

## Molybdenum isotope signatures in recent sediments of the Black Sea

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The present study investigates the pathways of Mo scavenging under reducing conditions using Mo isotope measurements. For this purpose we analyze Black Sea surface samples from different depths.

The isotopic signature of Molybdenum is a relatively new proxy to reconstruct the paleo-redox conditions of earth atmosphere and the oceanic system. Barling et al. 2001 were the first to suggest that the  $\delta^{98/95}\text{Mo}$  values of seawater may reflect changes in the relative proportions of anoxic to oxic sedimentation in the ocean through time, and that this variation can be archived in anoxic sediments.

Molybdenum is a redox-sensitive trace metal with a high solubility and a low chemical reactivity which results in a long residence time of ~800 k.y. (Nägler et al. 2005, Emerson & Huested 1991, Colodner et al. 1995). Therefore its isotopic composition in seawater is homogeneous, as shown by Siebert et al. 2003. It exists in seawater as the very unreactive oxyanion  $\text{MoO}_4^{2-}$ . The scavenging of Mo under reducing conditions is strongly dependent on the amount of free  $\text{H}_2\text{S}$ . Still there is a large ongoing debate whether Mo scavenged from pore waters during early diagenesis, or is scavenged from the water column in this environment (s. discussion in Lyons et al. 2003). The transition from  $\text{MoS}_4^{2-} \ll \text{MoO}_4^{2-}$  to  $\text{MoS}_4^{2-} \gg \text{MoO}_4^{2-}$  is very sharp. The so called 'Action Point of Switch' (APS, Erickson & Helz, 2000) describes the point in which  $\text{MoS}_4^{2-}$  largely dominates over  $\text{MoO}_4^{2-}$ . Neretin et al. 2001 shows a linear increase of  $\text{H}_2\text{S}$  with increasing water depth in the Black Sea. In this basin the APS is at about 400m water depth with a  $\text{H}_2\text{S}_{\text{aq}}$  concentration of  $11 \pm 3 \mu\text{M}$  (Erickson & Helz, 2000). Therefore, if Mo is scavenged from the water column, Black Sea samples from below 400m should carry seawater isotopic composition due to complete removal of Mo, while shallower samples should show Mo isotope fractionation. Nägler et al. 2005 shows a set of Molybdenum data from a Black sea sediment core, taken in 396 m water depth. Samples from the anoxic sediments show a slight fractionation from ocean water ( $0.7 \delta^{98/95}\text{Mo} \text{ ‰}$ ).

We investigate surface sediment samples from 80 – 2200m water depth to continue the work of Nägler et al. 2005. We additionally measured Mo and  $\text{H}_2\text{S}$  of the water column to address open questions concerning the Mo enrichment in chemical sediments. The data below 400m water depth mirror the seawater Mo isotopic composition. The oxic/suboxic sediments above 100m water depth (chemocline) as well as anoxic sediments between 100m and 400m water depth ( $< 11 \mu\text{M} \text{H}_2\text{S}_{\text{aq}}$ ) show a fractionation from seawater to more negative values reaching from -0.3 to  $1.9 \delta^{98/95}\text{Mo}$ . The low Aluminium/Molybdenum ratio of the anoxic sediment samples precludes significant detrital influence on the Mo isotopic signal. The latter results indicate directly incomplete Mo scavenging above 400m depth in relation to low  $\text{H}_2\text{S}$  concentrations. While these results seem to indicate Mo scavenging from the water column, a detailed study of the correlation of Mo isotopes with  $\text{H}_2\text{S}$  concentrations of pore water, bottom water and from the water column above will be applied to identify the locus of the Mo scavenging.

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