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H_2S dependence of Molybdenum isotope signatures in sediments of the Black Sea

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

The isotopic signature of Mo is a relatively new proxy to reconstruct the paleo-redox conditions of the earth atmosphere and the oceanic system. Mo is a redox-sensitive trace metal with a high solubility. In seawater Mo occurs predominately as the very unreactive oxyanion MoO_4^{2-}, which results in a long residence time of $\sim$800 ka. Therefore, its isotopic composition in seawater is homogeneous, as shown by Siebert et al. 2003. The scavenging of Mo under reducing conditions is related to TOC and the amount of free H_2S. The importance of TOC under strongly euxinic conditions is ambiguous. Furthermore, there is an ongoing debate whether Mo is scavenged from pore waters during early diagenesis, or from the water column. For euxinic conditions an answer can be found in recent Black shale sediments. The speciation transition from MoS_4^2 << $MoO_4^{2-}$to MoS_4^{2-} >> $MoO_4^{2-}$is very sharp. The ´Action Point of Switch‘ (APS), where MoS_4^{2-}largely dominates over MoO_4^{2-} is reached at a H_2S_{aq} concentration of 11$\pm$3*10E-6M (Erickson and Helz, 2000). In the Black Sea this corresponds to a water depth of about 400 m. Therefore, if Mo is scavenged from the water column in relation to H_2S concentration, Black Sea sediments from below 400 m should carry a seawater isotopic composition due to complete removal of Mo, while shallower sediments should show Mo isotope fractionation.

We measured surface sediments from 80 – 2200 m water depth and compared them with H_2S data. The sediment data below 400 m water depth mirror the seawater Mo

isotopic composition (+2.3 delta$^{98/95}$Mo). The oxic/suboxic sediments above 100 m water depth (chemocline) as well as anoxic sediments between 100 m and 400 m water depth ($<$11*10E-6 M H_2S_{aq}), show a fractionation from seawater to lower values (-0.3 to +1.9 delta$^{98/95}$Mo), which require an incomplete Mo scavenging. A plot of Mo isotopic composition shows a clear correlation with bottom water H_2S rather than pore water H_2S. These results indicate scavenging from the water column as main enrichment pathway for primary Mo in euxinic sediments.

References

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