Inorganic hints of Archean oxygenation in the ~2.7 Ga Roy Hill Shale

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Recent challenges to the Archean biomarker record greatly elevate the significance of continuing to develop inorganic tools for probing the ancient marine biosphere. Previous Archean sterane records (now discredited) were unique in their specificity for identifying the accumulation of biogenic O_2 in surface waters. In constrast, classic inorganic proxies for quantifying environmental O_2 typically reflect the abundance of atmospheric O_2 and/or oxidative weathering on the continents and, to date, have yielded limited but tantilizing glimpses into the history of dissolved, bioavailable O_2. Inorganic proxies, however, unlike biomarkers, have the distinct advantage of being relatively insensitive to the thermal history of their host rocks, which makes them ideal for exploring the redox structure of the Archean ocean.

We have used Fe speciation and trace metal records to reconstruct both local and global redox during deposition of the ~2.7 Ga Roy Hill Shale in the AIDP2 (onshore) and AIDP3 (offshore) cores. Our data suggest a redox-stratified system with juxtaposed ferruginous (iron-rich) and euxinic (sulfide-containing) conditions, and do not preclude oxic environments in the shallow ocean.

Although we have examined anoxic shales, our trace metal records imply ongoing oxidative processes. Enrichments of Mo and other redox-sensitive metals in both cores is consistent with at least transient oxidative weathering on the continents. Futhermore, systematic metal covariation—combined with evidence for enhanced delivery of reactive Fe—suggest the mutual delivery of trace metals to the sediments on the surface of Fe (and likely Mn) oxyhydroxides during ferruginous deposition in AIDP2. Conversely, the lack of metal covariation in AIDP3 among metals with a particular affinity for Mn vs. Fe oxides is inconsistent with the operation of an Mn oxide shuttle. On the modern Earth, Mn oxidation does not occur in the absence of O_2; therefore, the possible spatiotemporal variability in Mn oxidiation documented between the two cores may indicate geographically restricted or temporally limited O_2 accumulation in surface O_2 oases within an anoxic ocean.