



Oxygen isotope biogeochemistry of phosphate in brackish marginal seas: I. The Black Sea

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Phosphorus (P) is an important limiting nutrient for primary production in aquatic ecosystems. Therefore, it is important to understand the sources and biogeochemical cycling of different P species. Biotic and abiotic processes, like the uptake and metabolism of inorganic and organic P compounds, enzymatic regeneration of P, redox controlled sorption and release of phosphates and precipitation of apatite or other P containing solids can alter the isotopic composition of oxygen in dissolved and particulate phosphorus matter.

The Black Sea is known as the world's largest permanently modern euxinic basin – the Type System for anoxia in Earth's history. Strong gradients for dissolved species are observed across the redoxcline and a zonation of the biogeochemical processes occurs along the stratified water column and further within the sediments. Oxygen isotope analyses of phosphate were carried out as a additional tool to allow the evaluation of biotic and abiotic influences on the P cycle.

We analyzed for the first time, the oxygen isotope composition of DIP (d18OP) in the water column of the Black Sea and compared the results to inorganic P extracted from laminated brackish and limnic sediments. Samples were recovered during two cruises (M51/4, M72/5) of the research vessel RV METEOR.

Besides hydrographical and physical parameters, particulate P and Fe, as well as dissolved constituents, like DIP, O₂ and H₂S, were analyzed for water column samples. Oxygen isotope compositions of phosphate were measured after conversion to silver phosphate, and then results were compared with published values for oxygen isotope compositions of water. In addition, oxygen isotope compositions of inorganic phosphate bound to laminated brackish (MUC sample) and bioturbated (formerly limnic) sediments were determined.

We found an increase in 18OP from the redoxcline down to the deep anoxic waters. The isotope values even exceed the calculated equilibrium composition. The increase in d18OP with depth is assumed to be the result of: (1) the release of isotopically heavy Fe-bound P at depth; or (2) mixing with "heavy" DIP from the Mediterranean Sea. The seawater-like d18OP value at depth (about +24 per mil) and a positive correlation between salinity and d18OP support scenario (2), while the input of DIP to reach about 7 μ M supports scenario (1).

Furthermore, we observed oxygen isotope differences between the pelagic DIP and inorganic P extracted from sediments (d18O of about +18 per mil), which are likely caused by an enhanced benthic enzymatic decomposition of organic matter due to microbial sulfate reduction, which has a large kinetic isotope effect.