



Recent advances in fluid inclusion isotope analysis of speleothem calcite

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As early as in the 1970's, isotope analysis of fluid inclusion water in speleothem calcite was recognized to be of great value for paleoclimate reconstruction. However, initial experiments in different labs soon showed that production of accurate isotope data from fluid inclusion water was not a trivial task (see Vonhof et al., 2006 and refs therein). With the introduction of continuous-flow mass spectrometry, new equipment became available that allowed for simultaneous $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of sub-microliter amounts of water. Based on this technique the first fluid inclusion crushing devices we constructed that provided relatively accurate isotope analysis of the water captured in small chips of speleothem calcite. (Vonhof et al, 2006; van Breukelen et al., 2008; Dublyansky and Spoetl, 2009).

Approximately 5 years later, we have gradually improved the method, and gained better understanding of the benefits and limitations of this new analytical technique for speleothem studies. Some of the topics to be addressed in this presentation are:

Isotopic equilibrium:

Fluid inclusion isotope analysis has proven to be very useful for the better interpretation of isotope composition in speleothem calcite, because it provides direct information on the variability of drip water isotope composition through time. Less well understood at this point is the concept of isotope equilibrium, as inferred from the isotopic difference between drip water (captured in fluid inclusions) and the host calcite. Possible kinetic fractionation hampers the straightforward calculation of paleotemperatures from paired fluid inclusion – calcite $\delta^{18}\text{O}$ ratios and it appears difficult to interpret differences in fractionation behaviour between different stalagmites studied.

Combination with clumped isotope data:

Further quantification of non-equilibrium fractionation has recently been achieved by combining clumped isotope analysis with fluid inclusion isotope analysis in speleothem calcite (Wainer et al., 2011). Clumped isotope data of speleothems have been shown not to be in isotope equilibrium, but in combination with fluid inclusion isotope data, relatively accurate paleotemperature can be calculated.

Preservation of fluid inclusion isotope signal:

Further methodological innovation remains of importance to improve the quality of fluid inclusion isotope analysis. Analytical reproducibility within and between labs needs to be monitored and understood, to facilitate interlaboratory calibration. To achieve that, we not only need to identify reliable standard material, but more importantly we need to get a better grip on the preservation of the isotope signal in fluid inclusion water so that we can better screen for post-depositional alteration in fluid inclusion isotope data. In the work done over the past few years, isotopic offsets attributed to post-depositional alteration were suspected to have occurred in several cases.

Further applications:

The technique can be applied to various materials other than speleothems. We have meanwhile experimented with materials as diverse as hydrothermal minerals, marine fossils, evaporites and diagenetic calcite to explore the possibilities of fluid inclusion isotope analysis beyond speleothem calcite.

References:

- Breukelen, M.R. van, Vonhof, H.B., Hellstrom, J.C., Wester, W.C.G., and Kroon, D., 2008, Fossil dripwater in stalagmites reveals Holocene temperature and rainfall variation in Amazonia: *Earth and Planetary Science Letters*, v. 275, p. 54-60.
- Vonhof, H.B., van Breukelen, M.R., Postma, O., Rowe, P.J., Atkinson, T.C. and Kroon, D. 2006, A continuous-flow crushing device for on-line $\delta^2\text{H}$ analysis of fluid inclusion water in speleothems. *Rapid Communications in Mass Spectrometry*, v. 20, p. 2553-2558.

Dublyansky, Y.V. and Spoetl, C. 2009, Hydrogen and oxygen isotopes of water from inclusions in minerals: design of a new crushing system and on-line continuous-flow isotope ratio mass spectrometric analysis. *Rapid Communications In Mass Spectrometry*, v. 23, p. 2605-2613.

Wainer, K, D. Genty, D. Blamart, M. Daëron, M. Bar-Matthews, H. Vonhof, Y. Dublyansky, E. Pons-Branchu, L. Thomas, P. van Calsteren, Yves Quinif and N. Caillon, 2011, Speleothem record of the last 180 ka in Villars cave (SW France): Investigation of a large $\delta^{18}\text{O}$ shift between MIS6 and MIS5. *Quaternary Science Reviews*, v.30, Issues 1-2, p. 130-146.