

Iron redox cycling and subsurface offshore transport in the eastern tropical South Pacific oxygen minimum zone

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Iron (Fe) is well known as an essential element involved in a number of biochemical processes in the ocean such as nitrogen metabolism. The distribution of dissolved Fe in seawater depends on the nature and magnitude of the sources and sinks, and the transport mechanisms. The thermodynamically favored oxidation state of Fe, Fe(III), is strongly hydrolyzed and its removal is mainly constrained by the formation of strong complexes with natural organic ligands such as humic substances and siderophores. These organic ligands control not only the solubility of dissolved Fe in seawater, but also the bioavailability of Fe(III) for phytoplankton. Fe(III) in seawater can be reduced to Fe(II), which is more soluble and kinetically labile, although is rapidly oxidized in the oxygenated seawater. Recent studies have suggested that dissolved Fe(II) substantially exists in surface seawater (e.g., Hansard et al., 2009), suboxic layers in oxygen minimum zones (OMZs) (e.g., Kondo and Moffett, 2013), hypoxic shelf waters and sediments (Lohan and Bruland, 2007), hydrothermal vents and shallow submarine eruption (Santana-Casiano et al., 2013). Since Fe(II) is more bioavailable than Fe(III), the existence of Fe(II) could provide a big advantage for the organisms in these environments even though it is ephemeral. These results suggest the importance to investigate chemical and redox speciations of Fe to elucidate carbon and nitrogen cycles in the ocean.

The distribution of dissolved Fe, Fe(II) and Fe(III)-binding organic ligands were investigated in the upper 1000 meters of the eastern tropical South Pacific from January to March 2010, during El Nino event. Dissolved Fe concentrations were exceedingly low in surface waters, showed minima near chlorophyll maximum, and increased below that depth. While high rates of nitrogen fixation have been inferred for this region from models, our data suggest that surface Fe is much too low to support diazotrophs. Dissolved Fe and organic Fe(III) ligands concentrations at mid-depth were elevated in the nearshore stations, where virtually all dissolved Fe(III) was bound to these ligands. Maxima in the concentration of Fe(II) were seen in the oxygen-deficient and high-nitrite layers of the OMZ. Fully 8 to 68% of dissolved Fe existed as Fe(II) in the samples collected at these depths. Dissolved Fe concentration was higher in the OMZ where Fe(II) and nitrite were present. We propose that this region, the most reducing part of the OMZ, plays an important role in subsurface, offshore Fe transport.

Keywords: iron, Fe(II), oxygen minimum zone, eastern tropical South Pacific, organic ligand