

## Mo isotopes in modern euxinic environments: Water column and sediment data

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The present study investigates the pathways of molybdenum (Mo) scavenging under euxinic conditions following the fractionation of stable Mo isotopes in three modern settings: The Black Sea, the largest permanently euxinic basin, and two anoxic troughs of the Baltic Sea. Water column profiles, as well as surface sediment samples, were recovered from different water depths and analyzed for the concentration and isotopic composition of Mo, besides other geochemical parameters.

Mo is a redox-sensitive trace metal which is soluble as the molybdate oxyanion in oxic seawater with a residence time of about 800 ka. The isotope signature of Mo is a relatively new proxy used to reconstruct the paleo-redox conditions of the Earth's atmosphere and the oceanic system. The Mo isotope composition in seawater is homogeneous, as shown by [1]. Scavenging of Mo under euxinic conditions is related to the amount of free H<sub>2</sub>S. Near total removal of Mo from the water column is reached at a H<sub>2</sub>S<sub>aq</sub> concentration of 11±3 μM [2]. In the Black Sea this corresponds to a water depth of about 400 m. Sediment samples of the Black Sea from more than 400 m water depth show seawater isotopic composition, agreeing completely with the assumption of bulk Mo removal. However, shallower sediments deposited under lower H<sub>2</sub>S concentrations show significant Mo isotope fractionation.

Brackish Baltic Sea surface sediment samples are taken from two separate basins, the Gotland Deep and the Landsort Deep which have maximum water depths of 248 m and 459 m, respectively. The Baltic Sea oceanographic conditions, including temporary bottom water oxygenation due to sporadic North Sea water inflows, are more complex than in the Black Sea. The dissolved sulfide concentrations in the water column are less than 50 μM and the salinity is less than 22 PSU. In the anoxic part, Mo isotope signatures are shifted towards heavier values indicating *in-situ* fractionation upon scavenging under euxinic conditions. The surface sediments are the sink for reduced Mo and show Mo fractionation similar to the oxic to slightly euxinic sediments of the Black Sea. Intra-basinal differences and downcore variations can be explained by changes in the bottom water redox conditions due to episodes with different inflow intensities and reflect varying concentrations of dissolved sulfide in the water column.

### References

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## Extremely refractory oceanic lithospheric mantle and its implications for geochemical mass balance

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In several ocean islands (e.g. the Canary Islands, Kerguelen, Cape Verde and Savai'i) the mantle xenoliths population is dominated by extremely refractory spinel harzburgites. These harzburgites (OI1) show no petrographic evidence of metasomatism, and carry no primary clinopyroxene. However, minor metasomatism may be reflected in the incompatible trace elements and radiogenic isotopes. The major element and modal compositions of the OI1 harzburgites correspond to residual mantle formed from a primordial source after 25-30% partial melting, leaving a clinopyroxene- and garnet-free residue. These peridotites are, on average, significantly more refractory than MOR peridotites. Estimated P-T conditions (850-1200°C and 0.7-1.3 GPa) indicate that the OI1 peridotites last equilibrated within the abyssal mantle lithosphere. Their textures and high solidus temperatures imply that their strongly refractory nature cannot be the result of processes ("additional" partial melting or melt – wall-rock reactions) associated with the present plumes. Although interaction with plume melts has caused minor enrichment in radiogenic isotopic ratios and the most strongly incompatible elements, their original (pre-ocean-island) compositions are preserved in the most abundant major elements and in the modal relationships. Highly refractory OI1 spinel-harzburgites have higher solidi than more fertile, clinopyroxene-bearing peridotites, and are likely to be resistant to further partial melting. We interpret the OI1 peridotites as fragments of recycled, "sterile" asthenospheric material that have been trapped in the abyssal mantle lithosphere. These peridotites imply that the convecting mantle includes material that is significantly more refractory than MOR peridotites. The OI1 peridotites are buoyant relative to less refractory, denser mantle material and may preferentially accumulate at the top of the convecting mantle, where they freeze to the base of newly formed abyssal lithosphere.