

Inhibition of Molybdenum Adsorption to Manganese Oxides by Dissolved Silica: Implications for the Molybdenum Isotope Paleoredox Proxy

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Molybdenum (Mo) isotopes are used as a paleoredox proxy due to the contrasting behavior of Mo isotopes in oxic and anoxic conditions (e.g., Barling et al., 2001; Siebert et al., 2003). In oxic environments, Mo readily adsorbs to manganese oxides (MnO_x), preferentially removing lighter isotopes from solution (Barling and Anbar, 2004). This fractionation dominates the ocean Mo isotope budget. Past changes in the ocean Mo isotope budget, inferred from the sedimentary record, are interpreted under the assumption that the distribution coefficient for Mo adsorption (K_{OX}) and the fractionation factor during Mo adsorption ($\alpha_{\text{Mo-MnOx}}$) were not affected by changes in ocean chemistry. To date, Precambrian applications of this proxy have not considered the effect on adsorption of dissolved silica, which is thought to have been at higher concentrations in Precambrian oceans (Maliva et al., 2005). There are two potential impacts of silica on Mo isotope systematics: First, silica can adsorb to metal oxide surfaces, competing with dissolved metals for adsorption sites (Konhauser et al., 2007), thereby affecting K_{OX} . Second, adsorbed silica could affect the bonding geometry of surface-bound Mo, affecting $\alpha_{\text{Mo-MnOx}}$.

We are experimentally quantifying the effects of silica on K_{OX} and $\alpha_{\text{Mo-MnOx}}$ during Mo adsorption onto MnO_x . Adsorption reactions were performed in 0.1 M KNO_3 solution $\pm$ 2.20 mM silica at pH = 7.5, equilibrated for 48 hrs. Our results show that Mo adsorption is inhibited by silica across a range of Mo/Mn ratios, such that K_{OX} decreases by nearly 50% in the presence of silica. In simple 2-sink models of Mo isotope mass balance, the seafloor areal extent of oxic conditions (A_{OX}) inferred from Mo isotope data scales linearly with K_{OX} , in which case this effect could significantly affect paleoredox reconstructions. More sophisticated 3-sink models are in progress, as are experiments to determine the effect of silica on $\alpha_{\text{Mo-MnOx}}$.

References:

1. Barling et al. (2001), *EPSL* 193: 447-457.
2. Barling and Anbar (2004), *EPSL* 217: 315-329.
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4. Maliva et al. (2005) *GSA Bulletin* 117: 835-845.
5. Siebert et al. (2003) *EPSL* 211: 159-171.