Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.9700

Apparent Mo isotope anomalies resulting from non-exponential mass fractionation

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Mass-independent (nucleosynthetic) Mo isotope anomalies are a powerful tool to investigate genetic relationships among meteoritic and planetary materials and, therefore, to reconstruct Earth's accretion history [1]. Recently, growing evidence for the preservation of primordial mantle heterogeneities has sparked a search for Mo isotope anomalies in terrestrial rocks [2,3], which would provide key insights into the origin and nature of Earth's late-stage building blocks. Their reliable identification, however, critically depends on the accurate correction of mass-dependent isotope fractionation induced during natural processes, chemical separation, and mass spectrometry, which is conventionally assumed to follow the *exponential law*.

To assess whether this is a valid assumption, we obtained high-precision Mo isotope data for diverse terrestrial samples by MC-ICP-MS following [1]. After internal normalization (to $^{98}Mo/^{96}Mo$) using the exponential law, several samples (sediments, steel, igneous rocks) display a characteristic ∩- or ∪-shaped Mo isotope pattern, with anomalies up to ~1 ε-unit (for $\varepsilon^{92}Mo$) relative to typical reference materials. These residual anomalies broadly scale with the degree of mass-dependent fractionation (inferred from standard-sample bracketing), and are internally inconsistent with a nucleosynthetic origin. Instead, the data are in excellent agreement with theoretical predictions for the effects of equilibrium or Rayleigh fractionation imparted during sample formation, consistent with the observations in [4].

Our results demonstrate that non-exponential Mo isotope fractionation should be considered the norm rather than the exception, and that even a modest effect (<1 ‰/amu) can cause significant apparent Mo isotope anomalies. This is particularly critical as it can shift data points relative to the CC/NC-lines in the $\varepsilon^{95}Mo$–$\varepsilon^{94}Mo$ diagram [1], resulting in a spurious *s*-process excess near the CC-line or deficit near the NC-line. Consequently, assessing the origin and magnitude of mass-dependent fractionation will be essential for any efforts to precisely define the Mo isotope composition of bulk silicate Earth and to identify potential nucleosynthetic isotope anomalies in terrestrial rocks; particularly for samples with complex geological histories such as sediments or molybdenites [4].

[1] Budde et al. (2019) *Nat. Astron.* 3, 736-741. [2] Toboul et al. (2021) *Goldschmidt*, #7475. [3] Bermingham et al. (2022) *LPSC*, #1468. [4] Kendall et al. (2017) *RiMG* 82, 683-732.