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The effects of early diagenesis on Mo isotope compositions in Pacific abyssal sediments

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The molybdenum isotope (δ^{98}Mo) systematics is a robust proxy for reconstructing redox conditions in ancient oceans. In the modern oceans, Mo is present mainly as molybdate (MoO_4^{2-}) in seawater with a heavy isotopic value of ~2.3‰ due to the preferential removal of isotopically light Mo into Fe-Mn (oxyhydr)oxides under oxic condition. Abyssal sediments represent a key Mo sink in the global Mo cycle, however, Mo mobility and associated isotope fractionation during early diagenesis in this oxic setting remain poorly constrained. In this study, we investigated the Mo geochemistry (e.g., content and δ^{98}Mo) of bulk sediments throughout an 8-meter-long sediment core from the Central North Pacific. Fe-Mn (oxyhydr)oxides were found to be the main carrier of Mo in the sediments. Above 3 m below the seafloor (mbsf), Mo contents remain constant and δ^{98}Mo values display an increasing trend with burial depth ranging from −0.75‰ to 1‰. This isotope pattern likely reflects pore water geochemistry. Positive isotope excursion might result from Mo diffusing upward which is enriched in ^{98}Mo from below. Below 3 mbsf, Mo contents of sediments decrease with depth from ~26 to ~5 μg/g. Concomitantly, the Mo isotopic signals show a linearly decreasing trend from ~1‰ to ~0.5‰. The positive relation between Mo content and isotope composition indicates that the Mo carrier (i.e., Fe-Mn (oxyhydr)oxides) might preferentially release the isotopically heavy Mo during Mn reduction. This explanation is supported by the lower ratios of Mo/U of bulk sediments and Mn/Fe in the Fe-Mn micronodules in this horizon. Our findings thus provide new constraints on Mo cycling in oxic sedimentary environments.