



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 $\delta^{56}\text{Fe}$ 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 $\delta^{56}\text{Fe}$ values (up to $+0.41\text{‰}$), 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 ($2\text{--}9\text{ nmol dFe m}^{-2}\text{ d}^{-1}$). 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 CO_2 uptake (Le Quééré 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 \sim 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 μ m) concentrations typically range between <0.2 and ~ 1 nmol L⁻¹ (e.g., [Klunder et al., 2011, 2012](#); [Rijkenberg et al., 2014](#); [Resing et al., 2015](#); [Nishioka and Obata, 2017](#)) and are generally lowest in the surface ocean. However, dFe concentrations of 1–1.7 nmol L⁻¹ have been observed within oxygen minimum zones (OMZs) away from coastal seas ([Rijkenberg 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 ([Rijkenberg 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](#); [Schmidtko 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)).

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

The isotopic signatures of dFe for different sources are distinct. The continental crust has an average $\delta^{56}\text{Fe}$ value of $+0.09 \pm 0.10\text{‰}$ (2 SD, $n = 46$; [Beard et al. \(2003\)](#)). The $\delta^{56}\text{Fe}$ value of atmospheric dust in the North Atlantic ($\sim +0.07 \pm 0.11\text{‰}$; [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 $+0.7\text{‰}$ ([Conway and John, 2014](#)), although these heavy 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 $+0.5\text{‰}$ ([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 $+0.27 \pm 0.25\text{‰}$ ([Labatut et al., 2014](#)). The reported isotopic signal of dFe in rivers draining into tropical oceans is -0.27 to $+0.31\text{‰}$ ([Bergquist and Boyle, 2006](#)), although the range for all of the world's rivers is larger (-1.2 to $+0.8\text{‰}$; [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 $\Delta^{56}\text{Fe}_{\text{Fe(II)-FeS}} < +0.77\text{‰}$ ([Rouxel et al., 2008](#)). It is now clear that dFe is rapidly complexed 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

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