

Reconstructing past hydrology from annual cycles in trace elements in a Moroccan Stalagmite

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We present annually resolved trace element and stable isotope data from a laminated Mid-Holocene north Moroccan stalagmite. All reported analyses were performed on the same 200- μm micro-milled calcite samples, yielding an entirely inter-comparable dataset. In addition to $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg, Sr, Ba, U and P, we present the first measurements of Cd in speleothem carbonate. Recent cave-analogue experiments [1] demonstrate that Cd/Ca is highly sensitive to variation in the amount of calcite precipitated from solution, with high Cd/Ca particularly indicative of low degrees of prior calcite precipitation. We employ a multi-proxy approach, using Cd alongside other trace elements and stable isotopes to reconstruct changes in hydrology at this site.

With the exception of $\delta^{18}\text{O}$, highly distinct annual cycles occur in all reported proxies and correspond closely to changes in laminae colour. The observed annual cycle in Cd/Ca implies that % calcite precipitated is a major driver of annual trace element cycles in this sample. The agreement between the trace elements, laminae colour and $\delta^{13}\text{C}$ agrees well with that expected in calcite precipitated in a site where rainfall is highly seasonal. Weaker correlations with $\delta^{18}\text{O}$ reflect the more integrated nature of the information recorded by oxygen isotopes, indicating that some regional signal is being captured.

Despite differences in seasonal cave ventilation these observations show remarkable agreement with annual trace element cycles from a modern speleothem at St Michael's Cave, Gibraltar [2], which lies 27 km northwest of our site. Such a parallel between sites gives confidence that trace element geochemistry can potentially be used for robust regional palaeoclimate reconstruction, and perhaps also for the careful extrapolation of monitoring studies between sites.

[1] Day & Henderson, *Geochimica et Cosmochimica Acta*, in review. [2] Matthey, Lowry, Duffet, Fisher, Hodge, & Frisia (2008), *Earth and Planetary Science Letters* **269**, 80-95.

Ancient recycled nitrogen isotope signatures in Siberian xenoliths

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Siberian xenoliths display compelling evidence for a recycled crustal origin. In order to assess if nitrogen is also recycled in ancient subducted-oceanic crust we have measured N-isotopes ($\delta^{15}\text{N}$) and elemental (N_2/Ar) ratios for a suite of peridotitic and eclogitic xenoliths (n=10) from two petrologically-distinct kimberlite pipes (i.e., Udachnaya and Obnazhennaya). Additionally, all samples have been well-characterized, mineralogically, petrographically, and for major and trace element chemistry.

Crustally-derived xenoliths (Gt, Cpx and Ol) of Siberia are believed to originally be derived from subducted oceanic crust which has since amalgamated to form the Siberian craton. The occurrence of non-mantle-like oxygen isotope signatures in Siberian xenoliths suggests that these lithologies are artifacts of partially-melted subducted ocean crust [1, 2]. Subsequently, this material was transported to Earth's surface via kimberlitic volcanism. The age of Siberian xenoliths have been constrained to be within 2.7 - 3.1 Ga using Re-Os and Sm-Nd isotope dating techniques [3]. $\text{Mg}\#_{\text{Gt}}$ ranges from 86 - 96, suggesting relatively primitive magmas. Major and trace element chemistry indicates that these samples have been subjected to varying degrees of metasomatism. Due to the antiquity of these particular xenoliths, they represent prime targets for N-isotopes, which have been previously suggested to show a secular variation throughout Earth history [4].

N-isotopes ($\delta^{15}\text{N}$) of Siberian xenoliths range from -0.7 to -10.8 ‰ and are consistent with both upper mantle (MORB = -5 ± 2 ‰) and recycled contributions (modern sediments = $+6 \pm 2$ ‰). N_2/Ar values range from 32 to 178, spanning both atmospheric (84) and typical mantle values (84-164). Cpx mineral separates retained the most nitrogen gas. Notably, all Obnazhennaya samples display N-isotope values above the MORB range, indicating a larger contribution from a recycled component vs. Udachnaya samples, which span the MORB range. These results suggest xenoliths of different kimberlite pipes sample isotopically-distinct parts of the mantle, and may preserve varying mantle/crustal contributions throughout Earth history.

[1] MacGregor and Manton, (1986). [2] Taylor and Anand, (2004). [3] Pearson *et al.*, (1995). [4] Marty and Dauphas, (2003).