



Nitrate-dependent iron oxidation limits iron transport in anoxic ocean regions



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ABSTRACT

Iron is an essential element for life on Earth and limits primary production in large parts of the ocean. Oxygen-free continental margin sediments represent an important source of bioavailable iron to the ocean, yet little of the iron released from the seabed reaches the productive sea surface. Even in the anoxic water of oxygen minimum zones, where iron solubility should be enhanced, most of the iron is rapidly re-precipitated. To constrain the mechanism(s) of iron removal in anoxic ocean regions we explored the sediment and water in the oxygen minimum zone off Peru. During our sampling campaign the water column featured two distinct redox boundaries separating oxic from nitrate-reducing (i.e., nitrogenous) water and nitrogenous from weakly sulfidic water. The sulfidic water mass in contact with the shelf sediment contained elevated iron concentrations >300 nM. At the boundary between sulfidic and nitrogenous conditions, iron concentrations dropped sharply to <20 nM coincident with a maximum in particulate iron concentration. Within the iron gradient, we found an increased expression of the key functional marker gene for nitrate reduction (*narG*). Part of this upregulation was related to the activity of known iron-oxidizing bacteria. Collectively, our data suggest that iron oxidation and removal is induced by nitrate-reducing microbes, either enzymatically through anaerobic iron oxidation or by providing nitrite for an abiotic reaction. Given the important role that iron plays in nitrogen fixation, photosynthesis and respiration, nitrate-dependent iron oxidation likely represents a key-link between the marine biogeochemical cycles of nitrogen, oxygen and carbon.

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1. Introduction

Metabolic processes that regulate carbon fixation in the surface ocean and export into the ocean interior (nitrogen fixation, photosynthesis and respiration) require bioavailable iron (Fe). In many ocean regions, the Fe supply is insufficient relative to the supply of the macronutrients nitrogen and phosphorous. Therefore, Fe availability is regarded one of the key-limiting factors for primary and export production in the ocean (Falkowski, 1997; Moore and Doney, 2007; Boyd and Ellwood, 2010). Traditionally, Fe supplied by atmospheric dust was considered the main source

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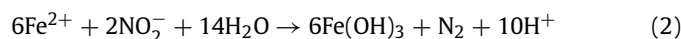
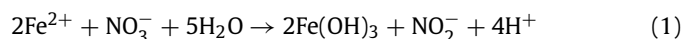
of bioavailable Fe to the ocean (Jickells et al., 2005). More recently, however, sedimentary processes have been highlighted as important in mobilizing and transferring Fe into the water column (Lam and Bishop, 2008; Lohan and Bruland, 2008; Severmann et al., 2010; Homoky et al., 2013; Scholz et al., 2014a; Dale et al., 2015). The highest sedimentary Fe fluxes have been recorded in oxygen-deficient ocean regions (oxygen minimum zones, OMZs) where reductive dissolution of ferric Fe (oxyhydr)oxide minerals, either by Fe-reducing bacteria or through reaction with hydrogen sulfide (H₂S), liberates dissolved ferrous Fe (Fe²⁺) into the sediment pore water (Severmann et al., 2010; Noffke et al., 2012). Due to the absence of oxygen within the surface sediment, the mobilized Fe escapes re-oxidation and -precipitation as Fe (oxyhydr)oxide and may therefore diffuse across the sediment-water interface.

Whether sediment-derived Fe can support nitrogen fixation and primary production in the surface ocean critically depends on

the extent of re-precipitation and demobilization during transport within the water column. The distribution of dissolved Fe concentrations in the water column overlying continental margin sediments suggests that most of the Fe discharged from the seabed is rapidly re-precipitated and thus prevented from reaching the surface ocean and becoming transported offshore (Lohan and Bruland, 2008; Bruland et al., 2005; Vedamati et al., 2014). According to current thinking, sediment-derived ferrous Fe is demobilized through re-oxidation with oxygen (O_2) to ferric Fe (Fe^{3+}) and precipitation of nanoparticulate or colloidal Fe (oxyhydr)oxides, followed by aggregation or scavenging by larger particles (Lohan and Bruland, 2008; Boyd and Ellwood, 2010). A small fraction of the sediment-derived Fe remains in solution as ferric Fe through complexation with organic ligands (Kondo and Moffett, 2015; Noble et al., 2012) or in suspension as colloids or nanoparticles (Raiswell and Canfield, 2012). This Fe fraction can be transported over longer distances within oxygenated seawater.

Fe oxidation with oxygen, either abiotically or microbially induced, is a viable explanation for rapid Fe removal in ocean regions where at least trace amounts of oxygen are present in the water column. However, this process cannot explain Fe removal from effectively anoxic waters columns such as the OMZs off Chile and Peru. Previous studies have reported total dissolved Fe (dFe) concentrations >100 nM (sum of dissolved Fe^{2+} and Fe^{3+} , with Fe^{2+} being dominant) in near-bottom waters overlying the Peruvian shelf (Hong and Kester, 1986; Bruland et al., 2005; Vedamati et al., 2014). Despite anoxia (<10 nM O_2) (Thamdrup et al., 2012) and pervasive sedimentary Fe release in this area of the Peru OMZ (Noffke et al., 2012; Scholz et al., 2014b), dFe concentrations in the water column rapidly decline offshore to a level that is typical for well-oxygenated, near-shore seawater (<5 nM dFe). As the zone of dFe removal is located well below the photic zone (e.g., <10 m in the water column overlying the Peruvian shelf), phototrophic Fe^{2+} oxidation (Widdel et al., 1993) can also be excluded as a mechanism of Fe removal.

It has recently been hypothesized that in the nitrate-containing OMZs of the contemporary ocean ferrous Fe is oxidized anaerobically with nitrate (Raiswell and Canfield, 2012). Anaerobic Fe oxidation with nitrate (NO_3^-) results in the production of nitrite (NO_2^-), nitrogenous gases (N_2O or N_2) or ammonium (NH_4^+) (Straub et al., 1996; Weber et al., 2006a; Carlson et al., 2013) and, depending on pH and ambient water chemistry, a variety of authigenic Fe minerals (Kappler et al., 2005; Miot et al., 2009; Pantke et al., 2012), e.g.:



If nitrite is present, e.g., from heterotrophic nitrate reduction, Fe oxidation with nitrite (Equation (2)) has also been shown to take place abiotically at circum-neutral pH, especially when reactive Fe (oxyhydr)oxide mineral surfaces are available to catalyze the reaction (Picardal, 2012; Klueglein and Kappler, 2013). Microbial and partly abiotic mechanisms by which ferrous Fe is oxidized with nitrate as the terminal electron acceptor are hereafter summarized under the term “nitrate-dependent Fe oxidation” (Carlson et al., 2013; Picardal, 2012; Klueglein and Kappler, 2013).

Nitrate-dependent Fe oxidation has been demonstrated in laboratory cultures (Straub et al., 1996) and in a variety of marine and freshwater sediments (Edwards et al., 2003; Weber et al., 2006b; Laufer et al., 2016). By contrast, direct evidence for nitrate-dependent Fe oxidation in the water column of the ocean is missing. Particularly in OMZs, nitrate-dependent Fe oxidation could represent a key-process in biogeochemical cycling. For instance, sediments underneath the Peru OMZ release high amounts of Fe into the anoxic water column (Noffke et al., 2012;

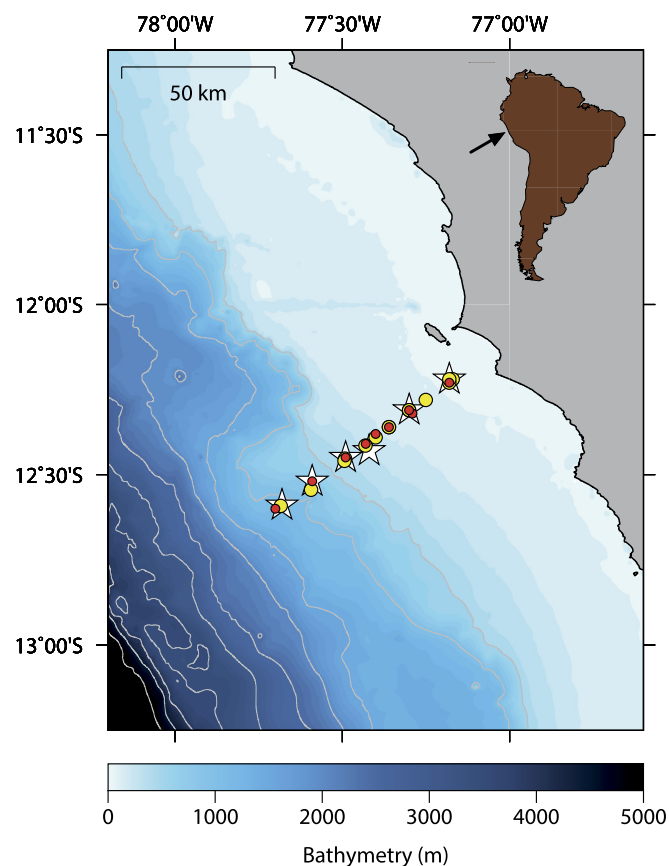


Fig. 1. Bathymetric map of the Peruvian continental margin (bathymetric data were taken from GEBCO). GO-FLO stations are depicted by red dots, CTD stations by yellow dots and MUC stations by white stars. The location of the study area off South America is indicated on the upper right side. The coordinates of all sampling stations are contained in the Electronic Supplement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Vedamati et al., 2014), yet primary production in the eastern equatorial Pacific high-nitrate-low-chlorophyll (HNLC) region off Peru has been shown to be Fe-limited (Hutchins et al., 2002). Moreover, much of the Fe released from Peru margin sediments is not transported offshore within the OMZ but re-deposited and buried close to its source (Scholz et al., 2014b). Nitrate-dependent Fe oxidation within the anoxic water column could be a meaningful explanation for both of these puzzling observations.

Here, we report geochemical and metagenomic data for sediment, water and suspended particulate matter samples from the Peruvian continental margin. Collectively, these data provide evidence that nitrate-dependent Fe oxidation is an active process in OMZ waters, limiting the transport of sediment-derived Fe. Implications for nutrient cycling and redox dynamics in the ocean are discussed.

2. Methods

2.1. Sampling

Samples for this study were collected during the M92 cruise of research vessel Meteor in January 2013 (Fig. 1). Water samples for dissolved and particulate Fe analyses were collected using an array of six PTFE-coated 8 l GO-FLO bottles (General Oceanics) individually mounted on a Kevlar wire. Upon recovery the GO-FLO bottles were transferred to a laboratory and pressurized with nitrogen gas (0.2 bar). The water was filtered in-line through polyethersulfone filters (0.2 μ m pore size, 47 mm diameter) (PALL Corporation) in a laminar flow bench. Prior to filtration the filters were cleaned

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