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Biological fractionation of Mo isotopes during N_2 fixation by *Trichodesmium sp.* IMS 101

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There is increasing interest in heavy stable isotopes as proxies in oceanography. Mo is an obvious choice given its isotopic range, the potential for redox shifts in the oceanic environment and its importance in biological processes. Enzymes for nitrate and nitrite uptake, nitrogen fixation, and dentrification all contain Mo cofactors. If these different processes result in different Mo isotopic signatures, Mo could turn out to be a valuable proxy for paleo-nitrogen utilization, complementary to nitrogen isotope studies. Initial studies of Mo isotopic systematics in the oceans concentrated on abiotic processes. Preliminary data on Mo isotope variations related to biological processing are presented here. Mo isotope fractionation during N_2-fixation by the filamentous non-heterocystous cyanobacteria *Trichodesmium sp.* IMS 101 has been investigated. Cells were grown in batch cultures on YBC II media. Uptake of Mo and Mo isotope ratios were measured using MC-ICP-MS. The external standard reproducibility is 0.1 per mil for the $^{98}Mo/^{95}Mo$ ratio (2 σ). Average Mo uptake by *Trichodesmium sp.* was approximately 0.5 ng Mo l^{-1} h^{-1} , within expectations based on known Mo uptake in cyanobacteria. First results indicate that the average net effect of Mo isotopic fractionation during nitrogen fixation by *Trichodesmium* results in lighter isotopic composition, but fractionation (-0.3 delta $^{98/95}Mo$) is only 10% relative to inorganic oxic sedimentation in the oceans. There is a slight gradient from -0.5 delta $^{98/95}Mo$ in the initial states (chlorophyll = 10 ug l^{-1}) to -0.1 δ $^{98/95}Mo$ in the late stages (chlorophyll = 80 ug l^{-1}) that might indicate a more complex process than just one constant biologically mediated isotope fractionation. Further studies will involve cultures grown under low Mo conditions, as well as investigations on the isotope effects of denitirification and nitrate uptake.

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Molybdenum, uranium, and vanadium diagenesis in marine sedimentary systems: Relation to organic carbon flux and isotopic constraints on Mo diagenesis

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We present sediment pore water and solid-phase data from a range of reducing continental margin environments to assess the utility of Mo, U, and V as a proxies for past oceanic conditions. Each of these elements display varying relationships with sedimentary oxygen penetration depth, which is a combination of bottom water oxygen penetration and the organic carbon flux. For example, in sites along the California continental margin U exhibits a close correlation with organic carbon flux that is independent of bottom water oxygen concentration above ~3 μM. In addition, to the elemental concentration data, we present sediment and pore water data on Mo isotope composition. These data further allow us to refine our interpretation of sedimentary diagenetic processes. More specifically, consistent with previous hypotheses, our data suggest that Mo uptake into reducing sediments (i.e., those where Mn reduction has occurred) may be a two-stage process, where initial removal may be via an organic Mo complex followed by a second stage removal process as sediments become increasingly reducing. It is apparent that the initial stage of uptake is associated with isotope fractionation causing the build-up of an isotopically heavy pore water Mo pool relative to seawater. Initial solid-phase results support this contention in that that the solid-phase authigenic pool is isotopically light relative to the pore waters, but continues to be enriched in the heavier isotope as diagenesis proceeds.