Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.36289

Investigation of tungsten stable isotope fractionation by extremophile organisms as biosignatures

ICHIKO SUGIYAMA[1], HANIKA RIZO[1], DANIEL S. GRÉGOIRE[1], ALLYSON L. BRADY[1], MATTHEW R MCILVIN[2] AND MAK SAITO[2]

[1]Carleton University
[2]Woods Hole Oceanographic Institution

Tungsten (W) is a redox-sensitive trace metal, and its isotopic fractionation in the geologic record is increasingly recognized as a promising proxy for tracking shifts in Earth's surface redox conditions. In addition, W-dependent microbes often possess enzymes deeply rooted in the tree of life. Metabolic evolution models suggest that W-dependent biochemistry predates molybdenum (Mo)-dependent pathways, with Mo utilization increasing along with the rise of atmospheric oxygen and the proliferation of aerobic prokaryotes in early Earth environments. Despite advances in our understanding of W biogeochemical cycles through time, microbial assimilation and isotopic fractionation of W and Mo remain poorly constrained.

Here, we quantify W uptake and isotopic fractionation in a model W-utilizing microbe to evaluate the potential of W isotopes as a biosignature in paleoenvironmental archives. We conducted metalloproteomic analyses to improve our mechanistic understanding of W-dependent pathways that contribute to isotopic fractionation. *Moorella thermoacetica*, an acetogen that utilizes W and Mo-dependent enzymes for CO_2 fixation, was cultured anaerobically at pH 7 with varying W and/or Mo concentrations. Metal speciation in the growth medium was modeled using PHREEQC, while growth rates were quantified via OD600 and cell counts (OD600 ~1.2; cell counts: $2.3x10^9$ (W) and $3.5x10^9$ cells/mL (W+Mo)), enabling calculation of cellular metal quotas. Metal concentrations in cells and solutions were measured by ICP-MS, and W isotopic fractionation was measured by MC-ICP-MS. Metalloproteomic analyses were used to identify differential protein expression across W and/or Mo treatments, with investigations of potential enzymes/proteins incorporating these metals into biochemical pathways. Parallel experiments with *Pyrococcus furiosus*, a W-obligate archaeon, repeated the use of this framework to further constrain W uptake and isotopic fractionation in a model organism posited to be more representative of early Earth habitats.

Our study explores the potential W and Mo biosignatures in microbes that reflect conditions in early Earth's environments. Through this approach, with our preliminary results, we investigate the evolutionary transition from W- to Mo-dependent metabolisms in the geological record. We also evaluate how microbial W and Mo utilization may serve as proxies for reconstructing early Earth redox conditions and for tracing the co-evolution of microbial metabolism and environmental change.