

Experiments demonstrate that Uranium isotopes fractionate during adsorption to Mn-oxides

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In natural waters, manganese oxides scavenge large amounts of various metals, including U [1]. This process is frequently coupled with isotope fractionation. Recently uranium in marine Mn nodules was determined to be isotopically lighter than seawater by $\sim 0.2\%$ ($\delta^{238}\text{U}$) [2].

To study this phenomenon, we conducted a time series of experiments similar to prior studies of Mo isotope fractionation during adsorption [3]. Synthetic Mn-oxide particles (birnessite) were suspended in slightly acidic media doped with known amounts of U. At various time intervals (0.17, 2, 10, 24 and 48 hours) the suspensions were filtered, halting exchange between dissolved and adsorbed U. Uranium was extracted and purified by ion exchange chromatography. Isotope compositions were determined using double-spike MC-ICP-MS [2].

Measurements of the oxides and filtrate solutions in all experiments yielded the same magnitude and direction of fractionation; U adsorbed to the Mn-oxides is isotopically $0.2 \pm 0.03\%$ ($\delta^{238}\text{U}$) lighter than U in the filtrate. Approach to equilibrium (both concentration and isotopic) appears to occur rapidly, with approximately 75-80% of the uranium budget adsorbed to the Mn-oxides in ≤ 2 hours.

These results confirm the hypothesis of Weyer *et al.* (2008) that adsorption to Mn-oxides causes U isotope fractionation. The close match between our experimental results and natural samples, despite differences between seawater and our solutions, suggests that the isotope fractionation factor is insensitive to pH and ionic strength. Further work is required to fully understand the fractionation mechanism, but the results support the use of U isotopes in paleoredox and other applications.

[1] Koschinsky & Hein (2003) *Marine Geology* **198**, 331-351.

[2] Weyer *et al.* (2008) *GCA* **72**, 345-359. [3] Barling & Anbar (2004) *EPSL* **217**, 315-329.

Speleothem reconstructions of palaeomonsoon dynamics from Flores, Indonesia over the last 24 kyr

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The summer monsoon is a critical component of the global climate system, distributing heat and moisture to higher latitudes. The southern half of the Australasian monsoon dominates the climate of tropical Australia and Indonesia, yet little is known about the magnitude of its response to changing boundary conditions during the late Quaternary.

We present high-resolution, U-series dated $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records from multiple stalagmites from Liang Luar cave in Flores, southern Indonesia (8°S , 120°E) spanning the last 24 kyr. Speleothem $\delta^{18}\text{O}$ in southern Indonesia reflects changes in rainfall amount brought about by large-scale shifts in the position of the Intertropical Convergence Zone (ITCZ). Liang Luar is situated such that the seasonal isotopic contrast between winter tradewind (orographic) rainfall (ave. -2.8%) and summer ITCZ rainfall (ave. -8.3%) is $\sim 5.5\%$.

The speleothem $\delta^{18}\text{O}$ record shows that the post-glacial onset of the Australian monsoon lagged the Asian monsoon by several thousand years. The driest period in Flores occurred ~ 15 -13 kyr ago, well after the LGM and Heinrich 1, which are dry elsewhere. Also, Holocene rainfall amounts do not exceed modern values, in contrast with the strong Holocene monsoon in Asia. Speleothem $\delta^{18}\text{O}$ in Flores reflects the opposing "push and pull" of the Australian monsoon across the hemispheres on orbital timescales.

The $\delta^{13}\text{C}$ record reaches modern values ~ 13 kyr ago, suggesting that tropical vegetation cover and strong soil CO_2 production was established thousands of years before the onset of the Australian summer monsoon. The landscape response follows the deglacial rise and early Holocene maximum in Warm Pool sea surface temperatures, rather than rainfall amount alone. Results suggest that the post-glacial landscape response may be linked to air temperature and humidity, or to the more even distribution of rainfall associated with a weaker El Niño-Southern Oscillation.