

Sulfur Isotope Biogeochemistry Related to Intense Microbial Sulfate Reduction and Anaerobic Methane Oxidation in Marine Deep-Sea Sediments (Hydrate Ridge)

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Short sediment cores were recovered in August 1999 from the Hydrate Ridge by the use of a TV-guided multicoring device during cruise 143 of RV SONNE. Sediment at station 173 (760m water depth) was covered by a dense bacterial mat of *Beggiatoa sp.*, and sediment at station 185 (785m water depth) was recovered from a mussel field of bivalves *Calymene sp.* Pore waters were analyzed for the concentrations and sulfur isotopic composition of dissolved sulfur species (H₂S and sulfate), and chloride. The sediments were additionally analyzed for the contents in total organic carbon (TOC), acid volatile sulfide (AVS), pyrite, elemental sulfur, and ³⁴S/³²S ratios of the sedimentary sulfur species. The vertical abundance of free and aggregate-related sulfate-reducing bacteria (SRB) was quantified by fluorescence in-situ hybridization (FISH). The activity of SRB was measured using the ³⁵S-radiotracer technique. Results from the methane-containing near-surface sediments are compared to those from a reference site (127, 2890m water depth).

Due to bacterial sulfate reduction associated with anaerobic methane oxidation at stations 173 and 185 a depletion of the pore waters in dissolved sulfate took place within the first 5-10cm and a corresponding increase in dissolved bisulfide up to more than 10 mM. In contrast, no change in the sulfate concentrations was found at station 127 within the first 35 centimeters, indicating that no significant net sulfate reduction took place. Extremely high sulfate reduction rates were measured in the surface sediments of stations 173 and 185 (up to more than 5000 nmol cm⁻³ d⁻¹) with corresponding high numbers of SRB. The cell numbers were about an order of magnitude higher at stations 173 and 185 compared to the reference site. The SRB community in the first cm of the sediment was dominated by *Desulfosarcina/Desulfococcus sp.* and *Desulfobacter sp.* *Desulforhopalus sp.* contributed to cells at Site 185. The community composition changed with depth and hydrogen sulfide concentrations. Calculated cellular sulfate reduction rates based on free and aggregate-related SRB are in the range previously reported from culture

experiments (Knoblauch, 1999). Compared to the isotopic composition of modern seawater sulfate (+20.6 per mil vs. V-CDT; Böttcher et al., 2000), bacterial sulfate reduction caused dissolved sulfate at stations 173 and 185 to become significantly enriched in ³⁴S (up to +56 per mil vs. V-CDT). The products of the dissimilatory metabolism H₂S, AVS (essentially H₂S), pyrite and S were enriched in ³²S, accordingly. An apparent sulfur isotope enrichment factor of about -30 per mil is estimated from coexisting pore water sulfate and AVS of surface sediments at Sites 173 and 185. Combined ³⁴S/³²S discrimination and corresponding cellular sulfate reduction rates are similar to results from pure culture studies (Chambers & Trudinger, 1979). Below about 5cm (Site 173) or 10cm (Site 185) the delta-³⁴S values of H₂S / AVS reached or even exceeded the isotopic composition of seawater sulfate (up to +25 per mil vs. V-CDT at Site 173), in agreement with a limited supply rate of sulfate from the sediment-water interface. A TOC content of 2% dwt. in the surface sediment of Site 173 corresponds to 1.2% dwt. in reduced inorganic sulfur. The first centimeters of surface sediments at both stations 173 and 185 were enriched in elemental sulfur due to the bacterial and chemical reoxidation of hydrogen sulfide. S was isotopically enriched in ³²S w.r.t coexisting AVS/H₂S and pyrite, most likely due to isotope effects related to the reoxidation and/or bacterial disproportionation reactions. The isotope ratios of pyrite were generally positioned between those for coexisting AVS and S and increased with depth. Most pyrite was formed within the first 5cm of the sediments, but additional pyritization still took place in deeper sediment sections. Based on the sulfur isotope data AVS/H₂S contributes to the deeper pyrite formation.

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