Calcium isotope systematics of caves: Implications for speleothem palaeoclimatology

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Cave carbonates are widely used continental palaeoclimate archives, providing some of the highest resolution and best dated records available for the past 500,000 years. Numerous speleothem-based proxies have been developed and applied to palaeoclimate problems; in particular $\delta^{18}O$ and trace-metal analyses have shown promise in reconstructing changes in regional and local rainfall.

Little attention has been paid to the isotopic composition of calcium ($\delta^{44}Ca$) incorporated into speleothems. In theory cave $\delta^{44}Ca$ shares many controls with Mg/Ca, Sr/Ca and other trace metal ratios, making speleothem $\delta^{44}Ca$ a potential proxy for local hydrological conditions. As a major element, calcium potentially avoids some of the pitfalls of trace-metal based proxies, namely uncertainty in source composition and potential bias towards non-carbonate phases [1]. However, no systematic study of $\delta^{44}Ca$ in natural cave systems has been published, although a lab-based study has indicated the level of Ca isotope fractionation expected in this environment [2].

We have conducted the first field study of calcium isotopes, in Heshang Cave (Central China). Dripwater and glass plate calcite were analysed at ca. monthly resolution to understand the modern cycling of calcium isotopes from source rock, through the cave system and into the speleothem record.

In addition, we have measured $\delta^{44}Ca$ in a section of stalagmite from the same drip site (HS-4) covering the 8.2 kyr climate event [3]. The event is characterised by a positive excursion in calcium isotopes, which can be explained by increased prior-calcite precipitation and aridity during the event. This time-series, combined with data from our monitoring study, allows us to quantitatively reconstruct changes in calcium cycling at Heshang Cave across the 8.2 kyr event and demonstrates the potential for calcium isotopes to elucidate past changes in cave calcium cycling.

[1] Fairchild et al. (2000) *Chem. Geo* **166**, 255-269. [2] Reynard et al. (2011) *Geochim. Cosmochim. Acta* **75**, 3726-3741. [3] Liu et al. (2013) *Nature Geosci* **7**, 117-120.