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Cover Photo:

Spongework in the Capitan Reef limestone near the Big Room of Carlsbad Cavern, New Mexico. This feature is commonly called “Boneyard” because of its appearance. This is commonly interpreted as a classic example of dissolution by slow-moving phreatic water. However, a more feasible process is condensation of moisture from moving air masses above the water table. Solutional aggressiveness can be produced by absorption of gases from the cave air—e.g., carbon dioxide to form carbonic acid, and/or a mixture of hydrogen sulfide and oxygen to produce sulfuric acid. This type of spongework is common where air has moved slowly through the porous limestone that separates large rooms. Photo by Art Palmer.

HERCULES AND DIANA HYPOGENE CAVES (HERCULANE SPA, ROMANIA): DISSIMILAR CHEMICAL EVOLUTIONS DOCUMENTED BY THEIR PRESENT-DAY THERMAL WATER DISCHARGES

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Abstract

Hercules Cave and Diana Cave are two small caves situated some 600 m apart, for which a hypogene origin has been previously suggested. Thermal water discharges (up to about 54°C) are hosted by each cave, and were recently made the object of an eight-month chemical monitoring operation. By plotting the concentrations of several chemical species (Na, K, Ca, Sr, Mg, SiO₂, Br) against the concentration of the conservative anion Cl, it was found that both caves discharged a binary water mixture, which was derived from the same saline (and hot) parent-fluid and the same fresh (and cold) parent-fluid. This fact was substantiated mainly by the conservative behavior that Na and Br displayed both in Hercules and Diana Cave's spring waters. Alternatively, the original water mixture appears to have systematically experienced, before reaching the sampling point in Diana Cave, significant depletions in terms of K, Ca, Sr, and SiO₂, while no such depletions were recorded in Hercules Cave. Inferred depletion mechanisms include K⁺-Na⁺ cation-exchange and Ca, Sr

and SiO₂ precipitation in minerals. Both processes could be favored by the possibility that upstream Diana Cave, water flow occurred slowly and in a diffuse manner through a network of cracks (likely across the shaly Iuta Layers). While the absence of analogous depletions at Hercules Cave was probably due to the fact that an extended network of penetrable passages presumably extended upstream the presently known length of that cave, such an underground environment is unlikely to favor precipitation of minerals or cation-exchange processes.

Introduction

The present study addresses the hydrochemical behavior displayed by two karst cavities—Hercules and Diana—both of which are located at Herculan Spa on Cerna Valley (Southern Carpathians, Romania). Extensive experimental datasets analyzed in the framework of several previous investigations (Onac et al., 2009, 2011, 2013; Wynn et al., 2010; Pușcaș et al., 2013) have strongly suggested a hypogene origin for these caves.

At present, both caves still host near-neutral pH NaCl-type thermal water discharges with temperatures up to about 54°C. Yet, until now, the corresponding spring waters have not been systematically and simultaneously monitored in terms of their hydrochemistry. Therefore, by filling this investigation gap, we aimed to elucidate the processes responsible for shaping the chemical character of the groundwater discharges, processes that could have been also involved in the corresponding hypogene speleogenesis.

Geological and Hydrogeological Setting

The concerned caves develop in a 200-250-m-thick stack of Late Jurassic–Early Cretaceous (J₃-K₁) limestones with cherts, underlain by sandstones and conglomerates of Early Jurassic (J₁) age, and overlain by the Late Cretaceous (K₂) shaly Iuta Layers (marly limestones and siltstones). Both cavities occur within the southeastern limb of a SW-NE oriented syncline (Figure 1). Karst water, supplied by several swallets located further northeast, is channeled southwestward along that syncline strike (Mitrofan et al., 2008; Povară et al., 2008). In the proximity of the two caves, there are also located (Figure 1) additional outlets (wells, impenetrable springs) that discharge thermo-mineral water, also of NaCl-type, frequently sulfide-rich, with TDS values up

to about 6 g/L and temperatures up to about 56°C.

For the Herculane Spa aquifers, hydrogen and oxygen stable isotopes' contents have been published by Crăciun et al. (1989), who had sampled three unspecified outlets with NaCl chemical types and discharge temperatures of 56-61.5°C. Studies were also published by Winn et al. (2010), who had sampled several thermal and non-thermal outflows, including the Hercules and Diana Caves. All data suggested that the discharged thermal fluids were basically of meteoric origin, and no significant alteration of the corresponding original isotopic signature had occurred as a result of metamorphic processes, which possibly acted along the hydrothermal flow paths.

This so-far acquired body of information seems insufficient for elucidating both the mechanisms involved in the heating of the discharged fluids and the origin of the water mineralization.

Data Collection and Processing

In the present study, discharge water samples for chemical analyses were collected from Hercules Cave and Diana Cave. The water sampling was performed from early June 2013 to mid-February 2014, twice a week at Hercules Cave and weekly at Diana Cave.

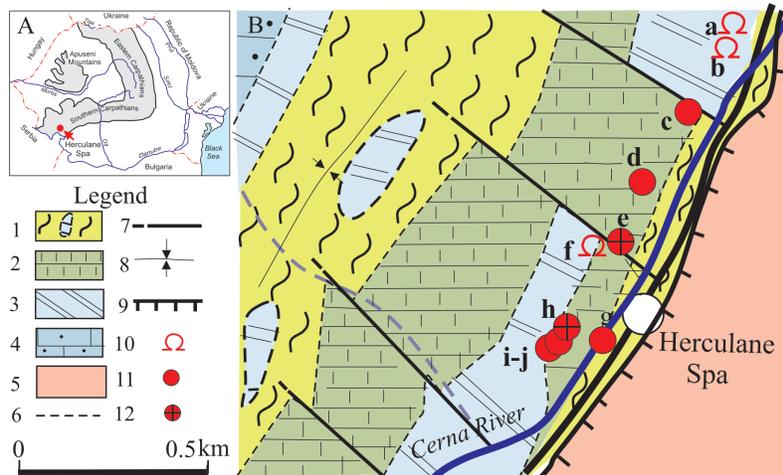


Figure 1.

(A) Location map of study area; (B) Sketch map illustrating the thermal water discharges' location and their associated geological setting.

Legend of symbols: (1) Black argillites with limestone olistoliths (K₂); (2) Marly limestones and siltstones (Iuta Layers, K₂); (3) Limestones with cherts (J₃-K₁); (4) Sandstones and conglomerates (J₁); (5) Getic crystalline schists; (6) Geological boundary; (7) Fault; (8) Syncline; (9) Overthrust boundary; (10) Cave; (11) Thermo-mineral spring; (12) Well. The indicated outlets are: (a) Hercules Cave; (b) Despicatora Cave; (c) Apollo outlet; (d) Hebe spring; (e) Diana well; (f) Diana Cave; (g) Venera outlets; (h) Neptun I+IV well; (i) Neptun II spring; (j) Neptun III spring.

The index map illustrates the location of the study region within Romania.

Nalgene High-Density Polyethylene bottles were used to store the collected samples. When collected, the samples were filtered using Thermo Scientific Chromacol Polyether Sulphone Syringe Filters (0.45 μm pore size). Suprapur (Merck) 65% nitric acid was used for the collected samples' pH adjustment.

The complete chemical analysis of all water samples was conducted in the Hydrogeochemistry Laboratory of the "Emil Racovița" Institute of Speleology. The techniques utilized for analyzing concentrations were as follows. The Na, K, Mg, Ca, and Sr concentrations were determined by the Dynamic Reaction Chamber – Inductively Coupled Plasma Mass Spectrometry technique (DRC-ICP-MS). The Cl, Br, and Si (expressed here as SiO_2) concentrations were determined in standard ICP-MS mode. Both approaches followed the USEPA (2007) standard. The determinations were carried out with a NexION 300S (PerkinElmer, Shelton, CT, USA) ICP-MS instrument, equipped with a S10 Autosampler. All solutions were prepared with ultrapure water (LaboStar TWF UV7 Ultrapure Water System, electric resistance 18.2 $\text{M}\Omega \times \text{cm}$).

Several lines of evidence (Bulgăr and Povară, 1978;

Povară and Marin, 1984; Mitrofan et al., 2015) had suggested that the Hercules Cave discharge was derived from the mixing of a cold freshwater flow component, with another hot, saline water component. Such a mixing pattern can be primarily investigated by plotting, against the concentration of the conservative anion Cl, the concentrations of several other chemical species (main cations, SiO_2 , Br). The purpose of this approach is to establish if the latter species behaved conservatively as well; otherwise stated, if those constituents' concentration fluctuations in the Hercules Cave spring water were controlled only by variable mixing ratios between the two above-indicated flow components, or if other altering processes also intervened. Figures 2-4 plot the data-points corresponding to Diana Cave's spring flow concentrations, and—where available—results of chemical analyses conducted several decades earlier (Institutul de Balneologie și Fizioterapie, 1973) at the two cave water discharges.

Figures 2 and 3 indicate that for most of the considered constituents of Hercules spring water (Na, K, Ca, Sr, SiO_2 , Br), very good correlations with the Cl cation concentration can be outlined. Thus, the assumption that

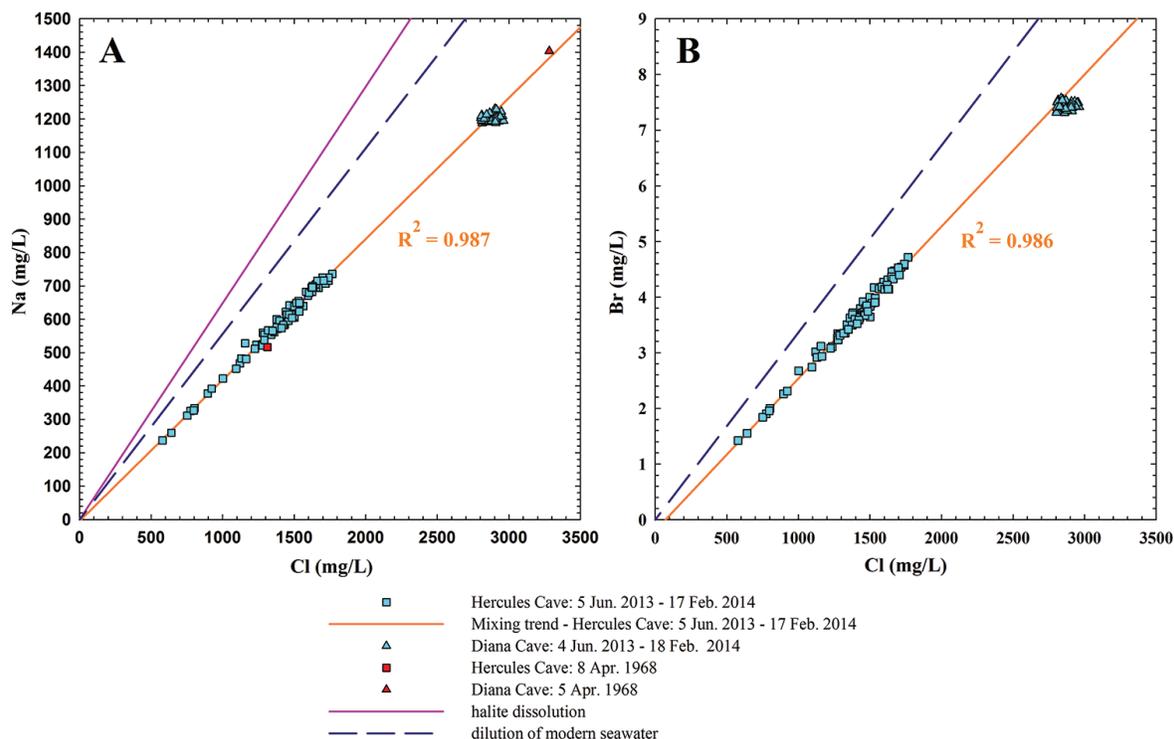


Figure 2.

Plots of Na (A) and Br (B) as a function of Cl. They indicate that both Hercules Cave and Diana Cave discharge a binary water-mixture derived from the same saline (and hot) and fresh (and cold) parent-fluids. Those two endmembers undergo virtually no time variations of their Na, Cl and Br contents.

the corresponding constituents behave conservatively is supported. Namely, concentrations are not altered by mechanisms other than variable mixing between a saline endmember, which has a virtually constant content of the concerned species, and a poorly mineralized groundwater, with fairly invariable concentrations as well.

Regression lines computed based exclusively on the concentrations of Hercules spring constituents (Figures 2 and 3, where the corresponding r^2 values are also indicated) were further used to assess whether the Diana spring water concentrations fell on the same regression lines, or if, alternatively, they were subject to significant shifts.

Results and Discussion

Figure 2A clearly indicates that the Na vs. Cl data-points fall on a mixing-line that is common to both Hercules and Diana Caves; the same also holds true for the Br vs.

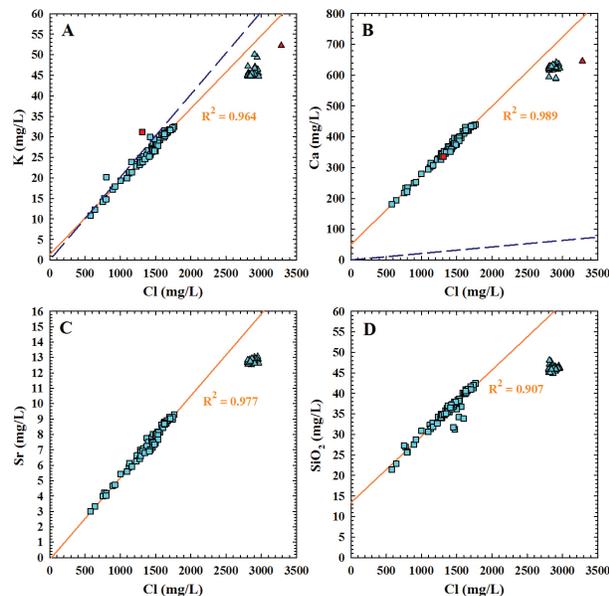


Figure 3. Plots of K (A), Ca (B), Sr (C), and SiO₂ (D) as a function of Cl (symbols as in Figure 2). In Hercules Cave, those constituents' contents were not altered by mechanisms other than variable mixing between the two endmembers (saline and fresh) of virtually constant concentrations. In contrast, it appears that after reaching the sampling point, the Diana Cave water-mixture had experienced significant depletions in terms of K (probably by cation-exchange) and of Ca, Sr and SiO₂ (probably by mineral precipitation).

Cl data-points (Figure 2B). It hence results that the same saline and fresh parent fluids contribute to the binary water mixture discharged by both caves. In this respect, the only difference between the two cave discharges is the much wider range of dilutions exhibited by the Hercules Cave water, whose concentrations moreover are, each time, considerably smaller than those measured at Diana Cave.

Another inference derived from Figure 2 is that Na and Br behave conservatively not only in the Hercules Cave spring water, but also in the Diana Cave discharge.

Yet a similarly conservative behavior fails to be obeyed by other chemical species in the Diana Cave water flow. Specifically, before reaching the sampling point in Diana Cave, the original water mixture appears to have systematically experienced significant depletions in terms of K, Ca, Sr and SiO₂ (Figure 3A, B, C, and D). Mechanisms possibly responsible for this setting could involve:

- K⁺-Na⁺ cation exchanges (the possible Na⁺ excess that would result from such a process being too small to be discerned in the Na vs. Cl plot of Figure 2A);
- precipitation of Ca (most likely involving associated Sr) and silica.

The distinct behavior recorded at Diana Cave might be a consequence of the fact that the cave was partly developed at the contact of an actual limestone body with the shaly Iuta Layers. It is therefore quite possible that upstream the cave, water flow occurred slowly and in a diffuse manner through a network of cracks, possibly across the shaly Iuta formation, where cation-exchange processes could be favored by the clayey environment. In contrast, although the currently known length of Hercules Cave is not much larger than that of Diana Cave (94 m and 22 m, respectively), there is a significant body of evidence (Mitrofan and Povară, 1992; Mitrofan et al., 2015), that suggests that an extended network of penetrable passages should continue upstream Hercules Cave. Accordingly, it seems unlikely that such an underground environment would favor processes that lead to significant depletions of the concerned constituents, by cation-exchange or mineral precipitation.

As already specified, in terms of their chemical species' contents, the two endmembers that contribute to the water mixture discharged by both the Hercules and Diana Caves, seem to undergo no time variations. Yet a different behavior is displayed by the Mg²⁺ cation, whose concentration in the freshwater flow-component

appears to be highly variable (Figure 4). This setting is highly conspicuous for the Hercules Cave discharge, where the freshwater fraction prevails; in contrast, the Mg concentration fluctuations are significantly dampened at Diana Cave, where the saline flow component results in a much larger contribution. It is important to stipulate that the Mg content of the involved saline endmember seems to be—as suggested by the overall pattern of the Mg vs. Cl diagram of Figure 4—extremely low. As for the rather elevated Mg concentration value determined in 1968 at Diana Spring, it is unclear whether it is indeed relevant or merely due to an analytical error.

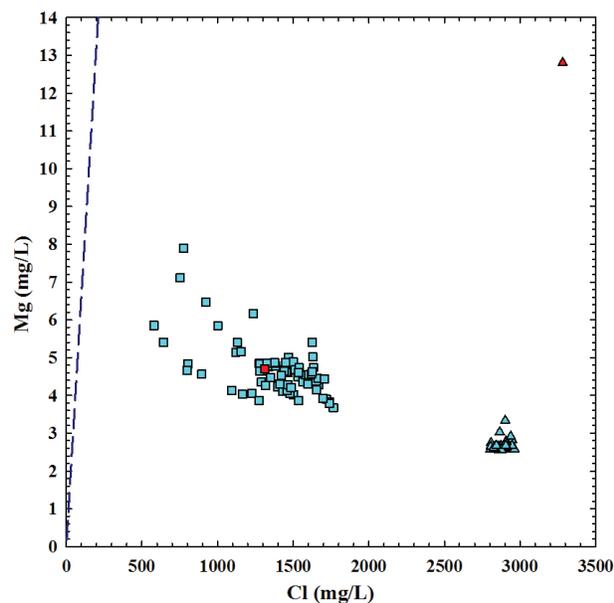


Figure 4. Plot of Mg as a function of Cl (symbols as in Figure 2). It is suggested that the Mg concentration in the freshwater endmember is highly fluctuating. This setting is highly conspicuous for Hercules Cave, in which the freshwater fraction prevails; in contrast, significantly dampened fluctuations occur at Diana Cave, where a much larger contribution is due to the saline endmember, whose Mg²⁺ content appears to be extremely low.

As a result of the hydrochemical monitoring of the Hercules and Diana Caves' water discharges, it became possible to reliably assess ratios between the main constituents of the saline parent-water. In particular, it became clear that those ratios did not correspond to the ratios expected as a result of diluting modern seawater (e.g., the Na vs. Cl and Br vs. Cl plots of Figures 2A and B; the K vs. Cl and Ca vs. Cl plots of Figures 3A

and B; the Mg vs. Cl plot of Figure 4). As for the Na vs. Cl mixing trend (Figure 2A), it did not match the halite dissolution line either. Consequently, one must admit that the saline parent-water composition essentially resulted from water-rock interaction—a conclusion that is potentially relevant for the circumstances under which hypogene speleogenesis might develop.

Further evidence that these caves are of hypogene origin comes from detailed mineralogical and stable isotope analyses performed on the thermo-mineral waters and the minerals precipitated within them. The $\delta^{34}\text{S}$ values of the sulfate in the thermal waters of these two caves are extremely ³⁴S-enriched, while dissolved sulfide increases sharply (especially in Diana Cave) and the $\delta^{34}\text{S}$ values of dissolved sulfide take on the isotopic signature of the initial dissolved sulfate (Wynn et al., 2010). This fact is documented by the $\delta^{34}\text{S}$ of gypsum crusts (~19‰) in the cave sulfates of Diana and Hercules, which indicates a more complete sulfate-limited thermochemical sulfate reduction. The negative correlation between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in the latter group of cave sulfates is consistent with increasing H₂S:SO₄²⁻ ratios downstream (higher $\delta^{34}\text{S}$ values), and more anoxic conditions downstream (lower $\delta^{18}\text{O}$ values). This trend culminates in $\delta^{18}\text{O}$ values of SO₄²⁻ indicating near complete exclusion of O derived from O₂ in sulfate minerals from Diana Cave (Onac et al., 2011).

Of the two caves, Diana Cave is by far the richer and more diverse in terms of minerals (Onac et al., 2009). Abundant steam and H₂S rises from the thermal water to condensate on the walls and ceiling of the cave. The sulfuric acid produced by H₂S oxidation/hydrolysis causes a strong acid-sulfate weathering of the bedrock, generating in combination with Al³⁺ and Na⁺ from the marls and thermal water, a paragenesis that includes native sulfur, bassanite, epsomite, halotrichite group minerals, alunite, anhydrite, tamarugite, and rapidcreekite. The last three sulfates have their type locality in this carbonate cave environment (Diaconu, 1974; Pușcaș et al., 2013; Onac et al., 2013).

Conclusions

The chemical composition of the thermal spring waters discharged by the Hercules and Diana hypogene caves was monitored for about eight months. It consequently became possible to ascertain that a common mixture between two endmembers (saline and fresh) supplied both indicated outlets. The contents of most chemical species in the two endmembers were invariable in time; one exception was the Mg²⁺ cation, whose concentration in the freshwater flow-component appeared to be highly fluctuating.

In Hercules Cave, the constituents' concentrations were only altered by the variable mixing between the saline and fresh endmembers. However, in Diana Cave, it appears that before reaching the sampling point, the original water mixture systematically experienced significant depletions in terms of K (probably by cation-exchange) and of Ca, Sr, and SiO₂ (probably by mineral precipitation). Both of these indicated processes could be favored by the possibility that upstream Diana Cave, the water flow occurred slowly and in a diffuse manner through a network of cracks, likely across the shaly Iuta Layers. The absence of analogous depletions at Hercules was probably due to the fact that an extended network of penetrable passages presumably extended upstream the presently known length of that cave, such an underground environment being unlikely to favor precipitation of minerals or cation-exchange processes.

Another significant issue clarified by the hydrochemical monitoring operation addressed the nature of the saline parent-water composition. It was ascertained that it was essentially a result of water-rock interaction—such a conclusion being potentially relevant for the circumstances under which hypogene speleogenesis might develop.

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