Picking apart paleoredox proxies: What regulates them?

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Certain trace elements that are oxyanions (broadly defined) with long seawater mean residence times (e.g. HVO_4^{2-}, CrO_4^{2-} AsO_4^{3-}, MoO_4^{2-}, $Sb(OH)_6^-$, WO_4^{2-}, ReO_4^{2-}, and $UO_2(CO_3)_2^{2-}$) are modestly to strongly enriched relative to Earth's crust in sediments below O_2-depleted waters. Their enrichment in sedimentary rocks is cited to support qualitative conclusions about redox conditions in ancient sedimentary basins. More nuanced, possibly quantitative conclusions require better knowledge of events that regulate conversion of these particle-inert oxyanions to particle-reactive species. Each of these elements exists in multiple oxidation states in nature, inviting the assumption that pE regulates conversions. But pE is indefinable in natural waters, so this is at best a superficial explanation. In some cases, abiotic or biotically mediated electron transfer, leading to insoluble products, is indeed a regulating mechanism (U the most studied example). In other cases (e.g. Re), evidence for an electron transfer mechanism is lacking. In sulfidic solutions, most of these oxyanions undergo O ↔ S exchange. If the particle reactivity of the thioanions exceeds that of the oxyanions, then O ↔ S exchange could be a deposition-regulating mechanism. Often exchanges are labile, probably abiotically and thermodynamically controlled, and thus invariant over geologic time. Important gaps remain in knowledge of what regulates deposition of these elements--for example, polysulfides' role. Recent evidence demonstrates polysulfides' importance, at least for Mo and As. Another gap concerns organic matter's role. Correlations between the above elements and TOC are well known in sediments beneath O_2-depleted waters. Correlations might be incidental or might point to specific biotic or abiotic organic reactions that participate in trace element deposition mechanisms. Good evidence exists for organic hosting of V and Re in TOC-rich sediments, but this may arise after deposition, during early diagenesis.

Rare Earth Element distributions as tracers of micronutrient input and Nd cycling in the South Atlantic

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Concentrations of the REEs in seawater reflect their inputs and their cycling in the water column. Because the behaviour of the REE have some similarities to that of micronutrient elements (such as Fe, Zn, Cu, Cd) but are not directly biologically utilised, their distribution has potential to constrain the cycling of micronutrients. The cycling of Nd is also of particular interest because Nd isotopes are widely used as tracers of past ocean circulation. In this study, we have measured REE concentrations on filtered samples collected during the UK-GEOTRACES GA10 cruises (D357, JC068) across the South Atlantic at 40ºS. CTD profiles and a full range of other chemical parameters provide a comprehensive context for these new REE measurements. REE samples were obtained for the full- water column and concentrations determined by isotope-dilution MC-ICP-MS on 250 ml samples. This samples all the major deep-water masses of the Atlantic, and a clear water-mass dependence is observed in the concentrations of heavy REEs. The light REEs show significantly less water-mass dependence, however, suggesting the importance of downward particulate transport for their cycling, with implications for the interpretation of Nd isotopes. Ce concentrations demonstrate the lack of significant input in intermediate waters, reflecting O_2 levels that are insufficiently depleted to drive Mn cycling in the sediment, but are notably high in surface waters due to additional inputs and active release from particles.

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