}$1), (01$\overline{1}$5) and (02$\overline{2}$1), respectively, do indicate the presence of norsethite. Furthermore, the reflections of norsethite located between 46 and 49° 2θ are shifted on the spectrum of dolomite, where they appear from 48.5 to 51.5° 2θ (values shown in italic in Table 2).

The chemical composition of norsethite, obtained by AAS, is 54.34 wt.% BaO, 14.27% MgO, 0.3% Fe$_2$O$_3$, and 31.09% CO$_2$. which corresponds to the structural formula BaMgFe$_{0.01}$(CO$_3$)$_{1.99}$. More investigations are planned to shed light on the way this mineral precipitated in the cave environment.

Calcite, CaCO$_3$

Calcite is by far the most common and abundant mineral, forming a large variety of types and subtypes of speleothems (Hill & Forti 1997). These include

TABLE 2. INDEXED POWDER PATTERN OF NORSETHITE AND COMPARISON WITH DIAGNOSTIC REFLECTIONS OF CALCITE AND DOLOMITE

Norsethite Băiţa, Bihor County			Calcite (24-27)		Dolomite (11-78)	
d (Å)	I	*hkl*	d (Å)	I	d (Å)	I
4.222	**10**	**101**	-	-		
3.8801	20	012				
			3.852	29		
			3.03	100		
3.021	100	104				
					2.886	100
2.6711	**10**	**015**	-	-	2.67	10
					2.405	10
2.506	35	110				
2.2939	20	113				
			2.284	18		
					2.192	30
2.157	**10**	**021**	-	-		
			2.094	27		
2.0144	30	202				
1.9355	*27*	*024*				
			1.9071	17		
1.8804	*20*	*018*				
			1.8726	34		
1.843	*126*	*116*			*1.848*	*5*
					1.804	*20*
					1.786	*30*
1.6294	31	211				
1.6121	22	122				
			1.604	15		
					1.545	10
1.5285	5	214				
1.5171	4	208				
1.4783	7	125				
					1.413	10

coralloids, coatings, crusts, stalactites, stalagmites, columns, flowstones, moonmilk, helictites and spars. Calcite speleothems in the skarn-hosted caves from Băiţa vary in color, depending on the quantity of trace impurities, from pure white to dark brown, passing through all shades of yellow and orange.

Investigations carried out on 27 calcite speleothems (*e.g.,* coatings, coralloids) suggest some are of hydrothermal origin. One hundred and twenty-one subsamples of calcite were analyzed for oxygen and carbon isotopic ratios in CO_2 expelled in a hot H_3PO_4 line on a Finnigan 251 mass spectrometer. The reproducibility of the system is 0.06‰ for $\delta^{13}C$ and 0.07‰ for $\delta^{18}O$, based on replicate measurements of an internal carbonate standard. Results are reported as ‰ *versus* PDB, using NBS19 as standard reference. The isotopic analyses reveal depleted $\delta^{18}O$ values (between –10 and –16.7‰) for the suspected hydrothermal calcite, whereas the $\delta^{18}O$ values are less strongly negative (*i.e.,* –4 to –8.3‰) in the low-temperature speleothems of the cave environment.

Hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$

Hydromagnesite is the main constituent of moonmilk and nodules found on the floor and walls of the two cavities in the Bolfu III mine. It typically forms on the walls, from where it may peel off and accumulate as granular aggregates. The color of hydromagnesite speleothems is cream to chalk white. The diffraction patterns obtained are complete and well resolved, fitting exactly the reference patterns of hydromagnesite. The mineral is derived from the solution of a dolomitic host-rock, and its deposition was influenced by carbon dioxide loss as well as by evaporation.

Malachite, $Cu^{2+}{}_2(CO_3)(OH)_2$ *and azurite,* $Cu^{2+}{}_3(CO_3)_2(OH)_2$

These two secondary minerals are widespread in the oxidation zones of copper-bearing ore deposits. The two mineral species, identified by X-ray powder diffraction, were found in cavities in the Elena and Karoli mines. In the Water Cave at the Codreanu mine, malachite is closely associated with rosasite and glaukosphaerite. In all these locations, bright green to olive-green malachite (Fig. 2), and dark blue, lustrous azurite (Fig. 3) generally stain and coat the bedrock, the calcite crusts, and the pebbles along the stream. In some parts of the cavities, these minerals fill small fissures or corrosion pockets in the cave walls. Malachite and azurite occur as short prismatic and tabular crystals or needles, commonly grouped in tufts, producing thick (up to 5 mm) crusts and botryoidal aggregates.

Both malachite and azurite were identified by their optical properties in thin sections (*i.e.,* optical character and sign, dispersion and pleochroism). Currently, an investigation of their oxygen and carbon isotope composition is in progress to establish the source material and the temperature of their formation.

Rosasite, $(Cu^{2+},Zn)_2(CO_3)(OH)_2$ *and glaukosphaerite,* $(Cu,Ni)_2(CO_3)(OH))_2$

Samples containing these minerals were collected in the Water Cave in the Codreanu mine. Rosasite appears as bluish green needles, 0.05 to 2 mm long, forming efflorescences on bedrock and calcite crusts. In a few of the samples, rosasite is associated with malachite or glaukosphaerite. Glaukosphaerite occurs typically as a thin coating of deep green color. Although it appears alongside rosasite, it has never previously been reported from a cave environment.

The identification of the two minerals is based on XRD, optical properties and results of chemical analyses. The diffraction data for rosasite and glaukosphaerite differ significantly, such that it is easy to distinguish them where they coexist. The unit cells of rosasite and glaukosphaerite correspond closely to those reported in their ICDD files, which account for the stoichiometry. In thin sections, rosasite appears transparent to pale blue, slightly pleochroic, biaxial negative, and shows parallel extinction (Fig. 4), whereas glaukosphaerite displays fibrous green spherulites and it is also biaxial negative (Fig. 5).

The AAS analyses show 42.21 wt.% CuO, 30.87% ZnO, 19.82% CO_2, and 7.27% H_2O^+ for rosasite and 41.87% Cu, 30.77% NiO, 18.64% CO_2, and 8.51% H_2O^+ for glaukosphaerite. The recalculated analytical result gave the following structural formulae: $Cu_{1.16}Zn_{0.84}(CO_3)_{0.99}(OH)_{1.78}$ for rosasite and $(Cu_{1.12}Ni_{0.88})(CO_3)_{0.90}(OH)_{2.02}$ for glaukosphaerite.

Aurichalcite, $(Zn,Cu^{2+})_5(CO_3)_2(OH)_6$

Stoici (1983) has described the occurrence of aurichalcite from two caves intercepted by the Karoli and Elena galleries, where it appears as scarce, fragile, pale green or light blue crusts lining the walls. As in the case of the other secondary hydrous carbonates of copper discussed, aurichalcite also is derived from the oxidation of the skarn copper ore (Stoici 1983). No further observations on this mineral were possible because the sampled part of those caves collapsed.

The hydrous carbonates presented above result from the two-step oxidation of bornite, chalcopyrite, or covellite (*i.e.,* various copper oxides or sulfides form in an intermediate stage). The Zn and Ni in these minerals are related to sphalerite and gersdorffite, respectively (Stoici 1983).

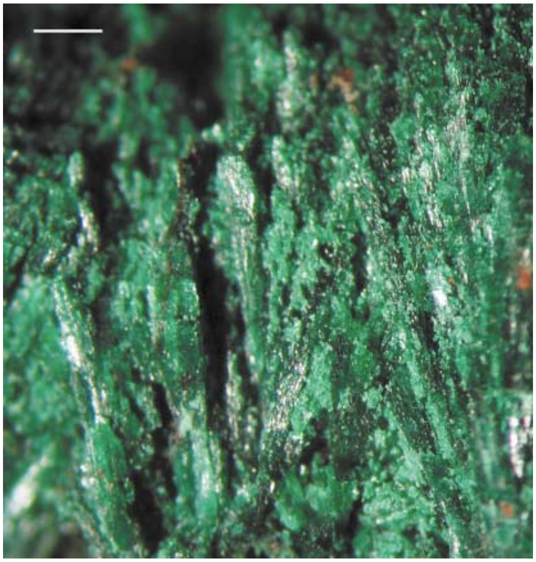

FIG. 2. Malachite tufts over calcite crusts, sample #1396. Scale bar: 1 mm. Water Cave, Codreanu mine.

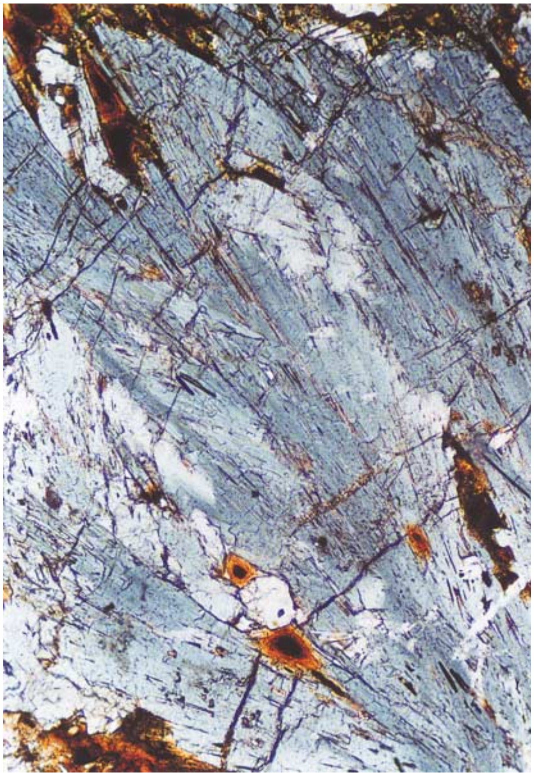

FIG. 4. Rosasite (crossed polars, ×10), sample #1396a. Water Cave, Codreanu mine.

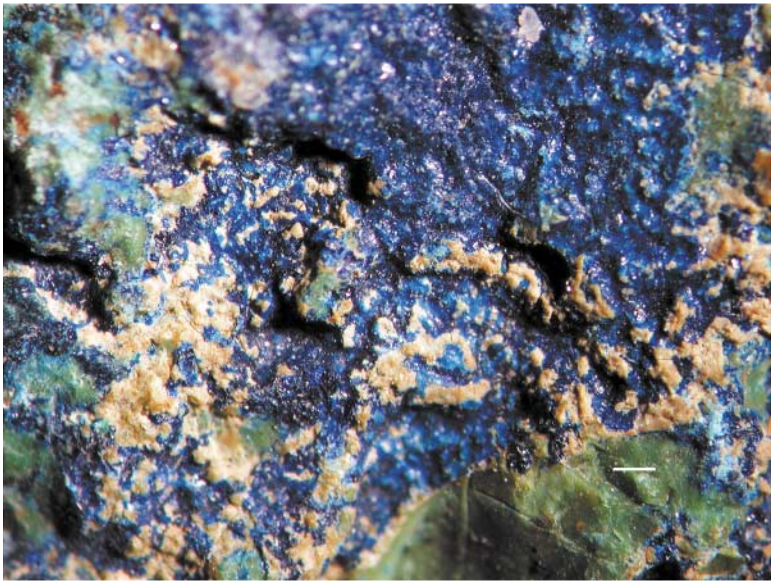

FIG. 3. Azurite overlying calcite and glaukosphaerite (light green crust), sample #1396. Scale bar: 1 mm. Water Cave, Codreanu mine.

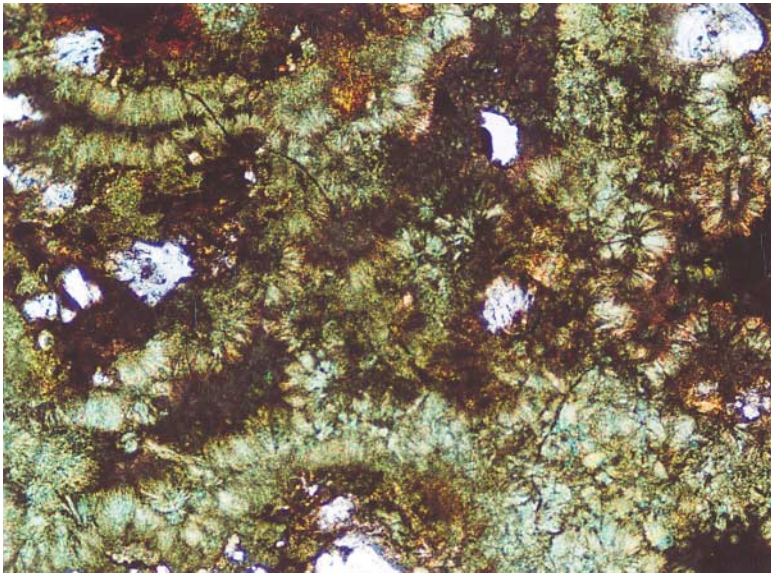

FIG. 5. Fibrous spherulites of glaukosphaerite (plane light, ×10), sample #1396.

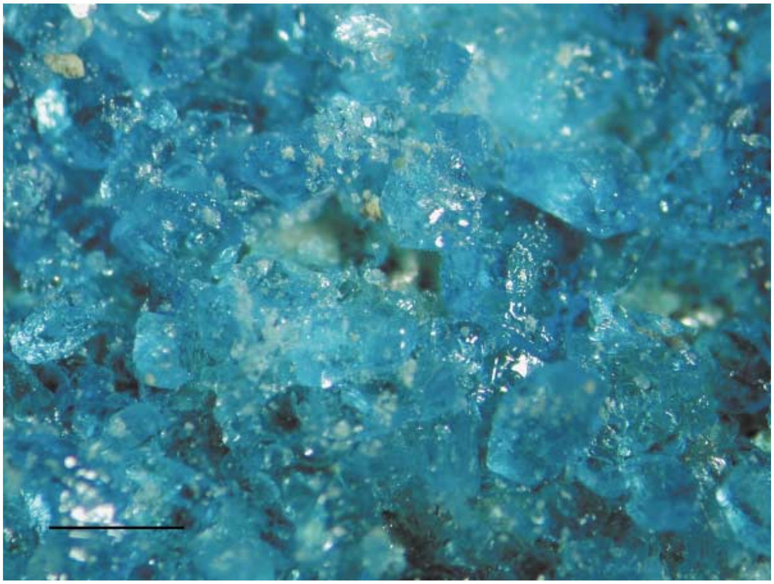

FIG. 6. Chalcanthite crystals, sample #1396b. Scale bar: 1 mm.

Chalcanthite, $CuSO_4 \bullet 5H_2O$

Millimetric granular crystals of chalcanthite colored sky blue and having a vitreous luster have also been found in the Water Cave from the Codreanu mine, along with malachite and azurite (Fig. 6). The only occurrence of this mineral is close to the intersection of the cave with the mine adits, where increased ventilation has lowered the humidity. Chalcanthite was identified by the characteristic *d* values on X-ray diffractograms. The crystallographic planes, *d* values, and relative intensity of the most important peaks of chalcanthite match perfectly those from the ICDD files. Both copper and sulfate in this occurrence comes from the action of acidic waters (from pyrite oxidation) upon chalcopyrite.

Quartz

Coralloids and subhedral crystals of quartz (0.5 to 15 mm in size) have been reported from the Water Cave in Codreanu mine. The coralloids never exceed 15 mm in length and are colorless or yellow-brown, being composed of fine crystals that build up concentric layers intermixed with calcite crystals and radially oriented, length-fast fibers of chalcedony. As the stable isotope composition of the calcite crystals suggests hydrothermal conditions of growth, we assume that quartz and chalcedony also were generated during a hydrothermal episode in the cave's history. Quartz was identified by means of XRD.

Natrolite, $Na_2[Al_2Si_3O_{10}]\bullet 2H_2O$

Natrolite forms glassy, opaque white patches that underlie calcite crusts in the Big Cave from Bolfu III mine. These patches are composed of aggregates of fibrous crystals up to 1–2 mm in thickness and 6 to 20 mm in diameter. Natrolite was identified by XRD. In thin section, it shows prismatic contours. The exact origin of the primary mineral from which the constituents of natrolite were derived is unknown. However, one possible scenario would be the presence of albite within the Upper Cretaceous calc-alkaline dykes occurring in the close vicinity of Bolfu III mine. If so, natrolite could be a product of alteration of albite in such a low-temperature hydrothermal setting.

DISCUSSION

Types of minerals

According to Hill & Forti (1997), if any secondary cave minerals formed *after* the cave passages were developed, due to a unique set of conditions in a cave (*i.e.,* high relative humidity, low and constant temperature, water composition), they can be considered to be genuine cave minerals. Yet, if they formed within the skarn during a metasomatic or a late hydrothermal stage and are exposed after the cave passage cut across the skarn body, they are not to be considered cave minerals.

The minerals presented in this contribution may be assigned to three different genetic categories: (a) minerals deposited from hydrothermal solutions (wittichenite, antimonian luzonite, quartz and, in part, calcite), (b) products of hydration or alteration of hydrothermal minerals (malachite, aurichalcite, rosasite, azurite, glaukosphaerite, chalcanthite, and goethite) or of some original constituents of the igneous rocks (*e.g.,* natrolite derived from albite), and (c) minerals precipitated from low-temperature vadose solutions (calcite, aragonite, hydromagnesite, and norsethite).

Following the definition of a cave mineral and knowing the common cations circulating in a groundwater karst system (Ca, Mg, Na), the minerals from category (c) are true cave minerals. Taking a closer look at the minerals in category (b), one can recognize them as secondary products formed within the skarn-hosted cavities at the expense of various primary, hydrothermal minerals.

Several authors consider karst openings of any size as ideal receptacles for various ore deposits (Dżułyński & Sass-Gustkiewicz 1989, Dublyansky 1997, Liaghat *et al.* 2000). Occasionally, hydrothermal minerals, such those reported under group (a), can be deposited in voids that are part of pre-existing karst channels of meteoric water. Although they cannot be considered true cave minerals, the presence of these minerals under normal cave settings would be the most diagnostic criterion for hydrothermal-related karst speleogenesis. The presence of such an "exotic" assemblage of primary or secondary minerals (*e.g.,* wittichenite, natrolite) provides supportive evidence of at least one hydrothermal episode in the cave history.

Model of skarn-hosted cave development

The speleogenesis of these cavities can be subdivided into three stages based on the geometry, morphology, position within or along the skarn bodies, and the mineral assemblages found. These stages of development, however, may not be related to each other.

Stage 1 (*deep-seated settings*). The earliest part of the speleogenesis in the Băiţa karst region is considered to have been a metasomatic one. Contact metamorphism of limestones involves decarbonation; the liberated CO_2 increases the acidity of the fluids escaping the system, and hence the dissolution capacity of these fluids is enhanced. At this stage, the circulation of hot metasomatic fluids may be responsible for some primitive dissolution-induced cavities along primary or secondary discontinuities. Cavities formed during this stage appear within the skarn bodies or following bedding planes, faults or geological boundaries (Fig. 7a). If such cavities did form, processes generated by subsequent stages obliterated them. None of the minerals (wittichenite and antimonian luzonite) precipitated during this stage would qualify as typical cave minerals.

Stage 2 (*shallow settings*). In the Băiţa metallogenic district, most of the skarn-hosted caves are probably connected to this stage. Two different processes are responsible for the caves: (a) upward flow of hydrothermal fluid, at which point the flow velocity was relatively high and dissolution outpaced deposition or replacement of the carbonate host-rocks, and (b) vigorous dissolution caused by mixing of ascending hydrothermal fluids with more oxygenated descending waters (Dublyansky 2000). The caves occur mostly along stratigraphic, metasomatic, and tectonic contacts. Therefore, they are closely related to the boundaries of the mineralized skarn bodies (Fig. 7b). Their morphology is indicative of cavities whose origins were either partially or completely hydrothermal in nature (Ford & Williams 1989). This category also includes cavities located at the edges of or within the mineralized skarn bodies. Stoici (1983) considered these cavities to have formed by dissolution of the mineralized bodies (Fig. 7c).

Minerals formed under shallow hydrothermal karst-forming conditions (natrolite, goethite, malachite, rosasite, azurite, glaukosphaerite) reflect an unstable geochemical environment.

Stage 3 corresponds to the latest part in cave genesis. In this stage, the karst conduits have been modeled to their actual morphology in either phreatic or vadose conditions. Alongside classical deposition of carbonate speleothems (calcite, aragonite, and hydromagnesite), the weathering of ore-related minerals continued, and hydrous carbonates were further produced.

CONCLUSIONS

Fourteen minerals assigned to one of three genetic categories, hydrothermal, alteration-hydration of primary igneous or hydrothermal parageneses, and vadose, were documented from 12 skarn-hosted cavities in the Băiţa region. Of these 14 minerals, five are described for the first time in a hydrothermal-activity-related karst environment (wittichenite, antimonian luzonite, norsethite, glaukosphaerite, and natrolite) and three are new occurrences for Romania (rosasite, glaukosphaerite, and norsethite). On the basis of the ubiquitous presence of these exotic minerals, combined with observations on the morphology, geometry, and position of the cavities within the skarn, most of the caves in the Băiţa area are part of an important hydrothermal karst generated by Upper Cretaceous postmagmatic solutions.

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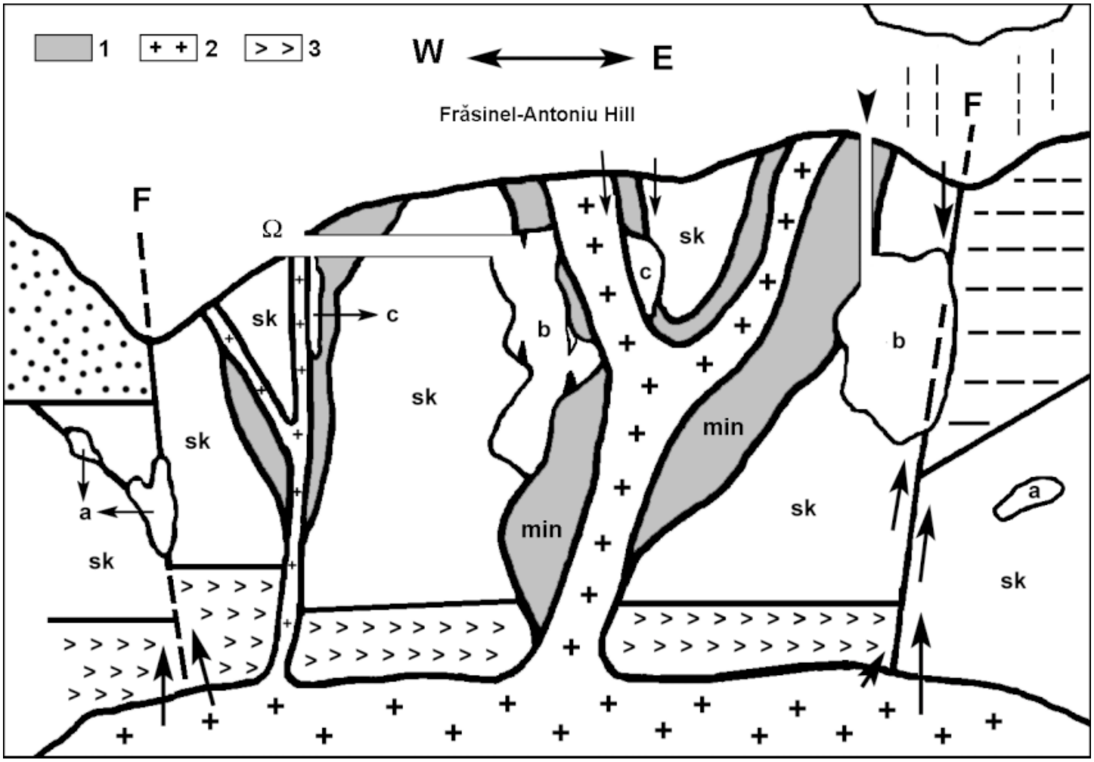

FIG. 7. Idealized east–west cross section across Frăsinel – Antoniu Hill, showing the location of different genetic types of skarn-hosted caves (labeled a, b and c; see text for explanation). 1: Mineralized skarns, 2: Upper Cretaceous pluton and dykes, 3: hornfels, sk: skarns. Other symbols are identical to those in Figure 1.

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