A dynamic magnesium cycle during the Cenozoic? Insights from the magnesium isotopic composition of pelagic carbonates

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Evidence from fluid inclusions in evaporites and systematic changes in the mineralogy of $CaCO_3$ ('aragonite seas' vs. 'calcite seas') suggest that the chemical composition of seawater has changed during the Cenozoic. In particular, magnesium in seawater is thought to have increased by as much as 20 mM since the early Cenozoic [1]. However, the mechanisms responsible for the observed chagnes in magnesium in seawater are not well understood. Proposed mechanisms include changes in the rate of high-temperature hydrothermal reactions at mid-ocean ridges as well as changes in the rate of dolomite precipitation [2-3].

Recent work on magnesium isotopes in deep-sea pore fluids shows that magnesium isotopes are fractionated very differently during the preciptiation of Mg-clays and dolomite [4]. A consequence of this is that the magnesium isotopic composition of seawater has likely changed with time. To reconstruct the magensium isotopic composition of seawater, we measured the magnesium isotopic composition of pelagic carbonates from two ODP sites (807 and 1265). Measured δ^{26}Mg values range from -4 to -5.5‰ and vary systematically with time. Similar changes in δ^{26}Mg are observed at both sites, though there appears to be a small offset (0.2-0.3‰) between sites. Although we cannot exclude changes magnesium isotope fractionation as the source of the observed variability, we tentatively interpret our data as reflecting changes in the δ^{26}Mg of seawater. Our results suggest a dynamic global magnesium cycle in the Cenozoic driven either by changes in the isotopic composition of the weathering flux [5] or the rate of dolomite precipitation.

[1] Horita, J. *et al.* (2001) *GCA* **66,** 3733-3756. [2] Holland & Zimmermann (2000) *Int. Geo. Rev.* **42**, 481-490. [3] Spencer & Hardie (1990) *Spec. Pub. Geochem. Soc.* **2,** 409-419. [4] Higgins & Schrag (2008) *GCA* **72**, A375. [5] Tipper *et al.* (2006) *EPSL* **250**, 241-253.

Revisiting Mediterranean sapropel formation: New insights from chlorin nitrogen isotope measurements

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Sedimentary nitrogen isotopic ratios are a useful tool for reconstructing past water column nutrient dynamics and budgets. However, isotopic values of bulk sediments may be prone to diagenetic alteration, especially in oxic environments. One way to circumvent potential isotopic alterations is to measure the isotopic composition of intact fossil chlorophyll molecules, which represent a primary signal from surface waters. The sedimentary record of the Mediterranean Sea contains several sapropel horizons during the late Pleistocene, which are characterized by high total organic carbon contents. Previous work utilizing a compound-specific nitrogen isotope approach suggested that in the Eastern Mediterranean, bulk nitrogen isotope measurements are enriched due to diagenetic processes in non-sapropel horizons [1]. However, past analytical limitations prevented the direct comparison of chlorins from non-sapropel and sapropel horizons, due to the low concentrations of nitrogen in non-sapropel samples, and this interpretation was based on an assumed isotopic composition for non-sapropel chlorins. The recent development of a new method for chlorin nitrogen isotopic analysis [2] allows for measurements of samples containing ~30 nmol N, enabling the measurement of chlorins from non-sapropel horizons. We have obtained chlorin fractions from sapropels S2-S5, and from the surrounding non-sapropel layers, from two sites in the Eastern Mediterranean. We will report on the nitrogen isotopic values obtained from these fractions, and compare the isotopic composition of sapropel and non-sapropel horizons to determine whether the difference in their bulk isotopic composition reflects different sources of nitrogen to surface waters, or is an artifact of sedimentary diagenesis.

[1] Sachs and Repeta (1999) Science **286,** 2485-2488.
[2] Higgins *et al.* (2009) *Anal. Chem.* **81,** 184-192.