

# Physical speciation and solubility of iron from baleen whale faecal material



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## ABSTRACT

Primary productivity in large areas of the Southern Ocean is limited by the availability of a key micronutrient—iron (Fe). Recently it has been suggested that marine animals could play an important role in recycling Fe through their diet and subsequent defecation, however there is no information on the relative bioavailability of faecal Fe for uptake. The bioavailability of Fe in seawater is controlled by a number of complex interactions. The physical separation between the dissolved ( $< 0.2 \mu\text{m}$ ) and particulate ( $> 0.2 \mu\text{m}$ ) fractions is one common measure used to determine element bioavailability. Here, the size fractionation of Fe from 3 whale faecal samples in 4 different size classes ( $< 0.2 \mu\text{m}$ ,  $0.2\text{--}10 \mu\text{m}$ ,  $10\text{--}60 \mu\text{m}$  and  $> 60 \mu\text{m}$ ) was investigated, along with the leaching of particulate Fe over time. Although the total particulate fraction ( $> 0.2 \mu\text{m}$ ,  $5026\text{--}22,526 \text{ nmol L}^{-1}$ ) dominated the total Fe pool, the concentrations of dissolved Fe in whale faecal samples ( $186\text{--}754 \text{ nmol L}^{-1}$ ) were three order of magnitude higher than published Southern Ocean surface seawater concentrations. Furthermore, results from the leaching experiment suggest that Fe is continually leached from faecal particles over an initial 12-hour period, thus increasing the concentration of bioavailable Fe in surface seawater. Although the concentrations measured here are some of the highest reported in the literature, the true supply of Fe back to surface seawater will be controlled by processes such as organic complexation, scavenging and sinking by particles, remineralisation, and vertical transport, not measured in this study.

## 1. Introduction

Large regions of the Southern Ocean are characterized by low phytoplankton biomass despite high concentrations of major nutrients (e.g. nitrate, phosphate and silicate), and have been characterized as High Nutrient Low Chlorophyll (HNLC) waters (Moore and Abbott, 2000). One factor responsible for limiting the growth of phytoplankton in HNLC waters has been the availability of iron (Fe) that is required for nitrogen acquisition and assimilation (Morel and Price, 2003). *In-situ* Fe fertilisation experiments and bottle assays have demonstrated that Fe deficiency limits the ability of phytoplankton to acquire nitrogen, consequently limiting photosynthetic yield (Martin, 1990; de Baar et al., 2005; Boyd et al., 2007).

Iron enters the surface waters through the deposition of atmospheric dust (Boyd et al., 2004; Cassar et al., 2007), weathering of shelf sediments (Sedwick et al., 2008; Bowie et al., 2009), hydrothermal vents (Tagliabue et al., 2010; Klunder et al., 2011), melting icebergs

(Smith et al., 2007; Lin et al., 2011; Duprat et al., 2016) and sea ice (Sedwick and Di Tullio, 1997; Lannuzel et al., 2007), and upwelling of nutrient rich deep water (de Baar et al., 1995). However, the concentration of Fe in Southern Ocean surface waters is at limiting concentrations ( $0.1\text{--}0.5 \text{ nmol L}^{-1}$ , Tagliabue et al., 2012) due to the remoteness of large areas of the Southern Ocean to many of these sources, and the short residence time of Fe in surface waters (Millero et al., 1987). Recently, it has been proposed that biological recycling by higher order marine animals, in particular baleen whales, could increase the availability of Fe to phytoplankton (Smetacek and Nicol, 2005; Nicol et al., 2010; Smith et al., 2013; Ratnarajah et al., 2014; Ratnarajah et al., 2016a; Ratnarajah et al., 2016b).

Antarctic krill (*Euphausia superba*) concentrate Fe through their diet (phytoplankton, copepods etc.) which is influenced by seasonal and regional differences, as well as surface or benthic feeding (Ratnarajah et al., 2016b). Baleen whales feed on Fe-rich Antarctic krill as their main dietary source (Lockyer, 1981; Nicol et al., 2010). Whales require

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Fig. 1. a) Defecating humpback whale in the Southern Ocean (source A.S. Friedlaender) b) Close-up of 5 mL of humpback whale faecal material from Sample 3.

Fe for the production of red blood cells and the oxygen storage protein in muscles (Ordway and Garry, 2004; Ganz and Nemeth, 2006); however, mammals are unable to excrete Fe through their kidneys. Therefore the Fe taken up for muscle growth and the production of red blood cells as a calf is retained and recycled for future use, and much of the Fe consumed as adults is defecated into surface waters, unless they are pregnant or injured, in which case they may retain some Fe for growth. The high concentrations of total Fe in whale faeces ( $119 \pm 30 \text{ mg kg}^{-1}$  dry weight for humpback whales,  $162 \pm 107 \text{ mg kg}^{-1}$  dry weight for blue whales and for  $237 \pm 45 \text{ mg kg}^{-1}$  dry weight fin whales, Nicol et al., 2010, Ratnarajah et al., 2014) demonstrate that it is a source of recycled Fe. However, not all Fe in the ocean is bioavailable and it is unclear if this recycled Fe is bioavailable for uptake by phytoplankton.

The bioavailability of Fe reflects the ability of phytoplankton cells to acquire Fe; with the dissolved Fe (dFe, operational cut-off of 0.2 or 0.4  $\mu\text{m}$ ) fraction being considered most accessible for biological uptake despite the particulate Fe (pFe) fraction being the dominant pool of total Fe in the water column (de Baar and de Jong, 2001). However, the particulate fraction could also be an important reservoir that can be solubilized (Wu et al., 2007; Schroth et al., 2009; Sugie et al., 2013). Multiple leaching experiments have been conducted to explore the dissolution of Fe under widely varying conditions (e.g. ultrapure deionized water leaching, weak acid, seawater leaching and semi-continuous flow-through leaching techniques) (Wu et al., 2007; Schroth et al., 2009; Aguilar-Islas et al., 2010; Mendez et al., 2010; Gao et al., 2013; Winton et al., 2015). These studies demonstrated the need for including the dissolved and particulate fractions, and the leachable fraction, in determining the total amount of Fe in seawater that is potentially bioavailable for uptake by phytoplankton.

Biological recycling of Fe by baleen whales could represent a large source of Fe into surface waters, however there is no information on the

potential bioavailability of faecal Fe in surface waters. The overall aim of this study is to provide the first quantitative estimate of the fraction of dFe to pFe in whale faeces, and the solubility of this recycled Fe source over time. Dissolved Fe represents the fraction passed through a 0.2  $\mu\text{m}$  pore size filter as a means to partition dFe and pFe. The solubility represents the concentration of dissolvable Fe from pFe at each size fraction. The dissolvable Fe may contain labile  $\text{Fe}^{2+}$ , organically complexed  $\text{Fe}^{3+}$ , and colloidal Fe (between 0.02  $\mu\text{m}$  to 0.2 or 0.4  $\mu\text{m}$ ) (Siefert et al., 1999; Trapp et al., 2010). Aluminium is commonly used as a tracer of lithogenic inputs (Ohnemus and Lam, 2014). Therefore the concentration of aluminium (Al) was also measured to determine the Fe/Al ratio to estimate whether the pFe in whale faeces is more likely to originate from biogenic or lithogenic sources.

## 2. Methods

### 2.1. Sample preparation

New 20 L low-density polyethylene (LDPE) carboys, 1 L LDPE bottles, silicon C-flex tubing, and 5 and 10 mL LDPE nutrient tubes were soaked in 2% Decon 90 (Decon Laboratories) cleaning solution for at least 7 days. Subsequently carboys, bottles, tubing, and nutrient tubes were acid leached in 10% (v:v) Hydrochloric acid (HCl, Merck, Analytical grade 32%, Germany) for 4 weeks prior to use for transferring freshly collected sub-Antarctic seawater samples for leaching experiment and the dilution and analysis of size fractionated samples. Teflon perfluoroalkoxy (PFA) screw cap digestion vials (15 mL; Savillex Corp., USA) were acid leached in 50% (v:v) HCl for 2 weeks. Following acid leaches, all materials were rinsed thoroughly (five times) with Ultra High Purity (UHP) water and left to dry in an HEPA filtered Class 100 laminar flow bench.

60  $\mu\text{m}$  (Nylon net filters, 47 mm, Merck Millipore), 10  $\mu\text{m}$  and 0.2  $\mu\text{m}$  membrane filters (polycarbonate (PC), 47 mm diameter, Sterlich and Merck Millipore, respectively) were soaked in 10% ultrapure HCl for 1 week, rinsed with UHP water 7 times, and stored in UHP water. Polycarbonate filtration units (Sartorius) were soaked in 2% Neutracon (Decon Laboratories) cleaning solution for 7 days and acid leached in 10% (v:v) HCl (Merck, Analytical grade 32%, Germany) for 3 days prior to use. Following acid leaches, all filtration units were rinsed thoroughly (five times) with UHP water and left to dry in a HEPA filtered Class 100 laminar flow bench.

## 2.2. Sample collection

Adult humpback whale faecal samples from 3 individuals, were collected opportunistically using new Nalgene 250 mL LDPE bottles in Antarctic waters during the 2014/2015 summer feeding season around Palmer Station, Anvers Island. Whale faeces are mostly liquid in nature, with some solid particles (Fig. 1b). Faecal samples were collected by dipping a Nalgene LDPE bottle into seawater from a 6-meter inflatable boat, as the whale was simultaneously defecating and then diving, and immediately frozen. Each sample consists of a mixture of faecal material and seawater, as it is not possible to solely collect the liquid fraction of whale faeces.

Seawater used for leaching experiments were collected from an HNLC region using a SeaBird trace metal clean rosette equipped with 12  $\times$  10 L externally closing Ocean Test Equipment Teflon-lined Niskin bottles, attached to a polyurethane powder-coated aluminium frame specially designed for trace metal work during the Heard Earth-Ocean-Biosphere Interactions (HEOBI) cruise (8 January–5 March 2016) in the vicinity of Heard Island, Southern Ocean. Bottles were tripped at pre-programmed depths using a pressure sensor. Seawater used for the leaching experiments was collected at a depth of between 28 and 83 m. Seawater samples were drawn through C-flex tubing and filtered in-line through 0.2  $\mu\text{m}$  pore-size acid-washed capsules (Pall Supor membrane Acropak 200). The dissolved fraction of the seawater collected is thus a combination of the colloidal and soluble ( $< 0.02 \mu\text{m}$ ) fraction. All sample processing was carried out under an ISO class 5 trace-metal-clean laminar flow bench in a HEPA filtered-air clean container.

## 2.3. Analysis of iron and aluminium

10 mL of faecal material from each humpback whale was sequentially vacuum filtered through 47 mm diameter acid washed 60  $\mu\text{m}$ , 10  $\mu\text{m}$ , and 0.2  $\mu\text{m}$  membranes to obtain the dissolved and particulate fractions. This volume of faecal material was chosen because high particle concentrations restrict the volume of sample that is able to be passed through the filters before clogging.

The dissolved and particulate fractions were measured using Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS, Thermo Fisher ELEMENT 2, Bremen, Germany), following methods described in Townsend (2000) and Bowie et al. (2010). Briefly, particulate samples were measured by digesting filters in 1 mL of concentrated nitric acid ( $\text{HNO}_3$ ), 1 mL of concentrated hydrofluoric acid (HF) and 0.125 mL of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (all Ultrapure, Seastar Baseline, Choice Analytical) inside Teflon PFA vials. Faecal material contains high concentrations of dissolved organic material. The addition of  $\text{H}_2\text{O}_2$  enhances the oxidation properties of  $\text{HNO}_3$  (especially in the digestion of organics), whilst the addition of HF allows for greater digestion of the Fe particles retained on the filters compared to  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  assisted digestion only (Sucharova and Suchara, 2006; Bowie et al., 2010; Ohnemus et al., 2014). Digests were heated at 125  $^\circ\text{C}$  for 8 h on a Teflon coated digestion hotplate, housed in a bench-top fume hood coupled with HEPA filters to ensure clean air input (Digiprep, France).

Following digestion, all samples were dry evaporated at 60  $^\circ\text{C}$  for 4 h on the Teflon coated digestion hotplate, cooled for  $\sim 2$  h, then

resuspended in 10 mL of 10% v:v  $\text{HNO}_3$  (Ultrapure, Seastar Baseline) for 2 days. Identical procedures were applied to procedural filter blanks ( $n = 9$ ) and to one certified referenced material (BCR-414 trace elements in plankton,  $n = 3$ ) to assess elemental recovery following digestion. Prior to analysis all particulate samples, certified reference materials (CRMs) and digest blanks were diluted 10-fold in 2% v:v  $\text{HNO}_3$  (Ultrapure, Seastar Baseline) in LDPE nutrient tubes. The dissolved fraction was diluted 10-fold in 2% v:v  $\text{HNO}_3$  (Ultrapure, Seastar Baseline) in LDPE nutrient tubes to reach final salinity  $< 3$ , thereby minimising sample matrix effects during SF-ICP-MS analysis.

Indium (In, High-Purity Standards, USA) was added to all samples at a final concentration of 10  $\mu\text{g L}^{-1}$  and used as an internal standard. Representative subsamples from each analytical sequence were also spiked with a multi-element solution (QCD Analysts, MISA suite of solutions, 10  $\mu\text{g L}^{-1}$ , Spring Lake, USA) to monitor the recoveries of Fe and Al in the sample matrices considered. The ELEMENT 2 SF-ICP-MS has three pre-defined spectral resolutions available enabling isotopes to be quantified with minimal spectral interferences. Iron and Al were measured using the “medium” resolution setting ( $m/\Delta m \sim 4000$ ). Four calibration standards with concentrations 0, 1, 5 and 10  $\mu\text{g L}^{-1}$  were prepared by serial dilution from multi-element stock solutions (QCD Analysts, MISA suite of solutions, Spring Lake, USA).

## 2.4. Leaching of particulate iron

Background dFe concentration of the HEOBI seawater used for this experiment was determined using a sample pre-concentration and matrix separation instrument for undiluted seawater (seaFAST S2, Elemental Scientific, USA) and subsequently measured on the SF-ICP-MS. Dissolved Fe concentration was determined to be  $0.17 \pm 0.02 \text{ nmol kg}^{-1}$  ( $n = 7$ ). Laboratory analysis of SAFe intercalibration sample D1 for dFe was determined to be  $0.69 \pm 0.05 \text{ nmol kg}^{-1}$  ( $n = 7$ ). This agrees with the consensus value for this standard of  $0.67 \pm 0.04 \text{ nmol kg}^{-1}$  (Wuttig et al., in prep).

Sample 3 was randomly chosen for the leaching experiment. Initially, a fresh 10 mL subsample of faecal material was sequentially filtered through acid washed 60  $\mu\text{m}$ , 10  $\mu\text{m}$ , and 0.2  $\mu\text{m}$  filters using the filtration devices coupled with a vacuum pump (Merck Millipore). 50 mL of filtered (0.2  $\mu\text{m}$ ) seawater was then added into the filtration chamber. Filters were soaked in this solution for 5 min, and 1 mL of the seawater and faecal material solution was subsequently filtered using a vacuum pump. Following that, 1 mL of the seawater and faecal material solution were filtered at 15, 30, 60 min, and 4 and 12 h intervals. The experiment was conducted in the dark at ambient seawater temperature (2  $^\circ\text{C}$ ) to mimic natural conditions. At the end of the experiment, the filters were digested and analysed as above. The seawater and faecal Fe leachates were diluted 20-fold in 2%  $\text{HNO}_3$  in LDPE nutrient tubes with 10  $\mu\text{g L}^{-1}$  In added as internal standard (as above).

## 3. Results

### 3.1. Analysis of iron and aluminium

Results for procedural blanks, limits of detection (defined as three times the standard deviation of the blank) and certified reference materials are presented in Tables 1 and 2 respectively, and were found fit for purpose. Spike recoveries of Fe in faecal digests were between 83 and 96% ( $n = 7$ ).

Whale faecal material is voluminous (Fig. 1a) and highly heterogeneous in nature, consisting of a mixture of dissolved, small and large particles (Fig. 1b). Measured dFe and pFe concentrations for the 3 samples are presented in Table 3 (in  $\text{nmol L}^{-1}$ ) and Fig. 2 (in %). The concentration of dFe in whale faecal material ranged from 186 to 754  $\text{nmol L}^{-1}$  (Table 3 and Fig. 2), which is comparable to marine and continental ice in East Antarctica (Table 4). The particulate fractions were individually measured at 3 different size fractions (0.2–10, 10–60

**Table 1**

Measurements of Fe and Al from procedural filter blanks. Averages shown are the mean of 3 replicates. The limit of detection (LOD) is 3 times the standard deviation of the filter blank.

	Fe	Al
0.2 $\mu\text{m}$		
Average filter blank ( $\mu\text{g L}^{-1}$ )	0.7 $\pm$ 0.1	1.1 $\pm$ 0.2
LOD ( $\mu\text{g L}^{-1}$ )	0.2	0.5
10 $\mu\text{m}$		
Average filter blank ( $\mu\text{g L}^{-1}$ )	1.1 $\pm$ 0.09	0.4 $\pm$ 0.06
LOD ( $\mu\text{g L}^{-1}$ )	0.3	0.2
60 $\mu\text{m}$		
Average filter blank ( $\mu\text{g L}^{-1}$ )	0.7 $\pm$ 0.3	1.1 $\pm$ 0.2
LOD ( $\mu\text{g L}^{-1}$ )	1.0	0.5

**Table 2**

Analysis of certified referenced material plankton (BCR-414) for Fe and Al. Reference values for Fe are certified, but Al values are indicative only. Averages shown are the mean of 3 replicates. Recovery values indicate the percentage difference between measured and certified values.

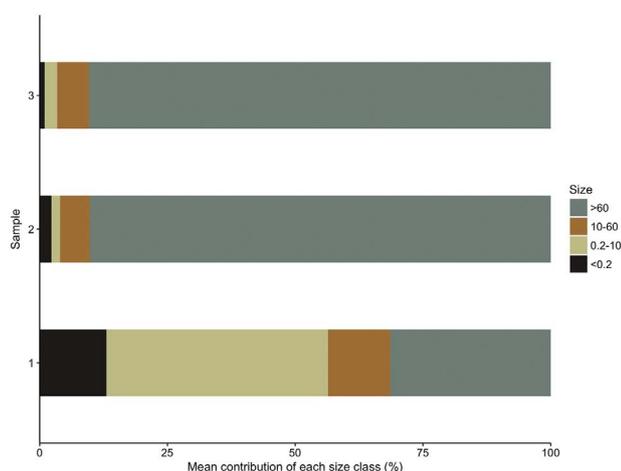
	Fe	Al
BCR-414 referenced values ( $\text{mg kg}^{-1}$ )	1850 $\pm$ 190	[1800 $\pm$ 30]
Measured average ( $\text{mg kg}^{-1}$ ) (n = 3)	1709 $\pm$ 22	2563 $\pm$ 46 <sup>a</sup>
Recovery (%)	92	142

<sup>a</sup> [Al] is a non-certified value only. Similarly high values for Al (2639  $\pm$  80) were also found using a combination of HCl, HF and HNO<sub>3</sub> under similar digestion conditions by Lannuzel et al. (2015).

**Table 3**

Iron concentration in  $\text{nmol L}^{-1}$  in the different size fractions, and percent (%) pFe (> 0.2  $\mu\text{m}$ ) for each sample of whale faecal material. Total pFe represents the sum of iron concentrations > 0.2  $\mu\text{m}$ , whilst Total Fe represents the sum of all size fractions.

	Sample 1	Sample 2	Sample 3
< 0.2 $\mu\text{m}$	754	527	186
0.2 $\mu\text{m}$	2508	389	486
10 $\mu\text{m}$	703	1353	1212
60 $\mu\text{m}$	1815	20,784	17,664
Total pFe	5026	22,526	19,362
% pFe	87	98	99
Total Fe	5780	23,053	19,548



**Fig. 2.** Mean percent (%) contribution of each size fraction ( $\mu\text{m}$ ) to total iron in whale faecal material.

and > 60  $\mu\text{m}$ ) (Table 3 and Fig. 2). The concentration of size-fractionated pFe varied greatly between each faecal sample and between each size fraction, ranging from 380 to 2508  $\text{nmol L}^{-1}$  for the 0.2–10  $\mu\text{m}$  fraction, 703–1353  $\text{nmol L}^{-1}$  for the 10–60  $\mu\text{m}$  fraction, and

1815–20,784  $\text{nmol L}^{-1}$  for the largest particles (> 60  $\mu\text{m}$ ).

The > 0.2  $\mu\text{m}$  fraction is the most commonly reported particulate fraction in the literature. ‘Total pFe’ in Table 3 was determined by summing the Fe concentrations measured in the 0.2–10, 10–60 and > 60  $\mu\text{m}$  fractions. Total particulate fraction in whale faecal samples ranged from 5026 to 22,526  $\text{nmol L}^{-1}$  (Table 3), which is comparable to marine ice, fast ice, hydrothermal vents and krill faecal pellets (Table 4). ‘Total Fe’ represents the sum of the dissolved (< 0.2  $\mu\text{m}$ ) and particulate (> 0.2  $\mu\text{m}$ ) fractions, which ranged from 5780 to 23,053  $\text{nmol L}^{-1}$  (Table 3). The particulate fraction consistently dominated the total Fe pool (87–99%, Table 3). Assuming that Al is solely lithogenic in origin, the pFe/pAl in whale faecal samples suggest that the pFe in whale faecal samples is highly biogenic in origin (between 50 and 80%).

### 3.2. Leaching of particulate iron

Although dFe is generally considered the most bioavailable fraction, Fe can be leached from the particulate fraction into the dissolved fraction over time. This fraction of leached Fe is overlooked in instantaneous size fractionation measurements.

At the start of the 12-hour leaching experiment, the total Fe concentrations on the 0.2  $\mu\text{m}$ , 10  $\mu\text{m}$  and 60  $\mu\text{m}$  filters were 1021  $\text{nmol L}^{-1}$ , 1557  $\text{nmol L}^{-1}$  and 17,229  $\text{nmol L}^{-1}$ , respectively. Initial dFe of the whale faecal material was measured at 207  $\text{nmol L}^{-1}$ . The pFe concentrations presented here were determined by summing the final Fe concentration in the filters, and at each subsampling time step as measured on the SF-ICP-MS.

The concentrations here are different from that presented for Sample 3 in Table 3 due to the inherent heterogeneity of the sample and the heavy particle load that would influence individual subsampling attempts (Fig. 1b). The leaching experiment demonstrated that most of the labile Fe within each size fraction is released within the first 5 min (1–7%, Fig. 3). After 12 h, between 0 and 2.5% of Fe was still being leached by the faecal particles.

## 4. Discussion

### 4.1. Dissolved fraction (< 0.2 $\mu\text{m}$ )

The highly heterogeneous nature of whale faecal material would influence the apparent variability of the measured dFe concentrations between these samples (186–754  $\text{nmol L}^{-1}$ ) because some faecal material might have more particulate matter in the volume sampled (Fig. 1b). However, the dFe concentrations in whale faecal material fall within the range of other dFe pools found in the Southern Ocean region (Table 4). The dFe concentrations measured in our samples are most comparable to marine ice and continental ice from the Amery Ice Shelf, which demonstrate similarly wide ranges in Fe concentrations (339–691  $\text{nmol L}^{-1}$  and 62–167  $\text{nmol L}^{-1}$  respectively), but much higher than in other pools, including background seawater concentrations from the Southern Ocean and the Polar Frontal region, sea ice, snow, glaciers, icebergs, Antarctic streams, upwelled subsurface waters, and hydrothermal sources (Table 4).

The large variability in dFe concentration measured here could also reflect the timing of sample collection (i.e. between defecation and collection) and the variability in ingested food quantity and quality. Although whale faecal samples were collected as soon as the whales defecated, the dilution and potential sinking of faecal material would significantly influence the Fe concentrations measured in these samples. In addition, there are no direct measurements of the daily krill consumption rates by baleen whales. However, tag data suggests that humpback whales in this region spend the vast majority of their time foraging (Friedlaender et al., 2013; Friedlaender et al., 2016a; Tyson et al., 2016) and remain in this state for extended periods of time punctuated by short transits between feeding areas (Friedlaender et al.,

**Table 4**  
Summary of dissolved iron (dFe) and particulate iron (pFe) concentrations from various sources in the Southern Ocean.

Location	Source	Fraction	Fe (nmol L <sup>-1</sup> )	Reference
Southern Ocean	Humpback whale faeces	dFe <sup>a</sup>	186–724	This study
	Surface seawater	dFe <sup>a</sup>	0.1–0.5	Tagliabue et al., 2012
Polar Frontal region	Surface seawater	dFe <sup>a</sup>	0.5–3.5	de Baar et al., 1995, Löscher et al., 1997
	Deep water	dFe <sup>a</sup>	0.4–2.8	Löscher et al., 1997
East Antarctica	Pack ice	dFe <sup>a</sup>	0.2–26	Lannuzel et al., 2007, van der Merwe et al., 2009, van der Merwe et al., 2011a
	Fast ice	dFe <sup>a</sup>	0.9–7.1	van der Merwe et al., 2011b
Ross Sea	Snow	dFe <sup>a</sup>	1–31.7	Edwards and Sedwick, 2001, Lannuzel et al., 2007
	Brine	dFe <sup>a</sup>	4.7–25.5	Lannuzel et al., 2007
	Marine ice	dFe	339–691	Herraiz-Borreguero et al., 2016
	Continental ice	dFe	62–167	Herraiz-Borreguero et al., 2016
	Sea ice	dFe <sup>a</sup>	1.1–6	Grotti et al., 2005
Taylor Glacier and Canada Glacier, Weddell Sea	Glacier	dFe <sup>a</sup>	0.1–2.2	Raiswell et al., 2008
Seymour Island and King George Island, Weddell Sea	Iceberg	dFe <sup>a</sup>	0.05–3.8	Raiswell et al., 2008
Antarctic Circumpolar Current (56°S, 15°W)	Deep water upwelling	dFe <sup>b</sup>	1	de Baar et al., 1995
Taylor Valley	Antarctic stream <sup>d</sup>	dFe <sup>c</sup>	190	Lyons et al., 2015
Bransfield Strait	Hydrothermal	dFe <sup>b</sup>	2.2–12.6	Klinkhammer et al., 2001
Southern Ocean	Humpback whale faeces	pFe	5026–22,526	This study
	Pack ice	pFe	0.1–213	Lannuzel et al., 2007, van der Merwe et al., 2009, van der Merwe et al., 2011a
East Antarctica	Fast ice	pFe	40.4–10,385	van der Merwe et al., 2011b, Lannuzel et al., 2015
	Surface snow	pFe	0.1–18.3	Lannuzel et al., 2007
	Brine	pFe	0.5–12	Lannuzel et al., 2007
	Marine ice	pFe	13,323–14,679	Herraiz-Borreguero et al., 2016
	Continental ice	pFe	26–31	Herraiz-Borreguero et al., 2016
Ross Sea	Sea ice	pFe	26–1160	Grotti et al., 2005
	Aeolian deposition	pFe	0.7–430	Winton et al., 2015 and Bowie et al., 2009
East Scotia Ridge	Hydrothermal	pFe	820,000–1,312,000	James et al., 2014
Pyrdz Bay	Krill faecal pellet	pFe	12,234,757–18,612,163 <sup>e</sup>	Ratnarajah et al., 2016b

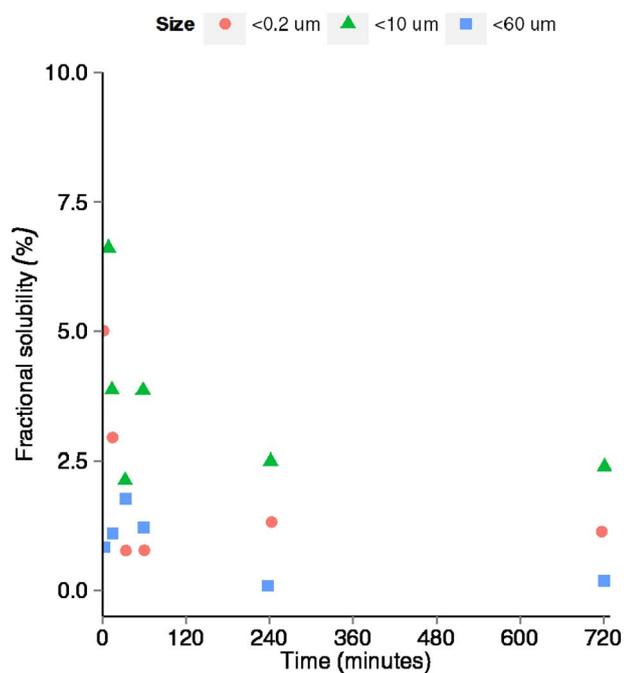
<sup>a</sup> dFe is < 0.2 μm.

<sup>b</sup> Unclear if dFe is < 0.2 μm or < 0.4 μm.

<sup>c</sup> dFe is < 0.4 μm.

<sup>d</sup> Potential sources of iron into the stream include chemical weathering of the stream channel sediments or aeolian inputs on glacial surfaces.

<sup>e</sup> pFe concentration in nmol kg<sup>-1</sup> dry weight.



**Fig. 3.** Leached Fe from whale faecal material as a function of time in each size fraction (Sample 3).

2016b). Daily krill consumption estimates for humpback whales range from 694 to 874 kg day<sup>-1</sup> wet weight and are calculated based on a number of factors (e.g. using daily prey consumption from average

body weight of 35 g kg<sup>-1</sup> body weight, and 2%, 2.5% and 3% of body mass, Lockyer, 1981 and Reilly et al., 2004). The variability in consumption rates would thus influence the amount of Fe digested and recycled.

#### 4.1.1. Potential processes influencing bioavailability of faecal dFe

Scavenging removes dFe when concentrations exceed the solubility (Johnson et al., 1997; Gordon et al., 1998; Boyd and Ellwood, 2010; Saito et al., 2013), which is controlled by chemical speciation according to the environmental conditions, especially the presence of Fe-binding ligands. Whilst the organic complexation of faecal dissolved Fe was not measured in this project, most of the dFe (99%) in the Southern Ocean is complexed by organic ligands (Boye et al., 2001; Croot et al., 2004; Boye et al., 2010; Ibisani et al., 2011; Thuróczy et al., 2011). Although the concentration of Fe complexing ligands in Southern Ocean waters is low ( $0.7 \pm 0.2$  nmol L<sup>-1</sup>, Boye et al., 2001), other sources of organic ligands could be important.

Antarctic sea ice contains some of the highest concentrations of organic ligands (4.5–72 nmol L<sup>-1</sup> of sea ice), potentially due to the high ice-associated algal and bacterial production (Lannuzel et al., 2015). Consequently, Southern Ocean seawater may not contain sufficient organic ligands to bind with a large pulse of faecal dFe, however release of recycled Fe close to the ice edge may increase the availability of faecal Fe through binding with organic ligands produced in sea ice. Marine animals could also be a source of organic ligands. Zooplankton have been demonstrated to produce Fe binding ligands (Sato et al., 2007). Accordingly, whales could release organic ligands produced by whale enterobacteria in their faecal material (e.g. enterobactin, a strong siderophore, which is produced by bacteria such as *Escherichia coli* Kraemer 2004, Butler and Martin, 2005) resulting in the

release of organically complexed Fe in their faecal material, however this has yet to be demonstrated.

In terms of chemical forms,  $\text{Fe}^{2+}$  is considered to be the more bioavailable fraction, due to the low solubility of the thermodynamically stable  $\text{Fe}^{3+}$  redox species. In copepods and krill, the acidic digestion process has been demonstrated to aid in the solubilization of Fe (Hutchins and Bruland, 1994; Barbeau et al., 1996; Tovar-Sanchez et al., 2007; Schmidt et al., 2016). In vertebrates, HCl and pepsin in the stomach coupled with the low oxygen environment in the intestine would favour the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (Slijper, 1962; Naikare et al., 2006). Although in an oxygenated environment  $\text{Fe}^{2+}$  could rapidly be oxidised to  $\text{Fe}^{3+}$ , if some of the dFe fraction of whale faeces is released already bound to ligands (similar to that of zooplankton), then the dissolved Fe solubility, bioavailability, and residence time would be greatly increased.

Dissolved Fe can be further partitioned into small soluble species and larger colloidal forms (not measured in this study). Within the dFe phase, soluble Fe may be more bioavailable than the more chemically dynamic colloidal Fe (Wu et al., 2001), and therefore may have a greater control over ocean primary productivity, because the colloidal fraction could aggregate into larger particles, scavenge Fe and settle to the ocean floor (Honeyman and Santschi, 1989; Gordon et al., 1998; Wu et al., 2001; Boyd and Ellwood, 2010). Conversely, Hassler et al. (2011) demonstrated the role of organic ligands in enhancing the colloidal fraction within the water column. Dissolved Fe could also be scavenged by other sinking particles, or precipitate from the water column (Wu et al., 2001; Boyd and Ellwood, 2010; Fitzsimmons and Boyle, 2014). However, complexation with organic ligands can protect dFe from particle scavenging and precipitation (Street and Payton, 2005; Fitzsimmons and Boyle, 2014) and bacteria can remineralise this sinking fraction and increase dFe concentrations again (Boyd and Ellwood, 2010).

Lateral transport of dFe is an important mechanism in supplying Fe to Fe-limited regions. The high dFe concentrations between 1000 and 2000 m in the tropical Pacific has been attributed to lateral transport from hydrothermally derived dFe ~500 km away (Boyle et al., 2005; Wu et al., 2011). Lateral supply was also observed in the plume region around the Kerguelen Plateau, whilst vertical supply was the dominant source on the plateau (Bowie et al., 2015). In addition, the lateral supply of dFe from the Kerguelen shelf was higher than the vertical upward dFe flux, and plays a significant role in the phytoplankton bloom observed around Elephant Island (South Shetland Islands; Dulaiova et al., 2009). Assuming that the solubility of the dFe pool in whale faeces is stabilized by organic complexation, whale faecal dFe could also be transported laterally great distances and play an important role in supplying Fe to distal HNLC regions of the Southern Ocean.

#### 4.2. Particulate fraction (> 0.2 $\mu\text{m}$ )

The particulate fraction constituted the dominant pool of the total Fe in these samples. Generally, Fe concentrations were highest in particles > 60  $\mu\text{m}$  (1815–20,784  $\text{nmol L}^{-1}$ ), followed by particles between 10 and 60  $\mu\text{m}$  (702–1352  $\text{nmol L}^{-1}$ ) and lastly between 0.2 and

10  $\mu\text{m}$  (389–2507  $\text{nmol L}^{-1}$ ) (Table 3, Fig. 2). Except for Sample 1 where the highest concentrations were observed in the 0.2–10  $\mu\text{m}$  fraction, the other samples demonstrated a decline in Fe concentrations with decreasing size fractionation (Table 3 and Fig. 2). The large variation in Fe concentrations between particulate fractions would again reflect the natural variability in the sample, as well as variability in feeding rates and/or assimilation efficiency, and timing of collection as mentioned earlier. Particle aggregation may also increase the Fe concentration in particles > 60  $\mu\text{m}$ .

The concentration of total pFe in the faecal materials was comparable to concentrations reported elsewhere for Antarctic land-fast sea ice and marine ice (Herraiz-Borreguero et al., 2016; van der Merwe et al., 2011b; Lannuzel et al., 2014); lower than in hydrothermal source solutions (James et al., 2014) and krill faecal pellets (Ratnarajah et al., 2016b); but higher than all other Southern Ocean sources including aeolian deposition, surface snow, brine, pack ice, continental ice and sea ice (Table 4). Although the pFe in krill faecal pellets is considerably higher than in whale faecal material, the larger size of krill faecal pellets would result in faster sinking rates, decreasing the residence time of Fe in surface waters.

##### 4.2.1. Potential processes influencing bioavailability faecal pFe

The particulate fraction is generally considered less bioavailable for uptake by phytoplankton due to its refractory composition, but could be converted into a more bioavailable pool through recycling of the biogenic pFe in surface waters, leaching of pFe, and remineralisation, or conversely be rapidly removed through aggregation and precipitation. The molar Fe/Al ratio is a useful proxy for estimating the lithogenic and biogenic composition and enrichment of elements in particles (Lannuzel et al., 2011; Lam et al., 2015; Ohnemus and Lam, 2015), which can then be used to help predict the lability of specific elements found in those particles.

Iron and Al are abundant in the Earth's crust and in continental and marine sediments, and although abundances vary, the mean crustal ratio of Fe/Al is approximately 0.2  $\text{mol mol}^{-1}$  (Wedepohl, 1995; Rudnick and Gao, 2003). The Fe/Al molar ratios for the 3 whale faecal material samples measured here were found to be between 0.4 and 0.99  $\text{mol mol}^{-1}$ . Assuming that Al is solely lithogenic in origin (however Al can be scavenged leading to an overestimate in lithogenic contribution—see Ohnemus and Lam, 2015), and using the Fe/Al molar ratio of 0.2 (Wedepohl, 1995), the lithogenic PFe (> 0.2  $\mu\text{m}$ ) contribution was calculated as  $(100 * [\text{PAI}]) * (0.2/[\text{PFe}])$ . These calculations suggest that between 20 and 50% of the faecal material is lithogenic in origin (Table 5). The biogenic PFe is considered as the difference between total PFe and lithogenic PFe, and ranged from 50 to 80% (Table 5). The enrichment factor (EF) determined as  $([\text{PFe}] * [\text{PAI}])_{\text{faecal sample}} / ([\text{PFe}] * [\text{PAI}])_{\text{crust}}$  was calculated at 2, 5 and 4 for faecal Samples 1, 2 and 3 respectively. Elements with EF > 3–5 suggest an enrichment of Fe in the water column whereas elements with EF < 3–5 is considered to fall within the natural variability inherent to crustal material (Duce et al., 1983). Although the Fe/Al ratios suggest a high biogenic load, the EF factors point towards natural variability in the samples.

The main prey of baleen whales, Antarctic krill, were found to be

**Table 5**

Iron-to-Aluminium molar composition and estimated lithogenic and biogenic contributions in the three faecal samples (for details see text). A comparative crustal Fe/Al ratio of 0.2<sup>a</sup> was used for calculations.

	Total [pAl] <sup>b</sup> $\text{nmol L}^{-1}$	Total [pFe] <sup>b</sup> $\text{nmol L}^{-1}$	Fe/Al	Lithogenic [pFe] $\text{nmol L}^{-1}$	Biogenic [pFe] $\text{nmol L}^{-1}$	Lithogenic (%)	Biogenic (%)
Sample 1	12,674	5026	0.40	2535	2491	50	50
Sample 2	22,677	22,526	0.99	4535	17,991	20	80
Sample 3	24,454	19,362	0.79	4891	14,471	25	75

<sup>a</sup> Wedepohl (1995).

<sup>b</sup> pFe and pAl is > 0.2  $\mu\text{m}$ .

feeding on the seabed in the Scotia Sea (Schmidt et al., 2011). Therefore, the lithogenic composition in whale faecal material could be attributed to benthic feeding by their prey, Antarctic krill or by accidental feeding of resuspended lithogenic sediments by the whales themselves when they filter krill. The biogenic fraction in whale faecal material from this study could be due to the Fe that had been incorporated into the krill body. The processing of both biogenic and lithogenic material by whales during digestion likely renders all particulate Fe more bioavailable before being defecated at the surface. Furthermore, the particulate Fe in whale faecal material released in surface seawaters could be further broken down and released by both micro- and meso-zooplankton (Sarhou et al., 2008; Strzepek et al., 2005; Maranger et al., 1998; Barbeau et al., 1996; Hutchins and Bruland, 1994), heterotrophic bacteria (Strzepek et al., 2005; Sarhou et al., 2008; Boyd et al., 2010) and viruses (Mioni et al., 2005), thus making it even more bioavailable to Fe-limited plankton.

The dissolution of digested and defecated lithogenic pFe could be an important source of dFe in this region (Blain et al., 2007; van der Merwe et al., 2014). For example, the high vertical dFe supply in the naturally fertilised region of the Kerguelen Plateau did not meet the dFe demand of phytoplankton, and the missing Fe supply could have been met through the extended dissolution of leachable Fe from resuspended marine particles (Blain et al., 2007). Similarly, the dissolution of pFe from faecal material, although largely biogenic in origin, could play an important role in the supply of dissolvable Fe into surface water prior to sinking.

To test the instantaneous and prolonged solubilization of Fe in faecal material, the three size fractions were subjected to seawater leach experiments over a 12-hour period from a single sample ("Sample 3"). The leaching experiment demonstrated that most of the labile Fe is released within the first 5 min (Fig. 3). At the 0.2 µm size fraction, approximately 5% of the material is leached into the dissolved pool. Approximately 7% is leached within the first 5 min from the 10 µm filter, and only approximately 1% from the 60 µm filter. The solubility of faecal particles decreased over time with approximately 1% being leached after 12 h for the 0.2 µm size fraction, 2.5% for the 10 µm size fraction and ~0% for the > 60 µm size fraction. Comparatively, the solubility of atmospheric dust particles is between 0.5 and 80% (Mahowald et al., 2005; Winton et al., 2015). However, these leaching experiments were performed using different leach solutions (UHP and weak acid such as acetic acid and hydroxylamine hydrochloride), and at different temperatures (heating step of 90–95 °C, Winton et al., 2015), which would influence solubility estimates (Wu et al., 2007; Schroth et al., 2009; Aguilar-Islas et al., 2010; Mendez et al., 2010; Gao et al., 2013; Morton et al., 2013; Winton et al., 2015). A similar seawater leach experiment using particles in sea ice (> 0.2 µm) at 4 °C found a maximum of 6% solubility (Kanna et al., 2016).

Although the % solubility of faecal particles is at the lower end of the scale, there is still a high concentration of dFe being leached from these particles. For instance, in the first 5 min, 51 nmol L<sup>-1</sup> of Fe is leached from the 0.2 µm filter, whilst 103 nmol L<sup>-1</sup> and 143 nmol L<sup>-1</sup> is leached from the 10 µm and 60 µm fractions respectively. The concentration of dissolvable Fe here could be an underestimate due to adsorption of dFe to container walls (Wu et al., 2007). In laboratory experiments, the ratio between particle load and leach solution have been shown to contribute to the variability in the estimates of aerosol Fe dissolution in seawater, where higher particle load resulted in a decrease in percentage Fe released (Bonnet and Guieu, 2004). However, this is not likely to be a problem in the open ocean, where the faecal material is dispersed over a large volume during defecation.

It is important to compare the leaching rates of pFe against the sinking rates to gain a better estimate of the residence time in the water column. The sinking velocity of pFe is a function of its particle density and size. The density of organic matter (1060 kg m<sup>-3</sup>, Logan and Hunt, 1987) is close to that of water (1027 kg m<sup>-3</sup>). Using Stoke's Law for the sinking of spherical particles, the sinking rate of faecal particles in

seawater was calculated for a particle with a diameter of 0.2 µm, 10 µm and 60 µm (using gravitational acceleration of 9.81 m s<sup>-2</sup> and dynamic viscosity of seawater of 1.88 × 10<sup>-3</sup> kg s<sup>-1</sup> m<sup>-2</sup>). A particle of 60 µm would sink at a rate of 3 m day<sup>-1</sup>, whilst a particle of 10 µm would sink at a rate approximately 0.08 m day<sup>-1</sup>. At the smallest fraction, a particle of 0.2 µm would sink at a rate of 3.3 × 10<sup>-5</sup> m day<sup>-1</sup>.

Assuming a euphotic depth of 100 m, the larger particles (60 µm) would remain in the euphotic zone for 33 days, whilst the medium-sized particles (10 µm) would remain for 3.4 years (1250 days), and the smallest particles (0.2 µm) would remain for > 10 years. However, these sinking rate estimates are only approximations and assume that particles are spherical. Furthermore, particle aggregation will reduce the residence time in surface waters, the exact particle density for these samples is unknown, and rapid dilution in seawater, dissolution, scavenging, uptake and remineralisation processes will heavily influence the magnitude and settling rate of sinking particles.

As the pFe fraction sinks due to a combination of scavenging and gravitational forces, the bacterial community gradually remineralizes the organic matter, consequently returning Fe to the dissolved phase (Boyd and Ellwood, 2010). Furthermore, using particles > 53 µm, Boyd et al. (2010) demonstrated that bacteria are capable of releasing weak Fe-binding ligands during particle remineralisation. Therefore as faecal pFe sinks, not only will zooplankton and bacteria rapidly recycle the biogenic pool, the fraction that sinks will also be remineralised by the bacterial community.

Lateral transport of pFe has been demonstrated to play a crucial role in the supply of Fe to Fe-limited waters (Johnson et al., 2005; Lam et al., 2006; Lam and Bishop, 2008; Bowie et al., 2009). The wintertime phytoplankton bloom observed in the HNLC region of the subarctic North Pacific Ocean has been attributed to the lateral transport of pFe from the continental margin of the Aleutian Islands (Lam et al., 2006). Similarly, the high subsurface concentrations of pFe southeast of Tasmania is thought to be from shelf sediments laterally transported from Tasmania or from eastern mainland Australia, or Australian dust initially deposited in waters north of the sampling region and transported laterally towards the southeast (Bowie et al., 2009). Consequently, faecal-derived pFe could also be transported laterally to fertilise Fe-limited HNLC waters further afield.

The dilution of faecal samples in seawater, as well as particle aggregation and precipitation will also influence the bioavailability of Fe to phytoplankton. The rate of defecation or exact volume of faecal material defecated by a whale is unknown, however the image of a defecating humpback whale (Fig. 1a) suggests that it is voluminous. The pFe sinking rates calculated above are for individual particles. However, a major removal pathway of pFe from surface waters is through aggregation into larger particles (Frew et al., 2006; van der Merwe et al., 2014). van der Merwe et al. (2014) demonstrated that the aggregation of particles onto phyto-aggregates resulted in a 70% decrease in the pFe concentration within the mixed layer. In addition, when Fe concentrations exceed the solubility, Fe will be removed through scavenging and precipitation, as discussed earlier. Therefore, much of this faecal pFe could be rapidly exported via sinking aggregates, and a true concentration of bioavailable Fe will reflect a balance between the accumulation and removal mechanisms discussed here.

## 5. Conclusion

The distribution of bioavailable Fe in the ocean reflects a balance between Fe sources, biological uptake, speciation (chemical and physical), scavenging, precipitation, aggregation, remineralisation and lateral transport. Therefore it is critical to understand the role of marine animals in Fe recycling to better constrain biogeochemical budgets of Fe in the Southern Ocean. This study provided the first quantitative estimate on the physical speciation of Fe in recycled organic material. Biological recycling of Fe through large marine animals such as whales

could play an important role in the resupply of Fe to the Fe-limited waters of the Southern Ocean.

The measured concentrations of dFe and pFe in whale faecal material are some of the highest compared to all other sources into the region, and a time series leaching experiment suggests that Fe is continually leached from these particles over time. Although the particulate fraction dominated the total Fe pool, zooplankton and microbial solubilization of biogenic pFe, coupled with leaching of pFe over time and the slow sinking rates of organic matter, may imply that the faecal material would be rapidly recycled in the surface for biological uptake. Furthermore, as demonstrated in other studies, lateral transport of dFe and pFe could be an important mechanism in transporting Fe to other Fe-limited regions further away. There is a constant transfer dFe to pFe and vice versa. It is now important to: (i) determine if whales, like zooplankton, release organic Fe-binding ligands in their faecal material that would keep the dFe in suspension in the water column; (ii) understand the uptake response of phytoplankton to a faecal-derived Fe source; (iii) consider the supply of Fe by whales compared to other sources in the region, and (iv) examine the influence of historical whaling practices.

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