



1 **Atmospheric Fe supply has a negligible role in promoting marine productivity in**
2 **the Glacial North Pacific Ocean**

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13 **Abstract**

14 Iron is a key element in the Earth climate system as it can enhance the marine primary productivity in the
15 High-Nutrient Low-Chlorophyll (HNLC) regions where, despite a high concentration of major nutrients, the
16 chlorophyll production is low due to iron limitation. One of the main Fe sources to the ocean is aeolian dust.
17 For this reason, ice cores provide a sensitive and continuous archive for reconstructing Fe fluxes over the last
18 millennia. Here we show the first Northern Hemisphere Fe record retrieved from the NEEM ice core, which
19 offers a unique opportunity to reconstruct the past Fe fluxes in the Arctic region over the last 108 kyr.
20 Holocene Fe fluxes to the Arctic were three times lower than the average recorded over the last glacial
21 period. They were greater during the Last Glacial Maximum (LGM) and the Marine Isotope Stage 4 (MIS 4).
22 Comparing our data with palaeoceanographic records retrieved from the HNLC North Pacific, we
23 demonstrated that during the coldest periods, characterized by the highest Fe fluxes, marine productivity in
24 the subarctic Pacific Ocean did not increase due to a greater sea-ice extent and the absence of upwelling
25 nutrient supply. This supports the hypothesis that Fe-fertilization was more effective in other regions, such as



26 the transition zone of the North Pacific, where a closer relationship between marine productivity and the
27 aeolian Fe fluxes was observed.

28 **1. Introduction**

29 Greenland and Antarctic ice cores are unique archives that can provide information about how
30 temperature, atmospheric dust load and atmospheric gas composition have changed during the Holocene and
31 the late Pleistocene (Lambert et al., 2008; Schüpbach et al., 2018). Glacial periods were dustier and with a
32 lower CO₂ concentration (≈ 180 ppm) than interglacials (≈ 280 ppm). This dichotomy was explained through
33 different hypotheses: the increase in aridity and in newly exposed continental shelves (Fuhrer et al., 1999),
34 the enhancement of the atmospheric circulation (Delmas and Legrand, 1989), the increase in the aerosol
35 atmospheric life-time (Yung et al., 1996), the enhancement of glacier mobilization of highly bioavailable
36 iron from the bedrock (Shoenfelt et al., 2018) and, lastly, the enhancement of the polar circulation that might
37 have entrained additional dust from lower latitudes (Mayewski et al., 1994). The higher atmospheric dust
38 loading during glacial periods affected climate in both physical and biological ways. On the one hand, dust
39 particles absorbed and scattered the incoming solar radiation and the outgoing infrared radiation with a direct
40 effect on the Earth energy budget. On the other hand, once deposited on the ocean surface, the mineral dust
41 provided major and micronutrients (including iron) that could have stimulated the biological carbon pump
42 (Martin et al., 1990). This iron mediated mechanism has been demonstrated for the High-Nutrient Low-
43 Chlorophyll (HNLC) regions, whose productivity is primarily Fe-limited, both through artificial (Smetacek
44 et al., 2012; Yoon et al., 2018) and natural (Duprat et al., 2016; Langmann et al., 2010) Fe-fertilization
45 processes. It has been inferred that the observed decrease in the atmospheric CO₂ concentration during
46 glacial periods was linked to the Fe-modulated enhancement of the biological carbon pump in the Southern
47 Ocean due to the increase in Fe availability (Martin et al., 1990). However, according to both modeling
48 (Lambert et al., 2015) and observational (Gaspari et al., 2006; Röthlisberger, 2004; Vallelonga et al., 2013)
49 studies, the Fe-fertilization mechanism itself cannot completely explain the ≈ 100 ppmv glacial-interglacial
50 atmospheric CO₂ variability, but only around 8-20 ppmv of it.

51 Studies on leachable iron in ice cores were performed in Antarctica from Talos Dome (TD) (Spolaor et
52 al., 2013; Vallelonga et al., 2013), Law Dome (LD) (Edwards et al., 2006; Edwards et al., 1998) and EPICA



53 Dome C (DC) (Wolff et al., 2006). During the Holocene, the average flux and concentration values varied
54 significantly among the different sites with similar values recorded at TD and LD and lower values at DC
55 (Table 3). For TD, this was explained both through changes in atmospheric transport patterns across
56 Antarctica and through a local input of dust from proximal Antarctic ice-free zones that affected coastal sites
57 more than the central plateau (Albani et al., 2012; Delmonte et al., 2010; Vallelonga et al., 2013). During the
58 LGM, the Fe fluxes were similar among the different Antarctic sites, suggesting a homogeneous atmospheric
59 load over the entire Antarctic continent.

60 Unfortunately, few reconstructions of Arctic Fe fluxes exist and they are limited to the last centuries
61 (Burgay et al., 2019; Hiscock et al., 2013). Reconstructing how the Fe concentrations and fluxes have
62 changed in the Northern Hemisphere in the last millennia is essential to understand the evolution of the
63 global atmospheric circulation, the human impact on dust mobilization (Mahowald et al., 2008) and to
64 evaluate the impact on Marine Primary Production (MPP) in the North Pacific HNLC regions. Here, we
65 present a 108 kyr record of leachable Fe retrieved from the North Greenland Eemian Ice Drilling (NEEM)
66 ice core (Rasmussen et al., 2013; Schüpbach et al., 2018), which provides a unique insight on the iron supply
67 in the Arctic both during the Holocene and the last Glacial. Furthermore, we performed a comparison
68 between the Fe NEEM record and different palaeoproductivity records from the HNLC North Pacific region
69 to evaluate if the increase in aeolian Fe fluxes was mirrored by an increase in marine productivity.

70 **2. Materials and methods**

71 **2.1 Sampling site**

72 In the framework of the NEEM project, a 2540 m-depth ice core was drilled in north-western
73 Greenland (77°45'N, 51°06'W) at 2479 m.a.s.l. The site is characterized by an average annual temperature
74 of -29°C and a modern accumulation of 22 cm ice equivalent per year. According to the GICC05modelext-
75 NEEM-1 timescale, the ice core covers the last 128 kyrs (Rasmussen et al., 2013). The ice cores were cut to
76 obtain ice sticks with a square cross section of 36x36 mm. They were continuously melted on a continuous
77 flow analysis (CFA) system with a typical melt-speed of 3.5 cm min⁻¹ (Schüpbach et al., 2018). A low-
78 resolution (110 cm) sampling apparatus, collecting discrete samples for ICPMS analyses, was coupled to the
79 CFA system. The CFA system provides meltwater from the inner and not contaminated part of the core, thus



80 we did not adopt any further decontamination procedure. The temporal resolution depends on the
81 accumulation rate and it decreases with depth because of the ice thinning. According to the available
82 timescale (Rasmussen et al., 2013) and considering the 110 cm sampling resolution, the temporal resolution
83 varies from decadal to millennial (Table 1).

84 Samples were collected in vials previously cleaned as follows: 7 days with HNO₃ 5% (Suprapure, Romil,
85 UK), rinsed three times with Ultrapure water (UPW, Elga, UK), 7 days with HNO₃ 2% % (Suprapure,
86 Romil, UK), rinsed three times with UPW and dried under a laminar flow hood Class 100. The samples were
87 kept frozen and shipped to Italy for analysis. Once melted, the samples were acidified to pH 1 using HNO₃
88 (Suprapure, Romil, UK). To ensure an effective dissolution of iron particles, samples were analysed 30 days
89 after the acidification.

90 **2.2 Analytical procedure and performances**

91 The ice samples were analysed with an Inductively Coupled Plasma Single Quadrupole Mass Spectrometer
92 (ICP-qMS, Agilent 7500 series, USA) equipped with a quartz Scott spray chamber. This allowed a
93 comparison with previous studies on Antarctic ice cores (Gaspari et al., 2006; Vallelonga et al., 2013). To
94 minimize any kind of contamination, all the instrument tubes were flushed before the analysis for 2 hours
95 with 2% HNO₃ (Suprapure, Romil, UK). A 120 seconds rinsing step with 2% HNO₃ (Suprapure, Romil, UK)
96 was performed after each sample to limit any possible memory effect, the vials used for the standard
97 preparation were cleaned following the same procedure adopted for the ice samples. Considering the isobaric
98 and polyatomic interferences affecting Fe, its quantification was performed using the interference-free
99 isotope ⁵⁷Fe. Its quantification was performed using external calibration curves with acidified standards (2%
100 HNO₃, Suprapure, Romil, UK) from dilution of a certified 1000 ppm ± 1% standard solution (Fisher
101 Chemical, USA). The resulting R² for the external calibration curves was 0.999. The Limit of Detection
102 (LoD) for ⁵⁷Fe, calculated as three times the standard deviation of the blank, was 0.8 µg L⁻¹. Accuracy and
103 precision were evaluated using the TM-RAIN04 certified reference material produced by the National
104 Research Council of Canada. The accuracy was determined as a recovery percentage calculated as O/T%,
105 where O is the determined value and T is the certified value. For Fe, the accuracy was 104%, while
106 precision, calculated as Relative Standard Deviation (RSD%), was 5%.



107 **3. Results**

108 **3.1 Iron fluxes from the NEEM core**

109 Iron concentrations and fluxes, calculated as $F = C \cdot A$ (where F is the Fe flux, expressed in $\text{mg m}^{-2} \text{yr}^{-1}$
110 ¹, C is the Fe concentration and A the accumulation, whose values are from Rasmussen et al., 2013) over the
111 last 108 kyrs are reported in Table 2 and Figure 1. A pattern of higher dust (expressed as nssCa^{2+}) and Fe
112 fluxes during colder climate periods and lower dust and Fe fluxes during warmer climate periods is clearly
113 recognizable.

114 The Holocene (Figure 1) was characterized by average Fe fluxes of $0.06 \text{ mg m}^{-2} \text{yr}^{-1}$ which varied
115 between $0.01 \text{ mg m}^{-2} \text{yr}^{-1}$ and $0.45 \text{ mg m}^{-2} \text{yr}^{-1}$. The Coefficient of Variability (CV), calculated as the ratio
116 between the standard deviation and the mean value, was 1.2. The last 4000 years were characterized by the
117 highest average Fe fluxes ($0.09 \pm 0.08 \text{ mg m}^{-2} \text{yr}^{-1}$). The lowest Fe fluxes were recorded between 4000 and
118 8000 years b2k ($0.03 \pm 0.02 \text{ mg m}^{-2} \text{yr}^{-1}$). During the Younger Dryas (YD, 11.7 – 12.9 kyr b2k), an abrupt
119 cooling was observed with a drop in the $\delta^{18}\text{O}$ value from -36.9‰ to -43.1‰ . The recorded average Fe fluxes
120 were $0.13 \pm 0.05 \text{ mg m}^{-2} \text{yr}^{-1}$, higher than both the 12.9-13.9 kyr b2k ($0.06 \pm 0.03 \text{ mg m}^{-2} \text{yr}^{-1}$) and the 10.7-
121 11.7 kyr b2k ($0.03 \pm 0.02 \text{ mg m}^{-2} \text{yr}^{-1}$) periods.

122 The glacial period (11.7-108 kyr b2k) showed Fe fluxes three-times higher ($0.2 \text{ mg m}^{-2} \text{yr}^{-1}$, CV =
123 1.0) than the Holocene, spanning from 0.01 to $1.80 \text{ mg m}^{-2} \text{yr}^{-1}$ (Figure 1). A significant variability during the
124 last glacial period was detected. During the LGM and MIS 4, average Fe fluxes were six ($0.4 \pm 0.3 \text{ mg m}^{-2}$
125 yr^{-1}) and ten-times ($0.6 \pm 0.3 \text{ mg m}^{-2} \text{yr}^{-1}$) greater than the Holocene average. Fe fluxes also increased during
126 MIS 5b (82-87 kyr b2k) when a concurrent decrease in $\delta^{18}\text{O}$ values was observed. During MIS 5c and MIS
127 5d, Fe fluxes were comparable with those detected during the Holocene. The high frequency of the
128 Dansgaard-Oeschger (D-O) events that characterized MIS 3 is mirrored by the high variability in both nssCa
129 and Fe fluxes. Each stadial period corresponded to an increase in both Fe and nssCa . However, their
130 variability was significantly different. During MIS 3, Fe fluxes showed maxima values greater than 0.7 mg
131 $\text{m}^{-2} \text{yr}^{-1}$ during D-O 15, 13 and 5 (0.729 , 0.819 and $0.933 \text{ m}^{-2} \text{yr}^{-1}$ respectively), and lower than $0.3 \text{ mg m}^{-2} \text{yr}^{-1}$
132 ¹ during D-O 12, 11, 10 and 8 (0.128 , 0.274 , 0.290 and $0.286 \text{ m}^{-2} \text{yr}^{-1}$ respectively). This variability was
133 significantly higher than the one recorded for nssCa , which showed maxima values closer to $2 \text{ mg m}^{-2} \text{yr}^{-1}$ for



134 all the D-O events. As an example, the nssCa maxima for D-O 15 and D-O 12 were 2.1 and 2.0 m² yr⁻¹
135 respectively.

136 **3.2 Comparison with Fe fluxes from Antarctic ice cores**

137 The NEEM iron ice core record allows the first comparison of leachable Fe concentrations and
138 fluxes between the Arctic and Antarctica (Figure 2) focusing on the Holocene, LGM and MIS 4 periods
139 (Table 3).

140 During the Holocene, average Fe fluxes in both NEEM (0.06 mg m⁻² yr⁻¹, CV = 1.2) and Talos Dome
141 (0.09 mg m⁻² yr⁻¹, CV = 1.2), were of the same order of magnitude suggesting a similar contribution from
142 aeolian mineral dust in both sites. They were significantly greater than the ones recorded in Law Dome (0.04
143 mg m⁻² yr⁻¹, CV = 0.5) and Dome C (0.007 mg m⁻² yr⁻¹, CV = 0.2). As previously mentioned, the greater Fe
144 fluxes in TD than in the other Antarctic sites, was related to the activation of a dust deflation area which
145 influenced Victoria Land more than the central Antarctic Plateau (Delmonte et al., 2013).

146 The LGM (19 – 26.5 kyr b2k) showed Fe fluxes on the same order of magnitude among NEEM (0.4 mg
147 m⁻² yr⁻¹, CV = 0.6), TD (0.4 mg m⁻² yr⁻¹, CV = 0.5), LD (0.4 mg m⁻² yr⁻¹, CV = 0.7) and DC (0.2 mg m⁻² yr⁻¹,
148 CV = 0.5). Considering that the atmospheric CO₂ concentration dropped down to 180 ppm (Köhler et al.,
149 2017), the global enhancement of the Fe fluxes likely contributed to part of this decrease, enhancing marine
150 productivity in some HNLC regions (Amo and Minagawa, 2003; Kawahata et al., 2000; Martínez-García et
151 al., 2011)

152 MIS 4 (60-71 kyr b2k) was characterized by higher Fe fluxes in NEEM (0.6 mg m⁻² yr⁻¹, CV = 0.5) than
153 in Antarctica. Indeed, Fe fluxes both in TD (0.2 mg m⁻² yr⁻¹, CV = 0.5) and DC (0.09 mg m⁻² yr⁻¹, CV = 0.7)
154 were substantially lower suggesting a particularly enhanced deflation from Asian deserts (e.g. high wind
155 speeds, enhanced dustiness over the East Asian desert regions, increased aridity related to changes in the
156 Asian monsoon system) (Schupbach et al., 2018).

157 **3.3 Iron and marine productivity in the Northern Hemisphere**

158 Considering the biological relevance of Fe and taking advantage from the Fe flux record retrieved from
159 the NEEM ice core, we questioned if the increase in its fluxes triggered the marine productivity in the HNLC



160 region of the North Pacific. Our interpretation is based on Fe fluxes retrieved from samples, which were
161 acidified with 2% HNO₃ for one month before the analysis. Therefore, they do not directly represent the
162 actual bioavailable Fe that can be dissolved into seawater at pH 8, but rather an upper limit of the aeolian Fe
163 potentially available for the phytoplankton (Edwards et al., 2006).

164 Geochemical evidence showed that the dust source that influences Greenland and the North Pacific
165 is the same and it originates in both cases from the East Asian deserts (Schüpbach et al., 2018; Serno et al.,
166 2014). A significant amount of Asian dust (250 Mt yr⁻¹) is mainly deposited over the HNLC region of the
167 subarctic Pacific (Serno et al., 2014; Zhang et al., 2003) and the marine productivity changes in this oceanic
168 region might reflect the possible Fe fertilization effects promoted by an increase in the atmospheric Fe
169 supply. Both increases in aeolian influx from Asia (Young et al., 1991) and sporadic Fe input from volcanic
170 eruptions (Langmann et al., 2010) caused an enhancement in MPP by more than 60% in this region.
171 Moreover, Fe-fertilization experiments performed south of the Gulf of Alaska (McDonald et al., 1999; Tsuda
172 et al., 2003), showed significant increases in the abundance of diatoms and in chlorophyll-a concentration
173 (Boyd et al., 1996). This indicates that the North Pacific is rather sensitive to atmospheric iron inputs.
174 However, no data are available to evaluate if the Fe-sensitivity of the subarctic Pacific Ocean holds over
175 even longer timescales and if an increase in the aeolian Fe supply, observed during glacial periods, could
176 explain the MPP variability in the subarctic Pacific Ocean. To address this point, we compared the NEEM Fe
177 record with different marine sediment cores. For the period that ranges from the LGM to the Holocene we
178 compared our record with the high-resolution SO202-27-6 (from the Patton-Murray Rise plateau, eastern
179 subarctic Pacific Ocean) and the SO202-07-6 (from the Detroit Seamount, western subarctic Pacific Ocean)
180 productivity records (Méheust et al., 2018). For a long-term record, we relied on the ODP887 (McDonald et
181 al., 1999) and the ODP882 (Haug et al., 1995) sediment cores, located close to SO202-27-6 and SO202-07-6,
182 respectively. A comparison over the last 108 kyr between the NEEM record and the S-2 sediment core (from
183 the Shatsky Rise, transition zone) was also performed (Amo and Minagawa, 2003) (Figure 3, Table 4). This
184 location shares, together with the northernmost sediment cores, the same Asian dust source and it is thus
185 considered representative for the evaluation of the possible Fe-fertilization effects on MPP (Kawahata et al.,
186 2000).

187 3.3.1 From the LGM to the Holocene



188 During the Last Glacial Maximum, the Fe fluxes recorded in the NEEM ice core were up to 7 times
189 higher than during the Holocene. However, marine productivity in the subarctic Pacific Ocean, expressed as
190 Si/Al ratio (McDonald et al., 1999), % biogenic silica (Haug et al., 1995) and Brassicasterol concentration
191 (Méheust et al., 2018), was at its lowest level (Figures 3, 4). Other records highlighted the same behaviour
192 with a minimum in palaeoproductivity during the LGM and a maximum during the Bølling-Allerød (B/A)
193 warm period (Ren et al., 2015). This can reflect the absence of key conditions that can intensify primary
194 production such as the presence of a well-developed water stratification (McDonald et al., 1999).

195 Reconstructions based on the foraminifera-bound $\delta^{15}\text{N}$ (FB- $\delta^{15}\text{N}$), a proxy which indicates the degree
196 of nitrate consumption by phytoplankton (Martínez-García et al., 2014), showed that, in the western
197 subarctic Pacific Ocean, the nitrate consumption was more complete during the LGM and the YD, when
198 MPP was low, than during the warmest periods (Ren et al., 2015). This apparent contradiction was explained
199 through an increase in the water stratification during the coldest periods (Francois et al., 1997) which led the
200 system towards a major-nutrient limitation. Indeed, the enhanced Fe supply from the aeolian mineral dust,
201 observed during the LGM and YD, determined an increase in the FB- $\delta^{15}\text{N}$ values, that is in the nitrate
202 consumption (Ren et al., 2015). However, because of the stronger water stratification (either by reduced
203 upwelling or vertical mixing), the nitrate supply from bottom waters was limited and this might have limited
204 the MPP (Kienast et al., 2004; Ren et al., 2015).

205 An additional explanation arises from the higher extent of perennial sea-ice that might have played a
206 role in creating a physical barrier between the atmosphere and the marine environment, reducing the amount
207 of available sunlight and the deposition of bioavailable Fe on seawater (Kienast et al., 2004; Méheust et al.,
208 2018). Marine sediment records, collected in the eastern and western subarctic Pacific and in the Bering Sea,
209 showed extended spring ice-cover during the LGM (Méheust et al., 2018; Méheust et al., 2016) when the Fe
210 fluxes were at their maxima. The progressive decrease in perennial sea-ice coverage recorded after the LGM
211 led to an increase in the marine productivity (Figure 4) with a maximum during the Bølling-Allerød (B/A)
212 warm event (\approx 13-15 kyr ago). The possible relevance of sea-ice in modulating MPP at the highest latitude of
213 the Pacific Ocean during the LGM is strengthened by a marine sediment record collected in the transition
214 zone (Amo and Minagawa, 2003), which, because of its southernmost location, did not experience any sea-
215 ice condition. During the LGM, contrarily to what is observed in the subarctic Pacific, a prominent



216 maximum in marine productivity was recorded, suggesting that Fe could have triggered an important
217 phytoplankton response (Figure 4). The Fe-sensitivity of the transition zone is confirmed during the
218 Holocene, when the Fe fluxes were at their minima and the productivity, expressed as MAR (Mass
219 Accumulation Rate) C_{37} alkenone ($\mu\text{g cm}^{-2} \text{ kyr}^{-1}$), was at its lowest level. A plausible explanation is that this
220 region was not characterized by stratified waters and thus it was not affected by the limitation of major
221 nutrients. Unfortunately, neither $\text{FB-}\delta^{15}\text{N}$ nor information about water stratification are available for this
222 record.

223 **3.3.1 From 108 kyr to the LGM**

224 According to the available records, marine productivity changed heterogeneously in the Pacific
225 Ocean during the last glacial period (Figure 3).

226 It is challenging to state, with a high degree of confidence, whether Fe-fertilization triggered a
227 phytoplankton bloom or not in the HNLC subarctic North Pacific. This is due to the different responses that
228 the western and the eastern sides showed with respect to the atmospheric iron supply (Figure 2). In the
229 eastern subarctic Pacific, the increase in the Aeolian Fe fluxes was mirrored by a phytoplankton response
230 during the MIS 5.2 and the MIS 5 / MIS 4 transition. The subsequent decrease in MPP during the MIS 4
231 suggests that the prolonged Fe supply during the coldest interstadial might have led the ecosystem towards
232 the limitation of other nutrients (Kienast et al., 2014) following the similar mechanisms described in the
233 previous section. The enhanced water stratification during those periods, as suggested by stable oxygen
234 isotope ratios in planktonic foraminifera (Zahn et al., 1991), did not allow a supply of macronutrients from
235 below the mixed layer. Thus, the additional atmospheric iron supply did not cause any additional effect on
236 the phytoplankton, providing additional clues that their growth was likely limited by the lack of major
237 nutrients (Kienast et al., 2004). In the western subarctic Pacific, the increase in productivity was recorded
238 also in periods with low atmospheric Fe fluxes (e.g. from 100 to 90 kyr at ODP882), strengthening the
239 hypothesis that other players (e.g. meltwater inputs, continental margin supply, sea-ice) had a more relevant
240 role (Kienast et al., 2004; Lam and Bishop, 2008).

241 On the contrary to what was observed in the subarctic Pacific, the S-2 sediment core collected in the
242 transition zone (Amo and Minagawa, 2003), showed a marked increase in primary productivity during MIS 4



243 and the overall last glacial period when the Fe fluxes were higher (Figure 3). This indicates that the MPP in
244 the transition zone of the North Pacific was sensitive to the atmospheric Fe supply, suggesting that the high
245 degree of upper ocean stratification that characterized the subarctic region of the Pacific Ocean did not likely
246 affect the transition zone. This, could have allowed a continuous supply of macronutrients so that the
247 increase in dust transport (and Fe deposition) could have stimulated the productivity (Kienast et al., 2004).

248 **4. Conclusions and future perspectives**

249 In this study, we provided the first Fe record retrieved from the NEEM ice core. Through the comparison
250 with other available Fe records, we observed that during the Holocene, the Fe fluxes were similar between
251 TD and NEEM, while during the LGM all the investigated records showed Fe fluxes on the same order of
252 magnitude. The greatest difference arose during the MIS 4, when Fe fluxes in NEEM were 3 and 7 times
253 higher than in TD and DC respectively.

254 Merging our record with marine productivity data, we found that a direct link between Fe transport and
255 ocean productivity holds only in the transition zone of the North Pacific. On the contrary, in the subarctic
256 Pacific, we did not find any overwhelming evidence that the increase in the atmospheric Fe fluxes triggered a
257 phytoplankton response. This indicates that other players, such as sea-ice and increased water stratification
258 during the coldest periods have a more relevant role in modulating the MPP in the HNLC region of the North
259 Pacific on a millennial time scale.

260 This study provided an upper limit for the potentially available Fe for the phytoplankton, meaning that
261 other studies, that aim to analyse the most labile and bioavailable Fe fractions, are needed to better constrain
262 the actual Fe bioavailability to the marine ecosystem.

263

264 **Data availability**

265 Data will be published on Pangaea

266 **Author contributions**



267 FB wrote the manuscript. FB, AS and CB designed the research. JG, CT and GC performed the analyses. PV
268 contributed to the interpretation of the results.

269 **Competing interests**

270 The authors declare that they have no conflict of interest.

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278 NSF, Office of Polar Programs).
279



280 **Figures and tables**

281

282 **Figure 1** $-\delta^{18}\text{O}$ (blue line) profile is from the NGRIP ice core, while $nss\text{Ca}^{2+}$ (red line) and Fe (black line)
283 fluxes are from the NEEM ice core. YD: Younger Dryas, BA: Bølling-Allerød. Numbers in the bottom panel
284 indicate the Dansgaard-Oeschger events.

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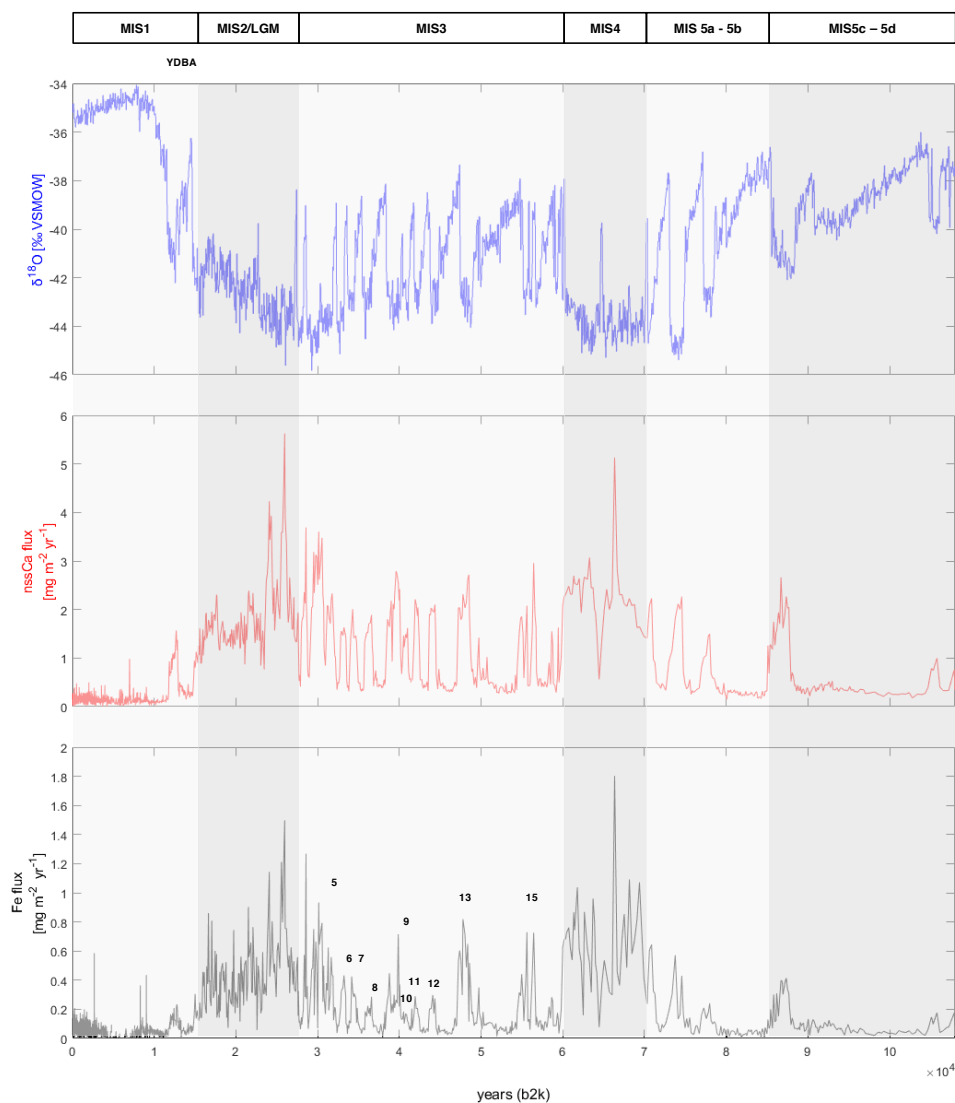
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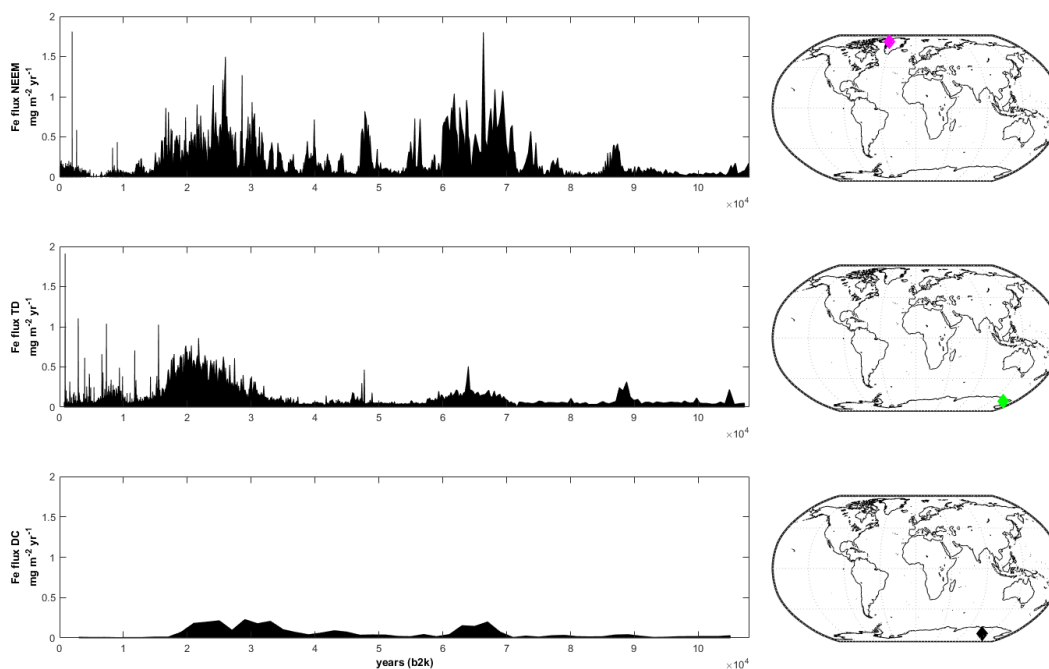




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313 **Figure 2** – Comparison of the Fe fluxes among NEEM (this work), TD (Vallelonga et al., 2013) and EDC
314 (Wolff et al., 2006)

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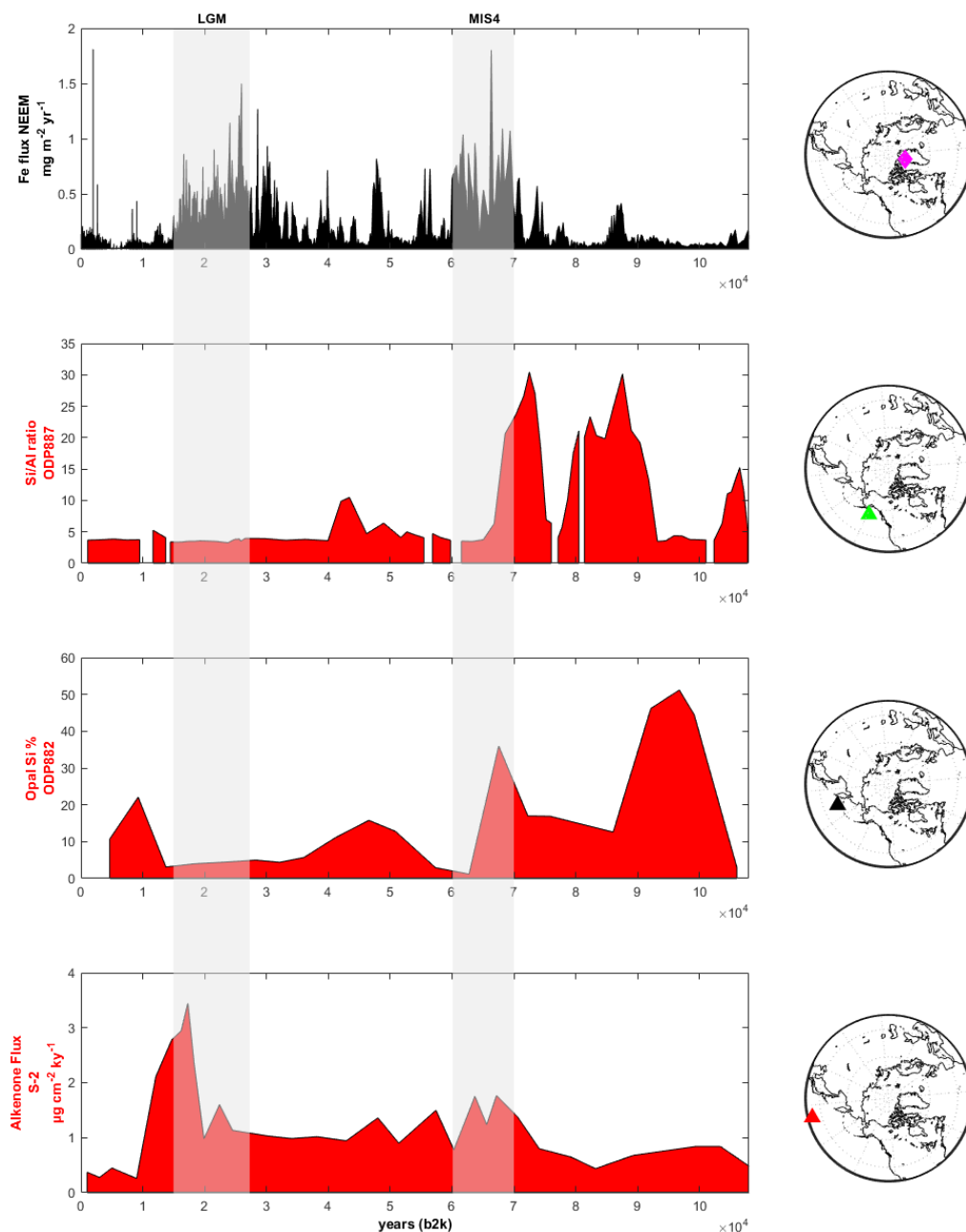
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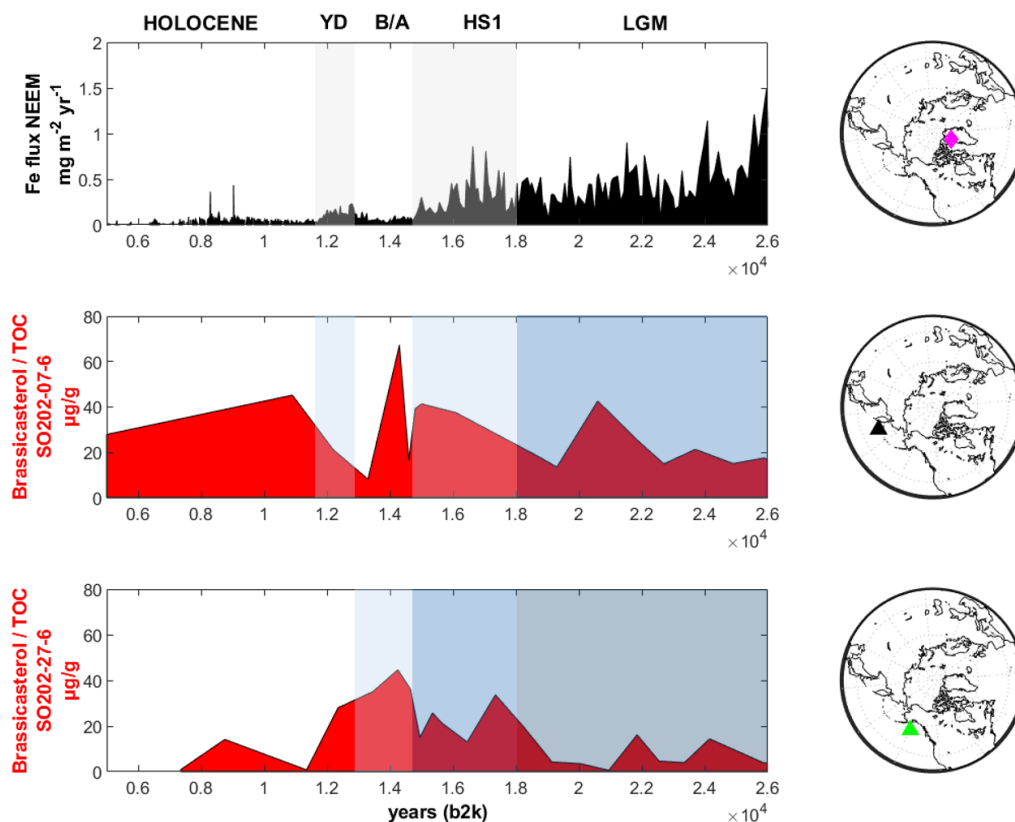
332 **Figure 3** – Comparison between Fe fluxes (black line) from NEEM (this work), with marine productivity
333 (red lines) from ODP887, eastern subarctic Pacific (McDonald et al., 1999), ODP882, western subarctic
334 Pacific (Haug et al., 1995) and S-2, transition zone (Amo and Minagawa, 2003). Due to their limited
335 temporal extension, productivity records from SO202-07-6 and SO202-07-26 are not discussed in this figure,
336 but in Figure 4.



337



338 **Figure 4** – Focus on the last 26 kyr and the possible influence of sea-ice in regulating MPP in the subarctic
339 Pacific Ocean. Sea-ice data are from Meheust et al. (2018): prevalently extended sea-ice (dark blue),
340 prevalently marginal sea-ice (blue), prevalently variable sea-ice (light blue), prevalently ice-free (white). Fe
341 flux record (black line), productivity in the eastern subarctic Pacific Ocean (SO202-07-6, red line, from
342 Meheust et al., (2018)), and productivity in the western subarctic Pacific Ocean (SO202-27-6, red line, from
343 Meheust et al (2018)). Productivity pulses were recorded when sea-ice changed its conditions towards ice-
344 free conditions. YD = Younger Dryas, B/A = Bolling-Allerod event, HS1 = Heinrich Stadial 1, LGM = Last
345 Glacial Maximum.



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351 **Table 1** - Ice samples for ICP-MS analysis were collected with a resolution of 110 cm. According to the
 352 GICC05modelext-NEEM-1 age scale (Rasmussen et al., 2013), the temporal resolution is reported below.

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Temporal resolution	Period
10 years	Holocene (post-7.2 kyr)
22 years	Holocene (pre-7.2 kyr)
110 years	Last Glacial Maximum
73 years	Interstadials
147 years	28-59 kyr
440 years	59-70 kyr
220 years	70-96 kyr
730 years	96-110 kyr

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357 **Table 2** – Fe average concentration (ng g^{-1}) and fluxes ($\text{mg m}^{-2} \text{yr}^{-1}$) from the NEEM ice core. More details in
 358 the text. The Coefficient of Variability (CV) was calculated for Fe fluxes and it is reported in bold

	Fe average concentration /ng g^{-1}	Fe average fluxes $\text{/mg m}^{-2} \text{yr}^{-1}$
Holocene <i>(0.042 -11.7 kyr b2k)</i>	2.9	0.06 (CV 1.2)
Glacial <i>(11.7– 108 kyr b2k)</i>	44.3	0.2 (CV 1.0)
Younger Dryas <i>(11.7 – 12.9 kyr b2k)</i>	18.2	0.1 (CV 0.4)
LGM <i>(14.5 – 26.5 kyr b2k)</i>	86.3	0.4 (CV 0.6)
MIS 3 <i>(26.5 – 60 kyr b2k)</i>	45.5	0.2 (CV 0.9)
MIS 4 <i>(60 - 71 kyr b2k)</i>	146.4	0.6 (CV 0.5)
MIS 5a-MIS 5b <i>(71-87 kyr b2k)</i>	17.0	0.15 (CV 1.0)
MIS 5c-MIS 5d <i>(87-108 kyr b2k)</i>	6.5	0.07 (CV 0.8)

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367 **Table 3** – Comparison of Fe concentration ([Fe] in ng g^{-1}) and Fe fluxes (in $\text{mg m}^{-2} \text{yr}^{-1}$) among four
 368 different ice cores: NEEM, Talos Dome (Vallelonga et al., 2013), Law Dome (Edwards et al., 2006) and
 369 Dome C (Gaspari et al., 2006; Wolff et al., 2006). n.a. = not available. Fe concentration at DC is not
 370 available since the accumulation rate at that site during MIS4 is unavailable. Data from Law Dome spans
 371 from 59 to 8.5 b2k (for the Holocene) and from 18.2 to 23.7 b2k (for the LGM). The Coefficient of
 372 Variability (CV) was calculated for Fe fluxes and it is reported in bold for all the cores.

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	Greenland		Antarctica					
	NEEM		Talos Dome		Law Dome		Dome C	
	[Fe] / ng g^{-1}	Fe flux / $\text{mg m}^{-2} \text{yr}^{-1}$	[Fe] / ng g^{-1}	Fe flux / $\text{mg m}^{-2} \text{yr}^{-1}$	[Fe] / ng g^{-1}	Fe flux / $\text{mg m}^{-2} \text{yr}^{-1}$	[Fe] / ng g^{-1}	Fe flux / $\text{mg m}^{-2} \text{yr}^{-1}$
Holocene (0.042 - 11.7 kyr b2k)	2.9	0.06 (CV 1.2)	1.4	0.09 (CV 1.2)	0.09	0.04 (CV 0.5)	0.2	0.007 (CV 0.2)
LGM (14.5 -26.5 kyr b2k)	86.3	0.4 (CV 0.6)	10.3	0.4 (CV 0.5)	2.4	0.4 (CV 0.7)	16	0.2 (CV 0.5)
MIS4 (60- 71 kyr b2k)	146.4	0.6 (CV 0.5)	3.1	0.2 (CV 0.5)	n.a.	n.a.	n.a.	0.09 (CV 0.7)

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376 **Table 4** – Summary of locations and data source for all the cores (both ice and sediment cores) discussed in
 377 the text (NH = Northern Hemisphere; SH = Southern Hemisphere)

Name	Core	Location	Reference	Latitude/Longitude
NEEM ice	Ice core	NH	<i>This work</i>	77°45'N, 51°06'W
Talos Dome	Ice core	SH	Vallelonga et al., 2013	73°0'S 158°0'E
Dome C	Ice core	SH	Wolff et al., 2006	75°06'S; 123°23' E
ODP882	Marine sediment	NH	Haug et al., 1995	50°22'N; 167°36'E
ODP887	Marine sediment	NH	McDonald et al., 1999	54°22'N; 148°27'W
SO202-27-6	Marine sediment	NH	Meheust et al., 2018	54°12'N; 149°36'W
SO202-07-6	Marine sediment	NH	Meheust et al., 2018	51°16'N; 167°42'E
SO202-18-6	Marine sediment	NH	Meheust et al., 2018	60°08'N; 179°26' W
S-2	Marine sediment	NH	Amo and Minagawa, 2003	33°22'N; 159°08'E

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