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## S and O isotope fractionation in the western Black Sea

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The Black Sea offers the opportunity to study the fundamental processes which have to be considered in the interpretation of the modern and fossil sedimentary isotope record. We analyzed Holocene/Pleistocene sediments of the western Black Sea (cruise M51/4 of RV METEOR in 12/2001) which were deposited both below an oxic and anoxic water column for the abundance and stable S isotopic composition of different dissolved and solid species. Dissolved sulfate and sulfide reflect in-situ microbial isotope discrimination and in deeper limnic sediments transport processes. Activity of sulfate reducing bacteria in surface sediments and the zone of anaerobic methane oxidation was analyzed using radiolabeled sulfate. In-situ isotope fractionation between sulfate and sulfide in surface sediments (upper 15 cmbsf) on a transect ranging from 80 to 2200 m water depth showed isotope discrimination up to 60% similar to water column results. Decreased values (about  $44 \pm 4\%$ ) are associated with turbidites. S and O isotope fractionation in anoxic brackish sediments is dominated by microbial sulfate reduction, which is influenced by several factors, such as the microbial SRR which is controlled by the availability of reactive organic matter, sedimentation rate, bottom water conditions, and probably the microbial community structure. Additional factors at the chemocline and in surface sediments under oxic bottom waters may include the metabolism of intermediate sulfur species via disproportionation processes. In limnic sediments counter diffusion processes (sulfate - methane and sulfide - iron(II)) and in-situ microbial activity due to anaerobic methane oxidation lead to an overprint of the original S isotope signals by extremely heavy sulfide, leading to the precipitation of iron sulfides with characteristic  $\delta^{34}$ S values up to +40%<sub>o</sub>.

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## The effects of submarine hydrothermal systems on ocean chemistry and deep-sea microbial processes

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Hydrothermal flux estimates are based on the assumption that the hydrothermal heat flux on the ridge axes is directly related to the magmatic heat input and that fluxes derived from compositions of vent fluids from few locations can be extrapolated to a global scale assuming constant element/heat ratios. Recent observations suggest that most hydrothermal systems are not at steady state, element/heat ratios are usually highly variable, hydrothermal flux is not directly proportional to magma supply rates, and substrate composition may range from peridotite to basalt to dacite to sediment. Slow and ultraslow spreading ridges are hydrothermally more active than predicted, based on their apparent low magma budgets. By length, more than 50% of the global ridge system spreads at full rates <20 mm/yr. At slow rates of mantle upwelling and increased conductive boundary layer thickness, detachment faulting and exhumation of peridotite at the seafloor is common. Hydrothermal fluids reacting with peridotite are chemically distinct from fluids in basalt-hosted systems (e.g., higher H<sub>2</sub> and CH<sub>4</sub>, variable pH). In recent years, research has focused on hydrothermal activity related to intraplate volcanoes and associated with volcanic arcs and forearcs as well as backarc basins. Hydrothermal fluid composition in these submarine settings is strongly influenced by substrate composition, pressure and temperature (phase separation), and magmatic volatile input. Two-thirds of the oceanic hydrothermal heat loss is due to circulation of seawater through the flanks of mid-ocean ridges. Despite their potentially important role, estimates of ridge flank chemical fluxes are based on rare direct fluid samples and reconstructions of chemical changes derived from few deep sections of veined and altered ocean crust. Global lithosphereocean budgets cannot be established if the considerable contributions of the various non-MOR hydrothermal systems cannot be estimated.

The subseafloor biosphere may make up a significant fraction of the global biomass, although the carbon turnover rates are likely low. Incorporation of chemo-lithoautotrophy in global carbon cycle modelling is nevertheless important. For example, deep-sea crenarchaeota make up one-third of the microbial biomass of the oceans and appear to be dominantly chemoautotrophic. These may represent extremophiles adapted to non-extreme conditions. Links between deepsea microbial ecosystems, ocean crust formation and hydrothermal alteration are yet to be explored. Energy considerations suggest seafloor hydrothermal systems may support primary production of biomass that is significant relative to the flux of photosynthetic organic carbon and the biomass associated with its remineralization.

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