Controls on seawater Fe(III) solubility in the Mauritanian upwelling zone

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[1] Iron solubility measurements in the Mauritanian upwelling and the adjacent Open Ocean of the Tropical Atlantic show for all stations lower values in the surface mixed layer than at depth below the pycnocline. We attribute this distribution to a combination of loss terms, chiefly photo-oxidation of organic ligands in the surface, and supply terms, predominantly from the release of ligands from the decomposition of organic matter. Significant correlations with pH, oxygen and phosphate for all samples below the surface mixed layer indicate that biogenic remineralisation of organic matter results in the release of iron binding ligands into the dissolved phase. The comparison of the \( \frac{c_{FeS}}{PO_4^-} \) ratio with other published data from intermediate and deep waters in the Pacific suggests an enhanced release of iron chelators in the more productive Mauritanian upwelling zone. Citation: Schlosser, C., and P. L. Croot (2009), Controls on seawater Fe(III) solubility in the Mauritanian upwelling zone, Geophys. Res. Lett., 36, L18606, doi:10.1029/2009GL038963.

1. Introduction

[2] Iron (Fe) is a micronutrient whose low availability in seawater restricts the growth of phytoplankton over broad swaths of the surface ocean [Boyd et al., 2000; Coale et al., 2004; Martin et al., 1994; Sato et al., 2007]. Fe in seawater exists in both dissolved (DFe < 0.2 \( \mu \)m) and particulate (PFe > 0.2 \( \mu \)m) phases, and it is believed that 99% of the dissolved Fe is organically complexed [Rue and Bruland, 1997]. The recent advent of microfiltration and ultrafiltration techniques has shown that the dissolved phase consists of both soluble (FeS < 0.02 \( \mu \)m) and colloidal (0.02 \( \mu \)m < FeC < 0.2 \( \mu \)m) fractions [Bergquist et al., 2007; Nishioka et al., 2005; Wu et al., 2001].

[3] Measurements of Fe solubility (cFeS) are performed by adding a saturating amount of Fe to seawater and then determining the concentration of the filtrate that has passed through a 0.02 \( \mu \)m, or smaller, filter. The pioneering works of Kuma et al. [1996] and Liu and Millero (2002), suggest that cFeS largely depends on temperature, pH, and ligand concentration, with higher concentrations of inorganic soluble Fe possible at lower pHs and temperatures. Fe solubility in both UV irradiated and artificial seawater (i.e., seawater containing no dissolved organic matter (DOM)) at 0.01 nmol L\(^{-1}\) between pH 7.5 and 9 has been shown to be lower than in untreated seawater (cFeS = 0.5 nmol L\(^{-1}\)) [Liu and Millero, 2002]. This difference can be explained by the existence of natural organic ligands [Kuma et al., 1996; Liu and Millero, 2002; Rue and Bruland, 1995], which enhance the Fe solubility in seawater by organic complexation.

[4] Concentrations of Fe binding ligands in surface seawater vary from region to region. Coastal seawater, related to its overall higher biological activity, has significantly higher ligand concentrations (7 to 70 nmol L\(^{-1}\) [Crook and Johansson, 2000]) than open ocean seawater (0.5 to 6 nmol L\(^{-1}\) [Crook et al., 2004a, 2004b; Powell and Donat, 2001]). A slight increase in Fe binding ligand concentrations with depth has also been seen in the Atlantic [Powell and Donat, 2001] and ascribed to the release of Fe binding organic ligands during the remineralization of settling organic matter.

[5] In other work cFeS is apparently correlated to concentrations of nutrients and humic-type fluorescent intensity (QSU, humic substances) [Tani et al., 2003; Takata et al., 2004]. Fe binding ligands could be released to seawater directly from phytoplankton when the cells are lysed [Gobler et al., 1997; Hutchins and Bruland, 1994], or indirectly by grazing [Sato et al., 2007]. In addition, Fe binding ligands are produced by bacteria [Martinez et al., 2000] in response to iron limitation. Fe-binding ligands may also be directly released to seawater by growing phytoplankton, which may often excrete dissolved organic matter (DOM, as waste product or intentional released), some of which may be able to bind Fe [Fuse et al., 1993].

[6] In an attempt to shed light on parameters influencing Fe solubility, which has implications for the bioavailability and transport of Fe in the surface ocean, we measured the solubility of Fe of seawater in a tropical upwelling zone to understand what processes were important in this region.

2. Methodology

2.1. Overview of the Study Site in the Mauritanian Upwelling Zone

[7] During springtime, when the trade winds blow from the northeast, the Mauritanian upwelling zone is marked by strong upwelling. In summer, however, the winds come more predominantly from the north and upwelling is confined closer to the coast. Our work was performed during Meteor cruise M68/3 in July 2006, when upwelling only occurred close to the coast.

2.2. Sampling of Subsurface Seawater

[8] Samples of seawater between 20 and 200 m were collected using trace metal clean GO-FLO bottles (General Oceanics, Miami, USA) deployed on a Kevlar line. The GO-FLO bottles were transferred into a class 100 clean container where all sample handling was performed. The

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collected seawater was filtered through a 0.2 μm membrane filter (Sartorius) under nitrogen overpressure (0.2–0.3 bar) into acid cleaned HDPE bottles (Nalgene).

2.3. Sample Treatment

Fe solubility measurements were performed immediately using the radioisotope, 55Fe (Hartmann Analytik, Braunschweig, Germany). The experimental setup (described below) was adapted from Kuma et al. [1996]. The 55Fe isotope had a specific activity of 157.6 MBq/mg Fe, a total activity of 75MBq, and was dissolved in 0.1 M HCl. 55Fe dilution standards were produced with Milli-Q (MQ) water and acidified with quartz distilled (QD) HCl to a pH below 2.

After the addition of 55Fe (t0 = 0h; total Fe, FeT = 20 nmol L⁻¹; pH 7.9; 20°C) to each sample, a small subsample was immediately filtered through a 0.02 μm Anotop syringe filter (Whatman) and acidified with (QD) HCl, to keep the Fe from adsorbing to the bottle walls [Schlosser and Croot, 2008]. Duplicates of the unfiltered and 0.02 μm filtered samples (400 μL) were transferred into 6 mL vials to which 4.5 mL of scintillation fluid (Lumagel Plus®) were then added. This procedure was repeated for subsamples taken at 3, 6, 24, 48 and 72h. Counts per minute of 55Fe were made in a scintillation counter (Packard, TriCarb 2900TR). This 55Fe technique was chosen to investigate the true capacity of seawater for soluble Fe.

The dissolved Fe concentration (DFe) (see auxiliary material) was measured onboard with the luminol chemiluminescence method [de Jong et al., 2000] in an online flow injection analysis (FIA) system. Macronutrient concentrations (nitrate, nitrite, phosphate and silicate) for each sample were measured on board with an auto-analyser flow injection analysis (FIA) system. The free pH of the samples was calculated using the CO2SYS software [Lewis and Wallace, 1998] (T. Steinhoff, personal communication, 2007).

3. Results

3.1. Iron Solubility

The solubility of Fe was lowest at the sites located furthest offshore (Station 258 and GO-FLO cast site 261; Figures 1 and 2). At these stations cFeS generally increased with depth from the minimum below around 40 m. The more shoreward casts (261, 284, 289, and 307) showed a Fe solubility minimum at 20 m (Figures 1 and 2). As with the offshore sites, Fe solubility at shoreward sites was highest at deeper depths below the pycnocline.

When the data are plotted together, they fall into two distinct groups (Figure 1). In the first group, that of samples taken from depths ≥40 m, values of cFeS are greater than 0.3 nM and show strong linear relationships with in situ pH (R² = 0.91), phosphate concentrations (R² = 0.77), and apparent oxygen utilization (AOU) (R² = 0.80). The shallower samples make up the second group, with values of cFeS that fall between 0.1 and 0.4 nmol L⁻¹ and do not sit on the trend lines.

3.2. Irradiance Attenuation Coefficient and Seawater Density

Light irradiance data (irradiance attenuation coefficient (PAR), Kd) are available for three locations (272, 284, and 307) (Figure 2). These data indicate the location of particle maxima in seawater and can be used as an indicator for the potential loss of organic ligands by adsorption onto particle surfaces [Campbell et al., 1997]. If adsorption onto particles is the reason for the lower Fe solubility in surface waters, increases in particle abundances as shown by Kd should be associated with decreases in cFeS. However, this was not observed at all three stations, suggesting that removal of ligands by particle scavenging is not the main parameter controlling cFeS and it is likely that photooxidation of organic ligands [Barbeau et al., 2003] and humic substances [Chen and Bada, 1992] is responsible for the lower cFeS values in these surface waters.

A distinct minimum in Fe solubility at 40 m at the Open Ocean stations 258 and 261 (Figure 2) was not
elements necessary for growth. The production/release of specific organic ligands (e.g., siderophores) by bacteria, however, is inhibited if cells are Fe-sufficient [Martínez et al., 2003]. At all the stations in the Mauritian upwelling zone higher dissolved Fe concentrations at depth (0.5–1.25 nmol L\(^{-1}\)) than in the surface (0.3–0.4 nmol L\(^{-1}\)) were observed. These dissolved Fe concentrations could be considered for many oceanic bacteria and phytoplankton Fe sufficient and suppressive of siderophore production particularly in light of the high aerosol Fe deposition rates and fast Fe turnover time in this region [Crook et al., 2004a, 2004b].

[19] Alternatively, the changes in Fe solubility may be associated with organic matter remineralisation [Kuma and Isoda, 2003; Tani et al., 2003], through a release of ligands and humic substances into the water [Chen et al., 2004]. DOM (including Fe-binding ligands) will be released directly into seawater from bacteria and phytoplankton cells following breakage of those cells via zooplankton grazing [Hutchins and Bruland, 1994], viral lysis [Gobler et al., 1997], or bacterial attack with ectoenzymes [Nagata et al., 1998]. Similarly, a rise in soluble ligand concentrations (and therefore Fe solubility) could be the result of production by heterotrophic bacteria obtaining their carbon via the oxidation of DOM but coming into Fe limitation. Thus the degradation of organic matter could see the production of siderophores in an effort to obtain Fe to fuel their growth. Finally, binding sites on ligands in the colloidal [Boye et al., 2005] or particulate phases could be converted to the truly soluble phase. This is an important point as though there are few data for iron binding ligands in the soluble and colloidal portions of the dissolved phase, results suggest that the soluble fraction is significantly smaller than the colloidal [Boye et al., 2005; Schlosser and Croot, 2008]. Thus comparison between measurements of dissolved ligand concentrations and cFe\(_S\) are only indicative as most of the ligand is in the colloidal phase and not in the soluble phase which determines cFe\(_S\).

[20] That it is some process related to remineralisation controlling Fe solubility in the samples ≥ 40 m depth is strongly supported by the significant correlations between cFe\(_S\) and pH, phosphate, and AOU (Figure 1). Both the solubilization, via microbial ectoenzymes, of Fe-binding materials present in phytoplankton cells and the release of Fe-ligands by bacteria as they grow remain plausible explanations for the observed patterns in Fe solubility (Figures 1 and 2).

[21] The high correlation with phosphate also suggests a simple alternative hypothesis for Fe solubility that has been seemingly overlooked – simple inorganic complexation by phosphate. Currently the methods [Rue and Bruland, 1995] used to measure organic complexation do not consider phosphate complexation and strong phosphate complexation would be interpreted as being organic with present methods. Interestingly data from Khoe and Robins [1988] for Fe-phosphate complexes indicate that these complexes could be significant: Fe(PO\(_4\))\(_4\) (log K = 19.50) and Fe(HPO\(_4\))\(_3\) (log K = 9.30). However a closer look at the Khoe and Robins [1988] study shows it was carried out at pH 2 (3 M NaNO\(_3\)) and there is no available data at seawater pH that would help to explain our correlation between phosphate and cFe\(_S\). For the sake of examination,
the stability coefficients of the Fe-phosphate complexes from Khoe and Robins [1988] were used to calculate the Fe solubility at our sampling sites with respect to phosphate species, pH, and temperature (Figure 1.). The dashed blue line in Figure 1 shows the solubility of Fe for phosphate-complexed and inorganic Fe species together. The closeness of the theoretical curve to the data suggests that the higher Fe solubility in the deeper samples could potentially be caused by complexation with phosphate or the formation of a meta-stable ferric phosphate phase. However correlation is not causation and solubility experiments in our lab with UV irradiated high phosphate Southern Ocean waters indicates much lower solubilities in agreement with only hydroxide irradiated high phosphate Southern Ocean waters indicates not causation and solubility experiments in our lab with UV 

4. Conclusions

In the Mauritanian upwelling zone, Fe solubility was lower in the upper mixed layer (20 m) than directly below the pycnocline (40–80 m). The lower Fe solubility in the surface appears to be tied to the phototioxidation of organic ligands. A significant correlation of pH, oxygen, and phosphate with cFeS of subsurface samples strongly suggests the conversion of POM to soluble organic Fe binding ligands. The exact mechanism of this process, be it via grazing or bacterial degradation is unclear at present and the further investigation of this pathway and elucidation of the mechanism and fluxes is clearly required if we are to truly understand what controls iron solubility in the ocean.

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