Carbon and oxygen isotope systematics in cave environments: Lessons from an artificial cave

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Variations in carbon and oxygen isotope ratios in cave carbonate deposits (stalagmites, stalactites, and flowstones) have been widely used as paleoclimate proxies. Carbon isotopes are used to infer changes in vegetation types (i.e. C3 and C4) or vegetation intensity above caves in the past, whereas oxygen isotopes have been interpreted as a paleotemperature and/or paleorainfall proxy. A critical assumption of these proxies is that cave carbonates have been deposited under isotopic equilibrium conditions and have not been modified by any kinetic effects during their formation. Unfortunately, no definite geochemical method exists to verify isotopic equilibrium in ancient cave carbonates. For example, the Hendy test has been criticized for its inability to identify isotopic disequilibrium conditions [1]. Similarly, the Replication test [2] may falsely indicate isotopic equilibrium when two (or more) cave carbonate samples have experienced a similar magnitude of kinetic effect. Moreover, there are still difficulties using the recently developed carbonate clumped isotope thermometer to examine isotopic equilibrium in cave carbonates due to discrepancies among the existing calibrations, and analytical challenges. Consequently, climatic and non-climatic isotope signals in cave carbonates are hard to differntiate and quantify.

We simulated the growth of cave carbonates under tightly controlled conditions (e.g., temperature., relative humidity, solution chemistry, and drip rate) in an artificial cave in order to characterize isotopic equilibrium/disequilibrium conditions in natural caves. Our data demonstrates that kinetic effects can obscure the climatic isotope signals for both carbon and oxygen, producing offsets as large as 25 ‰ and 3 ‰ in $\delta^{13}C$ and $\delta^{18}O$, respectively. Key mechanisms for these kinetic effects were investigated in our experiemnts, allowing us to identify a datum for isotopic equilibrium conditions in caves.

[1] Mickler *et al*. (2006) *Geological Society of America Bulltien* **118**, 65–81. [2] Dorale & Liu (2009) *Journal of Cave and Karst Studies*. **71**, 73–80.