

MINERALÓGIA A PETROLÓGIA

UNUSUAL TYPES OF SECONDARY CALCITE FROM THE SCĂRIȘOARA ICE CAVE, BIHOR MTS., ROMANIA

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Abstract: Several genetically different types of secondary cave calcite formed in connection with water freezing in the Scărișoara Cave (Bihor Mts, Romania) were studied using C and O stable isotopes and U-series dating. Fine-grained cryogenic calcite trapped within the ice mass and/or occurring on the ice surface was formed by rapid, complete water freezing, accompanied by a quick kinetic CO₂ degassing from the solution. Cave pearls sized from less than 1 mm to 25 mm occurring in periglacial zone in front of the main ice block were not formed by accumulation of fine-grained calcite aggregates occurring in the ice block. Stable isotope composition of the pearls is quite different. Pearls could have been formed in an open system by calcite precipitation during partial water freezing, with a part of the non-frozen fluid seeping away. The cave pearls are porous and highly contaminated by detrital Th, which precludes their precise age determination. Nevertheless, the results indicate that the dated pearls are not older than 2 thousands years.

Key words: secondary cave calcite, fine-grained cryogenic calcite, cave pearls, stable isotopes, U-series dating, Scărișoara Ice Cave, Romania

INTRODUCTION

Besides the prevailing processes of secondary cave carbonate (speleothem) formation by CO₂ degassing from calcium bicarbonate drip-waters or by CO₂ escape accompanied by water evaporation, another process of secondary cave calcite precipitation related to calcium-bicarbonate-water freezing in caves has been also described (Viehmann, 1960, 1963, 1993; Maximovich – Panarina, 1966; Savchenko, 1976; Mavludov, 1987; Lauriol et al., 1988; Clark – Lauriol, 1992, 1997; Andrejchuk – Galuskin, 2001; Žák et al., 2004). The formation of carbonate by expulsion (segregation) during the freezing of common low ionic strength Ca²⁺ – HCO₃⁻ waters is a frequent process in the nature, reported from numerous Arctic, Antarctic and high-altitude glacial environments. When karst waters enter cave passages with temperatures below zero, water freezing (accompanied by CO₂ escape) gradually concentrates the dissolved load in the residual fluid, finally leading to carbonate precipitation. Unstable hydrated forms of CaCO₃ can be primarily formed instead of calcite.

Rapid water freezing produces fine-grained precipitates whose C and O stable isotope chemistry is usually controlled by fast (i.e., from the viewpoint of C and O stable isotope non-equilibrium), kinetic escape of CO₂ from the freezing solution, usually resulting in high δ¹³C values of the carbonate. This process was repeatedly simulated experimentally, e.g. by Clark and Lauriol (1992), Fairchild et al. (1996), Killawee et al. (1998), Socki et al. (2001), and Niles et al. (2004). Coarse-grained carbonate precipitates formed by slow water freezing and slow CO₂ degassing (under isotopic equilibrium) have been described by Žák et al. (2004) from several Central European Caves.

The Scărișoara Cave is one of the world's most outstanding ice-hosting caves. Its entrance is located at the altitude of 1,165 m in the central part of the Bihor Massif, on the left bank of the Garda Seacă Valley, within the Ocoale – Scărișoara karst depression. The cave is developed in thickly bedded limestone of Upper Jurassic age (see Racoviță – Onac, 2000 for more data about the cave). The cave opens with an elliptical, funnel-shaped shaft 60 m in diameter and 48 m in depth. The main iced part of the cave is located below the shaft, in the “Sala Mare” (Great Hall). It is composed of a huge ice block, the volume of which was estimated at about 100,000 m³. Most of this space has a horizontal surface resulting from freezing of drip-waters and snow-melt and rain waters penetrating into the cave. Based on the available data, the main ice block is about 3 thousands years old at its base. Several types of ice speleothems are present in this large room and around the ice block, in the periglacial meroclimate zone. The cave also contains a variety of calcite speleothems, which mostly decorate the passages in the warm meroclimate zone.

Besides these usual speleothems of the warm zone of the cave, two types of secondary cave carbonates occur in the glacial and periglacial meroclimate zone of the cave. First of them is common cryogenic calcite powder, represented by fine-grained carbonate crystals either trapped in the ice or forming mealy deposits on the surface

of ice or around ice stalagmites. The second type is represented by the famous Scărișoara cave pearl nests (Viehmänn, 1960, 1963, 1993) that occur in the periglacial zone, at the limit of massive ice flow, in the cave section called Great Reserve. The pearls are less than 1 mm (micro-pearls) to 25 mm in size. Smaller pearls are usually more regular, spherical in shape, while larger pearls are frequently more irregular. Their color is white to light pink. When broken, the pearls are porous (up to 38 % porosity), show indistinct concentric zoning, and usually do not have any allogenic nuclei. The pearls form irregular accumulations on the surface of limestone scree and/or among limestone blocks. These cover areas of up to several square meters, and are up to several centimeters thick. Viehmänn (1960, 1963) formulated a theory that the pearls are formed during freezing of water, which first concentrates the dissolved substances into the form of a microcrystalline carbonate (“moonmilk”, “lublinite”), which is then collected on pearl surfaces. Scărișoara thus probably became the first cave in the world, where possible importance of water freezing for speleothem formation was recognized. The cave therefore offers a unique possibility to study the processes of cryogenic calcite formation.

SAMPLING AND ANALYTICAL METHODS

Cave pearls were sampled at several locations in the Great Reserve, either close to ice stalagmites or at a longer distance from them. Samples of fine-grained carbonate powder trapped in ice and on the ice surface were sampled at several locations within the cave.

The ice and carbonate powder samples were stored together in vapor-tight plastic containers to prevent water vapor loss during the transport to the laboratory. The ice melted to water immediately after leaving the cave. In the laboratory, water was removed by a syringe and used for oxygen isotope determination on water (using conventional CO₂ exchange). The carbonate sediment on the bottom of the plastic container was dried. Two procedures of drying were tested: rapid drying at elevated temperature, and slow vacuum freeze-drying. Due to a slow oxygen isotope exchange between solid carbonate and water, these procedures had no impact on the carbon and oxygen isotopic composition of the carbonate. Isotope data for pairs of sub-samples dried using both of the two alternative procedures were identical, within the analytical error. Cave pearls were analyzed either as bulk homogenized samples (one whole pearl, or several pearls) or in several points along a profile from centre to the rim (in large pearls). Carbon and oxygen isotope data on carbonate were measured after common digestion in 100 % H₃PO₄ under vacuum. All stable isotope measurements were performed on a Finnigan MAT 251 mass spectrometer in the Laboratories of the Czech Geological Survey in Prague.

One sample of cave pearls (about 5 to 10 mm in size) from Great Reserve was used for age determination. To reach the required sample size, several pearls had to be crushed and mixed together into one sample. Uranium and thorium were separated following the standard chemical procedure described by Ivanovich and Harmon (1992) for carbonates. The pearls were dissolved in ca. 6M HNO₃, and a ²²⁸Th – ²³²U spike mixture was added as an internal controller of chemical procedure efficiency. After oxidation of any organic matter by H₂O₂, spiked acid extracts were pre-concentrated by scavenger precipitation on Fe(OH₃). After ether extraction, U and Th nuclides were separated by ion exchange chromatography (DOWEX 1x8 resin in 9M HCl, then 0.1M HCl). After further purification steps, U and Th were electro-deposited on steel disks. Energetic spectra of alpha particles were collected using OCTETE PC spectrometer manufactured by EG&G ORTEC. Spectra analyses and age calculations were done using “URANOTHOR 2.6” software, which is standard software developed in the U-Series Laboratory in Warsaw (Gorka and Hercman, 2002). The quoted errors are 1σ.

RESULTS AND DISCUSSION

The stable isotope analyses of fine-grained carbonate powder from the main ice mass of the underground glacier yielded high and variable δ¹³C values (up to +12 ‰ vs. PDB), and high δ¹⁸O values, which is typical for cryogenic carbonate formed during rapid, complete water freezing accompanied by a swift kinetic CO₂ degassing. This carbonate “dust” cannot represent redeposited grains derived from the Mesozoic limestone bedrock (as has been sometimes interpreted) since the hosting marine limestone has a different isotopic composition (see Fig. 1).

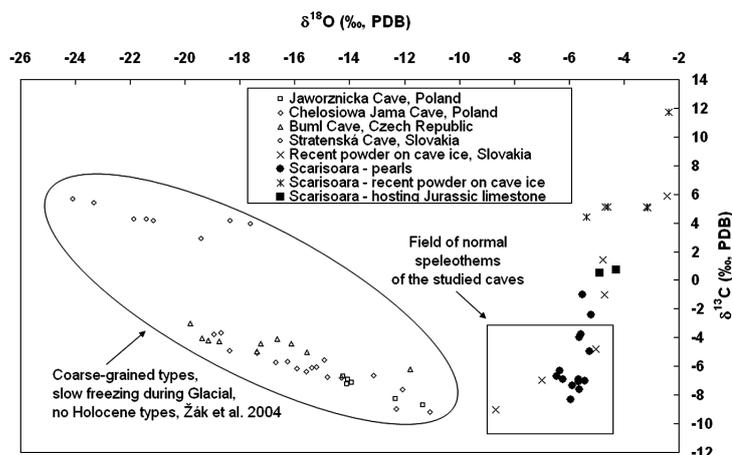


Fig. 1. Stable isotope data of the studied calcite types from the Scărișoara Cave. Data from Žák et al. (2004) are shown for comparison

Obr. 1. Data stabilních izotopů zkoumaných typů kalcitu z jeskyně Scărișoara. Na porovnání jsou uvedeny data od Žáka et al. (2004)

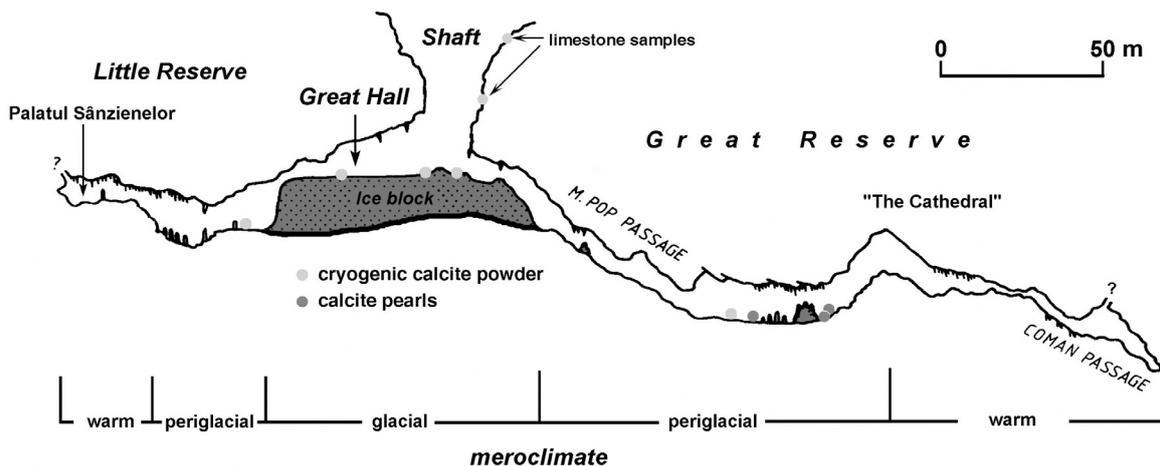


Fig. 2. Profile of the Scărișoara Cave with sampling points
 Obr. 2. Profil jeskynní Scărișoara s lokalizací odběru vzorků

The data on cave pearls occupy a different field in the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ diagram (Fig. 1) than the cryogenic carbonate powder. Therefore, the pearls cannot be formed by simple mechanical accumulation of fine-grained cryogenic carbonate redeposited from the main underground glacier, and a different process of cave pearl formation is required. Slow complete water freezing in a closed system under isotope equilibrium typically produces negatively-sloped trends in the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ space, and low $\delta^{18}\text{O}$ carbonate values (Žák et al., 2004, see also Fig. 1). Such trends were not observed in the studied pearls. The difference in $\delta^{18}\text{O}$ between the pearls and present-day cave ice (water) is close to the equilibrium value at 0 °C. The most plausible explanation is that the carbonate of the pearls precipitated during water freezing in a system open with respect to water, i.e., in a system of partial water freezing, when a portion of non-frozen solution flows away.

Dating of one cave pearl sample using the $^{230}\text{Th}/^{234}\text{U}$ method yielded the following results:

U content in the sample:	3.9070 +/- 0.0388 ppm
$^{234}\text{U}/^{238}\text{U}$ ratio:	0.9776 +/- 0.0076
$^{230}\text{Th}/^{234}\text{U}$ ratio:	0.0242 +/- 0.0009
$^{230}\text{Th}/^{232}\text{Th}$ ratio:	3.982 +/- 0.319

The content of U in the sample is much higher than in usual speleothems precipitated in the non-iced section of the Scărișoara Cave, where the U content is normally well below 1 ppm (Onac, 2001). During cryogenic calcite formation, the dissolved components are concentrated in the residual fluid, and finally in the precipitates, therefore cryogenic precipitates typically show higher contents of U, Si, Mg and other elements than speleothems of the same cave formed by ordinary deposition from supersaturated solutions. The very low $^{230}\text{Th}/^{232}\text{Th}$ ratio of the studied sample indicates a significant detrital contamination. Thus, a precise age could not be calculated (for a successful dating, this ratio should be above 20). Nevertheless, the extremely low $^{230}\text{Th}/^{234}\text{U}$ ratio suggests that the sample is relatively young, probably not older than 2 thousands years.

CONCLUSIONS

1. The Scărișoara Cave contains several genetically different types of calcite speleothems precipitated in connection with water freezing.
2. Abundant, fine-grained cryogenic calcite trapped within the ice mass and/or occurring on the ice surface was formed by rapid, complete water freezing, accompanied by a swift kinetic CO_2 degassing from the solution.
3. Cave pearls of the Great Reserve are not formed by accumulation of fine-grained calcite aggregates occurring in the ice block. Stable isotope composition of the pearls is quite different.

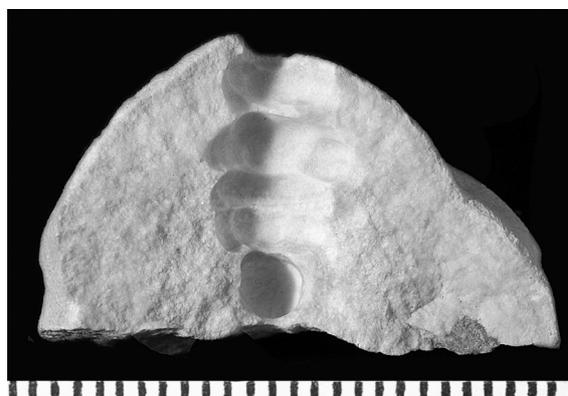


Fig. 3. Profile of a 24 mm large pearl with sampling points for C and O isotope measurements
 Obr. 3. Profil 24 mm velkou jeskynní perlou se vzorkovacími body pro stanovení izotopů C a O

4. Pearls could have been formed in an open system by calcite precipitation during partial water freezing, with a part of the non-frozen fluid seeping away.

5. The cave pearls are porous and highly contaminated by detrital Th, which precludes their precise age determination. Nevertheless, the results indicate that the dated pearls are not older than 2 thousands years.

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ZVLÁŠTNÍ TYPY SEKUNDÁRNÍHO JESKYNNÍHO KALCITU ZE ZALEDNĚNÉ JESKYNĚ SCĂRIȘOARA, BIHOR, RUMUNSKO

S o u h r n

Ledová jeskyně Scărișoara v pohoří Bihor v Rumunsku je jednou z nejznámějších zaledněných jeskyní světa a pravděpodobně první jeskyní světa, ze které byl Josifem Viehmannem v 60. letech popsán vznik jeskynního kalcitu kryogenním procesem, tedy srážením kalcitu při mrznutí vody. V jeskyni se vyskytuje jednak běžný jemnozrný kryogenní kalcit v hlavní mase podlahového ledu a potom silně porézní, obvykle nepravidelně kulovité jeskynní perly s velikostí od méně než 1 mm do zhruba 25 mm, které tvoří akumulace na sutí v předpolí hlavní akumulace ledu. Tyto neobvyklé typy sekundárního jeskynního kalcitu byly podrobeny výzkumu s využitím geochemie stabilních izotopů C a O v kalcitu a datování metodou $^{230}\text{Th}/^{234}\text{U}$.

Jemnozrný kalcit v hlavní mase ledu vzniká během rychlého mrznutí vody za rychlého kinetického úniku CO_2 z roztoku. Tento typ je vznikem i izotopovým složením blízký jemnozrnému kryogennímu kalcitu, který se vyskytuje v zaledněných jeskyních na Slovensku. Jeskynní perly jeskyně Scărișoara nevznikly nabalováním recentního jemnozrného kryogenního kalcitu, jejich izotopové složení je odlišné a naznačuje vznik nejspíše během částečného mrznutí vody, kdy podíl nezmrzlé vody stéká pryč. datování jednoho vzorku perel vykazovalo vysoký obsah detritického Th a přesné určení stáří není proto možné. Lze však odhadnout, že perly nejsou starší než zhruba 2-tisíce let.