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

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ABSTRACT

The distributions of dissolved iron (Fe), Fe(II) and Fe(III)-binding organic ligands were investigated in the upper 1000 m of the eastern tropical South Pacific from January to March 2010, during an El Niño event. Dissolved Fe concentrations were exceedingly low in surface waters, showed minima near the chlorophyll maxima, and increased below that depth. High rates of nitrogen fixation have been inferred for this region from models, but our data suggest that surface Fe is frequently too low to support diazotrophs. Dissolved Fe and organic Fe(III) ligand concentrations at mid-depth were elevated in the nearshore stations, where virtually all dissolved Fe(III) was bound to these ligands. Subsurface Fe(II) maxima were observed in the secondary nitrite maxima of the oxygen minimum zone (OMZ), comprising 8 to 68% of dissolved Fe. Dissolved Fe concentrations displayed local maxima coinciding with the maxima in Fe(II) and nitrite. We propose that this zone, the most reducing part of the OMZ, plays an important role in Fe transport in the upper 400 m of the water column.

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1. Introduction

Iron (Fe) is well known as an essential element involved in a number of biochemical processes in the ocean including respiration, photosynthesis and nitrogen metabolism (e.g., Sunda et al., 1991). The distribution of dissolved Fe in seawater depends on the nature and magnitude of the sources and sinks, and in situ processes. 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, but also the bioavailability of Fe(III) for phytoplankton (e.g., Kondo et al., 2013). 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. Fe(II) has been reported in surface seawater (e.g., Roy et al., 2008; Hansard et al., 2009), anoxic layers in oxygen minimum zones (OMZs) (Hopkinson and Barbeau, 2007; Moffett et al., 2007; Kondo and Moffett, 2013), hypoxic shelf waters and sediments (Lohan and Bruland, 2008), hydrothermal vents and shallow submarine eruptions (Santana-Casiano et al., 2013). Since Fe(II) is more bioavailable than Fe(III)-ligand complexes, the existence of Fe(II) has important implications in waters where Fe may become a limiting element. This includes OMZs, where the processes of denitrification and anammox have high

Fe requirements (Granger and Ward, 2003; van de Vossenberg et al., 2013).

While dissolved Fe concentration has been measured throughout the oceans, there are few data for the eastern tropical South Pacific (ETSP). The ETSP is considered to be one of the lowest dust deposition areas in the world ocean (Mahowald et al., 1999; Moore et al., 2002; Jickells et al., 2005), and the concentration of dissolved Fe ([D-Fe]) in the upper 400 m in the ETSP is low (Blain et al., 2008). The region also contains one of the world's most extended and intense oceanic OMZs where there is active removal of fixed nitrogen by denitrification and anammox (Ward, 2013). The reducing conditions within the OMZ influence Fe geochemistry. Reducing conditions over the Peruvian shelf result in [D-Fe] as high as 50 nM (Bruland et al., 2005) which is predominantly Fe(II) (Hong and Kester, 1986; Vedamati et al., 2014). Nevertheless, Fe decreases dramatically over the shelf-slope break (Vedamati et al., 2014) and it has been suggested that primary production is Fe-limited (Hutchins et al., 2002; Eldridge et al., 2004).

Recent Fe(II) studies in the OMZs have reported Fe(II) maxima in the anoxic waters of the OMZs (Hopkinson and Barbeau 2007; Moffett et al., 2007; Kondo and Moffett 2013). The Fe(II) feature is surprising because Fe(II) is thermodynamically unstable in the presence of nitrate and nitrite, even in the absence of oxygen. Moreover, nitrate and nitrite can oxidize Fe(II) chemoautotrophically (Straub et al., 1996). Witter et al. (2000) and Hopkinson and Barbeau (2007) showed that Fe(III) is complexed by strong organic ligands that exist in the Arabian Sea and eastern tropical North Pacific, respectively, further shifting redox equilibria away from Fe(II).

Previous studies off Peru have reported detectable Fe(II) at the west-ernmost stations of their cruise tracks (Hong and Kester, 1986; Vedamati et al., 2014). This is the first study to track the Fe(II) feature westward to its disappearance. In this study, Fe(II) measurements were made on two zonal transects at 10°S and 20°S from 80°W to 100°W in March 2010. The objective was to determine how far the Fe(II) feature extends and to obtain more information about its role in the transport of Fe from the eastern boundary to the ocean interior in the Pacific Ocean.

2. Methods

2.1. Study area and sampling collection

Seawater samples were collected in the ETSP during the R.V. *Atlantis* AT-15-61 cruise from 29 January to 3 March in 2010 (Fig. 1) when it was under an El Niño event (Dekaezemacker et al., 2013). The El Niño-Southern Oscillation (ENSO) subjects the ETSP to interannual climate variability, which controls the strength of the upwelling and modifies the biogeochemical functioning of this ecosystem. During El Niño events, marine productivity usually decreases because of the weaker upwelling of nutrient-rich waters. Seawater samples were obtained using acid-cleaned Teflon-coated 5-L external-spring "Niskin-like" bottles (Ocean Test Equipment) mounted on a trace metal clean rosette (Sea-Bird Electronics). Sub-sampling from the Niskin-like bottles was performed under nitrogen pressure inside a laminar-flow clean van immediately after recovery. All plastic apparatus used in this study were acid-cleaned. Filtered seawater samples (<0.2 μm, Acropack, Gelman) for dissolved Fe(II) analysis were collected in 35-mL Teflon bottles (Nalgene). Samples for total dissolved Fe analysis were stored in 250-mL low density polyethylene (LDPE, Nalgene) bottles, and those for Fe(III) speciation were stored in 500-mL fluorinated polyethylene (Nalgene) bottles. Measurement of dissolved Fe(II) was conducted shortly after Niskin-like bottle recovery to minimize the potential oxidation, finishing within 2 min of subsampling. Seawater samples for total dissolved Fe analyses were acidified to pH < 2 with trace-metal-grade HCl (Optima, Fisher Chemical) and stored at room temperature for at least half year. Seawater samples for Fe(III) speciation were stored at −20 °C immediately after sampling. These samples were kept frozen until just before analysis.

2.2. Total dissolved Fe analysis

The concentration of total dissolved Fe ([D-Fe]) was determined using a single batch nitrilotriacetic acid (NTA) resin extraction and isotope dilution inductively coupled plasma mass spectrometry (ICP-
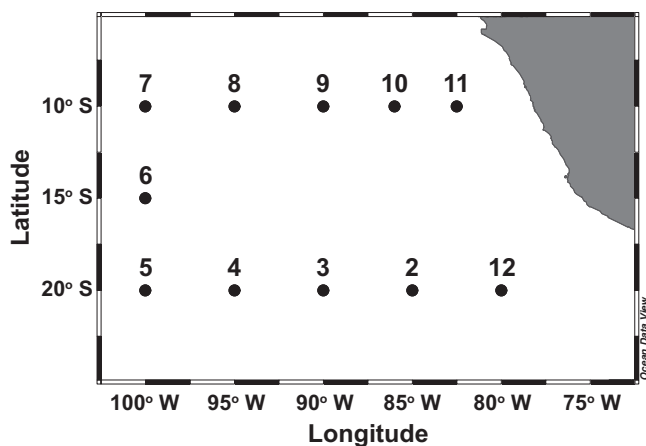

Fig. 1. Map of the cruise track in the eastern tropical South Pacific from 29 January to 03 March 2010 aboard the *R/V Atlantis*.

MS) method adapted from Lee et al. (2011) with a Thermo Element 2 Mass Spectrometer coupled to an APEX desolvation system (ESI). All reagent and sample preparations were carried out in a Class 100 clean laminar flow bench or recirculating fume hood in a positive pressure clean lab. The 15 mL polypropylene centrifuge tubes (VWR) used for the sample preparation were cleaned with HCl (both reagent grade and trace metal grade).

NTA Superflow resin (Qiagen Inc) used in this study comprises NTA covalently-bonded by a linker to Superflow chromatography matrix. The NTA resin was cleaned by multiple steps using trace metal grade HCl and HNO_3 (Optima, Fisher Chemical) in acid-cleaned polypropylene centrifuge tubes (Lee et al., 2011; Jacquot et al., 2013). The detail of its cleaning protocol in this study was described elsewhere (Jacquot et al., 2013). A 0.15 μM stable-isotope-enriched spike ^{57}Fe (BHD Arister Plus) was prepared in 5% HNO_3 (Optima, Fisher Chemical). Trace metal grade 1.5 M hydrogen peroxide (H_2O_2) (Optima, Fisher Chemical) was prepared in a LDPE bottle. An ammonium acetate buffer was prepared by combining 0.1 M trace metal grade NH_4OH (Optima, Fisher Chemical) and 0.1 M acetic acid (Optima, Fisher Chemical). Total dissolved copper (Cu) was also measured simultaneously with our method, the results have been reported in Jacquot et al. (2013).

Approximately 7.5 mL of seawater sample was poured to the centrifuge tube with the exact volume determined gravimetrically. A 50 μL aliquot of the 0.15 μM ^{57}Fe solution was spiked to the sample, which gave approximately 1 nM of ^{57}Fe (precise final concentration of ^{57}Fe in each sample was calculated using the exact volume of sample). Because Cu was measured simultaneously as well as Fe, the pH of the samples was then increased to ~3 with 1.5 mL of the ammonium acetate buffer (Jacquot et al., 2013). The 0.1 mL aliquot of 1.5 M H_2O_2 solution was added to each vial and left for 1 h at laboratory temperature in order to oxidize Fe^{2+} to Fe^{3+}. Approximately 800 beads of the NTA resin were then added to each sample, and the samples were placed on a shaker for 2 to 5 days at laboratory temperature. At the end of shaking period, the samples were centrifuged for 10 min at 4000 rpm, and supernatant seawater was carefully siphoned off to leave only the NTA resin beads at the bottom. The NTA resin beads were washed with ~3 mL Milli-Q water 3 times to remove salts. After the final Milli-Q wash, 1 mL of 5% trace metal grade HNO_3 was added to each tube, and the samples were placed on the shaker again for 1 to 2 days. The samples were centrifuged for 10 min at 4000 rpm just before the analyses. The isotope ratios of Fe ($^{57}Fe/^{56}Fe$) and Cu ($^{65}Cu/^{63}Cu$) were then determined on the instrument in medium resolution mode. Surface seawater obtained in the North Pacific during the 2009 U.S. GEOTRACES intercalibration cruise was used for the procedural seawater blanks. The procedural seawater blanks were prepared the same way using ~0.2 mL seawater instead of ~7.5 mL (Jacquot et al., 2013). All of the samples including procedural blank were prepared in triplicate. The detection limits for both Fe and Cu were 0.030 nM, and blanks were 0.055 nM and 0.030 nM, respectively. SAFe reference standards S1 and D1 (Johnson et al., 2007) were measured during the course of sample analysis. The results for the Fe with respect to S1 and D1 samples (consensus value: 0.093 ± 0.008 nM (S1), 0.67 ± 0.04 nM (D1)) were 0.081 ± 0.026 nM (n = 3) and 0.71 ± 0.006 nM (n = 3), respectively. The results are within the range of the latest consensus values (GEOTRACES website (2013): http://www.geotraces.org/science/intercalibration). The results for Cu were also within the range of the consensus values (Jacquot et al., 2013).

2.3. Dissolved Fe(II) analysis

The concentration of dissolved Fe(II) ([Fe(II)]) was determined on board by a luminol-based chemiluminescence method using a FeLume flow injection analysis system (Waterville Analytical) (King et al., 1995), as described in Kondo and Moffett (2013). The setup of the instrument was continuous mode which was similar to previous Fe(II)