

Molybdenum Isotope Fractionation in Saanich Inlet, British Columbia

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Molybdenum concentrations and isotope ratios have been identified as a potential paleoredox proxy in ancient environments. Marine sediments are important sinks for Mo due to (1) adsorption onto Mn-oxyhydroxides under oxic conditions and (2) accumulation as particle-reactive thiomolybdate in euxinic environments. This removal is associated with an isotopic fractionation ranging from 3‰ in fully oxic settings to 0‰ in euxinic environments where reductive Mo removal is complete [1, 2]. However Mo isotopic fractionation associated with partial reduction has not been yet fully described [3].

In order to refine our understanding of Mo cycling and associated isotopic fractionation, we investigate Mo concentration and isotopic composition of the stratified waters and anoxic sediments of Saanich Inlet, British Columbia. Mo isotopes were measured by MC-ICPMS using a ¹⁰⁰Mo/⁹⁷Mo-double spike [4]. The data are reported as $\delta^{98/95}\text{Mo}$ relative to NIST-SRM-3134 = +0.25‰. Analytical precision is <0.05‰ (2sd).

Mo concentration in anoxic surface sediments deposited in the central basin of the inlet rises to >20ppm, and $\delta^{98/95}\text{Mo}$ varies between 1.26‰ and 1.63‰, well within the range reported for marine sediments in non-euxinic settings [3]. In the water column, $\delta^{98/95}\text{Mo}$ in bottom anoxic water is significantly heavier (2.55±0.05‰; 2sd) and Mo concentration significantly lower (6.695±0.001 ng/g) than in surface water ($\delta^{98/95}\text{Mo}$ = 2.23±0.05‰; [Mo] = 8.997±0.002 ng/g). Assuming Rayleigh fractionation in a closed system, a tentative -1.1‰ fractionation factor during Mo reduction is derived, which is consistent with sediments ca. 1‰ lighter than seawater. [Mo] and $\delta^{98/95}\text{Mo}$ measured in the water column at the seawater redox boundary deviates from this simple Rayleigh fractionation calculation suggesting additional processes linked to Mn cycling, which further fractionate Mo isotopes. Saanich Inlet thus shows promise as a natural laboratory to study Mo isotope dynamics in the marine environment.

[1] Barling *et al.* (2001) *Earth Planet Sci Lett* **193** (447-457). [2] Siebert *et al.* (2006) *Earth Planet Sci Lett* **241** (723-733). [3] Scott *et al.* (2012) *Chem Geol* **324-325** (19-27). [4] Skierszkan *et al.* (2015) *Anal Bioanal Chem* **407**, 1925-1935.