

1 **Where bio- meets geochemistry: Zooplankton gut passage mobilises**
2 **lithogenic iron for ocean productivity**

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23 **Summary**

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

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48 **Results and Discussion**

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

61 Antarctic krill (*Euphausia superba*) is central to the South Georgia foodweb transferring
62 primary production to higher trophic levels including fish, seals, penguins, albatrosses and whales
63 [21]. Highest krill abundances on the eastern side of the island coincide with low chlorophyll *a* (chl *a*)
64 concentrations and the dominance of fecal pellets in the suspended matter of surface waters, which
65 indicates intensive grazing by krill (Fig. 1B-E). However, stomach content analysis reveals that krill
66 do not only feed on phytoplankton but also ingest lithogenic particles and copepods when those are
67 abundant (Fig. 1F). As a consequence, the amount of lithogenic particles in krill stomachs increased
68 exponentially towards the main glacial outlets at Cumberland Bay, reaching >100 fold higher values
69 than at a reference station ~ 170 km away (Fig. 2A). In concert with the increased ingestion of
70 lithogenic particles, krill had up to three-fold higher iron concentrations in their muscle tissue and 1-2
71 orders of magnitude higher iron concentrations in their fecal pellets (Fig. 2B,C). Regardless of the
72 sampling location, krill fecal pellets contained typically higher proportions of labile iron than the
73 suspended material in surface waters [pellets: $2.4 \pm 2.0\%$; suspended material dominated by diatoms:
74 $0.5 \pm 0.5\%$ 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 [$\text{DFe} = -25.07 + 3.59 (\text{Diatoms}), R^2 = 0.624, p =$
96 0.011] (Fig. 2E), while the TDFe release rates were a function of both the amount of ingested diatoms
97 and lithogenic particles [$\text{TDFe} = -679 + 66.7 (\text{diatoms}) + 31.3 (\text{lithogenic particles}), R^2 = 0.659, p =$
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 excretion rates are at the

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 ($3600 \pm 330 \mu\text{mol Fe mol}^{-1}$) 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 likelihood 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.

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

184 **Iron measurements** In a trace metal clean laboratory container onboard ship, water samples for DFe
185 (< 0.2 µm) and TDFe (unfiltered) were acidified with ultra pure HNO₃ to pH 1.66 for subsequent
186 analysis by inductively coupled plasma-mass spectrometry (ICP-MS). The labile particulate iron
187 fraction was remobilised with a 25% acetic acid solution at room temperature for 3h. The refractory
188 particulate iron was digested in a mixture of concentrated HNO₃, HCl and HF acids at 140°C for 4 h.
189 Both labile and refractory particulate iron were analysed by ICP-MS.

190

191 **Author contributions**

192 Conceptualization, K.S., A.A. and E.P.A.; Methodology, C.S., A.A., K.S. and S.F.; Investigation,
193 C.S., A.A., K.S., S.F., H.J.V. and C.M.W.; Writing – Original Draft, K.S.; Writing – Review &
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367 **Figure legends**

368 **Figure 1 | Phytoplankton distribution and krill grazing at South Georgia (Southern**
369 **Ocean). A,** The Southern Ocean with the study area at South Georgia (red box) - overlaying a
370 chlorophyll *a* (chl *a*) climatology derived from MODIS-Aqua (Jul 2002 - Feb 2015). **B-F,**
371 Results from our study period: 25th Dec 2010 - 19th Jan 2011. **B,** Distribution of chl *a* ($\mu\text{g L}^{-1}$).
372 **C,** Distribution of krill density (g wet mass m^{-2}). **D,** Proportion of diatoms in the suspended
373 particulate matter (PM) at 20 m water depth. **E,** Proportion of fecal pellets in the suspended
374 particulate matter at 20 m water depth. **F,** Stomach content of freshly-caught krill. (See also
375 Fig. S1)

376

377 **Figure 2 | Krill iron cycling.**

378 **A-D,** Characteristics of freshly-caught krill in relation to the distance from major glacial
379 outlets (Cumberland Bay). **A,** Volume of lithogenic particles in krill stomachs. **B,** Total
380 particulate iron content in krill muscle tissue. **C,** Total particulate iron content in krill fecal
381 pellets. **D,** Labile iron content in suspended particulate matter (PM) at 20 m water depth and in
382 krill fecal pellets. dm - dry mass. TPFe – total particulate iron. **E-F,** Results from short-term
383 shipboard incubations of freshly caught krill. **E,** DFe excretion rates in relation to the volume
384 of diatoms in krill stomachs. **F,** TDFe release rates in relation to the dry mass of fecal pellets
385 produced during 3h-incubations. (See also Table S2)

386

387 **Figure 3 | Schema of iron flux through krill and pathways of DFe supply.** Blue numbers
388 indicate the partitioning of ingested iron between body tissue, fecal pellets and ambient water
389 ($\text{nmol Fe g}^{-1} \text{ dm d}^{-1}$). Black and open arrows schematically represent the relative fractions
390 sourced from lithogenic- and biogenic iron respectively. Grey arrows indicate processes that
391 remain to be quantified. In the upper mixed layer, iron ingested and mobilised by krill can lead
392 to DFe supply via several pathways: A) Fragmentation and digestion of food by krill, B)
393 Dissolution of particulate iron in fecal pellets due to photochemical reactions and
394 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)

397

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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