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Isotope biogeochemistry of sulfide and sulfate in the Black Sea

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The modern Black Sea offers the opportunity to study the fundamental processes in the sulfur cycle of natural euxinic systems. The Black Sea is the largest permanently euxinic system on Earth and provides, as a 'type system', the geochemical references for the interpretation of past marine anoxia preserved in the fossil sedimentary record. In the low-temperature sulfur cycle, sulfur and oxygen isotope discrimination have been found to be of particular value for evaluation of fundamental biogeochemical process mechanisms and rates.

We have analyzed the concentrations and stable sulfur isotope compositions of dissolved and solid sulfur species (sulfide, sulfate, FeS, CrII-reducible sulfur (S° and pyrite)) and the oxygen isotope composition of sulfate in the water column and Holocene surface sediments, recovered during Legs M51/4 and M72/5 of RV Meteor. Results are compared to measurements from previous cruises. As a synthesis, we present the a data set for the sulfur isotope composition of sulfide for whole the (deep) Black Sea.

The magnitude of sulfur isotope discrimination between dissolved sulfate and sulfide in the anoxic water colum is close to 60 per mil that decreases in the upper part close to the pelagic redoxcline. Isotope discrimination is by far higher than observed in previous batch experiments with pure cultures of sulfate-reducing bacteria, indicating very low cellular activities probably dominated by strains, not isolated so far. The lowered overall isotope effect below the redoxcline accompanied by a steep gradient in dissolved sulfide is caused by the oxidation of dissolved sulfide at the redoxcline. Sulfur isotope discrimination in the water column is close to results from the surface sediments, indicating similar processes leading to the overall isotope discrimination. Disproportionation of sulfur intermediates may play a role close to the pelagic redox-cline but can be neglected in the surface sediments below anoxic bottom waters.
The oxygen isotope composition of dissolved sulfate below the redox-cline is enriched in the heavier isotope compared to open Ocean seawater. This indicates enhanced turnover in the sulfur system. In the sediments further 18O enrichment is associated with net sulfate reduction and reaches isotope exchange equilibrium with pore water at higher depths.