Causes and consequences of isotopically heavy dissolved molybdenum in rivers

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The molybdenum (Mo) isotopic composition of the dissolved load of rivers is isotopically heavy relative to likely average continental crust. Two key aspects of this finding are not understood. The first is the origin of this isotopic fractionation. The second is the degree to which the riverine dissolved load reflects the delivery of Mo isotopes from the continents to the oceans. Both of these issues are crucial to the intrepretation of oceanic Mo isotope records, and to their use as redox indicators. Here we address both these issues, the first using new data from soil profiles that constrain processes by which Mo and its isotopes are released during weathering, and the second through data and models that have implications for the release of Mo from riverine particulate material in estuaries and shallow seas.

We have studied Mo isotope systematics in a range of soil chronosequences, and the data suggest that the behaviour of Mo and its isotopes in the weathering environment is dependent on an array of controls. In one key chronosequence from Scotland, however, there is a previously un-heralded role implied for biological processes. In these soils, there is pronounced retention of Mo in organic material at the top of the profile, that becomes more pronounced as the soil ages. In these soils Mo isotope retention/release in/from soils is controlled by both Fe-Mn oxides and organic material. These data are consistent with recent findings that Mo is limiting in many terrestrial ecosystems and that soil bacteria take up the light isotope.

A key issue for oceanic Mo isotope records is the isotopic composition of the input from the continents. The heavy dissolved load of rivers presents some severe problems for models of the Mo isotope mass balance in the modern oceans. Recent data from continental margin settings, however, particularly those that are marginally sub-oxic, suggests that diagenetic reactions could release the light particulate Mo washed into the oceans as the counterpart of the heavy dissolved load. The implications of this suggestion for the oceanic Mo isotope budget will be explored.

GEOTRACES intercalibration results for Nd isotopes and REE on seawater and particulate samples

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One of the key activities during the initial phase of the international GEOTRACES program was an extensive international intercalibration effort for all trace elements and isotopes (TEIs) targeted by the program, to ensure that results from different cruises and from different labs can be compared in a meaningful way. Two intercalibration cruises sailed in 2008 and 2009 to enable systematic testing of sampling equipment and methods, and to collect large amounts of homogenous seawater samples to check whether results for dissolved and particulate TEIs obtained by different laboratories are accurate and reproducible.

Here we present the results from the intercalibration efforts on neodymium isotopes and rare earth elements in seawater and marine particulates. For seawater, we obtained Nd isotope results from 11 different laboratories on duplicate seawater samples from two different water depths (2000m and 15m) at the Bermuda Atlantic time series study site (BATS). Average ε_{Nd} values are -13.1 \pm 0.6 and -9.1 \pm 0.6. This is a very satisfactory result for the community, as individual labs typically achieve external reprodibilities of 143Nd/144Nd measurements between 0.2 and 0.4 ε units (2 σ standard deviation). In an attempt to test whether the spread in reported isotope ratios is due to differenct protocols used for preconcentration and ion chromatography, or rather due to different methods applied on the mass spectrometry end, we distributed an isotopic standard of unknown composition to all labs. Averaged results from all laboratories reveal a very similar external reproducibility of 60 ppm (2σ SD) on ¹⁴³Nd/¹⁴⁴Nd, indicating that mass spectrometry is the main variable in achieving accurate and precise Nd isotope ratios.

We will furthermore present Nd isotope results on systematic shipboard filtration tests, a comparison of different sampling systems, as well as intercalibration results for Nd isotopes in marine particulates and REE patterns in seawater and particulates. While the community is definitely ready for Nd isotope measurements in seawater, the analyses of marine particulates seems to require a common methodology to provide comparable results.