Experimental confirmation of isotope fractionation in thiomolybdates using ion chromatographic separation and detection by multi-collector ICP-MS

C. F. KERL[1], R. LOHMAYER[1], E. BURA-NAKIĆ[2], D. VANCE[2], B. PLANER-FRIEDRICH[1]*

[1] Department of Environmental Geochemistry, Bayreuth Center for Ecology and Environmental Research (BayCEER), University of Bayreuth, 95440 Bayreuth, Germany (*b.planer-friedrich@uni-bayreuth.de)

[2] Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, 8092 Zürich, Switzerland

Bulk molybdenum isotope ratios ($^{98}Mo/^{95}Mo$) in marine sediments are used as paleo proxies to reconstruct the redox state of the ancient ocean. Under oxic conditions, molybdate (MoO_4^{2-}) is the dominant species. With increasing sulfide concentrations, thiomolybdates ($MoO_{4-x}S_x^{2-}$, where x = 1-4) form by stepwise sulfidization of MoO_4^{2-}. If MoO_4^{2-} is quantitatively transformed to MoS_4^{2-} and precipitated, no fractionation between seawater and sediment should be observed. However, for incomplete sulfidation quantum mechanical calculations [1] suggested isotopic fractionation for thiomolybdates relative to MoO_4^{2-} (about 1.5‰ per sulfidization step). To experimentally confirm isotope fractionation in thiomolybdates, a new approach for determination of isotope ratios in individual species was developed. Individual thiomolybdates were chromatographically separated by HPLC-UV [2] and isotope ratios were determined with multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in individually collected peaks after sample purification. Method evaluation was done using commercially available MoO_4^{2-} and MoS_4^{2-} standards. Isotope fractionation occurred within peaks with longer retention times, but excellent reproducibility and accuracy were obtained when chromatographic peaks were collected completely. During formation of thiomolybdates, reacting MoO_4^{2-} with 20-fold or 50-fold sulfide excess, isotopic fractionation for each thiomolybdate species could be experimentally proven for the first time [3]. Further optimization and online-coupling of the HPLC-MC-ICP-MS approach for determination of low concentrations in natural samples will greatly help to obtain more accurate species-selective isotope information.

[1] Tossel (2005) *GCA* **69**, 2981–2993. [2] Lohmayer *et al.* (2015) *Anal. Chem.* **87**, 3388–3395. [3] Kerl *et al*. (2017) *Anal. Chem*. **89**, 3123–3129.