A record of Northern Hemisphere climate variability during the Penultimate Glacial from high resolution speleothem data

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Numerous paleoclimate records have contributed to our understanding climate change during the Last Glacial. Data for previous glacial cycles are rare however, due to the lack of absolutely dated continuous records. Here we present stable isotope and elemental data of an absolutely dated stalagmite (FS-TR3) from Fort Stanton Cave, New Mexico, that reveal the character and timing of Northern Hemisphere (NH) climate variability during the Penultimate Glacial (MIS 6). These data show links to summer insolation, rapid North Atlantic cold/warm anomalies or lack thereof, and climatic oscillations resembling the 1500-year cycle.

Previous results from the study area showed that δ18O values from stalagmite FS2 mimic the δ18O record of the Greenland Ice Core in both general trends and higher frequency variations such as the Dansgaard–Oeschger (DO) and Heinrich events (HEs) (Asmerom et al., 2010 ref 1) . The new FS-TR3 stalagmite extends our record to the Penultimate Glaciation. Stalagmite FS-TR3, based on high-resolution U-series chronology, grew continuously from 165 to 130 ka. At the orbital scale, the trend is dominated by insolation, upon which are superimposed millennial scale variations. The millennial scale variations are more muted than HE and DO events during the Last Glacial. In contrast to the millennial scale variability, the transition to peak cooling during MIS 6 was abrupt and pronounced, and followed by a very rapid Termination II. Time series analyses of the stable isotope and elemental data show climatic oscillations similar to those exhibited by NH Last Glacial records, such as the 1500-yr cycle. A growth hiatus at 130.3 ka is coincident with the termination of NH Glacial-II from other records. Our record is comparable to that of stalagmite SB11 from Sanbao Cave, China (Wang et al. 2008 ref 2), and this comparison shows that the atmospheric teleconnections between Greenland, the SW USA, and China are likely hemispherical in scale through the Penultimate NH Glacial.

[1] Asmerom (2010) *Nature* **3**, 113-117.
[2] Wang (2008) *Nature* **451**, 1090-1093.

Stable isotope tracing of ZnO nanoparticles in complex systems

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Whilst nanomaterials are employed in an increasing range of commercial and industrial products, analytical difficulties obstruct the scientific understanding of their toxicological properties and environmental fate. ZnO nanomaterials (NMs) are of particular interest as these are used in sunscreens and cosmetics as a UV filter, and reach the biosphere through a variety of routes. Due to the high natural background levels of Zn, the detection of ZnO NMs in ecotoxicologically relevant exposures cannot be attained through concentration data alone. However, highly sensitive detection can be achieved using purpose-made ZnO nanoparticles (NPs) labelled with a stable Zn isotope [1]. This approach also negates handling difficulties and time restrictions associated with radioactive tracing. Even with relatively inexpensive ^{68}Zn as the isotope label, ZnO nanoparticle concentrations as low as 5 ng/g can be precisely quantified against a background of 100 μg/g Zn when measured using MC-ICP-MS.

ZnO NPs (30 nm, TEM) labelled with ^{68}Zn were synthesized by hydrolysis from an acetate precursor [2]. Parallel 10-day exposures of *Corophium volutator* to labelled ^{68}ZnO NPs, bulk ^{68}ZnO and soluble $^{68}ZnCl_2$ were performed in artificial seawater in the presence of sediment [3]. Dialysis experiments were used to determine the rate and extent of dissolution for both bulk and nanoparticulate ^{68}ZnO in the test medium. The subsequent analyses of organisms, sediment and water samples for Zn isotope compositions and concentrations were carried out by MC-ICP-MS following preconcentration of Zn by anion exchange chromatography [4].

For all exposures, including those utilizing dissolved $^{68}ZnCl_2$, the sediments accumulated the largest pool of the ^{68}Zn label. This finding and the low final ^{68}Zn contents of the aqueous media are indicative of significant Zn transfer from the water column to sediments, presumably as a result of Zn sorption [5]. The observations that (i) the ^{68}Zn levels determined for the organisms were approximately scaled in proportion to the dissolved ^{68}Zn concentrations that are expected based on the dialysis experiments and (ii) the organisms featured $^{68}Zn/^{66}Zn$ isotope ratios lower than those measured for the corresponding water samples, suggest that the uptake of ^{68}Zn by the organisms from ^{68}ZnO NPs occurred through the dissolved state.

[1] Croteau *et al*., (2011) *Nanotoxicology*, **5**, 79-90 [2] Dybowska *et al.,* (2011) *Environ. Poll.,* **159**, 266-273 [3] Scarlett *et al*., (2007) *Mar. Environ. Res.,* **63**, 457-470 [4] Arnold *et al*., (2010) *Anal. Bioanal. Chem.,* **398**, 3115-3125 [5] Jain *et al*., (2004) *J. Haz. Mat.*, **B114**, 231-239