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Evidence for regulation of Fe(II) oxidation by organic complexing ligands in the Eastern Subarctic Pacific

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ABSTRACT

Redox cycling of iron in natural seawater is an important process that can affect iron availability to marine phytoplankton. In this work, luminol chemiluminescence was used to measure picomolar Fe(II) oxidation rate constants in continental shelf waters and oceanic surface (upper 200 m) waters of the iron-limited eastern subarctic Pacific. In both cases, Fe(II) oxidation rate constants were faster within the chlorophyll maximum than in UV oxidized seawater (UVOS), while rate constants were comparable to UVOS rate constants in waters from below the mixed layer. The larger Fe(II) oxidation rate constants in surface waters converged with UVOS rate constants upon stepwise additions of either Fe(II) or Fe(III), while Fe titrations did not affect Fe(II) oxidation rate constants in waters from below the mixed layer. Direct measurements of hydrogen peroxide, a common Fe(II) oxidant in surface waters, do not explain the high Fe(II) oxidation rate constants. We hypothesize that excess concentrations of strong Fe(III)-complexing organic ligands measured in surface seawater increase Fe(II) oxidation, and that titration of these ligands with added Fe explains the observed slowing of Fe(II) oxidation rates. Given that Fe(III)-complexing ligands are found in both surface and deep waters, and higher Fe(II) oxidation rate constants were measured only near the chlorophyll maximum, we suggest that the chemical nature and perhaps origin of natural Fe(III)-complexing organic ligands differ between in surface and deep waters.

1. Introduction

Marine primary production by phytoplankton is an important factor regulating net carbon dioxide flux across the air-sea interface, and thus affects atmospheric CO_2 concentrations. It now is well established that phytoplankton production is limited by the trace element iron in up to 40% of the world's ocean, including the subarctic Pacific, equatorial Pacific, and Southern Ocean, even though total dissolved iron concentrations in these surface waters (~50–100 pM Fe) in principle are sufficient to support a diatom bloom (Wells, 2003; and references therein). The bulk of dissolved Fe appears then to be poorly available to at least diatoms and other large eukaryotic phytoplankton. We still lack fundamental insights into the control and dynamics of the chemical speciation of iron in seawater, and how these restrict or enhance iron availability to marine phytoplankton.

It is known that the marine chemistry of Fe, at equilibrium, is controlled by strong organic Fe(III) chelators (Gledhill and Van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995) but there is a growing body of evidence that Fe speciation in surface seawater deviates from equilibrium conditions, with Fe(II) becoming quantitatively significant in oceanic surface waters (Hansard et al., 2009; Johnson et al., 1994; Rose and Waite, 2003b; Roy et al., 2008). These dynamics are important because Fe uptake models for marine phytoplankton predict that Fe(II) is a biologically active species (Salmon et al., 2006; Shaked et al., 2005). However, our ability to explain Fe acquisition by marine eukaryotic phytoplankton is challenged by our lack of understanding of Fe redox dynamics in seawater.

Fe(II) is generated photochemically in surface waters either by direct photolysis of organic complexes and colloids (Barbeau et al., 2001; Wells et al., 1991), or indirectly through reduction by photoproduced superoxide (Rose et al., 2005a; Rose and Waite, 2005; Voelker and Sedlak, 1995). Based on the action spectra of these photochemical reactions, Fe(II) can be produced deep in the photic zone (Laglera and Van den Berg, 2007; Wells et al., 1991). In addition to photochemical production, Fe(II) is thought to be generated through biological processes, by released superoxide (Kustka et al., 2005; Rose et al., 2005b) cell surface reductases (Maldonado and Price, 2001; Wells et al., 2005), and thermal reduction of organically complexed Fe(III) (Hansard et al., 2009). Once formed, the ephemeral Fe(II) is reoxidized inorganically in oxic seawater by the four-step Haber-Weiss process:

$$Fe(II) + O_2 \rightarrow Fe(III) + O_2^{\bullet -} \quad (1)$$

$$Fe(II) + O_2^{\bullet -} + 2H^+ \rightarrow Fe(III) + H_2O_2 \quad (2)$$

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$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH^{\bullet} \quad (3)$$

$$Fe(II) + OH^{\bullet} \rightarrow Fe(III) + OH^- \quad (4)$$

Superoxide and hydrogen peroxide can accumulate in the sample when Fe(II) is at high nanomolar and micromolar concentrations, producing a 4:1 product stoichiometry ($Fe:O_x$). But Fe(II) concentrations in most oceanic surface waters are too low to generate significant concentrations of O_2^-, and hydrogen peroxide (H_2O_2) concentrations also are low (<200 nM), so dissolved oxygen (O_2) becomes the dominant oxidant for Fe(II) (Santana-Casiano et al., 2006).

Past studies have shown that solution composition has a profound effect on Fe(II) oxidation rate constants (King, 1998; Millero, 1989; Santana-Casiano et al., 2005). The overall Fe(II) oxidation rate in seawater is well described as the sum of the product of distribution coefficients (α_i) and second order rate constants for each Fe(II) species (k_i).

$$\frac{dFe(II)}{dt} = -[Fe(II)][O_2]\sum_i \alpha_i k_i \quad (5)$$

Although the traditional assessment from these measurements is that Fe(II) is a transient species in seawater at pH 8.0 (King et al., 1995) this perception has been challenged recently, where oxidation kinetics have been slower than expected in some regions of the ocean (Croot et al., 2001; Croot and Laan, 2002; Hansard et al., 2009; Roy et al., 2008). Complexation by Fe(II) binding organic ligands has been proposed in some cases as an underlying mechanism for these lowered Fe(II) oxidation rates (Roy et al., 2008; Kieber et al., 2003).

While organic Fe(II) complexing ligands contribute to Fe redox dynamics in rainwater (Kieber et al., 2001, 2005; Willey et al., 2008) and freshwater (Emmenegger et al., 1998; Theis and Singer, 1974), their existence in seawater remains speculative. The potential effects of model organic ligands on Fe(II) oxidation rates have been demonstrated in well-defined laboratory conditions at high Fe(II) concentrations (Rose and Waite, 2003a; Santana-Casiano et al., 2000). But it is difficult to extrapolate these findings to natural waters where Fe(II) and ligand concentrations are orders of magnitude lower than tested in the laboratory.

Here we show evidence that Fe(II) oxidation rate constants in the eastern subarctic Pacific are markedly higher than rate constants measured in UV oxidized seawater near the chlorophyll maximum, and agree with model predictions below the surface mixed layer. The higher than expected Fe(II) oxidation rate constants converged with to rate constants measured in UV oxidized seawater with stepwise Fe additions. In this manuscript, we consider the possibility that these results are due to the influence of Fe(III) complexing ligands, which are found in ubiquitous excess in surface seawater.

2. Materials and methods

2.1. Sampling

Seawater samples were collected while underway during two cruises to the eastern subarctic Pacific Ocean on the R/V Thomas G. Thompson using a trace metal clean pumping and tow fish system described elsewhere (Roy et al., 2008). Samples for Fe(II) oxidation studies were collected at two stations: Ocean Station PAPA (50 °N 145 °W) on 13 Jun 2006 and 25 May 2007 (hereafter referred to as OSP 2006, OSP 2007) and from a continental shelf station north of Vancouver Island, British Columbia, Canada (51° 15.3′ N 129° 01.7′ W) on 14 May 2007 (hereafter referred to as Shelf 2007). On the 2006 cruise, all deep (>5 m) trace metal clean samples were collected by attaching the tow fish to a 150 m spool of 1 cm inner diameter acid-cleaned high density polyethylene (HDPE) tubing, lowering the fish to depth, and pumping the sample directly to a shipboard clean room. The tubing was allowed to flush for 25 min at each depth and the time delay between depth and the deckboard instrument was ~1.5 min. On the 2007 cruise, deep trace metal samples were collected using a 5 L, Teflon-coated Go Flo bottle (General Oceanics) on a Kevlar line, tripped using a Teflon messenger. Once back on deck, the Go Flo bottle was sampled under a high-efficiency particle air (HEPA) filter, inside the shipboard fabricated clean room. The time between closing the Go Flo bottle and sample introduction to the instrument was slightly longer (≤3 min.) for deeper samples using this approach. Samples for oxidation studies were filtered through a 0.2 μm polyethersulfone capsule (PCI Membrane Systems, Inc.) or 0.45 μm Teflon capsule filters (Sterlitech — Go Flo samples) at low pressure (<70 kPa) and collected in rigorously cleaned fluorinated polyethylene (FPE) bottles. Additional filtered and unfiltered samples were pulled from the Go Flo bottle for later Fe(II) oxidation studies, that probe the effect of sample filtration. Samples for H_2O_2 analysis were collected in black HDPE bottles from Niskin bottles on the sampling rosette.

2.1.1. Reagents

All solutions were prepared using >18 MΩ water from a Barnstead Nanopure Diamond Lab Water System. Chemicals were purchased immediately prior to each cruise and used as received; luminol (5-Amino-2,3-dihydro-1,4-phthalazinedione) (Fluka), ferrous ammonium sulfate hexahydrate, ferric iron atomic absorption standard, potassium carbonate, and sodium sulfite were purchased from Sigma. Catalase, concentrated hydrochloric acid (Optima), ammonia (Optima), and glacial acetic acid (Optima) were purchased from Fisher. Acridinium ester was a gift from D. Whitney King. The luminol reagent and carrier solutions for Fe analysis are described elsewhere (Roy et al., 2008) and were stored in acid-cleaned HDPE bottles. The reagents for H_2O_2 analysis by acridinium ester chemiluminescence were prepared according to Miller et al. (2005) and stored in black HDPE bottles.

2.2. Flow injection analysis for total dissolved Fe, Fe(II), and H_2O_2

An automated flow injection-based FeLume system (Waterville Analytical) was used for analysis of Total Dissolved Fe, Fe(II), and H_2O_2 . The optimized analytical methods and steps taken to minimize contamination for Fe(II) are described elsewhere in detail (King et al., 1995; Roy et al., 2008), and for H_2O_2 (Miller et al., 2005). Total dissolved Fe was measured by reducing all Fe to Fe(II) in filtered seawater samples using sulfite prior to chemiluminescent detection (Lannuzel et al., 2006). We also found that the reproducibility of the reduction step was improved by first removing oxygen from the Total Fe samples by bubbling with nitrogen for 30 min prior to adding the reducing agent. For all reaction chemistries, a seawater sample mixes with a chemiluminescent reagent (luminol for Total Dissolved Fe and Fe(II), acridium ester for H_2O_2) in a reaction spiral seated beneath a photomultiplier tube (PMT). The FIA system, reagents, and samples to be analyzed were kept in a separate HEPA-filtered air bench surrounded by a heavy black plastic curtain to minimize light interference with the analyses. Detection limits (3 standard deviations of Chelex-treated seawater blank solutions) for Fe(II) ranged between 3 and 11 pM , 8–22 pM for Total Dissolved Fe, and between 2 and 4 nM for H_2O_2.

2.3. Fe(II) oxidation experiments

The FeLume system was adapted to determine apparent Fe(II) oxidation rate constants by bypassing the injection valve, thereby allowing a continuous stream of sample and luminol through the plexiglas reaction coil. Plumbed in this way, the system enabled uninterrupted measurement of Fe(II) over time. All samples (both filtered and unfiltered) used in the Fe(II) oxidation studies were stored at room temperature in the dark for 24 h to allow for complete decay of any Fe(II), O_2^-, and other radicals present at the time of sample