



Fractional iron solubility of atmospheric iron inputs to the Southern Ocean



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ABSTRACT

Deposition of iron (Fe) bearing aerosols to Fe deficient waters of the Southern Ocean may drive rapid changes in primary productivity, trophic structure and the biological uptake of carbon dioxide. The fractional solubility (i.e., the ratio of water leachable Fe to total Fe) of aerosol Fe is an important variable determining its availability for biological uptake, and is a function of both particle type and the experimental conditions used to leach the particles. There have been few studies of fractional Fe solubility over the Southern Ocean where the aerosol loading is the lowest in the world. To investigate Southern Ocean aerosol Fe solubility, the fractional solubility of Fe was determined in cryogenically archived Southern Ocean aerosols. Samples were collected at the Cape Grim Baseline Air Pollution Station (CGBAPS), Tasmania, Australia from February 1999 to April 2000. Fractions determined included water soluble Fe ($<0.45 \mu\text{m}$), labile Fe ($>0.45 \mu\text{m}$; acetic acid and hydroxylamine hydrochloride leachable Fe) and refractory Fe ($>0.45 \mu\text{m}$; total digestion using nitric and hydrofluoric acids). Extremely low Fe mass concentrations were observed for baseline Southern Ocean air during the study period. An inverse hyperbolic relationship was observed between fractional Fe solubility (0.5 to 56%) and total Fe mass concentration (0.04 to 5.8 ng m^{-3} ; excluding an anomalously high sample). A peak of 4.6 ng m^{-3} of labile Fe occurred during May/June 1999 and was linked to atmospheric transport from South Western Australia over the Southern Ocean. Bioavailable Fe was estimated by summing the water soluble and labile Fe fractions, and this likely represents the upper bound of long range transport aerosol over the Southern Ocean. The results confirm previous reports of a range of fractional Fe solubility within all atmospheric particles measured and also suggest that a large fraction of the Fe from Australian mineral aerosols is labile and potentially bioavailable.

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1. Introduction

Limitation of Southern Ocean primary productivity due to low iron (Fe) availability is well established and has been the focus of a large body of research (e.g. Martin et al., 1990, 1991; Blain et al., 2007). These waters are characteristically replete with nitrate and phosphate and depleted with respect to Fe. In-situ oceanic Fe-fertilisation experiments have demonstrated an almost explosive response of the ecosystem to relatively small additions of dissolved Fe (e.g. Coale et al., 2004; de Baar et al., 2005; Boyd et al., 2007). Inputs of new Fe to pelagic surface waters can occur through upwelling of deep waters (de Baar et al., 1995), deep winter mixing and entrainment (Bowie et al., 2014; Tagliabue et al., 2014), transport from continental margins by ocean currents (Johnson et al., 1999; Elrod et al., 2004), from sea-ice and ice

bergs (Sedwick and DiTullio, 1997; Lannuzel et al., 2007, 2008; Raiswell et al., 2008), hydrothermal vents (Tagliabue et al., 2010), deep winter mixing (Tagliabue et al., 2014), and atmospheric aerosol deposition (e.g. Jickells et al., 2005). Aerosol deposition to remote Southern Ocean surface waters is extremely low ranging from 0.3 to $2.5 \text{ mg m}^{-2} \text{ d}^{-1}$, and has been investigated in relation to the distribution and transport of mineral dust (Duce et al., 1991; Luo et al., 2005; Mahowald et al., 2005; Bowie et al., 2009) and the episodic input of volcanic ash (Narcisi et al., 2005). Episodic changes in mineral dust deposition to the Southern Ocean have been linked to 20th-century climate change and land use modification (Bhattachan and D'Odorico, 2014). Mineral dust proxy records from Antarctic ice cores (Edwards et al., 2006; Gaspari et al., 2006; Spolaor et al., 2012; Vallelonga et al., 2013) and Southern Ocean marine sediments from several regions (e.g. Moore et al., 2000; Martínez-García et al., 2009; Smetacek et al., 2012) display higher deposition rates during glacial stages. Recent Southern Ocean marine sediment studies link enhanced glacial atmospheric Fe

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deposition to higher rates of Southern Ocean primary productivity (Martínez-García et al., 2014). While other studies postulate that higher rates of Fe inputs to the Southern Ocean during glacial periods were sourced from the upwelling of water enriched by sediments (Latimer and Filippelli, 2001; Latimer et al., 2006).

Aerosol Fe bioavailability data is required to constrain the biogeochemical impact of present and past atmospheric Fe variability. Aerosol Fe bioavailability will depend on the residence time of the Fe aerosol in the euphotic zone, and thus it is a function of its chemical composition and physical characteristics (e.g. particle size, surface area). Therefore, an upper limit of aerosol Fe bioavailability can be estimated by measuring the instantaneous water solubility (i.e., the concentration of Fe that passes through a 0.2 or 0.45 μm aerosol-laden filter when leached with ultra-pure water) and the labile Fe fraction (i.e., a chemically defined measure using weak acid to estimate the portion of the particulate trace metal pool that is potentially bio-available on the time frame of phytoplankton generation (days) (Berger et al., 2008)) from aerosol particles over longer time scales (Berger et al., 2008; Boyd et al., 2010). Reported values of the Southern Ocean fractional Fe solubility (i.e., the ratio of water leachable Fe to total Fe) range from 0.01 to 90% (Edwards and Sedwick, 2001; Mahowald et al., 2005; Bowie et al., 2009; Baker and Croot, 2010; Heimbürger et al., 2013a). This large range may reflect differences in mineral dust concentrations, particle size, atmospheric weathering, cloud chemistry and aerosol leaching methods (Zhuang et al., 1990, 1992; Spokes and Jickells, 1995; Chen and Siefert, 2003; Meskhidze et al., 2003; Bonnet and Guieu, 2004; Mackie et al., 2005; Baker and Jickells, 2006; Buck et al., 2006; Meskhidze and Nenes, 2006; Aguilar-Islas et al., 2010; Trapp et al., 2010). Laboratory studies have indicated that aerosol Fe solubility is enhanced by acid processing (Spokes et al., 1994; Desboeufs et al., 1999), although this relationship was not observed in the remote Atlantic and Pacific ocean (Hand et al., 2004; Baker et al., 2006). An alternative hypothesis for the observed solubility range is that it results from a mixture of aerosol Fe source types with different mineralogy and Fe solubilities (Sholkovitz et al., 2012). Sholkovitz et al. (2012) show that global scale fractional aerosol Fe solubility displays an inverse hyperbolic relationship with the total Fe mass concentration. This relationship is consistent with a low Fe solubility for mineral dust (~1–2%) and the presence of other soluble Fe sources such as those originating from fire and oil combustion with higher Fe solubilities (Chuang et al., 2005; Guieu et al., 2005; Sedwick et al., 2007; Luo et al., 2008; Sholkovitz et al., 2009; Kumar et al., 2010; Paris et al., 2010; Ito, 2011; Gao et al., 2013). Gao et al. (2013) recently measured soluble Fe as Fe(II) in the Southern Ocean southwest of Australia and this species of Fe has been operationally defined as labile (e.g. Chen and Siefert, 2004). Studies of labile Fe species (Fe(II)) over the Atlantic Ocean show that the highest percentage of labile Fe (mean value of 32%) was observed in winter corresponding to low mass concentrations of total Fe and air mass trajectories influenced by anthropogenic activities over North America (Chen and Siefert, 2004). Conversely, the lowest concentrations of labile Fe (mean value 5%) were observed in summer with higher mineral aerosol concentrations associated with African dust.

This study reports fractional Fe solubility and estimates of the upper bound of Fe bioavailability for Southern Ocean aerosols sampled from the Cape Grim Baseline Air Pollution Station (CGBAPS) in Tasmania, Australia. Data from the aerosol samples have previously been reported with respect to lead (Pb) pollution and its source apportionment (Bollhöfer et al., 2005).

2. Methods

2.1. Sampling site

This study used archived aerosol filter samples collected from February 1999 to April 2000 at CGBAPS (40.68° S, 144.69° E), located

at the northwest tip of Tasmania, Australia (Fig. 1). Fractions of filters were previously studied for Pb isotopic composition and are described in detail by Bollhöfer et al. (2005). Samples were collected during baseline conditions using a sector-controlled ultra-trace clean aerosol filter system suspended 70 m above the ground (164 m a.s.l.) on a communication tower (~100 m from the ocean, adjacent to 94 m high coastal cliffs). Meteorological baseline air conditions for CGBAPS are described by Ayers et al. (1987) and occur when the winds are from the west to southwest (wind direction from 190 to 280°) (Fig. 1) and total aerosol particle counts are <600 cm^{-3} . These conditions occur ~30% of the time (Keywood, 2007) and are representative of air masses over the remote Southern Ocean.

2.2. Sample collection

Stringent trace-metal clean techniques were used throughout the sampling campaign (Bollhöfer et al., 2005). Briefly, aerosols were collected on 47 mm acid-cleaned polytetrafluoroethylene (PTFE) filters (0.45 μm front, 60 μm back) in single-stage perfluoroalkoxy alkane (PFA) filter assemblies (acid-cleaned). The filter assembly housing consisted of trace-metal clean cylindrical inlet units, with a baseline sector controlled pump at the tower base and a pneumatically actuated seal on the top of the inlet unit. The samples were collected over time periods varying from one to seven weeks. Exposure blanks ($n = 5$), collected with every 3rd to 4th sample, were run as for normal samples but the pump switched off (Bollhöfer et al., 2005). These exposure blanks were used to determine the Fe contribution from sampling, laboratory procedures and analysis. Air volumes were measured using a calibrated gas flow meter. Thirteen cryogenically archived (−18 °C) filter sub-samples (Supplementary Table 1) from the Bollhöfer et al. (2005) study were used in this work to investigate the aerosol Fe mass concentration and fractional Fe solubility.

2.3. Partial filter sizing

During the original study, the filters were cut into halves or quarters with an acid cleaned stainless steel scalpel blade (Bollhöfer et al., 1999, 2005). These filter sub-samples were the focus of this aerosol Fe study. Filter samples were visually inspected in a laminar flow hood under clean-room conditions with minimal handling.

2.4. Aerosol iron leaching experiments

All bottles and filtration parts used in the Fe leaching experiments were acid-cleaned following GEOTRACES protocols (Cutter et al., 2010). Leaching experiments were conducted sequentially using a trace metal clean flow-through reactor (Fig. 2) (e.g. Wu et al., 2007; Aguilar-Islas et al., 2010). This reactor consisted of the sub-sampled filter supported on acid-cleaned 0.45 μm acid cleaned backing filter that was mounted in a single-stage PFA filter assembly with a PFA funnel front face. Leaching solutions were pulled through the reactor under vacuum, into 250 ml low-density polyethylene bottles (LDPE). The PTFE filters were hydrophobic and required exposure to high-purity methanol to initiate water flow. Prior to the leaching experiments, the system was rinsed with several litres of ultra-pure water (>18 M Ω -cm) and ultra-pure 1% HCl (baseline Seastar), followed by another ultra-pure water rinse.

2.4.1. Soluble iron

The instantaneous water soluble Fe fraction (Fig. 2) was investigated using two successive 50 ml aliquots (“a” and “b”) of ultra-pure water. The mean procedural blank ($n = 10$) for this Fe fraction was $0.07 \pm 0.005 \text{ nmol g}^{-1}$ of soluble Fe. The mean exposure blank ($n = 5$) was $0.1 \pm 0.003 \text{ nmol g}^{-1}$ of soluble Fe. The mean ultra-pure water blank ($n = 5$) was $0.001 \pm 0.002 \text{ nmol g}^{-1}$. On average 90% of the water soluble Fe was leached in the first leach. Other ultra-pure water leaching

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