

Distribution and Redox Speciation of Dissolved Vanadium in the South Pacific Ocean: Implications for Its Biogeochemical Cycling

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Vanadium is known as a redox-sensitive element having three redox species in natural aqueous system. Its speciation is a complex function of pH, redox conditions, concentration and also biological activities. In contrast to the oxidized form V(V) the reduced vanadyl V(IV) is highly reactive and forms a large number of strong complexes with inorganic and organic ligands, including humic and fulvic acids and V(V) can potentially even be reduced by humics. Vanadium redox species play an important role for biogeochemical cycles in the marine environment because V(V) is an essential nutrient for phytoplankton in the photic zone. The understanding of V speciation is also important for understanding V isotopic signatures in the ocean.

The separation of vanadium redox species in coastal and open ocean seawater in the South Pacific Ocean collected during GEOTRACES research cruise (GP21, SO289) has been carried out using a solid phase extraction with chelating resin chelex-100, followed by the determination of the concentration of each V redox species with ICP-MS (Kurahashi et al. 2024).

In depth profiles of V(V) and V(IV) from coastal seawater close to the Maipo river mouth, coastal seawater, and open ocean seawater, V(V) was the dominant redox species throughout the entire profiles from all sampling locations (16.8 - 32.9 nmol/kg), however, V(IV) was also successfully detected (0.9 - 1.9 nmol/kg). Coastal seawater close to the river mouth contains highest V(V) and V(IV) concentrations. The ratios of V(V)/V(IV) of coastal seawater have larger variations with water depth relative to the rather constant ratios from the other sampling locations.

Despite low oxygen concentrations down to 25 $\mu\text{mol/kg}$ in the upper 500 m water depth, the ratios of V(V)/V(IV) from the shallower region including the oxygen minimum zone do not show any correlation with the dissolved oxygen concentration. However, the V(V)/V(IV) ratios from the deeper layers in coastal seawater (500 - 2500 m water depth) showed a positive correlation with the dissolved oxygen concentration. This suggests that the behavior of vanadium redox species in the shallower region may be influenced by more complex biogeochemical interactions.

Kurahashi et al. (2024), *Deep-Sea Research I*, **206**, 104261.