Dissolved iron(II) in the Pacific Ocean: Measurements from the PO2 and P16N CLIVAR/CO$_2$ repeat hydrography expeditions

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ABSTRACT

The redox speciation of dissolved iron in seawater was evaluated at 121 locations in the Pacific Ocean at depths of 15-1000 m, using the method of luminol chemiluminescence. The results indicate that reduced iron, Fe(II), is ubiquitous in surface seawater with a relatively consistent pattern of occurrence. Surface maxima were present in most profiles, with median concentrations of 25-30 pM representing 12-14% of the total dissolved iron. Concentrations decreased monotonically with depth to < 12 pM within the upper euphotic zone. This pattern was observed during both day and nighttime sampling events, which suggests that non-photochemical production mechanisms can produce photochemical-like signatures. Further, if theoretical rates of Fe(II) oxidation are applicable to the open ocean, then the employed sampling methods precluded assessment of photochemically-produced Fe(II), regardless of ambient light conditions. For this and other reasons, the concentrations reported here for the upper water column likely represent lower limits of labile iron concentration, and suggest that dissolved iron may be more available for uptake than previously believed. Deeper in the water column, Fe(II) was also frequently detected, though it constituted a small fraction of the total dissolved iron. Possible source mechanisms at these depths include thermal (dark) reduction of Fe(III) organic complexes or remineralization of sinking biogenic particles containing Fe(II). In the northern Philippine Sea between the Japanese coast and the Izu-Bonin volcanic arc system, Fe(II) concentrations were found to be atypically high, possibly because of high atmospheric dust deposition near the surface and transport of sediment-derived iron at depth.

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1. Introduction

Iron is an essential trace element for all organisms, yet its aqueous concentration in the modern open ocean is very low because of its low solubility with respect to oxyhydroxide precipitation and its strong tendency to adsorb to particle surfaces (Landing and Bruland, 1987;

Johnson et al., 1997; Waite, 2001). For this reason, it has been estimated that primary production is iron-limited in 15-40% of the world ocean (Martin et al., 1991; de Baar and de Jong, 2001). This discovery has led to research into the sources of iron to the open ocean, the chemical forms in which it occurs and is biologically utilized, and its potential role as a key determinant in global carbon cycling (Cooper et al., 1996).

The manner in and extent to which iron is partitioned into various chemical species are subjects of fundamental importance, as the distribution of these species may further limit or enhance its bioavailability. In particular,

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processes that maintain the pool of dissolved iron species are of special significance, because colloidal and particulate fractions are not thought to be directly available to marine phytoplankton (Rich and Morel, 1990). In seawater, iron has been observed to occur in two oxidation states, Fe(II) and Fe(III) (Waite and Morel, 1984a). In the presence of oxygen, Fe(III) is thermodynamically favored. However, the solubility of $Fe(OH)_3^\circ$, the hydrolysis species that is predicted to form under seawater conditions, is extremely low, resulting in an overall Fe(III) solubility of 0.2-0.4 nM (Liu and Millero, 2002). Several studies have now shown that most of the Fe(III) present in seawater is bound to organic ligands, which form strong complexes with Fe(III), thereby keeping it in solution (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther III, 1995). Though organic complexation serves to maintain the pool of dissolved iron, most research suggests that these organometallic complexes are not directly available to marine phytoplankton. Instead, uptake rates appear to be more closely related to the concentration of dissolved inorganic iron species (Anderson and Morel, 1982; Hudson and Morel, 1990; Sunda and Huntsman, 1995; Hutchins et al., 1999; Maldonado and Price, 1999). Thus, models of iron cycling and phytoplankton uptake usually invoke some mechanism by which the organometallic complex, Fe(III)-L, is dissociated prior to uptake, a process that nearly always involves the reduction of Fe(III) to Fe(II) (Rose and Waite, 2003; Shaked et al., 2005; Weber et al., 2005).

In contrast to Fe(III), Fe(II) is highly soluble and forms much weaker complexes with organic ligands. However, Fe(II) is unstable in oxic seawater, and will eventually be oxidized to Fe(III), the thermodynamically stable state. The oxidation rate of Fe(II) in seawater has been studied extensively (Millero et al., 1987; Millero and Sotolongo, 1989; King et al., 1995; King, 1998; King and Farlow, 2000; Gonzalez-Davila et al., 2005; Santana-Casiano et al., 2005), and has been shown to exhibit first-order oxidation kinetics with respect to dissolved oxygen and hydrogen peroxide (H_2O_2). In surface waters, both of these oxidants are present in significant quantities, as oxygen is typically high because of exchange with the atmosphere and H_2O_2 is produced *in situ* by biotic and photochemical processes. In deeper water, oxygen is depleted by the respiration of organic matter, and hydrogen peroxide concentrations are negligible (Yuan and Shiller, 2005). Consequently, Fe(II) oxidation rates in deep waters are predicted to be much slower than in surface waters.

The oxidation rate is also governed by factors that influence the relative distribution of Fe(II) species, as different species oxidize at different rates. In seawater, with relatively uniform ionic strength, the main determinants on Fe(II) speciation are pH and temperature. At high pH and temperature, equilibrium speciation models predict increased percentages of readily oxidizable hydroxo ($Fe(OH)^+$, $Fe(OH)_2^\circ$) and carbonato ($Fe(CO_3)^\circ$, $Fe(CO_3)_2^{2-}$) complexes (Millero et al., 1995; King and Farlow, 2000). Because both pH and temperature typically decrease with depth, an Fe(II) speciation gradient is predicted that favors rapid oxidation at the surface and slower oxidation at depth. Coupled with diminished

concentrations of oxidants, the half-life of Fe(II) in deep water can be on the order of several hours or days. Conversely, at the surface, in warm oxygenated seawater of pH > 8, with 100 nM H_2O_2, Fe(II) is predicted to have a half-life of 1-2 min (Gonzalez-Davila et al., 2005; Santana-Casiano et al., 2005; Trapp and Millero, 2007).

Several Fe(II)-producing mechanisms have been proposed and are reviewed by Sunda (2001). These include reduction of dissolved Fe(III) hydroxides by photochemically-produced superoxide (Voelker and Sedlak, 1995), direct photoreduction of dissolved Fe(III) hydroxide complexes (King et al., 1993), direct photoreduction of dissolved Fe(III) organic complexes (Kuma et al., 1992; Miller et al., 1995; Barbeau et al., 2001; Rijkenberg et al., 2006), photoreductive dissolution of colloidal and particulate Fe(III) (Rich and Morel, 1990; Wells et al., 1991), bioreduction of Fe(III)-L at cell surfaces (Maldonado and Price, 1999; Maldonado and Price, 2001), extracellular reduction of Fe(III)-L by biogenic superoxide (Kustka et al., 2005; Rose and Waite, 2005), viral lysis of cells (Gobler et al., 1997), grazing (Hutchins and Bruland, 1994), recycling of particulate organic matter containing Fe(II) (Moffett et al., 2007; Hopkinson and Barbeau, 2007), and microbial reduction in isolated suboxic and anoxic microenvironments, such as settling fecal pellets and aggregates (Alldredge and Cohen, 1987). In addition to *in situ* processes, Fe(II) can be physically transported elsewhere by advection and turbulent mixing. Aerosols contain photochemically-produced Fe(II) that can be readily solubilized upon deposition (Buck et al., 2006a). Fe(II) produced in sediments by anaerobic bacteria can be transported elsewhere by advective and diffusive processes (Elrod et al., 2004; Lohan and Bruland, 2008). Fe(II) can also be supplied to seawater via submarine groundwater discharge (Charette and Sholkovitz, 2003; Windom et al., 2006), and via hydrothermal activity (Coale et al., 1991; Chin et al., 1994; Statham et al., 2005).

All of these processes are potential sources of aqueous Fe(II). However, there are relatively few open-ocean measurements of Fe(II) available to support specific hypotheses of Fe cycling (Weber et al., 2005). This is due to the inherent difficulties of making shipboard measurements of "picomolar concentrations of ephemeral species" (Morel and Hering, 1993; Bruland and Rue, 2001). The few field studies conducted to date have been geographically restricted (O'Sullivan and Hanson, 1991; Bowie et al., 2002; Boye et al., 2006; Roy et al., 2008) or focused on unique environments, such as suboxic zones (Moffett et al., 2007; Hopkinson and Barbeau, 2007). In addition, many of the methods used to determine Fe(II) have not had sufficient analytical power to detect natural levels of Fe(II). This has led to an inconsistent set of observations, which in turn has resulted in widely different models of iron cycling, some that have incorporated redox transformations (Weber et al., 2005) and some that have not (Archer and Johnson, 2000). To gain more information regarding iron redox speciation in the open ocean, we conducted systematic surveys of open ocean Fe(II) along two Pacific Ocean transects. Here, oceanographic sections of Fe(II) are presented, both as absolute concentrations and as the relative fraction of total dissolved iron (Fe_{DISS}).