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Iceberg-hosted nanoparticulate Fe in the Southern Ocean: Mineralogy, origin, dissolution kinetics and source of bioavailable Fe

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ABSTRACT

Sediments from icebergs and glaciers contain nanoparticulate Fe(III) oxyhydroxides (including ferrihydrite) which form in aqueous, oxic (micro)environments where Fe(II)-bearing rock minerals oxidise and high degrees of supersaturation are promoted by freezing and thawing. An ascorbic acid extraction dissolves only labile Fe present in fresh (loosely aggregated) ferrihydrite that is directly or indirectly bioavailable. Glacial and iceberg sediments contain ferrihydrite aggregates that provide 0.04 to 0.17% Fe soluble in ascorbic acid, rather larger than the concentrations in a limited suite of atmospheric dusts. The dissolution behaviour of labile Fe from glacial and iceberg sediments by ascorbic acid is controlled by the access of reactant, or removal of solute, through micropores to or from active sites in the interior of ferrihydrite aggregates. A first-order kinetic model is presented to examine the rates at which bioavailable Fe can be supplied by melting icebergs in the Weddell Sea. The model utilizes rate constants from the literature for the processes which solubilise Fe from nanoparticulate ferrihydrite (dissolution, photochemical reduction and grazing) and the processes that remove Fe nanoparticulates (sinking, scavenging and incorporation in faecal material), and render them less reactive (transformation, aging). Model results demonstrate that icebergs can supply bioavailable Fe to the Weddell Sea by the dissolution of nanoparticulate ferrihydrite (despite loss/removal of nanoparticles by sinking, aging, transformation, scavenging and incorporation into faecal pellets) at rates that are comparable to atmospheric dust. Dissolution enhanced by photochemical reduction and grazing provides the most rapid rates of bioavailable Fe production.

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1. Introduction

Bioavailable Fe is supplied to surface waters in the Southern Ocean from a variety of sources, including atmospheric dust, continental shelf sediments and porewaters, upwelling and vertical diffusion from deep waters, sea ice and sediment released by melting icebergs (see Cassar et al., 2007). For many years atmospheric dust has been considered to be the main source of bioavailable Fe external to the marine reservoir although the links between dust and productivity may be weaker than previously believed (Boyd et al., 2010). However recent work has shown that icebergs may be a significant source of bioavailable Fe to the Southern Ocean. Ice rafting is clearly a major source of sediment to the Southern Ocean but this sediment has usually been considered as essentially inert. Recent data suggest otherwise. First, Smith et al. (2007) observed that melting icebergs in the Weddell Sea were associated with hot spots of biological activity and suggested that enhanced productivity was caused by the release of terrigenous debris that supplied bioavailable Fe. Furthermore iceberg-hosted sediment was demonstrated to stimulate productivity

in experiments carried out with diatoms under Fe-limited conditions, such as those existing in the Southern Ocean. Second, Raiswell et al. (2006, 2008a) showed that glacial and iceberg-hosted sediment contained nanoparticles of Fe oxyhydroxides that were potentially bioavailable and were present in sufficiently large concentrations to influence the Fe biogeochemical cycle in the Southern Ocean. Hence iceberg-hosted sediment clearly has the potential to stimulate significant primary productivity in the Southern Ocean.

Quantifying this potential presents considerable difficulties. First, it is necessary to identify the reactive iron-bearing minerals that exist in iceberg sediment. Second, it is necessary to determine whether Fe is present in these minerals in a form that can be directly or indirectly rendered as bioavailable. Third, it is necessary that the kinetics of Fe release from such minerals are rapid relative to the processes which remove particulates from the water column. This contribution begins by briefly describing the characteristics and origin of the main iron oxyhydroxides found in glacial and iceberg sediments. The paper continues by evaluating the use of an ascorbic acid extraction to estimate bioavailability and the kinetics of iron release during ascorbic acid extraction of glacial and iceberg sediments. Finally, a simple kinetic model of iron release from iceberg-hosted sediment is presented that assesses whether bioavailable iron can be released at rates that exert a significant regional influence on the Fe biogeochemical cycle.

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2. Potentially bioavailable forms of Fe in glacial sediments

Iron, although the fourth most abundant element in the crust, is poorly soluble and may be biologically scarce in seawater. Iron (III) is the thermodynamically stable form of iron in surface environments but generally occurs in minerals that are stable and poorly-soluble in oxic environments. Common iron (II) minerals (e.g. pyrite and iron-bearing carbonates and aluminosilicates) are formed in sub-surface environments where oxygen is depleted but slowly weather to form Fe(III) oxyhydroxides when exposed to oxygen and water. In general truly dissolved iron occurs mainly as inorganic complexes or low molecular weight Fe (III) organic complexes which are regarded as being capable of supplying bioavailable Fe. Uncomplexed Fe (III) (and Fe (II) produced by reduction) are more readily available than their equivalent organic complexes (Sunda, 2001). The most thermodynamically stable dissolved form of iron in seawater is Fe(III) but Fe(II) can be transiently present as a consequence of photochemical reduction of Fe(III) (Moffett, 2001). Both inorganic and organic complexes of dissolved Fe (III) are photochemically active (Waite and Morel, 1984; Moffett, 2001) and in seawater systems photochemical reactivity is mainly controlled by dissolved Fe (III) complexed by organic ligands (Barbeau, 2006) although colloidal Fe may also undergo photochemical reduction in seawater (see later).

However the colloidal forms of iron in seawater cannot always be distinguished analytically from the truly dissolved species. Dissolved iron is usually determined operationally following passage through membrane filters that have a nominal cut off of 0.2–0.45 μm . Thus measurements of dissolved Fe exclude some colloidal material (generally defined < 1 μm diameter) but include nanoparticulates (defined as < 100 nm diameter) not attached to sediment grains (nor present as large aggregates) as well as truly dissolved Fe. Thus these measurements of iron using membrane filters include nanoparticulate iron as well as truly dissolved species and in some cases nanoparticulate Fe may be predominant. For example, Bergquist et al. (2007) found that $\sim 90\%$ of the Fe passing a 0.45 μm filter actually occurred in the 400–20 nm fraction (and only $\sim 10\%$ was truly dissolved at North Atlantic sites with low dust loadings (see also Kuma and Matsunga, 1995). Fe nanoparticles measured as dissolved Fe behave differently to aqueous inorganic species in that their reactivity may vary with time (Raiswell et al., 2010; Raiswell, 2011). Fe nanoparticulates may also be attached to sediment grains and the relative abundance of free-standing and attached nanoparticles is unknown. However nanoparticulate forms of iron are physically and chemically intermediate between soluble and particulate forms, and their small size increases solubility and reactivity by several orders of magnitude. Nanoparticulates may thus be important in maintaining a reservoir of iron that can be transformed into a bioavailable form. Glacial and iceberg sediments have been shown to contain potentially bioavailable iron oxyhydroxides nanoparticulates as described below.

2.1. Characteristics of iron oxyhydroxide nanoparticulates in glacial and iceberg sediments

Fe-bearing nanoparticulates have been described in suspended sediments in glacial meltwaters (Poulton and Raiswell, 2005) in proglacial, supraglacial and subglacial sediments (Raiswell et al., 2006), and in icebergs and glaciers (Raiswell et al., 2008a; 2009). These studies have found nanoparticulates of ferrihydrite, goethite, lepidocrocite, hematite and schwertmannite along with unidentified Fe-rich phases containing Ti and Si. The occurrence of Fe oxyhydroxide nanoparticles in a wide range of glacial weathering environments, and on widely different lithologies, provides compelling evidence for an origin from common Fe-bearing minerals in ubiquitous, oxic weathering processes. The existence of metastable

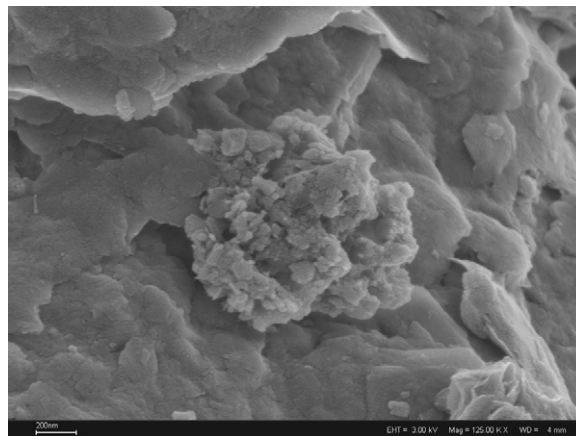


Fig. 1. Aggregate of ferrihydrite nanoparticles in iceberg-hosted sediment, Seymour Island, Antarctica.

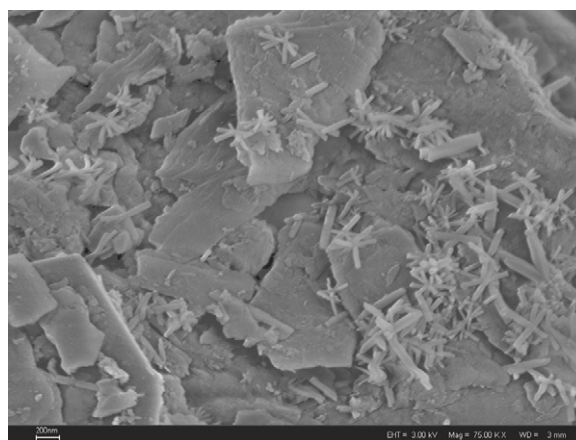


Fig. 2. Goethite laths in iceberg-hosted sediment, Seymour Island, Antarctica.

nanoparticulate Fe oxyhydroxides clearly indicates an authigenic origin in these weathering environments, with their preservation attributable to freezing that limits access to water and slows down transformation to more stable phases. Cornell and Schwertmann (2003) describe the characteristics of the main nanoparticulate iron minerals as below.

2.1.1. Ferrihydrite

The precise composition of ferrihydrite has yet to be established but the formula $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ is thought to be more accurate than $\text{Fe}(\text{OH})_3$ (Towe and Bradley, 1967). Ferrihydrite is metastable and is formed by the rapid oxidation of Fe(II) which produces a poorly ordered structure. The degree of ordering is variable and the two extremes of crystal ordering are referred to as 2-line and 6-line ferrihydrite. 2-line ferrihydrite is often referred to in the literature as amorphous or hydrous ferric oxide (HFO). Once formed, 2-line ferrihydrite alters to 6-line ferrihydrite or goethite/hematite mixtures (see later). It is important to recognise that all ferrihydrite is nanoparticulate (Janney et al., 2000; 2001) and hereafter the 'nano' prefix will only be used for other minerals where appropriate. Ferrihydrite characteristically occurs as sub-spherical to hexagonal nanoparticulates that are often assembled into rubbly aggregates in glacial and iceberg sediments (Fig. 1).

2.1.2. Goethite

The Fe in goethite is in octahedral coordination with each Fe^{3+} ion surrounded by three O^{2-} and three OH^- giving $\text{FeO}_3(\text{OH})_3$

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