Clumps and carbonatites: A preliminary investigation into post-deposition alteration of Δ_{47}

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Clumped isotope paleothermometry, as quantified by Δ_{47}, the measured deviation in acid-liberated mass-47 CO_2 (predominantly $^{13}C^{18}O^{16}O$) from that expected if isotopes were randomly distributed, shows much promise as a technique for reconstructing temperature in the geologic record [1, 2, 3]. It is particularly advantageous for determining the temperature of terrestrial carbonates [4] and carbonates precipitated from waters with unconstrained isotopic histories [3]. However, little work has been done to assess the integrity of the clumped isotope proxy over million year timescales.

As a preliminary investigation into the robustness of Δ_{47}, we have analyzed over 20 carbonatite samples from 11 different sites with ages ranging from recent to 140 Ma, and one carbonatite from the early Paleozoic. Using the temperature calibration of [1], carbonatites with a primary carbonatite $\delta^{18}O$ signature retain a temperature on the order of 150 to 200°C. Repeat analyses of an Italian marble standard also fall into this range. If re-crystallization of a carbonatite has occurred (as indicated by a heavier $\delta^{18}O$), we find Δ_{47} is also re-set, and records much lower temperatures. Replicate analyses of carbonatites yield a median Δ_{47} standard error of 0.013‰ ($n = 3$ to 8, mean $n = 4.5$), while recent analyses of the marble standard give a standard error of less than 0.005‰ ($n = 10$).

The temperature calibration given in [1] was conducted over the range of 1 to 50°C and it may not be valid to extrapolate this relationship to high temperatures. We will conduct high temperature precipitation experiments to refine constraints on the clumped isotope thermometer above 50°C. This will enable us to assess if Δ_{47} is recording the temperature at which isotopic exchange ceases and the clumped isotope signature is locked-in, analogous to noble gas blocking temperatures, or if the carbonatite signatures represent temperatures closer to that of formation.

[1] Ghosh *et al*. (2006) *Geochimica et Cosmochimica Acta* **70**, 1439-1456. [2] Eiler (2007) *Earth and Planetary Science Letters* **262**, 309-237. [3] Came *et al*. (2007) *Nature* **449**, 198-201. [4] Ghosh *et al*. (2006) *Science* **311**, 511-515.

Nitrogen deposition in the world's ocean: An assessment of uncertainties in models and measurements

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Recent model studies as well as observations suggest an important flux of reactive nitrogen (NHx and NOy) from the atmosphere into the world's oceans. It has been recently suggested (Duce *et al.* 2008) that these N inputs play an important role in the uptake of atmospheric CO_2 on the hand, and on the other hand may lead to increased N_2O emissions.

One of the overarching questions is how much, where and when reactive N is entering the coastal and open oceans.

Our two tools to address these questions, models and measurements, both suffer from specific problems.

Models have often incomplete descriptions of atmospheric formation, transport and removal of reactive nitrogen in the atmosphere, and are poorly evaluated over oceanic regions. The amount of high quality coastal and open ocean measurements is very limited, and it is difficult to estimate their representativeness for larger regions.

We combine available datasets from models and measurements, and try to make an updated best estimate of N inputs into oceans around the world and discuss the uncertainties and potential impact related to these estimates.