

Glacial-interglacial paleotemperatures and paleohydrology in the Jourdan River Valley from clumped isotopes in fresh water snails.

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Oxygen isotope composition of carbonate minerals is the most popular proxy in paleo-climate research and is especially common in the marine environment; however, since implementation of $\delta^{18}\text{O}$ records for reconstruction of environmental temperatures requires an independent estimate of paleo-water composition, it is difficult to interpret this proxy in terrestrial records. Carbonate clumped isotopes thermometry is based on the relationship of ^{13}C - ^{18}O bond abundance in the carbonate lattice (measured as Δ_{47}) with the carbonate formation temperature. Most marine biogenic carbonates are consistent with the laboratory precipitation experiments that are used as calibration for the clumped isotopes thermometer.

We examine Δ_{47} in fresh water snails, focusing on *Melanopsis* snails that were collected in various water-bodies along the Jordan Rift Valley (Israel). The modern samples cover a range of $\sim 10^\circ\text{C}$. As in marine biogenic carbonates, the temperatures derived from clumped isotopes in these modern shells are consistent with the water temperatures. Measured oxygen isotopic compositions of sampled water-bodies broadly agrees with $\delta^{18}\text{O}_{\text{water}}$ values calculated from clumped isotope temperatures and living-shell $\delta^{18}\text{O}$. This suggests that clumped isotopes in *Melanopsis* shells, as in marine organisms, reflect isotopic equilibrium and agree with the same clumped isotopes thermometer calibration.

We further analysed fossil *Melanopsis* snails collected in the Northern Jordan Valley and at sites near the modern-day northern and the southern banks of the Sea of Galilee. Our samples ages range from MIS 3 to Late-Holocene. We find fairly constant temperatures during the glacial period with low temperatures and $\delta^{18}\text{O}_{\text{water}}$. Post-glacial temperature increase to a peak in Mid-Holocene, followed by a decrease to intermediate modern values. River and lake water temperatures are generally warmer than estimated Mediterranean Sea surface temperatures [1]. Mid-Holocene Jordan River and northern Sea of Galilee water are ^{18}O -enriched by $\sim 2\%$ relative to both the LGM and modern values, and southern Sea of Galilee waters are highly enriched.

This enrichment is opposite to the depletion glacial-interglacial trend observed in other regional records such as Dead Sea sediments, Soreq cave speleothems, and Mediterranean Sea foraminifera. It is likely to reflect a change in the hydrological balance, mainly in the contribution of snow-melt to the Jordan River. The difference between the northern and southern Sea of Galilee sites are likely to reflect a change in lake evaporation following the partitioning of the glacial Lake Lisan into 2 basins with the difference observed between Southern Sea of Galilee and Northern Jordan River Valley reflecting the hydrological evolution of the northern basin through the Holocene.

[1] Almogi-Labin et al. (2009) *Quaternary Science Reviews* **28**, 2882-2896.

Silica-stabilized actinide(IV) colloids at near-neutral pH

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Due to their low solubility, tetravalent actinides, An(IV), are usually assumed to be immobile in natural waters. However, it is also well known that insoluble precipitation products can be mobile if they occur as colloids. For An(IV) oxyhydroxides this phenomenon has thoroughly been studied [1]. Here we describe the formation of a new type of An(IV) colloids [2].

Evidence is provided that uranium(IV) and Th(IV) can form silicate-containing colloids in near-neutral solutions containing background chemicals of geogenic nature (carbonate, silicate, sodium ions). These particles remain stable in aqueous suspension over years. A concentration of up to 10^{-3} M of colloid-borne An(IV) was observed which is a concentration significantly higher than the concentrations of truly dissolved or colloiddally suspended waterborne An(IV) species hitherto reported for the near-neutral pH range. The prevailing size of the particles is below 20 nm. The higher the silicate concentration and the pH, the smaller (and obviously the more stable) are the particles that are formed (however, silicate at the concentrations tested does not form particles in the absence of the actinides). Electrostatic repulsion due to a negative zeta potential caused by the silicate stabilizes the nanoparticles. The isoelectric point of the nanoparticles is shifted toward lower pH values by the silicate. The mechanism of colloidal stabilization can be regarded as "sequestration" by silicate, a phenomenon well known from trivalent heavy metal ions such as iron(III) [3] or curium(III) [4], but never reported for tetravalent actinides so far. U-O-Si bonds, which increasingly replace the U-O-U bonds of the amorphous uranium(IV) oxyhydroxide with increasing silicate concentrations, make up the internal structure of the colloids. The next-neighbor coordination of U(IV) in the U(IV)-silica colloids is comparable with that of coffinite, USiO_4 .

The assessment of actinide behavior in the aquatic environment should take the possible existence of An(IV)-silica colloids into consideration. Their occurrence might influence actinide migration in anoxic waters.

[1] Altmaier *et al.* (2004) *Radiochim. Acta* **92**, 537-543. [2] Dreissig *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 352-367. [3] Robinson *et al.* (1992) *J. Am. Water Works Assn.* **84**, 77-82. [4] Panak *et al.* (2005) *Radiochim. Acta* **93**, 133-139.