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Speleothem aragonite trace element partitioning: insights from cave monitoring

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Speleothems are well established climate archives. Most research focusses on calcite specimens, but aragonite is a common mineralogy in cave environments and has the advantage of high uranium contents and thus excellent dating potential. The use of trace elements as environmental proxies in speleothem aragonite is still understudied compared to calcite. In this study, we present Sr/Ca, Ba/Ca, U/Ca and Mg/Ca data from drip water samples collected at 3-day intervals with an autosampler from Grotte de Piste, a cave in northern Morocco. Although watchglasses did not provide enough aragonite for trace element analysis, the drip water results can be used to examine trace element partitioning coefficients.

Prior carbonate precipitation (PCP) is a process taking place in the epikarst above the cave and can be recognized in dripwaters by analyzing their trace element to Ca ratios since the carbonate incorporates trace elements disproportionally with respect to Ca. The monitored drip site has a seasonally varying drip rate and shows a clear bi-modal trace element behaviour in U/Ca and Sr/Ca but not in Mg/Ca. We assign this to a switch between prior calcite and prior aragonite precipitation. The preliminary Ba/Ca data seem similar to the Mg/Ca data. Interestingly, the wet part of the year is associated with high drip rates and prior calcite precipitation, whereas progressive drying of the drip site leads to prior aragonite precipitation. Enhanced prior calcite precipitation results in higher Sr/Ca and Mg/Ca dripwater ratios but lower U/Ca ratios, whereas prior aragonite precipitation results in lower U/Ca and Sr/Ca but higher Mg/Ca ratios. We further investigate the drip water trace element composition with a simple prior carbonate precipitation model that allows us to fit the model by changing the trace element partitioning coefficients for the prior calcite and aragonite precipitation phases, improving estimates of these important parameters and future interpretations of trace elements in aragonite speleothems. A linear regression model shows that there is potential for reconstruction of quantitative drip rates and thus rainfall variability. This study provides one of the first empirical evidences for prior aragonite precipitation in cave drip waters.