

Controls of Ancient Geochemical Records: Global Oceans Versus Local Water Masses

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A growing body of efforts seeks to reconstruct the evolution of global ocean chemistry over Earth's four-billion-year history. Due to sparseness of the rock record, studies of Earth's early history often leverage samples from a single stratigraphic succession to constrain the global-scale marine chemistry for specific time periods. This approach relies on the assumption that these rocks were deposited in settings hydrologically connected to the open ocean. However, that assumption is not universally valid. In this presentation, we will illustrate this issue with two examples and demonstrate that many geochemical archives used to trace redox and nutrient cycling in Earth history are instead linked to hydrologically restricted environments, thus heavily influenced by the local depositional conditions.

First, we focus on a mid-Proterozoic shale sequence (the Atar and El Mreiti groups, Mauritania)—the same sediments previously interpreted to have recorded the rise of oxygen at ~1.1 Ga. Our iron speciation data suggest that the local redox state was dynamic. Unexpectedly, even in the euxinic intervals, concentrations of redox-sensitive trace metals are extremely low. The most parsimonious interpretation is that the basin was hydrologically restricted, which is consistent with our thallium isotopic signatures. In light of this, the data from the location cannot be used to extrapolate global marine chemistry. Therefore, we challenge the suggestion of a transient oxygenation at ~1.1 Ga. Next, we focus on the Permian Phosphoria Formation, a phosphorus-rich shale sequence deposited in a subtropical epicontinental sea along western Pangaea. While previous models attribute the extensive phosphogenesis to upwelling as in modern analogs, our new and existing data suggest that these environments were instead (semi)-restricted and salinity-stratified. Notably, we find exceptionally high $\delta^{15}\text{N}$ values ($> 15\text{‰}$), which may result from NH_3 volatilization in a redox-stratified, NH_4^+ -enriched water column. If true, this may imply a unique local water mass

chemistry with elevated pH and alkalinity, conditions that would favor PO_4^{3-} accumulation and eventually lead to phosphorus enrichment in sediments. These findings emphasize the importance of local controls in shaping geochemical records and caution against broad extrapolations of global marine conditions from localized sedimentary successions.