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Speleothems in the "Earth and Man" National Museum in Sofia (Bulgaria) – an example of moveable storage of mineral diversity

Пещерните образувания в Националния музей „Земята и хората" – пример за съхраняване на минералното разнообразие

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Moveable geological heritage includes rocks, ores, fossils and others, that are stored in museums and private collections. The "Earth and Man" National Museum in Sofia, Bulgaria, is a big cultural and scientific institution, where the mineral collections are stored, systematized and studied. They are: collection "Giant crystals" – one of the two largest crystal collections in the world, collection "Gemstones" – includes mineral specimens representing almost all of the currently known minerals with gemstone characteristics, collections "Minerals of the Earth", "Mineral resources of the Earth", "Minerals of Bulgaria", "Mineral resources of Bulgaria", collection of cave formation and others.

Collection of cave formation

Various speleothems are formed in the karst caves. All they are resulted from the slow accumulation of calcite after degassing of CO_2 from percolation water in caves (Baldini, 2010; Perrin et al., 2014). As speleothems grow in response to specific physical and chemical processes within the caves, every cave is characterized by its individual set and characteristics of speleothems and minerals (Self, Hill, 2003). In the cave's deposits formed in limestones and marbles, calcite is the main mineral – about 95%, the other polymorphic modification of calcium carbonate – aragonite is 2–3%, gypsum is to 2%, and other minerals occur in minor amounts and their presence mainly depends on the host lithological medium.

The collection of speleothems in the "Earth and Man" National Museum is of particular interest. Todays, it includes more than 600 museum pieces of 49 caves of Bulgaria and 14 caves from abroad. The collection mainly includes cave formations from caverns and mining excavations discovered during mining activity, and a smaller part is donations of private persons. The mineral composition of stored speleothems is relatively simple. They are mainly composed of calcite, aragonite, gypsum, and minor minerals as hydromagnesite, huntite, dolomite, magnesite, alumohydrocalcite, barite, celestine, diaspore, todorokite, hematite (Janakieva, Maleeva, 2011). Totally 53 mineral species have been identified in speleothems in Bulgaria so far (Shopov, 2005). The collection of cave formations in the museum started to fill up in 1987 firstly with samples from the now-nonexistent karst cave Obrechenata (Doomed). Because of the impossibility of preserving the cave in the limestone quarry, all speleothems – 296 samples were taken from the cave. Stalactites, coralloids and helictites are the most widespread in the cave, while stalagmites and crystallictites are rare. Today this collection is a subject of scientific investigations of the karst and associated mineral-forming processes.

Mineralogical investigations

Mineralogical investigations in the present work is carried out on coralloids of this cave with a specific tower-type morphology, covering the bottom of a small sinter pool, which were found to have grown over earlier formed fragments of cave rafts and spherulites. These coralloids occur as single formations or groups up to 25 cm high colored in brawn. Their longitudinal and transverse cross-sections reveal complex internal structure (Fig. 1A, B). It is found that the coralloid bodies include plates of cave rafts 1–2 mm in thickness (Fig. 1B) and spherulites, all colored from white to different nuances of yellow and brawn. The cave rafts are flat planar speleothems formed on the surface of pool. Dripping water breaks them causing their randomly oriented deposition on the pool bottom. Besides planar material, the formed heapings contain also spherulites. These primary aggregates then are

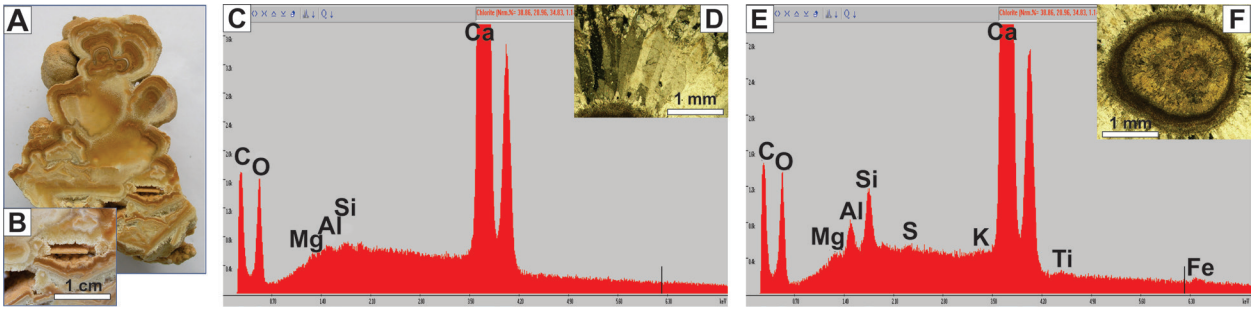

Fig. 1. *A*, longitudinal cross-section of coralloid showing spherulites and plates of cave rafts; *B*, detail of Fig. 1A; *C*, EDX spectrum of radially arranged calcite crystals; *D*, colorless and transparent calcite crystals overgrowing the spherulites; *E*, EDX spectrum of spherulite core; *F*, spherulite core of fine calcite crystals

overgrown by spheroidalite individuals forming the coralloid body (tower). The raft plates as well as the internal spherulites are observed at different places throughout the height of coralloids, thus indicating that the mineral forming processes were periodical.

It is found that among the all parts of coralloid body, the internal spherulites are more intensively colored in brawn and contain a central dark-brawn round core with diameter 1–2 mm (Fig. 1F). Optical microscopy and scanning electron microscopy examinations of coralloid cross-sections show very good correlation between the coloring in brawn and the size of crystals constituting the coralloid body. The smallest crystals of 1–3 μm in size are determined for the most dark-brawn cores (Fig. 1F) of internal spherulites while the largest crystal individuals up to 1–3 mm are found in the colorless and transparent zones (Fig. 1D) overgrowing the cores and fragmented cave raft plates. The colored in brawn micro-inclusions are found in calcite crystals and in the boundaries between growth zones of radial calcite (Figs. 1D, F).

Electron probe microanalyses (Figs. 1C, E) of differently colored parts show that the Ca is a prevailing chemical element in all examined areas of coralloid cross-sections (CaO 51.7–55.3 wt%). The Mg, although in small quantities, (MgO 0.1–0.3 wt%) is present in all analyzed areas. It is found that the coloring in brawn well correlates with the presence of such elements as Si, Al and Fe – their maximal contents are detected in the spherulite cores (in wt%): SiO_2 up to 1.69, Al_2O_3 up to 0.9 and Fe_2O_3 up to 0.41, which indirectly points to the presence of clay minerals (Figs. 1B, C). Other minor elements as K and S well correlate with the Fe being (in wt%) up to 0.05 (K_2O) and up to 0.20 (SO_3).

Powder X-Ray diffraction (XRD) analysis of the coralloid fragments shows that well crystallized calcite is an absolutely dominant mineral in them. No any diffraction reflections of clay minerals were found on the XRD patterns thus indicating that they are presented by structurally strongly disordered varieties. Besides calcite, the XRD analysis reveals traces of jarosite ($KFe_3(SO_4)_2(OH)_6$) in the studied material. This finding although well correlated with the chemical composition of the spherulite cores intensively colored in brawn, raises a question about the physicochemical conditions of mineral deposition in the cave as jarosite is a mineral stable in strongly acid media (pH <3) and this mineral is found by us in a very aggressive alkaline carbonate surrounding. It is assumed that the observed very intensive coloring of the spherulites cores is due to the replacement of initial jarosite by ferric iron oxides as is expected to be in alkaline media.

Conclusion

The Obrechenata cave, though a small karst formation, is characterized by a variety of speleothems. Coralloid speleothems formed in the sinter pool and studied by us in more detail represent a unique cave formation not only because of the specific tower type morphology, but also because of the complex internal structure and the presence of jarosite, for the first time identified in the cave formation of Bulgaria.

Although the Obrechenata cave is a bitter example of destruction of natural phenomena by humans, the preserved collection of all the speleothems from this cave in the "Earth and Man" National Museum is also an example of positive thinking and concern for the future generations.

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