



Towards reliable fluid inclusion measurements of oxygen isotopes in speleothems

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Fluid inclusions in speleothems preserve samples of meteoric water for measurement of stable isotope ratios. Because of the wide distribution of speleothems, and because precise ages can be assigned by U/Th dating of the host calcite, fluid inclusions are an archive that may track the changing isotopic composition of ancient precipitation in both space and time. However, there are formidable technical difficulties in recovering and measuring isotope compositions without fractionation. Considerable success has been achieved with $\delta^2\text{H}$ in recent years^{1,2,3} but very few successful $\delta^{18}\text{O}$ measurements have been published¹. We now report the application of the “Amsterdam device” to measuring $\delta^{18}\text{O}$ and $\delta^2\text{H}$ simultaneously in fluid inclusions, by continuous flow mass spectrometry.

The “Amsterdam device”⁽³⁾ relies on crushing a chip of calcite (~ 0.3 g) at 150°C in a stream of He carrier gas. Fluid inclusion waters ($\sim 0.1 - 0.3$ μl) were analysed using a Thermo-Finnigan TC/EA and Delta Plus XP mass spectrometer. The water released by crushing was cryo-focused by trapping at -80°C , then released from the trap at 200°C , and reacted with glassy carbon at 1400°C to produce H_2 and CO gases for analysis of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ respectively.

A measurement protocol has been developed in which corrections for the effects of sample size were established using injections of a reference water via a septum directly into the crushing cell. Each fluid inclusion measurement was preceded and followed by several injections of the same reference water. Fluid inclusion measurements were replicated using 29 analyses of multiple samples cut from nine individual layers in several British speleothems. Between two and six replicates were performed on each

layer, with overall precisions of ± 1.4 per mille for $\delta^2\text{H}$ and ± 0.5 per mille for $\delta^{18}\text{O}$. About two thirds of these measurements lie very close to the Global Meteoric Water Line on a $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ plot. The remainder trend to the left of the GMWL with a gradient of ~ 2 , suggesting the possibility of fractionation caused by diffusion of water vapour. This may be diffusion through cracks linking partially-opened inclusions to the surfaces of the grains produced by crushing. If these evidently fractionated values are excluded, replication errors improve to ± 1 per mille for $\delta^2\text{H}$ and ± 0.2 per mille for $\delta^{18}\text{O}$.

Preliminary interpretation of fluid inclusions in British speleothems suggests that cave drip waters in the mid-Holocene were 6-8 per mille heavier for $\delta^2\text{H}$ than today. In two caves in NW England these mid-Holocene waters plot close to the Global Meteoric Water Line, suggesting they may directly reflect changes in the isotopic composition of precipitation. In a cave in SW England, the mid-Holocene waters trend along a gradient of ~ 5 to the right of the GMWL, suggesting enhanced evaporation of rainfall before recharge. These examples illustrate the potential value of paired $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements for distinguishing different processes by which palaeo-climate may be recorded isotopically in speleothem fluid inclusions.

¹Dennis et al. 2000 *Geochimica et Cosmochimica Acta*, **65**, 871-884.

² Atkinson et al. 2005 *Geophysical Research Abstracts*, **7**, EGU05-A-06961; SSP9-1WE4O-004.

³ Vohnhof et al 2006 *Rapid Communications in Mass Spectrometry* **20**, 2553-2558)