Defining an uniquely euxinic molybdenum signal

CLINT SCOTT AND TIM LYONS[1]

[1]University of California, Riverside

The redox chemistry of molybdenum and the implications of its enrichment in black shales is generally understood and often employed in the geochemical analysis of ancient marine environments. The conservative nature of the common oxidized species (MoO_4^{2-}) in sea water and its conversion to highly particle-reactive thiomolybdate ions (MoS_4^{2-}) where Σ H_2S exceeds ~ 10 μM suggests that its enrichment in black shales is indicative of the presence of reduced sulfur. Enrichments in black shales typically fall within a wide range of 5 to 400 ppm relative to an average crustal value of 2 ppm. This wide range of Mo concentrations has thus far prohibited the use of Mo enrichments as an unambiguous indicator of an anoxic/sulfidic (euxinic) water column.

On closer inspection we can demonstrate a distinct bimodality in the enrichment of Mo in modern sulfidic sediments. Mo concentrations in sediments where the sulfide interface remains below the seafloor do not exceed 16 ppm whereas those in euxinic environments are represented by a range of values of 20 to 200 ppm. This relationship suggests the presence of a barrier to the diffusion of Mo that disappears where dissolved sulfide reaches the sediment/water interface. We propose that this inhibition is associated with the presence of Mn-oxides in the sediment surface layer. The affinity of MoO_4^{2-} for Mn-oxides results in a subsurface maximum in dissolved Mo when these Mn-oxides are buried and dissolved, thus masking the Mo gradient between sulfidic sediments below and the water column above and prohibiting direct diffusion of Mo from sewater into the sulfidic pore waters . As the sulfide interface reaches the sea floor, and euxinia sets in, this Mn cap disappeares and the enrichment of Mo is then controlled by other factors such as Mo limitation in the water column, seasonal euxinia, sedimentation rate or the nature of organic matter present.

This barrier to the diffusion of Mo into sulfidic/noneuxinic sediments and the observed distribution of Mo concentrations in such environments should allow us to define an uniquely euxinic Mo signal of ~20 ppm or greater. This would allow for the characterization of euxinia where DOP is inconclusive or of Mo limitation where DOP is indicative of euxinia but Mo concentrations are subdued. Additionally, Mo concentrations between 6 and 16 ppm are indicative of sulfidic sediments below an oxic to suboxic water column.

Unexpected denitrification in oxic shelf sands: A consequence of redox dynamics?

RICHARD JAHNKE, ALEXANDRA RAO, MARY RICHARDS AND DEBORAH JAHNKE

Skidaway Institute of Oceanography, Savannah GA 31411 (rick@skio.peachnet.edu)

The South Atlantic Bight (SAB) continental shelf seafloor is sandy with elevated permeabilities. Bottom currents, primarily driven by tides, efficiently drive bottom waters into and out of the upper 5-8 cm of the sediments. Because tidal flows and directions alternate with a period of approximately 6 hours, the direction of pore water flow and redox conditions vary on the same time scales. Sun light also reaches the sediment surface supporting significant rates of photosynthesis. Diel variations in photosynthetic oxygen production in the upper 1-2 mm of the sediments add further complexity to the benthic redox dynamics.

To investigate sedimentary remineralization reactions in this dynamic environment, laboratory column reactors were employed to mimic advective pore water transport and diagenesis. Multiple column lengths were employed to yield nominal pore water residence times of 3, 6 and 12 hours. High respiration rates are observed in all columns, consistent with previous estimates based on whole core incubations. Unexpectedly, however, the remineralized nitrogen appears primarily as dinitrogen gas (N_2) as measured directly via inlet membrane mass spectrometry. These direct measurements of N_2 are consistent with measurements of nitrite, nitrate, ammonium, nitrous oxide and dissolved organic nitrogen that reveal little change in these other constituents. Estimates based on the measured oxygen consumption and the Redfield oxygen:nitrogen ratio of planktonic organic matter suggest that most of the regenerated nitrogen is denitrified.

This efficient generation of N_2 is especially unexpected in the 3 and 6 hour residence time columns because the bulk pore waters remain oxic throughout the column reactors. Follow-up experiments in which the influents of the column reactors were amended with ^{15}N labelled nitrate revealed a significant delay in the incorporation of the tracer into the N_2. These results suggest that the pool of nitrogen that is undergoing denitrification is significantly isolated from the bulk pore waters, at least for periods of days. We speculate that the dynamics of redox conditions in this permeable system have led to the development of this unexpected denitrification pathway.