Both soluble and colloidal iron phases control dissolved iron variability in the tropical North Atlantic Ocean

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Abstract

The size partitioning of dissolved iron (dFe, <0.4 μm) into soluble (sFe, <0.02 μm) and colloidal (0.02 μm $<$ cFe < 0.4 μm) phases was investigated at seven stations in the tropical North Atlantic Ocean, and the results are compared to the dFe size fractionation study of Bergquist et al. (2007) in the same region. Downwind of the North African dust plumes, cFe comprised $80 \pm 7\%$ of the surface dFe pool at six stations, supporting the hypothesis that atmospherically-derived Fe is maintained in the colloidal size fraction. At the deep chlorophyll maximum, colloidal Fe had minimum concentrations or was completely absent, suggesting that cFe was either preferentially taken up by microbes and/or scavenged/aggregated at these depths. At remineralization depths, sFe was the dominant fraction both in the subtropical gyre-like stations (76% sFe; [sFe] $= 0.42 \pm 0.03$ nmol/kg) and in the oxygen minimum zone (56% sFe; [sFe] $= 0.65 \pm 0.03$ nmol/kg). Only at remineralization depths of stations with intermediate oxygen concentrations (100–110 μmol/kg) did colloidal Fe dominate (contributing 58% of dFe) , indicating that cFe may be serving as a conduit of dFe loss during mixing of high-Fe OMZ and low-Fe gyre waters. North Atlantic Deep Water (NADW) had a typical sFe concentration of 0.34 ± 0.05 nmol/kg. In the deepest samples composed of a NADW/Antarctic Bottom Water mixture where the bottom water may have attained a ~ 0.1 nmol/kg hydrothermal Fe input during transit past the Mid-Atlantic Ridge, sFe did not increase coincidentally with dFe, indicating that any potential hydrothermal Fe contribution was colloidal. In general, the results of this study counter the previous hypothesis of Bergquist et al. (2007) that the colloidal Fe fraction predominately controls dFe variability, instead suggesting that both soluble and colloidal Fe are variable, and both contribute to the observed dFe variability throughout the North Atlantic. The nearly 50–50% dFe partitioning into soluble and colloidal phases below the DCM suggest one of two partitioning mechanisms persists: (1) soluble and colloidal Fe exchange rates reach a "steady state," over which regional, uniquely-partitioned Fe sources can be overlain, or (2) the partitioning of Fe-binding ligands between the two size fractions is variable in the open ocean and directly controls dFe partitioning.
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1. INTRODUCTION

For decades an understanding of the limitation of marine primary productivity by the micronutrient iron (Fe;

Martin and Fitzwater, 1988; Morel et al., 2003) has been hampered by the scant knowledge of its global distribution. With the advent of the international GEOTRACES program, however, global transects of dissolved Fe (dFe) are being measured, and the new data will generate a much improved understanding of the sources and sinks of this important micronutrient. These developments will allow a shift in the objectives of trace metal research from establishing the distribution of trace metals to determining the processes that control those distributions. One such process, the transfer of metals from the dissolved pool into the

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sinking particulate pool ("scavenging"), is in particular need of illumination. Several metal loss mechanisms are encompassed by the term "scavenging," including adsorption/surface complexation, precipitation, and aggregation into successively larger particles, as well as microbiological uptake.

Colloids, the focus of this study, are an understudied physico-chemical group of compounds defined as particles so small that they are operationally included in the dissolved size fraction, but they retain their status as particles because they are physically distinct from the fluid via a surface boundary. Because of their diminutive size, colloids remain suspended until they aggregate to a size experiencing significant gravitational settling. Colloids thus serve the important role of transporting material between the dissolved and sinking particulate phases, thereby coupling two of the aforementioned "scavenging" processes: a rapid initial adsorption of dissolved metal onto colloidal/particulate material in solution, followed by a slow aggregation of the colloids into particulate material of filterable size (the Brownian-pumping model, Honeyman and Santschi, 1989). Additionally, while suspended, colloidal material can mediate chemical processes that further alter the bulk seawater solution including sorption of solutes, ligand exchange, surface redox reactions, and photochemical reactions.

For Fe, a hybrid-type element demonstrating both nutrient-type profile shapes as well as scavenged-type surface maxima and concentration loss along global thermohaline circulation (Bruland and Lohan, 2003), scavenging plays an important role in its marine biogeochemical cycle. Under oxic conditions, Fe(III) has a very low inorganic solubility in seawater (Millero, 1998). Instead, marine dissolved Fe is complexed by natural organic ligands that elevate dFe concentrations above the <0.1 nM solubility observed in UV-irradiated seawater (Kuma et al., 1996; Liu and Millero, 2002)., while excess Fe above these ligand concentrations is rapidly precipitated. Of this marine dFe, a large fraction, often 30–70% and as high as 90%, of the dissolved Fe in the ocean exists in the colloidal size fraction (Wu et al., 2001), which is operationally defined in this study as the dFe between 0.02 μm and 0.4 μm (cFe, "colloidal Fe", and "Fe colloids" will be used interchangeably in this paper; soluble Fe, sFe, is the Fe passing through a 0.02 μm filter; sFe + cFe = dFe). Thus, although dissolved Fe is classically envisioned as bound to soluble, siderophore-like organic ligands in seawater, a large portion of marine dFe is actually composed of tiny particles (colloids) that may have a different chemical composition and behavior than truly dissolved (soluble) Fe.

Using transmission electron microscopy imaging and energy dispersive spectroscopy composition analyses, it was concluded that colloidal Fe is organically bound in the open ocean (Wells and Goldberg, 1991, 1992). This is consistent with electrochemical measurements of Fe ligand concentration and binding strength that indicate that >99% of marine dFe, which contains the colloidal fraction, is bound by organic Fe-binding ligands (Rue and Bruland, 1995; Gledhill and Buck, 2012). However, due to their differences in size and chemical composition, soluble and colloidal Fe have unique behaviors that affect the Fe biogeochemical cycle in two ways. First, because soluble and colloidal Fe undergo different chemical transformations (sFe experiencing sorption and cFe experiencing aggregation), the two phases may have inherently different residence times. Thus, the measured size partitioning at any site could influence, for instance, whether new dFe sources escape abiotic scavenging long enough to be taken up by microbes, and consequently modelers must understand the size distribution of dFe in order to best predict dFe concentrations down current.

Second, and even more important to studies of micronutrient limitation, soluble and colloidal Fe may not be equally bioavailable. Laboratory experiments have conclusively shown that inorganic Fe colloids (here called nanoparticles) as small as 6–50 Fe atoms per colloid are not directly bioavailable to diatoms (Rich and Morel, 1990). However, since most marine colloidal Fe is thought to be organically bound, incubations using natural, organic-dominated colloidal Fe assemblages were also executed to reflect more realistic marine compounds, and the results indicated that natural colloidal Fe is only indirectly bioavailable, requiring first a dissociation from the colloid into the soluble phase before being taken into the cell. The smaller soluble Fe fraction, in contrast, was always taken up faster and is thus thought to be preferred (Chen and Wang, 2001). An assessment of the bioavailability of natural colloidal Fe is essential in order to ensure that nutrient limitation models do not underestimate the geographic extent of Fe limitation simply because they parameterize the bioavailable Fe pool as dFe instead of sFe.

In their Atlantic Ocean size partitioning study of dFe, Bergquist et al. (2007) concluded that much of the dFe variability in the tropical and subtropical Atlantic Ocean was due to a dynamic colloidal fraction, while the soluble Fe concentration remained relatively constant with depth. This highlighted the importance of studying dFe size partitioning, as it suggested that the cycling of the two size fractions is distinct. In this study, we have measured dFe size partitioning at several more stations across the tropical North Atlantic, reaching further along the southwestern boundary of the subtropical gyre and east into the heart of the oxygen minimum zone (OMZ). We find that both soluble and colloidal fractions determine the dissolved Fe variability in this broader region, instead of just the colloidal fraction as in Bergquist et al.'s study. In this paper we will establish the similarities and differences between the Bergquist et al. study and the new data presented here, and we will attempt to illuminate the major facets of dFe size partitioning and its contribution to Fe biogeochemistry in the tropical North Atlantic.

2. SAMPLING & ANALYSIS METHODOLOGY

In August 2008, trace metal clean seawater samples were collected aboard the R/V Oceanus (cruise OC449-2 sailing from Bridgetown, Barbados, to Mindelo, Cape Verde Islands) in the tropical North Atlantic (see cruise track in Fig. 1). A review of the sample collection and Fe analysis protocols for this cruise can be found in Fitzsimmons