

CONDENSATION CORROSION IN MOVILE CAVE, ROMANIA

SERBAN M. SARBU

Department of Biological Sciences, University of Cincinnati, Cincinnati OH 45221- 0006 USA

CRISTIAN LASCU

“Emil Racovita” Speleological Institute, Str. Frumoasa 11, 78114 Bucharest ROMANIA

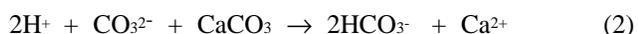
Condensation corrosion is the dissolution of carbonate by acidic vapors condensing above the water table. This process is rarely noted and receives little attention in the mainstream cave literature. The oolitic limestone walls in Movile Cave’s upper dry passages are severely altered by a selective corrosion mechanism. Temperature differences between the water in the lower passages and the walls in the upper passages and high concentrations of CO₂ in the cave atmosphere create favorable conditions for condensation corrosion to take place. Carbon and oxygen stable isotope data support the hypothesis that condensation corrosion is the major mechanism currently affecting the morphology of Movile Cave’s upper dry level.

Condensation corrosion is the dissolution of carbonate by acidic vapors condensing above the water table (Ford & Williams, 1989). This carbonate dissolution process is rarely noted and receives little attention in the mainstream cave literature (Jameson, 1991). The effects of condensation corrosion were reported from several non-thermal caves (Jameson, 1991; 1995) as well as from many hydrothermal caves which exhibit specific dissolution patterns (Bakalowicz et al., 1987; Cigna & Forti, 1986; Collignon, 1983; Palmer & Palmer, 1989). Cupola-form solution pockets have also been modeled as condensation corrosion cells (Szunyogh, 1984). It appears that condensation corrosion is a quantitatively important force of speleogenesis in semi-desert karst areas of Central Asia according to A. Maltsev (personal communication) as well as in the Mediterranean region (Pasquini, 1973). Several studies performed in caves developed in soluble rocks (i.e. gypsum), attempted to determine the amount of bedrock dissolved by condensation corrosion (Cigna & Forti, 1986; Calaforra et al., 1993).

The mechanism proposed for condensation corrosion is simple: water vapors condense when the temperature decreases reaching the dew point; drops of water or thin water films result when condensation occurs on walls; water drips from walls and ceiling if condensation rates are sufficiently large (Jameson, 1995); carbon dioxide from the cave atmosphere dissolves in the condensate to form carbonic acid [1].



Carbonic acid reacts with the carbonate bedrock forming bicarbonate [2] which is transported by the condensate as it drains down the cave walls.



High concentrations of carbon dioxide in the cave atmosphere favor the production of large quantities of carbonic acid thus accelerating the process of limestone dissolution (James, 1994).

Movile Cave in southeastern Romania was discovered in 1986 when an artificial shaft intercepted a natural cave passage at the depth of 18 m below the surface (Lascu, 1989; Sarbu & Kane, 1995; Sarbu et al., 1996). It consists of an upper dry level (total explored length: 200 m) and a lower submerged level (total explored length: 40 m). For information on the location and detailed map of Movile Cave see Sarbu & Kane (1995). The cave is developed in oolitic and fossil-rich limestone of Sarmatian age (i.e., late Miocene, about 12.5 Ma) that contains numerous molluscan fossils (Lascu, 1989). Following the examination of the cave’s morphology, Constantinescu (1989) concluded that the cave has a phreatic origin. He also pointed out that the upper level of the cave is extremely dry as a consequence of the lack of water infiltration from the surface and considered that the lack of speleothems is the effect of the dry climate in the region. (Average annual precipitation in southeastern Dobrogea is 350 mm). The lower level is flooded by thermal water (20.9°C) flowing at a rate of 5 l/s (Sarbu & Kane, 1995). The water contains significant amounts of sulfide (0.3mMol/l), ammonium (0.3mMol/l) and methane (0.2mMol/l). An abundant and diverse microbiota lives in the sulfidic waters and on the cave walls adjacent to the water (Sarbu et al., 1994). The food produced *in situ* by chemoautotrophic microorganisms supports a rich community of cave limited invertebrates (Sarbu et al., 1996). The atmosphere in Movile Cave is rich in carbon dioxide and depleted in oxygen (Sarbu & Kane, 1995). Hydrogen sulfide is present in the cave atmosphere in the lower level of the cave, but has not been detected in the upper dry cave level (Sarbu, unpublished).

In the upper dry level of Movile Cave, the surface of the cave walls is soft, and petrographic analysis showed that the bedrock is severely corroded (Horoi, 1994). Individual oolites

detached from the cave walls by selective corrosion accumulate at the base of the walls (Horoi, 1994).

The current study was performed in the upper dry level of Movile Cave, located five meters above the water level. The experimental sites were chosen at distances of 15 to 45 m from the water surface. The cave passages in the upper dry level of Movile Cave have a cylindrical cross-sectional morphology and their diameter ranges between one and two meters.

The presence of corroded walls in the upper cave passages led to the hypothesis that condensation corrosion may represent the major limestone dissolution mechanism currently affecting the morphology of Movile Cave's upper dry level.

METHODS

Measurements of oxygen, carbon dioxide, and water vapor concentrations in the cave atmosphere were performed *in situ* using Draeger tubes and a Draeger hand pump. Gas samples, which were later analyzed by gas chromatography, were also collected in 50 ml glass vials sealed with Teflon lined rubber septa. These measurements were performed at three-month intervals between 1993 and 1996.

Temperature measurements of water, air, and cave walls were performed with an EXTECH digital thermometer. These measurements were performed at 15-day intervals for a period of one year.

Glass plates with an area of 200 cm² were suspended 10 cm from the cave walls and one meter above the passage floor in various locations in the cave to estimate the amount of liquid condensing on the cave walls. Plastic funnels placed under the plates collected the condensed water in containers for subsequent analysis. The amounts of condensate were determined each month and stable isotope measurements were performed.

Fluorescein grains were applied to the cave walls to visualize the movement of the condensate along the cave walls. Observations were performed at 30 day intervals.

A three-millimeter-thick stainless steel wire was used to measure the thickness of the soft, corroded layer of bedrock throughout the entire cave.

Samples of rock and of water collected in Movile Cave were sent to the Department of Geological Sciences, University of Michigan for carbon and oxygen stable isotope analysis. Samples of atmospheric carbon dioxide were analyzed at the Department of Geology, University of Illinois. Results are expressed as δ values. [Values of δ (per mil) are calculated as $X = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 10^3$ where X is $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ and R is $^{13}\text{C}/^{12}\text{C}$ or $^{18}\text{O}/^{16}\text{O}$. Standards are Pee Dee belemnite for carbon and oxygen. Precision of measurements was 0.2‰ or better.]

RESULTS AND DISCUSSION

The temperature of the water in the lower cave passage is 20.9°C. The temperature of the cave walls reaches 20.7 to 20.9°C in the lower level of the cave and 19.0 to 20.1°C in the

upper level. Additionally, the floor of the dry cave passages is 0.2 to 0.3°C warmer than the ceiling due to the thermal flux (Figure 1) generated by the warm sulfidic reservoir. The air temperature ranged between 20.7 and 20.9°C in the lower cave passage, while in the upper cave passage the air was on average 0.5°C warmer than the cave walls. The warm vapor produced at the surface of the sulfidic lake (Figure 1) ascends along the cave passages into the upper cave level where it condenses on the cooler cave walls and especially on the ceiling. Amounts of 10 to 15 ml of condensate / 100 cm² / month were collected in several locations in the upper cave passage, supporting the above hypothesis. No seasonal variations were noticed in the amount of condensate collected. The upward movement of the warm and moist air from the lower to the upper cave level is slow and it is difficult to determine how much air ascends per unit time. Due to the decreased wall temperature, condensation is greater in the upper cave level and is lacking almost completely in the proximity of the lake where the cave walls are warmer. Through capillary movement, the condensate drains down along the walls at rates of up to 10 cm/month.

Compared to the surface atmosphere, the atmosphere in the upper dry level of Movile Cave is depleted in oxygen (reaching 19.5 to 20%), and is enriched in carbon dioxide (up to 1.5%; Figure 1). There are no local or seasonal variations in the chemical composition of the atmosphere in the upper cave level. The high levels of carbon dioxide in the atmosphere of Movile Cave accelerate dissolution by the condensed water on the surface of the limestone walls. Carbon dioxide in the cave atmosphere is isotopically light ($\delta^{13}\text{C} = -22$ to -24 ‰; $\delta^{18}\text{O} = +4.9$ to 5.7 ‰; Figure 2) compared to surface carbon dioxide ($\delta^{13}\text{C} = -7.8$ ‰), indicating that methane oxidation (Vlasceanu, unpublished) and metabolic activity of the cave biota (Sarbu et al., 1996) are the main sources of carbon dioxide in Movile Cave.

The superficial corroded layer of bedrock reaches a thickness of up to eight centimeters and consists of uncemented oolites. Due to preferential dissolution of the carbonate matrix (Horoi, 1994), oolites become detached from the wall and accumulate on the floor of the cave passage primarily at the base of the walls. Not being affected by condensation corrosion, the noncarbonate component of the bedrock accumulates on the surface of the corroded walls or may become detached and accumulate at the base of the walls along with oolites (Figure 1).

The deep limestone bedrock which has not been exposed to the cave atmosphere is isotopically heavy both for carbon and oxygen ($\delta^{13}\text{C} = -2.6$ to -0.2 ‰; $\delta^{18}\text{O} = 0$ to 1.2 ‰; "A"s in Figure 2). The surface of the cave walls affected by corrosion and the detached oolites, as well as the boulders of bedrock lying on the passage floor are isotopically lighter than the limestone bedrock ("B"s and "C"s in Figure 2). The enrichment in light carbon isotopes of the bedrock exposed to the cave atmosphere may be the result of an interaction between the bedrock and the isotopically light CO₂, but the mechanism of this hypothetical

Figure 1. Schematic profile view of Movile Cave. A. Lower passage; B. Upper dry passage.

1.- Evaporation of water at the surface of the lake.

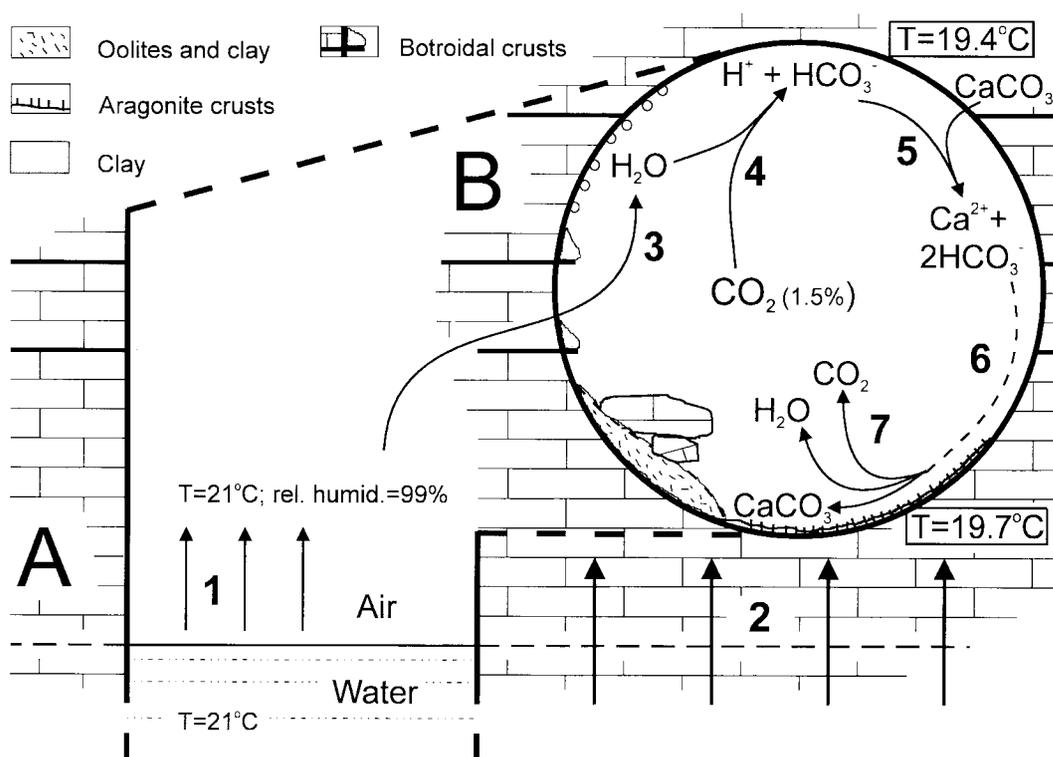
2.- Thermal flux through the bedrock.

3.- Condensation of water vapors onto the colder cave walls and ceiling in the upper cave passage.

4.- Dissolution of CO₂ into the condensate and formation of carbonic acid.

5.- Reaction between carbonic acid and the carbonate bedrock with formation of bicarbonate.

6.- Transport of bicarbonate along the walls.



7.- Precipitation of aragonite crusts and dissociation of bicarbonate.

interaction is unknown.

Numerous botryoidal calcite crusts interbedded within the limestone (Diaconu & Morar, 1993) fill the fractures within the bedrock and appear to be more resistant to corrosion compared to the bedrock. They often protrude from the cave walls, forming small ledges on which the uncorroded limestone residue (i.e. clays) accumulates (Figure 1). Examination of the edges of these crusts shows that they are eventually affected by corrosion which transforms them into a fine white powder often found on the passage floor. The botryoidal crusts that are in contact with the cave atmosphere are also isotopically lighter than the bedrock ("D"s in Fig. 2).

The floor of the cave passage as well as the base of the walls are covered by carbonate crusts that consist of aragonite as the main mineral (Diaconu & Morar, 1993; Engel & Lascu, 1996). This work proposes that the water film covering the cave wall is loaded with bicarbonate when it reaches the floor of the cave passage. Upon reaching warmer temperatures and evaporative conditions at the base of the walls and at the floor of the upper passage, the capillary water approaches saturation with respect to calcite. Evaporation can actually drive the solution to supersaturation with respect to the more soluble aragonite. Magnesium ions present in the water inhibit precipitation of calcite, causing the aragonite to be the main precipitate, even though aragonite is more soluble. Bicarbonate dissociates as a consequence of aragonite precipitation [3].



The aragonite crusts are isotopically light both with respect to carbon and to oxygen ($\delta^{13}\text{C} = -16.6$ to -21.4‰ ; $\delta^{18}\text{O} = -10.9$ to -11.17‰ ; "E"s in Figure 2). This suggests that the bicarbonate generating the crusts results from the isotopically light carbon dioxide in the cave atmosphere ("F"s in Figure 2), the water vapor condensing on the cave walls ($\delta^{18}\text{O} = -41\text{‰}$), and the isotopically light limestone bedrock. The very negative $\delta^{13}\text{C}$ values for the crusts also suggest a possible epigenetic interaction between the crusts and the light carbon dioxide in the cave atmosphere.

CONCLUSION

Carbon and oxygen stable isotope data support the hypothesis that condensation corrosion is the major mechanism currently affecting the morphology of Movile Cave's upper dry level. The peculiar morphology of the cave passages, the unusual temperature regime of this cave, and the high concentrations of CO₂ in the cave atmosphere favor the process of condensation corrosion. As supported in this work, water vapor is produced in the warm lower level of the cave, it ascends into the upper dry cave level condensing onto the cold cave walls. Carbon dioxide from the cave atmosphere dissolves in the condensate and forms carbonic acid. This reacts with the carbonate cave walls forming bicarbonate. The condensate containing bicarbonate is transported downward along the cave walls, reaching the warmer cave floor to precipitate aragonite. Water evaporates and CO₂ is released in the cave

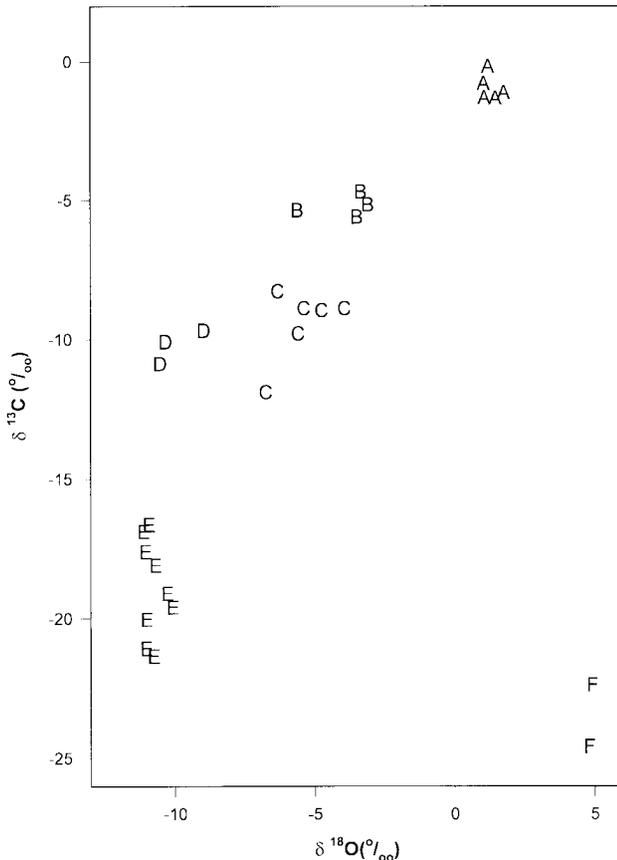


Figure 2. Carbon and oxygen stable isotope ratios in samples of carbonate and carbon dioxide from Movile Cave. A.- Limestone bedrock not affected by corrosion. B.- Corroded surface of passage walls and detached oolites. C.- Boulders of limestone bedrock lying on the passage floor. D.- Botryoidal calcite crusts filling the fractures within the bedrock. E.- Aragonite crusts covering the passage floor and the base of the walls. F.- Carbon dioxide from Movile Cave.

atmosphere.

ACKNOWLEDGMENTS

The authors are grateful to all those who made this study possible. Special thanks to the members of the GESS Group who assisted us during field work. We thank J. B. Risatti and M. Buck for their help with the stable isotope work. T. Algeo, A. Badescu, M. Buck, A. S. Engel, P. Forti, S. Galdenzi, B. B. Jorgensen, T. C. Kane, A. N. Palmer, F. L. Wefer, offered useful suggestions during the different stages of the preparation of this paper. This research was supported by the National Speleological Society, the Cave Research Foundation, the National Geographic Society (Grant 5460-95), the National Science Foundation (DEB-9420033), the Romanian Academy of Sciences (Grant #3919-95), the Fulbright Program and the NSF-NATO Postdoctoral Program.

REFERENCES

- Bakalowicz, W.J., Ford, D.C., Miller, T.E., Palmer, A.N., & Palmer, M.V. (1987). Thermal genesis of dissolution caves in the Black Hills, South Dakota. *Geological Society of America Bulletin*. 99:729-738.
- Calaforra, J.M., Dell'Aglio, A. & Forti, P. (1993). The role of condensation corrosion in the development of gypsum karst: the case of the Cueva del Agua (Sorbas-Spain). *Proceedings International Congress of Speleology*. Beijing: 63-65.
- Cigna, A.A. & Forti, P. (1986). The speleogenetic role of airflow caused by convection. 1st contribution. *International Journal of Speleology* 15:41-52.
- Collingnon, B. (1983). Spéléogénèse hydrothermale dans les Bibans (Atlas Tellien-nord de l'Algérie). *Karstologia* 2:45-54.
- Constantinescu, T. (1989). Considerations sur la zone karstique de "La Movile" (Mangalia, Dobrogea de Sud, Roumanie). *Misc. speol. Rom. Bucharest* 1:7-12.
- Diaconu, G. & Morar, M. (1993). Analyses mineralogiques dans la grotte "Pestera de la Movile" (Mangalia - Dobrogea de Sud). *Karstologia* 22:15- 20.
- Engel, A. S. & Lascu, C. (1996). Clays of Movile Cave, Southern Dobrogea, Romania: speleogenetic indicators of cavern formation. *Program and Abstracts of the 33rd Annual Meeting of the Clay Minerals Society*. Gatlinburg, Tennessee: 53 p.
- Ford, D. & Williams, P. (1989). *Karst geomorphology and hydrology*. UNWIN HYMAN, London: 601 p.
- Horoï, V. (1994). The corrosion process in "Pestera de la Movile" Cave (Southern Dobrugja - Romania), *Theor. Appl. Karstol.* 7:187-191.
- James, J.M. (1994). Microbially produced carbon dioxide and studies on its effects on speleogenesis. In Sasowsky, I.D. & Palmer, M.V. (Eds.), *Breakthroughs in karst geomicrobiology and redox geochemistry*. Karst Water Institute special publication 1: 28-30.
- Jameson, R.A. (1991). Features of condensation corrosion in caves of the Greenbrier karst, West Virginia, *National Speleological Society Bulletin* 53:44.
- Jameson, R.A. (1995). Condensation, condensation corrosion, & associated features. In Snedegars & Greenville Saltpeter Caves, *Guidebook, 1995 NSS Convention, Blacksburg, Virginia*: 122-125.
- Lasclu, C. (1989). Paleogeographical and hydrogeological hypothesis regarding the origin of a peculiar cave fauna. *Misc. speol. Rom. Bucharest* 1:13-18.
- Palmer, A. N. & Palmer, M.V. (1989). Geologic history of the Black Hills caves, South Dakota. *National Speleological Society Bulletin* 51:72-99.
- Pasquini, G. (1973). Aggressive condensation. *Internat. Speleol. III*: 315-318.
- Sarbu, S.M., Kinkle, B.K., Vlasceanu, L., Kane, T.C. & Popa, R. (1994). Microbiological characterization of a sulfide-rich groundwater ecosystem. *Geomicrobiology Journal* 12:175-182.
- Sarbu, S.M. & Kane, T.C., (1995). A subterranean chemoautotrophically based ecosystem. *National Speleological Society Bulletin* 57:91-98.
- Sarbu, S.M., Kane, T.C. & Kinkle, B.K. (1996). A chemoautotrophically based groundwater ecosystem. *Science* 272:1953-1955.
- Szunyogh, G. (1984). Theoretical investigation of the origin of spherical caverns of thermal origin (Second Approach). *Karszt-es Barlang* 1984:19-24.