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Carbonate bedrock alteration during low-temperature hydrothermal karstification: a potential tool for hydrogeological paleothermometry using oxygen isotopes

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Movement of heated aqueous fluids through carbonate rocks commonly causes isotopic alteration of the latter. Halos of altered δ^{18}O values were reported around magmatic intrusions, scarn deposits (500 to 350°C), and hydrothermal ore deposits (350 to <80°C). The lateral extent of reported isotope halos ranges over five orders of magnitude, from <1 m to several km. Alteration halos were mostly studied in association with ancient mineral- and/or ore-depositing systems. We report that characteristic alteration zones could also be produced by lukewarm to thermal waters, which are undersaturated with respect to the carbonate wall-rock, dissolved it and thus forming karst cavities, instead of depositing minerals.

Isotope alteration profiles were studied in several sites in the Austrian Alps including the Entrische Kirche cave in the Gastein valley, the hypogene Stegbachgraben deposit in the Grossarl valley, and calcite-lined solutional vugs in the Tux valley. At all three sites the host carbonate rock (calcite marble) shows clear macroscopic indications of alteration (discoloration). Fine-resolution profiles measured perpendicularly to the cave walls revealed that the rock is depleted in ^{18}O by up to 10-15 per mill near the cave walls. The values return to unaltered background values (δ^{18}O = -3 to -5 per mill V-PDB) within 10 to 40 mm from cave wall. In two cases isotopic profiles showed characteristic sigmoid shape, indicating that the rock at the cave wall reached isotope equilibrium with cave-forming water. This conclusion is supported by the observation

that the δ^{18}O values of the altered marble near the cave wall coincide with the δ^{18}O values of low-temperature hydrothermal euhedral calcite lining the cave.

Traditionally, secondary minerals are viewed in paleo-hydrogeology as the most common "footprints" left behind by waters, which circulated through the rocks in the geological past. The isotope alteration zones identified in carbonate rocks suggest that footprints of aggressive to neutral waters can also be detected. In those cases when the rock near cave wall reached isotopic equilibrium with the water (as determined from the shape of the isotope profiles), the isotope properties of altered rock can be used to assess the temperature of the paleo water by solving the isotope mass-balance equation for water-rock interaction. Similarly to mineralogical δ^{18}O -based thermometry this approach requires an independent estimate of the oxygen isotopic composition of the paleo water. For the two case-studies, Entrische Kirche and cavities in Tux valley, paleo-temperatures were assessed at 30-35 and 70-80°C, respectively.