

Sulfides in oxic seawater over the submarine hydrothermal area of Kikai Caldera south of Kyushu Island, Japan

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Vertical distributions of metal sulfide and free sulfide ($\text{H}_2\text{S}_{\text{gas}} + \text{HS}^- + \text{S}^{2-}$) as a ligand to stabilize and to preserve trace metals in oxic seawater over the submarine hydrothermal field were obtained for the first time at the Kikai Caldera south of Kyushu Island, Japan. free sulfide was found to be gradually increasing with depth (max. 31.1 pmol/kg in the surface layer and max. 59.5 pmol/kg below ~330 m within the Caldera rim), whereas total metal sulfide was virtually constant throughout the water column (~345 pmol/kg). Interestingly, total and dissolved metal sulfide exhibited uniform and quite similar concentrations within the water column, showing that metal sulfide exists in the dissolved phase (“truly” dissolved and/or particulate form with dia. $< 0.2 \mu\text{m}$), and is quite stable even in an oxic environment. A mass balance calculation suggested that 70% of the total sulfide originating from hydrothermal vents reached the upper layer without oxidation. The present results clearly show that dissolved metal sulfide originating from hydrothermal vents contributes to a large portion of the observed high dissolved total sulfide concentration even in the surface water, indicating that metal-sulfide complex is quite stable in preventing its rapid removal from the water column by metal precipitation and/or oxidation in an oxic environment. The present study suggests that metal-sulfide complexation/nanoparticle play an important role in transporting trace metals far from their sources in oxic environments and biogeochemical cycles of trace metals in the ocean.