Determination of thiomolybdates in natural waters by IPC-ICP-MS

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Molybdenum in sediments is used as indicator for reducing conditions during the time of deposition and hence serves as important paleoproxy. Thiomolybdates ($MoO_{4-x}S_x^{2-}$ with x = 1-4) are assumed to play a key role in the process of molybdenum precipitation in form of molybdenum (iron) sulfides but have not yet been determined in natural waters. This is due to the lack of a suitable analytical method with sufficiently low detection limit.

We adapted an ion-pair chromatographic (IPC) separation method [1] to be able to use inductively coupled plasma-mass spectrometry (ICP-MS) as detection system. Therefore, previously used acetonitrile was replaced by 2-propanol to reduce the carbon load into the plasma. Detection limits of the newly developed IPC-ICP-MS method were ~10 nM. Salt concentrations higher than 2 mM were found to have a negative effect on molybdate elution but not on higher thiolated molybdates.

In synthetic solutions, kinetics and degree of thiomolybdate formation increased with increasing sulfide excess and were highest at pH 7. Tetrathiomolybdate was most stable at pH 9; higher pHs led to direct transformation to molybdate, lower pHs to stepwise hydrolysis and precipitation from solution. Flash-freezing preserved tetrathiomolybdate with less than 4% transformation over more than two months.

In the environment, spontaneous formation of thiomolybdates was observed after adding a molybdate spike to a euxinic saline water sample of Lake Rogoznica, for which the natural occurrence of thiomolybdates was predicted by modeling [2]. Moreover, we were able to determine considerable amounts of di- to tetrathiomolybdate in several hot springs of Yellowstone National Park.

With the newly developed IPC-ICP-MS method, we provide the first evidence for thiomolybdate occurrence in natural waters. Thus, this method is the basis for elucidating the molybdenum-sulfur cycle in nature.

[1] Weiss *et al.* (1988) *Chromatogr.* **439**, 93-108. [2] Helz *et al.* (2011) *Chem. Geol.* **284**, 323-332.