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Mo behaviour in deep pelagic sediments of the North and South Pacific over the past 70 Myr

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Molybdenum isotopes (δ^{98}Mo) are used as a proxy to investigate past redox conditions, because markedly different systematic isotopic signatures are recorded in oxic and anoxic sediments. Therefore, mass balance calculations allow the assessment of past oceanic oxygenation. In the present day ocean, dissolved Mo has an isotopic value of +2.3‰. This heavy value is attributed to the oxic Mo sink, in which molybdate is adsorbed onto Mn oxides with fractionation of ~-2.8‰ [1] relative to seawater, leaving seawater enriched in heavy isotopes. In agreement with these data, Fe-Mn crusts and Quaternary pelagic clays published so far show an average δ^{98}Mo value of -0.5‰ [2].

However, few long-term records of the oxic Mo sink have been reported to date. We measured δ^{98}Mo in two cores: one in the North Pacific Gyre and one in the South Pacific Gyre, covering 70 Myr of deposition in areas of low sedimentation rates and low biological activity. The pore waters of these cores have been oxic throughout their geological history and are an excellent archive to evaluate the seawater evolution of Mo isotopes in oxic settings. In near-surface samples, the cores show low δ^{98}Mo values near -0.5‰. In contrast, in deeper samples, δ^{98}Mo ranges from -0.5 to +0.3‰. We investigate whether the results reflect primary variation in ocean oxygenation or whether the values result from (secondary) diagenesis. We find that the latter interpretation is more plausible given that mass balance calculations show that the extent of ocean oxygenation required to produce an observed signature of +0.3‰ is not realistic within the age range of the cores. However, oxic diagenesis can explain observed signatures, for example, through the recrystallisation of birnessite to todorokite and the release of trace metals[3]. Our findings suggest that the overall oxic Mo sink is isotopically heavier and more variable than currently assumed in mass balance calculations, which may have implications for paleo-reconstructions.

1. Barling & Anbar, *EPSL*. **217**, 315–329 (2004).
2. Siebert et al., *EPSL*. **211**, 159–171 (2003).
3. Atkins et al., *GCA*. **189**, 158–183 (2016).