Light Mo isotopic signatures in Chesapeake Bay sediments

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Parts of the Chesapeake Bay water column experience seasonal oxygen depletion, possibly due to eutrophication; historical records indicate this is largely a 20th century phenomenon. Anoxia that penetrates into the sediments affects the authigenic deposition and down core distribution of molybdenum and possibly Mo isotopes. Insufficient understanding of fractionation processes as they relate to the conversion of the molybdate ion to thiomolybdate, and the search for a sedimentary environment that captures the intermediate reaction products and preserves their isotopic compositions prompted this research.

We present an exploratory Mo-isotope data set of recent shallow core material from the upper deep channel of Chesapeake Bay. Complementary trace metal (Re, Mn) and major element (C, N, S, Fe) concentrations have also been obtained for these sediments in order to constrain any influence these ubiquitous sedimentary constituents may have on the Mo isotopic composition in the Bay.

Molybdenum isotopes were analyzed using a ^{97}Mo-^{100}Mo double spike (via MC-ICP-MS and TIMS). Compared to both average 'lithogenic' (assumed to be δ^{98}Mo ~0 per mil) and seawater (+2.3 per mil) isotopic compositions, considerable variation in amount and direction of fractionation down-core is observed. The total range of the measured values is ~0.55 per mil (with maximum error of ~±0.1 per mil), with all δ^{98}Mo values <0. The isotopic compositions do not appear to be correlated with excess Mo (relative to crustal abundance) in the sediment column. δ^{98}Mo values are positively correlated with sulfur concentration, but negatively correlated with Mn and Re concentrations.

There are several possible explanations for excursions into the light Mo isotopic realm: fractionation by diffusion into the sediments, during capture by Mn oxyhydroxides; or through deposition from isotopically fractionated reaction intermediates, such as thiomolybdates. All samples are fractionated from the inferred δ^{98}Mo of the overlying water by least 0.7 per mil and as much as 1.2 per mil, suggesting that there must be processes occurring at the sediment-water interface, or during sediment diagenesis, that are driving the measured materials away from a heavy isotopic composition.

Ice sheet regulation of weathering fluxes during the Eocene Oligocene transition

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A high resolution neodymium (Nd) isotope record, generated from fossil fish teeth recovered from lower Oligocene to upper Eocene sediments from Ocean Drilling Program (ODP) Site 738 (Kerguelan Plateau, (62.7°S, 82.8°E, 2253 m), reveals an Nd isotope excursion toward continental (i.e., nonradiogenic) compositions. Two shifts to nonradiogenic compositions (arrows in figure 1) are synchronous with previously published oxygen isotope steps [1] during the Eocene Oligocene transition (EOT). The source of extremely nonradiogenic Nd is probably glacial weathering of Precambrian basement rocks in the Prydz Bay region of Antarctica. Rare earth element and yttrium (REE+Y) anomalies in the fish teeth do not support the alternate hypothesis that nonradiogenic compositions reflect post-depositional uptake of REE+Y from ice rafted debris. Instead the excursion reflects a transient increase in the weathering flux from Antarctica as a result of glacial weathering. Silicate weathering of exhumed Antarctic bedrock and marine productivity stimulated by increased nutrient delivery may have acted to rapidly drawdown pCO_2 during the EOT. These results provide a detailed history of the weathering flux during the EOT and support the interpretation of inflections in the marine osmium and strontium records [2, 3].

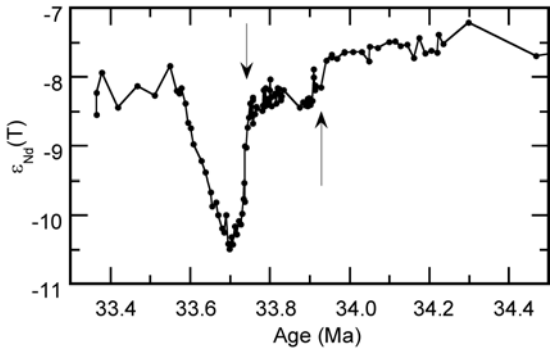

Figure 1: Nd isotope results from 115 fossil fish teeth samples from 18-24 meters below sea floor in ODP Site 738.

[1] Coxall *et al.* (2005) *Nature* **433**, 53-57. [2] Dalai *et al.* (2006) *EPSL* **241**, 477-492. [3] Zachos *et al.* (1999) *Chem. Geol.* **161**, 165-180.