6.5.34

Temporal trends in Mo enrichment in Precambrian black shales as an indicator of Earth's oxidative history

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Recent studies of Phanerozoic black shales and modern sediments have demonstrated the utility of Mo enrichment as a paleoredox indicator. While research continues to clarify the specific controls on enhanced Mo burial, the environmental parameters are generally known. The primary requirement for Mo enrichment is the presence of hydrogen sulfide resulting in the formation of particle-reactive thiomolybdate ions. This requirement links Mo enrichment to the presence of reactive organic matter, sulfate, and bacterial sulfate reduction in the absence of oxygen. Any historical or spatial shifts in the balance among these parameters will result in concomitant shifts in Mo distributions in the ocean.

While application of Mo as a paleoredox indicator is well established for Phanerozoic systems, its use in reconstructions of Precambrian paleoenvironments has been limited. This is surprising in light of recent studies wherein C and S isotopes track the evolving oxidation state of surface environments during the Proterozoic. Because this isotopic variability records organic matter burial and evolving marine sulfate concentrations, it is likely that patterns of Mo enrichment during this period would mirror the C-S trends. Our model calls for Archean marine sulfate limitation and minimal riverine contributions of Mo. Across the Great Oxidation Event, sedimentary Mo abundances increased with increasing fluxes of sulfate and Mo as well as increased organic matter burial associated with elevated nutrient supply. This initial period of Mo accumulation in marine sediments was followed by an extended period of depressed Mo enrichment as sulfidic conditions spread throughout the deep ocean, and Mo sequestration occurred over a broad portion of the global ocean. During this period, the magnitude of sedimentary enrichment was ultimately controlled by the mass balance between supply to the ocean and the regional extent of environments favoring Mo burial. Later oxygenation of the deep ocean reversed the expansion of these environments, giving rise to the more-local occurrences of the highly Mo-enriched black shales that typify euxinic settings in the Phanerozoic. Our preliminary data compilation for the Precambrian is consistent with this model but is ultimately weakened by the scarcity of suitable data.

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From dissolved organic carbon to marine snow in the prokaryote dominated Precambrian oceans

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It has been suggested that production of fecal pellets from eukaryote grazers was not of importance until the end of the Neoproterozoic. Today, discrete fecal pellets constitute 10-30% of organic matter collected in sediment traps, where as the rest is marine snow, of which up to 37% may be fecal pellets. Thus, fecal pellets are an important component of the vertical transport of carbon in the present ocean. If this is so, how was organic carbon cycled and sedimented to the ocean floor in the prokaryote dominated Precambrian ocean, before the evolution of grazing eukaryote and the production of fecal pellets?

At present we have limited qualitative and quantitative knowledge on the formation and degradation properties of prokaryote-formed aggregates, as well as the their sinking properties. This, lack of knowledge, prevents us from developing quantitative models of the ancient carbon cycle and thereby understanding the biogeochemical evolution on the early Earth.

In the Archean oceans where the food-web most likely was characterized by only lateral competition without grazers, carbon export from the euphotic zone might have been driven by DOC advection and/or aggregation of prokaryote cell material. Individual bacteria are nearly neutrally buoyant, however sticky transparent exopolymers from bacteria and cell lysis could aggregate the prokaryote cells and particles into larger aggregates, possible marine snow, that would eventually sink. The formation and sinking properties would have depended on the concentration of bacteria, dissolved organic carbon (DOC) and inorganic particles (dust and newly formed oxides formed at the chemocline).

Here we analyze the sensitivity of conditions for formation of aggregates and marine snow in the a prokaryote dominated world using aggregation kernels, and simple growth models for cyanobacteria (nutrient and light limited). Our analysis provides estimates of the concentration of DOC and quantify of the organic particle size spectra, which will enable us to approach a quantification of the sizes of the different carbon pools in the ocean and vertical chemical structure of a prokaryote dominated world.