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

C. Schlosser[1] and P. L. Croot[1]

[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 cFe_S/PO_4^{3-} 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 μm) and particulate (PFe > 0.2 μm) 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 (Fe_S < 0.02 μm) and colloidal (0.02 μm < Fe_C < 0.2 μm) fractions [*Bergquist et al.*, 2007; *Nishioka et al.*, 2005; *Wu et al.*, 2001].

[3] Measurements of Fe solubility (cFe_S) 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 μm, or smaller, filter. The pioneering works of *Kuma et al.* [1996] and *Liu and Millero* [2002], suggest that cFe_S 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 (cFe_S = 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} [*Croot and Johansson*, 2000]) than open ocean seawater (0.5 to 6 nmol L^{-1} [*Croot 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 cFe_S 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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[1]FB2 Marine Biogeochemistry, Leibniz-Institut für Meereswissenschaften, Kiel, Germany.
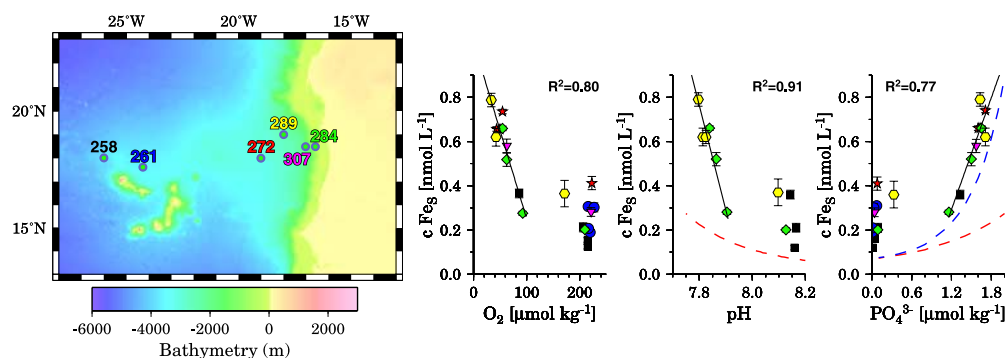
Figure 1. Shown are the sampling positions in the Mauritanian upwelling zone, combined with bathymetric data. Each sampling location has a different color on the diagrams. All subsurface samples ($\geq$40 m) from the onshore casts show a linear correlation of cFe_S with O_2, pH and PO_4^{3-}. The dashed red lines illustrate the capacity of seawater for the inorganic soluble Fe species. The dashed blue line indicates the capacity of seawater for the inorganic and phosphate complexed Fe species.

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

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

[10] After the addition of ^{55}Fe (t_0 = 0h; total Fe, Fe_T = 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 ^{55}Fe were made in a scintillation counter (Packard, Tri-Carb 2900TR). This ^{55}Fe technique was chosen to investigate the true capacity of seawater for soluble Fe.

[11] The dissolved Fe concentration (DFe) (see auxiliary material[1]) 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 following the methods outlined by *Grasshoff et al.* [1999]. Dissolved oxygen (O_2) was also measured on board via classic Winkler titration. Chlorophyll a concentrations were measured via high performance liquid chromatography (HPLC) [*Hoffmann et al.*, 2006]. 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

[12] 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 cFe_S 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.

[13] When the data are plotted together, they fall into two distinct groups (Figure 1). In the first group, that of samples taken from depths $\geq$40 m, values of cFe_S are greater than 0.3 nM and show strong linear relationships with *in situ* pH (R^2 = 0.91), phosphate concentrations (R^2 = 0.77), and apparent oxygen utilization (AOU) (R^2 = 0.80). The shallower samples make up the second group, with values of cFe_S 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

[14] Light irradiance data (irradiance attenuation coefficient (PAR), K_d) 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 K_d should be associated with decreases in cFe_S. However, this was not observed at all three stations, suggesting that removal of ligands by particle scavenging is not the main parameter controlling cFe_S 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 cFe_S values in these surface waters.

[15] A distinct minimum in Fe solubility at 40 m at the Open Ocean stations 258 and 261 (Figure 2) was not
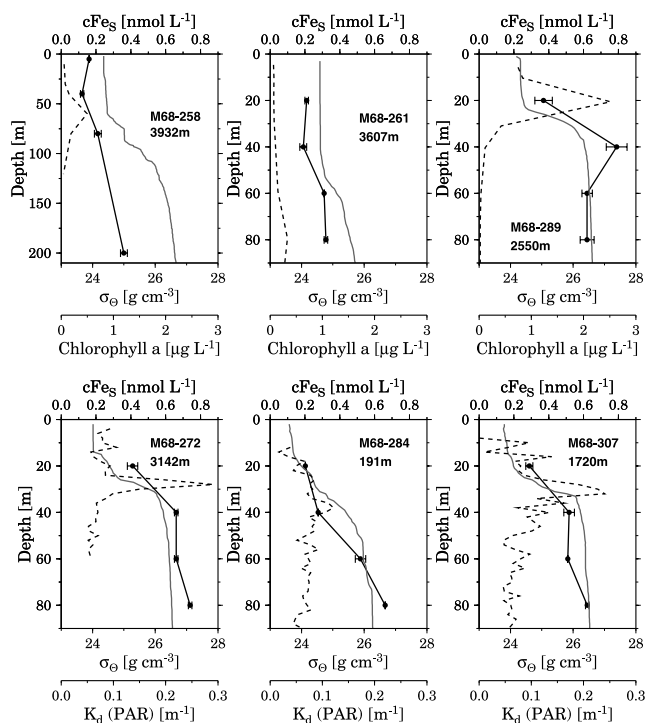
Figure 2. Shown are the results of cFe_S (black squares), density (σ_θ, solid grey line), chlorophyll a (dashed black line, upper diagrams) and irradiance attenuation coefficient (PAR), K_d (dashed black line, lower diagrams) versus water depth. Note that the top left plot uses a different depth scale.

apparently related to any other measured parameter (chlorophyll a, density (σ_θ), etc.). It appears that this minima represents a region where processes that remove Fe ligands dominates over production terms and it is intriguing that it is immediately above the deep chlorophyll maximums that are found in these oligotrophic waters.

[16] Seawater density (σ_θ) shows a strong positive correlation with cFe_S (Figure 2). This suggests that the pycnocline acts as a strict barrier at these sampling locations, between primary production, above, and remineralisation of biomass, below.

3.3. Nutrient Regeneration and Relationship to cFe_S

[17] The simplest possible explanation for the increasing Fe solubility at greater depths and lower pHs is that the solubility of inorganic Fe is higher at lower pHs. It should also be remembered here that our experiments were all conducted at 20°C and thus the solubility is not dependent on the *in situ* temperature that the samples were collected from. The expected solubility of inorganic Fe (where $Fe' = Fe(OH)^{2+} + Fe(OH)_2^+ + Fe(OH)_3 + Fe(OH)_4^-$) can be calculated using the equations of *Liu and Millero* [1999] and is shown by the dashed red line in Figure 1. It is clear in Figure 1. that inorganic solubility is insufficient to account for the high Fe solubility at deeper depths, nor the lower levels of Fe solubility in the near surface, and thus organic complexation is required.

[18] Iron complexing ligands are known to be produced by bacteria or phytoplankton, and released to the environment as metabolites or in a strategy for obtaining trace

elements necessary for growth. The production/release of specific organic ligands (e.g., siderophores) by bacteria, however, is inhibited if cells are Fe-sufficient [*Martinez et al.*, 2003]. At all the stations in the Mauritanian 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 [*Croot 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: $Fe(PO)_4$ (log K = 19.50) and $Fe(HPO)_4^+$ (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,

Table 1. cFe_S/PO_4^{3-} Ratios of This and Reference Studies

Location	Filtration [μm]	cFe_S/PO_4^{3-} ratio [$\times 10^{-3}$]	Reference
Mauritanian upwelling zone	0.02	0.682 ± 0.094	This study
Western North Pacific Ocean	0.025	0.143 ± 0.026	[Kuma and Isoda, 2003]
Eastern Indian Ocean	0.025	0.076 ± 0.013	
Subarctic WN Pacific Ocean	0.025	0.220 ± 0.029	[Tani et al., 2003]
Subtropical WN Pacific Ocean	0.025	0.181 ± 0.012	
Boundary Zone	0.025	0.230 ± 0.026	
Okhotsk Sea	0.025	0.352 ± 0.041	
Okhotsk Sea	0.025	0.292 ± 0.026	
NWN Pacific Ocean	0.025	0.377 ± 0.035	
NWN Pacific Ocean	0.025	0.343 ± 0.024	

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 complexation, seemingly ruling out phosphate as an important complexing agent. Though, the match is striking enough to warrant further study of phosphate-Fe species complexes with a view to assessing their contribution to Fe solubility in deeper waters.

3.4. Ratio of cFe_S/PO_4^{3-}

[22] The cFe_S/PO_4^{3-} ratio in the Mauritanian upwelling zone, calculated from the linear part of the cFe_S and phosphate diagram (i.e., essentially the nutricline) is $2-9$ fold higher than in studies carried out in the Pacific and Indian Ocean [*Kuma et al.*, 1996] (Table 1). However, in these previous studies cFe_S/PO_4^{3-} ratios were estimated for deep water masses (i.e., between 80 and 800 m) whereas the Mauritanian samples come from the upper 80 m of the water column. The higher Fe solubility with respect to phosphate concentrations in our shallower samples are more likely from the presence of fresher, more labile dissolved organic matter released in the more productive Mauritanian upwelling zone, than in deeper waters, below 100 m.

4. Conclusions

[23] 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 photooxidation of organic ligands. A significant correlation of pH, oxygen, and phosphate with cFe_S 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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P. L. Croot and C. Schlosser, FB2 Marine Biogeochemistry, Leibniz-Institut für Meereswissenschaften, Dienstgebäude Westufer, Düsternbroo-ker Weg 20, D-24105 Kiel, Germany. (cschlosser@ifm-geomar.de)