

Phase-specific geochemistry of trace metals: Development of a novel biosignature

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Substantial effort is being made to better understand metal cycling in modern settings with varying O₂ and H₂S availability, with the aim of interpreting geochemical signatures in sediments from the geological record. Here we explore a new approach, based on phase-specific analyses rather than bulk sediment analyses, to understanding the location of authigenic metal enrichments in modern sediments, and their transition metal isotope signatures. We subsequently apply the method to organic-rich sediments from the geological record, to investigate feedbacks between environmental conditions and the geochemical behaviour of trace metals.

An acid digestion procedure followed by a high pressure ashing step allows the separation of bulk sediment metal inventories into an HF-extractable phase and a second phase, which we identify as “organic material + pyrite”. We present data from modern sediments of the Peru Margin for Fe, Zn, Mo, Cu, and their isotopes. Both sediment fractions have isotopic signatures that, in the most reducing settings, with lowest bottom water O₂ and highest TOC (12-16 wt%), are closest to seawater. In the case of Cu and Zn this isotopic signature is close to that of deep seawater, whereas δ⁹⁸Mo is at the typical value for such settings of +1.6‰. In contrast, the isotopic composition of the two fractions are much more variable at the most oxic site (bottom water O₂ at about 80 μM and TOC contents <2 wt%). At this site, where pyrite is absent, the organic fraction always contains lighter metal isotopes than both the HF-extractable fraction and seawater. Whether this represents an artefact of the acid digestion or a genuine biogenic signature is currently being tested. Nonetheless, these data suggest fundamental differences in the processes of authigenic enrichment and fixation of these metals in sediments in different environmental settings.

Metalloproteome analyses suggest that trace metals, such as Cu, Fe, Mo, Ni, Zn, were selectively utilised by different organisms and metabolisms at different times throughout the evolution of the biosphere. Thus the geochemical and isotopic study of separate phases within organic rich sediments has great potential as a tool to probe the co-evolution of the Earth’s dynamic geosphere and biosphere through time.