Intercomparison of dissolved iron isotope profiles from re-occupation of three GEOTRACES stations in the Atlantic Ocean

Conway, T. M.^{1,2,*}, John, S. G.^{2,3} and Lacan, F.⁴

¹ Dept. Earth Sciences, ETH Zürich, Zürich, Switzerland

² Dept. Earth and Ocean Sciences, University of South Carolina, Columbia, S.C., United States

³ Dept. of Earth Sciences, University of Southern California, Los Angeles, USA (present address)

⁴ LEGOS, Université de Toulouse, CNES, CNRS, IRD, UPS, Toulouse, France

*Corresponding author: *conway.tm@gmail.com*; Phone: Tel: +41 44 632 4797

Keywords: trace metals, GEOTRACES, biogeochemistry, intercomparison

Abstract

Intercomparison of trace metal data is a key aspect of the International GEOTRACES program, allowing data from multiple laboratories and countries to be combined to produce high-resolution datasets for the oceans. The use of crossover stations by the GEOTRACES program provides the opportunity both for comparison of analytical techniques and assessment of temporal variability in the cycling of trace metals such as iron (Fe). Here, we present the first comparison of dissolved Fe stable isotope ratio ($\delta^{56}\text{Fe}$; relative to IRMM-014) profiles in the oceans, from re-occupations of three locations in the Atlantic Ocean; (1) the Bermuda Atlantic Time Series Station (31.75°N 64.17°W) during the U.S. GEOTRACES IC1 cruise (June 2008) and the U.S. GEOTRACES GA03 cruise (Nov. 2011); (2) a station near Cape Verde (17.4°N 24.5°W) during the U.S. GEOTRACES GA03 cruises (2010; 2011), and (3) two nearby stations in the Cape Basin close to South West Africa (31.1-31.4°S 36.5°W) during the French GEOTRACES GIPY4 Bonus Good Hope Cruise (Feb. 2008) and the U.K. GEOTRACES GA10 D357 cruise (Oct. 2010). These datasets provided us with the opportunity not only to compare sampling and analysis techniques by two different laboratories (USC and LEGOS), but also the temporal variability of $\delta^{56}\text{Fe}$ at these locations on a 1-3 year timescale. A good agreement between data and profiles generated by different laboratories does allow assessment of temporal variation of $\delta^{56}\text{Fe}$ in the water column, as well as spatial variability and synthesis of datasets from different regions of the ocean. Comparison of $\delta^{56}\text{Fe}$ at the three locations in this study demonstrates a remarkable consistency between the shape of ocean $\delta^{56}\text{Fe}$ profiles measured 1-3 years apart, pointing to the overall stability of Fe cycling at all three locations on these timescales, despite the expected dynamic nature of the Fe cycle. This consistency is highlighted by strong agreement in $\delta^{56}\text{Fe}$ throughout the whole water-column at Bermuda, and in waters deeper than 500 m in the Cape Basin, which suggests that different water masses may carry distinct $\delta^{56}\text{Fe}$ signatures. In contrast to the stable $\delta^{56}\text{Fe}$ at these locations, we observe some apparent variability in $\delta^{56}\text{Fe}$ between cruises at other locations, both throughout the water column at Cape Verde, and in Agulhas-leakage influenced surface waters in the Cape Basin. Such variability may provide information about changes in internal Fe cycling or external Fe sources on these timescales. Overall, this study highlights the usefulness of repeat $\delta^{56}\text{Fe}$

measurements to provide information on the variability of Fe cycling throughout the oceans.

1. Introduction

Seawater dissolved iron (Fe) is an important limiting nutrient for phytoplankton over much of the surface oceans (Moore *et al.*, 2001). Understanding the global distribution and biogeochemical cycling of Fe is a central aim of the international GEOTRACES program which seeks to measure global distributions of a range of trace elements and their isotopes. Fe concentrations are a GEOTRACES key parameter, meaning their analysis is required on all GEOTRACES cruises (Anderson and Henderson, 2005; Henderson *et al.*, 2007). Fe stable isotopes ($\delta^{56}\text{Fe}$) have been measured on several GEOTRACES cruises, although they are not a key parameter. The resulting ocean sections of dissolved Fe concentration from the Atlantic, Indian and Pacific Oceans, and similar sections in progress, are beginning to provide new insights into the marine sources, sinks and cycling of Fe at both the regional and global scale throughout the oceans (e.g. Conway and John, 2014a; Klunder *et al.*, 2012; Nishioka *et al.*, 2013; Resing *et al.*, 2015; Rijkenberg *et al.*, 2014; Saito *et al.*, 2013).

GEOTRACES cruises all follow internationally agreed methods for clean sampling and handling (The GEOTRACES Cookbook; Cutter *et al.*, 2010; 2014), meaning that datasets can be collated to form regional and global pictures of the distribution of trace metals and their isotopes in the ocean. Recently, such data as been combined to form the GEOTRACES Intermediate Data Product and the GEOTRACES eAtlas (Mawji *et al.*, 2015; Schlitzer, 2015). To ensure compatibility of datasets from different groups and nations, given the range of collection and analytical techniques deployed on different cruises, it is essential to carry out intercomparison of data collected from the same location and/or in the same samples by multiple groups. Accordingly, intercomparison is an important aspect of the GEOTRACES program, with the recommended reporting of measurements of SAFe reference standards for dissolved trace metal concentrations, the use of cross-over stations for comparison between different GEOTRACES cruises (see Fig. 1), and a number of studies comparing sampling systems (Cutter, 2013). Inter-comparison of trace metal

concentrations and stable isotope ratios was a goal of two U.S. GEOTRACES cruises in the Atlantic (IC1, June 2008) and North Pacific (IC2, May 2009) Oceans (Boyle *et al.*, 2012; Cutter and Bruland, 2012; Cutter, 2013; and others), and recent work has compared the clean sampling system of the Dutch and US GEOTRACES programs as well as different analytical techniques (Middag *et al.*, 2015).

The GEOTRACES program and similar cruises have also facilitated the application of dissolved Fe isotope ratios ($\delta^{56}\text{Fe}$) as a useful parameter for understanding the marine Fe cycle. Although a challenging measurement, due to the low concentration of Fe in seawater and the difficulties of analysis, advancement in chemical techniques and high-resolution mass spectrometry has allowed a number of groups to develop methods to measure seawater-dissolved $\delta^{56}\text{Fe}$ over the full range of observed oceanic dissolved Fe concentrations (~ 0.02 to >2 nmol kg⁻¹). These methods have utilized either NTA or Nobias PA-1 chelating resins (Boyle *et al.*, 2012; Conway *et al.*, 2013; John and Adkins, 2010; Lacan *et al.*, 2010, 2008; Rouxel and Auro, 2010), extraction with dithiocarbamate (Ellwood *et al.*, 2014) or co-precipitation with magnesium (de Jong *et al.*, 2007), followed by analysis with multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS). Such methods have to date led to the publication of dissolved $\delta^{56}\text{Fe}$ depth profiles from a number of ocean basins (e.g. Chever *et al.*, 2015; John and Adkins, 2012; John *et al.*, 2012; Labatut *et al.*, 2014; Lacan *et al.*, 2008; Radic *et al.*, 2011; Staubwasser *et al.*, 2013), and a high resolution ocean section of dissolved $\delta^{56}\text{Fe}$ across the North Atlantic (Conway and John, 2014a). Dissolved $\delta^{56}\text{Fe}$ measurements were also part of the focus of a previous intercomparison effort utilizing seawater collected from the Bermuda Atlantic Time Series onboard the U.S GEOTRACES IC1 cruise in 2008, where four different laboratories demonstrated strong agreement on both surface and deep water samples at concentrations of 0.4 and 0.8 nmol kg⁻¹ (Boyle *et al.*, 2012; see Fig. 2c-d).

Different marine sources of Fe have different $\delta^{56}\text{Fe}$ signatures, and these isotope signatures have been used to trace Fe as it mixes through the oceanic water column, including non-reductive sediment dissolution (Labatut *et al.*, 2014; Radic *et al.*, 2011), reductive sediment dissolution (Chever *et al.*, 2015, John *et al.*, 2012), and Fe from multiple sources (Conway and John, 2014a). As such, studies of seawater-dissolved $\delta^{56}\text{Fe}$ show promise for understanding the cycling and differing sources of

Fe to the ocean; however, application of this tracer is still limited to a small number of laboratories. Thus, spatial coverage of $\delta^{56}\text{Fe}$ measurements throughout the oceans remains sparse. Additionally, although changing conditions over time are important to our understanding of changes in Fe sources and cycling, logistics and cost have meant that repeat-sampling to assess temporal variability has rarely been carried out. However, re-occupation of crossover stations as part of the GEOTRACES program provides us with the opportunity to begin to address this lack of knowledge of variability, as well as to compare sampling and analysis by different groups.

Here we compare measured Fe and $\delta^{56}\text{Fe}$ profiles from three locations in the Atlantic Ocean (Fig. 1): 1) Occupation of a GEOTRACES crossover station at the Bermuda Atlantic Time Series (BATS; 31.75°N 64.17°W; Fig. 2a) by the U.S. GEOTRACES IC1 cruise in June 2008 and the U.S. GEOTRACES GA03 KN204 cruise in Nov. 2011 (Superstation USGT11-10) allows us to compare $\delta^{56}\text{Fe}$ data measured by Conway and John (U.S.C.; GA03; Conway and John, 2014a) with $\delta^{56}\text{Fe}$ data measured by five laboratories on the IC1 cruise (Boyle *et al.*, 2012). 2) Re-occupation of the Tenatso Time Series station near Cape Verde (17.4°N 24.5°W) by the 2010 (KN204) and 2011 (KN199) cruises of the U.S. GEOTRACES GA03 section (USGT10-12 in Nov. 2010, USGT11-24 in Dec. 2011; Fig. 3a) allow us to compare $\delta^{56}\text{Fe}$ profiles at this location a year apart. 3) Occupation of a GEOTRACES crossover station in the South Atlantic by the U.K. GEOTRACES GA10 D357 Cruise in 2010 (Superstation 3; 31.4°S 36.5°W) and the French GEOTRACES GIPY4 Bonus Good Hope Cruise in 2008 (Superstation S1; 31.1°S 36.5°W) allow us to compare $\delta^{56}\text{Fe}$ profiles from nearby locations three years apart (Fig. 4a), measured using different collection and analytical techniques by Conway and John (GA10; USC) and Lacan (GIPY4; LEGOS). Interpretation of the $\delta^{56}\text{Fe}$ profiles measured at these locations is the focus of other articles (Abadie *et al.*, in review; Conway and John, 2014a; John and Adkins, 2012), and so here we instead focus largely on intercomparison and assessment of temporal variability of Fe and $\delta^{56}\text{Fe}$.

2. Materials and Methods

2.1 Seawater collection and handling

2.1.1. U.S. GEOTRACES IC1 and GA03 cruises

Seawater collection and sampling were previously described for these cruises by Boyle *et al.* (2012) and Conway and John (2014a), but are briefly summarized here for ease of reference. Clean seawater was collected similarly on all three U.S. GEOTRACES cruises (IC1, KN199, KN204) onboard the RV Knorr, using either underway Teflon towed-fish (surface samples; ~2 m; Cutter and Bruland, 2012) or the U.S. GEOTRACES rosette with 24x12 L GO-Flo bottles on a Kevlar cable (Cutter and Bruland, 2012). Following collection, the GO-Flo bottles were transferred to a clean van and the water filtered through 0.45 µm Osmonics cartridge filters (towed-fish samples) or 0.2 µm Pall Acropak capsule filters (GO-Flo samples).

As part of IC1 at the BATS station (31.75°N 64.17°W; Figs 1-2) on June 22nd 2008, a 500 L surface isotope sample (GSI) was pumped from the towed-fish and filtered into a clean 500 L acid-cleaned polyethylene tank, where it was acidified with the equivalent of 1 mL 12 M HCL per litre (Boyle *et al.*, 2012; John and Adkins, 2012). Similarly a 250 L deep isotope sample (GDI) was collected from 2000 m using the GEOTRACES rosette, filtered and then homogenized and acidified in an identical polyethylene tank (Boyle *et al.*, 2012). An 8 point profile for isotope comparison (GPri) from depths of 75-3500 m and a single sample for Fe isotope measurement at 4200 m were also collected using the GEOTRACES rosette and similarly filtered and acidified (Boyle *et al.*, 2012; John and Adkins, 2012). Supporting oceanographic parameters were made shipboard and are taken from John and Adkins (2012).

As part of the GA03 section cruises, seawater samples were collected using towed-fish or GEOTRACES Rosette and water filtered into 1 L acid-cleaned Nalgene low density polyethylene (LDPE) bottles from: 1) Station USGT10-12 (17.40°N 24.50°W; 25 point profile, 2-3498 m) on the 02/11/2010; 2) Superstation USGT11-12 at the BATS station (31.75°N, 37 point profile 2-4526 m) on November 19th-21st 2011; and 3) Station USGT11-24 (17.40°N 24.50°W; 25 point profile, 2-3517 m) on December 9th-10th 2011. (Figs 1-3). Seawater samples were acidified back on shore to pH ~2 with conc. Aristar Ultra HCl. Supporting oceanographic parameters were made shipboard and are supplied by the Ocean Data Facility (Jenkins *et al.*, 2015).

2.1.2. U.K. GEOTRACES GA10 D357 cruise

Seawater samples were collected from Station 3 (13.39°S 36.46°W; 13 point profile, 2-4724 m) on October 23rd 2010 as part of the GA10 D357 cruise on board the RRS Discovery. Clean seawater samples were collected broadly as described by Wyatt *et al.* (2014); briefly, seawater was collected into twenty four 10 L clean Teflon-coated OTE samplers on a Titanium CTD frame on a plasma (polyethylene) rope. The OTE bottles were transferred to a clean container, and water samples were filtered using Millipore 25 mm 0.4 µm polyethersulfone (PES) filters (>75 m depth) or 0.2 µm AcroPak Supor Pall PES capsules (<75 m depth or fish samples). Filtered seawater was collected into acid-cleaned and seawater-rinsed 1 L Nalgene LDPE bottles. Seawater samples were acidified back on shore to pH ~2 with conc. Aristar Ultra HCl. Salinity, temperature and oxygen were measured shipboard using standard methods as described by Wyatt *et al.* (2014).

2.1.3. French GIPY4 cruise

Seawater samples were collected from Super-Station 1 (St. 18) (13.12°S 36.51°W; 9 point profile, 31-4068 m) on February 20th 2008 as part of the GIPY4 MD166 Bonus Good Hope cruise on board the RV Marion Dufresne. Clean seawater samples were collected and filtered as described previously (Abadie *et al.* in review, Lacan *et al.* 2008, Lacan *et al.*, 2010); briefly, 10 L seawater samples were collected into acid-cleaned 12 L Go-Flo bottles mounted on a Kevlar wire. Go-Flo bottles were brought inside a clean container and seawater was filtered using Savillex PFA Teflon filtration units with 0.45 µm 90 mm nucleopore membranes into 10 L flexible LDPE containers with PP closure, within a few hours of collection. Samples were acidified onboard with 1.7 mL per L of 9 M twice-distilled HCl.

2.2. Analytical Methods

Stable Fe isotope ratios ($\delta^{56}\text{Fe}$) are expressed for all laboratories in this paper in standard delta notation, relative to IRMM-014:

$$\delta^{56}\text{Fe} (\text{‰}) = \left[\frac{\frac{^{56}\text{Fe}}{^{54}\text{Fe}}_{\text{sample}}}{\frac{^{56}\text{Fe}}{^{54}\text{Fe}}_{\text{IRMM-014}}} - 1 \right] * 1000$$

2.2.1. IC1 Intercomparison Exercise

Analytical methods for the four laboratories taking part in the IC-1 exercises were described in full by Boyle *et al.* (2012) and by the respective labs (John and Adkins, 2012; Lacan *et al.*, 2010, 2008; Rouxel and Auro, 2010), with subsequent analysis by USC described below. For reference, three laboratories (WHOI, Caltech, LEGOS) used extraction of Fe from seawater with Qiagen NTA-Superflow resin, whilst one laboratory used extraction using purified ammonium pyrrolidinedithiocarbamate and sodium diethyldithiocarbamate and chloroform (ANU). All laboratories performed analysis by Thermo Neptune MC-ICPMS, either with Ni and standard-sample bracketing (WHOI, Caltech, ANU) or ^{57}Fe - ^{58}Fe double spike technique (LEGOS) for instrumental mass-bias correction. Uncertainty on $\delta^{56}\text{Fe}$ is expressed as 2SE error for ANU, and WHOI (Boyle *et al.* 2012), as 2σ external error for Caltech (John and Adkins., 2012) and as the 2SD on mean $\delta^{56}\text{Fe}$ for LEGOS (see Suppl. Data).

2.2.2. IC1, GA03 and GA10 (USC)

Samples were processed and analyzed at USC for Fe concentration and $\delta^{56}\text{Fe}$ analysis following several months of storage at pH 2, following already published methods, with extraction by Nobias PA-1, purification by AGMP-1 resin and analysis by Thermo Neptune MC-ICPMS with mass bias correction by ^{57}Fe - ^{58}Fe double spike technique (Conway *et al.*, 2013; Conway and John 2014a) in ‘high’ resolution (HR) mode to resolve polyatomic interferences such as ArN^+ and ArO^+ . ^{54}Cr and ^{58}Ni isobaric interferences on ^{54}Fe and ^{58}Fe were corrected for using the measured abundances of ^{53}Cr and ^{60}Ni . A background correction was applied to each sample using the blank 0.1 M HNO_3 acid, with this blank acid measured twice for every group of 4-6 samples. $\delta^{56}\text{Fe}$ were calculated relative to an IRMM-double spike mixture, which was concentration and matrix matched to the samples, and run twice with each group of 4-6 samples. Seawater samples were spiked in a 1:2 sample:spike

ratio, purified from 1 L and measured twice by MC-ICPMS with a mean value calculated.

Following Conway *et al.* (2013), uncertainty on mean $\delta^{56}\text{Fe}$ in figures and Suppl. Data is expressed as 2σ internal error, calculated from replicates and bracketing standards, based on the previous observation that uncertainty with this technique is dominated by internal error (John, 2012). For this study, 2σ internal analytical error varied from 0.04 to 0.18‰, largely dependent on sample Fe concentration. As an indication of external precision for the method we also calculated the 2SD (0.05‰) of the offset of duplicate analyses from the mean of 60 South Atlantic GA10 seawater samples (0.1–1.8 nmol kg⁻¹), with duplicates measured in different analytical sessions (following Steele *et al.*, 2011). This calculated external precision is similar to or smaller than internal error for most samples, suggesting that for these samples internal error is a good representation of overall uncertainty.

Fe concentration measurements were made via isotope-dilution, with a procedural blank of 0.005 nmol kg⁻¹, with 2% uncertainty applied for weighing and pipetting errors (Conway *et al.*, 2013). We have previously shown strong agreement with other laboratories for SAFE standards and profile concentration data produced with this method (Conway *et al.*, 2013; Middag *et al.*, 2015). For some IC1 samples multiple subsamples were purified separately and then each measured twice by MC-ICPMS; here, a mean $\delta^{56}\text{Fe}$ is used in figures.

2.2.3. GIPY4 (LEGOS)

Samples were processed and analysed at LEGOS for $\delta^{56}\text{Fe}$ following previously described methods (Lacan *et al.*, 2008, 2010). Briefly, Fe was pre-concentrated from 4 to 10 L of seawater using an NTA resin column and then purified with AG 1-x4 anionic exchange resin, before redissolution in ~0.7 mL 0.3 M HNO₃ for analysis by MC-ICPMS using a Neptune (Thermo Scientific) coupled with a CETAC Aridus II desolvation system. Instrumental mass bias and potential procedural fractionation was corrected for using the double-spike technique, also following the iterative method of Siebert *et al.* (2001). A ⁵⁷Fe-⁵⁸Fe double spike with a composition of 0.1% ⁵⁴Fe, 2.94% ⁵⁶Fe, 54.90% ⁵⁷Fe and 42.06% ⁵⁸Fe was added to samples in a 1:1 natural:spike

ratio at least 12 hours prior to pre-concentration. Samples were analyzed in medium resolution mode (MR) to resolve polyatomic interferences, using the older Thermo MR slits (30 μm), which correspond more closely to the newer HR slits (18-25 μm). Isobaric interferences on ^{54}Fe and ^{58}Fe were corrected for using the measured abundances of ^{53}Cr and ^{60}Ni .

As described by Lacan *et al.* (2010), each analytical session began with analysis of the in-house ETH Zürich hematite standard relative to IRMM-014 (both mixed with the double-spike), and then the hematite standard was analysed after every two samples as a check on accuracy and precision of the instrument. Each sample was bracketed by the blank acid, with 25 cycles of 8.4 s for samples and standards and 10 cycles of 8.4 s for blanks. This method has been shown to give excellent precision and accuracy over the full range of expected Fe concentrations in seawater (0.05-1 nmol kg^{-1}) in volumes of 2-20 L, with full details described previously (Lacan *et al.*, 2010). Final values are either means calculated from multiple Neptune analysis of a single 10 L sample, calculated from separate extractions of 5 L aliquots, or a combination of the two. 2σ uncertainty on measurements is expressed as the long term reproducibility of the ETH Zürich standard (0.07‰), as the repeatability from seawater samples yielded better results (2σ from 0.01 to 0.05‰). Fe concentration measurements were made by isotope dilution, with a procedural blank corresponding to 0.002 nmol kg^{-1} and uncertainty is expressed as 2SD of replicate analyses (Lacan *et al.*, 2010).

3. Results and Discussion

The $\delta^{56}\text{Fe}$ and Fe data discussed in this study are reproduced from other interpretive studies (Abadie *et al.*, in review; Boyle *et al.*, 2012; Conway and John, 2014a; John and Adkins, 2012; Lacan *et al.*, 2008), with the exception of GA10 results, which are presented here for the first time. All data shown in figures are available as Suppl. Data.

3.1 GA03 (2011) and IC1 at Bermuda (2008)

The water column profiles of Fe and $\delta^{56}\text{Fe}$ for the BATS station from the IC1 and GA03 cruises are shown in Fig 2b, with the $\delta^{56}\text{Fe}$ values for the IC1 intercomparison

depths shown in Fig. 2c-d. Good agreement within error was previously observed between the labs taking part in the IC1 cruise in these samples, for the GSI surface (7 m; Fig. 2c) and GDI deep tanks (2000 m; Fig. 2d), with $\delta^{56}\text{Fe}$ ranging from +0.24 $\pm$ 0.10‰ to +0.41 $\pm$ 0.04‰ for the surface tank and +0.42 $\pm$ 0.11‰ to +0.52 $\pm$ 0.07‰ for the deep tank (Boyle *et al.*, 2012, see Suppl. Data), with all labs reporting data within 2SD of the mean of the five labs (GSI +0.34 $\pm$ 0.13‰ and GSD +0.48 $\pm$ 0.10‰; 2SD), demonstrating the ability of the individual labs to accurately measure $\delta^{56}\text{Fe}$ at dissolved Fe concentrations of 0.4 and 0.8 nmol kg⁻¹.

For comparison of the IC1 and GA03 cruise, although samples were not taken at exactly the same depth, we can compare samples of similar depth (Fig 2c-d). At the surface, the GA03 towed fish sample (~2 m) is within 2SD of the mean $\delta^{56}\text{Fe}$ of the GSI tank (+0.23 $\pm$ 0.07‰ and +0.34 $\pm$ 0.13‰; Fig. 2c), and Fe concentrations show similar good agreement (0.46 vs. 0.41-0.45 nmol kg⁻¹). For the deep ocean, the GA03 samples collected at 1951 and 2101 m are also both within error of 2SD of the mean $\delta^{56}\text{Fe}$ of the GDI tank (+0.35 $\pm$ 0.06‰, +0.43 $\pm$ 0.07‰ and +0.48 $\pm$ 0.10‰; Fig. 2d), and the $\delta^{56}\text{Fe}$ of the GA03 sample at 2101 m is identical within error to the GSD Tank mean $\delta^{56}\text{Fe}$. Fe concentrations measured for this depth interval on the GA03 cruise (0.61-0.65 nmol kg⁻¹) were slightly lower than those for the GSD tank (0.74-0.84 nmol kg⁻¹). Very similar temperature, oxygen and salinity profiles are also observed between the cruises, suggesting consistent water mass structure (Fig. 2b); despite this, given the dynamic nature of the marine Fe cycle, such consistency in $\delta^{56}\text{Fe}$ at both depths from the two cruises is remarkable. This is especially remarkable for the surface ocean in different seasons (June and November) three years apart, when this region of the ocean is prone to episodic atmospheric supply of Fe with both storm activity and seasonality causing variability in the deposition of more-soluble anthropogenic aerosol Fe vs. lower-solubility lithogenic aerosol Fe (e.g. Fishwick *et al.*, 2014; Sedwick *et al.*, 2005; Sedwick *et al.*, 2007; Wu and Boyle, 2002).

A lack of variability may in fact point to the stability of the Fe cycle in this region on this timescale in terms of overall Fe sources and internal cycling processes such as scavenging and biological uptake/release. Since anthropogenic and lithogenic aerosols might be expected to alternately dominate deposition in winter and summer respectively and have been suggested to have different $\delta^{56}\text{Fe}$ signatures (Conway, T.

M., unpublished data; Fishwick *et al.*, 2014; Mead *et al.*, 2014; Sedwick *et al.*, 2005), it is perhaps surprising that there is such little variability in surface water dissolved $\delta^{56}\text{Fe}$. However, since the surface of neither profile is characterized by the very high Fe concentrations that have been attributed to episodes of lithogenic dust deposition in summer months (1-2 nmol kg⁻¹; Sedwick *et al.*, 2005), it may be that both profiles reflect the longer-timescale combined effect of different Fe sources, equilibrium and kinetic processes in concert with dust particles rather than the primary $\delta^{56}\text{Fe}$ signature of each dust source. We previously suggested that the heavy $\delta^{56}\text{Fe}$ signature might represent an equilibrium effect of dust particles being in contact with organic ligands (Conway and John, 2014a), with the exchange/dissolution process in the presence of ligands perhaps ultimately more important than the $\delta^{56}\text{Fe}$ signature of either lithogenic or anthropogenic aerosols. However, this remains a hypothesis and clearly more process and experimental studies will be required to fully test this and to understand what is ultimately responsible for heavier-than-crustal $\delta^{56}\text{Fe}$ in surface Atlantic waters. As such, we cannot presently assess on the basis of these datasets whether episodic dust fluxes might cause dramatic effects on surface ocean dissolved $\delta^{56}\text{Fe}$, perturbing the profiles observed here, or whether the magnitude of local dust flux has a negligible effect on $\delta^{56}\text{Fe}$ because the surface ocean $\delta^{56}\text{Fe}$ in this region is typically dominated by an internal cycling process.

Higher resolution comparison of $\delta^{56}\text{Fe}$ at BATS through the water column is also possible because of the measurement of a 10 point $\delta^{56}\text{Fe}$ profile on IC1 samples by Caltech (John and Adkins, 2012; Boyle *et al.*, 2012), and a 34 point profile for $\delta^{56}\text{Fe}$ measured on samples from the GA03 cruise (Conway and John, 2014a). A general homogeneity of $\delta^{56}\text{Fe}$ through the full water column (+0.32‰ to +0.55‰ with one exception; Fig. 2b) for the IC1 samples was previously commented upon by John and Adkins (2012), who attributed heavy $\delta^{56}\text{Fe}$ to dust and the homogeneity to buffering of the dissolved phase by particles. They also attributed one exceptionally heavy $\delta^{56}\text{Fe}$ value (+0.78±0.07‰) at 2500 m to a hydrothermal source. However, further study called into question whether the heavy $\delta^{56}\text{Fe}$ value at 2500 m (bracketed point, Fig. 2b) was representative of the ocean. Whilst the heavy $\delta^{56}\text{Fe}$ value reported by John and Adkins (2012) was confirmed by analyses at USC, this sample had anomalously low Zn and Cd concentrations, poor reproducibility of Fe concentration, and unexpectedly light $\delta^{66}\text{Zn}$ in this sample, compared to the typically homogenous deep

ocean $\delta^{66}\text{Zn}$ value (-0.1 vs. +0.5‰; Conway and John, 2014b; Conway and John 2015a; Conway *et al.*, 2013; Zhao *et al.*, 2014), suggesting that it was not representative of 2500 m seawater, but rather that the Go-Flo bottle probably tripped at the wrong depth. Additional analysis of $\delta^{56}\text{Fe}$ over for the whole IC1 profile from the same sample bottles at USC showed good overall agreement, within 2σ quoted uncertainty for most depths (Fig. 2b; Conway *et al.*, 2013a; 2013b, Suppl. Information). However, it is worth noting that at 1500 m, $\delta^{56}\text{Fe}$ measurements from USC and Caltech were slightly greater (0.13‰) than the combined 2σ uncertainty (0.12‰) apart, and that, while typically within 2σ uncertainty, the USC $\delta^{56}\text{Fe}$ dataset was generally heavier than Caltech by $\sim 0.1\text{‰}$. These differences could point to a slight underestimation of true analytical uncertainty by one or other of the methods, or some effect of 5 years of sample storage.

A similar broad homogeneity in $\delta^{56}\text{Fe}$ through the water column to that observed on IC1 was reported for BATS from the GA03 cruise, with $\delta^{56}\text{Fe}$ varying from +0.22 to +0.58‰, with the exception of one data point at 420 m (+0.7‰). Upon direct comparison of $\delta^{56}\text{Fe}$ data from the two cruises we observe very similar $\delta^{56}\text{Fe}$ profile shapes (Fig. 2b); in fact, with the exception of the IC1 samples at 250 m and 500 m (where we have no direct comparison between cruises) and 2500 m (the flagged sample), $\delta^{56}\text{Fe}$ from the other 7 depths from the Caltech IC1 cruise agree well with their depth counterparts from GA03, extending the observation of consistent $\delta^{56}\text{Fe}$ in GSI and GSD samples with GA03 to the full depth profile. Whilst most USC IC1 cruise data also agree well with GA03 within 2σ uncertainty, the previously mentioned $\delta^{56}\text{Fe}$ data point at 1500 m appears to be slightly anomalously heavy compared to the other two datasets, and the USC IC1 value at 4200 m ($+0.45 \pm 0.06\text{‰}$) is also slightly outside of 2σ internal uncertainty of GA03 ($+0.29 \pm 0.06\text{‰}$), whilst agreeing with Caltech ($+0.35 \pm 0.07\text{‰}$). These differences could also point to small variability between datasets, whether from natural variability, sampling contamination or a slight underestimation of true analytical uncertainty. Nevertheless, the overall agreement of the three datasets is strong, agreeing within $\sim 0.1\text{‰}$, and so differing by much smaller amounts than the range of variability observed elsewhere in the ocean (e.g. Fig 2-4).

The higher resolution of the GA03 profile compared to IC1 permits the observation of systematic variability in the deep ocean, with depth intervals where $\delta^{56}\text{Fe} \leq +0.3\text{‰}$ (800-1800 m and >3600 m) and $>0.3\text{‰}$ between 1800-3600 m, corresponding to the influence of Upper Labrador Seawater and deep nepheloid layers respectively (Jenkins *et al.*, 2015; Ohnemus and Lam, 2015), and attributed to the influence of non-reductive sedimentary Fe (Conway and John, 2014a). Whilst the presence of similar $\delta^{56}\text{Fe}$ structure can not be assessed for IC1 due to the depth resolution, the consistency of the full water column profile between the cruises does suggest that the broad external source addition and internal cycling processes that determine dissolved $\delta^{56}\text{Fe}$ throughout the water column in this region are likely to be similar at both times. In terms of dissolved Fe concentration, the profiles for both cruises are very similar above 1500 m (Fig. 2a), including a surface enrichment ($\sim 0.4\text{--}0.5 \text{ nmol kg}^{-1}$) and pronounced dissolved Fe minimum at 120-140 m ($0.1 - 0.2 \text{ nmol kg}^{-1}$) in both cruises. Below 1500 m, Fe concentrations were slightly higher on the IC1 cruise ($0.1\text{--}0.2 \text{ nmol kg}^{-1}$) at the two comparable depths.

3.2. GA03 (2010 and 2011) at Cape Verde

The GA03 section was completed on two cruises in 2010 and 2011, with station identification defined as USGT, then 10 or 11 for year, then station number (e.g. USGT10-12). The cruises overlapped with reoccupation of the Tenatso Time Series station ($17.40^{\circ}\text{N } 24.50^{\circ}\text{W}$) near Cape Verde by the GA03 cruise in Oct. 2010 (USGT10-12) and Nov. 2011 (USGT11-24). Depth and density profiles of dissolved $\delta^{56}\text{Fe}$ and Fe are shown for these two stations in Fig. 3b-c.

Both occupations were characterized by very similar temperature, salinity and oxygen vertical profiles on both density and depth scales, with oxygen slightly higher in 2010 (Fig. 3b-c). The vertical structure is strongly dominated by the Mauritanian Oxygen Minimum Zone (OMZ) present between $\sim 200\text{--}1000 \text{ m}$, with dissolved oxygen as low as $60 \mu\text{mol kg}^{-1}$, as well as a very shallow mixed layer ($\sim 40\text{--}50 \text{ m}$; Hatta *et al.*, 2015). The dissolved Fe concentration profiles for both stations reflect this vertical structure, with both showing a surface enrichment of $0.3\text{--}0.4 \text{ nmol kg}^{-1}$ in the mixed layer, presumably from atmospheric dust, a dissolved Fe minimum of $0.1\text{--}0.2 \text{ nmol kg}^{-1}$ just below the mixed layer (associated with the fluorescence maximum; $60\text{--}70 \text{ m}$),

elevated concentrations of 0.8-1.2 nmol kg⁻¹ through the OMZ horizon, and Fe concentrations declining to 0.6 nmol kg⁻¹ in the deep ocean (Conway and John, 2014a; Fig. 3b). Although dissolved Fe profiles from both years show very similar overall shapes, and strong consistency in waters >1000m, there is some apparent variability within surface waters and especially throughout the OMZ horizon (Fig. 3b), a feature also reported by other investigators reporting dissolved Fe, Fe-binding ligands, Fe size fractionation and other parameters such as Pb concentrations and Cd isotopes on GA03 (Buck *et al.*, 2015; Conway and John, 2014a; 2015b; Fitzsimmons *et al.*, 2015; Hatta *et al.*, 2015; Noble *et al.*, 2015). Potential inter-annual variability is discussed in the context of $\delta^{56}\text{Fe}$ later in this section.

$\delta^{56}\text{Fe}$ measurements through the water column at this location show greater variability in a single profile than at the BATS station (Section 3.1), with both USGT10-12 and USGT11-24 spanning a range of 0.7‰ (between 0 and +0.7‰). Similar to the consistency in dissolved Fe concentrations, the $\delta^{56}\text{Fe}$ profiles for both years are broadly similar in shape, with heavy $\delta^{56}\text{Fe}$ values in the mixed layer (> +0.4‰), a sub-surface minima (0‰), values of 0 to +0.3 ‰ within the OMZ region, and values increasing from +0.2 to as high as +0.7 in deep water, as Fe concentrations decline (Fig. 3b). This structure was previously attributed to isotopically heavy Fe released from dust (+0.7‰) in the surface mixed layer and the deep ocean, mixing with a reductive sediment light Fe (<-1‰) that is transported throughout the water column, (but mostly within OMZ waters) from reducing sediments on the Mauritanian margin (Conway and John, 2014a).

Samples were collected at the same depth on each cruise, allowing direct comparison of $\delta^{56}\text{Fe}$ values for each profile. For the surface dissolved Fe enrichment in the mixed layer, $\delta^{56}\text{Fe}$ were very similar between cruises (2-50 m; +0.52±0.09‰ and +0.41±0.09‰ in 2010, +0.60±0.09‰, +0.60±0.09‰, and +0.63±0.09‰ in 2011; Fig. 3b). In density space, these surface values show poorer agreement (Fig. 3c), perhaps due to changes in the relative importance of North Atlantic Central Water or Atlantic Equatorial Water between the two years (Hatta *et al.*, 2015; Jenkins *et al.*, 2015). However, if isotopically heavy values are the result from local surface dissolution of sinking dust, then variability in vertical density may not be an appropriate parameter for comparison. Below the mixed layer, from 70-240 m depth, the two profiles are

equivalent within error for $\delta^{56}\text{Fe}$, with $\delta^{56}\text{Fe}$ values of +0.2‰ associated with both the subsurface dissolved Fe concentration minimum and fluorescent maximum, as well as a $\delta^{56}\text{Fe}$ minimum of 0.0‰ just below the Fe minimum, when Fe concentrations begin to rise. While it is not yet clear what process causes this intriguing subsurface structure, such as regeneration, uptake or scavenging, it is reproduced for both years here, and was also observed associated with the Fe minimum in other nearby GA03 profiles (Conway and John, 2014a). Surface variability in the top 300 m may be induced by not only changes in atmospheric dust deposition and biological processes, but also in the relative importance of different surface water masses with different characteristics, so it is notable that Fe and $\delta^{56}\text{Fe}$ are so consistent at shallow depths.

Set against the broad similar $\delta^{56}\text{Fe}$ profile shapes, there is poorer agreement between $\delta^{56}\text{Fe}$ depth pairs throughout both the OMZ horizon and the deeper ocean (>200 m). With the exception of $\delta^{56}\text{Fe}$ data from 3198 m, the $\delta^{56}\text{Fe}$ profile from 2011 is notably isotopically heavier than that of 2010 (by 0.03 to 0.3‰). While some of these differences (8 of the 17 depths) are within combined 2σ uncertainty ($\geq 0.10\text{‰}$), some are larger (Fig. 3b; Suppl. Data). Indeed, throughout the OMZ horizon (~200-1000 m; shown as a blue bar in Fig 3b), where most of the Fe concentration measurements are different between the two cruises (by 0.1 to 0.2 nmol kg⁻¹), four of the seven $\delta^{56}\text{Fe}$ data points are outside of error of each other. Deeper in the ocean (below 1000 m), while Fe concentrations show strong consistency, $\delta^{56}\text{Fe}$ show more variability between the cruises, identical within error between 1000 and 1300 m, 2000-2300 and >3000 m, but differing between 1500-1750 and 2500-3000 m. Whilst Fe concentrations are consistent for most of these depths (differing by <0.02 nmol kg⁻¹, similar to expressed error of 0.01-0.02 nmol kg⁻¹), the largest differences in $\delta^{56}\text{Fe}$ in this interval (0.19‰ and 0.26‰ at 1500 and 2748 m respectively) are found at depths where Fe concentrations are subtly more different (0.06-0.1 nmol kg⁻¹). Thus, while it is possible that some of this variability in $\delta^{56}\text{Fe}$ in the deep ocean represents differences in background contamination or under-estimation of $\delta^{56}\text{Fe}$ analytical uncertainty, especially when it is not accompanied by changes in Fe concentration, it is consistent with observed variability in other oceanographic parameters. Variability in Fe cycling would also not be unexpected, given the dynamic oceanographic nature of this region. Upwelling of nutrient and Fe rich deep water, high productivity in surface waters, an OMZ at intermediate depths facilitating potential advection of shelf

Fe, and the presence of Antarctic water masses at intermediate depths could all lead to variability in Fe cycling and hence $\delta^{56}\text{Fe}$ signatures.

Variability in $\delta^{56}\text{Fe}$ and Fe in the deep ocean is also consistent with the idea that dissolved Fe in this region is dominantly locally sourced from atmospheric dust or reductive sediments that have very different $\delta^{56}\text{Fe}$ signatures (Conway and John, 2014a); thus, small changes in either sediment or dust supply could dramatically influence $\delta^{56}\text{Fe}$, while having only a small effect on Fe concentrations. A shelf source of Fe might be expected to have a waning influence with distance from Africa, as well as varying with strength over time, while dust supply would also be episodic and seasonal. If we examine data from stations USGT10-12 and 11-24 in the context of nearby stations (USGT10-11 and USGT11-24; Fig. 3a; Suppl. Fig. 1), it can be observed that USGT11-22, a 2011 station further from Africa (Fig. 3a), is characterized by much lower Fe concentrations throughout the water column as well as generally heavier $\delta^{56}\text{Fe}$, while USGT10-11, a 2010 station nearer to Africa, is practically identically to USGT10-12 for $\delta^{56}\text{Fe}$ below 500 m. Given that USGT11-24 looks more similar to USGT11-22 below 800 m within the depth intervals at which USGT10-12 and USGT11-24 disagree (lower Fe concentrations and higher $\delta^{56}\text{Fe}$), it is possible to interpret the full water-column variability as being driven by a changing component of isotopically light Fe from reductive sediments that is slightly greater in 2011 than 2010. At shallower depths (286-451 m), USGT11-24 is characterized by higher Fe concentrations and heavier $\delta^{56}\text{Fe}$ than both USGT10-11 and USGT10-12, as well as slightly lower oxygen (Suppl. Fig. 1; Fig 3b; Hatta *et al.*, 2015); thus, this difference could not be explained by an increased source of light Fe in 2011, but perhaps rather by a greater dissolution of atmospheric dust or regeneration of Fe within the OMZ.

3.3 GIPY4 (2008) and GA10 (2010)

Water-column profiles of dissolved $\delta^{56}\text{Fe}$ and Fe for and GIPY4 Super-Station S1 (2008) and GA10 D357 Station 3 (2010) from the Cape Basin in the Eastern South Atlantic are shown, together with supporting oceanographic parameters, plotted against both depth and density in Fig. 4. Below 700 m, similar temperature, oxygen and salinity profiles are observed for both cruises, whilst in surface waters the GIPY4

cruise was characterized by much warmer, fresher, less dense water than GA10 (Fig. 4b-c). This difference can be most clearly observed in density space for $\sigma_\theta < 26.75 \text{ kg m}^{-3}$ (Fig. 4c), indicative of different surface waters dominating the upper water column (<700 m) during the two cruises. This difference could be due to movement in the position of the South Subtropical Convergence, which is located near this station (Fig. 1 of Browning *et al.*, 2014), and/or the variable influence of the Agulhas current, which variably transports warm salty surface water from the Indian Ocean to the South Atlantic within mesoscale structures (Lutjeharms, 2006). Indian ocean water is transported into the Atlantic within the Agulhas retroflection, typically in the form of large anticyclonic eddies ('Agulhas rings'; Lutjeharms, 2006). Such rings, characterized both on the GA10 and GIPY4 cruises by elevated temperature, salinity and nutrients ($S > 35$; $T \text{ } 15\text{-}23^\circ\text{C}$; Arhan *et al.*, 2011; Wyatt *et al.*, 2014), can have an important effect on both biogeochemical cycling in surface waters (Viller *et al.*, 2015); indeed, it was recently shown that Agulhas rings transport an Indian Ocean Pb isotope signature to the North Atlantic (Paul *et al.*, 2015), suggesting that they could also play a role in influencing the surface ocean cycling of Fe and other trace metals.

The difference in surface water characteristics is also reflected in the Fe concentration profiles, which show broad similarity for both cruises below 400 m, but disagreement in surface waters <100 m where dissolved Fe was $0.2\text{-}0.3 \text{ nmol kg}^{-1}$ in 2008 and $<0.09 \text{ nmol kg}^{-1}$ in 2010, perhaps due to the transport of higher Fe concentrations within warmer saltier Indian Ocean water compared to colder more-Fe depleted Atlantic waters. As might be expected, with the surface variability in surface waters and Fe concentrations, $\delta^{56}\text{Fe}$ between the cruises show differences between the two cruises (Fig. 4b); $\delta^{56}\text{Fe}$ from GIPY4 are rather homogenous over the top 400 m, and close to crustal ($+0.09\text{‰}$; Beard *et al.*, 2003; Lacan *et al.*, 2008), varying only between $+0.04\pm 0.07\text{‰}$ and $+0.21\pm 0.07\text{‰}$. In contrast, although subject to larger uncertainties at low surface Fe concentrations, $\delta^{56}\text{Fe}$ from GA10 show more variability in the top 500 m, ranging from $-0.22\pm 0.10\text{‰}$ to $+0.51\pm 0.22\text{‰}$. When compared in density space (Fig. 4c), it becomes clear that much of the GIPY4 data are from lower density waters; this, together with the documented agreement of data from the two labs at BATS (Section 3.1) and in the deep ocean at this location (see below), suggests that this variability in $\delta^{56}\text{Fe}$ may be natural rather than analytical and could perhaps also be attributed to the greater influence of Indian Ocean water in 2008.

Although to date no $\delta^{56}\text{Fe}$ data has been reported from the Indian Ocean, the near-crustal homogenous $\delta^{56}\text{Fe}$ in Indian Ocean water above 400 m could reflect non-reductive release of Fe from sediments as suggested in the Equatorial Pacific and North Atlantic Oceans (Radic *et al.*, 2011; Conway and John, 2014a, Labutut *et al.*, 2014) and observed *in situ* within sediment pore waters (Homoky *et al.*, 2013).

In terms of the ocean below ~500 m, the South Atlantic at this location is dominated by the lateral South-North or North-South movement of Southern- and Northern-sourced water masses, especially for nutrients and trace metals such as Zn (Wyatt *et al.*, 2014). The depth intervals of these water masses, specifically Antarctic Intermediate Water (AAIW), Upper Circumpolar Deep Water (UCDW), North Atlantic Deep Water (NADW), and Antarctic Bottom Water (AABW), are shown in Fig. 4b-c, and are defined following Wyatt *et al.* (2014), based either on salinity, with NADW >34.75 (~1700-4000 m) and AAIW <34.4 . For $\delta^{56}\text{Fe}$ below 700 m, the two $\delta^{56}\text{Fe}$ profiles are identical within 2σ uncertainty (Fig. 4b). Above this, between 500-700 m, although there are no direct comparable samples, there appears to be a disagreement in $\delta^{56}\text{Fe}$. However, for comparison purposes it is important to note that the salinity minimum corresponding to AAW was from ~500-950 m for GA10 (as shown in Fig. 4b), but deeper (750-950 m) for GIPY4, suggesting that the isotopically light $\delta^{56}\text{Fe}$ of $-0.18 \pm 0.09\text{‰}$ at 594 m from GA10 is in fact most comparable to the $-0.17 \pm 0.07\text{‰}$ at 763 m from GIPY4; this can be seen more clearly in density space (Fig. 4c). With this adjustment in mind, $\delta^{56}\text{Fe}$ can be considered identical within uncertainty for both cruises over the entire water column below 500 m. This remarkable consistency in water-column $\delta^{56}\text{Fe}$, in contrast to surface waters at this location, highlights the quality of data being produced by both laboratories, as well as again pointing to the stability of Fe sources and cycling in the ocean at this location on this timescale, similar to that suggested at Bermuda.

Little temporal variability on this timescale suggests that the deep water masses at this location may have relatively stable transported $\delta^{56}\text{Fe}$ signatures, similar to that observed in the Western North Atlantic (Section 3.1). Such signatures can be observed when water mass horizons are shown on the $\delta^{56}\text{Fe}$ profile (Fig. 4b), with AABW ($+0.21 \pm 0.07\text{‰}$, and $+0.21 \pm 0.09\text{‰}$) slightly isotopically heavier than crustal, NADW ($+0.29 \pm 0.06\text{‰}$, $+0.33 \pm 0.07$, and $+0.27 \pm 0.07\text{‰}$) distinctly isotopically

heavier than crustal, while UCDW ($-0.12 \pm 0.07\text{‰}$ and $-0.09 \pm 0.15\text{‰}$) and AAIW ($-0.17 \pm 0.07\text{‰}$ and $-0.18 \pm 0.09\text{‰}$) are both isotopically light. One additional GA10 sample from 2000 m, from shallower depths of NADW, was slightly lighter ($+0.17 \pm 0.08\text{‰}$), perhaps reflecting mixing with the above-lying isotopically lighter UCDW. While it is not clear what might cause these differences in water mass $\delta^{56}\text{Fe}$ signatures, it could point to $\delta^{56}\text{Fe}$ retained from different dominant Fe sources (e.g. reductive versus non-reductive sediment dissolution), or to fractionation processes during formation or transport of these water masses. These ideas are explored in greater detail in the context of the full GIPY4 section in Abadie *et al.* (in review).

4. Conclusions

We have presented the first oceanic comparison of dissolved $\delta^{56}\text{Fe}$ depth profiles from three locations in the Atlantic Ocean, including the first full profile inter-lab comparison, and comparison with a previous inter-calibration exercise. We find that: (1) There is strong agreement between data and profiles produced by the two laboratories compared in this study, and the five laboratories compared in the previous exercise, which allows the combination and interpretation of $\delta^{56}\text{Fe}$ datasets from different laboratories. Where discrepancies exist between laboratories, they are typically on the order of 0.1‰ , which is occasionally greater than stated analytical uncertainty, but much less than the overall variability in $\delta^{56}\text{Fe}$ observed within the global ocean. While some of this discrepancy may be due to true analytical error or sample storage/handling, our data suggest that variability between cruises may also be driven by true natural variability in $\delta^{56}\text{Fe}$. Thus, repeat occupation of oceanic stations by different GEOTRACES cruises and $\delta^{56}\text{Fe}$ analysis by different laboratories is essential for continued evaluation and comparison of analytical methods, but also permits evaluation of temporal variability in oceanic Fe cycling. (2) At all three locations compared in this study, there was remarkable agreement in the overall shape of $\delta^{56}\text{Fe}$ profiles on a 1-3 year timescale, including almost complete agreement over the full water column at Bermuda in the Western North Atlantic and for the water column below 500 m in the South Atlantic. (3) Set against this overall homogeneity in $\delta^{56}\text{Fe}$, we observe apparent natural variability in $\delta^{56}\text{Fe}$ in shallow waters in the South Atlantic, and throughout the water column in the Eastern subtropical North Atlantic, close to North Africa. Overall, where $\delta^{56}\text{Fe}$ invariance is observed, we suggest that

the internal cycling and sources of $\delta^{56}\text{Fe}$ is stable on these timescales, in regions of the oceans dominated by stable water-masses or single Fe sources (e.g. atmospheric dust). However, $\delta^{56}\text{Fe}$ may be more dynamic in surface waters with variable currents, upwelling/regeneration or low-oxygen waters, which may either facilitate the supply of Fe from different sources with different $\delta^{56}\text{Fe}$ signatures or changes in the internal cycling of Fe. Taken together, this work lends weight to the use of $\delta^{56}\text{Fe}$ as a tracer to increase our understanding of the variability in supply from different Fe sources and transport of Fe through the oceans, or in internal Fe cycling.

Acknowledgements

We thank the Captains, crew, chief scientists and sampling teams for water collection on the cruises described here, as well as the GEOTRACES scientific steering committee and all those involved in coordinating the GEOTRACES program and inter-comparison efforts. We especially thank M. Lohan on the GA10 cruise for water collection (funded by NERC grant NE/H004475/1), and J. Wu, R. Middag, K. Bruland, C. Schlosser and G. Sarthou for providing concentration data which was helpful in planning double-spike additions on GA03, GA10 and GIPY4. We also thank A. Rosenberg for technical assistance at the University of South Carolina, C. Pradoux, A. Radic and J. Chmieleff for help in the lab and with ICPMS at LEGOS, M. Boyé, S. Speich and their collaborators for providing the nutrient and physical parameters for GIPY4, and G. de Souza for useful discussions. We thank two anonymous reviewers for their helpful comments which allowed us to improve this manuscript. Ocean data facility provided supporting nutrient and oceanographic parameters for GA03. This study was funded by National Science Foundation grant OCE-1131387 to S. John, ETH Zürich, the Swiss National Science Foundation, and the French National Center for Scientific Research (CNRS).

Figure Captions

Figure 1. Atlantic Ocean showing GEOTRACES crossover stations and locations described in this study. Cruises included in the GEOTRACES Intermediate data product 2014 are shown for reference, based on eGEOTRACES graphics (Mawji *et al.*, 2015; Schlitzer, 2015). The three locations sampled in this study are shown as black dots.

Figure 2. Comparison of $\delta^{56}\text{Fe}$ and Fe data from Bermuda Atlantic Time Series (BATS) in the subtropical North West Atlantic (31.75°N 64.17°W) from the U.S. GEOTRACES IC1 (June 2008) and GA03 cruises (Nov. 2011). **a)** Regional location map showing BATS and GA03 stations sampled for Fe isotope ratios. **b)** dissolved Fe concentration (nmol kg^{-1}) and dissolved $\delta^{56}\text{Fe}$ (relative to IRRM-014) profiles shown with other oceanographic parameters. **c)** dissolved $\delta^{56}\text{Fe}$ from the IC1 surface tank and from GA03 towed-fish sample. **d)** dissolved $\delta^{56}\text{Fe}$ from the IC1 2000 m depths deep tank and from GA03 rosette samples from similar depths. The dashed lines and grey shaded region in b) and c) represent the mean and 2SD $\delta^{56}\text{Fe}$ respectively of the five labs that have published measurements for the GSI and GDI tanks. Data are reproduced from Boyle *et al.* (2012); Conway and John (2014a); Conway *et al.* (2013a; 2013b); John and Adkins (2012). Error bars for ANU and WHOI are from Boyle *et al.* (2012), error bars for LEGOS represent 2SD on $\delta^{56}\text{Fe}$ (see Suppl. Data), error bars for Caltech are from John and Adkins (2012) and error bars for USC are from Conway *et al.* (2013) and Conway and John (2014a). For GA03, temperature and salinity are from the GEOTRACES rosette and dissolved oxygen is from the ODF rosette.

Figure 3. Comparison of $\delta^{56}\text{Fe}$ and Fe profiles from GA03 Station USGT10-12 and USGT11-24 (17.4°N 24.5°W) from the Tenatso Time Series station in the North East Atlantic. **a)** Regional location map showing GA03 stations sampled for Fe isotope ratios. Dissolved Fe concentration (nmol kg^{-1}), dissolved $\delta^{56}\text{Fe}$ (relative to IRRM-014) and oceanographic parameters shown against depth (b) or σ_θ density (c). Data and 2σ error bars are from Conway and John (2014a). Temperature and salinity are from the GEOTRACES rosette and dissolved oxygen is from the ODF rosette.

The shaded below denotes the influence of the Mauritanian Oxygen Minimum Zone (OMZ; dissolved oxygen $<120 \mu\text{mol kg}^{-1}$).

Figure 4. Comparison of $\delta^{56}\text{Fe}$ and Fe profiles from Superstation 3 of GA10 D357 cruise and Super-Station 1 (station 18) of GIPY4 cruise in the South East Atlantic. **a)** Regional location map showing GIPY4 and GA10 stations sampled for Fe isotope ratios. Dissolved Fe concentration (nmol kg^{-1}) and dissolved $\delta^{56}\text{Fe}$ (relative to IRRM-014) shown against depth (**b**) or σ_θ density (**c**). Data are from Abadie *et al.* (in review), Lacan *et al.* (2008), or are previously unpublished. Error bars are 2σ as described in the text. GA10 temperature and salinity are from the titanium rosette and oxygen from the stainless steel rosette, corrected to match bottle measurements. GIPY temperature, salinity and oxygen data are from the Niskin Rosette. The horizontal shaded bars represent the presence of different water masses based on salinity (see text; Antarctic Intermediate Water, AAIW; Upper Circumpolar Deep Water, UCDW; North Atlantic Deep Water, NADW; Antarctic Bottom Water, AABW). N.B. The position of AAIW in depth space is based on GA10 and was deeper for GIPY4.

References

- Abadie, C. Lacan, F., Radic, A., Pradoux, C., Poitrasson, F. In review. Iron isotopes reveal distinct dissolved iron sources and pathways in the intermediate versus deep Southern Ocean. *Proc. Natl Acad. Sci. USA*.
- Anderson, R.F., Henderson, G.M., 2005. GEOTRACES A global study of the marine biogeochemical cycles of trace elements and their isotopes. *Oceanography* 18, 76–79. doi:10.5670/oceanog.2005.31
- Arhan, M., Speich, S., Messenger, C., Dencausse, G. Fine, R., and Boye, M., 2011. Anticyclonic and cyclonic eddies of subtropical origin in the subantarctic zone south of Africa. *J. Geophys. Res.* 116, C11, doi:10.1029/2011JC007140
- Beard, B.L., Johnson, C.M., Von Damm, K.L., Poulson, R.L., 2003. Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans. *Geology* 31, 629–632. doi:10.1130/0091-7613(2003)031<0629:IIICOFC>2.0.CO;2
- Boyle, E.A., John, S.G., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M.J., Flegal, A. R., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkämper, M., Rouxel, O., Sohrin, Y., Stirling, C., Thompson, C., Vance, D., Xue, Z., and Yhao, Y. 2012. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnol. Oceanogr. Methods* 10, 653–665. doi:10.4319/lom.2012.10.653
- Browning, T.J., Bouman, H.A., Moore, C.M., Schlosser, C., Tarran, G.A., Woodward, E.M.S., Henderson, G.M., 2014. Nutrient regimes control phytoplankton ecophysiology in the South Atlantic. *Biogeosciences* 11, 463–479. doi:10.5194/bg-11-463-2014
- Buck, K.N., Sohst, B., Sedwick, P.N., 2015. The organic complexation of dissolved iron along the U.S. GEOTRACES (GA03) North Atlantic Section. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 116, 152–165. doi:10.1016/j.dsr2.2014.11.016
- Chever, F., Rouxel, O.J., Croot, P.L., Ponzevera, E., Wuttig, K., Auro, M., 2015. Total dissolvable and dissolved iron isotopes in the water column of the Peru upwelling regime. *Geochim. Cosmochim. Acta* 162, 66–82. doi:10.1016/j.gca.2015.04.031
- Conway, T.M., John, S.G., 2014a. Quantification of dissolved iron sources to the North Atlantic Ocean. *Nature* 511, 212–215. doi:10.1038/nature13482
- Conway, T.M., John, S.G., 2014b. The biogeochemical cycling of zinc and zinc isotopes in the North Atlantic Ocean. *Global Biogeochem. Cycles* 28, 1111–1128. doi:10.1002/2014GB004862

- 753 Conway, T.M., John, S.G., 2015a. The cycling of iron, zinc and cadmium in the North
754 East Pacific Ocean - insights from stable isotopes. *Geochim. Cosmochim. Acta.*
755 164 (1), 262-283. doi:10.1016/j.gca.2015.05.023
- 756 Conway, T.M., John, S.G., 2015b. Biogeochemical cycling of cadmium isotopes
757 along a high-resolution section through the North Atlantic Ocean. *Geochim.*
758 *Cosmochim. Acta.* 148, 269-283. doi:10.1016/j.gca.2014.09.032
- 759 Conway, T.M., Rosenberg, A.D., Adkins, J.F., John, S.G., 2013a. A new method for
760 precise determination of iron, zinc and cadmium stable isotope ratios in seawater
761 by double-spike mass spectrometry. *Anal. Chim. Acta* 793, 44–52.
762 doi:10.1016/j.aca.2013.07.025
- 763 Conway, T.M., Rosenberg, A.D., Adkins, J.F., John, S.G., 2013b. Corrigendum to "A
764 new method for precise determination of iron, zinc and cadmium stable isotope
765 ratios in seawater by double-spike mass spectrometry." [*Anal. Chim. Acta* 793,
766 44–52]. *Anal. Chim. Acta* 801, 97. doi:10.1016/j.aca.2013.09.010
- 767 Cutter, G., Andersson, P. Codispoti, L. Croot, P., François, R., Lohan, M. C. , Obata,
768 H., Rutgers van der Loeff, M., 2010. Sampling and Sample-handling Protocols
769 for GEOTRACES Cruises. Version 1.0, December 2010,
770 [http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook_v](http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook_v1_2010.pdf)
771 [1_2010.pdf](http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook_v1_2010.pdf)
- 772 Cutter, G.A., 2013. Intercalibration in chemical oceanography-Getting the right
773 number. *Limnol. Oceanogr. Methods* 11, 418–424. doi:10.4319/lom.2013.11.418
- 774 Cutter, G.A., Bruland, K.W., 2012. Rapid and noncontaminating sampling system for
775 trace elements in global ocean surveys. *Limnol. Oceanogr. Methods*, 10(6), 425–
776 436. doi:10.4319/lom.2012.10.425
- 777 Cutter, G., Andersson, P. Codispoti, L. Croot, P., François, R., Lohan, M. C. , Obata,
778 H., Rutgers van der Loeff, M., 2014. Sampling and Sample-handling Protocols
779 for GEOTRACES Cruises. Version 2.0, December 2014,
780 [http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.p](http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.pdf)
781 [df](http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.pdf)
- 782 de Jong, J., Schoemann, V., Tison, J.L., Becquevort, S., Masson, F., Lannuzel, D.,
783 Petit, J., Chou, L., Weiss, D., Mattielli, N., 2007. Precise measurement of Fe
784 isotopes in marine samples by multi-collector inductively coupled plasma mass
785 spectrometry (MC-ICP-MS). *Anal. Chim. Acta* 589, 105–119. doi:
786 10.1016/j.aca.2007.02.055
- 787 Ellwood, M.J., Hutchins, D.A., Lohan, M.C., Milne, A., Nasemann, P., Nodder, S.D.,
788 Sander, S.G., Strzepek, R., Wilhelm, S.W., Boyd, P.W., 2014. Iron stable
789 isotopes track pelagic iron cycling during a subtropical phytoplankton bloom.
790 *Proc. Natl. Acad. Sci. USA.* 112, E15–20. doi:10.1073/pnas.1421576112

791 Fishwick, M.P., Sedwick, P.N., Lohan, M.C., Worsfold, P.J., Buck, K. N., Church, T.
792 M., Ussher, S. J., 2014. The impact of changing surface ocean conditions on the
793 dissolution of aerosol iron. *Glob. Biogeochem. Cyc.* 28 (11), 1235-1250. doi:
794 10.1002/2014GB004921

795 Fitzsimmons, J.N., Carrasco, G.G., Wu, J.F., Roshan, S., Hatta, M., Measures, C.I.,
796 Conway, T.M., John, S.G., Boyle, E.A., 2015. Partitioning of dissolved iron and
797 iron isotopes into soluble and colloidal phases along the U.S. GEOTRACES
798 North Atlantic Transect. *Deep. Res. Pt II.* 116, 130-151. doi:
799 10.1016/j.dsr2.2014.11.014

800 Hatta, M., Measures, C.I., Wu, J., Roshan, S., Fitzsimmons, J.N., Sedwick, P.,
801 Morton, P., 2015. An overview of dissolved Fe and Mn distributions during the
802 2010–2011 U.S. GEOTRACES North Atlantic cruises: GEOTRACES GA03.
803 *Deep Sea Res. Pt II.* 116, 117–129. doi:10.1016/j.dsr2.2014.07.005

804 Henderson, G.M., Anderson, R.F., Adkins, J.F., Andersson, P., Boyle, E.A., Cutter,
805 G., de Baar, H.J.W., Eisenhauer, A., Frank, M., Francois, R., Orians, K., Gamo,
806 T., German, C.R., Jenkins, W.J., Moffett, J.W., Jeandel, C., Jickells, T.D.,
807 Krishnaswami, S., Mackey, D., Measures, C.I., Moore, J.K., Oschlies, A.,
808 Pollard, R., van der Loeff, M.R.D., Schlitzer, R., Sharma, M., von Damm, K.,
809 Zhang, J., Grp, S.W., 2007. GEOTRACES - An international study of the global
810 marine biogeochemical cycles of trace elements and their isotopes. *Chemie Der*
811 *Erde-Geochemistry* 67 (2), 85–131. doi:10.1016/j.chemer.2007.02.001

812 Homoky, W.B., John, S.G., Conway, T.M., Mills, R.A., 2013. Distinct iron isotope
813 signatures and supply from marine sediment dissolution. *Nat. Comm.* 4 2143.
814 doi: 10.1038/ncomms3143

815 Jenkins, W.J., Smethie, W., Boyle, E.A., Cutter, G.C., 2015. Water mass analysis for
816 the U.S. GEOTRACES North Atlantic Sections. *Deep. Res. Pt II.*, 116, 6-20. doi:
817 10.1016/j.dsr2.2014.11.018

818 John, S.G., 2012. Optimizing sample and spike concentrations for isotopic analysis by
819 double-spike ICPMS. *J. Anal. At. Spectrom.* 27, 2123–2131.
820 doi:10.1039/c2ja30215b

821 John, S.G., Adkins, J.F., 2010. Analysis of dissolved iron isotopes in seawater. *Mar.*
822 *Chem.* 119, 65–76. doi:10.1016/j.marchem.2010.01.001

823 John, S.G., Adkins, J.F., 2012. The vertical distribution of iron stable isotopes in the
824 North Atlantic near Bermuda. *Global Biogeochem. Cycles* 26 (2). doi:
825 10.1029/2011GB004043

826 John, S.G., Mendez, J., Moffett, J.W., Adkins, J.F., 2012. The flux of iron and iron
827 isotopes from San Pedro Basin sediments. *Geochim. Cosmochim. Acta* 93, 14–
828 29. doi:10.1016/j.gca.2012.06.003

829 Klunder, M.B., Laan, P., Middag, R., de Baar, H.J.W., Bakker, K., 2012. Dissolved
830 iron in the Arctic Ocean: Important role of hydrothermal sources, shelf input and
831 scavenging removal. *J. Geophys. Res.* 117, C04014. doi:10.1029/2011JC007135

832 Labatut, M., Lacan, F., Pradoux, C., Chmeleff, J., Radic, A., Murray, J.W.,
833 Poitrasson, F., Johansen, A.M., Thil, F., 2014. Iron sources and dissolved-
834 particulate interactions in the seawater of the Western Equatorial Pacific, iron
835 isotope perspective. *Global Biogeochem. Cycles*. 28, 1044-1065. doi:
836 10.1002/2014GB004928

837 Lacan, F., Radic, A., Jeandel, C., Poitrasson, F., Sarthou, G., Pradoux, C., Freydier,
838 R., 2008. Measurement of the isotopic composition of dissolved iron in the open
839 ocean. *Geophys. Res. Lett.* 35, L24610, doi:10.1029/2008GL035841

840 Lacan, F., Radic, A., Labatut, M., Jeandel, C., Poitrasson, F., Sarthou, G., Pradoux,
841 C., Chmeleff, J., Freydier, R., 2010. High-precision determination of the isotopic
842 composition of dissolved iron in iron depleted seawater by double spike
843 multicollector-ICPMS. *Anal. Chem.* 82, 7103–7111. doi:10.1021/ac1002504

844 Lutjeharms, E., 2006. *The Agulhas Current*. Springer Berlin Heidelberg, Berlin,
845 Heidelberg.

846 Mawji, E., Schlitzer, R., Dodas, E.M., Abadie, C., Abouchami, W., Anderson, R.F.,
847 Baars, O., Bakker, K., Baskaran, M., Bates, N.R., Bluhm, K., Bowie, A., Bown,
848 J., Boye, M., Boyle, E.A., Branellec, P., Bruland, K.W., Brzezinski, M.,
849 Bucciarelli, E., Buesseler, K., Butler, E., Cai, P., Cardinal, D., Casciotti, K.,
850 Chavez, J., Cheng, H., Chever, F., Church, T.M., Colman, A., Conway, T.M.,
851 Croot, P., Cutter, G., de Baar, H.J.W., de Souza, G., Dehairs, F., Deng, F., Dieu,
852 H.T., Dulaquais, G., Echegoyen-Sanz, Y., Lawrence Edwards, R., Fahrbach, E.,
853 Fitzsimmons, J., Fleisher, M., Frank, M., Friedrich, J., Fripiat, F., Galer, S.,
854 Gamo, T., Solsona, E.G., Gerringa, L.J.A., Godoy, J., Gonzalez, S., Grossteffan,
855 E., Hatta, M., Hayes, C.T., Heller, M.I., Henderson, G., Huang, K.-F., Jeandel,
856 C., Jenkins, W.J., John, S., Kenna, T.C., Klunder, M., Kretschmer, S.,
857 Kumamoto, Y., Laan, P., Labatut, M., Lacan, F., Lam, P.J., Lannuzel, D., le
858 Moigne, F., Lechtenfeld, O.J., Lohan, M., Lu, Y., Masqué, P., McClain, C.R.,
859 Measures, C., Middag, R., Moffett, J., Navidad, A., Nishioka, J., Noble, A.,
860 Obata, H., Ohnemus, D.C., Owens, S., Planchon, F., Pradoux, C., Puigcorbé, V.,
861 Quay, P., Radic, A., Rehkämper, M., Remenyi, T., Rijkenberg, M.J.A., Rintoul,
862 S., Robinson, L.F., Roeske, T., Rosenberg, M., van der Loeff, M.R., Ryabenko,
863 E., Saito, M.A., Roshan, S., Salt, L., Sarthou, G., Schauer, U., Scott, P., Sedwick,
864 P.N., Sha, L., Shiller, A.M., Sigman, D., Smethie, W., Smith, G.J., Sohrin, Y.,
865 Speich, S., Stichel, T., Stutsman, J., Swift, J.H., Tagliabue, A., Thomas, A.,
866 Tsunogai, U., Twining, B.S., van Aken, H.M., van Heuven, S., van Ooijen, J.,
867 van Weerlee, E., Venchiarutti, C., Voelker, A.H.L., Wake, B., Warner, M.J.,
868 Woodward, E.M.S., Wu, J., Wyatt, N., Yoshikawa, H., Zheng, X., Xue, Z.,

869 Zieringer, M., Zimmer, L.A., 2015. The GEOTRACES Intermediate Data
 870 Product 2014. *Mar. Chem.* 177(1), 1-8. doi:10.1016/j.marchem.2015.04.005

871 Mead, C., Herckes, P., Majestic, B. J., Anbar, A. D., 2013. Source apportionment of
 872 aerosol iron in the marine environment using iron isotope analysis. *Geophys.*
 873 *Res. Lett.* 40(21), 1944-8007. doi: 10.1002/2013GL057713

874 Middag, R., Séférian, R., Conway, T.M., John, S.G., Bruland, K.W., de Baar, H.J.W.,
 875 2015. Intercomparison of Dissolved Trace Elements at the Bermuda Atlantic
 876 Time Series Station. *Mar. Chem.* 177(3), 476-479.
 877 doi:10.1016/j.marchem.2015.06.014

878 Moore, J.K., Doney, S.C., Glover, D.M., Fung, I.Y., 2001. Iron cycling and nutrient-
 879 limitation patterns in surface waters of the World Ocean. *Deep Sea Res. Part II*
 880 *Top. Stud. Oceanogr.* 49, 463–507. doi:10.1016/S0967-0645(01)00109-6

881 Nishioka, J., Obata, H., Tsumune, D., 2013. Evidence of an extensive spread of
 882 hydrothermal dissolved iron in the Indian Ocean. *Earth Planet. Sci. Lett.* 361,
 883 26–33. doi:10.1016/j.epsl.2012.11.040

884 Noble, A.E., Echegoyen-Sanz, Y., Boyle, E.A., Ohnemus, D.C., Lam, P.J., Kayser,
 885 R., Reuer, M., Wu, J., Smethie, W., 2015. Dynamic variability of dissolved Pb
 886 and Pb isotope composition from the U.S. North Atlantic GEOTRACES transect.
 887 *Deep Sea Res. Pt II.* 116, 208–225. doi:10.1016/j.dsr2.2014.11.011

888 Ohnemus, D.C., Lam, P.J., 2015. Cycling of Lithogenic Marine Particulates in the US
 889 GEOTRACES North Atlantic Transect. *Deep Sea Res. Part II Top. Stud.*
 890 *Oceanogr. Deep Sea Res. Pt II.* 116, 283-302. doi:10.1016/j.dsr2.2014.11.019

891 Paul, M., van de Flierdt, T., Rehkämper, M., Khondoker, R., Weiss, D., Lohan, M.C.,
 892 Homoky, W.B., 2015. Seawater Lead Isotopes Trace Agulhas Leakage.
 893 *Geophys. Res. Lett.* 42, 8515-8521. doi:10.1002/2015GL065625

894 Radic, A., Lacan, F., Murray, J.W., 2011. Iron isotopes in the seawater of the
 895 equatorial Pacific Ocean: New constraints for the oceanic iron cycle. *Earth*
 896 *Planet. Sci. Lett.* 306, 1–10. doi:10.1016/j.epsl.2011.03.015

897 Resing, J.A., Sedwick, P.N., German, C.R., Jenkins, W.J., Moffett, J.W., Sohst, B.M.,
 898 Tagliabue, A., 2015. Basin-scale transport of hydrothermal dissolved metals
 899 across the South Pacific Ocean. *Nature* 523, 200–203. doi:10.1038/nature14577

900 Rijkenberg, M.J.A., Middag, R., Laan, P., Gerringa, L.J.A., van Aken, H.M.,
 901 Schoemann, V., de Jong, J.T.M., de Baar, H.J.W., 2014. The distribution of
 902 dissolved iron in the West Atlantic Ocean. *PLoS One* 9, e101323.
 903 doi:10.1371/journal.pone.0101323

904 Rouxel, O.J., Auro, M., 2010. Iron Isotope Variations in Coastal Seawater
 905 Determined by Multicollector ICP-MS. *Geostand. Geoanalytical Res.* 34, 135–

906 144. doi:10.1111/j.1751-908X.2010.00063.x

907 Saito, M.A., Noble, A.E., Tagliabue, A., Goepfert, T.J., Lamborg, C.H., Jenkins, W.J.,
908 2013. Slow-spreading submarine ridges in the South Atlantic as a significant
909 oceanic iron source. *Nat. Geosci.* 6, 775–779. doi:10.1038/ngeo1893

910 Schlitzer, R., eGEOTRACES - Electronic Atlas of GEOTRACES Sections and
911 Animated 3D Scenes, <http://www.egeotraces.org>, 2015.

912 Sedwick, P.N., Church, T.M., Bowie, A.R., Marsay, C.M., Ussher, S.J., Achilles,
913 K.M., Lethaby, P.J., Johnson, R.J., Sarin, M.M., McGillicuddy, D.J., 2005. Iron
914 in the Sargasso Sea (Bermuda Atlantic Time-series Study region) during
915 summer: Eolian imprint, spatiotemporal variability, and ecological implications.
916 *Global Biogeochem. Cycles* 19, GB4006. doi:10.1029/2004GB002445

917 Sedwick, P.N., Sholkovitz, R., and Church, T. M., 2007. Impact of anthropogenic
918 combustion emissions on the fractional solubility of aerosol iron: Evidence from
919 the Sargasso Sea. *Geochem. Geophys. Geosys.* 8. 1525-2027 doi:
920 10.1029/2007GC001586

921 Siebert, C., Nagler, T.F., Kramers, J.D., 2001. Determination of molybdenum isotope
922 fractionation by double-spike multicollector inductively coupled plasma mass
923 spectrometry. *Geochemistry Geophys. Geosystems* 2.
924 doi:10.1029/2000GC000124.

925 Staubwasser, M., Schoenberg, R., von Blanckenburg, F., Krüger, S., Pohl, C., 2013.
926 Isotope fractionation between dissolved and suspended particulate Fe in the oxic
927 and anoxic water column of the Baltic Sea. *Biogeosciences* 10, 233–245.
928 doi:10.5194/bg-10-233-2013

929 Steele, R. C. J., Elliott, T., Coath, C. D., Regelous, M., 2011. Confirmation of mass-
930 independent Ni isotopic variability in iron meteorites. *Geochim. et Cosmochim.*
931 *Acta* 75(24), 7906-7925. doi:10.1016/j.gca.2011.08.030

932 Villar, E., Farrant, G.K., Follows, M., Garczarek, L., Speich, S., Audic, S., Bittner, L.,
933 Blanke, B., Brum, J.R., Brunet, C., Casotti, R., Chase, A., Dolan, J.R.,
934 d’Ortenzio, F., Gattuso, J.-P., Grima, N., Guidi, L., Hill, C.N., Jahn, O., Jamet,
935 J.-L., Le Goff, H., Lepoivre, C., Malviya, S., Pelletier, E., Romagnan, J.-B.,
936 Roux, S., Santini, S., Scalco, E., Schwenck, S.M., Tanaka, A., Testor, P.,
937 Vannier, T., Vincent, F., Zingone, A., Dimier, C., Picheral, M., Searson, S.,
938 Kandels-Lewis, S., Acinas, S.G., Bork, P., Boss, E., de Vargas, C., Gorsky, G.,
939 Ogata, H., Pesant, S., Sullivan, M.B., Sunagawa, S., Wincker, P., Karsenti, E.,
940 Bowler, C., Not, F., Hingamp, P., Iudicone, D., 2015. Ocean plankton.
941 Environmental characteristics of Agulhas rings affect interocean plankton
942 transport. *Science* 348, 1261447. doi:10.1126/science.1261447

943 Wu, J.F., Boyle, E.A., 2002. Iron In The Sargasso Sea: Implications for the processes

944 controlling dissolved Fe distribution in the ocean. *Global Biogeochem. Cycles*
945 16(4), 1086. doi:10.1029/2001GB001453

946 Wyatt, N, J., Milne, A., Woodward, E.M.S., Rees, A.P., Browning, T.J., Bouman,
947 H.A., Worsfeld, P.J., Lohan, M.C., 2014. Biogeochemical cycling of dissolved
948 zinc along the GEOTRACES South Atlantic transect GA10 at 40°S. *Global*
949 *Biogeochem. Cycles* 28, 44-56. doi:10.1002/2013GB004637

950 Zhao, Y., Vance, D., Abouchami, W., de Baar, H.J.W., 2014. Biogeochemical cycling
951 of zinc and its isotopes in the Southern Ocean. *Geochim. Cosmochim. Acta* 125,
952 653–672. doi:10.1016/j.gca.2013.07.045

953

Figure 1

Figure 2
a) Location Map

b) BATS Water column

c) Surface (<10 m)

d) Deep (1950-2100 m)

a) Location Map

Figure 3

b) vs. Depth

c) vs. Density

Figure 4

a) Location Map

b) vs. Depth

c) vs. Density