Re-evaluation of Fe speciation and Mo isotopes as paleo-redox proxies: Impact of post-depositional alteration

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Ratios of highly reactive Fe to total Fe (Fe_{HR}/Fe_T) and of pyrite to highly reactive Fe (Fe_{Py}/Fe_{HR}) have been applied to distinguish between different redox states in the water column. However, these ratios can also be influenced by changing lithogenic influx, sedimentation rates, or Fe-remobilization. This can be addressed by application of a recently proposed systematic that is based on total Fe to aluminum (Fe_T/Al) vs. Fe_{HR}/Fe_T relationships [1]. The Mo isotope redox proxy in contrast is based on the distinct geochemical behavior of Mo and fractionation of its isotopes (reported as $\delta^{98}Mo$) under oxic and sulfidic conditions. However, different modes of Mo supply to the sediment (e.g., diffusive versus particulate) and diagenesis also play an important role in the recorded $\delta^{98}Mo$ signature. These (post-)depositional factors often complicate the interpretation of the detected signatures in the paleorecord.

Here we investigate the Fe- and Mo-based redox-proxies in anoxic marine environments in order to understand their modification during diagenesis. Sediment cores from three oxygen minimum zone (OMZ) settings in the Gulf of California and the Peruvian margin covering the last 10,000 years were analyzed. Although all these settings are anoxic, they differ in environmental conditions including water depth, primary productivity, particle rain in the water column and biogeochemical interactions between sediment and bottom water. Application of Fe_T/Al vs. Fe_{HR}/Fe_T relationships reveals that all records are affected by post-depositional pyritization of Fe in silicate minerals in the zone where sulfate reduction is coupled to anaerobic methane oxidation. Sediments from the OMZ of the Gulf of California show Mo isotope values that remain constant at $+1.76 \pm 0.15$ ‰ (2SD) throughout this interval indicating that the Mo isotope proxy remains unaffected by late-stage pyrite formation. The conclusion is that late-stage pyrite formation can generate Fe-based proxy signatures that can falsely imply euxinic conditions. Here, Mo isotopes are a more robust redox proxy to trace such conditions.

[1] Scholz (2018) *Earth-Science Reviews* 184, 29-45