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Speleothems from Spannagel Cave, Austria: no link between trace elements and climate?

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We performed a high-resolution study of the stable isotope (δ18O and δ13C) and trace element (Mg, Sr, Ba, P, Al, U, Fe, Cu, Zn, REE) composition of speleothems from Spannagel Cave in order to investigate the potential use of these elements as paleoenvironmental proxies. Stable isotopes were analyzed using IRMS on subsamples milled at 100 micrometer resolution, while trace elements were measured in continuous transects by LA-ICP-MS using a 30 micrometer circular laser mask.

Absolute values are variable and high compared to many limestone caves and reflect the geologic setting of Spannagel Cave, i.e. calcite marble tectonically sandwiched between gneiss. Minimum and maximum values of Mg, Sr, Ba, P and U are 164 to 11,100 ppm, 69 to 1,240 ppm, 0.9 to 741 ppm, 0.1 to 565 ppm and 0.5 to 442 ppm, respectively.

Mg and Sr concentrations of recently deposited calcite are consistent with measured values in drip water and partition coefficients reported in the literature.

The Mg/Ca ratio has been repeatedly proposed as a potential thermometer in speleothems, but as in many other caves the slight temperature dependence of the partition coefficient is overwhelmed by natural variations in the Mg/Ca ratio of Spannagel drip waters (0.04 to 0.21). The Sr/Ca ratio in modern drip waters also scatters widely (0.002-0.017), albeit intra-site variability is much smaller. Mg and Sr are highly correlated in the analyzed speleothem samples which is commonly attributed to prior calcite precipitation in the karst aquifer.

Several other trace element show statistically significant correlations, including Sr-Mg-Ba-U, Fe-Al and Cu-Zn-U-La, but none of these elements is correlated with either δ13C or δ18O. The lack of a climate link is corroborated by the fact that there are no systematic trends in trace element concentrations (or ratios) at times of known climate shifts, e.g., at D/O events.

In essence, Spannagel Cave is an example of a karst hydrological regime dominated by complex leaching processes within metamorphic rocks fueled by carbon dioxide from the soil zone and by sulfide oxidation within the aquifer. These reactions give rise to exceptionally high trace element contents in the seepage waters and speleothems - e.g., up to 34 ppb and 442 ppm U, respectively – but mask any climate control (e.g., Mg/Ca) even at decadal to annual time scales.