



## Isotopic indications of water-rock interaction in the hypogene Tavrskaya cave, Crimea, Ukraine

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The Inner Range of the Crimea Mountains has recently been identified as an area of previously unrecognized hypogene speleogenesis (Klimchouk et al. 2009). The entrance of the Tavrskaya cave is located in the middle of the 25 m-high scarp of the cuesta built up of Paleocene limestone. The cave comprises two parallel major passages (ca. 180 m long, up to 7-8 m high and up to 5-6 m wide) connected by a smaller passage. The major passages are slightly inclined toward the north-west following the dip of bedding. The morphology of the cave bears strong indications of dissolution at conditions of ascending flow in a confined aquifer setting.

A massive calcite crust, studied in this paper, was first found in a small cave located ca. 200 m from Tavrskaya cave along the cuesta scarp. According to its position and morphology, the cave corresponds to the rift-like “feeder” zone of Tavrskaya cave. Recently, similar calcite crust was found in Tavrskaya cave, in a rift-like passage of the near-scarp zone. The crust is built up of a brownish translucent calcite whose columnar crystals (bounded by competitive growth surfaces) are arranged in a characteristic radiating pattern. Calcite contains only all-liquid inclusions indicating deposition at less than ca. 50°C. It also contains filamentous biological material (possibly fungi or cyanobacteria), which sometimes facilitated entrapment of fluid inclusions. This calcite body is tentatively interpreted as a paleo-spring deposit (ascending flow). In order to characterize the isotopic properties of this calcite and the bedrock limestone we drilled small-diameter cores through the calcite formation, as well as through the wall of a cavity devoid of calcite. Stable isotope analyses were performed along these cores. To provide a basis for comparison several samples from the same lithostratigraphic units were collected far from the cave.

Along a 15 cm-long profile, both oxygen and carbon isotopes of the limestone remain stable at  $\delta^{18}\text{O} = -4.3 \pm 0.2 \text{ ‰}$  and  $\delta^{13}\text{C} = -1.7 \pm 0.3 \text{ ‰}$  ( $1\sigma$ ). Only within the 1.5 cm-thick zone immediately underlying the calcite  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values plunge to ca.  $-8 \text{ ‰}$  and  $-9 \text{ ‰}$  respectively. It appears from this data that water rock-interaction associated with the deposition of this calcite produced only a thin alteration halo in the limestone. However, when data from the cave-wall cores are compared with those collected far from the cave, it appears that the “constant” values from cave walls are shifted relative to the presumably unaltered limestone values toward lower values by ca.  $1.5\text{--}3.0 \text{ ‰}$  (oxygen) and  $3\text{--}4 \text{ ‰}$  (carbon). On the  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  cross-plot the data for unaltered limestone, cave wall limestone, alteration halo, and secondary calcite plot along a well-defined line ( $R^2=0.99$ ).

We propose that the Paleocene limestone in the vicinity of the Tavrskaya cave has experienced a two-stage alteration. During the first stage, presumably associated with the process of cave excavation, the bedrock has been altered ( $\delta^{18}\text{O}$  depleted by  $1.5$  to  $3.0 \text{ ‰}$  and  $\delta^{13}\text{C}$  by  $3$  to  $4 \text{ ‰}$ ). The thickness of this zone of early alteration is unknown but must be larger than 15 cm (length of our cores). The second stage of alteration was associated with the deposition of calcite; during this stage the isotopic composition was further depleted (by  $4\text{--}5 \text{ ‰}$  in  $\delta^{18}\text{O}$  and  $8\text{--}10 \text{ ‰}$  in  $\delta^{13}\text{C}$ ). The extent of alteration was much smaller, though, and restricted to zones where calcite was deposited (ca. 15 mm beneath the calcite).

REFERENCE: Klimchouk et al. (2009) Hypogene Speleogenesis in the Piedmont Crimea Range. UISK, Special Paper 1. pp. 159-171.