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THE RELATIONSHIP BETWEEN CAVE MINERALS AND H_2S-RICH THERMAL WATERS ALONG THE CERNA VALLEY (SW ROMANIA)

POVEZAVA MED JAMSKIMI MINERALI IN TERMALNIMI VODAMI BOGATIMI Z ŽVEPLOVODIKOM V DOLINI CERNE (JZ ROMUNIJA)

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Bogdan P. Onac, Jonathan Sumrall, Tudor Tămaş, Ioan Povară, Joe Kearns, Veronica Dărmiceanu, Daniel Veres, Cristian Lascu: The relationship between cave minerals and H_2S - rich thermal waters along the Cerna Valley (SW Romania)

Within the Cerna Valley in southwestern Romania, over a 100 caves were formed in the Jurassic and Cretaceous limestone that outcrops on the valley walls. Three aspects are prominent when entering most of the caves in this region: the presence of considerable gypsum deposits, the amount of guano, and the cave temperature. High temperature anomalies are uncommon in the cave environment. In certain caves in the lower part of Cerna Valley, however, one can measure air temperatures as high as 40°C. This situation is due to the presence of thermal water pooling or flowing through the caves or to the hot steam that rises along fractures from deeper thermal water pools. As a result, these caves provide a unique set of conditions that allowed for the deposition of a suite of unusual minerals. This study presents the results of fifty-seven mineral samples that were investigated by means of X-ray diffraction, geochemical, Fourier-transformed infrared spectroscopy, and scanning electron microscope analyses with the scope of linking the cave minerals with likely hypogene speleogenetic processes. Here we document the occurrence of twenty-two secondary cave minerals, among which, apjonite and tamarugite are the first recorded occurrences in a limestone cave environment. The minerals fall into three distinct associations: sulfate-dominated (Diana Cave), phosphate-dominated (Adam Shaft), and sulfate-phosphate-nitrate-rich assemblage (Great Sălitrari Cave). Additional isotopic measurements (δ34S) performed on sulfate speleothems contribute valuable information on both minerals and cave origins.

Keywords: cave minerals, thermal water, stable isotopes, hypogene speleogenesis, Cerna Valley, Romania.

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Bogdan P. Onac, Jonathan Sumrall, Tudor Tămaş, Ioan Povară, Joe Kearns, Veronica Dărmiceanu, Daniel Veres, Cristian Lascu: Povezava med jamskimi minerali in termalnimi vodami bogatimi z žveplovodikom v dolini Cerne (JZ Romunija)

V dolini Cerne, na jugozahodu Romunije, je bilo v jurskih in krednih apnencih oblikovano več kot 100 jam. Za jame v tej regiji so izstopajoče tri značilnosti: prisotnost velikih količin izločene sadre, veliko guana in visoka jamska temperatura. Visoko temperaturne anomalije niso značilne za običajno jamsko okolje. V določenih jamah, v nižjih delih doline Cerne, ponekod temperatura doseže 40ºC. Ta situacija je posledica prisotnosti termalnih vod, ki tečejo skozi jamo ali se nabirajo v bazenih ter vročih par, ki se dvigajo iz globin skozi razpoke. Posledica naštetih posebnosti so izjemni pogoji v jamskem okolju, ki dovoljujejo izločanje niza redkih mineralov. Ta študija predstavlja rezultate preiskav 57 vzorcev z rentgensko difrakcijo, geokemijo, Fourierjevo-transformacijsko infrardečo spektroskopijo in elektronsko mikroskopijo z namenom, da povežemo prisotnost jamskih mineralov z verjetnimi hipogenimi speleogenetskimi procesi. Tukaj dokumentiramo prisotnost dvaindvajsetih sekundarnih jamskih mineralov, med katerimi je prisotnost apjonita in tamarugita prvič zabeležena v okolju jame razvite v apnencih. Minerali pripadajo trem različnim združbam: s prevladujočimi sulfati (Diana Cave), s prevladujočimi fosfati (Adam Shaft), in sulfatno-fosfatno-nitratno bogata združba (Great Sălitrari Cave). Dodatna merjenja izotopov (δ34S) izvedena na sulfatnih kapnikih, so prispevala dodatne informacije o izvoru mineralov in jam.

Ključne besede: jamski minerali, termalne vode, stabilni izotopi, hipogena speleogeneza, dolina Cerne, Romunija.

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INTRODUCTION

Cerna Valley in SW Romania is famous for its enormous cliff faces, and rugged landscape. Above all, it has been known since pre-Roman times because of its thermal springs (Cristescu 1978). The Băile Herculane Spa is located in the lower part of the Cerna Valley (Fig. 1), directly above an important positive geothermal anomaly. Thermal gradients of the anomaly are six fold higher than the average normal value (Veliciu 1988). Hydrochemical investigations by Povară (1973) and Marin (1984) indicated that the waters in the Cerna River basin are either carbonate (typical for karst regions) or chloride-sodic type. Most of the thermo-mineral sources which show high contents of H_2S and SO_4^{2-} (> 76 mg/l and > 90 mg/l, respectively) fall in the chloride-sodic category (Povară *et al.* 2008; Sumrall 2009). The water temperature from these thermal springs may reach 58°C (Povară *et al.* 1972). In most cases, the presence of H_2S allows native sulfur to be precipitated at thermal spring mouths along the lower part of the Cerna Valley.

In the neighborhood of Băile Herculane, a number of caves such as Diana, Despicătură, and Hercules are currently under the influence of thermal waters, which either flow or pool in them. In other caves (e.g., Grota cu Aburi and Adam) the thermal anomalies are related to the presence of hot steam that ascends along deep paths (faults, fractures, and voids along folded strata).

It has been documented that many caves affected by thermal and/or sulfide-rich solutions (either during their development or in later stages) display a rich and diverse mineral association (Povară *et al.* 1972; Diaconu & Medeşan 1973; Cody 1978; Hill 1987; Maltsev & Self 1992; Onac *et al.* 2000, 2001, 2007; Dublyansky 1997, DuChene 1997; Maltsev 1997; Onac 2002; Forti *et al.* 2006; Audra & Hobléa 2007). Onac (2004, 2005) has shown that in many situations, exotic mineralogy in a cave environment could be a diagnostic feature for hypogene speleogenesis or some special conditions under which the mineral assemblage was precipitated.

This paper provides an overview on the mineralogy of caves in the middle and lower section of the Cerna Valley, once or presently influenced by sulfide-rich thermal water activity. The study has three objectives: 1) to identify and preliminary characterize the mineralogy of selected caves, 2) to reveal the genetic pathways of all documented cave minerals, and 3) to ascertain the relationship (if any) between specific cave mineral associations and possible hypogene processes.

GEOLOGICAL SETTINGS

The southwestern part of the "Transylvanian Alps" (South Carpathians) is mainly composed of pre-Alpine basement nappes (e.g., Berza *et al.* 1994; Kräutner 1996). The Cerna Valley is a complex region, both geologically and tectonically. Stratigraphically upward, the units documented in this region include: the Danubian nappe complex with a metamorphic basement intruded by granitoids of Panafrican age and the Getic nappes (both with Cadomian and/or Variscan basement and Mesozoic covers; Năstăseanu 1980; Liégeois *et al.* 1996; Bojar *et al.* 1998; Kräutner & Krstic 2002). The Getic Nappe is represented by elongated strips of crystalline schists, sunken into the Cerna Graben or situated at 150-200 m above it.

The basement of the Danubian nappes is a transgressive sequence capped mainly by Mesozoic carbonate sediments. The Jurassic sedimentary deposits are best developed and preserved on the right slope of Cerna Valley. They are represented by basal conglomerates, sandstones, shales, clastic and spathic limestones varying from 50 to 75 m in thickness (J1-J2). These are overlain by a thick carbonate sequence (180-200 m) of late Jurassic to early Cretaceous (Berriasian) age, consisting of sandy limestones with chert nodules and massively bedded (in metric banks) limestones. The rest of the early Cretaceous (Valanginian-Hauterivian) follows in depositional continuity and is represented by 50 to 75 m thick carbonate deposits with frequent marly intercalations. The Barremian-Aptian interval is mainly represented by the schistous marly limestones of the Iuta Layers (200-250 m in thickness). The sedimentary sequence ends with terrigenous flysch deposits of Turonian to Senonian age (Năstăseanu 1980).

From a tectonic point of view, two major structures are involved in the functioning of the thermo-mineral aquifer in the vicinity of Băile Herculane: the Cerna Syncline (developed on the right slope of the river) and the Cerna Graben (formed between two deep fractures, NNE-SSW oriented, and sunk more than 1,000 m), respectively. The most important transversal fractures in the Băile Herculane perimeter are the Hercules, Munk, Diana, Neptun, and Vicol faults. On the intersections with the western fault of the Cerna Graben or immediately nearby, thermo-mineral waters emerge either directly to the surface or into natural karst cavities.

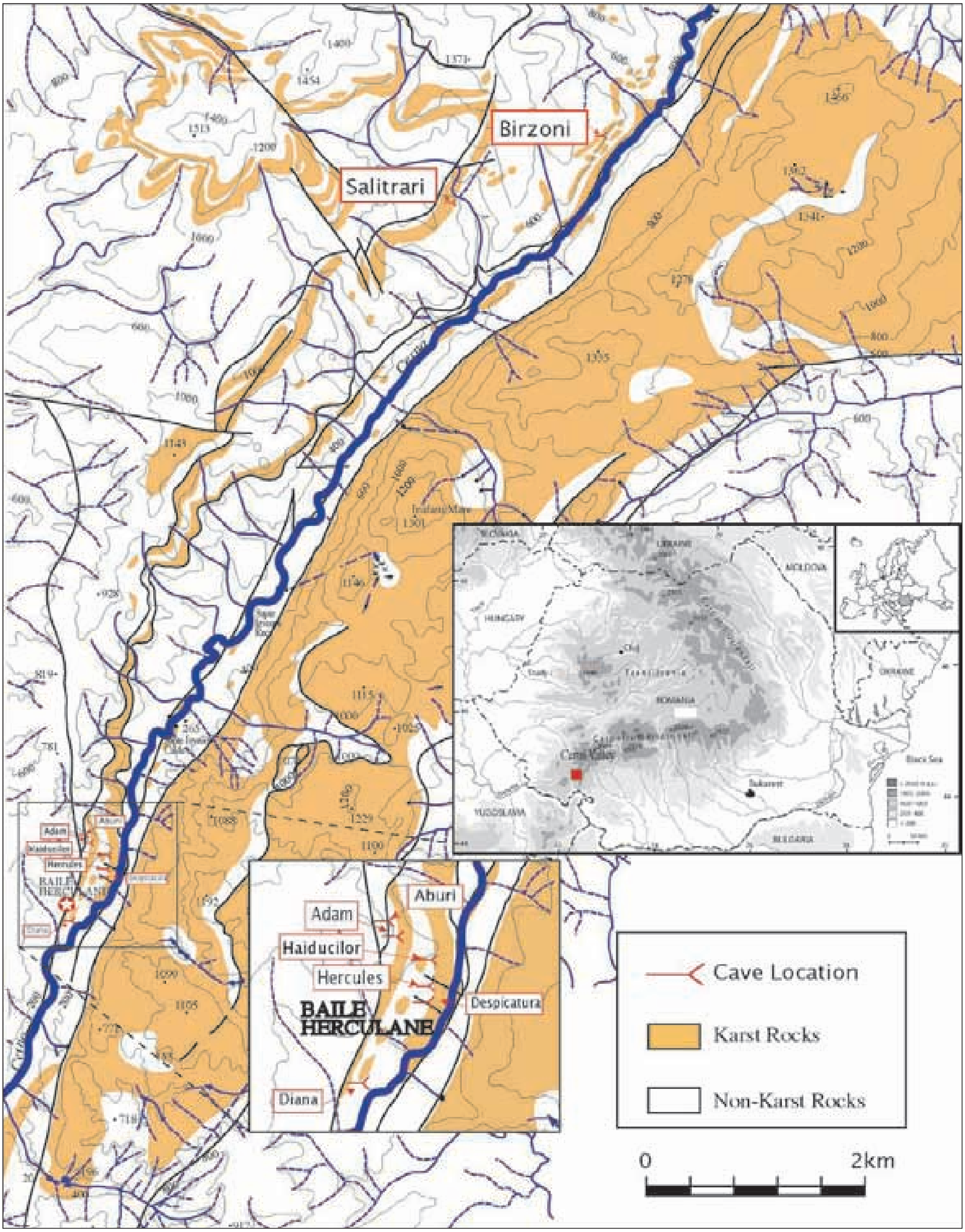

Fig. 1: Location map showing the major cave sites along Cerna Valley, SW Romania.

SAMPLING AND ANALYTICAL METHODS

Water and mineral sampling was performed during the 2008 field season. Samples of thermo-mineral water were collected from three caves (Diana, Despicătură, Hercules) and ten thermal sources (springs and wells) (Neptun 1+4, Neptun 2, Neptun 3, Venera, Traian, Diana 3, Scorilo, Şapte Izvoare Calde (The Seven Hot Springs; left and right of Cerna), and Crucea Ghizelei). Temperature, pH, total dissolved solids (TDS), and electrical conductivity (EC) were measured in the field using a Hanna HI 9828 Multiparameter instrument.

Over 50 mineral samples (mostly sulfates) were collected from thirteen caves (Diana, Despicătură, Hercules, Haiducilor, Adam, Aburi, Sălitrari 1 and 2, Sălitrari 6 to 9, Great Sălitrari Cave, and Bîrzoni) and the Hercule Mining Gallery (Fig. 1). Visual inspection of all mineral specimens was made using a Nikon SMZ1500 stereo zoom microscope, equipped with a fiber-optic ring illuminator and a high-definition DS-5M standard CCD camera. Additional images were collected using a Hitachi S-3500N scanning electron microscope. Samples were routinely analyzed by means of X-ray powder diffraction (XRD) method using a Rigaku MiniFlex II instrument at the Department of Geology, University of South Florida. Operating parameters were 30 kV and 15 mA using a Ni Kβ-filtered CuKα radiation. The patterns were collected using fixed 1.25° scattering slit and a 0.3 mm receiving slit. All samples were continuously scanned (speed was 0.5 and 1°/s) from 5 to 70° 2θ with a fixed step size of 0.02° 2θ per second. Silicon (NBS-640b) was used as the internal standard.

The Fourier-transformed infrared (FT-IR) spectra were recorded at room temperature using a Brucker Equinox 55 spectrometer (In-GaAs detector and KBr pellets) at “Babeş-Bolyai” University in Cluj. The spectral resolution was 4 cm-1. Two hundred scans were accumulated.

A Thermo Delta V Isotope Ratio Mass Spectrometer (IRMS) at University of South Florida Stable Isotope Lab was used to measure $\delta^{34}S$ values ($^{34}S/^{32}S$ ratio expressed in δ-notation) in water and mineral samples by coupled Elemental Analysis (EA)-IRMS by conversion of S to SO_2. The method that this study used for continuous flow sulfur isotope analysis follows Grassineau *et al.* (2001). The standards used for the analysis were IAEA S-2 and IAEA S-3 for sulfides and IAEA SO-5 and IAEA SO-6 for sulfates.

RESULTS AND DISCUSSIONS

Prior to this study, only seven minerals were identified in four caves (Diana, Despicătură, Adam, and Great Sălitrari Cave) located in the middle and lower section of the Cerna Valley (Povară *et al.* 1972; Diaconu & Medeşan 1973; Diaconu 1974; Diaconu & Lascu 1999). Our present study reinvestigated these caves along with nine others, adding 16 more mineral species to the mineral inventory, which now totals twenty-two (Tab. 1). What is important is not the number of new minerals, but the way they associate and the types of information they carry. To better understand the mineralogical results, a brief presentation of the chemical and the $\delta^{34}S$ values of the thermo-mineral waters are given below. Since this is not the main focus of the paper we only present those thermal sources that are related to some of the investigated caves (Tab. 2). These analyses will allow insight into how isotopic values are transferred from the dissolved sulfur in thermal water to solid mineral forms.

CHEMICAL AND STABLE ISOTOPE COMPOSITION OF THERMO-MINERAL WATERS

Chemical analyses of the thermo-mineral sources along Cerna Valley show that the dissolved sulfate is almost completely reduced by the time it reaches Diana 3 Well. The lowest concentration of dissolved sulfate is 9 mg/l with an elevated (41.2 mg/l) concentration of total dissolved sulfur (Tab. 2). The dissolved sulfide produced in Diana 3 Well (and downstream) shows a complete reduction of sulfate, resulting in the dissolved sulfide having the isotopic value of the original marine sulfate. The dissolved sulfide effervesces into the atmosphere of the cave, where it is oxidized to produce sulfuric acid. The sulfuric acid reacts to form the suite of sulfate minerals. There is little to no fractionation associated with these reactions, which is reflected in the isotopic values of the samples in Diana, Despicătură, and Hercules caves.

Upstream from Băile Herculane, the sources show very negative sulfide $\delta^{34}S$ values (-19.5 to -14.1 ‰) suggesting towards an incomplete reduction of sulfate, which accounts for the ^{34}S-depleted sulfides. In addition, TDS data correlate well with the total dissolved sulfur in these sources. The TDS values in the lower springs, however, appear less influenced by total sulfur content but being mostly controlled by dissolution of other soluble species.

Tab. 1: List of minerals found in caves from Cerna Valley during this study in comparison with minerals previously documented from this region.

Mineral	***Composition***	***This study***	***Previous studies***[1]	***Cave***[2]
Native elements				
Sulfur	S	X	X	D
Carbonates				
Calcite	$CaCO_3$	X	X	all caves
Aragonite	CaCO3	X	-	D
Monohydrocalcite	$CaCO_3·H_2O$	X	-	H, S1
Sulfates				
Anhydrite	$CaSO_4$	X	X	D
Aluminite	$Al_2(SO_4)_2·(OH)_4·7H_2O$	X	-	S
Alunite	$KAl_3(SO_4)(OH)_6$	X	-	S
Apjohnite	$Mn^{2+}Al_2(SO_4)_4·22H_2O$	X	-	D
Chalcanthite[3,4]	$Cu^{2+}SO_4·5H_2O$	X	-	HM
Epsomite	$MgSO_4·7H_2O$	X	-	D
Gypsum	$CaSO_4$·2H2O	X	X	all caves
Halotrichite	$Fe^{2+}Al_2(SO_4)_4·22H_2O$	X	?	D
Pickeringite	$MgAl_2(SO_4)_4·22H_2O$	X	X	D
Tamarugite	$NaAl(SO_4)_2·6H_2O$	X	-	D
Nitrates				
Darapskite	$Na_3(SO_4)(NO_3)·H_2O$	X	X	S
Nitratine	$NaNO_3$	-	X	S
Phosphates				
Apatite-(CaF)	$Ca_5(PO_4)_3F$	X	-	Ad, S
Apatite-(CaOH)	$Ca_5(PO_4)_3(OH)$	X	-	Ad, Ab, S, S2
Ardealite	$Ca_2(SO_4)(HPO_4)·4H_2O$	X	-	S
Brushite	$CaHPO_4·2H_2O$	X	-	Ad, S
Taranakite	$K_3(Al,Fe)_5(HPO_4)_6(PO_4)_2·18H_2O$	X	-	S
Variscite	$AlPO_4·2H_2O$	X	-	S
Other minerals[4]				
Kaolinite	$Al_5Si_2O_5(OH)_4$	X	-	S
Illite[5]	$K_{0.65}Al_{2.0}\square Al_{0.65}Si_{3.35}O_{10}(OH)_2$	X	-	Ad, S
Quartz	SiO_2	X	-	Ad, S, S2

According to the data published by Marin (1984) and Povară *et al.* (2008), all thermo-mineral sources in Tab. 2 are of sodium-calcium-chloride and high-sulfide composition type (± bromide and iodide). This observation is crucial when discussing the mineralogy of the precipitates within the cave environment along Cerna Valley.

MINERALOGICAL DATA

Tab. 1 lists all minerals positively identified in thirteen caves and one mining gallery. The twenty-two mineral species belong to five chemical groups. The only native element found was sulfur. It occurs as bright yellow powder sprinkled over halotrichite-group minerals within Diana Cave. The presence of sulfur in this environment is likely related to the oxidation of hydrogen sulfide rich water vapors.

Apart from calcite and gypsum, which were identified in every cave investigated, all the other minerals fall into three distinct associations resulting from specific reactions under highly particular settings in caves such as Diana, Adam, and Great Sălitrari. These three remarkable cave mineral occurrences are considered below, along with a presentation of the gypsum deposits from Bîrzoni Cave and a general summary of the remaining minerals.

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[1] Studies by Povară *et al.* (1972), Diaconu & Medeşan (1973), Diaconu (1974) and Diaconu & Lascu (1999)

[2] D: Diana; H: Hercules; HM: Hercule Mining Gallery; S: Great Sălitrari Cave; S1: Sălitrari 1; S2: Sălitrari 2; Ad: Adam; Ab: Aburi.

[3] Found in the Hercule Mining Gallery

[4] Not secondary cave minerals

[5] Series name for incompletely-investigated, interlayer-deficient micas (Back & Mandarino 2008)

Tab. 2: Characteristics of selected thermo-mineral sources in the lower section of the Cerna Valley, Romania (data collected in July 2008).

Name	***Temp (°C)***	***pH***	***TDS (ppm)***	***EC (mS/cm)***	***S^{2-} (mg/l)***	***SO_4^{2-} (mg/l)***	***$\delta^{34}S$ sulfide (‰)***	***$\delta^{34}S$ sulfate (‰)***
Diana Cave	52.44	6.63	1247	2.1	36.9	44	23.7	27.2
Diana 3 Well	43.2	7.3	3175	6.332	41.2	9	19	71.3
Hercules Cave (Hercules I Spring)	36.33	7.76	2375	5.679	-	125	-	17.7
Despicătură Cave (Hercules IIα Spring)	18 to 53.4	7.26	1681	3.362	-	124	-	16.6

DIANA CAVE (SULFATE-DOMINATED ASSOCIATION)

The thermo-mineral spring (~51°C) and the highly steam condensate-related alteration environment in Diana Cave are responsible for the unusual mineral association (nine species) precipitated at water/bedrock interface. Diana Cave is a short cavity (14 m in length) developed along the Diana Fault line, at the contact between the upper Jurassic limestones and the marls of Iuta formation (Năstăseanu 1980). It is located in the older part of Herculane Spa on the right side of Cerna Valley. In order to capture and use the thermal spring for cure, an artificial gallery was constructed. Therefore, much of the original cave morphology is hidden behind precast concrete segments. Due to the aggressiveness of thermal sulfidic waters and steam, however, the concrete was weathered and the cave walls are exposed on limited surfaces allowing for sample collection.

The first report on the mineralogy of this cave is presented in Povară *et al.* (1972), where gypsum, sulfur, and halotrichite are briefly described. One year later, a detailed study undertaken by Diaconu and Medeşan (1973) concluded that the main mineral phase of the efflorescences developed over the marl debris is pickeringite and not halotrichite. The genesis of this mineral is related to the reaction between the acidic sulfate-rich solutions (pH ~ 4) and the clay minerals within the marls.

In 1974, Diaconu described acicular and prismatic crystals of anhydrite precipitated along with gypsum on cave wall crusts and on the ceiling. The $NaCl^-$ and $MgCl_2^-$ enriched thermal waters and the thermal cave microclimate are considered responsible for the precipitation of anhydrite.

A reexamination of earthy aggregates and efflorescences from Diana Cave, reconfirmed the presence of sulfur, anhydrite, and pickeringite. In addition, we detected four other sulfates, namely: apjonite, halotrichite, epsomite, and tamarugite (Tab. 1). In one sample (associated with gypsum), few diffraction lines match those of rapidcreekite. However, further investigations are needed to confirm the occurrence of this rare mineral. The presence of the halotrichite-group minerals (apjonite, halotrichite, and pickeringite) is not surprising. A complete series between the Fe^{2+} end-member (halotrichite) and the Mg^{2+} analogue (pickeringite) is supposed to exist, extending also towards the Mn^{2+} end-member (apjonite). Under binocular microscope, the efflorescences and the mammillary/botryoidal crusts in which these three minerals were identified appear to be composed of fibrous and short acicular to prismatic crystals. Pickeringite is shiny white-yellowish to silver white and is closely associated (intergrown) with orange/yellowish-brown halotrichite (Fig. 2). Apjonite forms fibrous microcrystals that have a silky luster and are tinted yellow to pale green. The XRD spectra of these minerals are practically indistinguishable; their identification relies on chemical microanalyses (electron microprobe) and FT-IR.

The genetic mechanism proposed by Diaconu and Medeşan (1973) for pickeringite also holds true for the

Fig. 2: Acicular to fibrous aggregates composed of pickeringite (1) and halotrichite (2) crystals in Diana Cave (Photo: B.P. Onac).

other two mineral members of this series. Capillary action draws sulfate-rich solutions through the porous marls of Iuta formation. Upon reaching the surface, the water evaporates resulting in the deposition of halotrichite-group minerals.

Epsomite forms delicate fibrous (microcrystals elongated after [001]), patchy white efflorescences on the cave walls. The epsomite is precipitated from Mg-rich sulfidic thermal waters.

Tamarugite is a hydrated Na-Al sulfate first documented in Grotta dello Zolfo, Italy by Zambonini (1907). Since then, it has been identified only in Alum Cave in Sicily and Ruatapu Cave in New Zealand (Forti *et al.* 1996; Rodgers *et al.* 2000). However, at all these locations the mineral is precipitated in a volcanic environment. Diana Cave seems to be the first truly karst setting in which the reaction between alkali-type sulfidic thermal waters and kaolinite and illite of Iuta marls resulted in the precipitation of tamarugite. It occurs as colorless to dull white, porous aggregates (Fig. 3) developed along with gypsum crusts, in the same areas where halotrichite-group minerals were identified.

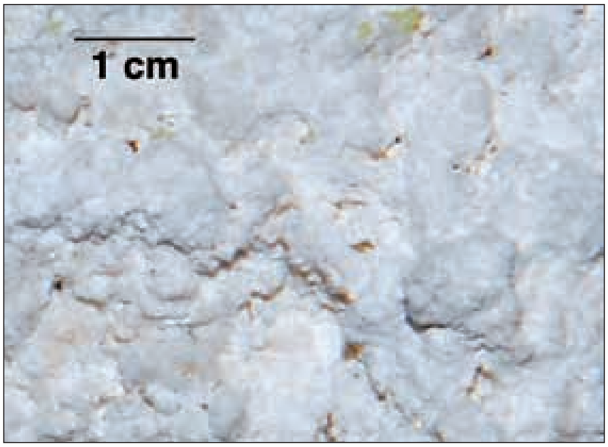

Fig. 3: Porous aggregates of tamarugite (Photo: B.P. Onac).

The isotopic compositions of sulfate minerals from Diana Cave range from +18.0 to +19.5 ‰ for $\delta^{34}S$ in gypsum, tamarugite, halotrichite, and pickeringite. These values are typical for marine sulfates. We know, however, that the thermal water in Diana Cave is sulfidic, indicating that the sulfates were not derived from the simple dissolution and reprecipitation of marine evaporite sulfate within the stratigraphic section. Our argument to support this statement is the absence of evaporite rocks in the lithology of Cerna Valley region (Năstăseanu 1980) and the presence of H_2S in thermal water of Diana Cave (Tab. 2).

GREAT SĂLITRARI CAVE (SULFATE/PHOSPHATE/ NITRATE ASSOCIATION)

The entrance to Great Sălitrari Cave is located in the right slope of the Presacina Valley (right side tributary of Cerna Valley in its middle section) at 480 m absolute altitude (Ponta & Solomon 1982). Its passages have a Y shape (Fig. 4). From a topoclimatic and mineralogical point of view, the cave can be divided in two very distinct sectors: 1) the Nitrate Passage (125 m from the cave entrance) and 2) the rest of the cave passages. With the exception of the Nitrate Passage, the cave is cold (< 10°C) and its air is near saturated or saturated with water vapor, i.e., the relative humidity ranges between 96 and 100 %. The only minerals identified in these sectors were calcite, gypsum, and apatite-(CaOH). Calcite forms a variety of speleothems (including spectacular eccentrics and helictites), gypsum was found to occur only as sub-millimeter to centimeter thick wall or floor crusts, whereas apatite-(CaOH) is restricted to those parts of the cave that host various size bat colonies.

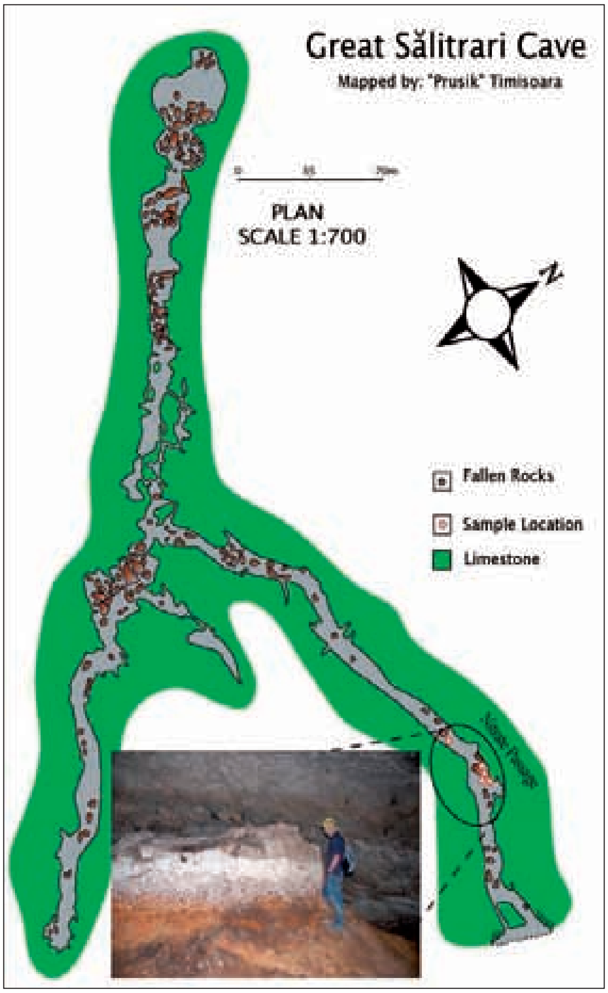

Fig. 4: Map of Great Sălitrari Cave showing the Nitrate Passage and the investigated sediment profile.

The Nitrate Passage (ca. 30 m in length) lies along the Main Gallery and differs from the rest of the cave by its low relative humidity (below 75 % year around) and slightly high temperature (~11.7°C). These conditions prevailed at least over the last 125 years as wood fragments used by Turkish while mining saltpeter sediments for gunpowder manufacture are well preserved in this part of the cave (Diaconu & Lascu 1999). The main mineral association is located in the upper part (~80 cm) of a ~2.30 m thick sediment sequence that consists of (from bottom to top, Fig. 4, inset):

a) 1 m of detrital sediments (sand, cobbles, gravels, and limestone boulders);

b) ~0.5 m of fine-laminated ochre-brown clays having their fissures filled with white powdery material;

c) 15 cm of white-grayish material, in which lenses of brown clay and small size nodules occur;

d) ~15 cm of gray crumbly material that contains randomly spread, irregular dull-white nodules (up to 3-5 cm across);

e) 20 cm of gray crumbly material with very few, small-size white nodules;

f) a discontinuous blanket of dry guano (up to 30 cm thick), in which white nodules might be observed.

Ardealite was identified in the composition of the white nodules found within the gray phosphatic sediment immediately underlying the guano deposit. We interpret the presence of ardealite as a direct result of the reaction between bat guano, which supplied the phosphate, and small limestone chunks (that fell into the guano deposit), which supplied the calcium. The sulfate ion comes from gypsum that is a common phase throughout the sediment pile.

The three horizons in the upper sediment sequence consist of a mixture of darapskite, aluminite, alunite, gypsum, calcite, and quartz. All these minerals produce distinguishable peaks in the XRD spectra. The quartz is not a true cave mineral; its presence is related to the detrital sediments introduced by the underground stream. Some of the identified quartz, however, might have resulted from the reaction between kaolinite and the sulfuric acid generated by the oxidation of H_2S from the thermal waters, although this supposition has to be confirmed by further studies. Aluminite occurs mostly as white, chalky irregular nodules in horizon d (Fig. 5) but also as earthy-masses in the mineral assemblage of layers c, d, and e. The largest recovered nodule is 4 x 2.6 cm. Alunite was identified as transparent, euhedral, and subhedral microcrystals (millimeter size) randomly spread within the earthy masses horizons and coating aluminite nodules (Fig. 5). Darapskite seems to be responsible for the grayish appearance of the sediment sequence. The mineral was positively identified in both the whitish nodules and the matrix that host them. In the matrix, it is intermixed with calcite, gypsum, quartz, and aluminite. Nitratine was also reported by Diaconu and Lascu (1999) from this sequence, but was not found in the present work. Considering the genesis of these minerals it is plausible (preliminary supporting evidences are available and discussed within the Conclusion Section) that thermo-mineral waters, or more likely hot ascending steam, converted the guano-rich sediments and the detrital material accumulated along the Nitrate Passage into a mixture of sulfates and nitrates.

Fig. 5: Microcrystals of alunite over chalky nodules of aluminite (Photo: B.P. Onac).

Calcite and gypsum also occurs as microcrystals and fine-grained aggregates mixed with the other minerals within layers c, d, and e, while variscite is the common mineral phase in the lower part of the sediment pile. It occurs as white crisscrossing veins within the laminated clays (Fig. 6). The formation of variscite is attributed to the reaction between the phosphate-rich leachates derived from bat guano and the aluminum supplied by the underlying clay sediments.

In the lower part of the clay horizon (near the boundary with the detrital material), taranakite appears as white dull crumbly material forming nodules and veins (Fig. 6). The aluminum and potassium come from the clay (illite and kaolinite), the sandstone gravels supplied the iron while the phosphoric acid was derived from bat guano. Given that the location of these two minerals is well below the present-day dry guano deposit, we believe at the time of their precipitation there must have been a significant (thick and fresh) guano cover on top of the clay horizon. It is also plausible, however, that in a later stage of sediment accumulation history, phosphate-rich solutions trickled down the sediment pile and reacted with the floor clays to produce these minerals.

Fig. 6: Veins and nodules of variscite (1) and taranakite (2) in the lower part of the sediment sequence (Nitrate Passage, Great Sălitrari Cave; Photo: B.P. Onac).

White dull, crumbly nodules and earthy aggregates occurring within a 15 cm long lens (partly covered by guano material) have been collected in the lower part of the left sidewall, just before reaching into the Nitrate Passage. The XRD analysis of both bulk sample and nodules, confirms that brushite is the dominant mineral phase. This acid calcium phosphate formed when phosphate-rich solutions drained out from the overlying bat guano and reacted with the limestone bedrock.

ADAM SHAFT (PHOSPHATE-DOMINATED ASSOCIATION)

Adam Shaft is located outside Băile Herculane on the right bank of the Cerna River at 135 m above its thalweg (Povară *et al.* 1972). The passages are developed along a system of faults that intercept at depth the drainage of the Hercules thermal spring (Diaconu 1987). Adam Shaft is famous for its "tropical" biotope rendered from continuous hot (~47°C) steam emissions along these tectonic fractures (Decu *et al.* 1974). The bat colony in Adam Shaft is considered one of the oldest in Europe, a fact that was confirmed by the ^{14}C age of the guano deposit dated to ~8,500 cal yr BP (Carbonnel *et al.* 1999).

Considering these settings, it was not surprising to identify three, rather common cave phosphate minerals in this cavity: apatite-(CaOH), brushite, and apatite-(CaF). The first two minerals develop ochre to dark brown crusts (few millimeters in thickness) in the lower part of the cave walls, fringing the guano deposits, as well as on wall ledges beneath freshly accumulated guano. All three minerals were primary identified by means of XRD, but apatite-(CaF), which is associated with apatite-(CaOH) was further confirmed by FT-IR analysis. The FT-IR spectrum of apatite-(CaF) confirms the absence of OH- stretching and libration peaks, which are common in apatite-(CaOH) at about 3,570 and 635 cm^{-1}, respectively (Ross 1974).

Moreover, we calculated a smaller length for the *a*-axis for the unit cell of apatite-(CaF) but the same length for the c-axis as in apatite-(CaOH). It is possible that the difference in lattice parameter is due to the change centered in the calcium triangle. In other words, the F ions lie at the intersection of the plane with the six-fold screw axis, whereas the OH ions of apatite-(CaOH) lie with their inter-nuclear axis coincident with the six-fold screw axis, but at a distance of 0.3 Å from the nearest trigonal calcium triangle.

BÎRZONI CAVE (ONLY GYPSUM)

Bîrzoni Cave is the most upstream cavity investigated. The entrance is high in the right cliffs of Cerna Valley making the access to it extremely difficult (Avram *et al.* 1964). The cave has three small entrances (close to each other) and a total length of 570 m. Close to the entrances, the cave mineralogy is dominated by calcite speleothems. Further in, thick (up to 8 cm) granular or fibrous gypsum crusts (Fig. 7) cover most of the cave passages. Massive gypsum blocks lie on the cave floor along some of the galleries. The inner parts of these gypsum speleothems are white, to white-yellowish, but at the surface they are tinted ochre to dark brown. Sulfur isotope values of gypsum were determined for seven samples collected throughout the cave. The mean $\delta^{34}S$ value for these samples is around -27 ‰. A tentative U/Th dating (using alpha spectrometry) on a gypsum crust from this cave produced an age of 41,500 years (±3.95). This age, however, needs to be confirmed by either additional age determinations of this type or through another, independent dating method (Constantin 2003).

Fig. 7: Gypsum crusts and blisters covering walls in Bîrzoni Cave (Photo: B.P. Onac).

ADDITIONAL MINERALS

Monohydrocalcite occurs as millimeter size light white to light yellow-white patchy crusts and efflorescences up to several centimeters across, encrusting calcite crusts at the entrance to Sălitrari 1 Cave. At first glance, it closely resembles hyalite opal. Monohydrocalcite was verified using X-ray powder diffraction methods and microprobe analysis, which documented only Ca, with no Mg, Fe, Mn, or Zn present in detectable amounts. In addition, it was also characterized by IR spectroscopy. The asymmetric C–O stretching vibration is split (1,407 and 1,487 cm^{-1}). Monohydrocalcite shows bands at 590 (lattice), 698/725 (ν4 of carbonate), 765 (lattice), 871 (ν2 of carbonate), 1,066 (ν1 of carbonate), 1,407/1,487 (ν3 of carbonate), 1699 (H2O deformation), and 3,234 cm^{-1} (O–H stretch), in good agreement with the literature data (Tilli *et al.* 2001; Coleyshaw *et al.* 2003). Under scanning electron microscope, the monohydrocalcite crystals form trigonal platelets that seem to be precipitated along presumptive (based on morphology) bacterial filaments.

Taking into consideration its occurrence close to the cave entrance, in an evaporative environment rich in allochthonous organic matter entering from outside, the monohydrocalcite identified in this cave could have either a biochemical or evaporation-aerosol origin (Fischbeck & Müller 1971; Broughton 1972; Polyak *et al.* 1994).

Aragonite was identified only in Diana Cave as a minor phase in most of the gypsum samples investigated by XRD. The high temperature and Mg/Ca ratio (in the thermal water) within this particular cave triggered the precipitation of aragonite as submillimeter-sized crystals. This mineralogical paragenesis is rather common in the cave environments in Romanian as suggested by Diaconu (1983).

A light-blue moonmilk-like floor deposit was observed and sampled from a side niche along the Hercule Mining Gallery. The XRD analysis of a bulk sample confirmed the presence of chalcanthite. Because the gallery has been abandoned for quite some time, it is possible that this unusual mineral occurrence relates to the oxidation of copper materials left behind by miners (cables or device parts) in a sulfate-rich, 100 % relative humidity environment. Considering its location in a man-made cavity, chalcanthite might be regarded as a border mineral.

As previously mentioned, gypsum was found in all investigated caves. The significance of its presence, however, in Adam Shaft and Aburi Cave is important in understanding the minerogenic processes, therefore, additional information are given below. In both caves, gypsum is the principal component of millimeter-size dull white to ochre crusts occurring abundantly around active steaming vents. The mineralogy of these crusts was confirmed by XRD analyses. The sulfur isotope composition shows values that range between 0.5 and 6.5 ‰.

CONCLUSIONS

Our first results demonstrate that detailed investigations of the secondary minerals found in caves along Cerna Valley are useful for predicting the neoformation of minerals assemblages and to infer the speleogenetic pathways. It is clear that during the evolution of the thermo-mineral activity along the Cerna Valley interaction has occurred on a wide scale between the cave host rock (and/or cave sediments) and the ascending hot steam (and/or thermal solutions of all types, mainly sulfide-rich). The present work documents the mineral products of these processes and records the occurrence of twenty-two secondary cave minerals (both of primarily or replacement origin) precipitated under particular cave environments. Among these, apjonite and tamarugite are new to the cave minerals inventory. Tamarugite was previously documented from volcanic cavities, however, Diana Cave is the first limestone karst occurrence to host this mineral.

Since the sulfate minerals in Diana Cave have the same $\delta^{34}S$ values as the sulfate and sulfide ions in the thermal spring, they are byproducts of the reaction of sulfuric acid with the limestone and marls occurring within the cave. Therefore, the cave belongs to the H_2SO_4-acid speleogenetic type formed by the oxidation/hydrolysis of H_2S escaping from Diana spring water.

As the time of this writing, the only $\delta^{34}S$ values available for the sediment profile in Great Sălitrari Cave come from the sulfur isotope composition of ardealite, darapskite, and gypsum. The $\delta^{34}S$ values range between -2.6 and +6.5 ‰. Comparing these values to those obtained for gypsum samples (0.5 to 6.5 ‰) precipitated around hot steam vents in active thermal caves (e.g., Adam and Aburi), it is safe to assume that the minerals in Great Sălitrari Cave (at least those from the upper part of the Nitrate Passage sediment profile) inherited the same $\delta^{34}S$ signature of the deep sulfidic water reservoir.

The gypsum crusts from Bîrzoni Cave formed when isotopically light H_2S ascending with the thermal water was oxidized within the cave to form sulfuric acid (in the presence of meteoric water) which then reacted with the limestone to produce ^{34}S depleted gypsum. The ~41,500 years age reported by Constantin (2003) gives an approximate age for the deposition of gypsum. However, U/Th dated calcite speleothems from the same cave (Constantin 2003; Onac, unpubl. data) indicate that the cavity is probably older than 350,000 years. Taking into consideration the overall cave pattern (the passages parallel to the cliff face), we believe that the cave formed as a meander in relation to the Cerna River. We suggest that in a later stage, H_2S in the thermal water or steam reacted with descending oxygenated water to produce sulfuric acid, which dissolved the cave passages and precipitate gypsum. Evidences for one such hypogenic phase are provided by the large amounts of isotopically depleted gypsum crusts and particular morphological features (subspherical voids and ascending narrow passages). The original and hypogenic morphology of the cave passages were modified more recently by vadose processes such as collapse (probably caused by gypsum crystallization) and calcite speleothems deposition.

These results suggest that the initial assumptions on the peculiar minerogenetic pathways on caves along the Cerna Valley and the likely hypogene origin for some of these caves (or at least hypogene phases in their evolution) are correct. More investigations are planned in order to provide additional information on the relevance and implications of thermal activity in hypogene speleogenesis and deposition of unique secondary cave mineral associations.

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