



The challenge of identifying oxic, anoxic, and euxinic conditions by the chemical and isotopic composition of sedimentary sulfides

V. Brüchert (1), A. Dale (2)

(1) Department of Biogeochemistry, Max-Planck Institute for Marine Microbiology, Bremen, Germany, (2) Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands (vbrucher@mpi-bremen.de / Fax: +49- 421-2028690 / Phone +49-421-2028634)

The chemical and isotopic composition of sedimentary sulfides and reactive iron are widely used parameters for the discrimination of oxic, anoxic, and euxinic water column conditions in sediments and sedimentary rocks. Here we test these parameters in a systematic study of organic-rich shelf and slope sediments from the Benguela upwelling system off Namibia. These sediments deposit under (1) sulfidic, (2) anoxic, but non-sulfidic, and (3) fully oxic conditions below an oxygen minimum zone. Due to the high accumulation rates of organic matter, sulfate reduction and formation of sedimentary sulfides are observed at the sediment-water interface in all three environments. We find that the overall isotope difference between dissolved sulfate and pyrite increases from 25 permil in sulfidic, to 45 permil in anoxic, to 65 permil in fully oxic bottom waters. These isotope fractionations are only net isotope fractionations and are composed of two opposing isotope fractionations, one produced by sulfate-reducing bacteria and one by sulfide-oxidizing nitrate-reducing bacteria. Reaction transport modeling indicates that in the case of the anoxic, but non-sulfidic bottom waters, the isotope fractionation by sulfate-reducing bacteria substantially exceeds the net effect of 45 permil and may be as high as 85 permil. The isotope effect by sulfate-reducing bacteria, however, is reduced by superposition of normal isotope effects during the anaerobic oxidation of sulfide with nitrate, by the large sulfur-storing bacteria *Beggiatoa* and *Thiomargarita* sp., which may be as high 45 permil.

The ^{34}S -enrichment of dissolved sulfide in the zone of anaerobic methane oxidation varies between +14 and +19 permil vs. CDT and depends on the isotopic composition

of the initial hydrogen sulfide formed at the sediment-water interface rather than the depth of the sulfate-methane transition zone. Diagenetic overprinting by continuing sedimentary sulfide precipitation during burial is negligible in these sediments due to general iron limitation. Nevertheless, the isotopic composition of sulfides formed at the sediment-water interface is not preserved because of isotopic exchange of a fraction of the pyrite and organic sulfide pool with coexisting dissolved sulfide. In these sediments, this exchange leads to ^{34}S -enrichment of about 15 permil relative to the initial isotope composition of the respective sulfide pools. Our observations indicate that buried sediments never preserve the initial isotope composition of sulfides formed at the sediment-water interface or in the water column. However, the isotopic imprints of oxic, anoxic, and sulfidic bottom water conditions are sufficiently distinct from each other that they remain preserved as relative isotopic differences in the isotopic composition of buried sedimentary sulfides.