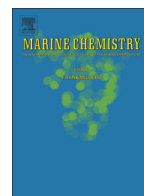




Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

The composition of dissolved iron in the dusty surface ocean: An exploration using size-fractionated iron-binding ligands

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ARTICLE INFO

Article history:

Received 16 June 2014

Received in revised form 27 August 2014

Accepted 1 September 2014

Available online xxx

Keywords:

Iron

Iron ligands

CLE-ACSV

Colloids

Ultrafiltration

Trace metals

GEOTRACES

North Atlantic Ocean

Chemical oceanography

ABSTRACT

The size partitioning of dissolved iron and organic iron-binding ligands into soluble and colloidal phases was investigated in the upper 150 m of two stations along the GA03 U.S. GEOTRACES North Atlantic transect. The size fractionation was completed using cross-flow filtration methods, followed by analysis by isotope dilution inductively-coupled plasma mass spectrometry (ID-ICP-MS) for iron and competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) for iron-binding ligands. On average, 80% of the 0.1–0.65 nM dissolved iron ($<0.2 \mu\text{m}$) was partitioned into the colloidal iron (cFe) size fraction ($10 \text{ kDa} < \text{cFe} < 0.2 \mu\text{m}$), as expected for areas of the ocean underlying a dust plume. The 1.3–2.0 nM strong organic iron-binding ligands, however, overwhelmingly (75–77%) fell into the soluble size fraction ($<10 \text{ kDa}$). As a result, modeling the dissolved iron size fractionation at equilibrium using the observed ligand partitioning did not accurately predict the iron partitioning into colloidal and soluble pools. This suggests that either a portion of colloidal ligands is missed by current electrochemical methods because they react with iron more slowly than the equilibration time of our CLE-ACSV method, or part of the observed colloidal iron is actually inorganic in composition and thus cannot be predicted by our model of unbound iron-binding ligands. This potentially contradicts the prevailing view that greater than >99% of dissolved iron in the ocean is organically complexed. Disentangling the chemical form of iron in the upper ocean has important implications for surface ocean biogeochemistry and may affect iron uptake by phytoplankton.

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1. Introduction

Since iron (Fe) is known to limit primary production in large portions of the global ocean (Boyd et al., 2007; Martin et al., 1994; Moore et al., 2002), much of the exploration of marine Fe biogeochemistry is focused on the association between Fe fluxes in the surface ocean and biological uptake of dissolved Fe by microorganisms. The utilization of Fe during photosynthesis, nitrogen fixation, and respiration (Morel et al., 2003; Sunda, 2012) unequivocally links Fe biogeochemistry to the global carbon cycle and ultimately climate. However the conversion efficiency of “new” dissolved Fe from lithogenic source to cell-assimilated form (Morel et al., 2008; Shaked et al., 2005) is ultimately controlled by the many elusive physicochemical forms that dissolved

Fe assumes. Processes such as scavenging/precipitation, Fe exchange, and photochemistry are sensitive to and responsible for controlling the physicochemical speciation of Fe, and thus both the chemical reactivity and fate of dissolved Fe are altered at each step along its transformation pathway.

Much has been learned about the physicochemical form of dissolved Fe over the last several decades. Dissolved Fe (dFe, here defined as $<0.2 \mu\text{m}$) has a broad size distribution composed of both “truly dissolved” soluble Fe (sFe $<10 \text{ kDa}$) and “very small particulate” colloidal Fe ($10 \text{ kDa} < \text{cFe} < 0.2 \mu\text{m}$) size fractions, with colloidal Fe contributing 0–90% of total dFe across the global ocean (Bergquist et al., 2007; Chever et al., 2010; Fitzsimmons and Boyle, 2014b; Fitzsimmons et al., in press; Nishioka et al., 2001; Ussher et al., 2010; Wu et al., 2001). Incubation studies have shown that while a limited number of cFe forms are highly bioavailable (such as exopolymeric saccharides, Hassler et al., 2011b), sFe is typically preferred and is taken into the cell much faster than cFe (Chen et al., 2003; Chen and Wang, 2001; Wang and Dei, 2003). Crystalline inorganic cFe (such as nanoparticulate Fe oxyhydroxide) is not directly available to marine phytoplankton at all (Rich and Morel, 1990; Wells et al., 1983), although freshly precipitated amorphous cFe

Abbreviations: cFe, colloidal iron ($10 \text{ kDa} < \text{cFe} < 0.2 \mu\text{m}$); CLE-ACSV, competitive ligand exchange adsorptive cathodic stripping voltammetry; CFF, cross flow filtration; dFe, dissolved iron ($<0.2 \mu\text{m}$); Fe, iron; ID-ICP-MS, isotope dilution inductively-coupled plasma mass spectrometry; sFe, soluble iron ($<10 \text{ kDa}$).

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<http://dx.doi.org/10.1016/j.marchem.2014.09.002>

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Please cite this article as: Fitzsimmons, J.N., et al., The composition of dissolved iron in the dusty surface ocean: An exploration using size-fractionated iron-binding ligands, Mar. Chem. (2014), <http://dx.doi.org/10.1016/j.marchem.2014.09.002>

nanoparticles have been found to be somewhat bioavailable to coastal species (Kuma and Matsunaga, 1995). In addition to this physical description of dFe speciation, studies using competitive ligand exchange electrochemical measurements have suggested that >99% of marine dFe, including both soluble and colloidal sized species, is complexed by organic ligands (Rue and Bruland, 1995; van den Berg, 1995; Wu and Luther, 1995). It is generally accepted that it is this binding of marine Fe by organic complexes that bolsters dFe concentrations above the ~0.1 nM inorganic solubility limits of organic-free seawater (Liu and Millero, 2002; Millero, 1998). While a few marine Fe-binding organic ligands have been identified as hydroxamate siderophores (Mawji et al., 2011; Velasquez et al., 2011; Vraspir and Butler, 2009), structurally characterized ligands only comprise a small percentage of the total dFe pool (<5%), and in general the identity of marine Fe-binding ligands is largely unknown (Gledhill and Buck, 2012).

However, the finding that nearly all marine dFe is organically bound is only an inference that relies on the assumption of thermodynamic equilibrium between dFe and dissolved Fe-binding ligands during electrochemical analysis and in the open ocean. Additionally, electrochemical characterization of Fe-binding ligands is somewhat limited, as only the Fe-binding ligands that are kinetically labile over the period of equilibrium with the added ligand can be detected, causing any refractory forms of dFe to be measured as a strong, Fe-bound ligand. In fact, Town and van Leeuwen (2005) asserted that kinetic limitation should prohibit many of the Fe-complexes detected by electrochemistry from being organic in composition, which precipitated an active debate on what is actually measured in competitive ligand exchange electrochemical measurements. Despite these shortcomings, electrochemical measurements are currently the predominant source of information on the chemical speciation of marine dFe, since almost no studies have conducted direct chemical speciation measurements, largely due to analytical hurdles. One analysis of colloidal Fe composition by energy dispersive spectroscopy showed that open ocean cFe is mostly organically bound (Wells and Goldberg, 1992), while in contrast a recent study using synchrotron technology demonstrated that a portion of the surface colloidal Fe underlying dust plumes in the Southern Ocean is inorganic, composed of tiny fragments of magnetite (von der Heyden et al., 2012). Thus, while the long-standing assumption is that the overwhelming majority of dFe is bound by strong organic Fe-binding ligands, there is a possibility that some dFe, especially in the colloidal phase, is inorganically bound (nanoparticulate). This might be especially true in regions where continental Fe sources are abundant, such as underlying dust plumes, downstream of hydrothermal vents, near the continental margin, and in regions containing glacial meltwater (Fitzsimmons et al., in press).

The chemical composition of dFe influences productivity the most in the upper ocean where phytoplankton are active, and simultaneously the surface ocean receives atmospheric dust deposition of Fe, arguably the most significant Fe input to the ocean (Jickells et al., 2005; Mahowald et al., 2005). The solubility of aerosol Fe is variable and depends on a suite of factors including aerosol composition, source (anthropogenic or crustal), and size, as well as seawater pH and Fe-binding ligand concentration (Baker and Croot, 2010). Studies of the size partitioning of dFe have consistently shown that in the surface ocean underlying dust plumes, dFe is predominantly colloidal in size (Berquist et al., 2007; Fitzsimmons and Boyle, 2014b; Fitzsimmons et al., in press; Ussher et al., 2010; Wu et al., 2001), while in the surface ocean of low-dust regions, the smaller soluble size fraction dominates the dFe pool (Boye et al., 2010; Chever et al., 2010; Nishioka et al., 2003; Wells, 2003). Colloidal Fe has also been shown to be the dominant Fe size fraction yielded in seawater leaches of natural dust (Aguilar-Islas and Mehalek, 2013; Aguilar-Islas et al., 2010).

These patterns raise two important questions: what is the physicochemical speciation of the abundant cFe in the surface ocean after recent dust deposition, and how much of this dust-derived cFe is bioavailable? It is possible for the dust-derived surface cFe maximum to have any of

three possible chemical compositions: Fe bound by colloidal-sized organic ligands after solubilization from dust, colloidal-sized fragments of dust that physically separated from aerosol particles upon impact with the surface ocean (resulting in an inorganic cFe composition of the same composition as the dust), or Fe that was initially solubilized from dust in the surface ocean but then re-precipitated *in situ* and aggregated to colloidal size (also resulting in an inorganic cFe composition, presumably amorphous Fe oxyhydroxides and mixed organic/inorganic precipitates). Each of these three Fe forms has a unique chemical lability and thus would have a different propensity for scavenging, aggregation, or biological uptake. Thus, the distinction between these physicochemical forms is at the crux of the problem linking dust deposition to biological uptake of dFe.

In this paper, we explore the physicochemical speciation of dFe in the upper 150 m of the high-dust North Atlantic Ocean where dFe falls predominantly into the colloidal size fraction, as is typical of dusty marine environments (Fitzsimmons et al., in press). Using an analysis of the Fe-binding ligand concentration and strength in both the soluble and dissolved Fe pools, we aim to consider whether there could be a natural inorganic component to the colloidal Fe pool of the surface ocean of this dusty environment, which could provide an exception to the prevailing view that >99.9% of dFe is believed to be bound by organic ligands.

2. Methods

2.1. Sample collection

Seawater samples from the upper 150 m of the ocean were collected from two stations on the U.S. GEOTRACES GA03 North Atlantic Zonal Transect 2011 cruise (Nov–Dec 2011): Station 10 at 31.933°N, 64.733°W near the Bermuda Atlantic Time Series (BATS) site and Station 23 at 18.39°N, 26.765°W near the Cape Verde Islands (Fig. 1). Hydrographic parameters defining these regions were measured using a Seabird SBE9 + CTD and an SBE43 dissolved oxygen sensor, which was calibrated by Winkler titrations (Langdon, 2010). Trace metal clean seawater was collected using the U.S. GEOTRACES GO-FLO rosette by the methods described in Cutter and Bruland (2012). Briefly, GO-FLO bottles were individually carried into an ISO 5-rated clean van, where the seawater was filtered through pre-cleaned 0.2 µm Pall Acropak-200™ Supor® capsule filters under ~0.4 atm of HEPA-filtered air. Surface samples were collected using the GeoFish system (Bruland et al., 2005), which employs all-perfluoroalkoxy alkane (PFA) tubing attached to a vane that coasted at ~3 m depth while suspended from a boom off the starboard side of the ship during forward ship motion of up to 12 knots. An all-PFA diaphragm pump drew clean seawater through this system at ~0.5 atm pressure, and filtration was completed first through a 0.45 µm Osmonics (Teflon™, MSI) filter and then through a 0.2 µm polycarbonate track etched filter mesh held in a polypropylene housing (Nuclepore™). Filtrates were taken into acid cleaned 4 L low density polyethylene (LDPE) bottles after three bottle rinses. Sub-samples of this 4 L were taken into 30 mL high density polyethylene (HDPE) bottles for Fe concentration analysis and into 500 mL fluorinated polyethylene (FLPE) bottles for the dFe-binding ligand analysis. LDPE and HDPE bottles were cleaned in 1 M reagent grade HCl, including an overnight heating to 60 °C, after which they were rinsed and filled with pH 2 ultrapure acid until use (Fitzsimmons and Boyle, 2012). FLPE bottles were cleaned in 3 M trace metal grade HCl for a month and then were conditioned with ultra clean Milli-Q water for more than a month prior to sample collection in order to remove all acid residues (Buck et al., 2012).

To collect the sFe fraction (< 10 kDa), the remainder of the 4 L filtrate was immediately ultrafiltered through an all-Teflon cross-flow filtration (CFF) system in static mode (CFF filter cleaning and ultrafiltration protocol described in detail in Fitzsimmons and Boyle, 2014a). Briefly, a Millipore Pellicon XL (PLCGC) 10 kDa regenerated cellulose CFF membrane was employed, and 300–350 mL of sample seawater was first

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