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Dynamics of Dissolved Inorganic and Organic Sulfides in Upwelling Sediments off Namibia

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The upwelling sediments off Namibia represent an ideal setting for a study of sulfide cycling in organic-rich sediments because most organic matter degradation proceeds via bacterial sulfate reduction. Furthermore, the benthic environment in this upwelling system is very diverse and changes from sulfidic bottom waters on the shelf via low-O_2 conditions in the oxygen minimum zone to fully oxygenated conditions on the lower continental slope. Porewater data for dissolved sulfide, sulfate, and dissolved organic sulfides are presented for 15 stations that cover the whole range of these benthic conditions. In addition to high resolution porewater sampling down to 30cm sediment depth, two 10m-long gravity cores were collected on the shelf and slope that penetrated the sulfate-methane transition zone. High concentrations of dissolved sulfide up to 22mM in the shallow-water near-surface sediments not only reflect the extremely high rates of bacterial sulfate reduction in these sediments. They are also reflect incomplete sulfide precipitation by iron and when compared to other continental margin upwelling areas. In the sulfidic bottom waters, some oxidation of sulfide proceeds via the bacterial oxidation with nitrate by the giant sulfide-oxidizing bacteria *Thioploca* and *Beggiatoa*. Oxidation of sulfide by oxygen increases in importance on the continental slope. In the gravity cores, dissolved sulfide displays a characteristic maximum with the highest concentrations near 12mM between 5 and 6m sediment depth. This maximum always occurred below the sulfate-methane transition zone. The decrease in dissolved sulfide below this maximum indicates a deep sink that may represent macromolecular organic matter and/or slowly reacting Fe released from Fe-silicates. Evidence for the increase of organic sulfides comes from porewater analysis of individual dissolved organic sulfides that increase to micromolar concentrations in the bottom 3m of the gravity cores. Organic polysulfides, ethanethiol, and methanethiol represent the dominant dissolved organic sulfides. These low-molecular weight thiols likely represent an important metabolic source for methanogenic bacteria and may contribute significantly to methane flux to sulfate-methane transition zone.