Re-visiting the redox-sensitive trace metal record of the Neoproterozoic Oxygenation Event

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It is widely believed that Earth's oxygenation proceeded in two steps, with the second occurring in the late Neoproterozoic (the 'Neoproterozoic Oxygenation Event'). Yet, the direct evidence for this latter event is not necessarily clear-cut. One of the strongest lines of evidence comes from the record of redox-sensitive trace metals (RSMs) in anoxic/euxinic shales. RSMs show marked increases in abundance in the Ediacaran and Phanerozoic compared to the remainder of the Proterozoic, and this is interpreted to represent a decrease in the proportion of seafloor area covered by reducing sinks. Here, we re-visit the record of RSMs using a large dataset of geochemical data and associated geological context data assembled by the Sedimentary Geochemistry and Paleoenvironments Project.

Analyses accounting for spatial-temporal sampling density re-capitulate the rise in Mo (in euxinic shale) and U (in anoxic shale) through the Ediacaran-Cambrian seen in previous publications. However, the new analyses show either constant levels (Mo) or lower levels (U) in the Ordovician-early Devonian, followed by a second rise to even higher levels in the mid-Devonian. When normalized to TOC, the Ediacaran-Cambrian RSM increase disappears: metal/TOC ratios are essentially flat until the middle and late Paleozoic. Machine learning analyses that simultaneously account for TOC, detrital input, 'degree of pyritization,' basin type, latitude/longitude, lithology, site type, depositional environment and metamorphic grade confirm these results.

Overall, our increased data density and ability to account for sampling and geological biases suggest that the visually dramatic increase between the Proterozoic and Phanerozoic in plots of raw trace metal data was due to 1) over-emphasis of outlier points, and 2) the large increase in TOC contents of sampled Phanerozoic shale compared to the Neoproterozoic. The analyses do not rule out some degree of oxygenation in the Ediacaran-Cambrian, or re-organization of the seafloor redox landscape. However, such as metal/TOC ratios proxy the area of reducing seafloor, the major long-term inflection point is not Neoproterozoic but rather Devonian.