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The mineral assemblage of the Great Şălitrari Cave (Cerna Valley, Romania): speleogenetic implications

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Muntele Şălitrari, meaning Saltpeter Mountain, suggesting the presence of saltpeter deposits, is a toponym within the upper Cerna River basin in SW Romania, which raised a relatively recent interest in investigating the mineral assemblages of the caves in the area. Here we present results from the Great Şălitrari Cave, which holds testimony of early saltpeter mining under the Ottoman and Austro-Hungarian empires' rule, as well as a rich mineral assemblage. The cave, 1500 m long, is developed in massive Jurassic limestone and hosts large deposits of alluvial sediments that were altered by percolating N- and P-rich solutions sourced from bat guano and cave bear bones, and once active sulfide-rich steam vents or thermal springs. One passage, close to the entrance, namely the *Nitrate Passage* has temperature and relative humidity values different than the rest of the cave ($\sim$11.7ºC and $<$75%, as compared to $<$10ºC and 96-100%). Unlike most of the cave, this passage lacks speleothems and contains thick sediment deposits, ranging from sand and pebbles at the base, an intermediate clay level (crisscrossed by white veins rich in phosphate minerals) and in the upper part silt-sized material containing nitrates, sulfates, and phosphates, topped by a layer of guano. Approximately thirty samples represented by nodules, crusts, aggregates, acicular or fibrous crystals, and highly weathered limestone fragments or earthy masses, have been analyzed. Carbonates, phosphates (apatite-CaOH, apatite-CaF, brushite, taranakite, ardealite, and variscite), and silicates (quartz, kaolinite, illite) were identified by means of XRD, whereas EMPA, SEM and EDS were additionally used to acquire further chemical data on more peculiar minerals, such as alunite and aluminite. Gypsum was positively tested by all of the methods presented above. Some of the minerals identified here are common in caves (e.g. calcite, gypsum, brushite), whereas others require very particular environments in order to form and persist (e.g., alunite, aluminite, darapskite) and may hold the key to diagnose this particular cave's genesis. δ^{34}S values of ardealite, darapskite, and gypsum range between -2.6 and +6.5‰ and are inherited from an incomplete oxidation of the sulfide-rich thermal fluids rising from depth as springs or steam [1, 2]. Observations of morphological features (e.g., ceiling cupolas, blind ascending passages, etc), coupled with unusual sulfate minerals and their isotopic signature suggest that several different speleogenetic pathways overlap, but at least one must have been hypogene.

[1] Onac, B.P., Sumrall, J., Tămaş, T., Povară, I., Kearns, J., Dârmiceanu, V., Veres, D., Lascu, C., 2009. The relationship between cave minerals and H_2S-rich thermal waters along the Cerna Valley (SW Romania). Acta Carsologica 38 (1), 67-79.

[2] Wynn, J.G., Sumrall, J., Onac, B.P. (2010). Sulfur isotopic composition and the source of dissolved sulfur species in thermo-mineral springs of the Cerna Valley, Romania, Chemical Geology, doi:10.1016/j.chemgeo.2009.12.009