



Total dissolvable and dissolved iron isotopes in the water column of the Peru upwelling regime

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Abstract

Vertical distributions of iron (Fe) concentrations and isotopes were determined in the total dissolvable and dissolved pools in the water column at three coastal stations located along the Peruvian margin, in the core of the Oxygen Minimum Zone (OMZ). The shallowest station 121 (161 m total water depth) was characterized by lithogenic input from the continental plateau, yielding concentrations as high as 456 nM in the total dissolvable pool. At the 2 other stations (stations 122 and 123), Fe concentrations of dissolved and total dissolvable pools exhibited maxima in both surface and deep layers. Fe isotopic composition ($\delta^{56}\text{Fe}$) showed a fractionation toward lighter values for both physical pools throughout the water column for all stations with minimum values observed for the surface layer (between -0.64 and -0.97‰ at 10–20 m depth) and deep layer (between -0.03 and -1.25‰ at 160–300 m depth). An Fe isotope budget was established to determine the isotopic composition of the particulate pool. We observed a range of $\delta^{56}\text{Fe}$ values for particulate Fe from $+0.02$ to -0.87‰ , with lightest values obtained at water depth above 50 m. Such light values in the both particulate and dissolved pools suggest sources other than atmospheric dust deposition in the surface ocean, including lateral transport of isotopically light Fe. Samples collected at station 122 closest to the sediment show the lightest isotope composition in the dissolved and the particulate pools (-1.25 and -0.53‰ respectively) and high Fe(II) concentrations (14.2 ± 2.1 nM) consistent with a major reductive benthic Fe sources that is transferred to the ocean water column. A simple isotopic model is proposed to link the extent of Fe(II) oxidation and the Fe isotope composition of both particulate and dissolved Fe pools. This study demonstrates that Fe isotopic composition in OMZ regions is not only affected by the relative contribution of reductive and non-reductive shelf sediment input but also by seawater-column processes during the transport and oxidation of Fe from the source region to open seawater.

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1. INTRODUCTION

Iron (Fe) is an essential micronutrient for marine organisms (Martin and Fitzwater, 1988). It is now well established that this element plays a key role in the functioning of the marine ecosystems (Moore et al., 2002; Boyd and

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Ellwood, 2010). *In-situ* and natural Fe fertilisations have demonstrated that Fe inputs enhance phytoplankton biomass and affect the major biogeochemical cycles (e.g. carbon (C) and nitrogen (N)) (Boyd et al., 2000, 2007; Coale et al., 2004; Jickells et al., 2005; Blain et al., 2007; Pollard et al., 2009). However, the importance of new and regenerated sources of Fe to the water column as well as the fractions that are truly bioavailable to the phytoplankton, are still subject of debate.

Whereas atmospheric deposition was commonly thought to be the predominant external source of Fe in remote areas (Jickells et al., 2005), inputs from sediments coupled to upwelling or advection are now considered to provide significant supply of Fe to surface waters of the open ocean (Bucciarelli et al., 2001; Elrod et al., 2004; Lam and Bishop, 2008; Tagliabue et al., 2009; Nishioka et al., 2011). In contrast to the open ocean, shelf environments may receive additional Fe input from fluvial sources and sediment resuspension (Croot and Hunter, 1998; Hutchins and Bruland, 1998; Johnson et al., 2001; Elrod et al., 2004; Lam and Bishop, 2008; Lohan and Bruland, 2008). Even if Fe supply is significant in those regions, some studies have shown that, due to the complex physico-chemical speciation of Fe in coastal systems, its bioavailability can be limited (Hutchins and Bruland, 1998).

In seawater, Fe occurs in two redox states, Fe(II) and Fe(III) (Waite and Morel, 1984). In oxic seawater, the thermodynamically stable state Fe(III) is highly insoluble (Liu and Millero, 2002) and rapidly hydrolyzes resulting in the precipitation of various Fe(III) oxyhydroxides. Organic ligands complex most of the dissolved Fe in seawater and control the solubility of Fe(III) (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Millero, 1998; Barbeau et al., 2001; Liu and Millero, 2002; Gledhill and Buck, 2012). Fe(II) is more soluble but is rapidly oxidized by oxygen (O₂) and hydrogen peroxide (H₂O₂) (Millero et al., 1987; Millero and Sotolongo, 1989; Gonzalez-Davila et al., 2005; Santana-Casiano et al., 2005; Sarthou et al., 2011). Reduction of Fe(III) to Fe(II) with possible stabilization by organic ligands is a potential mechanism by which Fe is made more bioavailable to phytoplankton (Anderson and Morel, 1980; Maldonado and Price, 2001). The release of Fe(II) from reducing continental-margin sediments (Hong and Kester, 1986; Lohan and Bruland, 2008) as well as Fe(II) supply from seafloor hydrothermal vents (Bennett et al., 2008; Toner et al., 2009; Tagliabue et al., 2010; Wu et al., 2011a; Nishioka et al., 2013; Vedamati et al., 2014) are now recognized as possible sources of Fe(II) in seawater. Under anoxic conditions as those encountered in relatively organic-rich marine sediments, when sulfide generation is limited and thus precluding the precipitation of FeS minerals reductive dissolution of Fe oxides or clay minerals can result in dissolved Fe(II) concentrations up to 1 mM (Sell and Morse, 2006). In open ocean surface waters, the photoreduction of Fe(III) to Fe(II) has also been clearly observed (Croot et al., 2008).

The Peruvian coast is characterized by an intensive mid-depth region of low oxygen associated with an upwelling and high surface productivity (Hong and Kester, 1986; Bruland et al., 2005; Stramma et al., 2010). Major changes

to marine sources and sinks of important nutrients such as nitrogen, phosphorus and Fe occur when oceanic oxygen concentrations decrease below threshold levels (Stramma et al., 2008). Along the continental shelf off the Peruvian coast, labile Fe (i.e. Fe(II)) concentrations up to 73 nM were attributed to intense redox cycling occurring at the sediment–water interface (Hong and Kester, 1986; Vedamati et al., 2014). This process can result in a greatly enhanced source of Fe available to upwell to surface waters, potentially increasing phytoplankton productivity (Lohan and Bruland, 2008). The Oxygen Minimum Zones (OMZs) of the tropics are key regions of low oxygen in today's ocean. The effects of nutrient cycling under oxygen deficient conditions are carried into the rest of the ocean by the thermohaline circulation (Stramma et al., 2008). Hence processes occurring in the OMZs, impacting nutrients and Fe cycles, may have an impact on the biological productivity and carbon cycle of the global ocean (Helly and Levin, 2004; Pennington et al., 2006). Given the fact that expansion of the OMZs will continue to occur in the future (Stramma et al., 2008), a better understanding of Fe biogeochemical cycle in those environments is of great interest.

Recent studies of Fe isotopes in open seawater and coastal regions have shown variability in $\delta^{56}\text{Fe}$ and have demonstrated how Fe isotopes may be used to constrain the global Fe cycle. The Fe isotope composition is expressed by $\delta^{56}\text{Fe}$ defined as: $\delta^{56}\text{Fe} = \left[\frac{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}}} - 1 \right] \times 10^3$. Values are reported relative to the IRMM-14 international iron isotope reference material (the $\delta^{56}\text{Fe}$ of igneous rocks relative to IRMM is of $+0.09 \pm 0.1\%$, 2SD; Beard et al., 2003a).

In nature, $\delta^{56}\text{Fe}$ variations are mainly controlled by both biotic and abiotic redox processes along with a range of isotope (kinetic and/or equilibrium) fractionations arising from non-redox processes (e.g. Welch et al., 2003; Croal et al., 2004; Johnson et al., 2004; Balci et al., 2006; Dauphas and Rouxel, 2006). Numerous studies were initially led at the ocean boundaries to characterize Fe sources to the ocean such as aerosols, sediment porewaters, groundwaters, rivers and hydrothermal vents (Sharma et al., 2001; Severmann et al., 2004, 2006, 2010; Bergquist and Boyle, 2006; Rouxel et al., 2008a,b; Bennett et al., 2009; Escoube et al., 2009; Homoky et al., 2009; Roy et al., 2012). Those studies demonstrated that benthic sources of Fe are often characterized with light isotopic values. In the case of benthic input from reducing sediments, Fe isotope composition of pore-fluid at the sediment–seawater interface is highly sensitive to local redox conditions, with most light $\delta^{56}\text{Fe}$ values being generated through the combination of microbial Fe reduction and partial Fe oxidation (Severmann et al., 2006; Homoky et al., 2009). Heavy $\delta^{56}\text{Fe}$ values have been also found in anoxic sediment porewater as a result of the development of sulfidic conditions and the precipitation of isotopically light Fe sulfides (Severmann et al., 2006; Roy et al., 2012). Homoky et al. (2013) recently highlighted the importance of the 'non-reductive' dissolution of continental margin sediments as a source of dissolved Fe in seawater that is characterized by $\delta^{56}\text{Fe}$ values close to crustal values.

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