

THE HYPOGENE ORIGIN OF DIANA CAVE (ROMANIA) AND ITS SULFURIC ACID WEATHERING ENVIRONMENT

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The Diana Cave in SW Romania develops along a fault line at the contact between Late Jurassic limestones and Early Cretaceous marls. It formed through corrosion of bedrock (limestone and marls) by sulphuric acid-rich steam condensate resulted after oxidation/hydrolysis of H₂S escaping from the thermo-mineral water emerging from depth in the cave. The sulfuric acid causes a strong acid sulfate weathering of the bedrock generating a sulfate-dominated secondary cave-mineral assemblage that includes gypsum, anhydrite, bassanite, epsomite, alunite, and halotrichite group minerals. Closely associated with these minerals are two rare sulfate species, namely rapidcreekite and tamarugite that represent new occurrences in limestone caves. Traditional X-ray diffraction and single crystal analyses were used along with scanning electron microscope (SEM), stable isotope, and electron microprobe investigations to fully characterize the primary and secondary speleogenetic by-products of Diana Cave.

1. Introduction

Sulfates are the largest group among cave minerals with 89 species which form in a variety of settings (Hill and Forti 1997; Onac and Forti 2011a, b). Of these, only gypsum, epsomite, and mirabilite may be considered common for the cave environments, with gypsum perhaps the second most frequent cave mineral after calcite (Onac 2012). The majority of the other sulfates only occur under very particular settings, such as in caves located nearby ore deposits or thermo-mineral water sources and in areas with abundant post-volcanic activities.

This paper provides an overview of the mineralogy of Diana Cave, an active sulfide-rich thermal water geochemical system. The study emphasizes the sulfuric acid origin of this cavity and the rich mineral assemblage precipitated in its steam-condensate environment.

2. Geology and cave settings

The geology of the Cerna Valley is complicated by the occurrence of several nappe complexes, such as Getic, Danubian, etc (Balintoni et al. 2010). Diana Cave develops at the contact between nodular limestones (Late Jurassic; J₃) and dark grey Iuta marls (Late Cretaceous; K₁), both part of the sedimentary cover of the Danubian nappe (Năstăseanu 1980) (Fig. 1). The major clay minerals within the Iuta marls (forming the floor and lower part of the cave walls) are illite, kaolinite, and chlorite (Diaconu and Medeașan 1973). Their importance resides in the ions released to the cave geochemical system upon reacting with the H₂SO₄ that condenses on cave walls. Relevant to this paper is that the cave passage formed along the Diana Fault (Fig. 2), which brings in contact the Late Jurassic limestones with the gray marls of Iuta strata (Năstăseanu 1980).

The regional hydrogeology of the region is rather complex;

its relationship with the karst of the Cerna Valley has been described in details elsewhere (Povară et al. 2008; Wynn et al. 2010).

The Diana Cave is located in the lower section of the Cerna Valley (SW Romania), in the old center of Băile Herculane, a famous thermal spa known for over 2000 years (Fig. 1). It opens on the right bank of the Cerna River and consists of a 22 m long cave passage at the far end of which the Diana thermal springs emerge (Povară et al. 1972).

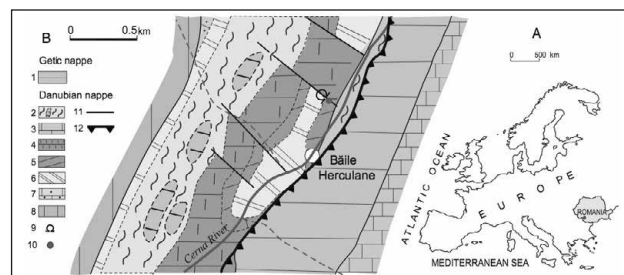


Figure 1. Location of Diana Cave and the geology of the lower Cerna Valley (from Pușcaș et al. 2013). 1. crystalline schists; 2. wildflysch with olistoliths (K₂); 3. Urgonian limestones (K₁); 4. Iuta strata (K₁); 5. bedded limestones (K₁); 6. nodular limestones (J₃); 7. conglomerates (J₁); 8. crystalline basement (PreC); 9. Diana Cave; 10. Diana 1 and 2 springs; 11. normal fault; 12. thrust fault (Cerna fault).

Diana Cave hosts two thermal springs (referred to as Diana 1 and 2, respectively; Povară et al. 2008). The waters are of sodium-chloride-calcium type, contain on average 1,392.5 mg/L Na⁺, 725 mg/L Ca²⁺, 3,370 mg/L Cl⁻, and abundant H₂S degasses into the cave atmosphere. The thermo-mineral water has a nearly neutral pH (~6.5), the total dissolved solids amount ~5,760 mg/L, and its total sulfide and sulfate concentration 37 and 92 mg/L, respectively (Marin 1984; Wynn et al. 2010). In the early 70's, the narrow cave passage heading SE (Fig. 2) was enlarged to drain the thermal water outside in a retention basin for further therapeutic uses. During this work, the entrance cave

passage was also enlarged and the walls, especially where the marl outcrops, were reinforced using concrete. Therefore, the original cave morphology was heavily altered, but since this happened, the strong acid sulfate weathered the concrete and the cave walls are now exposed on restricted areas allowing for sample collection.

Corroborating the regional hydrogeology with springs hydrochemistry, temperature, and sulfur isotopic composition, Povară et al. (2008) and Onac et al. (2011) concluded that the thermal waters around Băile Herculane Spa (including the Diana Springs) represent deeply circulating meteoric waters that are upwelling along stratigraphic boundaries or faults.

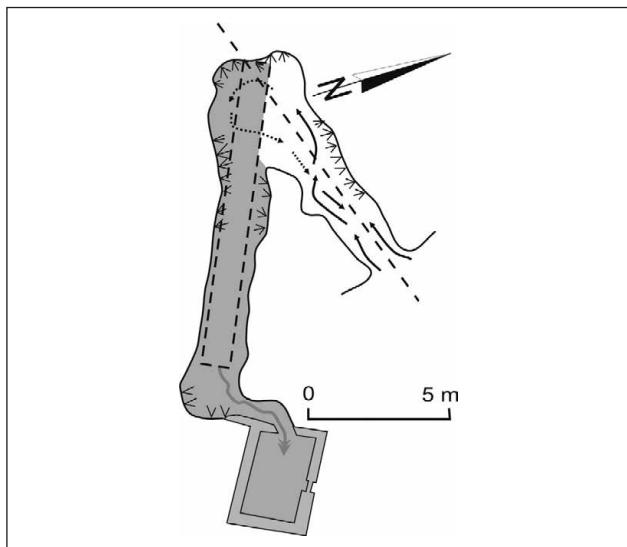


Figure 2. Map of the Diana Cave and the location of samples (∇, ∇); dashed line = Diana Fault; arrows = air circulation pattern (modified from Povară et al. 1972).

The water in the cave is milky due to suspended elemental sulfur and sub-millimeter thin gypsum rafts precipitating at its surface. The abundant sulfidic steam released by the hot waters emerging from the Diana Springs condenses on the colder bedrock surface. Subsequent oxidation/hydrolysis of sulfides creates a sulfuric acid solution (pH between 2 and 4.5), which reacts with the bedrocks to form a variety of sulfates and controls the resulting cave steam-condensed weathering environment of the Diana Cave.

3. Methods

Chemical analyses were performed using a JEOL 8900R Superprobe electron microprobe (EMPA) instrument at the Department of Earth Sciences, Florida International University. The SEM investigations were carried out on a JEOL 6490 LV operated in low vacuum mode and equipped with an EDS analytical system in the Lisa Muma Weitz Imaging Core Laboratories (University of South Florida). Sulfur and oxygen isotopic composition of SO_4^{2-} in bulk sulfates and in specific minerals (hand picked under the microscope) was measured in the Stable Isotope Laboratory of the Department of Geology (USF) on a Delta V Isotope Ratio Mass Spectrometer (IRMS) using a Costech Elemental Analyzer. Analytical conditions and methods for all these methods are available in Wynn et al. (2010), Onac et al. (2009, 2011, 2013), Pușcaș et al. (2013).

4. Results

Using the methods listed in the previous chapter, we positively identified 14 minerals that belongs to the group of native elements, halogenides, carbonates, and sulfates (Table 1).

Sulfur was first mentioned in this cave by Povară et al. (1972) covering the halotrichite earthy aggregates. Later, it has been documented as tiny aggregates suspended in the upper part of the water column and as earthy masses associated with other halotrichite-group minerals (Pușcaș et al. 2013). The elemental sulfur forms when the sulphides mobilized from deep anoxic reservoirs are rapidly oxidised in the oxic section of the cave (see reactions below).



Halite occurs as sub-millimeter crystals intermixed with tamarugite (Pușcaș et al. 2013). Its origin is most likely related to the reaction between the Na^+ in the Iuta marls and the cave chloro-sodic thermal water (Diaconu 1974).

Calcite and *aragonite* are the only minerals in this cave that are not related to the H_2S -rich environment, being precipitated by the percolating waters entering the cave.

Table 1. Minerals identified in the Diana Cave, type of speleothems they form, and abundance (C: common; R: rare; VR: very rare).

Mineral name	Chemical composition	Speleothem type and frequency
Sulfur	S	earthy aggregates, C
Halite	NaCl	crystals, R
Calcite	CaCO_3	crusts; C
Aragonite	CaCO_3	crystals, R
Alunite	$\text{KAl}_3(\text{SO}_4)(\text{OH})_6$	efflorescences; R
Anhydrite	CaSO_4	crystals; R
Apjohnite	$\text{Mn}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	efflorescences; C
Bassanite	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	crystals, R
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	crystals; R
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	crusts, rafts, flowers; C
Halotrichite	$\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	efflorescences; C
Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	efflorescences; C
Rapidcreekite	$\text{Ca}_2(\text{SO}_4)(\text{CO}_3) \cdot 4\text{H}_2\text{O}$	crystals; VR
Tamarugite	$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	earthy aggregates, R

The first reported presence of *anhydrite* as a cave mineral came from Diana Cave (Diaconu 1974), where it occurs as acicular and prismatic crystals closely associated with *gypsum*. Responsible for its precipitation seems to be the presence in the CaSO_4 solutions of high amounts of sodium and magnesium. Gypsum is the primary speleogenic by-product in Diana Cave and it occurs as crusts, crystals, anthodites, moonmilk, and delicate rafts (Fig. 3a).

Halotrichite was one of the minerals identified and reported by Povară et al. (1972). However, a year later Diaconu and Medeașan (1973) published a more detailed study of the yellowish-greenish efflorescences occurring on the Iuta marls suggesting that the mineral is in fact *pickeringite*. The

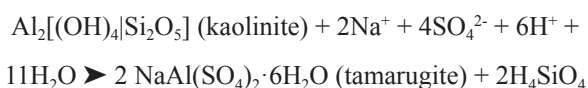


Figure 3. Diana Cave. Gypsum rafts (a); halotrichite-group minerals (b); SEM image of rapidcreekite (c).

site was resampled in 2007 and 2008 and X-ray analyses not only confirmed the presence of halotrichite and pickeringite, but also identified the Mn^{2+} end-member of this group, *apjohnite* (Onac et al. 2009) (Fig. 3b). On three of the X-ray spectrum peaks for *alunite* were also identified. All these minerals formed in the acid-condensate micro-environment on the expanse of the clay minerals from Iuta marls.

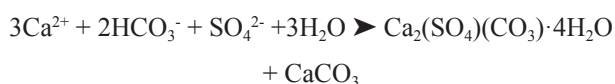
Both *bassanite* and *epsomite* appear as fibrous micrometer size crystals in patchy white efflorescence covering the cave walls. The precipitation of epsomite is favored by the presence of magnesium in the thermal water and limestone bedrock, which combines with the sulfate-rich solutions condensing on the walls. Bassanite likely resulted through the partial dehydration of gypsum during winter seasons when cold, drier air enters the cave and evaporation occurs.

Tamarugite forms dull white earthy aggregates that under SEM reveal tabular subhedral crystals smaller than 15 μm in length. The sulfuric acid alteration of marls (which contributes Al^{3+} and Na^+ ; see reaction below) seems to be responsible for this unique occurrence of tamarugite (Puşcaş et al. 2013).



This is the first time when this minerals forms in a typical limestone cavity that has no relationship to any past or present volcanic activity.

The sulfate-dominated primary and secondary cave-mineral assemblage also includes *rapidcreekite*, intimately associated with gypsum and halotrichite group minerals. Rapidcreekite forms bundles of colorless tabular rhombic crystals elongated along [001] and reaching up to 1.5 mm in length (Fig. 3c). The reaction suggested by Onac et al. (2013) to lead to rapidcreekite deposition is:



For a confident identification of rapidcreekite from a karst cave, a precision single-crystal study was performed at the University of Vienna (Onac et al. 2013). The crystal structure was refined starting from the atomic coordinates given by Cooper and Hawthorne (1996). The increased accuracy is mainly based on the larger number of observed reflections due to the use of an area detector, which allowed establishing the location of the H atoms in a difference Fourier summation and the refinement of their atomic

coordinates. Rapidcreekite unit-cell parameters are: a 15.524(2), b 19.218(3), c 6.161(1) Å; V 1838.1 Å³, $Z=8$, space group *Pcnb*. Chemical composition (wt.%): CaO 35.65, SO₃ 24.97, CO₂ 13.7, H₂O 23.9, Na₂O 0.291, MgO 0.173, Al₂O₃ 0.07, total 98.75%. The empirical formula based on 11 oxygen atoms per formula unit is: $Ca_{1.98}Na_{0.029}Mg_{0.013}Al_{0.004}(S_{0.971}O_4)(C_{0.97}O_3) \cdot 4.13H_2O$, very close to the ideal chemical formula.

The isotopic composition ($\delta^{34}S$ and $\delta^{18}O$) of rapidcreekite, gypsum, and bulk sulfate minerals occurring as crusts and efflorescences is homogeneous, showing ³⁴S-enriched $\delta^{34}S$ values (18 to 19.5 ‰ CDT) whereas the $\delta^{18}O$ values (in the sulfate site) range from -9.7 to -7.8 ‰ VSMOW.

5. Conclusions

Considering that Diana Cave's passages were heavily impacted by the mining activities described earlier, it is impossible to recognize any diagnostic features (cupolas, feeders, etc.) of sulfuric acid speleogenesis. However, the cave is an active sulfuric acid environment generated by the oxidation/hydrolysis of the H₂S in the hot thermal water and cave atmosphere:



Due to the presence of abundant H⁺ in the system (both in the water and steam), limestone weathers according to the reaction below:



This very efficient aggressive weathering of the carbonate bedrock (Polyak and Provencio 2001; Palmer 2007) extends from below the water table up to the ceiling of the cave, being responsible for the development and further enlargement of its passages. In addition, the H₂S-rich steam condensate favors the development of an acid-sulfate weathering environment that is conducive to the precipitation of the primary and secondary speleogenic minerals described above.

The $\delta^{34}S$ values of the sulfate samples from the Diana Cave indicate an almost complete, sulfate-limited thermo-sulfate reduction (high H₂S/SO₄²⁻) under anoxic conditions; they are consistent with an oxidation of dissolved sulfide in springs of the lower Cerna Valley described by Wynn et al. (2010). This suggests that S in the investigated sulfate minerals is derived from dissolution of primary evaporites from marine limestone followed by reduction in the thermal

aquifer and re-oxidation in the cave atmosphere. The $\delta^{18}\text{O}$ values of the sulfate minerals indicate an abundant ^{18}O exchange with $\text{H}_2\text{O}_{(l)}$ during hydration and near complete exclusion of oxygen derived from $\text{O}_{2(aq)}$ in sulfate minerals from the Diana Cave (Onac et al. 2011).

The results reported in this note provide further evidence that apart from expected speleogenic primary by-product minerals such as gypsum and alunite, other rarer phases (i.e. tamarugite and rapidcreekite) precipitate in the sulfide-rich steam condensate environment of Diana Cave if optimal pH, geochemical ingredients, and relative humidity conditions are met. These settings, however, are essentially different from other non-carbonate caves or terrestrial records previously documented for the last two minerals.

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