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Geochemical behavior of tungsten and molybdenum in anoxic continental margins – implications for trace metal-based paleoredox-proxies

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Tungsten (W) and molybdenum (Mo) concentrations and isotopes are applied as geochemical proxies to reconstruct redox-conditions in the sedimentary rock record. Here, they are investigated in modern sediments of anoxic open-marine margins, which are a major sink of trace metals and thus important for the global mass balance. The Mo isotope redox-proxy (reported as δ^{98}Mo) is well-investigated in various redox zones and environmental settings. It has been revealed on anoxic upwelling regimes from the Gulf of California and the Peruvian margin that different modes of Mo supply to the sediment (e.g., diffusive versus particulate) play an important role in the recorded δ^{98}Mo signature. Tungsten, the geochemical twin of Mo, shows a similar geochemical behavior in the oxygenated ocean, but reveals differences in the presence of sulfide. Thus, the W isotope composition (reported as δ^{186}W) is considered as a new promising paleo-redox proxy, complementing ambiguous Mo-based proxy signatures. However, there are still knowledge gaps on the geochemical behavior of W. For this purpose, W concentrations and isotope compositions were analyzed on sediment and pore water samples from the anoxic shelf off Namibia (Banguela upwelling system). Sediment samples show W depletion relative to the crustal background and δ^{186}W signatures ranging from 0.043 to 0.312 ‰, with a tendency to heavier signatures with increasing depletion. Pore water profiles show increasing W concentrations with depth under sulfidic conditions and δ^{186}W values between 0.168 and 0.486 ‰. Results indicate a crustal component as the main W source, although another W source cannot be excluded, and isotope fractionation towards heavier values under sulfidic conditions. In contrast, Mo contents are enriched relative to the crustal background by a factor of 7 to 57 in sulfidic sediments and show δ^{98}Mo values clustering from 1.57 to 2.06 ‰, indicating a Mo influx controlled by both, diffusion and particles. This study improves our knowledge of different geochemical mechanisms of Mo and W fixation and indicates that paleo-records of anoxic and sulfidic settings will show W depletion and Mo enrichment, while W isotope signatures are more affected by diagenetic processes and Mo isotope signatures are mainly influenced by the delivery mode.