1 **Where bio- meets geochemistry: Zooplankton gut passage mobilises**

2 **lithogenic iron for ocean productivity**

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Summary

   Iron is an essential nutrient for phytoplankton, but low concentrations limit primary production and associated atmospheric carbon drawdown in large parts of the world's oceans [1,2]. Lithogenic particles deriving from aeolian dust deposition, glacial runoff or river discharge can form an important source, if the attached iron becomes dissolved and therefore bioavailable [3-5]. Acidic digestion by zooplankton is considered a potential mechanism for iron mobilisation [6], but evidence is lacking. Here we show that Antarctic krill sampled near glacial outlets at the island of South Georgia (Southern Ocean) ingest large amounts of lithogenic particles and contain three-fold higher iron concentrations in their muscle than specimens from off-shore, which confirms mineral dissolution in their guts. About 90% of the lithogenic- and biogenic iron ingested by krill is passed into their fecal pellets, which contain ~5-fold higher proportions of labile (reactive) iron than intact diatoms. The mobilised iron can be released in dissolved form via multiple pathways involving microbes, other zooplankton and krill predators. These pathways can deliver substantial amounts of bioavailable iron and therefore contribute to iron-fertilisation of coastal waters and the ocean beyond. In line with our findings, phytoplankton blooms downstream of South Georgia are more intensive and longer-lasting during years of high krill abundance on-shelf. Thus, zooplankton not only crop phytoplankton, but also boost new production via their nutrient supply. Understanding and quantifying iron mobilisation by zooplankton is essential to predict ocean productivity in a warming climate where lithogenic iron inputs from deserts, glaciers and rivers are increasing [7-10].

Results and Discussion

While most of the remote Southern Ocean is a high-nitrate low-chlorophyll (HNLC) area, primary productivity can be elevated for hundreds of kilometres downstream of islands, including South Georgia (Fig. 1A). This is considered a consequence of iron supply from the island shelves and its subsequent transport and recycling within the current flow [11-15]. Our *in situ* measurements of dissolved iron (DFe; < 0.2μm), total dissolvable iron (TDFe; unfiltered) and surface water salinity suggest that high iron concentrations over the northern shelf of South Georgia are also associated with a freshwater source: melting glaciers (Fig. S1). Glacial runoff has been found an important iron source in other polar regions [4,16,17], due to its high sediment load and the attached aggregations of iron oxyhydroxide nanoparticles [4,18]. However, most of the iron associated with glacial runoff is removed from surface waters during transition from low to high salinity [19], and the fate and chemical processing of iron during transport from glaciers to the adjacent ocean is not well understood [20].

Antarctic krill (*Euphausia superba*) is central to the South Georgia foodweb transferring primary production to higher trophic levels including fish, seals, penguins, albatrosses and whales [21]. Highest krill abundances on the eastern side of the island coincide with low chlorophyll *a* (chl *a*) concentrations and the dominance of fecal pellets in the suspended matter of surface waters, which indicates intensive grazing by krill (Fig. 1B-E). However, stomach content analysis reveals that krill do not only feed on phytoplankton but also ingest lithogenic particles and copepods when those are abundant (Fig. 1F). As a consequence, the amount of lithogenic particles in krill stomachs increased exponentially towards the main glacial outlets at Cumberland Bay, reaching >100 fold higher values than at a reference station ~170 km away (Fig. 2A). In concert with the increased ingestion of lithogenic particles, krill had up to three-fold higher iron concentrations in their muscle tissue and 1-2 orders of magnitude higher iron concentrations in their fecal pellets (Fig. 2B,C). Regardless of the sampling location, krill fecal pellets contained typically higher proportions of labile iron than the suspended material in surface waters [pellets: $2.4 \pm 2.0\%$; suspended material dominated by diatoms: $0.5 \pm 0.5\%$ of total particulate iron, T-value = 4.85, *p*-value = 0.0001, DF = 31] (Fig.2D).

75   When feeding on lithogenic particles, both the enhanced iron concentrations in krill muscle

76   tissue and the higher content of labile iron in krill fecal pellets compared to their food suggest that

77   some of the lithogenic iron is mobilised and even dissolved during gut passage. Such a mechanism

78   has been proposed previously [6] and shown for benthic- and intertidal species including annelids,

79   bivalves and harpacticoid copepods [22-24], but until now evidence was missing for zooplankton. The

80   mobilisation of lithogenic iron is likely due to the acidic digestion typical for crustaceans [25,26]. A

81   gut pH of 5.4, as found in pelagic copepods [26], enhances the Fe(III) solubility ~100-fold compared

82   to carbonate-buffered seawater [27]. Other factors associated with feeding such as mechanical- and

83   enzymatic impact on particles, anoxia and the release of iron-binding ligands [22,26,28] may

84   complement the effect of a lowered pH. However, the uptake of lithogenic particles during filter

85   feeding is not restricted to Antarctic krill near glacial outlets, but is known from copepods, mysids,

86   salps, other euphausiids and ciliates in river plumes, fjords, at the seabed or in the open ocean after

87   dust deposition [29-35]. We therefore suggest that the mobilisation of lithogenic iron by zooplankton

88   is a widespread phenomenon.

89   To quantify the role of iron mobilisation by krill in ocean fertilisation, individual iron release

90   rates have to be measured and scaled up to the local abundance of krill. Only if the total iron release

91   by krill covers a significant part of the phytoplankton iron demand, these processes can be considered

92   important. Therefore, we conducted short-term shipboard incubations of krill as in a previous study

93   [36], with the difference that not only TDFe release rates were measured [36] but also excretion rates

94   of the bioavailable DFe. Stomach content analysis revealed that the DFe excretion rates increased

95   with the initial amount of diatoms in krill stomachs [DFe = -25.07 + 3.59 (Diatoms), R^2 = 0.624, p =

96   0.011] (Fig. 2E), while the TDFe release rates were a function of both the amount of ingested diatoms

97   and lithogenic particles [TDFe = -679 + 66.7 (diatoms) + 31.3 (lithogenic particles), R^2 = 0.659, p =

98   0.025, General Linear Model]. Moreover, there was a strong correlation between TDFe release rates

99   and the dry mass of fecal pellets egested during 3 h-incubations, indicating that fecal pellets were the

100   main source of the released TDFe (Fig. 2F). The total iron supply rates by krill in the upper mixed

101   layer ranged from 0.1 to 31 pM DFe d^{-1}and 5 to 355 pM TDFe d^{-1}. These DFe excetion rates are at the

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102   mid-range of values previously reported for micro- and mesozooplankton and covered up to 30% of

103   the phytoplankton iron demand under bloom conditions (Table S1, S2). These are conservative

104   estimates as on average two-thirds of the krill population resided below the mixed layer and additional

105   DFe released by those krill may have entered surface waters through vertical transport [15].

106   Our study shows that on average >90% of iron ingested by krill is re-packaged into fecal

107   pellets rather than excreted as DFe or incorporated into body tissue (Fig. 3). This is because iron

108   concentrations were 3-4 orders of magnitude higher in krill fecal pellets than in muscle tissue and

109   >90% of the iron released by krill during short-term incubations was in particulate rather than

110   dissolved form. Therefore the cycling of iron ingested by krill is closely linked to the fate of their

111   fecal pellets. We found on average 3.5 times (range: 0.1-17, median: 1.6 times) more fecal material at

112   150 m water depth than at 20 or 50 m, but in the upper depths pellets still accounted for high

113   proportions of the suspended particulate matter (Fig. 1E). This suggests that even though many pellets

114   sink to depth [37,38] and therefore export iron from surface waters, a substantial proportion remains

115   in the upper mixed layer where intensive fragmentation and degradation occur [39,40] and iron is

116   resupplied.

117   Regardless of the fate of these pellets, krill gut passage increases the proportion of labile iron

118   and therefore the likelihood of subsequent iron dissolution due to either photochemical reactions,

119   ligand activity, microbial recycling or zooplankton coprophagy [5,40-42]. Radiotracer experiments

120   have shown that 6-96 pM DFe d^{-1} can be released from copepod fecal pellets, which is similar in

121   extent to iron regeneration from phytoplankton either due to viral lysis or grazing [42]. Thus, in

122   addition to immediate DFe excretion by krill, further DFe may derive from the degradation of fecal

123   pellets and the digestion of krill tissue by predators [42,43]. In conclusion, krill uptake and

124   mobilisation of lithogenic and biogenic iron provides the basis for several pathways of DFe supply.

125   These pathways involve the activity of other organism - microbes, zooplankton, krill predators - as

126   well as abiotic processes (Fig. 3), and in their sum they can deliver a substantial part of the

127   phytoplankton iron demand.

128   In line with our findings, phytoplankton blooms downstream of South Georgia are more

129   intensive and longer-lasting during years of high krill abundance on the shelf (Fig. 4A, Fig. S2).

130   Correlations between median chl a concentration and annual krill abundance show negative slope

131   values across the northern shelf, but positive values in the main bloom area further downstream (Fig.

132   4B). A negative relationship between krill density and phytoplankton abundance has previously been

133   observed at the eastern side of South Georgia, and calculations confirmed that krill grazing rates

134   exceeded the phytoplankton growth rates leading to 'top-down' control [45]. However, the here

135   observed pattern of inverse correlations (negative on-shelf, positive downstream) suggests that high

136   krill grazing pressure has a dual effect: in their main habitat it leads to substantial phytoplankton

137   removal, but phytoplankton benefits from fertilisation after water masses have passed through this

138   area. At our outermost sampling station, ~170 km downstream of the main glacial outlet, subsurface

139   DFe and TDFe concentrations were still enhanced (0.9 nM DFe; 45 nM TDFe, Schlosser unpublished

140   data) relative to HNLC waters (0.1 nM DFe; 3 nM TDFe) (9). Here, the Fe:C ratios of diatom-

141   dominated suspended matter were 2 orders of magnitude higher (3600 ± 330 µmol Fe mol^{-1}) than

142   values reported for diatoms under Fe replete conditions [46]. This indicates that high amounts of both

143   DFe and TDFe can be transported away from South Georgia with the currents and aid subsequent

144   phytoplankton development. Our study shows that iron mobilisation and recycling by krill, combined

145   with the activity of other organisms, significantly enhances DFe supply and recycling in surface

146   waters. Therefore we suggest a causal link between high krill feeding activities on the shelf and

147   intensive, long-lasting phytoplankton blooms downstream.

148   There are undoubtedly other factors that contribute to the exceptional phytoplankton blooms

149   downstream of South Georgia, e.g. shallow mixed layer depths, eddy activities, enhanced availability

150   of macronutrients and luxury iron-uptake by abundant pennate diatoms [15, 47-49]. However, a state-

151   of-the-art hydrodynamic-biogeochemical model without krill was unable to simulate the high chl a

152   concentrations of the South Georgia bloom [50]. The discrepancy between observations and model

153   output suggests that important mechanisms of bloom fertilisation were not addressed in the model.

154   The mobilisation of lithogenic iron by zooplankton has rarely been considered [6], but our study

155   confirms the relevance of this mechanism, especially in regions with high zooplankton abundances

156   such as South Georgia.

157   In conclusion, zooplankton grazers can play a unique role in the marine iron cycle. Firstly, they

158   have efficient access to iron-rich material (e.g. lithogenic particles, large diatoms) and their acidic

159   digestion does not only recycle iron but also lifts new iron from lithogenic sources into the foodweb.

160   Secondly, zooplankton overlap spatially with phytoplankton and therefore the released iron can

161   directly benefit primary production, while DFe from benthic sources [51,52] requires vertical

162   transport into the euphotic zone. Third, zooplankton channel labile iron into fecal pellets which

163   enhances the likelyhood of DFe release via microbial activity or coprophagy. Our study indicates that

164   ocean fertilisation does not only depend on physical iron supply but also on the prevailing foodweb

165   structure that facilitates iron mobilisation and recycling. We are only beginning to understand the

166   complexity of these processes.

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168   **Experimental Procedures**

169   This text summarises the methods used, with the *Supplemental Experimental Procedures* providing

170   full details.

171   **Sampling** Our study took place during a research cruise at the northern shelf of South Georgia

172   (Southern Ocean, 53-54°S; 35-39°W), from December 2010 to January 2011 onboard RRS *James*

173   *Clark Ross*. The station activities included (1) an acoustic survey to estimate local krill densities over

174   the diurnal cycle, (2) live krill sampling for stomach content analysis, fecal pellet production, iron

175   measurements and incubation experiments, (3) collection of suspended particulate matter by Stand-

176   Alone Pump Systems (SAPS) and CTD rosettes for taxonomic identification and iron measurements,

177   (4) water sampling with towed fish and GO-FLO bottles for respective horizontal and vertical profiles

178   of DFe and TDFe.

Krill incubations Under iron-clean conditions, freshly caught krill were rinsed and placed in 9L-polycarbonate carboys filled with 0.2 µm filtered seawater from surface-towed trace metal clean fish. At each station, 2-3 replicate carboys each containing 10-20 krill and 2 control carboys without krill were run at 2°C. The incubation water was sampled for DFe and TDFe initially, after 1h and 3h. At termination of the experiment, the remaining fecal pellets were collected for dry mass estimates.

Iron measurements In a trace metal clean laboratory container onboard ship, water samples for DFe (< 0.2 µm) and TDFe (unfiltered) were acidified with ultra pure HNO_3 to pH 1.66 for subsequent analysis by inductively coupled plasma-mass spectrometry (ICP-MS). The labile particulate iron fraction was remobilised with a 25% acetic acid solution at room temperature for 3h. The refractory particulate iron was digested in a mixture of concentrated HNO_3, HCl and HF acids at 140°C for 4 h. Both labile and refractory particulate iron were analysed by ICP-MS.

Author contributions

Conceptualization, K.S., A.A. and E.P.A.; Methodology, C.S., A.A., K.S. and S.F.; Investigation, C.S., A.A., K.S., S.F., H.J.V. and C.M.W.; Writing – Original Draft, K.S.; Writing – Review & Editing, K.S.,A.A., E.P.A. and C.S.; Funding Acquisition, A.A. , K.S. and E.P.A.

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Figure legends

Figure 1│ Phytoplankton distribution and krill grazing at South Georgia (Southern

Ocean). A, The Southern Ocean with the study area at South Georgia (red box) - overlaying a

chlorophyll *a* (chl *a*) climatology derived from MODIS-Aqua (Jul 2002 - Feb 2015). **B-F,**

Results from our study period: 25th Dec 2010 - 19th Jan 2011. **B,** Distribution of chl *a* (μg L^{-1}).

C, Distribution of krill density (g wet mass m^{-2}). **D,** Proportion of diatoms in the suspended

particulate matter (PM) at 20 m water depth. E, Proportion of fecal pellets in the suspended

particulate matter at 20 m water depth. **F,** Stomach content of freshly-caught krill. (See also

Fig. S1)

Figure 2│ Krill iron cycling.

A-D, Characteristics of freshly-caught krill in relation to the distance from major glacial

outlets (Cumberland Bay). **A,** Volume of lithogenic particles in krill stomachs. **B,** Total

particulate iron content in krill muscle tissue. **C,** Total particulate iron content in krill fecal

pellets. **D,** Labile iron content in suspended particulate matter (PM) at 20 m water depth and in

krill fecal pellets. dm - dry mass. TPFe – total particulate iron. **E-F,** Results from short-term

shipboard incubations of freshly caught krill. **E,** DFe excretion rates in relation to the volume

of diatoms in krill stomachs. **F,** TDFe release rates in relation to the dry mass of fecal pellets

produced during 3h-incubations. (See also Table S2)

Figure 3│Schema of iron flux through krill and pathways of DFe supply. Blue numbers

indicate the partitioning of ingested iron between body tissue, fecal pellets and ambient water

(nmol Fe g^{-1} dm d^{-1}). Black and open arrows schematically represent the relative fractions

sourced from lithogenic- and biogenic iron respectively. Grey arrows indicate processes that

remain to be quantified. In the upper mixed layer, iron ingested and mobilised by krill can lead

to DFe supply via several pathways: A) Fragmentation and digestion of food by krill, B)

Dissolution of particulate iron in fecal pellets due to photochemical reactions and

complexation with ligands. C) Dissolution of particulate iron in fecal pellets due to microbial

395   degradation and zooplankton coprophagy. D) Digestion of krill tissue by predators. (See also

396   Table S3)

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398   **Figure 4│ Interannual differences in krill abundance as a predictor for chl *a***

399   **concentrations at South Georgia. A**, Average chl *a* concentrations in years with low (left)

400   and high (right) krill abundances on the South Georgia shelf. Years with low krill abundances:

401   2002/3, 2003/4, 2004/5, 2008/9, 2010/2011, 2012/2013. Years with high krill abundances:

402   2005/6, 2007/8, 2009/10, 2011/2012. **B**, Spatial distribution of negative (blue-purple) and

403   positive (yellow-red) slope values for the regression between median chl *a* concentration and

404   summer krill abundance at South Georgia for the years 2002-2013. Chl *a* concentrations were

405   derived from ocean colour radiometry (MODIS 2002-2013, mid August-mid April, 8-day

406   composites)**.** The black lines are drifter trajectories, which indicate that the surface current

407   flow links the northern shelf of South Georgia to the main phytoplankton bloom area

408   downstream with a transit time of 20-50 days [44]. (See also Fig. S2)

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