Partitioning of dissolved iron and iron isotopes into soluble and colloidal phases along the GA03 GEOTRACES North Atlantic Transect

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Abstract

The size partitioning of dissolved Fe ($dFe < 0.2 \mu m$) into soluble ($sFe < 0.02 \mu m$) and colloidal ($0.02 \mu m < cFe < 0.2 \mu m$) species was investigated at 28 stations along the GEOTRACES GA03 North Atlantic Transect. Upper ocean dFe size partitioning was highly variable with depth: $79 \pm 6\%$ of aerosol-derived surface dFe was maintained in the colloidal size fraction, while cFe disappeared completely at the deep chlorophyll maximum, presumably a result of preferential cFe biological uptake and/or scavenging. In the intermediate and deep ocean, however, dFe was evenly partitioned $\sim 50:50\%$ into sFe and cFe phases, which we hypothesize results from a "steady state" of dFe exchange reactions during and following remineralization including ligand exchange, sorption/desorption, and aggregation/disaggregation. There were only two exceptions to this constant partitioning in the intermediate/deep ocean. First, cFe dominated ($82-96\%$) at and downstream of the Mid-Atlantic Ridge hydrothermal system. Also, along Line W between Woods Hole and Bermuda the dFe partitioning

favoring ~60-80% cFe, with the excess cFe likely resulting from inorganic cFe inputs from the margin. Thus, in the North Atlantic Ocean we propose a new model of dFe size partitioning where a "steady state" of dFe exchange reactions during and following remineralization re-partitions intermediate and deep ocean dFe into constantly fractionated sFe and cFe pools, while in the upper ocean, downstream of the Mid-Atlantic Ridge, and along Line W, sFe and cFe appear to cycle more independently, as either not enough time has passed to reach a new dFe exchange steady state or one of the dFe phases is non-labile to dFe exchange. This surface-subsurface decoupling model of North Atlantic dFe size partitioning is supported by Fe isotope ratio analyses of the sFe and dFe size fractions, which recorded isotopically heavy sFe ($\delta^{56}\text{Fe}$ of +1.3 to +1.5‰) relative to dFe ($\delta^{56}\text{Fe} \sim +0.5‰$) in the surface ocean where sFe and cFe cycle independently, and identical sFe and dFe isotope ratios below 250m where sFe and cFe are constantly partitioned and exchanged.

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1. Introduction

The international GEOTRACES program endeavors to determine the global distribution of trace elements and their isotopes while also constraining the fluxes and processes controlling these distributions. One of the highest priority elements investigated by GEOTRACES is dissolved iron (dFe), which is known to be an essential micronutrient for marine phytoplankton (Morel *et al.*, 2003; Sunda, 2012). Fe(III), the thermodynamically favored oxidation state of dFe in the oxic ocean, is largely insoluble, causing dFe to exist at very low concentrations that are predicted to limit phytoplankton growth in nearly 40% of the surface ocean (Moore *et al.*, 2002). Based on electrochemical data, organic Fe-binding ligands are thought to bind >99.9% of marine dFe (Rue and Bruland, 1995), buffering its concentration above biologically limiting levels in many regions of the global ocean. However, assessing the chemical composition of individual marine dFe species has yet to be accomplished due to analytical challenges (Gledhill and Buck, 2012), and this has made it difficult to understand the chemical

transformations involved in the conversion of Fe between source and sink. The identity and rates of these transformations remain one of the biggest unknowns in marine Fe biogeochemistry today.

One tool we can use to explore the form, composition, and cycling of dFe in the ocean is the size partitioning of dissolved Fe species. We know that dFe (here defined as $<0.2\ \mu\text{m}$) is composed of both soluble ($\text{sFe} < 0.02\ \mu\text{m}$) and colloidal ($0.02\ \mu\text{m} < \text{cFe} < 0.2\ \mu\text{m}$) size fractions, and the partitioning across both geographic locations and depths is highly variable, with colloids contributing 0-90% of the dFe phase (Bergquist *et al.*, 2007; Fitzsimmons and Boyle, 2014b; Wu *et al.*, 2001). Colloidal Fe comprises submicron Fe particles so small that they do not sink, and these colloids pass through the $0.2\ \mu\text{m}$ filter separating dissolved from particulate Fe. Soluble Fe, in contrast, comprises the smallest, often considered "truly dissolved" Fe species. Resolving this physical description of dFe size partitioning with the chemical composition of dFe is, however, a significant challenge.

Since nearly all dFe is assumed to be organically bound in the open ocean (Rue and Bruland, 1995), we can assume to a first degree that both sFe and cFe are organically bound. Very few studies directly measuring the chemical binding environment of Fe have been completed. Some energy dispersive spectroscopy measurements on colloids imaged by electron microscopy supported the hypothesis that marine colloidal Fe is organically bound, while estuarine and coastal colloidal Fe contain an inorganic colloidal Fe oxyhydroxide component not observed in the open ocean (Wells and Goldberg, 1992). However, recent studies have found exceptions to the first order assumption that dFe is organically bound. Using synchrotron technology, von der Heyden *et al.* (2012) found that colloidal and particulate Fe in the Southern Ocean surface layer had an inorganic magnetite component. While we will also consider the possibility of an inorganic colloidal Fe component, we will work from the primary assumption that both sFe and cFe are organically-bound, a hypothesis largely supported in the literature (Gledhill and Buck, 2012; Rue and Bruland, 1995; Wells and Goldberg, 1992).

The size partitioning of dFe affects marine Fe biogeochemistry in two important ways. First, cFe has been shown to have aggregated to colloidal size from smaller "granules" of soluble material (Wells and Goldberg, 1992); thus, cFe has been hypothesized to be an actively aggregating pool that links the soluble and particulate phases of Fe via initial sorption followed by successive aggregation (Honeyman and Santschi, 1989). Not only does this size partitioning have implications for the chemical composition of the dFe pool, but it also can impact the fate and lifetime of dFe in any given location, depending on the relative rates of sorption/desorption and aggregation/disaggregation between the various Fe size fractions. Secondly, the speciation of Fe has a direct impact on its bioavailability, with different phytoplankton species preferring different dFe forms (Hassler and Schoemann, 2009; Hutchins *et al.*, 1999). While very few studies have assessed the bioavailability of dFe from various size fractions, the few existing studies have suggested that sFe is preferred, and cFe is only indirectly bioavailable after release into the sFe pool

(Chen and Wang, 2001; Wang and Dei, 2003) or as a result of protozoan grazing (Barbeau *et al.*, 1996). Only a few colloidal Fe forms have been found to be highly bioavailable, including Fe bound to exopolymeric saccharides (Hassler *et al.*, 2011b). In contrast, inorganic Fe colloids (synthetic Fe oxyhydroxides) as small as 6-50 Fe atoms were not bioavailable to diatoms (Rich and Morel, 1990). If these studies are taken as representative of total dFe bioavailability in the open ocean, then an understanding of the dFe partitioning between soluble and colloidal phases is required in order to best assess dFe bioavailability.

In this paper, we describe the size partitioning of dFe between soluble and colloidal species across the U.S. GEOTRACES North Atlantic Transect (international GEOTRACES section GA03), and we compare this to previous studies of dFe size partitioning in the North Atlantic. Several papers exploring the size fractionation of dFe in the Atlantic have been published (see map of sampling locations in Fitzsimmons and Boyle, 2014a, and in Figure 1 for the North Atlantic), yet these studies show different patterns in different regions. First, Bergquist *et al.* (2007) reported that sFe concentrations in the central Atlantic were constant with depth at ~0.35 nmol/kg, while cFe concentrations were highly variable. They concluded that a dynamic colloidal phase controls dFe variability alongside relatively invariant sFe. Then with increased spatial coverage in a similar region, Fitzsimmons and Boyle (2014b) found sFe to be much more variable than measured by Bergquist *et al.* (2007) and concluded that both sFe and cFe must play an active role in controlling dFe distributions.

The GA03 data presented here encompass the first full ocean-basin transect of dFe size partitioning ever obtained, with higher spatial and depth resolution than any prior study globally. This transect identifies the major dFe size fractions present across multiple water masses (surface currents, mode waters, Labrador Sea Water and Antarctic Intermediate Waters, and both North Atlantic Deep Water and Antarctic Bottom Water). It also characterizes the dFe size partitioning unique to four major dFe inputs in the North Atlantic: the North African dust flux to the surface ocean, the Mid-Atlantic Ridge hydrothermal plume, sedimentary resuspension along the western Atlantic margin, and the dFe maxima of Mauritanian oxygen minimum zone (OMZ). Our description of the dFe size patterns as a function of depth in the North Atlantic shows that most of the external Fe sources to the North Atlantic partition into the colloidal fraction, while biological/particle reactive processes near the deep chlorophyll maximum quantitatively remove colloidal Fe, and remineralization and the subsequent Fe exchange reactions balance the concentrations of sFe and cFe in the intermediate and deep oceans. We conclude with a synthetic model and discussion of the general size partitioning patterns of dFe in the North Atlantic Ocean, also using the Fe isotopic signature of the soluble and dissolved size fractions to corroborate our proposed model.

2. Methods

2.1 Sample Collection

The size fractionation of dFe was determined at 28 stations in the North Atlantic Ocean aboard the R/V *Knorr* on the U.S. GEOTRACES North Atlantic Transect cruise (GA03; station locations in Figure 1). Sampling took place on two cruise legs: the 2010 cruise (USGT10), which sailed from Lisbon, Portugal, to Mindelo, Cape Verde Islands, from 14 October to 4 November, 2010, and the 2011 cruise (USGT11), which sailed from Woods Hole, Massachusetts, to Praia, Cape Verde Islands, from 6 November to 11 December, 2011. In order to keep the station names from these two cruises distinct, we refer to stations from the 2010 cruise as USGT10-xx, and from the 2011 cruise as USGT11-xx, where "xx" is the two-digit station number. All sample handling was completed in ISO 5-rated flow benches or clean rooms. Ultrapure water used in this study was first de-ionized by reverse osmosis, then purified through a Barnstead ultrapure deionizing cartridge, and finally distilled in a Corning vycor still. Unless otherwise indicated, all ultraclean hydrochloric (HCl, 6M) acid used for cleaning, filtration, and acidification was obtained by four consecutive distillations of reagent grade HCl in a vycor still. This HCl was verified to have low Fe blanks (~ 0.1 nmol/kg) by ICP-MS analysis after evaporation to dryness and a 10x pre-concentration in dilute nitric acid.

Clean seawater was collected using the U.S. GEOTRACES GO-FLO rosette by the methods described by Cutter and Bruland (2012). After rosette recovery, GO-FLO bottles were carried individually into an ISO 5-rated clean van, where the seawater was filtered through 0.2 μm Pall Acropak-200™ Supor® capsule filters under ~ 0.4 atm of HEPA-filtered air. Filtration protocols were identical to those described by Fitzsimmons and Boyle (2012), except that the Acropak filters were pre-cleaned by soaking overnight in filtered surface seawater acidified to pH 2 with clean HCl, after which they were flushed with 5L of unacidified 0.2 μm -filtered surface seawater and stored empty in the refrigerator until use. Surface seawater was collected using the GeoFish system, which employed PFA tubing attached to a vane that coasted at $\sim 3\text{m}$ depth, suspended from a boom off the starboard side of the ship during forward motion at ship speeds up to 12 knots. An all-PFA diaphragm pump sipped clean surface seawater through this system at ~ 0.5 atm pressure, passing first through a 0.45 μm Osmonics (PFA) filter and then through a 0.2 μm polycarbonate track-etched (PCTE) filter mesh housed in a polypropylene holder. Surface GeoFish and GO-FLO <0.2 μm filtrates for dFe analyses were collected in 1L LDPE bottles and acidified to pH 2 with Seastar 12 N HCl (containing < 0.09 nmol/kg Fe) onboard the ship within 2 days of collection. Additional <0.2 μm filtrates for further sFe ultrafiltration were first collected into 500 mL HDPE bottles after three bottle rinses, followed by secondary ultrafiltration as described below.

A different sFe:cFe ultrafiltration method was used on each of the two cruises, and these two methods are described, summarized, and compared in Fitzsimmons and Boyle (2014a). In 2010, a cross

flow filtration (CFF) technique using a Millipore Pellicon XL (PLCGC) regenerated cellulose membrane with a 10 kDa nominal molecular weight cutoff (Pellicon) was used in static mode to collect sFe samples after system conditioning using 300-350 mL of sample seawater. In 2011, 47 mm Anopore membrane filters made of alumina with 0.02 μm pores were utilized on an offline, fluorocarbon filter rig (Savillex) to collect sFe samples after the filters were rinsed with >50 mL of pH 1.5 HCl, >50 mL of ultrapure water, and >50 mL of sample seawater. All sFe samples were acidified to pH 2 with vycor-distilled 6M HCl. Using these operational size-cutoffs, dFe is defined in this paper as $\text{Fe} < 0.2 \mu\text{m}$, sFe is defined as $\text{Fe} < 0.02 \mu\text{m}$ (Anopore) or $< 10 \text{ kDa}$ (CFF), and cFe is calculated as dFe minus sFe. These size definitions directly influence the interpretation of the data, since the use of Anopore filters assigns the 10 kDa-0.02 μm dFe compounds as sFe (USGT11 samples), while the 10 kDa-0.02 μm size fraction is assigned as cFe using CFF (USGT10 samples). In a previous intercalibration effort the average sFe through the CFF system was only $68 \pm 23\%$ of that passing through the Anopore filters ($n=23$ depths from the North Atlantic and Pacific Oceans), indicating that CFF has a smaller nominal pore size overall. Any comparison of sFe passing through both filter types is ultimately influenced by the natural spatial variability of the 10 kDa - 0.02 μm size distribution and thus will vary spatially (Fitzsimmons and Boyle, 2014a).

Both dFe and sFe samples were also collected for dFe stable isotope ratio analysis on the USGT11 cruise at several stations: four depths at station USGT11-11, the surface of station USGT11-21, and one depth at station USGT11-23. In each case, 0.2 μm filtered seawater was collected in 4 L LDPE bottles by the methods described above. 1 L of this was poured off into a 2 L HDPE bottle for dFe isotope ratio analysis and acidified to pH 2 with vycor-distilled 6M HCl. The rest was ultrafiltered through the CFF system following ~500 mL CFF system conditioning with sample seawater, followed by collection of ~1 L of permeate (sFe) into a 2 L HDPE bottle and acidification to pH 2 with vycor-distilled 6M HCl. CFF was chosen over Anopore filtration for the ultrafiltration because of the faster filtration times facilitated by CFF for large volumes (Fitzsimmons and Boyle, 2014a).

2.2 Analytical methods

dFe ($< 0.2 \mu\text{m}$) samples were analyzed in the Wu laboratory at the RSMAS at the University of Miami on a Thermo Neptune multi-collector ICP-MS using the isotope dilution and magnesium co-precipitation methods described in Wu and Boyle (1998). sFe ($< 0.02 \mu\text{m}$) samples were analyzed in triplicate in the Boyle laboratory at MIT by isotope dilution MC-ICP-MS on a hexapole collision cell IsoProbe ICP-MS (Lee et al., 2011). This method employs an ^{54}Fe -spike and batch pre-concentration with nitrilotriacetate resin (NTA Superflow®, Qiagen). Fe procedure blanks and reported detection limits for both methods are shown in Table 1, along with comprehensive lab analyses of SAFe standard reference

materials. The measured dFe concentrations in the SFe reference samples are shown to be consistent with consensus values, indicating the high integrity of the Fe analyses reported here.

dFe and sFe stable isotope ratio analyses were conducted in the MTEL and CEMS laboratories at the University of South Carolina following the methods described in Conway et al. (2013). This method involves addition of a ^{57}Fe - ^{58}Fe double spike in a 1:2 sample to spike ratio, batch pre-concentration onto Nobias PA-1 chelating resin, and purification for Fe by anion-exchange chromatography with AGMP-1 resin. Purified samples were analyzed using a Thermo Neptune MC-ICP-MS in high-resolution mode, with a jet interface and APEX-Q (ESI) desolvation system without membrane. Isobaric interferences from Ni and Cr were corrected by monitoring ^{60}Ni and ^{53}Cr . Stable Fe isotope ratios were calculated using a data reduction scheme following the iterative method of Siebert et al. (2001), and are reported as $\delta^{56}\text{Fe}$ in standard delta notation (‰) relative to the IRMM-014 isotope standard. It has been shown (Conway *et al.*, 2013; John, 2012) that the uncertainty on stable isotope measurements using this technique is dominated by internal analytical error, and so all uncertainties are expressed based on 2σ standard internal error of samples and standards.

3. Results and Discussion

The distribution of dFe and the measured partitioning into soluble and colloidal phases across the transect are shown in Figure 2, and all dFe and sFe data are tabulated in the Supplementary Material and also along with all cruise data online at the Biological and Chemical Oceanography Data Management Office (BCO-DMO: <http://www.bco-dmo.org/project/2066>) under the project "U.S. GEOTRACES North Atlantic Transect." An assessment of North Atlantic dFe biogeochemical cycling, in light of previous studies and general North Atlantic hydrography, is the subject of a companion paper (Hatta *et al.*, this issue); however, the major hydrographic sections and a temperature-salinity diagram summarizing the major water masses of this section are included in the Supplementary Material accompanying this paper. The major Fe sources along GA03 are summarized below and can be inferred from Figure 2a.

The most noticeable feature of the GA03 dFe distribution is the hotspot of up to ~68 nmol/kg that is observed at 3000-3500m at USGT11-16, which is attributable to the TAG (Trans-Atlantic Geotraverse) hydrothermal vent field centered at 26° 8.2' N along the Mid-Atlantic Ridge (Rona *et al.*, 1986), which contains black smoker vents known to consistently source fluids containing ~5 mM Fe into the abyssal ocean (Chiba *et al.*, 2001). Additionally, in the surface ocean (Figure 3) dFe enrichments in excess of 1 nmol/kg are attributed to the solubilization of aerosol Fe blown in from continental sources predominantly from the North African continent but also from North America and Europe. Finally, there appear to be dFe maxima emanating from both margins at intermediate depths. The western margin dFe maximum from 1000-2500m in excess of 1 nmol/kg corresponds to the depth range of Labrador Sea

Water (LSW, as defined by Jenkins *et al.*, this issue), extending across the western boundary to the Bermuda Atlantic Time Series (BATS) station (USGT11-10). The eastern dFe maximum, also in excess of 1 nmol/kg, is coincident with the Mauritanian OMZ and is not thought to derive from a margin Fe source but rather from remineralization of high Fe:C organic material (Fitzsimmons *et al.*, 2013; Wu *et al.*, this issue).

This Results & Discussion section is organized as follows. In section 3.1, we present and discuss the major patterns of dFe size partitioning in the North Atlantic as a function of depth (surface, deep chlorophyll maximum, and intermediate/deep ocean) and region (west, central, and east Atlantic). In Section 3.2, we propose a synthesis model of dFe size partitioning in the North Atlantic that allows a consensus between the results of this study and all other published studies of dFe size partitioning in the North Atlantic. In Section 3.3, we present the Fe isotope ratios of sFe and dFe in the North Atlantic, and we discuss how these data support our synthesis model of dFe size partitioning. We conclude in Section 3.4 with a discussion of the open questions concerning marine dFe physicochemical state.

3.1 dFe size partitioning results

3.1.1 Surface ocean

The southern portion of the North Atlantic Ocean is directly downwind of North African dust sources and is thus expected to receive one of the highest dust loadings on the planet (Jickells *et al.*, 2005). As 3.5% of dust by weight is composed of Fe (Taylor and McLennan, 1985), high dust loadings and subsequent dust solubilization should result in high Fe inputs to the surface ocean, and accordingly there are several reports of elevated surface dFe concentrations in the North Atlantic (Bergquist and Boyle, 2006; Croot *et al.*, 2004; Fitzsimmons *et al.*, 2013; Measures *et al.*, 2008; Rijkenberg *et al.*, 2008; Rijkenberg *et al.*, 2012). On GA03, both total aerosol Fe loading and the Fe solubility varied over more than an order of magnitude across the four aerosol end-members (North Africa, North America, Europe, and "marine"), with the highest Fe loading but lowest Fe solubility deriving from North African sources (Shelley *et al.*, this issue). Thus, high surface dFe concentrations over much of GA03 were expected, and elevated surface ocean dFe concentrations ≥ 1.0 nmol/kg during GA03 were in fact observed (Figure 3; Hatta *et al.*, this issue).

Despite the surface enrichment of dFe, sFe occurred at very low concentrations averaging 0.16 ± 0.05 nmol/kg during USGT11 (Figure 3, also expanded in Supplementary Material Figure S3), while the colloidal contribution to dFe (hereafter referred to as %cFe) dominated at $79 \pm 6\%$. This high colloidal contribution is the same within error as the $80 \pm 7\%$ cFe determined from six stations in the tropical North Atlantic (Fitzsimmons and Boyle, 2014b; station locations shown in Figure 1) and thus appears to be representative of dFe size partitioning in the tropical and subtropical surface Atlantic

underlying the North African dust plume. Aerosol-solubilized Fe seems to be preferentially maintained in the colloidal size fraction, which has been observed previously by others (Bergquist *et al.*, 2007; Fitzsimmons and Boyle, 2014b; Wu *et al.*, 2001), while lower dust regions such as the Subarctic Pacific (Nishioka *et al.*, 2001b) and Southern Ocean (Boye *et al.*, 2010) do not show these cFe surface maxima.

It is possible that aerosol Fe is predominantly released into the colloidal size fraction, which would directly explain the observed surface cFe maxima. Alternatively, aerosol Fe could be released as both sFe and cFe, after which most of the sFe is taken up rapidly by microorganisms, leaving only cFe in the mixed layer. Another possibility is that sFe addition exceeds organic complexation capacity (or does not react with organics on relevant timescales) and thus is converted or aggregated into inorganic colloids. If there was an aerosol-derived sFe component, enhanced surface sFe might have been expected somewhere along our cruise track, given the variability in surface primary production from the gyre to the upwelling region along Mauritania; however, surface sFe was ≤ 0.22 nmol/kg at all stations except USGT10-07. This might suggest that the first hypothesis of direct aerosol Fe solubilization into the colloidal size fraction is more likely. Lab-based aerosol leaching experiments are consistent with aerosol Fe release directly into the colloidal-sized dFe pool (Aguilar-Islas *et al.*, 2010), although one should be concerned whether excess Fe binding ligands are saturated during these experiments, which would generate colloidal Fe oxyhydroxides and bias the resulting dFe size observed. Our data cannot resolve whether dust-derived Fe is deposited directly into the soluble or colloidal size fractions but simply indicate that cFe always ends up dominating much of the aerosol-derived dFe surface maximum. Finally, it is also worth noting that dFe size partitioning at USGT11-02, which receives aerosol inputs derived from anthropogenic North American sources (as determined by Shelley *et al.*, this issue), shows the same surface dFe partitioning into the colloidal phase as stations receiving dFe inputs from North African desert aerosols.

The observed dust-derived surface cFe maxima could have any of three possible chemical compositions: 1) Fe bound by colloidal-sized organic ligands after solubilization from dust, oxidation of photochemically-produced Fe(II), and/or biological cycling, 2) colloidal-sized pieces of dust that physically eroded from the aerosol particles upon impact with the surface ocean (resulting in a dust-like, inorganic cFe composition), or 3) sFe that was released initially from dust in the surface ocean but then re-precipitated *in situ* (also resulting in an inorganic cFe composition, likely amorphous Fe oxyhydroxides). Whichever of these three Fe forms composes the surface colloidal Fe pool has important implications for dFe availability to phytoplankton and thus Fe's influence on the carbon cycle. Organically-bound cFe species may be bioavailable, either directly (Hassler *et al.*, 2011a; Hassler *et al.*, 2011b) or after solubilization through the sFe phase (Chen *et al.*, 2003; Chen and Wang, 2001; Wang and Dei, 2003). However, inorganic cFe of Fe-oxyhydroxide (Rich and Morel, 1990) or Fe-silicate

composition is not thought to be bioavailable. A large inorganic component of surface cFe could significantly change our understanding of the bioavailability of this dFe pool and warrants further study. We will return to the question of cFe chemical composition in Section 3.4 below.

3.1.2 Deep chlorophyll maximum (DCM)

Several profiles of sFe and cFe in the tropical and subtropical North Atlantic have demonstrated cFe minima in the deep chlorophyll maxima (DCM) (Bergquist *et al.*, 2007; Fitzsimmons and Boyle, 2014b; Ussher *et al.*, 2010). Similarly, along GA03 we found that at most stations cFe reached a minimum in the DCM, and at many stations DCM cFe disappeared completely (Figure 4). An exception to this was the western margin Line W transect (Figure 4a), where cFe was high throughout the upper ocean, presumably reflecting an external margin source of cFe (see Section 3.1.3.3). However, at most open ocean stations cFe disappeared completely at the DCM (Figure 4b-e), even along the more northern stations of USGT10 nearer to Europe (Figure 4d, USGT10-05 example shown). We suggest several possible explanations for the absence of cFe in the DCM:

(1) *Colloidal Fe is bioavailable and is preferably taken up by microorganisms over sFe in the DCM.* Experimental studies have suggested that sFe is biologically preferred over cFe (Chen *et al.*, 2003; Chen and Wang, 2001; Wang and Dei, 2003), especially when the cFe occurs in inorganic forms such as oxyhydroxides (Rich and Morel, 1990). However, some forms of cFe may be utilized by microorganisms, and if this cFe was taken up preferentially over sFe in the DCM, an absence of cFe in the DCM might be expected. A controlled ecosystem enclosure experiment by Nishioka *et al.* (2001a) showed that cFe decreased the most out of all dFe size fractions during a simulated phytoplankton bloom, some of which was attributed to biological uptake of cFe species (although also to cFe aggregation). Additionally, studies of Fe bound to colloidal-sized exopolymeric saccharides (EPS) found Fe-EPS to be highly bioavailable (Hassler *et al.*, 2011a; Hassler *et al.*, 2011b), supporting the hypothesis that some cFe may be biologically utilized by organisms in the DCM. Moreover, phytoplankton living in the light-limited DCM have higher cellular Fe requirements (Sunda and Huntsman, 1997) that could encourage their more aggressive utilization of any dFe phase available, including cFe, which might further explain a DCM-specific minimum in cFe.

(2) *Colloidal Fe is scavenged and/or aggregated to the particulate phase in the DCM.* Because colloidal aggregation rates have been modeled as a second order reaction with respect to particle concentration (Stumm and Morgan, 1996), then when the number of particles increases in the DCM, aggregation rates should increase as well and could aggregate all of the colloidal Fe into particulate Fe phase in this layer. While it is well known that the fluorescence maximum designated as the DCM does not necessarily indicate a biomass maximum (Taguchi *et al.*, 1988), we compared the fluorescence trace

used to derive the depth of the DCM to the light transmission trace, which indicates depths with higher particulate loadings. As the example shown in Figure 4f shows, at many stations the DCM depth did match the depth of minimum light transmission, indicating that the DCM is the relative particle maximum that would be expected to promote increased cFe aggregation rates that favor the formation of particulate Fe (pFe). We must note, however, that pFe ($> 0.45 \mu\text{m}$) concentrations also reach a relative minimum at the DCM (Ohnemus and Lam, this issue), which might not be expected if dFe was being converted into pFe at these depths. However, low DCM pFe may occur because these particles are large enough to experience gravitational forcing and, thus, may sink quickly out of the DCM. Ohnemus and Lam (this issue) successfully modeled how a DCM pFe minimum results when dust-derived pFe is incorporated into large aggregates in the mixed layer and sink through the DCM to disaggregate below, resulting in low pFe in the DCM. This same model could extend to dust-derived cFe and explain the cFe minimum at the DCM. Importantly, this pattern only results when the DCM occurs below the mixed layer depth, which excludes Line W stations where accordingly there was no DCM cFe minimum observed (Figure 4a).

(3) *A unique Fe-ligand partitioning pattern in the DCM with an absence of colloidal ligands or a low concentration of anomalously weak colloidal ligands favors the formation of soluble-sized Fe-ligand compounds at the DCM.* The current consensus based on electrochemical measurements of seawater is that nearly all marine dissolved Fe is bound by both strong and weak organic Fe-binding ligands (Gledhill and Buck, 2012; Rue and Bruland, 1995; van den Berg, 1995; Wu and Luther, 1995). Thus, at equilibrium the concentrations and strengths of the ligands in the soluble and colloidal size fractions should directly determine the observed size partitioning of dFe. If the DCM had no colloidal ligands or soluble ligands were significantly stronger there, we might expect organically bound dFe to fall more in the soluble size fraction at the DCM. To date there are only three studies containing size fractionated Fe ligand data (Boye *et al.*, 2010; Cullen *et al.*, 2006; Thuróczy *et al.*, 2010), and none have sufficient depth resolution to capture the DCM. The few size-fractionated Fe-ligand samples collected on GA03 are the subject of another paper (Fitzsimmons *et al.*, in press) but show a predominance of soluble-sized Fe ligands throughout the entire upper ocean with no large change in ligand partitioning at the DCM. Thus, the existing data do not support this hypothesis that ligand partitioning produces a unique dFe size partitioning at the DCM.

It is also important to note that while cFe concentrations were quite variable in the upper ocean, sFe was nearly constant from the surface through the DCM at concentrations of 0.05-0.20 nmol/kg (Figure 4). Additionally, sFe was never depleted to zero concentration in the euphotic zone, which might be expected if it was the more bioavailable fraction (Chen *et al.*, 2003; Chen and Wang, 2001; Rich and Morel, 1990; Wang and Dei, 2003). Fitzsimmons and Boyle (2014b) hypothesized that this persistent sFe

fraction might be relatively more refractory, potentially bound by ligands so strongly that the Fe is not biologically accessible. An alternate explanation is that this sFe is so labile that we are measuring a pseudo-"steady state" sFe concentration that is biologically/photochemically cycled so rapidly that it is never fully depleted. Up to 50% of the dFe in the western subarctic Pacific was found to be composed of Fe(II) at mid-day (Roy *et al.*, 2008), but we do not know which size fraction of dFe this Fe(II) would comprise. Free Fe(II) would fall in the soluble size fraction, but if marine Fe(II) were ligand bound, it could be either soluble or colloidal. Marine Fe(II) has only been hypothesized to be bound by organic ligands (Roy and Wells, 2011), but experiments suggest that Fe(II) in rainwater is ligand-bound (Kieber *et al.*, 2005; Willey *et al.*, 2008). Notably, the surface sFe concentrations across GA03 were very similar to Fe(II) concentrations measured by Sedwick *et al.* (this issue), despite the very different methods used to measure these two concentrations, and thus Fe(II) may compose a portion of the sFe pool. However, there is no evidence precluding a colloidal Fe(II) fraction. Unfortunately, too few surface samples were collected at night to fully resolve a day-night cycle in surface dFe size fractionation, and thus the relative impact of biology/photochemistry on the sFe persistence could not be determined.

3.1.3 Intermediate and deep ocean

The intermediate and deep ocean dFe distribution and relative size partitioning can be seen in Figure 2a and is discussed relative to circulation and major subsurface dFe sources in Hatta *et al.* (this issue). Here, we discuss first in section 3.1.3.1 the subsurface dFe partitioning away from external Fe sources, with a goal of identifying the influence of remineralization and deep ocean circulation on the size fractionation of subsurface dFe. In addition to remineralization, it is clear that the North American and North African margins and the Mid-Atlantic Ridge supply dFe to the deep ocean (Figure 2), potentially with uniquely partitioned dFe signatures. We discuss the effects of those Fe sources in section 3.1.3.2-3.1.3.4. Although we have included a T-S diagram in the Supplementary Materials that summarizes the major water masses of GA03, we predominantly use the intermediate and deep ocean water masses defined by an Optimum Multi Parameter Analysis (OMPA) applied by Jenkins *et al.* (this issue) along the entire GA03 cruise transect. Importantly, each water mass in this model was defined using a suite of conservative water mass properties from "proximal" locations to GA03 rather than from the formation regions of the water masses. This must be kept in mind when quantitatively estimating the end-member contributions of non-conservative species, such as dFe.

3.1.3.1 Non-margin deep ocean & remineralization effects

Intermediate and deep ocean waters of the North Atlantic away from the margins and the Mid-Atlantic Ridge (MAR) had a very reproducible dFe distribution and size partitioning. In intermediate

waters (DCM through ~1000m), dFe concentrations were low, ranging from ~0.2-0.5 nmol/kg Fe, with higher concentrations on the western and eastern margins (Figure 2, Hatta *et al.*, this issue). Both sFe and cFe were also very low (≤ 0.2 nmol/kg) at intermediate depths, and each contributed about 50% of the dFe. Away from the margins, these intermediate waters were dominated by North Atlantic Central Water, Antarctic Intermediate Water, Irminger Sea Water, and Mediterranean Outflow Water. In the deep waters below 1000m dFe was typically ≥ 0.6 nmol/kg, except in the deepest samples of station 12 and station 22 where dFe dropped below 0.5 nmol/kg (at these stations, Antarctic Bottom Water, AABW, contributed $\geq 40\%$, as defined by Jenkins *et al.*, this issue). sFe and cFe concentrations in these deep waters were nearly equal at ~0.3 nmol/kg each, except in the AABW-impacted regions where cFe was depleted to ≤ 0.2 nmol/kg. The sFe:cFe partitioning in intermediate and deep waters was very similar at ~50:50% (white hues in Figure 2d). Exceptions to this include the sFe excess in AABW-influenced regions, a slight trend towards excess sFe near ~1000m depth, and a clear cFe excess in Line W stations (USGT11-02 through USGT11-10).

Traditionally, deep ocean dFe is believed to arise from remineralization (Johnson *et al.*, 1997). Thus, in order to assess the influence of remineralization on dFe partitioning, we examined the relationship between dFe species and the apparent oxygen utilization (AOU), which is a measure of the integrated oxygen loss due to remineralization in a water parcel since it was last in contact with the atmosphere. We completed Type-I regressions between AOU and dFe, sFe, or cFe in the oxycline (Figure 5, oxygen section in Figure S1d), which happens to fall in the Central Water layer (potential density 25.8-27.1, which corresponds to ~100-600 m depth, see Figure S1c potential density section). In order to avoid the influence of external Fe sources on our dFe regressions, we followed Hatta *et al.* (this issue) and eliminated USGT11-02 (influenced by North American margin dFe inputs), the hydrothermally affected portions of USGT11-14 and USGT11-16, and stations USGT10-09 and USGT10-10, which are hypothesized to receive African margin Fe inputs, from these regressions to evolve the remineralization-only dFe size partitioning pattern. We also subdivided the remaining stations of our transect into three regions: Line W (a), the subtropical gyre (b), and the margin-unaffected 2010 stations (c). Finally, the resulting Fe:AOU slopes were converted to Fe:C slopes using an AOU:C ratio of 1.6 (Martin *et al.*, 1987), as in previous studies of dFe biogeochemistry in the North Atlantic (Bergquist and Boyle, 2006; Fitzsimmons *et al.*, 2013). The Fe:C (slope) and pre-formed Fe (y-intercept) for both dFe and sFe are tabulated in Table 2.

The strong relationship between AOU and all three dFe size fractions (Figure 5) implies that the dFe size partitioning observed in the intermediate and deep North Atlantic Ocean results directly from remineralization or any subsequent Fe exchange/scavenging reactions following remineralization. The sFe:C and cFe:C all fall within error of each other (Table 2), explaining to a first order why the average

partitioning is split 50:50% sFe:cFe across much of GA03 (white in Figure 2d). We also note that this average 50:50% partitioning is set by the 0.02 μm filter used on the 2011 cruise. If a smaller pore size filter was utilized, such as the 10 kDa filter on the 2010 cruise, a partitioning favoring more cFe might be expected. Following this, while not statistically significant because of the large standard errors for the regressions, the sFe:C ratio for the 2010 non-margin stations ($2.26 \pm 1.20 \mu\text{mol/mol}$) was lower than that of the nearby gyre stations ($2.83 \pm 0.36 \mu\text{mol/mol}$), which may to some extent reflect the smaller pore size (10 kDa) used on the 2010 cruise compared to the 2011 cruise (0.02 μm).

At intermediate depths, dFe must either be pre-formed or delivered by remineralization, where pre-formed dFe is defined here as the dFe that was present when the water was last at the surface and/or the dFe that has been added to the water parcel by processes other than remineralization before it reached the sampling site. We aimed to distinguish how much of the 50:50% sFe:cFe partitioning arose from remineralization and how much resulted from the partitioning of pre-formed dFe, working from a starting assumption that these Fe pools do not exchange rapidly. Thus, we calculated the ratio of sFe:C to dFe:C, which is tabulated in Table 2 as %sFe_{REMIN}, to indicate the fraction of dFe that is partitioned into the soluble phase via remineralization, since any "pre-formed" Fe (the y-intercept of the Fe:AOU plot) is not included in this ratio calculated from the slopes. It is important to note that we constrained this calculation to a narrow water mass band (potential density 25.8-27.1 kg/m^3 , mostly NACW), within which we assume that pre-formed Fe is identical in each region. The %sFe_{REMIN} was the same ~45% at all stations investigated (Table 2), suggesting that remineralization or the exchange/scavenging reactions following remineralization partition 45% of remineralized dFe into the soluble phase and 55% into the colloidal phase throughout the North Atlantic.

However, the non-margin Line W stations (USGT11-03 through USGT11-08) still showed an absolute excess of cFe in the Central Waters of Figure 2d (orange) that must have been contributed from an excess pre-formed cFe component. To determine the %cFe of the pre-formed Fe, the ratio of pre-formed sFe to pre-formed dFe was calculated by dividing the y-intercepts of the sFe-AOU and dFe-AOU plots; these ratios are tabulated as %sFe_{PF} in Table 2. As expected, the Line W stations had a significantly lower %sFe_{PF} ($27 \pm 13\%$) than that of the gyre stations ($57 \pm 15\%$), indicating that there was a higher contribution of pre-formed cFe to the Line W stations at intermediate depths than at the other stations. Also, the %sFe_{PF} and the %sFe_{REMIN} for the gyre and USGT10 stations were identical within error, which suggests that the pre-formed dFe of these stations may readily exchange with the remineralized dFe pools to produce an equally partitioned total dFe fraction. In contrast, along Line W the %sFe_{PF} (27%) was lower than the %sFe_{REMIN} (44%), suggesting that the pre-formed cFe excess may not exchange as rapidly with the remineralized dFe pool. A further discussion of the implications of this on the composition of the Line W excess cFe can be found in section 3.1.3.3.

In deep waters, the dFe size partitioning along different water masses was assessed and compared to the dFe size in the same water masses in previously published studies. Below 1000m, sFe concentrations in North Atlantic Deep Water (NADW) were consistently between 0.25-0.35 nmol/kg (Figure 6), agreeing well with the nearly-constant, ~0.30 nmol/kg sFe concentrations previously reported for NADW in the North Atlantic (Fitzsimmons and Boyle, 2014b; Wu *et al.*, 2001), through the South Atlantic (Bergquist *et al.*, 2007), and into the Southern Ocean (Chever *et al.*, 2010).

At USGT11-12 (Figure 6b), however, the water below 5000 m depth was determined to have ~40% OMPA-defined AABW influence (Jenkins *et al.*, this issue), which was also evident from a drop in potential temperature to below 1.8°C (McCartney, 1992) and elevated concentrations of dissolved silica (53 $\mu\text{mol/kg}$). Waters shallower than 5000 m depth were instead composed of NADW components, namely Denmark Strait Overflow Water, Central Labrador Sea Water, and Iceland-Scotland Overflow Water. dFe concentrations dropped from ~0.52 nmol/kg in NADW above 5000 to ~0.43 nmol/kg below 5000 m, with the %cFe remaining roughly constant 52% in NADW, 46% at AABW depths. sFe concentrations below 5000m were 0.20-0.25 nmol/kg, significantly lower than the 0.33 nmol/kg sFe found upstream in AABW-influenced waters near 25°S (Bergquist *et al.*, 2007), which are thought to have much less diluted AABW evidenced by their higher dissolved silicate concentration (118 $\mu\text{mol/kg}$) than the USGT11-12 AABW samples (53 $\mu\text{mol/kg}$). This drop of 0.1 nmol/kg sFe from 25°S to 30°N cannot be attributed solely to increasing dilution with NADW because NADW has a higher sFe (0.25-0.35 nmol/kg) than the most dilute 30°N data deeper than 5000m (0.23 nmol/kg). This sFe decrease can likely be attributed to sorption/aggregation of sFe into cFe. In support of this we note that the cFe increased by the same ~0.10 nmol/kg that sFe decreased along the AABW flow path, from 0.10 nmol/kg at 25°S to ~0.20 nmol/kg at USGT11-12.

In summary, in abyssal waters we find rather constant sFe concentrations along NADW flow paths and increasing cFe concentrations along AABW flow paths. These patterns imply that transformations between soluble, colloidal, and particulate Fe pools are dynamic in the deep ocean and involve active exchange between soluble and colloidal pools via aggregation/disaggregation and/or sorption/desorption. As a result of this active exchange, scavenging residence times of individual Fe size fractions could not be calculated along the advective routes of these abyssal water masses, as these calculations require a quantitative accounting of these exchanges (such as the potential production of cFe from pFe and/or the reversible conversion between sFe and cFe), which cannot be gleaned from the existing data.

3.1.3.2 Eastern margin: Mauritanian oxygen minimum zone (OMZ)

Nearest Africa, a dFe maximum within the oxygen minimum zone (OMZ) reached concentrations of 1.85 nmol/kg (Figure 7a; USGT10-09 OMZ oxygen profile shown in Figure 6d). This dFe maximum extended westward past the TENATSO time-series station (station USGT10-12, reoccupied as USGT11-24, Figure 7) to station USGT11-22 (Figure 2a) where maximum dFe concentrations were ~1.0 nmol/kg. The dFe peak extended from the DCM to ~1500m depth but was most intense between 350-500m depth, coincident with the OMZ where oxygen concentrations were as low as 40 μ mol/kg near Mauritania (Figure 6d; Hatta *et al.*, this issue; Wu *et al.*, this issue). dFe enrichments in the tropical North Atlantic OMZ have been reported previously (Bergquist and Boyle, 2006; Fitzsimmons *et al.*, 2013; Measures *et al.*, 2008; Rijkenberg *et al.*, 2012). Linear dFe:AOU correlations in these tropical North Atlantic studies have been used to show that this dFe maximum, extending from ~50°W to the Cape Verde Islands, is caused by remineralization of high Fe:C organic material (Fitzsimmons *et al.*, 2013; Wu *et al.*, this issue). Hatta *et al.* (this issue) show in their discussion of dFe-AOU regressions that while remineralization is surely the cause for the enhanced dFe in USGT11-22 through -24 and USGT10-11 and -12, there is an excess dFe at stations USGT10-09 and -10 that is likely derived from reducing African margin sediments. This distinction of a reducing margin source to USGT10-09 and USGT10-10 is corroborated by small increases in Fe(II) (Sedwick *et al.*, this issue), dissolved manganese (Hatta *et al.*, this issue), and isotopically light Fe (Conway and John, 2014), all of which are indicative of the influence of reduced porewaters.

Thus, an examination of the dFe size partitioning along the Mauritanian transect (stations USGT10-09 through USGT10-12) allowed a possible distinction of the size partitioning of sediment-derived dFe from that of remineralized dFe. The observed dFe size fractionation for these stations (Figure 7) demonstrated that both soluble and colloidal Fe had maxima coincident with the dFe maximum. In Figure 7d, it can be seen that the %cFe through the region was ~55-70%, which is higher than the 40-60% cFe at stations USGT11-22 and USGT11-24 (Figure 2d). This apparent cFe increase arose at least in part because of the change in sFe:cFe filtration on the two cruises: the 0.02 μ m Anodisc membranes used on USGT11 have a larger pore size than the 10kDa CFF filter used on USGT10 (Fitzsimmons and Boyle, 2014a). Notably, however, in the margin stations USGT10-09 and USGT10-10 (Hatta *et al.*, this issue), peak sFe concentrations of ~0.6 nmol/kg and peak cFe of ~1.25 nmol/kg resulted in the same ~55-70% partitioning into the colloidal fraction as at the stations less influenced by the margins, USGT10-11 and USGT11-12. Thus, remineralization and reducing sediments appear to partition dFe identically, or exchange between dFe size fractions in this region is rapid enough to produce a constant dFe size partitioning, regardless of dFe source.

No enhanced cFe signature associated with dFe fluxes from reducing sediments was observed, and also no enhanced cFe signature associated with the Fe- and Mn-rich nepheloid layer near 3000m at USGT10-09 (defined in Ohnemus and Lam, this issue) was observed either. In fact, as can be seen in Figure 6d, the dFe concentration at USGT10-09 dropped below 1.0 nmol/kg in the two deepest samples at ~3000m, indicating that the nepheloid layer may have promoted some dFe sorption/aggregation. The sFe concentrations decreased by a smaller magnitude than dFe, such that the %cFe decreased from >60% throughout most deep water column to ~50% near 3000m, implying a greater role for the sorption/aggregation of cFe in this nepheloid layer.

In their tropical North Atlantic study, Fitzsimmons and Boyle (2014b) found that along the edges of the OMZ where oxygen concentrations are 100-110 $\mu\text{mol/kg}$, a unique dFe partitioning favors the formation of excess colloids. They corroborated this theory with data from Bergquist *et al.* (2007) showing an identical partitioning pattern favoring cFe on the western edge of the same tropical North Atlantic OMZ. On GA03 only one station satisfying this intermediate oxygen concentration was sampled: USGT11-22 (oxygen section in Figure S1d). At this station, the sFe was 0.375 ± 0.014 nmol/kg ($n=3$), identical to the ~0.4 nmol/kg reported by Fitzsimmons and Boyle, and cFe composed 55-60% of dFe, identical to the $58 \pm 2\%$ cFe determined in Fitzsimmons and Boyle. Thus, our GA03 data from the more northern edge of the OMZ capture the same excess of colloidal Fe as Fitzsimmons and Boyle (2014b), despite being 1400-2000 km away from their western OMZ stations. While only an assessment of the Fe content in sediments along the edge of the OMZ could confirm this, the excess cFe along the edges of the OMZ could serve as an output pathway for the enhanced dFe from the OMZ. This has been shown in sediments surrounding the Peruvian OMZ where Fe redox chemistry plays a role in driving precipitation and loss of OMZ Fe(II) (Scholz *et al.*, 2012). A non-redox mechanism involving aggregation through the cFe phase would be implied instead in the North Atlantic where oxygen concentrations are not as low.

In addition, the occupation of the TENATSO time series station on both cruise legs (stations USGT10-12 and USGT11-24) afforded us an opportunity to compare the two sFe:cFe ultrafiltration methods used in this manuscript over a full-depth profile (Figure 8). Oxygen and dFe concentrations were relatively constant over the two sampling years (Figure 8a), so natural variability in dFe was not a significant issue during this comparison (see more on dFe comparison at the TENATSO time-series station in Hatta *et al.*, this issue). At the 24 depths sampled at TENATSO, sFe from the 10 kDa CFF system used on USGT10 was on average $75 \pm 21\%$ of the sFe from the 0.02 μm Anopore filters used on USGT11 (Figure 8d), which is within error of the $68 \pm 23\%$ CFF/Anopore sFe ratio seen in 23 samples collected from the North Atlantic and Pacific Oceans (Fitzsimmons and Boyle, 2014b). The majority of this difference is attributed to a larger effective pore size in the 0.02 μm Anopore filters (USGT11) than in the 10 kDa CFF filters (USGT10).

However, there is also spatial variability in the size distribution and/or composition of the 10 kDa-0.02 μm Fe colloids that comprise the difference between the pore sizes of the two ultrafilters. This spatial variability explains the large (21%) standard deviation in the sFe CFF/Anopore ratio measured at TENATSO and provides an oceanographic application of this filter comparison effort. As shown in Figure 8d, from the DCM through the upper portion of the OMZ (~500m depth) the CFF/Anopore sFe ratio was $\leq 60\%$, indicating where there was the largest component of 10kDa-0.02 μm material (the smallest possible cFe measured here). Three processes could result in an enhanced abundance of these small colloids: (1) an external input of the small colloids, (2) increased *in situ* aggregation/disaggregation into the small colloid fraction, or (3) a unique ligand partitioning that forced dFe to favor the smallest colloid sizes. The low dFe concentrations at the DCM make the likelihood of an analytical bias quite high, so we will not consider the DCM partitioning comparison further. By ~230 m, however, dFe concentrations had begun to increase (Figure 2, 4, and S3; Hatta *et al.*, this issue) and also the suspended particulate Ba, Fe, and Al had reached their maxima (Ohnemus and Lam, this issue), indicating that by 230m the disaggregation of large particles had begun to outcompete aggregation. Thus, the enrichment of small-colloidal Fe at 230 m is likely a result of particle disaggregation all the way to the smallest 10kDa-0.02 μm sizes. In contrast, these small colloids in the 10kDa-0.02 μm size fraction were negligible in the abyssal ocean (2500-3500 m), despite the abundance of larger colloids (0.02-0.2 μm) at elevated concentrations of 0.35-0.55 nmol/kg (Figure 8c). These patterns indicate that the size distribution of marine dFe is variable both with space and with depth and warrants future exploration.

3.1.3.3 Western boundary (Line W)

A dFe maximum of 0.8-1.2 nmol/kg is apparent at intermediate depths of the western region of GA03 (USGT11-02 through USGT11-10), which we refer to as the Line W transect due to its overlap with the Line W time-series transect between Woods Hole and Bermuda (Joyce *et al.*, 2005). The Line W dFe enrichment extended offshore from the margin along Line W at 500-2500 m depth, reaching eastward even beyond the BATS station along a narrower depth window of 900-2000 m (Figure 2a). As described in Hatta *et al.* (this issue), this dFe feature is coincident with elevated CFC concentrations that identify the presence of Labrador Sea Water (LSW). LSW can also be identified by the relatively lower silicate concentrations flowing along these aforementioned depths (Figure S2c). LSW has been found to circulate along the deep western boundary current of North America along the continental slope (Talley and McCartney, 1982) but also into the subtropics via an additional interior pathway that splits off to the east of the Grand Banks (Bower *et al.*, 2011; Bower *et al.*, 2009). Hatta *et al.* (this issue) hypothesize that LSW dFe was acquired from deep western boundary sediments during transport from the Labrador Sea. They support this hypothesis by noting coincident dissolved Mn and Al (Measures *et al.*, this issue)

maxima in LSW, both of which are hypothesized to be margin derived, as well as an excess of ^{228}Ra (Charette *et al.*, this issue), which indicates that LSW along Line W has been in contact with sediments during the last ~30 years.

The Line W dFe enrichment in LSW is partitioned 60-80% into the colloidal size fraction (Figure 2d), a much higher cFe contribution than in intermediate waters from the rest of GA03, where an ~50:50% sFe:cFe partitioning is hypothesized to result from remineralization (Section 3.1.3.1). As a first approximation, the maximum possible cFe concentration derived from external sources to LSW can be calculated by assuming a 45:55% sFe:cFe remineralization ratio (Table 2) and that all of the sFe measured in LSW derived from remineralization: the resulting LSW cFe excess is 0.10-0.38 nmol/kg. This Line W cFe enrichment must be either pre-formed cFe from the Labrador Sea surface ocean or cFe acquired from margin sediments during LSW transit. The SF_6 age of LSW along Line W is approximately 25 years since contact with the surface ocean (William Smethie, personal communication), which is shorter than estimates of cFe scavenging times in NADW of 140 ± 100 years (Bergquist *et al.*, 2007). This suggests that it would be possible for pre-formed Labrador Sea cFe to escape scavenging during transit to the subtropics, so long as the scavenging residence times in LSW and tropical NADW are the same. There is no published surface dFe data from the Labrador Sea, and thus we cannot confirm or reject a pre-formed cFe source. However, we do note that dust models do not predict large dust inputs to the Labrador Sea (Jickells *et al.*, 2005; Mahowald *et al.*, 2005), and surface dissolved Al concentrations in the Labrador Sea are very low (Hall and Measures, 1998), minimizing the potential for an atmospheric pre-formed dFe source. While surface Labrador Sea waters could have acquired cFe enrichments from sea ice or glacial meltwaters (Bhatia *et al.*, 2013; Lannuzel *et al.*, 2007), a more likely mechanism of Line W pre-formed cFe enrichment in LSW is cFe resuspension during passage along the continental slope, following Hatta *et al.*'s discussion of the continentally-derived Mn, Al, and ^{228}Ra in LSW.

Regardless of which individual process added the cFe to LSW, all possible sources are lithogenic. We also know that this cFe was maintained in excess of sFe throughout the LSW water mass, while in the other intermediate/deep waters of GA03 where the only source was remineralization the sFe and cFe concentrations were more equal. To explain this difference, we suggest that some or all of the excess cFe in LSW may be inorganic in composition (such as colloidal Fe oxyhydroxides or silicates) as opposed to being bound by organic ligands, which would be the working assumption since >99.9% of dFe is thought to be organically bound in the open ocean (Rue and Bruland, 1995). An inorganic composition of the LSW cFe component would make sense if the cFe was directly swept up from sediments during the flow of LSW along the continental margin and slope. In fact, previous studies have shown that a portion of the cFe phase is inorganic in coastal and nearshore environments (Wells and Goldberg, 1992, 1994). Furthermore, an inorganic cFe component to LSW, which would presumably be quite refractory, would

explain why pre-formed cFe in LSW does not exchange with the sFe phases and re-equilibrate to a 50-50% partitioning, as observed in the rest of GA03 (Table 2, discussed above). Moreover, the Fe isotope ratio of dFe in LSW close to the western margin (USGT11-01 through USGT11-03) ranged from 0.0 to +0.2‰, which is noticeably lower than the dFe $\delta^{56}\text{Fe}$ at similar depths of surrounding stations (Conway and John, 2014). These LSW $\delta^{56}\text{Fe}$ values are similar to the +0.1‰ crustal signature (Beard *et al.*, 2003), which would be expected if the LSW excess cFe included a significant contribution of inorganic Fe with a crustal composition. While these data are not sufficient to determine definitely whether cFe in the western basin is inorganic (since organically-bound dFe fractionated uniquely from that at similar depths nearby could also result in this isotope composition), the potential presence of inorganic cFe is biogeochemically relevant because it may be significantly less bioavailable than the organically-bound cFe in the N. Atlantic (Rich and Morel, 1990).

Above and below the intermediate LSW depth range, however, the entire Line W water column had an enhanced %cFe of 60-70% (Figure 2d and Figure 6a). The upper 500m of Line W was composed of Shelf/Slope Waters (USGT11-01 and USGT11-02), which flow southward along the continental margin, and Gulf Stream Waters (USGT11-03), which flow northward farther offshore (see the ADCP data from these stations for water mass assignment in Hatta *et al.*, this issue; the physical oceanography of the upper ocean of Line W is summarized in Joyce *et al.*, 2005). Only the Shelf/Slope Water-impacted USGT11-02 showed dFe concentrations greater than 0.4 nmol/kg, which Hatta *et al.* (this issue) attribute to direct dFe inputs from the North American shelf. In both water masses, upper ocean waters contained a $\geq 60\%$ cFe composition, and we propose that, similar to LSW, this colloidal Fe could contain inorganic cFe acquired from the continental shelf.

Finally, we note that the Line W nepheloid layers of stations USGT11-06 through USGT11-10 may have contributed the cFe excesses along the deep western boundary (Figure 2d). It has been known for some time that in this region particulate material can be resuspended into the water column hundreds of meters above the seafloor (Brewer *et al.*, 1976). On GA03 an example of these increased particle loadings is recorded at USGT11-06 by the reduction in the transmissometer signal (Figure 6a). Ohnemus and Lam (this issue) further defined the depths of each of these nepheloid layers using their measured particulate loadings, even recording a >1000 m resuspension above the bottom at USGT11-10. In the Line W nepheloid layers, the dFe was ~55-65% colloidal, and thus these nepheloid layers may serve as the source of excess colloids to the water column. Similarly, very near the Line W stations, Wells and Goldberg (1994) found evidence for increased colloid volume in nepheloid layers off the Scotian shelf, which they hypothesized was a result of episodic high-flow "storm" events that pushed sediments containing colloidal material into the deep water column (Gross *et al.*, 1988).

3.1.3.4 TAG hydrothermal system

Station USGT11-16 targeted the TAG (Trans-Atlantic Geotraverse) hydrothermal field centered at 26° 8.2' N along the Mid-Atlantic Ridge in order to sample the proximal influences of the known black smoker hydrothermal venting of high-Fe fluids on the geochemistry of the deep North Atlantic water column (Figure 9). The TAG hydrothermal field is located on the eastern wall of the slow-spreading (<2 cm/y) Mid-Atlantic Ridge rift valley in 3650m water depth (Rona *et al.*, 1986). TAG black smoker vents have been found to release fluids with extremely high dFe concentrations of ~5.0-5.5 mM (Chiba *et al.*, 2001), nearly six orders of magnitude higher concentration than typical North Atlantic abyssal dFe concentrations. A decrease in light transmission >3000 m at USGT11-16 (Figure 9c) indicates that we encountered the particle-rich neutrally buoyant plume. In the portion of the seawater mixed, non-buoyant plume that we sampled proximal to the TAG site, an elevated dFe concentration of 66.4 nmol/kg was detected, 89-96% of which was partitioned into the colloidal size fraction (Figure 9c), with sFe concentrations in the five highest-dFe samples reaching only 2.0-7.4 nmol/kg. While colloidal Fe oxyhydroxides have previously been hypothesized to account for the high concentrations of dFe at TAG (James and Elderfield, 1996), the discovery that 58-100% of this dFe is composed of Fe(II), not Fe(III) (Sedwick *et al.*, this issue), instead point toward a TAG non-buoyant plume dFe composition of colloidal Fe sulfide nanoparticles (Yucel *et al.*, 2011) and/or organically-bound colloidal Fe(II) species (Toner *et al.*, 2009).

The two stations flanking the TAG station afforded us the opportunity to determine whether hydrothermal-derived dFe is transported away from the MAR vent system in the dissolved phase, and if so which size fraction of dFe persists. Stations USGT11-14 and USGT11-18 were each ≥ 500 km away from the MAR (to the west and east, respectively, Figure 1). The recently proposed "leaky vent" hypothesis posits that instead of quantitatively precipitating at the vent site, some hydrothermal Fe is transferred long distances in the dissolved phase and contributes significantly to the deep ocean dFe inventory (Bennett *et al.*, 2008; Boyle and Jenkins, 2008; Fitzsimmons *et al.*, 2014; Toner *et al.*, 2012). This distal contribution of hydrothermal Fe to deep ocean dFe has been modeled (Saito *et al.*, 2013; Tagliabue *et al.*, 2010), and in the Pacific distal hydrothermal dFe transport thousands of kilometers from the vent site has been demonstrated (Fitzsimmons *et al.*, 2014; Nishioka *et al.*, 2013), confirming the "leaky vent" hypothesis. Determining whether this also occurs at higher abyssal oxygen concentrations in the North Atlantic (Field and Sherrell, 2000), and if so how the dFe size partitioning plays a role in this dFe persistence, was a major goal of this investigation.

While no hydrothermal dFe excess was recorded at USGT11-18 to the east of the MAR (Hatta *et al.*, this issue), a hydrothermal signal of ~1 nmol/kg dFe at USGT11-14 to the west of the MAR was recorded at a depth of 2500m, shallower than the TAG site (Figure 9a). The only possible source of this

enhanced dFe at USGT11-14 is the Mid-Atlantic Ridge, which demonstrates distal transport of dFe at least 500 km in the North Atlantic, confirming the "leaky vent" hypothesis in the North Atlantic (Bennett *et al.*, 2008; Boyle and Jenkins, 2008; Fitzsimmons *et al.*, 2014; Toner *et al.*, 2012). If background NADW dFe concentrations of ~0.6 nmol/kg are subtracted from the maximum dFe concentrations at USGT11-14, a hydrothermally-derived excess of ~0.4 nmol/kg remains between 2100-3000m at this site.

Of this ~0.4 nmol/kg hydrothermal dFe, soluble Fe contributed 9-18% (subtracting background NADW sFe of ~0.27 nmol/kg; Figure 9a). This is higher than the 4-11% sFe found proximal to the TAG site at USGT11-16 (Figure 9c). Although this could be attributed to a different Fe chemistry in the hydrothermal vent sourcing the dFe enrichment at USGT11-14, which is potentially not TAG since there is no direct abyssal circulation route between USGT11-16 and USGT11-14, another explanation is that the percent of truly soluble dFe actually increases with increasing distance from vent fields. The same pattern has been observed in the eastern South Pacific for dFe released from East Pacific Rise hydrothermal vents (Fitzsimmons *et al.*, 2014). If true, this would indicate that the soluble fraction more efficiently "leaks" from hydrothermal vents, providing a clue about the mechanism of hydrothermal dFe preservation during "leaky vent" hydrothermal dFe persistence.

3.2 Synthesis model of dFe size partitioning in the North Atlantic

The North Atlantic Ocean has been sampled more extensively for the size fractionation of dFe into soluble and colloidal phases than any other ocean basin (see global map of previous studies in Fitzsimmons and Boyle, 2014a). Nonetheless, a consensus on the factors controlling dFe size partitioning in this region has not yet emerged. We believe that the GA03 transect captures most of the major dFe inputs into the North Atlantic that might influence dFe partitioning and also provides the highest spatial and depth resolution sampled for size fractionated dFe in the Atlantic to date. Thus, this GEOTRACES dataset is optimally suited for resolving hypotheses of which processes control the size partitioning of marine dFe in the Atlantic Ocean.

First, we review the findings of previous North Atlantic dFe size partitioning studies (cruise locations indicated on the Figure 1 map). Originally, Bergquist *et al.* (2007) posited that variability in the cFe phase was responsible for the variability in North Atlantic dFe, while sFe remained relatively constant with depth at ~0.3 nmol/kg. This partitioning pattern is apparent in a reproduction of their size fractionated dFe data in Figure 10a, where dFe was well correlated with cFe but did not correlate with invariant sFe. In contrast, over a larger swath of stations in the tropical North Atlantic, Fitzsimmons and Boyle (2014b) found that both sFe and cFe contributed to dFe variability at nearly constant 50:50% distributions (Figure 10b). They concluded that either the size partitioning of organic Fe-binding ligands controls the overall partitioning of dFe in the North Atlantic or that North Atlantic dFe has a "steady

state" dFe partitioning pattern where exchange rates between soluble and colloidal fractions are set and produce the constant observed dFe partitioning (potentially overlain by inert or fresh Fe inputs containing uniquely size-fractionated Fe in some places).

To discriminate between these alternatives, we focused on the correlations between different dFe size fractions from the GEOTRACES transect for the 2011 (c-d) and 2010 (e) cruises (Figure 10). Importantly, the regressed data only includes depths below the DCM, and hydrothermally-affected depths of USGT11-14 and USGT11-16 were also excluded. As the data in Figure 10c-e shows, since sFe and cFe both increase as dFe increases, both size fractions must contribute to dFe variability. Thus we conclude that Bergquist *et al.*'s hypothesis of direct cFe control on dFe variability does not apply broadly across the North Atlantic.

It is difficult to evaluate Fitzsimmons and Boyle's first hypothesis (2014b) that the size partitioning of organic Fe-binding ligands directly controls the size partitioning of dFe, since there is so little data available on the size partitioning of organic Fe-binding ligands in the ocean, especially in the intermediate and deep ocean. The existing published measurements from the upper ocean, however, have suggested that the size partitioning of organic Fe-binding ligands does not predict the size partitioning of dFe (Boye *et al.*, 2010; Cullen *et al.*, 2006; Thuróczy *et al.*, 2010). Cullen *et al.* (2006) interpreted this result as being caused by a missing "inert" colloidal Fe-binding ligand fraction that is not detected electrochemically. Using size-fractionated Fe ligand data from the upper ocean of GA03, Fitzsimmons *et al.* (in press) question whether inorganic cFe might be the cause of this divergence between the ligand-predicted and observed dFe size fractionation. However, since unique dFe sources and transformation processes related to biological activity and particle dynamics occur in the upper ocean that could drive deviations in dFe size partitioning from what is expected by the ligand size partitioning (see Sections 3.1.1-3.1.2), we must leave open the possibility that in the intermediate and deep ocean ligand size partitioning and associated ligand exchange does control dFe size partitioning.

Nonetheless we instead focus on the hypothesis of Fitzsimmons and Boyle (2014b) that there is a "steady state" dFe re-partitioning into soluble and colloidal phases that is constant for a given region, and we develop a dFe partitioning model for all depths below the DCM based on this hypothesis. An exchange model must be implicated because new dFe inputs such as dust, margin sediments, and hydrothermal venting all result in cFe-enriched inputs (see sections 3.1.1 and 3.1.3.3-4) that cannot by themselves explain the ~50:50% sFe:cFe partitioning observed in the subsurface North Atlantic Ocean. Thus, we consider other potential pathways for dFe inputs/transformations in the deep ocean: remineralization, scavenging, and Fe exchange. First, we considered whether remineralization could alone create the ~50:50% sFe:cFe partitioning via equal input directly into sFe and cFe pools. While we have no evidence against this, any subsequent scavenging or exchange of Fe between size fractions would change

the observed dFe size partitioning, and also uniquely partitioned pre-formed dFe pools would impart an unequal partitioning to deep waters that is not supported by the equally-partitioned results in Figure 10b-e. Instead, we suggest that the constant partitioning is driven by a "steady state" of the sum of dFe exchange processes directly following remineralization (including ligand exchange, sorption/desorption, and aggregation/disaggregation, indicated with solid black arrows in Figure 11a); in other words, the rates of these dFe exchange processes are equal and result in the constant partitioning observed in the subsurface North Atlantic Ocean. Thus, rather than dFe in a given seawater parcel having a fixed concentration of sFe and a variable concentration of cFe that determines the magnitude of dFe (Bergquist *et al.*, 2007), the dFe in a given water parcel will have a fixed percentage of sFe and cFe set by the relative rates of exchange between sFe and cFe fractions (Figure 11a).

This "steady state" model of dFe partitioning is supported by the Fe:C errors from the three regions of GA03 in Table 2. The fact that the %sFe_{REMIN} across the three regions are identical within error indicates that a single process is informing the dFe size partitioning in all three regions, which we propose is remineralization and/or the immediate exchange reactions following remineralization. Furthermore, the similarity between the %sFe_{REMIN} and the %sFe_{PF} for most of GA03 likely indicates that the pre-formed and remineralized dFe pools are exchanging with each other, forming the total steady state 50:50% sFe:cFe partitioning observed in the subsurface of Figure 2d.

The only region where the overall partitioning was not 50:50% sFe:cFe was along Line W, where in Section 3.1.3.3 we argue that a portion of the cFe is inorganic Fe. This highlights the single caveat to the steady state partitioning model: in order to reach the observed 50:50% sFe:cFe partitioning, all measurable dFe must be labile to exchange with sFe and cFe pools. If the Line W pre-formed cFe is composed of inorganic Fe, it may not be exchangeable with the otherwise organically-bound sFe and cFe pools of the deep ocean on the timescales of the transit between the margin source and our sampling locations. Thus, the Line W pre-formed dFe remains mostly colloidal, and Line W appears to have a cFe excess (Figure 2d).

Thus, the "steady state" dFe size partitioning model fails under two conditions: 1) not enough time has passed for the exchange reactions to reach steady state, or 2) some of the dFe is not kinetically labile to exchange on relevant timescales. A prime example of this situation is the upper ocean of the North Atlantic (Figure 11b), where one or both of these conditions prevents dFe from reaching the constant 50:50% sFe:cFe partitioning observed in the subsurface ocean. As discussed in sections 3.1.1 and 3.1.2 (and observed in Figure 10c-e, open circles), surface dFe was mostly colloidal (Figure 2), while DCM dFe was mostly soluble (Figure 4), with a nearly constant sFe concentration above the DCM. The surface cFe excess likely arises from recent dust inputs that have not had sufficient time to exchange with the ambient dFe pools or that are potentially inorganic in composition and cannot exchange with the

ambient surface dFe (Section 3.1.1). Additionally, biological organisms take up dFe rapidly at these depths, potentially favoring one dFe size fraction over another, and sFe:cFe exchange kinetics may not be able to keep up. At the DCM, cFe may be favored after rapid scavenging/aggregation kinetics that outcompete the regular sFe:cFe exchange kinetics. Thus, steady state dFe partitioning is not reached, and euphotic zone sFe and cFe appear to cycle independently.

Some subsurface regions along GA03 also failed to reach dFe size partitioning steady state. At and downstream of the MAR, hydrothermal inputs of inorganic dFe may not readily exchange with deep ocean sFe and cFe pools on relevant exchange timescales. Alternatively, the aggregation and scavenging reactions in these fluids with modified chemistry and particulate loadings may have had faster kinetics (or were simply more abundant) than the sFe:cFe exchange reactions in the deep ocean. We also note that the subsurface dFe profiles of Bergquist *et al.* (2007, Figure 10a) may also not have re-partitioned to steady state for reasons of dFe composition and/or kinetics. At their 30°N site, a LSW influence at mid-depths likely resulted in their observed a cFe excess, just as in the Line W stations of GA03 (Section 3.1.3.3), and at their 10°N site, oxygen concentrations were at the intermediate concentration that Fitzsimmons and Boyle (2014b) showed favors the formation of cFe, presumably via non-steady state exchange of dFe during mixing of low-Fe gyre water with high-Fe OMZ water (Section 3.1.3.2).

Thus, our model of steady-state exchange between the sFe and cFe pools explains the near-constant 50:50% sFe:cFe partitioning of the subsurface North Atlantic Ocean (Figure 11). This is most clearly visualized in the sFe:cFe regressions on the right panel of Figure 10 (c-e), where it is shown that subsurface sFe and cFe cycle synchronously in the North Atlantic: where sFe was low, cFe was also low, and vice-versa. The relation of the sFe:cFe trend to the 1:1 line also gives an indication of the general partitioning of the dFe in water from a given region: in North Atlantic gyre waters, half of the dFe was cFe and half was sFe, while in Line W waters, more than half of the dFe was colloidal. We must emphasize that these "steady state" dFe partitioning patterns are dependent on the operational definitions of sFe utilized: using the 0.02 μm sFe size cutoff, typical "steady state" dFe partitioning was ~50% sFe (Figure 2d), but using a smaller 10 kDa sFe pore size in the 2010 cruise, "steady state" partitioning was only ~35% sFe (Figure 4d).

3.3 Size fractionated dFe stable isotope ratios

We also investigated the Fe isotopic signature ($\delta^{56}\text{Fe}$) of the sFe and dFe pools in order to test the "steady state" dFe partitioning model described above. Seawater dissolved Fe isotopes have previously been used both to trace different sources of Fe to the oceans and to study the transformations of dissolved Fe between species and phases (John and Adkins, 2012; John *et al.*, 2012; Lacan *et al.*, 2008; Radic *et al.*, 2011). Measurements of seawater dissolved $\delta^{56}\text{Fe}$ from GA03 have been used to constrain sources of Fe

to the North Atlantic (Conway and John, 2014), while measurements of particulate $\delta^{56}\text{Fe}$ have been used to investigate sources of particulate Fe to the North Atlantic and explore dissolved-particulate interactions (Revels *et al.*, this issue). We focus here on what $\delta^{56}\text{Fe}$ suggests about the sources and cycling of the individual sFe and cFe fractions.

The size partitioned Fe isotope ratio results are shown in Figure 12, and the data and errors are tabulated online in the Supplementary Materials. To separate sFe from cFe in these isotope samples, the 10 kDa CFF system was chosen over Anopore filtration because of the large sample volumes required for isotopic analysis (Fitzsimmons and Boyle, 2014a). However, as discussed for the TENATSO time-series station (Figure 8; Section 3.1.3.2), the general dFe size partitioning pattern resulting from CFF was the same as that derived from Anopore filtration: surface dFe was dominated by cFe (85% and 56% using CFF at USGT11-11 and USGT11-21, respectively), while intermediate/deep ocean dFe partitioning neared 50:50% sFe:cFe, ranging from 48-63% cFe.

Similar to the concentration partitioning patterns, the dFe isotope partitioning was different in the surface compared to subsurface waters (>300 m, Figure 12). In the surface, the $\delta^{56}\text{Fe}$ of sFe was quite heavy at both stations ($+1.33 \pm 0.11\text{‰}$ and $+1.49 \pm 0.18\text{‰}$ at USGT11-11 and USGT11-21, respectively, $\pm 2\sigma$ SE) relative to the $\delta^{56}\text{Fe}$ of bulk dFe ($+0.52 \pm 0.06\text{‰}$ and $+0.45 \pm 0.07\text{‰}$, respectively). If cFe is calculated as dFe minus sFe and the $\delta^{56}\text{Fe}$ of cFe is calculated by isotope mass balance, then the $\delta^{56}\text{Fe}$ of surface cFe was more variable ($+0.38 \pm 0.12\text{‰}$ and $-0.36 \pm 0.22\text{‰}$, respectively). In contrast, the $\delta^{56}\text{Fe}$ of subsurface sFe and bulk dFe were identical within error at all but one subsurface depths sampled (see Figure 12). We note that the bulk dFe $\delta^{56}\text{Fe}$ values reported here are in good agreement with those reported by Conway and John (2014) for similar depths of nearby stations. We also emphasize that these sFe and dFe isotope ratios are not likely to have been fractionated during filtration for three reasons. First, sFe appears to be wholly recovered using this CFF system and thus would not be fractionated as a result of poor recovery (Fitzsimmons and Boyle, 2014a). Second, sFe samples collected from the surface Pacific Ocean using the same CFF system did not result in positively fractionated sFe $\delta^{56}\text{Fe}$ (Fitzsimmons and Conway, unpublished results). Finally, stepwise ultrafiltration through 0.4 μm , 0.22 μm , 0.1 μm , 100 kDa, 10 kDa, and 1 kDa membranes resulted in equivalent <1 kDa sFe isotope ratios as direct filtration from 0.4 μm to 1 kDa using similar ultrafiltration membranes in a river water study (Ilina *et al.*, 2013), suggesting that ultrafiltration does not fractionate Fe isotopes in natural waters.

The size fractionated dFe isotope patterns are consistent with the dFe partitioning and exchange model presented in Figure 11. The fact that the sFe and cFe $\delta^{56}\text{Fe}$ are different in the surface but similar in the intermediate/deep ocean indicates either a change in the sources of Fe to the colloidal and soluble phases in the surface than in the deep ocean or the presence of different fractionation pathways at different depths. For example, the identical $\delta^{56}\text{Fe}$ values for sFe and dFe (and thus cFe) in the subsurface

suggest that subsurface sFe and cFe have either the same source and undergo exchange reactions that are non-fractionating, have different sources with identical $\delta^{56}\text{Fe}$ signatures, or have been isotopically equilibrated via Fe exchange. The isotopic similarity between sFe and cFe across the entire section in the deep ocean is particularly surprising given the wide variety of processes which could influencing subsurface $\delta^{56}\text{Fe}$ including variable remineralization rates (as reflected in changing AOU values, Figure 5), different pre-formed dFe and $\delta^{56}\text{Fe}$ ratios in different water masses (e.g. the Surface Waters, Central Waters, Atlantic Equatorial Waters, Mediterranean Outflow Waters, and Irminger Sea Waters; Jenkins *et al.*, this issue), and variable scavenging and exchange reactions that occur in the subsurface ocean as a function of variable particle loading/composition and ligand composition. A contribution of pre-formed sFe and cFe with different concentrations and/or isotope ratios could explain the different Fe isotope values between sFe ($+0.37 \pm 0.16\text{‰}$) and dFe ($+0.78 \pm 0.08\text{‰}$) at 531m at USGT11-11 if the pre-formed sFe in the Southwest Atlantic Central Waters partially feeding that depth was isotopically lighter than the sFe in the North Atlantic Central Water fully feeding the 286 m sample at the same station. However, the fact that the sFe and cFe isotope ratios are nearly identical in the other intermediate/deep ocean samples, yet different water masses feed those stations as well, suggests instead another deep ocean process is regulating Fe isotope ratios at depth.

There is no evidence in the literature that remineralization fractionates Fe isotopes (John and Adkins, 2012), especially between soluble and colloidal phases, nor that scavenging induces an Fe isotope effect (Radic *et al.*, 2011). Thus, for the sFe and cFe to have both nearly identical Fe isotope signatures and equal concentrations in the intermediate/deep ocean, sFe and cFe would have to be equally influenced by non-fractionating remineralization and/or scavenging pathways as well as have identical isotope compositions in water masses delivering pre-formed Fe. More likely, the Fe exchange processes following remineralization (such as sorption/desorption or aggregation/disaggregation associated with scavenging) that we propose in the dFe size partitioning model of Figure 11 might produce, with sufficient reaction time, the constant 50:50% sFe:cFe partitioning and isotope equilibrium observed between sFe and cFe in the North Atlantic. This is similar to the isotopic buffering between particles and organic ligands that John and Adkins (2012) hypothesized to cause the nearly constant dFe isotope ratios nearby in the North Atlantic.

In the surface ocean, however, the isotopically heavier sFe relative to cFe and bulk dFe suggest that sFe and cFe have unique sources conferring different Fe isotope signatures or that sFe and cFe are fractionated separately. Surface dFe at USGT11-11 and USGT11-23 are both thought to have an aerosol source (Section 3.1.1), so a further Fe transformation process must be implicated to explain the different sFe and cFe $\delta^{56}\text{Fe}$ values. If North Atlantic surface cFe was composed of inorganic pieces of dust, it would likely have a crustal $\delta^{56}\text{Fe}$ value near $+0.1\text{‰}$ (Beard *et al.*, 2003). Neither station had a surface

calculated cFe $\delta^{56}\text{Fe}$ of +0.1‰, but both stations' colloidal $\delta^{56}\text{Fe}$ were close to +0.1‰ when propagated errors are considered, so this hypothesis cannot be rejected without future testing.

Nonetheless, Fe isotope fractionation must have occurred during dust solubilization and/or binding by organic ligands, since the dust-derived bulk dFe $\delta^{56}\text{Fe}$ of the surface ocean is isotopically heavier than the +0.1‰ measured in dust itself (Figure 12). Isotopically heavy aerosol-derived surface dFe is somewhat surprising, given that the only published results of the Fe isotope ratios derived from aerosol solubilization in aerosol leach solutions suggested no significant fractionation (pH 4.7 ammonium acetate leach, Waeles *et al.*, 2007). However, the isotope fractionation may be controlled over longer timescales (an equilibrium isotope effect), such as during the non-reductive dissolution of Fe from sediment particles (Homoky *et al.*, 2013; Radic *et al.*, 2011) or during the binding of Fe by organic ligands (Dideriksen *et al.*, 2008). One laboratory study has suggested that stronger ligands bind heavier Fe than weaker ligands, in accordance with expectations of equilibrium isotope fractionation (Morgan *et al.*, 2010). By this argument, the binding of sFe by very strong Fe-binding ligands could explain its enrichment relative to cFe, which is possibly more loosely associated/trapped inside bulky organics or is inorganic in composition. Alternatively, several other Fe transformations occurring in the surface ocean could favor sFe or cFe and fractionate surface sFe and cFe isotopes including photoreduction of Fe(III) to Fe(II), biological uptake of dFe, and scavenging of Fe onto particles. The potential isotope effects associated with these processes are unknown, and thus we cannot further constrain their possible impact on size fractionated $\delta^{56}\text{Fe}$.

Overall, the Fe isotopic signatures of the sFe fraction support our dFe size partitioning model (Figure 11) that sFe and cFe have either different sources or undergo different processes in the upper ocean, while they are sourced by identical remineralization pathways or are isotopically equilibrated by the exchange reactions following remineralization in the subsurface ocean. We also note that while the $\delta^{56}\text{Fe}$ of the bulk dFe was relatively invariant in this dataset (Figure 12), the $\delta^{56}\text{Fe}$ of the sFe and cFe phases were more variable and provided new information that could not be derived from dFe concentration or isotope ratios alone. Thus, Fe isotopic analysis of the sFe and cFe phases appears to be a useful new tool for investigating the sources, cycling, and potentially even the chemical composition of marine dFe.

3.4 Final thoughts on the physicochemical speciation of dFe

We conclude with a comment on resolving the physical size partitioning of dFe with the chemical composition of dFe. Gledhill and Buck (2012) define these as:

Physical partitioning: $\text{dFe} = \text{sFe} + \text{cFe}$

Chemical partitioning: $\text{dFe} = \text{Fe}' + \text{FeL} + \text{Fe}_{\text{inert}}$

where dFe is categorized by size into soluble and colloidal phases (as in this study) and by chemical composition as labile inorganic Fe complexes (Fe'), complexes of Fe to organic ligands labile on the order of hours (FeL), and relatively refractory Fe complexes (Fe_{inert}). Because different analytical methods are used to measure the physical and chemical size partitioning of dFe, it is difficult to reconcile them. However, it is reasonable to assume that Fe' falls entirely into the soluble phase, FeL is found in both soluble and colloidal fractions, and Fe_{inert} might encompass both size fractions as well, given the possibility that very strongly-bound FeL complexes of soluble size could appear inert and inorganically-bound colloidal Fe (Fe nanoparticles) would appear refractory by electrochemical speciation techniques.

We raise this distinction because we have hypothesized that in the surface ocean, along Line W, and downstream of TAG, an excess cFe pool exists that does not exchange with the "steady state" partitioned dFe throughout the rest of the North Atlantic Ocean. While we cannot confirm the chemical composition of this cFe from the observed size partitioning alone, we do know that dFe in these locations was derived from continental sources and does not appear to exchange with the ambient dFe pools on relevant timescales (see sections 3.1, 3.3.3, and 3.3.4). Thus our data are consistent with a hypothesis that this excess cFe fraction could be inorganic cFe that is so small that it remains suspended in the cFe phase, which is different from the more typical (assumed here organically-bound) cFe found throughout the rest of GA03 deep waters.

This suggestion of the presence of inorganic cFe is important because different compositional forms of cFe would be likely to undergo different exchange processes at very different rates. In other words, the individual exchange processes between cFe and sFe or pFe in the model of Fig. 10 would potentially be different for inorganic and organically-bound cFe. For example, inorganic cFe may be "inert" to biological processes and even have different exchange rates between the Fe size fractions than typical (organic) marine dFe. Others have previously suggested that nanoparticulate dFe could be stabilized/trapped inside colloidal-sized organics such as transparent exopolymer compounds (Stolpe and Hasselov, 2010). While an inorganic component to dFe would be no surprise in hydrothermal plumes where nanoparticulate pyrite has already been posited to exist in the dFe size fraction (Yucel *et al.*, 2011), a significant nanoparticulate component of dFe in the surface ocean or along Line W would provide an exception to the prevailing view that >99.9% of marine dFe is bound by organic ligands. However, our suggestion of a significant inorganic cFe pool is consistent with Fe-ligand size partitioning studies in the surface North Atlantic Ocean that report nearly no excess colloidal Fe ligands, despite there being a surface excess of cFe over sFe (Cullen *et al.*, 2006): potentially much of this "inert" cFe is inorganic Fe that does not have an "unbound" ligand pool capable of being analyzed electrochemically.

With the size partitioning data reported here, we cannot confirm an inorganic cFe composition. For confirmation, we look toward future analyses of the cFe phase by synchrotron (similar to von der

Heyden *et al.*, 2012) and flow-field flow fractionation methods (Stolpe *et al.*, 2010) to resolve the physical and chemical classifications of dFe. Only with this resolution could we justify a refined Fig. 10 model differentiating the exchange reactions and kinetics that unique chemical forms of cFe undergo.

4. Conclusions

We sampled 28 stations across the North Atlantic Ocean for the size partitioning of dFe into soluble ($<0.02\ \mu\text{m}$) and colloidal ($0.02\text{-}0.2\ \mu\text{m}$) phases with the highest depth resolution explored to date. Assisted by the multidimensional range of GA03 chemical tracers discussed in this issue and cited throughout this paper, we have reached a new view of dFe partitioning in the North Atlantic Ocean. Previously dFe was thought to have a constant sFe component and a more variable cFe component that alone controlled the variability in the observed dFe profile (Bergquist *et al.*, 2007). sFe was believed to be the more "nutrient-like" phase, while cFe had a more dynamic distribution related to new Fe inputs. Following this, we expected to find a relatively uniform sFe concentration in the intermediate and deep North Atlantic Ocean. Instead, we found that both sFe and cFe have variable concentrations in the North Atlantic Ocean, and both contribute to dFe variability nearly equally, which we hypothesize occurs via a "steady state" partitioning driven by constant exchange between the Fe pools following remineralization. We observe a near 50:50% dFe partitioning into sFe and cFe fractions in the North Atlantic below the deep chlorophyll maximum and a partitioning favoring 60-80% cFe along Line W. Using a smaller definition of sFe ($<10\text{kDa}$), we found a ~65% partitioning into cFe along the eastern North Atlantic (2010 stations).

However, several regions of the North Atlantic failed to reach the dFe size partitioning "steady state," either because not enough time had passed for the dFe to reach steady state or because some of the dFe was not kinetically labile to exchange. The clearest examples of these were the upper ocean, where cFe dominated in the surface ocean underlying the North African dust plume, and in waters in and downstream of the TAG hydrothermal plume. We hypothesize that there may be a significant inorganic cFe component to these continentally-derived Fe sources. In contrast, cFe disappeared in the deep chlorophyll maximum as a result of increased cFe biological uptake and/or scavenging/aggregation to the particulate Fe phase in upper ocean waters, after which the remaining dFe did not re-attain steady state size partitioning. Thus, we have found that sFe and cFe cycle synchronously through much of the North Atlantic ocean, except in the upper ocean and in regions experiencing significant lithogenic cFe inputs, where cFe cycles independently of sFe. The suggested constant partitioning of dFe accomplished by Fe exchange between phases was further supported by stable Fe isotope ratios of the sFe and dFe phases, where sFe and dFe had identical $\delta^{56}\text{Fe}$ in the subsurface (connoting successful steady state exchange) but had very different $\delta^{56}\text{Fe}$ in the surface ocean (where sFe and cFe are thought to cycle independently).

This dFe size partitioning could be incorporated into future models of dFe biogeochemistry in order to better predict Fe limitation and downstream dFe concentrations, since the two size fractions potentially behave uniquely during biouptake and scavenging. We also look forward to future studies that better combine size partitioning techniques with analyses resolving the chemical composition of the dFe pool in order to better constrain the physicochemical nature of marine dFe.

Figure Captions

Figure 1: Station map. Stations from the 2010 cruise are shown in red, and stations from the 2011 cruise are in blue. The TENATSO crossover station was occupied on both cruises (station USGT10-12 and station USGT11-24). The locations of the Line W stations (USGT11-02 through USGT11-08), BATS station (USGT11-10), TAG hydrothermal station (USGT11-16), and the Mauritanian transect (USGT10-09 through USGT10-12) are also indicated. Stations from the literature that are referenced in this paper are also indicated as open symbols (Bergquist *et al.*, 2007; Fitzsimmons and Boyle, 2014b).

Figure 2: Sections from the 2011 cruise of (a) dissolved Fe $<0.2\mu\text{m}$ analyzed by the Mg co-precipitation method of Wu and Boyle (1998), (b) soluble Fe $<0.02\mu\text{m}$ analyzed by the NTA method of Lee *et al.* (2011), (c) colloidal Fe calculated as $\text{dFe} - \text{sFe}$, and (d) %cFe calculated as cFe/dFe (in percent). Station numbers are shown at the bottom of each panel.

Figure 3: Surface dFe partitioning as a function of longitude from (a) the 2011 cruise and (b) the 2010 cruise. Station numbers are indicated at the top. Colloidal Fe can be calculated as dFe minus sFe. Recall that sFe is defined as $<0.02\mu\text{m}$ in (a) and $<10\text{ kDa}$ in (b). In (b), the gray points at -22°W are from USGT10-07, which lies somewhat north of the other three stations indicated (Mauritanian transect USGT10-10 through USGT10-12). Error bars show ± 1 standard deviation error on analytical replicates.

Figure 4: The speciation and size distribution of dissolved Fe in the upper 200m on (a-c) the 2011 cruise where sFe is defined as $<0.02\mu\text{m}$ and on (d-e) the 2010 cruise where sFe is defined as $<10\text{ kDa}$. The deep chlorophyll maximum (DCM) is designated as the fluorescence maximum in grey. Note that colloidal Fe ($\text{dFe} - \text{sFe}$) goes to zero at the DCM, except along the western North Atlantic margin (a: USGT11-06). Not surprisingly, the DCM also appears to be a depth of maximum particle loading at many stations, as the light transmission shows a coincident minimum with the DCM (f: USGT10-09, as an example).

Figure 5: dFe partitioning resulting from remineralization in the Central Water layer (potential density $25.8\text{--}27.1\text{ kg/m}^3$), shown as a function of apparent oxygen utilization (AOU) for (a) Line W USGT11-03 to -08 where the sFe size cutoff is $0.02\mu\text{m}$, (b) the subtropical gyre stations USGT11-10 to -24 where the sFe size cutoff is $0.02\mu\text{m}$, and (c) the 2010 cruise stations USGT10-07 to -12 where the sFe size cutoff is 10 kDa . Samples are only utilized in these regressions if they are below the DCM and away from external Fe sources (margin and hydrothermal stations are removed). Filled circles show dFe ($<0.2\mu\text{m}$), open circles show sFe ($<0.02\mu\text{m}$ in a-b, $<10\text{ kDa}$ in c), and crosses show cFe ($\text{dFe} - \text{sFe}$). Fe:C values (in

units of $\mu\text{mol/mol}$) are calculated from the Type-I regressions shown using an AOU:C ratio of 1.6 (Martin *et al.*, 1987). Errors are ± 1 standard error from the calculated regression slope.

Figure 6: Full-depth ocean profiles of dissolved Fe ($<0.2 \mu\text{m}$, closed circles) and soluble Fe ($<0.02 \mu\text{m}$ in a-c and $<10 \text{ kDa}$ in d). Station locations are (a) USGT11-06 with the transmissometry trace, (b) USGT11-12 with the silicate trace, (c) USGT11-20 with the silicate trace, and (d) USGT10-09 with the oxygen trace.

Figure 7: Sections from the 2010 cruise along the Mauritanian transect of (a) dissolved Fe $<0.2 \mu\text{m}$, (b) soluble Fe $<0.02 \mu\text{m}$, (c) colloidal Fe calculated as $\text{dFe} - \text{sFe}$, and (d) %cFe calculated as cFe/dFe . Station numbers are shown at the bottom of each panel.

Figure 8: A comparison of dFe size partitioning during the two years of cruises at TENATSO. (a) dFe ($<0.2 \mu\text{m}$) over the two years with the oxygen shown in gray to designate the OMZ. (b) sFe over the two years, with the 2010 sampling occurring by CFF ($<10 \text{ kDa}$) and the 2011 sampling occurring by Anopore filtration ($<0.02 \mu\text{m}$). (c) cFe over the two years, as $\text{cFe} = \text{dFe} - \text{sFe}$. (d) A ratio of the 2010 sFe collected by CFF divided by the 2011 sFe collected by Anopore filtration. Depths where this ratio is particularly low indicate depths where there is a significant component of dFe in the $10 \text{ kDa} - 0.02 \mu\text{m}$ size fraction. The dotted line at 70m is the DCM, , and the shaded region includes depths where the dissolved oxygen concentration is $<100 \mu\text{mol/kg}$ (the OMZ). Error bars indicate ± 1 standard deviation in replicate analyses of the same sample.

Figure 9: dFe size partitioning at (a) station USGT11-14, which is $\sim 500 \text{ km}$ to the northwest of the TAG site, and (b-c) station USGT11-16, the TAG site (note the much larger dFe scale in panel c). Colloidal Fe (cFe) can be taken as the difference between dFe and sFe at any depth. In (c), the grey line shows the transmissometer trace, where a drop in the signal designates light absorption by enhanced particles in the water column. In the portion of the water column influenced by hydrothermal venting, sFe comprises 9-18% of the dFe at USGT11-14 compared to only 4-11% of the dFe at TAG USGT11-16.

Figure 10: Relationships between dFe, sFe, and cFe in (a) Bergquist *et al.* (2007), (b) Fitzsimmons and Boyle (2014b), (c) Line W stations USGT11-02 through USGT11-08, (d) North Atlantic subtropical gyre stations USGT11-10 through USGT11-22, and (e) stations USGT10-05 through USGT10-12 from the 2010 eastern North Atlantic cruise including the Mauritanian/OMZ section. In panels c-e, depths below

the DCM are shown as filled circles and are included in the regressions, while depths at and above the DCM are shown as open circles and are not included in the regressions. Station USGT11-16 is excluded altogether, as are the TAG-influenced depths at Station USGT11-14. Regressions are Type-II, and in (a) the statistics are taken from Bergquist *et al.* (2007). The dashed line on the right panels shows the 1:1 sFe:cFe line.

Figure 11: Model of Fe size partitioning, focused on the processes controlling dFe partitioning into soluble and colloidal fractions (box size has no relation to relative Fe pool size in this figure) for (a) the subsurface ocean (below the deep chlorophyll maximum) and (b) the upper ocean (surface through the deep chlorophyll maximum). Measurable quantities are shown in the gray rectangles (sFe, cFe, dFe, pFe), and exchange rates are shown as arrows. The black arrows and bolded processes indicate the mechanism(s) driving the dominant partitioning pattern expressed in the partitioning plots of Figure 10 for each depth range.

Figure 12: Size partitioned dFe concentration and stable isotope ratio ($\delta^{56}\text{Fe}$) at (a) USGT11-11 near Bermuda and (b) USGT11-21 (at the surface) and USGT11-23 (at 475m). dFe ($<0.2\ \mu\text{m}$) is shown with filled circles and solid lines, sFe ($<10\ \text{kDa}$) is shown with open circles and dashed lines, and cFe ($10\ \text{kDa} < \text{cFe} < 0.2\ \mu\text{m}$) is shown as crosses and was calculated as dFe - sFe and by isotope mass balance. The dissolved oxygen CTD trace is indicated in gray for USGT11-11 and USGT11-23.

Parameter or SRM	Consensus [Fe]	[dFe]	2010 [sFe]	2011 [sFe]
Procedure blank range	--	0.078 $\pm$ 0.008 (n=11 sessions)	0.009-0.019 (n=11 sessions)	0.006-0.026 (n=18 sessions)
Detection limit (3 σ)	--	0.03-0.05	0.027	0.030
SAFe D2	0.933 $\pm$ 0.032	0.950 $\pm$ 0.035	0.931 $\pm$ 0.046 (#446, n=28)	0.930 $\pm$ 0.042 (#446, n=43)
SAFe surface underway (Boyle-lab internal standard)	0.093 $\pm$ 0.008 (assume SAFe S)	--	0.083 $\pm$ 0.035 (n=39)	0.079 $\pm$ 0.050 (n=73)
SAFe S	0.093 $\pm$ 0.008	0.103 $\pm$ 0.010	--	0.094 $\pm$ 0.006 (#16, n=3)
				0.108 $\pm$ 0.002 (#318, n=3)

Table 1: Reported procedure blanks, detection limits, and comprehensive lab analyses of the SAFe standard reference materials over the analytical sessions. dFe concentrations were analyzed in the Wu laboratory at RSMAS by the method described in Wu and Boyle (1998). sFe concentrations were

analyzed in the Boyle laboratory at MIT by the methods described in Lee *et al.* (2011). All Fe concentrations are in units of nmol/kg, and consensus values are taken from <http://www.geotraces.org/science/intercalibration> as of May 2013. The detection limit is calculated as three times the standard deviation of the procedure blank for each analytical session.

Year	Stations	Dissolved Fe		Soluble Fe		%sFe _{REMIN}	%sFe _{PF}
		dFe:C ($\mu\text{mol/mol}$)	Pre-formed dFe (nmol/kg)	sFe:C ($\mu\text{mol/mol}$)	Pre-formed sFe (nmol/kg)	sFe:C / dFe:C	Pre-formed sFe/dFe
2010	7,11,12	5.49 $\pm$ 0.82	0.45 $\pm$ 0.08	2.26 $\pm$ 1.06	0.16 $\pm$ 0.10	41 $\pm$ 25%	35 $\pm$ 29%
2011	Line W: 3-8	5.69 $\pm$ 1.30	0.26 $\pm$ 0.04	2.49 $\pm$ 0.69	0.07 $\pm$ 0.02	44 $\pm$ 22%	27 $\pm$ 13%
	Gyre: 10-22	6.02 $\pm$ 0.66	0.20 $\pm$ 0.03	2.83 $\pm$ 0.36	0.11 $\pm$ 0.01	47 $\pm$ 11%	57 $\pm$ 15%

Table 2: dFe:C and sFe:C relationships (in $\mu\text{mol/mol}$) and pre-formed dFe and sFe (in nmol/kg) Central Waters below the DCM in the potential density range 25.8-27.1 kg/m^3 (largely dominated by North Atlantic Central Water, with smaller contributions of Atlantic Equatorial Water, and Southwest Atlantic Central Water, Jenkins *et al.*, this issue). The %sFe_{REMIN} (% soluble Fe attributed to remineralization) is calculated as the ratio of sFe:C to dFe:C (ignores the partitioning contribution by pre-formed dFe). The %sFe_{PF} attributed to pre-formed dFe is calculated as the ratio of pre-formed sFe to pre-formed dFe (ignores the partitioning contribution by remineralization). Fe:C values are calculated from a Type-I regression of Fe and AOU, and the Fe:AOU slope was converted to an Fe:C using the AOU:C ratio of 1.6 (Martin *et al.*, 1987). Error values are ± 1 standard error from the calculated regression.

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(a)

USGT11-11

(b)

USGT11-21 and -23

(a) Subsurface Ocean Fe Exchange Model: sFe and cFe cycle *synchronously*

(b) Upper Ocean Fe Exchange Model: sFe and cFe cycle *independently*

(a) USGT11-06 **(b) USGT11-16 (TAG)** **(c) USGT11-20** **(d) USGT10-05** **(e) USGT10-09** **(f) USGT10-09**

(a) GEOTRACES 2011

(b) GEOTRACES 2010

Fig. 1 Station map. Stations from the 2010 cruise are shown in red, and stations from the 2011 cruise are in blue. The TENATSO crossover station was occupied on both cruises (station USGT10-12 and station USGT11-24). The locations of the Line W stations (USGT11-02 through USGT11-08), BATS station (USGT11-10), TAG hydrothermal station (USGT11-16), and the Mauritanian transect (USGT10-09 through USGT10-12) are also indicated. Stations from the literature that are referenced in this paper are also indicated as open symbols (Bergquist et al., 2007; Fitzsimmons and Boyle, 2014b).

Fig. 2 Sections from the 2011 cruise of (a) dissolved Fe $<0.2\mu\text{m}$ analyzed by the Mg co-precipitation method of Wu and Boyle (1998), (b) soluble Fe $<0.02\mu\text{m}$ analyzed by the NTA method of Lee et al. (2011), (c) colloidal Fe calculated as $\text{dFe} - \text{sFe}$, and (d) %cFe calculated as cFe/dFe (in percent). Station numbers are shown at the bottom of each panel.

Fig. 3 Surface dFe partitioning as a function of longitude from (a) the 2011 cruise and (b) the 2010 cruise. Station numbers are indicated at the top. Colloidal Fe can be calculated as dFe minus sFe. Recall that sFe is defined as $<0.02\mu\text{m}$ in (a) and $<10\text{kDa}$ in (b). In (b), the gray points at -22°W are from USGT10-07, which lies somewhat north of the other three stations indicated (Mauritanian transect USGT10-10 through USGT10-12). Error bars show ± 1 standard deviation error on analytical replicates.

Fig. 4 The speciation and size distribution of dissolved Fe in the upper 200m on (a-c) the 2011 cruise where sFe is defined as $<0.02\mu\text{m}$ and on (d-e) the 2010 cruise where sFe is defined as $<10\text{kDa}$. The deep chlorophyll maximum (DCM) is designated as the fluorescence maximum in grey. Note that colloidal Fe ($\text{dFe} - \text{sFe}$) goes to zero at the DCM, except along the western North Atlantic margin (a: USGT11-06). Not surprisingly, the DCM also appears to be a depth of maximum particle loading at many stations, as the light transmission shows a coincident minimum with the DCM (f: USGT10-09, as an example).

Fig. 5 dFe partitioning resulting from remineralization in the Central Water layer (potential density $25.8\text{--}27.1\text{kg/m}^3$), shown as a function of apparent oxygen utilization (AOU) for (a) Line W USGT11-03 to -08 where the sFe size cutoff is $0.02\mu\text{m}$, (b) the subtropical gyre stations USGT11-10 to -24 where the sFe size cutoff is $0.02\mu\text{m}$, and (c) the 2010 cruise stations USGT10-07 to -12 where the sFe size cutoff is 10kDa . Samples are only utilized in these regressions if they are below the DCM and away from external Fe sources (margin and hydrothermal stations are removed). Filled circles show dFe ($<0.2\mu\text{m}$), open circles show sFe ($<0.02\mu\text{m}$ in a-b, $<10\text{kDa}$ in c), and crosses show cFe ($\text{dFe} - \text{sFe}$). Fe:C values (in units of $\mu\text{mol/mol}$) are calculated from the Type-I regressions shown using an

AOU:C ratio of 1.6 (Martin et al., 1987). Errors are ± 1 standard error from the calculated regression slope.

Fig. 6 Full-depth ocean profiles of dissolved Fe ($<0.2\text{ }\mu\text{m}$, closed circles) and soluble Fe ($<0.02\text{ }\mu\text{m}$ in a-c and $<10\text{ kDa}$ in d). Station locations are (a) USGT11-06 with the transmissometry trace, (b) USGT11-12 with the silicate trace, (c) USGT11-20 with the silicate trace, and (d) USGT10-09 with the oxygen trace.

Fig. 7 Sections from the 2010 cruise along the Mauritanian transect of (a) dissolved Fe $<0.2\text{ }\mu\text{m}$, (b) soluble Fe $<0.02\text{ }\mu\text{m}$, (c) colloidal Fe calculated as $\text{dFe} - \text{sFe}$, and (d) %cFe calculated as cFe/dFe . Station numbers are shown at the bottom of each panel.

Fig. 8 A comparison of dFe size partitioning during the two years of cruises at TENATSO. (a) dFe ($<0.2\text{ }\mu\text{m}$) over the two years with the oxygen shown in gray to designate the OMZ. (b) sFe over the two years, with the 2010 sampling occurring by CFF ($<10\text{ kDa}$) and the 2011 sampling occurring by Anopore filtration ($<0.02\text{ }\mu\text{m}$). (c) cFe over the two years, as $\text{cFe} = \text{dFe} - \text{sFe}$. (d) A ratio of the 2010 sFe collected by CFF divided by the 2011 sFe collected by Anopore filtration. Depths where this ratio is particularly low indicate depths where there is a significant component of dFe in the $10\text{ kDa} - 0.02\text{ }\mu\text{m}$ size fraction. The dotted line at 70 m is the DCM, and the shaded region includes depths where the dissolved oxygen concentration is $<100\text{ }\mu\text{mol/kg}$ (the OMZ). Error bars indicate ± 1 standard deviation in replicate analyses of the same sample.

Fig. 9 dFe size partitioning at (a) station USGT11-14, which is $\sim 500\text{ km}$ to the northwest of the TAG site, and (b-c) station USGT11-16, the TAG site (note the much larger dFe scale in panel c). Colloidal Fe (cFe) can be taken as the difference between dFe and sFe at any depth. In (c), the grey line shows the transmissometer trace, where a drop in the signal designates light absorption by enhanced particles in the water column. In the portion of the water column influenced by hydrothermal venting, sFe comprises 9-18% of the dFe at USGT11-14 compared to only 4-11% of the dFe at TAG USGT11-16.

Fig. 10 Relationships between dFe, sFe, and cFe in (a) Bergquist et al. (2007), (b) Fitzsimmons and Boyle (2014b), (c) Line W stations USGT11-02 through USGT11-08, (d) North Atlantic subtropical gyre stations USGT11-10 through USGT11-22, and (e) stations USGT10-05 through USGT10-12 from the 2010 eastern North Atlantic cruise including the Mauritanian/OMZ section. In panels c-e, depths below the DCM are shown as filled circles and are included in the regressions, while depths at and

above the DCM are shown as open circles and are not included in the regressions. Station USGT11-16 is excluded altogether, as are the TAG-influenced depths at Station USGT11-14. Regressions are Type-II, and in (a) the statistics are taken from Bergquist et al. (2007). The dashed line on the right panels shows the 1:1 sFe:cFe line.

Fig. 11 Model of Fe size partitioning, focused on the processes controlling dFe partitioning into soluble and colloidal fractions (box size has no relation to relative Fe pool size in this figure) for (a) the subsurface ocean (below the deep chlorophyll maximum) and (b) the upper ocean (surface through the deep chlorophyll maximum). Measurable quantities are shown in the gray rectangles (sFe, cFe, dFe, pFe), and exchange rates are shown as arrows. The black arrows and bolded processes indicate the mechanism(s) driving the dominant partitioning pattern expressed in the partitioning plots of Fig. 10 for each depth range.

Fig. 12 Size partitioned dFe concentration and stable isotope ratio ($\delta^{56}\text{Fe}$) at (a) USGT11-11 near Bermuda and (b) USGT11-21 (at the surface) and USGT11-23 (at 475 m). dFe ($<0.2\ \mu\text{m}$) is shown with filled circles and solid lines, sFe ($<10\ \text{kDa}$) is shown with open circles and dashed lines, and cFe ($10\ \text{kDa} < \text{cFe} < 0.2\ \mu\text{m}$) is shown as crosses and was calculated as dFe - sFe and by isotope mass balance. The dissolved oxygen CTD trace is indicated in gray for USGT11-11 and USGT11-23.

Table 1 Reported procedure blanks, detection limits, and comprehensive lab analyses of the SAFe standard reference materials over the analytical sessions. dFe concentrations were analyzed in the Wu laboratory at RSMAS by the method described in Wu and Boyle (1998). sFe concentrations were analyzed in the Boyle laboratory at MIT by the methods described in Lee et al. (2011). All Fe concentrations are in units of nmol/kg, and consensus values are taken from <http://www.geotraces.org/science/intercalibration> as of May 2013. The detection limit is calculated as three times the standard deviation of the procedure blank for each analytical session.

Parameter or SRM	Consensus [Fe]	[dFe]	2010 [sFe]	2011 [sFe]
Procedure blank range	—	0.078±0.008 (n=11 sessions)	0.009–0.019 (n=11 sessions)	0.006–0.026 (n=18 sessions)
Detection limit (3 σ)	—	0.03–0.05	0.027	0.030
SAFe D2	0.933±0.032	0.950±0.035	0.931±0.046 (#446, n=28)	0.930±0.042 (#446, n=43)
SAFe surface underway (Boyle-lab internal standard)	0.093±0.008 (assume SAFe S)	—	0.083±0.035 (n=39)	0.079±0.050 (n=73)
SAFe S	0.093±0.008	0.103±0.010	—	0.094±0.006 (#16, n=3) 0.108±0.002 (#318, n=3)

Table 2 dFe:C and sFe:C relationships (in $\mu\text{mol/mol}$) and pre-formed dFe and sFe (in nmol/kg) Central Waters below the DCM in the potential density range $25.8\text{--}27.1\sigma_{\theta}\text{kg/m}^3$ (largely dominated by North Atlantic Central Water, with smaller contributions of Atlantic Equatorial Water, and Southwest Atlantic Central Water, Jenkins et al., this issue). The %sFe_{REMIN} (% soluble Fe attributed to remineralization) is calculated as the ratio of sFe:C to dFe:C (ignores the partitioning contribution by pre-formed dFe). The %sFe_{PF} attributed to pre-formed dFe is calculated as the ratio of pre-formed sFe to pre-formed dFe (ignores the partitioning contribution by remineralization). Fe:C values are calculated from a Type-I regression of Fe and AOU, and the Fe:AOU slope was converted to an Fe:C using the AOU:C ratio of 1.6 (Martin et al., 1987). Error values are ± 1 standard error from the calculated regression.

Year	Stations	Dissolved Fe dFe:C ($\mu\text{mol/mol}$)	Soluble Fe Pre-formed dFe (nmol/kg)	%sFe _{REMIN} sFe:C ($\mu\text{mol/mol}$)	%sFe _{PF} Pre- formed sFe (nmol/kg)	sFe:C / dFe:C	Pre- formed sFe/dFe
2010	7,11,12	5.49 ± 0.82	0.45 ± 0.08	2.26 ± 1.06	0.16 ± 0.10	$41\pm 25\%$	$35\pm 29\%$
2011	Line W: 3– 8	5.69 ± 1.30	0.26 ± 0.04	2.49 ± 0.69	0.07 ± 0.02	$44\pm 22\%$	$27\pm 13\%$
	Gyre: 10– 22	6.02 ± 0.66	0.20 ± 0.03	2.83 ± 0.36	0.11 ± 0.01	$47\pm 11\%$	$57\pm 15\%$