Temperature dependence of Mo isotope fractionation during adsorption to δ-MnO_2: implications for the paleoredox proxy

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Previous investigations [1,2,3] have shown that fractionation of Mo isotopes during adsorption to Mn oxyhydroxides (MnOx) likely dominates the Mo isotope budget of the oceans and that Mo isotope signatures in ancient rocks likely record changes in the extent of ocean oxygenation in the past. This paleoredox proxy requires that the fractionation between seawater and MnOx is relatively insensitive to other variables, such as temperature. Thus we are conducting adsorption experiments from 1°-50°C to measure the effect of temperature on Mo isotopic fractionation and to yield better understanding of the fractionation mechanism during adsorption. These experiments also result in a more precise determination of the magnitude of fractionation than previous experiments (at 25°C [1]) because of recent advances in analytical methods.

Our experiments reveal little sensitivity to temperature. We observe a fractionation factor of α = 1.0019±0.0001 (2s.d.; $\Delta = \delta^{97/95}Mo_{soln} - \delta^{97/95}Mo_{MnOx}$ =1.92±0.08‰) at 1°C, and α = 1.0016±0.0001 (1.62±0.06‰) at 50°C. This magnitude of fractionation is in excellent agreement with prior experimental work that documented a fractionation factor of 1.0018±0.0005 (Δ = 1.84±0.49‰) at room temperature [1].

The small observed temperature effect does not agree with recent theoretical treatments. Using quantum mechanical calculations, Tossell [4] predicts that equilibrium fractionation occurs between MoO_4^{2-} and MoO_3 in solution, followed by preferenctial adsorption of isotopically lighter MoO_3. The predicted soln-MnO_x fractionation factor is large (α = 1.0019) at 0°C, but decreases sharply with increasing temperature to α = 1.0010 at 25°C and 1.0006 at 100°C.

Our results are encouraging with respect to application of the Mo isotope paleoredox proxy. However, the disagreement with theory indicates that more work is needed to constrain the fractionation mechanism.

References

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