



Multi-isotope biogeochemistry of sulfur in the water column and surface sediments of the Baltic Sea

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The anoxic deeps of the modern Baltic Sea with the temporal development of a pelagic redoxcline offer the opportunity to study the fundamental processes in the sulfur cycle of natural dynamic euxinic systems. In the low-temperature sulfur cycle multi-sulfur isotope discrimination has been found to be of particular value for the evaluation of fundamental biogeochemical processes and has, therefore, reached a lot of attention within the past decade.

We analyzed the concentrations and stable sulfur isotope (S-32, S-33, S-34, S-36) compositions of dissolved sulfide and sulfate, as well as elemental sulfur in the water column, and of sulfate, acid-volatile sulfide (FeS + HS-) and CrII-reducible sulfur (essentially pyrite) in surface sediments of several stations in the Landsort Deep (LD) and the Gotland Basin (GB). Samples were recovered during several research cruises to the Baltic Sea. Water column samples were obtained via the IOW pump-CTD system or a conventional CTD-rosette system; short sediment cores were retrieved with a multi coring device. Special focus was set on the zone at and below the pelagic redoxcline. Stable isotope results are compared to previous measurements of the traditional sulfur isotopes (S-32, S-34), and findings from other euxinic systems.

The direct correlation between salinity and dissolved sulfate and the low concentrations of dissolved sulfide (below 40 μM in the LD and 130 μM in the GB) indicate that now significant net pelagic sulfate reduction took place. Most of the sulfide originates from microbial processes in the surface sediments and further diffusion into the water column. The magnitude of overall $34\text{S}/32\text{S}$ discrimination between dissolved sulfate and sulfide in the anoxic water column was 49 ± 1 (LD) and 46 ± 2 (GB) per mil, with only small vertical variations and significantly smaller than in the modern Black Sea. This partitioning is within the range of published results found in experiments with pure cultures of sulfate-reducing bacteria at low cellular activities using simple organic substrates. Sulfur isotope partitioning in the water column is close to results found in the (post-)modern surface sediments, but increases with sediment depth. Combined $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ results give no evidence for a substantial contribution from the bacterial disproportionation of sulfur intermediates on sulfur cycling.

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