

## **A decade of progress in studies of trace metals in the early oceans**

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About a decade ago we were asked to consider the possibility that minor elements in the oceans, rather than N and P, might have been the ultimate arbiters in the spatiotemporal patterns of life in the Precambrian oceans. Models centered initially on molybdenum (Mo) and its role in N cycling have branched subsequently to include diverse metals that are also essential enzymatic cofactors across wide-ranging biological pathways. At first, we estimated metal abundances based on thermodynamic predictions in light of hypothesized prevailing redox conditions in the global ocean. Quickly those approaches morphed into more direct measures of trace metal abundances in the oceans using enrichment patterns in black shales and iron formations—patterns that could be scaled at least semi-quantitatively through observations in the modern oceans and in the lab to metal concentrations in ancient seawater. Metals such as Mo in black shales have utility in identifying local paleoredox conditions. If we can constrain those conditions independently, as through Fe speciation, we can also use metal enrichment to quantify local and even global seawater inventories. From those inventories, we can infer the spatial extent of anoxic/euxinic metal-scavenging settings in the oceans as well as low seawater concentrations that may have restrained biological activity. At the same time, first-order shifts in inferred metal abundances in the oceans linked to oxidative weathering on the continents can point to fundamental trends in atmospheric oxygenation or to transient events as in the case of possible ‘whiffs’ of oxygen. And refined perspectives on metal behavior allow us to distinguish between oxygen limited to the surface oceans and/or microbial mats versus appreciable build up in the atmosphere.

This talk will explore the history of studies of metal distributions in the early oceans while also emphasizing the latest frontiers. Ironically, some of the most exciting recent work is focused on extending the lessons learned from the Precambrian to studies of oxygen deficiencies in the Phanerozoic—most notably oceanic anoxic events. Similarly, spikes in metal enrichment in euxinic shales spanning from the late Proterozoic to the early Paleozoic are suggesting transient oxygenation events in the oceans that may have driven innovation among metazoans. Indeed, the best studies are using subtle differences in trace metal redox sensitivities to nuance the redox landscape across time and space.