



Biogeochemistry and stable isotope geochemistry of sulfur in Thioploca-colonized surface sediments in the upwelling area off central Chile

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The biogeochemistry and stable isotope geochemistry of sedimentary sulfur was investigated on the continental shelf off central Chile under partial influence of an oxygen minimum zone. Dissolved and solid iron and sulfur species, including the sulfur intermediates sulfite, thiosulfate, and elemental sulfur, were analyzed at high resolution in the top 20cm. All stations were characterized by high rates of sulfate reduction, but only the sediments within the Bay of Concepcion contained dissolved sulfide. Due to advection and in-situ reoxidation of sulfide, dissolved sulfate was close to bottom water values. Whereas the concentrations of sulfite and thiosulfate were mostly in the submicromolar range, elemental sulfur was by far the dominant sulfur intermediate. Although the large nitrate- and sulfur-storing bacteria *Thioploca* were abundant, the major part of elemental sulfur was located extracellularly. The distribution of sulfur species and dissolved iron suggests the reaction of sulfide with FeOOH as an important pathway for sulfide oxidation and sulfur intermediate formation. This is in agreement with the sulfur isotope composition of co-existing elemental sulfur and iron monosulfides. In the Bay of Concepcion, sulfur isotope data suggest that pyrite formation proceeds via the reaction of FeS with polysulfides or sulfide. At the shelf stations, on the other hand, pyrite was significantly depleted in S-34 relative to its potential precursors iron monosulfide (FeS) and elemental sulfur. Isotope mass balance considerations suggest further that pyritization at depth includes light sulfide, potentially originating

from bacterial disproportionation of sulfur intermediates. The sulphur isotope values of pyrite down to -38 per mil vs. V-CDT are among the lightest found in organic-rich active marine sediments, and indicate an overall sulfur isotope fractionation wrt. pore water sulfate of at least 59 per mil. Seasonal variations in the sulfur isotopic composition of dissolved sulfate indicated a dynamic non-steady-state sulfur cycle in the surface sediments. The O-18 contents of porewater sulfate increased with depth compared to the bottom water composition due to intracellular isotope exchange reactions during microbial sulfur transformations.