Sources of dissolved iron to oxygen minimum zone waters on the Senegalese continental margin in the tropical North Atlantic Ocean: Insights from iron isotopes

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Abstract

Oxygen minimum zones (OMZs) cover extensive areas of eastern boundary ocean regions and play an important role in the cycling of the essential micronutrient iron (Fe). The isotopic composition of dissolved Fe (dFe) in shelf and slope waters on the Senegalese margin was determined to investigate the processes leading to enhanced dFe concentrations (up to 2 nM) in this tropical North Atlantic OMZ. On the shelf, the δ56Fe value of dFe (relative to the reference material IRMM-014) was as low as −0.33‰, which can be attributed to input of dFe from both reductive and nonreductive dissolution of sediments. Benthic inputs of dFe are subsequently upwelled to surface waters and recycled in the water column by biological uptake and remineralisation processes. Remineralised dFe is characterised by relatively high δ56Fe values (up to +0.41‰), and the contribution of remineralised Fe to the total dFe pool increases with distance from the shelf. Remineralisation plays an important role in the redistribution of dFe that is mainly supplied by benthic and atmospheric inputs, although dust inputs, estimated from dissolved aluminium concentrations, were low at the time of our study (2–9 nmol dFe m−2 d−1). As OMZs are expected to expand as climate warms, our data provide important insights into Fe sources and Fe cycling in the tropical North Atlantic Ocean.

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Keywords: Tropical Atlantic Ocean; Iron isotopes; Oxygen minimum zone; Benthic iron; Remineralisation; Dissolved aluminium; Dust; GEOTRACES

1. INTRODUCTION

Iron (Fe) is an essential element for marine phytoplankton (Martin and Fitzwater, 1988; Martin, 1990), including nitrogen fixing diazotrophs (e.g., Falkowski, 1997; Berman-Frank et al., 2001). Iron supply therefore influences the nitrogen cycle (Schlosser et al., 2014) and the strength of the biological carbon pump (Coale et al., 2004). Marine photosynthesis is responsible for about half of the global atmospheric CO2 uptake (Le Quéré et al., 2013), and diazotroph and phytoplankton growth are limited by Fe availability in, respectively, 35 and 50% of the world’s ocean (Moore et al., 2002). Proper constraints on

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the sources of Fe to the oceans, and the processes that regulate its distribution, are essential for global models that are used to calculate past and future climate scenarios (e.g., Boyd and Ellwood, 2010).

The supply of Fe to the oceans is temporally and spatially variable. The low solubility of Fe in oxygenated seawater (pH ~ 8.1) (Liu and Millero, 2002), its highly particle reactive nature (Goldberg, 1954), and its uptake by marine microorganisms (Coale et al., 2004) lead to rapid removal of Fe from the surface ocean. Therefore, Fe concentrations tend to be highest close to source regions. Iron is mainly delivered to the ocean from atmospheric dust deposition, margin sediments, rivers, groundwater discharge and hydrothermal vents (Boyd and Ellwood, 2010, and references therein).

In the open ocean dissolved Fe (dFe; i.e. filterable through 0.4 or 0.2 μm) concentrations typically range between <0.2 and ~1 nmol L^-1 (e.g., Klunder et al., 2011, 2012; Rijkerberg et al., 2014; Resing et al., 2015; Nishioka and Obata, 2017) and are generally lowest in the surface ocean. However, dFe concentrations of 1–17 nmol L^-1 have been observed within oxygen minimum zones (OMZs) away from coastal seas (Rijkerberg et al., 2012; Fitzsimmons et al., 2013; Ussher et al., 2010, 2013; Conway and John, 2014; John et al., 2017; Milne et al., 2017). The development of OMZs occurs in “shadow zones” of eastern boundary regions where the wind-driven supply of recently ventilated water is slowed, and oxygen consumption is accentuated due to elevated biological production in surface waters caused by upwelling of nutrient rich waters and degradation of sinking organic matter (Karstensen et al., 2008). OMZs usually extend between ~100 and ~700 m water depth in regions with sluggish circulation, such as the eastern tropical Atlantic and eastern tropical Pacific (Stramma et al., 2005). Elevated dFe concentrations encountered in OMZs are attributed to remineralisation of biogenic Fe that sinks from the surface (Rijkerberg et al., 2012; Fitzsimmons et al., 2013), and transport of high dFe – low oxygen waters from the adjacent continental shelf forms another source (Ussher et al., 2010; Conway and John, 2014; Chever et al., 2015). In addition, elevated dFe concentrations off the Peru margin of the eastern tropical South Pacific have been attributed to reversible scavenging of dFe from sinking particles (John et al., 2017). The relative importance of each of these processes for Fe supply to oxygen deficient waters is, however, poorly constrained. As anthropogenic climate change results in the expansion and intensification of OMZs in the world’s oceans (Stramma et al., 2008b; Brandt et al., 2010; Schmidtke et al., 2017) and is postulated to have important effects on the biogeochemical cycling of many redox-sensitive elements, including Fe, as well as ecosystem functioning (Chan et al., 2008; Keeling et al., 2010), the Fe sources to OMZs need to be constrained.

The isotopic composition of dFe is a relatively new tool that can help to identify Fe supply and removal mechanisms in the ocean as well as biogeochemical processing of Fe within the ocean (e.g., Lacan et al., 2008), that cannot be provided by concentration data only. Iron isotope ratios are expressed in delta notation relative to the international reference material IRMM-014 throughout this manuscript (Eq. (1)).

\[
\delta^{56}\text{Fe} (\%e) = \left[ \frac{({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}}}{({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}}} - 1 \right] \cdot 1000
\]

The isotopic signatures of dFe for different sources are distinct. The continental crust has an average \(\delta^{56}\text{Fe}\) value of ~+0.09 ± 0.10‰ (2 SD, n = 46; Beard et al., 2003). The \(\delta^{56}\text{Fe}\) value of atmospheric dust in the North Atlantic (~+0.07 ± 0.11‰; Waeles et al., 2007; Mead et al., 2013) is similar to the crustal value, but has been suggested to be modified during deposition and dissolution in surface seawater, leading to a \(\delta^{56}\text{Fe}\) signature of between +0.3 and +0.7‰ (Conway and John, 2014), although these heavy isotope signatures may include the influence of other processes, such as biological uptake. Fe reduction in anoxic sediments and the efflux of pore waters supply isotopically light Fe to the overlying water column, leading to typical \(\delta^{56}\text{Fe}\) values in oxygenated bottom waters of between −1.25 and −0.1‰ (Conway and John, 2014; Chever et al., 2015; Klar et al., 2017a), and as low as −3.5‰ in anoxic bottom waters (John et al., 2012). In contrast, non-reductive dissolution of lithogenic material on continental margins and in the water column is thought to lead to a \(\delta^{56}\text{Fe}\) of dFe between −0.3 and +0.5‰ (Radic et al., 2011; Homoky et al., 2013; Conway and John, 2014; Abadie et al., 2017), and an isotopic difference between dissolved and particulate Fe (\(\Delta^{56}\text{Fe}_{\text{dFe-PFe}}\)) of +0.27 ± 0.25‰ (Labatut et al., 2014). The reported isotopic signal of dFe in rivers draining into tropical oceans is ~−0.27 to +0.31‰ (Bergquist and Boyle, 2006), although the range for all of the world’s rivers is larger (~1.2 to +0.8‰; Escoube et al., 2009; Escoube et al., 2015). The \(\delta^{56}\text{Fe}\) values of all of these sources can nevertheless be modified by chemical and physical transformations within the ocean.

The main processes leading to modifications of dFe concentrations and their isotopic composition are redox reactions, organic complexation, biological uptake, remineralisation of organic matter and adsorption/desorption onto/from suspended particles. Upon delivery of dFe to the ocean from reducing sediments, rivers or hydrothermal vents, the change in ambient temperature, salinity, oxygen concentrations, pH and redox potential may lead to precipitation of Fe as, for example, Fe-(oxy)hydroxides and Fe-sulphides. Fe(II) that remains in solution after partial oxidation to Fe(III) followed by Fe(III)-(oxy)hydroxide precipitation could theoretically be up to 3.9‰ lighter than the initial Fe(II) pool (e.g., Bullen et al., 2001; Klar et al., 2017b). The formation of iron sulphide (FeS) minerals leads to an isotopic fractionation of \(\Delta^{56}\text{Fe}_{\text{Fe(II)-FeS}}\) ≤ −0.77‰ (Rouxel et al., 2008). It is now clear that dFe is rapidly cycled upon delivery to the ocean, with >99% of dFe bound to organic ligands (Gledhill and Buck, 2012, and references therein). It has been observed that organically complexed Fe has \(\delta^{56}\text{Fe}\) values up to 0.6‰ higher than inorganic dFe (Dideriksen et al., 2008; Morgan et al., 2010). However, this value might be ligand specific and variable. Recently reported data from the Peru margin OMZ is best modelled if the expression of isotopically light
dFe that remains in solution after partial oxidation of Fe (II) is muted due to formation of Fe(III)-ligand complexes (Chever et al., 2015). In the presence of sufficient light and macronutrients, Fe is rapidly taken up during primary production in the surface ocean. Opposing directions of Fe isotopic fractionation associated with biological uptake have been reported. The uptake of isotopically light Fe with an isotopic difference between the particulate and dissolved δ56Fe values, Δ56Fe_p-dfFe < −0.54‰ has been observed in the waters east of New Zealand and in the equatorial Pacific Ocean (Radic et al., 2011; Ellwood et al., 2015). In contrast, relatively low δ56Fe values of dFe (−0.01‰) were observed in the deep fluorescence maximum and dFe minimum in the North Atlantic Ocean (Conway and John, 2014). Thus, it appears that the sinking of dead phytoplankton cells and their remineralisation at depth may lead to the release of both isotopically light (Radic et al., 2011; Ellwood et al., 2015) or heavy (Conway and John, 2014) Fe to the dissolved pool. Iron is highly particle reactive (Goldberg, 1954), and it is thought that adsorption/desorption of Fe onto/from particle surfaces is continuously occurring throughout the water column (Milne et al., 2017). The effects of scavenging/desorption on the isotopic composition of dFe are however not yet clear. While one study found that scavenging resulted in the preferential uptake of heavy Fe onto particles (Δ56Fe_dFe-scavFe = −0.67‰; Ellwood et al., 2015), results from another study indicated that differences in δ56Fe values of scavenged Fe relative to dFe were only small (Δ56Fe_dFe-scavFe = +0.3 ± 0.5‰; Radic et al., 2011). To constrain the processes that regulate the behaviour of Fe within OMZs, we have determined the isotopic signature of dFe from four water column profiles in the West African shelf and slope region of the tropical North Atlantic Ocean. We use our data to identify the sources of dFe in the OMZ and assess the effects of internal processes, such as Fe-ligand formation, biological uptake, remineralisation and scavenging, as well as water mass transport and mixing, on the distribution of Fe. This work contributes to the international GEOTRACES program (www.geotraces.org).

2. MATERIALS AND METHODS

2.1. Cleaning procedures

Seawater samples were collected in one litre high density polyethylene (HDPE) bottles (Nalgene), which were acid cleaned following a three-step procedure. Firstly, the bottles were filled and submerged for at least 3 days in 2% Decon. After a thorough rinse in reverse osmosis water, the bottles were filled and submerged in a 6 M hydrochloric acid (HCl, analytical grade, Fisher Scientific) bath for one week. The bottles were then rinsed with purified deionised water (Milli-Q, Merck Millipore; resistivity = 18.2 MΩ cm) and transferred into a 7 M nitric acid (HNO3, analytical grade, Fisher Scientific) bath for another week. Finally, the bottles were thoroughly rinsed with purified deionised water, double bagged and stored in boxes until used for sampling on the ship.

Laboratory equipment used for sample processing was mainly polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA), with some low density polyethylene (LDPE) and polyethylene (PE) components, all cleaned thoroughly in dilute HCl and HNO3 before and between uses.

2.2. Sample collection

Samples were collected during RRS Discovery cruise D361 (GEOTRACES section GA06) between the 7th February and the 19th March 2011. Water was collected from four stations, ranging from 51 to 2656 m water depth (Fig. 1), using a trace metal clean conductivity-temperature-pressure (CTD) rosette system. The trace metal clean CTD (TM-CTD) rosette was equipped with 24 × 10 L OTE (Ocean Test Equipment, Inc.) bottles (with external springs, modified for trace metal work) that were mounted onto a titanium frame. The TM-CTD was deployed on a non-conducting Kevlar wire fitted with a Seabird auto-fire module that triggered the OTE bottles at pre-programmed depths. Sampling depths were selected according to salinity, temperature, dissolved oxygen concentration and transmission profiles, obtained immediately beforehand by a standard stainless steel CTD deployment. Immediately after recovery of the TM-CTD rosette, the OTE bottles were transferred into a trace metal clean container for subsampling.

For water filtration, OTE bottles were pressurised with oxygen-free N2 gas at a low overpressure of 10–50 kPa. Water samples were filtered through 0.2 μm Acropak 500 filter capsules (Pall Corp.), that were pre-rinsed with ~5 L surface seawater from the trace metal clean “tow-fish”, or through acid cleaned 0.45 μm polyethersulfone membrane filters (Supor, Pall Gelman). The filters were rinsed with several hundred mL of sample, followed by three rinses of the HDPE sample bottle before filling up. For Fe isotopes, three 1 L bottles were filled for each sample.

Surface seawater samples were collected with the trace metal clean “tow-fish”, deployed on the side of the ship. Seawater was pumped into the clean laboratory using a trace metal clean Teflon diaphragm pump through acid washed braided PVC tubing during the ships transit (10 knots). Samples were filtered in-line through a 0.8/0.2 μm cartridge filter (AcroPak1000) into acid-washed low-density polyethylene bottles for dFe and dAl analysis.

Samples were acidified to pH ~ 2 with concentrated HCl (Romil, Ultra Purity Acid, UpA). Isotope samples were double bagged and stored for shipping back to the National Oceanography Centre (NOC) in Southampton for analysis. Dissolved Al samples were allowed to equilibrate for at least 24 h prior analysis on board.

2.3. Analysis of dissolved Fe concentrations and isotopes

Dissolved Fe concentrations were analysed on board using chemiluminescence flow-injection-analysis following a method outlined by (Klunder et al., 2011) and are published in Schlosser et al. (2014) and Milne et al. (2017). Iron for isotope analysis was preconcentrated using a nitriloace-
tic acid (NTA) Superflow resin (Qiagen) and purified by anion exchange chromatography (BioRad AG1-x8 resin; ~0.5 ml loaded onto a homemade polyethylene column). Two preconcentration protocols were used, a batch method (~0.65 ml wet resin added directly to the seawater sample), modified from (John and Adkins, 2010) and a column method (~1 ml wet resin in homemade FEP columns), based on (Lacan et al., 2010). At least 24 h before preconcentration, already acidified (pH < 2) seawater samples were adjusted to a pH of between 1.75 and 1.80. To oxidize any remaining Fe(II) to Fe(III) in the sample, H$_2$O$_2$ (Romil, UpA, Ultra Purity Reagent) was added to the samples to

Fig. 1. Maps showing positions of sampling stations on the shelf and slope off the coast of Senegal in the tropical North Atlantic Ocean. The main upper ocean circulation (grey lines) was adapted from (Stramma et al., 2008a). The red dotted line shows the 70 μmol kg$^{-1}$ dissolved oxygen contour of the OMZ at 400 m depth (Stramma et al., 2008b). NECC = North Equatorial Countercurrent; nNECC = northern NECC; NEUC = North Equatorial Undercurrent; GD = Guinea Dome.
give a final concentration of 10 μM, 30 min before preconcentration. The average yield from both methods was 95 ± 8% Fe (n = 15) and the procedure blank was 1.7 ± 0.5 ng Fe (n = 11) for the batch method and 2.3 ± 0.7 ng Fe (n = 10) for the column method. Sample volumes ranged from 1 to 3 L, leading to a final sample size of 100 to 350 ng Fe. When dFe concentrations were <1.5 nmol L⁻¹, individual 1 L bottles were combined in 4 L LDPE cubitainers to increase the sample volume.

Isotopic measurements of samples were carried out in duplicate on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (Thermo Fisher Neptune) at the University of Southampton. The sample was introduced to the plasma via a desolvating inlet system, a membrane to increase sensitivity (Dauphas et al., 2009), introduced to the plasma via a desolvating inlet system, mass spectrometer (MC-ICP-MS) (Thermo Fisher Neptune were combined in 4 L LDPE cubitainers to increase the dFe concentrations were <1.5 nmol L⁻¹, leading to a final sample size of 100 to 350 ng Fe. When dFe concentrations were <1.5 nmol L⁻¹, individual 1 L bottles were combined in 4 L LDPE cubitainers to increase the sample volume.

Isotopic measurements of samples were carried out in duplicate on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (Thermo Fisher Neptune) at the University of Southampton. The sample was introduced to the plasma via a desolvating inlet system, either a CETAC Aridus II or an ESI Apex-Q without a membrane to increase sensitivity (Dauphas et al., 2009), using a 75 μL min⁻¹ Teflon nebuliser. The MC-ICP-MS was fitted with an x-type skimmer cone to increase ion transmission and was run in high-resolution mode using a narrow slit (25 μm). In addition to the four Fe isotopes (⁵⁶Fe, ⁵⁷Fe, ⁵⁸Fe, ⁵⁹Fe), ⁵³Cr and ⁶⁰Ni were also measured, to correct any isobaric interference of ⁵⁴Cr on ⁵⁴Fe and ⁵⁸Ni on ⁵⁶Fe, assuming that the instrumental mass bias is the same for Fe, Cr and Ni and that ⁵⁴Cr/⁵³Cr and ⁵⁸Ni/⁶⁰Ni ratios are equal to the natural average (Dauphas et al., 2009). Instrumental mass bias was corrected by addition of a double spike (0.49% ⁵⁴Fe, 0.71% ⁵⁶Fe, 45.73% ⁵⁷Fe and 53.08% ⁵⁸Fe) prior to sample processing at a ≈1:1 sample to spike ratio. The typical ⁵⁶Fe ion beam size was between 0.04 and 0.10 V ppm⁻¹. Measured ⁵⁶Fe/⁵⁴Fe ratios of the sample- or standard-spike mixture were instrumental blank subtracted (<0.06%) and the sample or standard ⁵⁶Fe/⁵⁴Fe ratios were obtained by iterative deconvolution, while at the same time correcting for instrumental mass bias and Cr and Ni interferences (Albarède and Beard, 2004). ⁵⁶Fe/⁵⁴Fe sample ratios are expressed as δ⁵⁶Fe relative to the average ⁵⁶Fe/⁵⁴Fe value for the Fe isotope reference material IRMM-014 (Institute for Reference Materials and Measurements) determined during the same analytical session (Eq. (1)). The external precision and accuracy of the isotope measurements was assessed by multiple analyses of an Fe isotope standard during each analytical session. The average value of ETH (Eidgenössische Technische Hochschule, Zürich) hematite standard for all analytical sessions was +0.52 ± 0.07‰ (2 SD, n = 54). This value compares well with previous measurements of the ETH hematite standard reported in (Lacan et al., 2010) (+0.52 ± 0.08‰, 2 SD, n = 81). Analytical replicates, which consisted of splitting the sample and replicating the entire analytical procedure, of samples 6_16 and 8_13 (Table 1), resulted in differences between replicates that are within the external reproducibility of the ETH standard.

We have further validated our Fe isotope method by blind analysis of two seawater samples that had already been analysed in F. Lacan’s lab (LEGOS, Toulouse, France). The seawater samples were collected from Station 14 during Cruise B/V Kilo Moana 0625 in 2006 and Fe isotope results obtained at LEGOS are published in Radic et al. (2011). Fe concentrations were sub nano-molar, which is characteristic of open ocean seawater. By preconcentrating a similar quantity of Fe to the samples in this study, we obtained δ⁵⁶Fe values of +0.07 ± 0.07‰ (n = 2) for sample 14–2 at 849 m depth (vs. +0.22 ± 0.05‰ in Radic et al., 2011) and +0.34 ± 0.06‰ (n = 2) for sample 14–6 at 198 m depth (vs. +0.40 ± 0.06‰ in Radic et al., 2011). These replicate analyses are within the range of inter-lab reproducibility (+0.17‰) for 0.4 nmol L⁻¹ dFe, reported in Boyle et al. (2012) and Conway et al. (2016).

2.4. Analysis of dissolved aluminium concentrations

Dissolved aluminium (dAl) concentrations were determined on board by flow injection analysis using a lumogallion-Al fluorescence technique originally developed by Resing and Measures (1994) and modified according to Brown and Bruland (2008). The analytical procedure was validated by analysing North Atlantic GEOTRACES Reference Seawater. GD-23 yielded 18.2 ± 1.0 nmol kg⁻¹ dAl, n = 4 (vs. a consensus value of 17.7 ± 0.2 nmol kg⁻¹) and GS-57 yielded 27.1 ± 1.1 nmol kg⁻¹, dAl, n = 5 (vs. a consensus value of 27.5 ± 0.2 nmol kg⁻¹).

2.5. Auxiliary data

A Sea-Bird 911 plus CTD sensor, fin-mounted secondary temperature and conductivity sensors, a Digiquartz pressure sensor, a fluorometer sensor and a transmissometer sensor were mounted on the titanium rosette frame. Sensors were cross-calibrated with discrete seawater analyses using the Winkler method for oxygen (Carpenter, 1965) and conductivity measurements of a certified reference material for salinity. Chlorophyll-a content was monitored using a fluorometer fitted on the rosette frame and the manufacturer’s calibration was applied. More details on sensors and calibration methods employed during D361 can be found at the British Oceanographic Data Centre (www.bodc.ac.uk).

Concentrations of seawater nitrate, nitrite, silicate, ammonium and phosphate were determined on board the RRS Discovery, using a 5-channel segmented flow autoanalyzer (Bran and Luebbe AAIII) (Woodward and Rees, 2001).

3. RESULTS

3.1. Hydrography and oxygen content

Off the coast of Senegal, four main water masses were identified from potential temperature, salinity and potential density signatures (Fig. 2). The surface 40 m consisted of Tropical Surface Water (TSW; σθ < 25.8 kg m⁻³) (Stramma et al., 2005; Stramma et al., 2008a). Between the isopycnals (σθ) 25.8 and 27.1 kg m⁻³, at temperatures above 8 °C, subsurface waters down to 500 m depth mainly consisted of South Atlantic Central Water (SACW) (Stramma et al., 2005), which is formed from Indian Ocean Central Water, and transferred to the Atlantic Ocean by the Aghulas and Benguela currents (Stramma and England, 1999). After flowing northwards with the Benguela Current, SACW flows westward into the tropical Atlantic with the
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<th>Water mass</th>
<th>dFe (nmol L⁻¹)</th>
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**Table 1**

Composition of seawater samples recovered from the Senegalese continental margin, shown from shallowest to deepest water depth. dFe data are from (Milne et al., 2017).

The flow field in the upper 800 m of the northeastern subtropical Atlantic is controlled by a wind driven subtropical gyre (Stramma et al., 2005) (Fig. 1). Upwelling occurs near the coast of Senegal and Mauritania, as well as in the Guinea Dome (Schott et al., 2004). Coastal upwelling replaces the water moved offshore by Ekman transport, driven by equatorward winds (Stramma et al., 2005). Upwelling in the Guinea Dome is due to cyclonic circulation, associated with the North Equatorial Counter Current (NECC), the northern NECC (nNECC) and the North Equatorial Undercurrent (NEUC) (Stramma et al., 2005, 2005).
the Guinea Dome and its related circulation are weakened during the winter, even though they exist throughout the year (Siedler et al., 1987).

In the upper 40 m of the water column, oxygen concentrations were >200 μmol kg⁻¹. Oxygen concentrations were <70 μmol kg⁻¹ at depths between ~40 and ~900 m (the approximate extension of these waters at 400 m depth is shown in Fig. 1). Oxygen depleted waters roughly coincided with the extension of SACW and the upper part of AAIW (Fig. 2). Oxygen concentrations reached a minimum of ~45 μmol kg⁻¹ at around 400 m depth at Stations 2 and 3. NADW was well oxygenated, and oxygen concentrations were >200 μmol kg⁻¹ near the seafloor. Our observations agree with previous reports of oxygen concentrations >35 μmol kg⁻¹ for the OMZ in the tropical North Atlantic Ocean, compared to concentrations within the OMZ of the eastern tropical Pacific Ocean of ~2 μmol kg⁻¹ (Stramma et al., 2008b). The OMZ in the tropical North Atlantic Ocean consists of poorly ventilated upwelled waters, flowing westward from the African coast. The OMZ is contained by ventilation from below by AAIW; in the north and south by the eastward flowing zonal jets; and in the west by subtropical gyre waters (Stramma et al., 2005).

3.2. Distributions of dFe, δ⁵⁶Fe and macronutrients

Dissolved Fe concentrations in the water column ranged between 1.33 nmol L⁻¹ and 6.3 nmol L⁻¹ (Fig. 4 and Table 1). On the shelf, the highest dFe concentrations were observed near the seafloor and lowest concentrations in the surface waters, indicating benthic supply. By contrast, the slope stations (2 and 3) showed a mid-depth maximum between 300 m and 1100 m (up to 3.77 nmol L⁻¹) and rather similar dFe concentrations above and below (~1.5 nmol L⁻¹) of this feature. Dissolved Fe showed an approximately linear relationship with nitrate and phosphate (Fig. 3), for which the slope of the regression line was steeper for the offshore stations 2 and 3 than for the two shelf stations 4 and 5.

δ⁵⁶Fe values for dFe ranged between −0.33 and +0.41‰ (Fig. 4 and Table 1). δ⁵⁶Fe values were lowest over the shelf (~−0.3‰) close to the seafloor, and increased towards the crustal value (+0.09 ± 0.1‰, 2 SD; Beard et al. (2003)) higher up in the water column and away from the shelf (Fig. 4 and Table 1).

On the slope, Station 3 (1041 m water depth) displayed lowest δ⁵⁶Fe values (between −0.27 and −0.15‰) in oxygen depleted waters. Higher δ⁵⁶Fe values were observed at 200 m (+0.06‰) and 600 m depth (~0.08‰). The highest δ⁵⁶Fe values (~0.06 to +0.41‰) were observed at the furthest offshore Station 2 (2656 m water depth). Here, δ⁵⁶Fe values increased from −0.06‰ at 200 m depth to +0.41‰ at 500 m depth. Between 600 m and the seafloor, there was little variation in δ⁵⁶Fe, with values around +0.1‰.

4. DISCUSSION

4.1. Benthic supply of dFe

On the Senegalese shelf, elevated dFe concentrations (up to 6.35 nmol L⁻¹) in the water column close to the seafloor are indicative of a sedimentary Fe source to the overlying waters. This is consistent with other studies that have shown that shelf sediments are a source of dFe to the overlying water column even if the water column is oxygen replete (e.g., Mackey et al., 2002; Planquette et al., 2007; Conway and John, 2014; Marsay et al., 2014; Klar et al., 2017a). Moreover, the consideration of benthic Fe supply to seawater in biogeochemical models leads to an improved reproduction of dFe distributions (Siedlecki et al., 2012; Tagliabue et al., 2017). The release of dFe from shelf sediment is broadly classified into three categories: (i) dissimilatory iron reduction (DIR), (ii) non-reductive dissolution (NRD) and (iii) decomposition of organic matter recently transferred to the surface layer of sediments. The low δ⁵⁶Fe values (down to ~0.3‰) associated with high dFe concentrations in bottom waters on the Senegalese shelf are indicative of a reduced Fe source. Previous studies (e.g., John et al., 2012; Chever et al., 2015; Klar et al., 2017a) have shown that low δ⁵⁶Fe values in bottom waters correspond to efflux of Fe(II) across the sediment-water interface; this Fe(II) is produced by DIR in reducing sediments. However, δ⁵⁶Fe values associated with DIR are usually lower than those observed in our study area. Hence, we explore the possible mechanisms that could lead to the observed isotopic signals.

DIR occurs under anoxic conditions by microbial reduction of Fe(III) to Fe(II) (e.g., Canfield, 1989; Burdige, 2006). Fe(II) is soluble and is released into pore waters, yielding Fe(II) concentrations in the millimolar range, that has a light isotopic signature (δ⁵⁶Fe = −2 to −1‰; Severmann et al., 2006; Homoky et al., 2009; Henkel et al., 2016; Klar et al., 2017a). Upward diffusing Fe(II) is rapidly oxidised to Fe(III) when it encounters oxygenated pore waters or overlying oxygenated bottom water (Millero et al., 1987), and the subsequent formation of insoluble amorphous Fe-(oxy)hydroxide minerals at
As Fe(III) is removed from pore waters, the isotopic composition of Fe that remains in solution shifts towards lower values approaching the sediment-water interface (down to $-3.5\%$; Severmann et al., 2010). These field observations agree with experimental observations that have shown that the equilibrium fractionation between Fe(II) and Fe(III) results in the $\delta^{56}$Fe value of aqueous Fe(III) being up to $3.5\%$ higher than that of the coexisting aqueous Fe(II) (e.g., Welch et al., 2003). Hence, the $\delta^{56}$Fe value of dFe depends on the proportion of Fe(III) removed from the dissolved phase through precipitation (e.g., Dauphas and Rouxel, 2006; Klar et al., 2017b). If DIR was the main process supplying high dFe concentrations to bottom waters on the Senegalese shelf, lower $\delta^{56}$Fe values are expected. For example, $\delta^{56}$Fe values of as low as $-3.45\%$ have been measured in low-oxygen (<5 $\mu$mol kg$^{-1}$) bottom waters overlying reducing sediments along the Californian margin (John et al., 2012). However, at the same location, $\delta^{56}$Fe values increased with increasing oxygen concentrations in the water column, such that at oxygen concentrations similar to those found within the OMZ in our study (~50 to 75 $\mu$mol kg$^{-1}$), dFe ranged from 2.4 to 4.3 nmol L$^{-1}$ and $\delta^{56}$Fe values ranged from $-1.13$ to $-0.8\%$. Our results are within the high-end spectrum of $\delta^{56}$Fe values found in OMZ waters on the western South American margin, ranging from $-1.3$ to $-0.3\%$ (Chever et al., 2015; Fitzsimmons et al., 2016; John et al., 2017), and are comparable with $\delta^{56}$Fe values found in OMZ waters on the West African margin further north (down to $-0.5\%$; Conway and John, 2014). Lowest $\delta^{56}$Fe values (down to $-1.25\%$) were associated with the highest proportions (up to 100%) of Fe(II) in the dissolved pool (Chever et al., 2015), which provided evidence for a benthic Fe(II) source. Similarly, Scholz et al. (2014) inferred a $\delta^{56}$Fe value of $-0.44\%$ for dFe supplied to OMZ waters by Peru margin sediments. In addition, a light benthic iron isotope signal ($\delta^{56}$Fe down to $-1.02\%$) was also observed in oxygen-saturated bottom waters in a temperate shelf sea (Klar et al., 2017a).

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**Fig. 4.** Profiles of Chl-a, transmittance, oxygen concentration, dFe concentration and $\delta^{56}$Fe values at shelf stations 4 and 5 (top panels) and slope stations 2 and 3 (bottom panels), shown from shallowest to deepest water depth. dFe data are from (Milne et al., 2017). Note change of scale for dFe concentrations between upper and lower plots. The average $\delta^{56}$Fe value of the continental crust is shown as a vertical black line (+0.09 ± 0.10\%, 2 SD, n = 46; Beard et al., 2003). Water masses are delimited by the horizontal green lines in the oxygen plots. TSW = Tropical Surface Water; SACW = South Atlantic Central Water; AAIW = Antarctic Intermediate Water; NADW = North Atlantic Deep Water.

seawater pH (Liu and Millero, 2002; Ussher et al., 2004). As Fe(III) is removed from pore waters, the isotopic composition of Fe that remains in solution shifts towards lower values approaching the sediment-water interface (down to $-3.5\%$; Severmann et al., 2010). These field observations agree with experimental observations that have shown that the equilibrium fractionation between Fe(II) and Fe(III) results in the $\delta^{56}$Fe value of aqueous Fe(III) being up to $3.5\%$ higher than that of the coexisting aqueous Fe(II) (e.g., Welch et al., 2003). Hence, the $\delta^{56}$Fe value of dFe depends on the proportion of Fe(III) removed from the dissolved phase through precipitation (e.g., Dauphas and Rouxel, 2006; Klar et al., 2017b). If DIR was the main process supplying high dFe concentrations to bottom waters on the Senegalese shelf, lower $\delta^{56}$Fe values are expected. For example, $\delta^{56}$Fe values of as low as $-3.45\%$ have been measured in low-oxygen (<5 $\mu$mol kg$^{-1}$) bottom waters overlying reducing sediments along the Californian margin (John et al., 2012). However, at the same location, $\delta^{56}$Fe values increased with increasing oxygen concentrations in the water column, such that at oxygen concentrations similar to those found within the OMZ in our study (~50 to 75 $\mu$mol kg$^{-1}$), dFe ranged from 2.4 to 4.3 nmol L$^{-1}$ and $\delta^{56}$Fe values ranged from $-1.13$ to $-0.8\%$. Our results are within the high-end spectrum of $\delta^{56}$Fe values found in OMZ waters on the western South American margin, ranging from $-1.3$ to $-0.3\%$ (Chever et al., 2015; Fitzsimmons et al., 2016; John et al., 2017), and are comparable with $\delta^{56}$Fe values found in OMZ waters on the West African margin further north (down to $-0.5\%$; Conway and John, 2014). Lowest $\delta^{56}$Fe values (down to $-1.25\%$) were associated with the highest proportions (up to 100%) of Fe(II) in the dissolved pool (Chever et al., 2015), which provided evidence for a benthic Fe(II) source. Similarly, Scholz et al. (2014) inferred a $\delta^{56}$Fe value of $-0.44\%$ for dFe supplied to OMZ waters by Peru margin sediments. In addition, a light benthic iron isotope signal ($\delta^{56}$Fe down to $-1.02\%$) was also observed in oxygen-saturated bottom waters in a temperate shelf sea (Klar et al., 2017a).
The relatively higher δ^{56}Fe values (down to −0.33‰) in low oxygen bottom waters (−50 to 100 μmol kg^{-1}) on shelf stations 4 and 5 (Fig. 4, Table 1) may therefore reflect the presence of benthic inputs of reduced Fe that has been modified during transport across the sediment-seawater interface and/or additional inputs of Fe from other sources. Non-reductive dissolution (NRD) of lithogenic material occurs in the presence or absence of oxygen in the water column (Radic et al., 2011) and sediment porewaters (Homoky et al., 2013). It is suggested that during this process, both dissolution of particles and adsorption of dFe onto particles occur simultaneously, with a net release of dFe from particles (Radic et al., 2011; Labatut et al., 2014; Abadie et al., 2017). Dissolved Fe with a heavier isotopic composition than particulate Fe (Δ^{56}Fe_{dFe-pFe} ~ +0.2‰; Radic et al., 2011; Labatut et al., 2014) has been attributed to NRD, with observed δ^{56}Fe values of +0.22‰ in oxic sediment pore waters (Homoky et al., 2013) and from −0.3 to +0.4‰ in seawater (Radic et al., 2011; Labatut et al., 2014; Abadie et al., 2017). However, along the coast of South Africa, where atmospheric deposition and the supply of lithogenic material to sediments are low, benthic Fe fluxes associated with NRD have been found significantly lower (0.11–0.23 μmol dFe m^{-2} d^{-1}; Homoky et al., 2013) than those associated with DIR (400–866 μmol dFe m^{-2} d^{-1}; Severmann et al., 2010; Noffke et al., 2012). By contrast, relatively high dFe concentrations associated with isotopic signals characteristic of NRD have been measured in the water column in the western North Atlantic Ocean (Conway and John, 2014), where atmospheric deposition fluxes are intermediate (Jickells et al., 2005). In addition, Labatut et al. (2014) calculated large fluxes of dFe (on average 860 μmol dFe m^{-2} d^{-1}) associated with NRD of continental particles in the water column close to Papua New Guinea. Our study area lies within a high dust deposition area (Jickells et al., 2005), and therefore, NRD of rapidly accumulating “new” lithogenic material on the seafloor may make an important contribution to the total benthic Fe flux in our study area, and would explain the shift towards higher δ^{56}Fe values than expected for DIR-sourced Fe in bottom waters. Rivers (the Gambia River and the Casamance River) may also be an important source of lithogenic material to our study area. However, to date there is no data of particulate fluxes from these rivers to the adjacent shelf.

The upwelling area of the eastern (sub)tropical North Atlantic Ocean is highly productive, leading to large amounts of organic material (dead phytoplankton cells, faecal pellets, etc) continuously being exported into deeper waters and deposited on the seafloor (Broecker, 1974; Eppley and Peterson, 1979). This organic matter can be rapidly remineralised in the surface layer of the sediments (e.g., Klar et al., 2017a), leading to the release of nutrients, including dFe, to pore waters and bottom waters. Though we have no supporting data, the decomposition of organic matter at the sediment-water interface could be releasing dFe with relatively high δ^{56}Fe values to bottom waters. The release of dFe from remineralisation of organic matter and its isotopic signature will be further discussed in Section 4.3.

The stabilisation of Fe in bottom waters by organic complexation could partly prevent precipitation of Fe (III)-(oxy)hydroxides, facilitating the transport of pore water Fe into overlying bottom waters (Jones et al., 2011; Hickli et al., 2014). Since relatively low benthic δ^{56}Fe signals (<−0.2‰) were also observed some >600 m above the seafloor in OMZ waters on the slope (Station 3, Fig. 4), we suggest that a significant proportion of the pore water dFe that is transferred to overlying waters is immediately complexed with organic ligands, allowing offshore transport. Organic ligands may be directly supplied to sediment pore waters by degradation of organic material. Complexation to organic ligands most likely favours heavy Fe isotopes, with the δ^{56}Fe of ligand bound Fe being up to 0.6‰ higher than that of the inorganic Fe fraction (Dideriksen et al., 2008; Morgan et al., 2010), hence, justifying a shift towards heavier isotopic compositions of the benthic Fe signal observed in bottom waters. Dissolved Fe stabilisation due to complexation with organic ligands at the sediment-water interface has also been suggested in previous studies (e.g. Klar et al., 2017a), where Fe isotopic shifts signaled from as low as −3‰ in anoxic pore waters to up to −0.1‰ in oxygen saturated bottom waters.

Hence, a combination of DIR and NRD of margin sediments, remineralisation of organic matter and complexation of dFe with organic ligands at the sediment-water interface may all influence bottom water δ^{56}Fe values (down to −0.3‰) on the Senegalese margin. Our iron isotope data are similar to those measured in bottom waters in the eastern tropical North Atlantic Ocean north of Cape Verde Islands, where low δ^{56}Fe values of down to −0.5‰ were attributed to dFe release from reducing sediments into a water column with oxygen levels >220 μmol kg^{-1} (Conway and John, 2014). In their study, however, the shallowest station close to the African shelf was ~3000 m deep. Our stations, located ~6° to the south in shallower waters therefore provide new information on δ^{56}Fe in slope and shelf waters. Benthic inputs of dFe on the Mauritian shelf, at ~18 °N, with diffusive Fe fluxes (10 and 30 μmol m^{-2} d^{-1}) from shelf sediments (<200 m depth) to bottom waters with <50 μmol kg^{-1} oxygen, determined from pore water Fe concentrations (Lomnitz, 2017) were somewhat lower than those measured on the Californian shelf (<10 to >300 μmol m^{-2} d^{-1}) using benthic chambers (Severmann et al., 2010). Thus high benthic dFe fluxes appear to be associated with very low bottom water oxygen concentrations (i.e., <2 μmol kg^{-1} on the Californian shelf versus ~50 μmol kg^{-1} on the west African margin). However, the generally higher δ^{56}Fe values on the west African margin (~−0.3‰; this study; Conway and John, 2014), compared to those on the western South American margin (~1.3 to −0.3‰; Chever et al., 2015; Fitzsimmons et al., 2016; John et al., 2017), provide new information on the processes that regulate the benthic flux of dFe.

4.2. Atmospheric supply of Fe to the surface ocean

The study area is located in close proximity to the Sahara and Sahel deserts, which deliver large amounts of dust to the North Atlantic Ocean (Kramer et al., 2004;
Dissolved aluminium (dAl) is a nearly conservative tracer of lithogenic material in seawater (Measures and Brown, 1996), as it is only removed by scavenging processes (Moran and Moore, 1992) with minor incorporation into siliceous frustules of diatoms (Gehlen et al., 2002). Assuming that dAl in the surface mixed layer is entirely supplied by atmospheric dust, that dust is composed of 8.2% w/w Al (Taylor, 1964), that Al solubility from Saharan dust is 13 ± 10% (Buck et al., 2010), and that the residence time of dAl is 1.2 ± 0.5 years in tropical Atlantic waters (Dammshäuser et al., 2011), the dust flux was estimated to be 0.019 ± 0.19 g m⁻² y⁻¹ on the shelf and 0.023-0.080 g m⁻² y⁻¹ on the slope (Table 2). Assuming that dust is composed of 5.6% w/w Fe (Taylor, 1964) and that Fe solubility from Saharan dust is 4 ± 2% (Buck et al., 2010), the dust-derived soluble Fe flux was between 0.002 and 0.009 μmol Fe m⁻² d⁻¹ (Table 2).

The soluble Fe fluxes from aerosols estimated from dAl concentrations were an order of magnitude lower than those determined from aerosol measurements during the same cruise (Milne et al., 2017), i.e., 0.002 ± 0.002 μmol m⁻² d⁻¹ versus 0.075 μmol m⁻² d⁻¹ on the shelf and 0.003-0.009 μmol m⁻² d⁻¹ versus 0.074 μmol m⁻² d⁻¹ on the slope, respectively. Slight differences between the methods are expected, as aerosol fluxes derived from dAl measurements in surface waters represent average fluxes over ~1.2 years, and aerosol fluxes calculated from dAl concentrations are highly dependent on Al residence time, which is, in turn, controlled by particle scavenging. More critically, however, dust fluxes are highly variable because of the episodic and complex nature of dust dynamics in the atmosphere (e.g., Jickells et al., 2016). Our results suggest that dust-derived dFe inputs were low on the Senegalese shelf and slope regions at the time of our study, and although the soluble Fe flux from aerosols was slightly higher in the open ocean during the same cruise (0.135 μmol m⁻² d⁻¹; Milne et al., 2017), they were also low relative to aerosol fluxes measured on the West African margin during dust storms (up to 74 μmol Fe m⁻² d⁻¹; Crook et al., 2004). Hence, atmospheric deposition and sedimentation of lithogenic material, and potentially input of dFe from NRD, is likely to be more significant at other times of the year in our study area, and could be contributing to background dFe concentrations in the water column, which may be stabilised by complexation to organic ligands (Conway and John, 2014).

Assuming a residence time of dFe of 0.7 years in North Atlantic tropical gyre surface waters (Ussher et al., 2013), soluble Fe fluxes from dust can be converted to dust-derived dFe concentrations in the surface mixed layer (Table 2). Measured dFe concentrations were consistently higher than dFe concentrations calculated from dAl derived fluxes, and lower than dFe concentrations obtained from aerosol measurements. Nevertheless, our data indicate that atmospheric dust was likely to supply >10% of dFe to surface waters in our study area.

We have no δ⁵⁶Fe measurements from within the surface mixed layer (SML, 11–19 m thick) and dFe isotopic compositions are likely significantly modified below the SML due to scavenging and remineralisation processes. Hence, we are not able to directly assess the isotopic composition of dust-derived dFe in our study area. However, surface waters at 25 m depth on the shelf were characterised by higher δ⁵⁶Fe values (−0.11 to +0.03‰), and lower dFe concentrations (up to 3 nmol L⁻¹), compared to bottom waters (Fig. 4). The shift towards higher δ⁵⁶Fe values between 40 m and 25 m depth is consistent with input of dust-derived dFe to the surface ocean. In support of this, NRD of sinking lithogenic material would lead to the release of dFe with δ⁵⁶Fe values of +0.27 ± 0.25‰ (Labatut et al., 2014), which is higher than that of the lithogenic material (δ⁵⁶Fe ~ +0.07 ± 0.11‰; Waeles et al., 2007; Mead et al., 2013). In addition, high δ⁵⁶Fe values of +0.3 to +0.7‰ have been measured in the SML to the north of the Cape Verde islands in the North Atlantic Ocean (Conway and John, 2014). This has been attributed to the formation of strong Fe-ligand complexes during dust dissolution, which preferentially incorporate the heavier Fe isotopes (Δ⁵⁶Feₕₑ₋₅⁶Feₐₑ = 0.6‰; Dideriksen et al., 2008; Morgan et al., 2010).

Hence, NRD of sinking dust particles may explain the high δ⁵⁶Fe values, relative to inputs of dFe from DIR (see Section 4.1), throughout the entire water column on the shelf. Since atmospheric dust inputs to our study area can be significantly more important on an episodic basis, these could produce high background δ⁵⁶Fe values of dFe in seawater (Conway and John, 2014). To properly assess the effects of atmospheric deposition on the isotopic composition of dFe in seawater, δ⁵⁶Fe analyses of aerosols and suspended particulate material offshore Senegal are required.

### 4.3. Fe isotopic fractionation by biological activity

Concentrations of chlorophyll-a indicated that levels of biological activity in the surface waters were high, with levels up to ~1.5 μg L⁻¹ on the shelf and up to 2 μg L⁻¹ on the slope (Fig. 4). Maximum Chl-a and lowest transmittance were measured immediately below the surface layer (0–15 m depth) and thus above the depth of our shallowest Fe isotope sample. It is important to note that significant changes in δ⁵⁶Fe values linked to high biological activity are expected in surface waters. Uptake of isotopically light Fe linked to biological activity has previously been observed (Δ⁵⁶Feₕₑ₋₅⁶Feₐₑ < −0.54‰; Radic et al., 2011; Ellwood et al., 2015). By contrast, (Conway and John, 2014) recorded relatively light δ⁵⁶Fe values of dFe (e.g., −0.01‰ vs. +0.20‰ above and below) associated with the deep fluorescence maximum (136 m) in the North Atlantic Ocean. John et al. (2017) observed a decrease in δ⁵⁶Fe of dFe in the upper few hundred metres and suggested this was due to biological uptake; however, this was not observed in all their profiles. The direction of Fe isotopic fractionation could depend on phytoplankton type.

Even though we were not able to assess the isotopic fractionation of Fe associated with biological uptake directly, we were able to do this indirectly by investigating remineralisation of sinking organic material throughout the water column. Remineralisation of sinking organic material plays an important role in recycling Fe in the ocean (e.g., Rijkenberg et al., 2012; Fitzsimmons et al., 2013). The
amount of remineralised dFe in the water column below 100 m depth was calculated from estimates of apparent oxygen utilisation (AOU), assuming an AOU/C ratio of 1.6 (Martin et al., 1987) and a Fe/C ratio of 15 μmol Fe/mol C, measured in phytoplankton cells on the west African margin (Twining et al., 2015) (Fig. 5). This ratio is similar to that estimated in the eastern tropical North Atlantic during cruise AMT15 (13 μmol Fe/mol C; Ussher et al., 2013). Our calculations suggest that remineralisation was a significant source of dFe, especially within the OMZ (between 40 and 900 m depth). The apparent common source of Fe and P or N, as indicated by the correlation between Fe and P or N in the water column (Fig. 3), is also suggestive of significant remineralisation of sinking dead phytoplankton cells. Note that, for some samples, remineralised Fe appears to constitute >100% of dFe (Fig. 5); this suggests that removal of dFe by particle scavenging processes was significant in the water column. Scavenging of dFe onto biogenic and non-biogenic particles and exchange of Fe between the dissolved and particulate phases are continuous processes and could overprint the isotopic signatures of benthic or atmospheric inputs and remineralisation. Since the extent of Fe isotopic fractionation associated with particle scavenging and desorption are not well known (Radic et al., 2011; Labatut et al., 2014; Ellwood et al., 2015), these processes are ignored in subsequent discussions.

Higher levels of remineralisation are associated with relatively heavy Fe isotope signatures (Fig. 6). It has been shown that remineralisation of organic material is less effective in OMZs (Cavan et al., 2017), and therefore, it is not certain if the high δ56Fe values reflect remineralisation of the entire biogenic Fe pool or that of an unknown fraction. Other processes such as adsorption/desorption of Fe onto/from particles and NRD of lithogenic particles could overprint δ56Fe values throughout the water column, however, we assume that these changes are relatively small where remineralisation is high. At Station 3, the proportion of remineralised dFe was highest at 600 m depth (Figs. 4 and 5), where the δ56Fe value of dFe was −0.08‰. At Station 2, the proportion of dFe supplied by remineralisation was highest within the OMZ and correlated positively with δ56Fe values (+0.02 to +0.41‰), including a highest δ56Fe value of +0.41‰ at 500 m depth. Interestingly, the highest δ56Fe values were associated with relatively low dFe concentrations at both stations, suggesting rapid scavenging onto particles. Hence, our data are consistent with biological uptake of heavy dFe isotopes in surface waters, followed by release of heavy dFe isotopes during remineralisation of this material as it sinks throughout the water column and rapid scavenging of some part of the remineralised dFe onto sinking particles. Our results contradict previous studies, which suggested that biological Fe uptake incorporates the lighter isotopes (Ellwood et al., 2015; Radic et al., 2011), but they are consistent with the findings of Conway and John (2014), who reported that isotopically light dFe was associated with the deep fluorescence maxima and the dFe concentration minima in the North Atlantic.

Table 2: Estimates for dust fluxes and dust derived dFe fluxes from dust measurements and dust supplied dFe concentrations (dFe, dust) in the surface mixed layer (SML). Measured dFe (dFe, meas) values are from Schlosser et al. (2014). The SMDL (SML depth) was calculated according to Monterey and Levitus (1997). The SMDL for samples F-46, F-47 and F-49 was not measured and is assumed to be 11 m.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Lat (°C)</th>
<th>Long (°E)</th>
<th>Stn</th>
<th>SMLD (m)</th>
<th>dAl meas (nmol L⁻¹)</th>
<th>dFe meas (nmol L⁻¹)</th>
<th>dFe, dust (nmol L⁻¹)</th>
<th>SD dFe, dust (nmol L⁻¹)</th>
<th>SD dust flux (g dust m⁻² y⁻¹)</th>
<th>SD dust flux (l mol dFe m⁻² d⁻¹)</th>
<th>SD dFe (nmol L⁻¹)</th>
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<td>F-44</td>
<td>12.590</td>
<td>17.653</td>
<td>4 &amp; 5</td>
<td>11</td>
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<td>0.4</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.09</td>
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<tr>
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<td>17.714</td>
<td>3</td>
<td>9</td>
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<td>0.4</td>
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<td>0.02</td>
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</tr>
<tr>
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<tr>
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<tr>
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<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.09</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Data from Milne et al. (2017).
4.4. Isotopic signatures within water masses

Between 700 and 1100 m water depth, AAIW was present at stations 2 and 3. The $\delta^{56}$Fe values in this water mass were $\approx +0.1\%$ ($n=3$) at Station 2 and $-0.30$ to $-0.08\%$ ($n=4$) at Station 3. AAIW was located immediately above the seafloor at Station 3, with enhanced dFe concentrations and low $\delta^{56}$Fe values indicating a relatively strong supply of benthic dFe to bottom waters, overwriting the isotopic signature of AAIW. In previous studies, it has been observed that AAIW transports isotopically light Fe ($-0.37$ to $-0.17\%$) within the southern hemisphere basins of the Atlantic and Pacific Oceans (Conway et al., 2016; Fitzsimmons et al., 2016; Abadie et al., 2017). The Fe isotopic signature of AAIW is significantly modified at the equator in the Pacific ($+0.22\%$, Radic et al., 2011) and close to Papua New Guinea ($+0.06$ to $+0.44\%$; Radic et al., 2011; Labatut et al., 2014). Abadie et al. (2017) observed that the light $\delta^{56}$Fe values may originate from the dilution of Upper Circumpolar Deep Water (UCDW; $\approx -0.8\%$), as AAIW originates from the subduction of Antarctic Surface Water (AASW), which in turn results from the upwelling of UCDW. We suggest that the $\delta^{56}$Fe values we observed in AAIW are significantly modified by remineralisation, sorption/desorption processes and benthic input of new dFe.

At Station 2, NADW was present at depths below 1100 m, and had a $\delta^{56}$Fe value of $+0.09$ to $+0.12\%$ ($n=2$) and dFe concentrations of 1.3–1.7 nmol L$^{-1}$. Reported $\delta^{56}$Fe values for NADW differ significantly in the literature. In the North Atlantic Ocean, Conway and John (2014) reported $\delta^{56}$Fe values of $+0.21\%$ at $\approx 2000$ m depth for a profile over the continental slope at $\approx 18^\circ$ W, and $\delta^{56}$Fe values of $+0.7\%$ at $2000$ m depth at $30^\circ$ W in the open ocean. Near Bermuda, the $\delta^{56}$Fe of NADW ranged from $+0.2$ to $+0.56\%$ (Boyle et al., 2012; John and Adkins, 2012; Conway et al., 2013, 2016; Conway and John, 2014). NADW measured at $\approx 3000$ m depth in the Southern Ocean has $\delta^{56}$Fe values of between $+0.17$ to $+0.33\%$ (Conway et al., 2016; Abadie et al., 2017). This suggests that the isotopic composition of NADW is slightly modified during its journey southwards. Isotopic modifications of dFe could be due to: (i) exchange between the dissolved and particulate Fe pools (Radic et al., 2011; John and Adkins, 2012; Labatut et al., 2014; Ellwood et al., 2015), and (ii) non-reductive dissolution of sinking particles (Abadie et al., 2017). Thus, due to the short residence times and reactivity of Fe, and the supply of new Fe close to source regions, the isotopic composition of the dissolved Fe pool is continuously modified and it is clear that $\delta^{56}$Fe cannot be applied as a conservative water mass tracer.

4.5. Origin of elevated dFe concentrations in low oxygen waters off the shelf

The elevated dFe concentrations observed in the OMZ (between 40 and 900 m depth) at Station 2 may originate from offshore advection of high dFe containing shelf waters (e.g., Conway and John, 2014), remineralisation of sinking particles (e.g., Fitzsimmons et al., 2013), and net release of dFe from particle surfaces (Milne et al., 2017). $\delta^{56}$Fe values can be explained by mixing between high dFe concentration, low $\delta^{56}$Fe shelf waters and low dFe concentration, high $\delta^{56}$Fe offshore water masses (Fig. 7a). On the shelf, a positive correlation between oxygen concentrations and $\delta^{56}$Fe values could be an artefact due to larger amounts of oxygen being consumed in deeper waters combined with poor ventilation (Fig. 7b). We cannot assume that isotopic signatures are solely governed by mixing processes, and hence, explore other possibilities below.

We have estimated the amount of dFe released to the water column due to remineralisation, and this was up to 2.1 nmol L$^{-1}$ within low oxygen waters on the slope (Figs. 4 and 5; Section 4.3). The contribution of remineralised dFe to the total dFe concentration measured in the low oxygen waters was 56–170% (average 88 ± 36%, $n=11$) at Station 3, and 94 to 150% (average 118 ± 22, $n=9$) at Station 2 (Fig. 5). Hence, the importance of remineralised dFe increased with distance from the shelf. The AOU was positively correlated with dFe concentrations ($R^2 = 0.4$; Fig. 6a), and samples with a high proportion of remineralised dFe tended to have the highest $\delta^{56}$Fe values on the slope (Section 4.3; Fig. 6b).

"Excess" dFe (dFe supplied from processes other than remineralisation) correlated with low $\delta^{56}$Fe values on the slope (Fig. 6b). For this reason, excess dFe is assumed to be principally derived from benthic Fe inputs that appeared to be advected laterally from the adjacent shelf. On the slope at Station 3, excess dFe concentrations were $0.6 \pm 0.7$ nmol L$^{-1}$ ($n=11$), constituted up to 1.6 nmol L$^{-1}$ of

![Fig. 5. Proportion of remineralised dFe, relative to measured dFe concentrations, in the water column on the continental slope.](image-url)
total dFe at 500 and 800 m depth in low oxygen waters and were associated to relatively low δ56Fe values (as low as −0.32‰ at 500 m depth). At Station 2, excess dFe concentrations were very low within low oxygen waters, so relatively high dFe concentrations are attributed to remineralisation.

The presence of benthic dFe in OMZ waters at slope Station 3 (Fig. 4) could be facilitated by advection of shelf waters by the westward flowing NECC and the nNECC. This is supported by observations of relatively high horizontal dFe fluxes below the SML on the shelf (5185 μmol dFe m⁻² d⁻¹) and slope (94.4 μmol dFe m⁻² d⁻¹ at Station 3; Fig. 8; Milne et al., 2017). Benthic sources of dFe are less obvious at Station 2, coincident with low horizontal dFe flux estimates (21.5 μmol dFe m⁻² d⁻¹; Milne et al., 2017). Estimates of the vertical flux of dFe to the bottom of the SML were considerably lower than the horizontal dFe fluxes on both the shelf (16 μmol m⁻² d⁻¹) and the slope (0.024–0.043 μmol m⁻² d⁻¹) (Fig. 8; Milne et al., 2017). It is important to consider the speciation and redox state of the dFe that is transported off the shelf, because Fe tends to form insoluble (oxy)hydroxides in the presence of oxygen in seawater. In addition to Fe-ligand complexation, dFe may be stabilised in the presence of low oxygen concentrations (>45 μmol kg⁻¹; Fig. 4) because oxidation of Fe(II) is slowed (Millero et al., 1987). Although we have no measurements of Fe(II) in our samples, the Fe(II) content of Peru margin waters with oxygen concentrations of >50 μmol kg⁻¹ was up to 20% of the dFe pool (Chever et al., 2015). Hence, it is likely that dFe in our OMZ samples partly consisted of Fe(II) derived from DIR. The Fe(II) half-life (t₁/₂) in bottom waters at station 4 and 5 was estimated to be ~30 to 70 min (using equations from Millero et al., 1987), and [O₂] = 79 to 93 μmol kg⁻¹, T = 16 to 17 °C, Sal = 35.62–35.67, pH = 7.75–7.80). Theoretical oxidation rates were slower in bottom waters at the slope Station 3, with Fe(II) t₁/₂ ~ 325 min ([O₂] = 130 μmol kg⁻¹, T = 5.4 °C, Sal = 34.84, pH = 7.81). Longer Fe(II) t₁/₂ at this station may have maintained the relatively high dFe concentrations supplied by sediment pore waters, and likely inhibited the formation of Fe-(oxy)hydroxides. This is also supported by relatively high dFe concentrations within the OMZ on the slope. Fe(II) oxidation was slowest in OMZ waters (Fe(II) t₁/₂ ~ 500 min; stations 2 and 3), which would facilitate offshore transport of a portion of shelf derived dFe. Since a shift towards lower δ56Fe values along potential Fe(II) oxidation pathways was not observed in this study, it is likely that as Fe is gradually oxidised, part of it is immediately complexed to organic ligands or that hypotethetical organic ligand bound Fe(II) is gradually oxidised to its Fe(III) form (Klar et al., 2017a). Nonetheless, δ56Fe values imply that an important proportion of benthic dFe was supplied in the form of Fe(III) from NRD and remineralisation, for which stabilisation with organic ligands plays a crucial role in terms of residence time in the dissolved phase (Gledhill and Buck, 2012).

Benthic dFe inputs from shelf and slope sediments and, to a lesser extent at the time of our study, atmospheric dFe inputs, therefore make an important contribution to the supply of “new” dFe to the study area. Input of dFe from remineralisation of organic material also becomes an important source of dFe within the OMZ with increasing distance from the shelf. We suggest that a considerable proportion of the remineralised dFe is initially derived from benthic and (to a minor degree at the time of our study, atmospheric inputs in our study area. Our data provide a snapshot of part of a continuous cycle of upwelling of high dFe bottom waters, biological uptake of this dFe, particle sinking and remineralisation, the overall result of which is a shift from relatively low δ56Fe values (dominated by benthic sedimentary input of dFe) within the OMZ on the shelf towards higher δ56Fe values (due to remineralisation of organic material) within the OMZ further offshore (Fig. 8). We envision that a significant part of sinking...
Fig. 7. Relationship between (a) $\delta^{56}\text{Fe}$ and $d_{\text{Fe}}$; and (b) $\delta^{56}\text{Fe}$ and $O_2$ on the shelf (stations 4 and 5) and on the slope (stations 2 and 3). The average $\delta^{56}\text{Fe}$ value of the continental crust (±0.09 ± 0.10‰; Beard et al., 2003) is shown by the horizontal black lines. Linear regressions of $\delta^{56}\text{Fe}$ vs. $d_{\text{Fe}}$ for all samples and $\delta^{56}\text{Fe}$ vs. $O_2$ on the shelf are shown by the black dotted lines.

Fig. 8. Schematic interpretation of the Fe cycle in our study area. Shelf sediments supply $d_{\text{Fe}}$ with a light isotopic composition (↓ $\delta^{56}\text{Fe}$) to bottom waters. $d_{\text{Fe}}$ is supplied to the surface mixed layer (SML) by atmospheric dust deposition and upwelled bottom waters, where phytoplankton takes up $d_{\text{Fe}}$ with a relatively heavy isotopic composition (↑ $\delta^{56}\text{Fe}$). Remineralisation of sinking organic material leads to the release of $d_{\text{Fe}}$ with a relatively heavy isotopic composition, which is mixed with benthic $d_{\text{Fe}}$ inputs and upwelled to the SML, where it is mixed with atmospheric $d_{\text{Fe}}$ inputs. The flux of benthic $d_{\text{Fe}}$ decreases with distance from the coast. The continuous recycling of $d_{\text{Fe}}$ by biological uptake and remineralisation leads to increasingly heavy isotopic compositions of $d_{\text{Fe}}$ in the water column with distance from the shelf. Atmospheric dust inputs (fluxes in $\mu$mol $d_{\text{Fe}}$ m$^{-2}$ d$^{-1}$, in brown) to the SML, calculated from $d$Al concentrations, were low at the time of sampling but are potentially higher at other times of the year (Croot et al., 2004). Fluxes of vertical transport to the SML (white) and horizontal transport between the bottom of the SML and 500 m depth (yellow) are from Milne et al. (2017) and are in $\mu$mol $d_{\text{Fe}}$ m$^{-2}$ d$^{-1}$.
organic material is not remineralised within the OMZ and is exported towards deeper waters, because remineralisation rates may be low in OMZs (Cavan et al., 2017). Hence, the supply of new Fe (benthic and atmospheric) must play an important role in maintaining the high dFe concentrations in the tropical North Atlantic OMZ.

Our results are consistent with the conclusions of previous studies based on the analysis of dFe concentrations, which inferred that remineralisation plays a key role in the supply of dFe to subsurface waters of offshore regions of the tropical Atlantic OMZ (Rijkenberg et al., 2012; Fitzsimmons et al., 2013). These studies observed a close correlation between dFe and AOU that indicated that the main dFe source was from remineralisation of sinking material with a fixed Fe:C ratio. Rijkenberg et al. (2012) observed a shift to higher Fe:C ratios north of 25 °N, indicative of shelf inputs. Accordingly, a study north of the Cape Verde islands suggested that a shelf isotopic dFe signal can be observed up to 1000 km outside the OMZ in the open ocean (with O2 > 160 μmol kg⁻¹) (Conway and John, 2014). In their study, the contribution of reduced dFe benthic inputs from the eastern margin to their ocean transect was estimated using an end-member δ⁵⁶Fe value of −2.4‰ (as observed on the Californian margin, John et al., 2012). We suggest that, due to the reactive nature of Fe in seawater, which is usually associated with isotopic fractionation, mass-balance calculations based on Fe isotopes should be used with caution. In addition, our data indicate that the δ⁵⁶Fe signal of dFe within the tropical Atlantic OMZ not only reflects input of benthic Fe derived from DIR, but also benthic inputs of dFe from NRD and inputs of dFe from remineralisation of organic material. Thus, the relatively higher δ⁵⁶Fe values observed in the eastern Atlantic OMZ waters (this study and Conway and John, 2014) compared to those observed in eastern Pacific OMZ waters (i.e., −1.3 to −0.3‰ (Chever et al., 2015; Fitzsimmons et al., 2016; John et al., 2017) may be ultimately due to the larger annual input of atmospheric dust to the North Atlantic Ocean and stronger overprinting of benthic signals from remineralisation in the Atlantic OMZ.

5. CONCLUSIONS

Our study confirms that remineralisation plays an important role in recycling dFe within the tropical North Atlantic OMZ, but we also provide evidence for significant benthic inputs of dFe derived from both DIR and NRD processes to low oxygen waters. At times of low atmospheric dust deposition, we suggest that “new” benthic inputs of dFe derived from both DIR and NRD of lithogenic material in the water column and on the seafloor means that the isotopic composition of dFe is relatively high compared to other OMZs where levels of atmospheric dust deposition are lower.

With oxygen concentrations of seawater influencing remineralisation rates and Fe speciation, the decline in oceanic oxygen concentrations due to global warming may have significant consequences for Fe cycling. This needs to be investigated further and incorporated into future modelling efforts of the linkages between biogeochemical cycles and climate.

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