

## Constraints from clumped isotope analyses of a stalagmite on maximum tropical temperature change through the late Pleistocene

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We analyzed modern and ancient speleothems from caves in Northern Borneo (4°N, 115°W) for their carbonate isotopologue, or 'clumped isotope', compositions. Although this method of paleothermometry appears to exhibit a common calibration in a variety of carbonates, speleothems have so far proven to be difficult archives for this technique. Most samples measured to date are out of equilibrium, yielding apparent temperatures that are too high [1,2].

Many samples analyzed in this study also exhibit non-equilibrium clumped isotope compositions, but we have discovered one cave where modern carbonate appears to have grown at equilibrium. An old stalagmite from that cave, which covers at least 500 kyr, is being analyzed for changes in temperature back in time. The  $\delta^{18}\text{O}$  in this sample varies by 3‰ from glacial to interglacials. If this signal were due to temperature changes, it would translate to roughly 8 K (taking into account variations in global seawater  $\delta^{18}\text{O}$ ).

The clumped isotope measurements from peak glacial and interglacial intervals (identified by  $\delta^{18}\text{O}$  maxima and minima) yield temperature estimates that are statistically indistinguishable from each other and from the modern cave temperature. The data are consistent with equilibrium carbonate precipitation (with respect to clumped isotope compositions) and invariant cave temperature throughout the growth of this speleothem.

The results suggest that cave temperature stayed constant within  $\pm 0.8$  K (1 $\sigma$  s.d. of 4 intervals analyzed so far) through several glacial-interglacial cycles. Thus most of the variations in  $\delta^{18}\text{O}$  in the stalagmites from Northern Borneo is likely due to changes in the  $\delta^{18}\text{O}$  of precipitation. Compared to reconstructed deglacial changes in sea surface temperature in the West Pacific Warm Pool of 3.5-5.0 K [3,4], our data suggest that ground temperature changes in the same area were apparently at most of similar magnitude, but likely smaller.

[1] Affek *et al.* (2008) *GCA* **72**, 5351-5360. [2] Daeron *et al.* (2008) *GCA* **72**, A193. [3] Visser *et al.* (2003) *Nature* **421**, 152-155. [4] Lea *et al.* (2000) *Science* **289**, 1719-1724.

## Discriminating fluid sources in Miocene cold seep systems using REEs in authigenic carbonates

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Authigenic carbonates are a common feature in cold seep environments, where fluids enriched in methane and other hydrocarbon gases escape from the seafloor. Seep-carbonates have been reported worldwide both in modern and ancient sedimentary deposits. In the northern Apennines (Italy), numerous outcrops of seep-carbonates are particularly well-preserved. Evidences from paleoecological, sedimentological, geochemical and isotopic (O and C stable isotopes) analyses clearly show that they were derived from the microbial oxidation of methane-rich fluids. REE patterns and abundances in fossil seep-carbonates may provide additional informations for better constraining the origin and the composition of the fluids from which they have precipitated.

Here, we report REE data for a series of Miocene carbonate samples recovered from various geological settings in the northern Apennines. Samples were leached with 5%  $\text{HNO}_3$ , prior to analysis by SF-ICPMS using the Tm addition method [1]. Total REE concentrations ( $\Sigma\text{REE}_N$ ) in our studied carbonates are very similar to those reported for modern authigenic carbonates [2], suggesting negligible post-depositional diagenetic alteration. The shale-normalized REE patterns vary significantly amongst the different authigenic carbonate samples analysed in this study. These data indicate that they were formed from fluids having distinct REE signatures. These results, coupled with other geochemical, petrographic and mineralogical data, allow us to reconstruct the variation of fluid seepage activity in the northern Apennines during the Miocene.

[1] Bayon *et al.* (2009) *Geostand. Geoanal. Res.* **33**, 51-62.

[2]. Rongemaille *et al.* (2009) *GCA*, this volume.