REVIEWER 1

This manuscript presents an important and timely contribution to our understanding of atmospheric iron deposition and its potential role in regulating marine productivity during the Pleistocene–Holocene transition. By generating the first continuous records of FeICP and operationally defined dissolved iron (DFe) from the EGRIP ice core, the authors provide a high-resolution perspective on how iron speciation, rather than total iron flux alone, varied across a major climatic transition. The study is carefully executed, clearly written, and well situated within the long-standing debate surrounding the "iron hypothesis" and its regional expression in HNLC systems. In particular, the finding that dissolved iron increased only modestly during the Younger Dryas, despite a large enhancement in total iron, represents a valuable constraint on the effectiveness of aeolian iron fertilization in the North Pacific region.

Overall, this study represents a significant methodological and conceptual advance. By shifting the focus from total iron flux to iron solubility and chemical form, the authors provide a more nuanced framework for evaluating the climatic impact of atmospheric iron deposition. With minor clarifications regarding bioavailability and broader oceanographic implications, this manuscript will be of high interest to the paleoclimate, biogeochemistry, and Earth system science communities.

We thank the reviewer for the feedback.

1. Age model and chronological constraints

- How sensitive are the observed millennial- to centennial-scale variations in FeICP and DFe to uncertainties in the EGRIP age model?

The age uncertainty of the EGRIP chronology over the studied interval is estimated to be between 89 and 141 years (L85–86). Given that the observed variations in the Fe records occur on centennial to millennial timescales (with progressively higher concentrations between 11.6-12.9 ka), this level of uncertainty does not affect the identification or interpretation of the main features associated with the Pleistocene–Holocene transition.

- Could short-term depositional variability or age-model smoothing influence the alignment between iron speciation, acidity, and climatic transitions (e.g., the Younger Dryas)?

The good alignment between iron, acidity and the $\delta^{18}O$ data is preserved both using the nominal 1-cm resolution (i.e., monthly resolution) and a 10-year moving average (Figure 1). This means that short-term depositional variability did not influence the alignment between the considered variables and the climatic transitions.

2. Analytical methods and proxy interpretation

- How robust is the operational definition of CFA-derived DFe as a "labile" iron fraction across different aerosol sources and depositional conditions?

We adopt the operational definition of CFA-derived DFe following Hiscock et al. (2013) and Traversi et al. (2004), where Fe quantified through online absorption measurements corresponds to the fraction readily leachable at pH ~1.6. This operationally defined pool includes dissolved and weakly bound Fe species, while excluding more refractory mineral

phases. Please note that, following comments from reviewer #3, we now define iron detected with the absorption methodology as labile iron (LFe).

The interpretation of CFA-derived LFe as a labile fraction is further supported by comparisons with FeICP measurements (Erhardt et al., 2019), where soluble iron, defined as the background signal from single-particle measurements, accounts for ~20–30% of Fe_{ICP} during the Holocene, consistent with the results presented here. As noted in L65–67, this labile fraction likely corresponds to the pool of iron most prone to become bioavailable, as it can be more readily complexed by phytoplankton siderophores.

In the introduction we added this paragraph:

This iron corresponds to an easily leachable and labile fraction, which accounts for 20-30% of FeICP (Erhardt et al., 2019). Due to methodological differences, however, this fraction cannot be directly compared with the standard operational definition of DFe discussed above and used in many oceanographic studies by the GEOTRACES community. To make this distinction, we refer to this fraction as labile iron (LFe). We interpret LFe as a proxy for the potentially bioavailable iron fraction (Hiscock et al., 2013), i.e., the iron fraction that is most prone to become available for complexation by phytoplankton siderophores once deposited in seawater (Yoshida et al., 2002). From this perspective, LFe should be interpreted as an upper bound on the pool of potentially bioavailable iron, rather than a direct measure of iron available for phytoplankton uptake.

- Are there potential analytical or post-depositional processes in snow and firn that could alter iron solubility or speciation prior to measurement?

That is a very good question and the answer is yes, that is possible. We added a new paragraph (3.3 Potential post-depositional effects), where we discuss two post-depositional effects that may have influenced the concentration of labile iron (LFe).

We acknowledge the existence of at least two post-depositional processes that may influence iron solubility in ice cores, potentially leading to an over- or underestimation of the true LFe deposited in the North Pacific Ocean. The first is related to microbial activity. Microorganisms are known to inhabit glaciers and to be metabolically active even at low temperatures. They can use inorganic species as energy sources, including iron (Boetius et al., 2015). Under localized low-oxygen conditions some bacteria can reduce Fe(III) to Fe(II) (Jung et al., 2019; Boetius et al., 2015). As Fe(II) is more soluble than Fe(III), this process may enhance iron solubility. However, the extent to which such processes affect iron speciation in polar ice remains poorly constrained and cannot be quantitatively assessed in this study. The second process involves changes in dust mineralogy during burial, which can affect iron solubility. Previous studies have shown that mineral transformations can occur after significant ice grain growth, for example through acidic-oxidative weathering leading to the formation of secondary minerals such as jarosite, which are less soluble (Baccolo et al., 2021a; Baccolo et al., 2021b). Such processes, which favor the formation of Fe(III)-bearing minerals, could reduce the fraction of labile/leachable iron and thus lead to an underestimation of the true LFe. Nevertheless, given the relatively shallow depth interval (less than 1300 m), the small ice grains (Stoll et al., 2021), and the limited depth span of ice core investigated (≈150 meters), it is likely that these

processes, if present, exert a limited and broadly uniform effect across the record, and therefore do not significantly affect the relative variations discussed in this study.

Boetius A, Anesio AM, Deming JW, Mikucki JA, Rapp JZ. Microbial ecology of the cryosphere: sea ice and glacial habitats. Nature Reviews Microbiology. 2015 Nov;13(11):677-90.

Jung, Jaewoo, et al. "Microbial Fe (III) reduction as a potential iron source from Holocene sediments beneath Larsen Ice Shelf." Nature Communications 10.1 (2019): 5786.

Baccolo, Giovanni, et al. "Deep ice as a geochemical reactor: insights from iron speciation and mineralogy of dust in the Talos Dome ice core (East Antarctica)." The Cryosphere Discussions 2021 (2021a): 1-24.

Baccolo, Giovanni, et al. "Jarosite formation in deep Antarctic ice provides a window into acidic, water-limited weathering on Mars." Nature Communications 12.1 (2021b): 436.

Stoll N, Eichler J, Hörhold M, Erhardt T, Jensen C, Weikusat I. Microstructure, Micro-inclusions and Mineralogy along the EGRIP ice core–Part 1: Localisation of inclusions and deformation patterns. The Cryosphere Discussions. 2021 Jul 6;2021:1-29.

- Can the authors further clarify how volcanic versus dust-derived iron is distinguished analytically, and whether their dissolution behavior differs under the CFA protocol?

Volcanic- and dust-derived iron cannot be distinguished analytically based solely on Fe measurements. Instead, volcanic inputs are identified by the occurrence of LFe peaks coinciding with well-characterized volcanic horizons, as defined by sulfate deposition and stratigraphic markers (Lin et al., 2022). In these layers, enhanced acidity is observed (as shown in the acidity and conductivity profiles), which promote more efficient dissolution of iron from particles.

As a result, under the CFA protocol, volcanic layers are characterized by higher LFe concentrations due to enhanced solubility under acidic conditions. In contrast, dust-derived iron is typically deposited under less acidic conditions (see acidity profile), leading to lower dissolution efficiency. Therefore, differences in LFe between volcanic and dust sources are reflected in their contrasting dissolution behaviors.

In the manuscript we will add this paragraph:

Volcanic-derived iron can be differentiated from dust-derived iron based on their contrasting dissolution behavior. During volcanic eruptions, increased acidity promotes more efficient iron dissolution, either within volcanic plumes or after deposition (or both). In contrast, dust-derived iron is typically less soluble under lower acidity conditions. However, the occurrence of volcanic horizons with sufficient acidity for this to happen is limited to individual events, while mineral dust is constantly deposited onto the Greenland ice sheet with a seasonal maximum in spring (Bory et al., 2002).

Bory, A. J. M., Biscaye, P. E., Svensson, A., & Grousset, F. E. (2002). Seasonal variability in the origin of recent atmospheric mineral dust at NorthGRIP, Greenland. Earth and Planetary Science Letters, 196(3), 123-134.

3. Bioavailable iron and global implications

- How do the authors evaluate the extent to which CFA-DFe represents iron that is truly bioavailable to marine phytoplankton, rather than merely chemically soluble?

We acknowledge that the true bioavailability of iron cannot be directly assessed in this study, as also noted in the manuscript (L69-70). The CFA-LFe represents an operationally defined fraction corresponding to the most mobile and readily leachable pool of iron under mild acidic conditions. As such, it likely reflects the fraction most prone to become bioavailable, for instance through complexation by organic ligands such as siderophores. From this perspective, CFA-LFe should be interpreted as an upper bound on the pool of potentially bioavailable iron, rather than a direct measure of iron available for phytoplankton uptake. We included this sentence in the introduction:

We interpret LFe as a proxy for the potentially bioavailable iron fraction (Hiscock et al., 2013), i.e., the iron fraction that is most prone to become available for complexation by phytoplankton siderophores once deposited in seawater (Yoshida et al., 2002). From this perspective, LFe should be interpreted as an upper bound on the pool of potentially bioavailable iron, rather than a direct measure of iron available for phytoplankton uptake.

- What additional constraints—such as iron speciation analyses, ligand-binding considerations, or experimental dissolution and incubation studies—would be required to directly link ice-core DFe to biological uptake in the ocean?

Regarding iron speciation, while Fe(II) is more soluble than Fe(III), it is rapidly oxidized to Fe(III) in oxic seawater. Also, marine phytoplankton does not discern between Fe(II) and Fe(III), therefore the distinction between Fe(II) and Fe(III) in ice-core samples alone is insufficient to constrain marine bioavailability. Experimental dissolution studies, such as the one provided by Conway et al., (2015), can be useful to evaluate Fe potential bioavailability. However, this approach is time consuming and it does not allow for continuous flow analyses.

Most generally, establishing a direct link between ice-core LFe and marine biological uptake remains challenging, as phytoplankton activity in the ocean (as we demonstrate in our paper) is also controlled by a range of other processes: water-column stratification, sea-ice extent, abundance of major nutrients etc. Consequently, while LFe provides a useful proxy for the potentially bioavailable iron pool, it cannot be directly translated into impacts on phytoplankton uptake or net primary productivity.

- Given that the ice-core record integrates long-range atmospheric transport, how representative are the inferred iron solubility patterns for North Pacific?

Previous studies have shown that abrupt changes in eolian dust fluxes are synchronous between the Subarctic North Pacific and the NGRIP ice core (Serno et al., 2015). Given that dust deposited in Greenland during the Younger Dryas is primarily derived from East Asian deserts (Stoll et al., 2022), it is reasonable to infer that the EGRIP record reflects the same large-scale atmospheric dust variability influencing EGRIP and therefore the North Pacific.

We add a paragraph in the manuscript better clarifying why the LFe record is representative of the labile iron deposited in the North Pacific:

The representativeness of the LFe ice-core record presented here with the amount of labile iron deposited in the North Pacific Ocean is supported by the comparison of dust fluxes from sediment core SO202-7-6 (Subarctic North Pacific Ocean), with the high-resolution dust flux record from the NGRIP ice core (Serno et al., 2015). The comparison shows a good coherence in temporal dust deposition changes in Greenland and the Subarctic North Pacific and therefore that atmospheric deposition of iron-bearing particles deposited in Greenland are representative of what has been deposited over the Subarctic North Pacific Ocean. What differs between marine sediments and ice cores is the amplitude of the observed changes, with NGRIP showing a much larger variability in dust fluxes. This enhanced amplitude has been attributed to more efficient dust transport to Greenland and extended atmospheric residence time, driven by climate-related shifts in atmospheric circulation and wet deposition en route. While concentration and flux values from Greenland ice cores are not directly representative of the absolute amount of iron deposited in the Subarctic North Pacific Ocean, they still provide a robust record of relative changes in atmospheric dust (and iron) input in this HNLC region.

Stoll, Nicolas, et al. "Microstructure, micro-inclusions, and mineralogy along the EGRIP (East Greenland Ice Core Project) ice core–Part 2: Implications for palaeo-mineralogy." ***The Cryosphere*** **16.2 (2022): 667-688.**

- Can the authors elaborate on the pathways by which similar iron species are deposited in both marine sediments and ice cores, and how post-depositional processes in snow, firn, and seawater may differentially modify iron speciation?

This question has been partially addressed in our previous answers. Specifically:

- **By comparing $^{4}He_{terr}$-based dust fluxes from sediment core SO202-7-6 (Subarctic Pacific Ocean, SNP) with the high-resolution dust flux record from the NGRIP ice core, Serno et al. (2015) provide evidence that there is a good coherence in temporal dust deposition changes in Greenland and the Subarctic North Pacific. This supports the idea that both the Subarctic Pacific Ocean and the Greenland ice sheets share the same air mass sources (i.e., Asian deserts) and that atmospheric deposition of iron-bearing particles deposited in Greenland are predominantly representative of what has been deposited over the Subarctic North Pacific Ocean. What differs between marine sediments and ice cores is the amplitude of the observed changes, with NGRIP showing a much larger variability in dust fluxes. This enhanced amplitude has been attributed to more efficient dust transport to Greenland, driven by climate-related shifts in atmospheric circulation (Serno et al., 2015) and extended atmospheric residence time during cold periods with low precipitation (Schupbach et al., 2018). Therefore, while concentration and flux values from Greenland ice cores are not directly representative of the absolute amount of iron deposited in the SNP, they still provide a robust record of relative changes in atmospheric dust (and iron) input in the SNP. This part has been included in the manuscript (see answer before).**
- **Regarding post-depositional processes, we previously acknowledged mechanisms that might occur in the snow/firn and deep ice such as microbial iron reduction, which can favor iron solubility, and mineralogical transformations leading to the formation of less soluble iron-bearing minerals. These processes may respectively lead to an**

overestimate or underestimate of the true amount of leachable iron at the time of deposition.

In seawater, iron undergoes a range of post-depositional transformations, including photochemical reduction, oxidation, complexation, and scavenging onto sinking particles (Achterberg et al., 2001). Iron can be taken up by bacteria and phytoplankton through multiple pathways, including siderophore-mediated uptake, direct uptake of dissolved or colloidal iron, and reductive uptake mechanisms requiring enzymatic Fe(III) reduction (Boyd and Ellwood, 2010). In addition, iron in seawater is subject to rapid biological recycling within the so-called *"ferrous wheel",* which maintains iron within the biologically active pool. While increases in atmospheric iron inputs could in principle enhance this recycling and support marine productivity, observational data from the SNP do not support this idea. Instead, the ferrous wheel may play a more significant role during or immediately following short-term events, such as volcanic eruptions. We did not add this last point in the manuscript, as our goal is to demonstrate that despite higher iron fluxes during the YD, marine productivity did not increase.

Achterberg EP, Holland TW, Bowie AR, Mantoura RF, Worsfold PJ. Determination of iron in seawater. Analytica Chimica Acta. 2001 Aug 31;442(1):1-4.

Boyd PW, Ellwood MJ. The biogeochemical cycle of iron in the ocean. Nature Geoscience. 2010 Oct;3(10):675-82.

Schüpbach, S., Fischer, H., Bigler, M., Erhardt, T., Gfeller, G., Leuenberger, D., Mini, O., Mulvaney, R., Abram, N., Fleet, L., Frey, M., Thomas, E., Svensson, A., Dahl-Jensen, D., Kettner, E., Kjaer, H., Seierstad, I., Steffensen, J. P., Olander Rasmussen, S., Vallelonga, P., Winstrup, M., Wegner, A., Twarloh, B., Wolff, K., Schmidt, K., Goto-Azuma, K., Kuramoto, T., Hirabayashi, M., Uetake, J., Zheng, J., Bourgeois, J., Fisher, D., Zhiheng, D., Xiao, C., Legrand, M., Spolaor, A., Gabrieli, J., Barbante, C., Kang, J. H., Hur, S. D., Hong, S. B., Hwang, H. J., Hong, S., Hansson, M., Iizuka, Y., Oyabu, I., Muscheler, R., Adolphi, F., Maselli, O., McConnell, J., & Wolff, E. W. (2018). Greenland records of aerosol source and atmospheric lifetime changes from the Eemian to the Holocene. Nature Communications, 9(1476), doi:10.1038/s41467-41018-03924-41463

4. Lastly, one minor comment: although the study period extends slightly beyond the Holocene, it represents only a very limited interval of the late Pleistocene. As such, the term "Pleistocene–Holocene" in the title may be somewhat misleading with respect to the actual temporal scope of the study. I suggest revising the title to refer more specifically to the "last deglaciation" or to explicitly highlight the focus on the Younger Dryas interval.

The title of the manuscript will be modified to: Limited atmospheric iron availability increase during the Younger Dryas in the Northern Hemisphere

REVIEWER 2

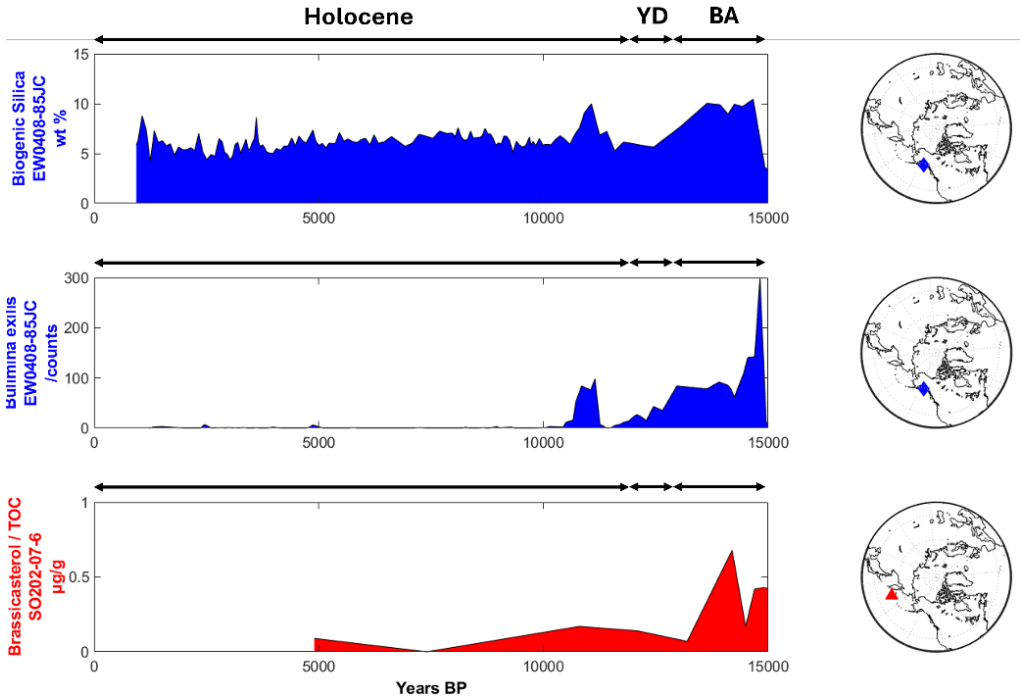
This manuscript reports high-resolution records of Fe_{ICP} and DFe from the EGRIP ice core in Greenland, covering the Pleistocene-Holocene transition (10.3–13.0 ka). The study demonstrates that while total iron concentrations increased 17-fold during the YD compared to the Early Holocene, the biologically active DFe fraction increased by only 29%. By integrating ice-core chemistry with marine productivity records from the North Pacific HNLC region, the authors effectively argue that aerosol alkalinity, rather than total dust flux, acted as a critical limit on iron fertilization during this climatic transition. The data are of high quality, utilizing CFA coupled with spICP-MS, and the findings provide significant new insights into the biogeochemical cycling of iron in the Northern Hemisphere. The manuscript is well-written and deserving of publication in Climate of the Past after addressing the following comments.

We thank the reviewer for the feedback

General comments

Comment 1: The manuscript effectively argues that aerosol alkalinity controls the iron solubility, however, the connection to marine primary productivity remains largely theoretical. The manuscript lacks a direct comparison with existing productivity records from the North Pacific HNLC region.

We agree with the reviewer. In the current version, we primarily refer to Burgay et al. (2021) and Kienast et al. (2004) for marine productivity proxy records; however, we acknowledge that including this information more explicitly in the main text would improve clarity. We added a reference to a new Figure (in the supplementary) reporting biogenic silica, *bulimina exilis* and brassicasterol records from the EW0408-85JC and the SO202-07-6 sediment cores from the Western and Eastern North Pacific Ocean covering the Holocene, Younger Dryas and Bolling-Allerod (Meheust et al., 2018, Praetorius et al., 2015, Davies et al., 2011). From this figure it appears clear ho productivity is higher during the BA than during the YD.



Méheust, M., Stein, R., Fahl, K., and Gersonde, R.: Sea-ice variability in the subarctic North Pacific and adjacent Bering Sea during the past 25 ka: new insights from IP 25 and U k' 37 proxy records, Arktos, 4, 1–19, 2018

Praetorius SK, Mix AC, Walczak MH, Wolhowe MD, Addison JA, Prahl FG. North Pacific deglacial hypoxic events linked to abrupt ocean warming. Nature. 2015 Nov 19;527(7578):362-6.

Davies, M., Mix, A., Stoner, J., Addison, J., Jaeger, J., Finney, B., and Wiest, J.: The deglacial transition on the southeastern Alaska Margin: Meltwater input, sea level rise, marine productivity, and sedimentary anoxia, Paleoceanography, 26, 2011.

Comment 2: L12-15: The manuscript excludes the correlation between atmospheric Fe deposition and productivity due to alkalinity constraints, while implies DFe is the key driver. However, this does not confirm that other factors (stratification, sea-ice, etc.) were more relevant without direct evidence. Additionally, the manuscript lack of the comparison between DFe and productivity records.

We agree with the reviewer and we expanded the Discussion section to include a more detailed consideration of the role of sea-ice (Méheust et al., 2016; Méheust et al., 2018) and enhanced water-column stratification (Ren et al., 2015) in regulating marine productivity. We add a more detailed discussion at the end of paragraph 3.2 (i.e., when we state that "[…] other players such as water stratification, iron remobilization from sediments, and sea-ice extent having a stronger contribution in modulating NPP" and we removed the following paragraph from section 3.1 (to avoid redundancy):

This pattern has been linked to ocean warming, which expanded the subsurface oxygen minimum zone and promoted seafloor hypoxia. Under these low-oxygen conditions, iron is remobilized from sediments, providing a source of bioavailable Fe that further stimulated marine productivity. An additional explanation for why NPP was higher during the BA warm period in the subarctic North Pacific is associated with an increase in sea level that inundated previously exposed lands, which in turn entrained iron and other nutrients to the marine ecosystems (Davies et al., 2011). Conversely, during the colder and dustier YD, either enhanced water stratification, which led to the consumption of major nutrients in surface waters, or a more extensive sea-ice cover, acting as a physical barrier between the atmosphere and ocean surface limiting aeolian iron deposition, played a more dominant role (Méheust et al., 2018; Kienast et al., 2004). In addition, atmospheric aerosol was more alkaline during the YD, potentially reducing Fe solubility (Delmas, 1994; Wolff et al., 1997).

Added in paragraph 3.2

Sea-ice has been proposed as one of the key factors controlling productivity, as it can act as a physical barrier between the atmosphere and the ocean, reducing both light availability and the direct deposition of bioavailable iron to surface waters. Marine sediment records from the eastern and western Subarctic North Pacific, as well as the Bering Sea, indicate extended spring sea-ice cover during the Last Glacial Maximum, coinciding with maximum iron fluxes (Burgay et al., 2021). The subsequent decline in perennial sea-ice coverage following the LGM is associated with an increase in marine productivity, which reached a maximum during the BA when prevalently ice-free conditions were recorded, and decreased during the YD, when variable sea-ice conditions were present (Figure S2) (Méheust et al., 2018).

Enhanced water stratification provides an additional mechanism to explain the decoupling between iron supply and productivity. Reconstructions based on foraminifera-bound $\delta^{15}N$, i.e., a proxy for

nitrate consumption, show that nitrate utilization was more complete during the Younger Dryas, despite low productivity, than during warmer periods (Ren et al., 2015). This apparent contradiction can be explained by stronger stratification during cold and dusty periods, which reduced vertical mixing and upwelling. As a result, nutrient-rich deep waters remained isolated from the surface, while nutrient-depleted, well-ventilated waters dominated the upper ocean (Kohfeld and Chase, 2017). This led to reduced nutrient supply to the euphotic zone and, consequently, to lower marine productivity despite elevated iron inputs.

Ren, H., Studer, A. S., Serno, S., Sigman, D. M., Winckler, G., Anderson, R. F., Oleynik, S., Gersonde, R., and Haug, G. H.: Glacial-to-interglacial changes in nitrate supply and consumption in the subarctic North Pacific from microfossil-bound N isotopes at two trophic levels, Paleoceanography, 30, 1217–1232, 2015.

Kohfeld, K. E. and Chase, Z.: Temporal evolution of mechanisms controlling ocean carbon uptake during the last glacial cycle, Earth Planet. Sci. Lett., 472, 206–215, 2017.

Comment 3: The manuscript suggest that volcanic eruptions can drive DFe atmospheric iron solubility. However, the ice core record primarily reflects local deposition near the EGRIP site. It remains unclear to what extent these volcanic events influenced the productivity in the North Pacific, which need more sedimentary record in the North Pacific. I suggest add a figure comparing the DFe of 10 volcanic eruptions with a productivity record in the North Pacific.

The identified volcanic eruptions caused sulphate deposition over the Greenland plateau larger than 30 kg km^{-2} yr^{-1} (up to 272 kg km^{-2} yr^{-1}). This indicates that these volcanic eruptions were exceptionally intense and they might have influenced the entire northern hemisphere. Three, occurring at 10 481, 12 917 and 13 028, were also observed in Antarctic ice cores (Lin et al. 2022), with an estimate stratospheric aerosol loading ranging between 150 and 220 Tg, proving a global deposition of sulfate (and also volcanic dust, including iron). Nevertheless, we agree with the reviewer that, for other volcanic eruptions, we don't know if the volcanic aerosol was also deposited in the Subarctic Pacific Ocean (SNP), because we do not know the location of the volcanos. Unfortunately, due to the coarse resolution of marine sediments, it is impossible to observe marine productivity blooms as consequence of volcanic eruptions, as already stated in the manuscript. We added a sentence:

Enhanced labile iron concentrations may have triggered local phytoplankton blooms in the HNLC North Pacific Ocean, in line with modern satellite observations (Olgun et al., 2011; Langmann et al., 2010). This can be particularly true for at least three interhemispheric eruptions occurring at 10481, 12917 and 13028 BP. However, due to the short time during which these bloom events develop, it is not possible to track them in sediment cores and their effect on biological productivity would be limited to a few years after the eruption.

Comment 4: There is a geographic distance between the study site and the North Pacific. Therefore, the manuscript should to discuss whether the characteristic (concentration and solubility) of DFe at the study site are truly representative of the aerosol deposition over the North Pacific, given the chemical evolution during long-range transport.

We thank the reviewer for this comment and we paste here the answer we gave to Rev. 1 who raised a similar concern.

The representativeness of the LFe ice-core record presented here with the amount of labile iron deposited in the North Pacific Ocean is supported by the comparison of dust fluxes from sediment core SO202-7-6 (Subarctic North Pacific Ocean), with the high-resolution dust flux record from the NGRIP ice core (Serno et al., 2015). The comparison shows a good coherence in temporal dust deposition changes in Greenland and the Subarctic North Pacific and therefore that atmospheric deposition of iron-bearing particles deposited in Greenland are representative of what has been deposited over the Subarctic North Pacific Ocean. What differs between marine sediments and ice cores is the amplitude of the observed changes, with NGRIP showing a much larger variability in dust fluxes. This enhanced amplitude has been attributed to more efficient dust transport to Greenland and extended atmospheric residence time, driven by climate-related shifts in atmospheric circulation and wet deposition en route. While concentration and flux values from Greenland ice cores are not directly representative of the absolute amount of iron deposited in the Subarctic North Pacific Ocean, they still provide a robust record of relative changes in atmospheric dust (and iron) input in this HNLC region.

Specific comments

Comment 1: L213-215: I suggest adding panel labels (a, b and c) to the Figure 2 and captions.

Ok

Comment 2: Move Figure S1 to the main text to better introduce the location of these three ice cores in the text.

We agree with the reviewer and will move Figure S1 to the main text. To better introduce the location of the ice cores, we will add the following sentence to Section 2.1:

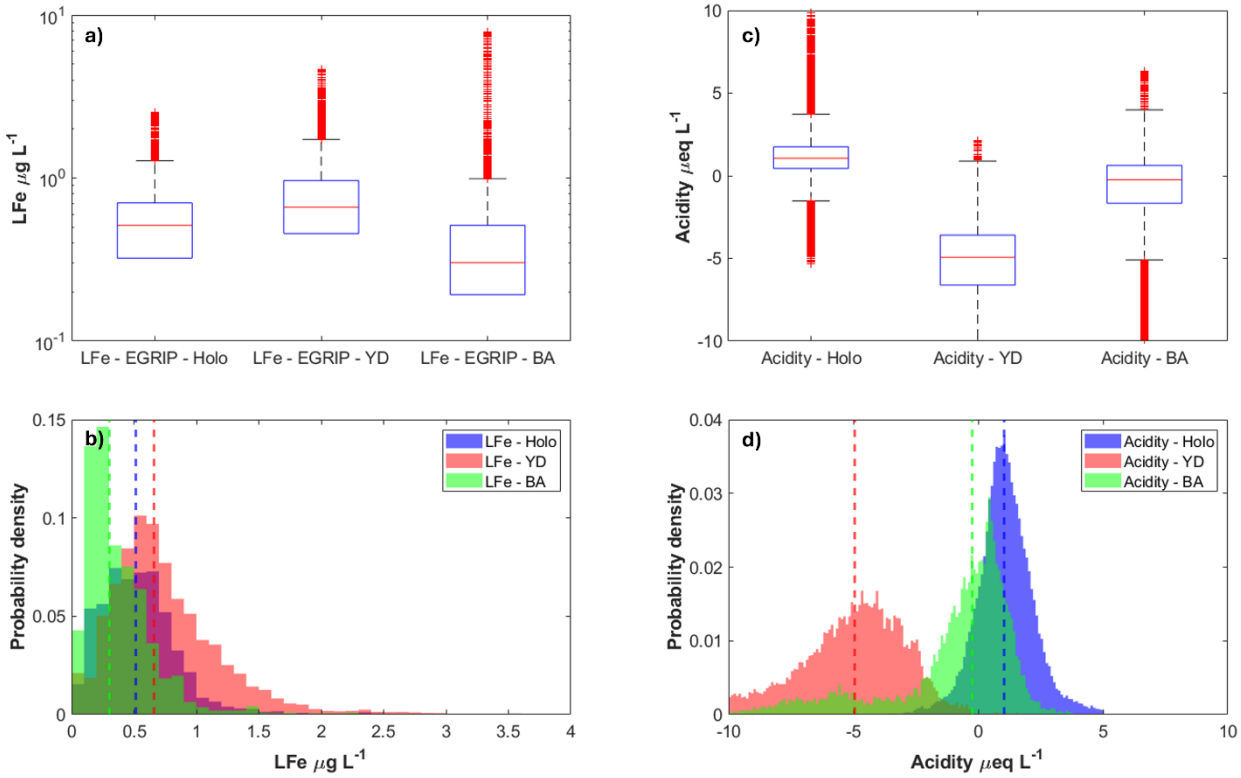
LFe and FeICP data from EGRIP are compared with other Greenland ice-core iron records, including NEEM (77.45°N, 51,06°W, blue star in Figure 1; Burgay et al., 2018) and GRIP (72.35°N, 37.38°W; green star in Figure 1; Hiscock et al., 2013). NEEM and GRIP are both located on the Greenland plateau at 2540 and 3230 m a.s.l., respectively, with modern accumulation rates of 22 and 23 cm ice equivalent per year (Schüpbach et al., 2018; Andersen et al., 2006). All three sites are predominantly influenced by dust originating from Asian deserts during the investigated time period.

To provide a comprehensive and inter-hemispherical comparison, the Fe records from Greenland were compared with an ice core from Antarctica (Epica Dome C, EDC96, 75°06'S; 123°21'E) (Traversi et al., 2004). EDC96 is located in the Antarctic Plateau at 3233 m. a.s.l., with a modern accumulation rate of 2.9 cm ice equivalent per year (Udisti et al., 2004).

Andersen KK, Ditlevsen PD, Rasmussen SO, Clausen HB, Vinther BM, Johnsen SJ, Steffensen JP. Retrieving a common accumulation record from Greenland ice cores for the past 1800 years. Journal of Geophysical Research: Atmospheres. 2006 Aug 16;111(D15).

Comment 3: The relationship between the acidity and DFe is important evidence of the argument. I suggest (1) moving Figure S3 and S4 to the main text, (2) combining these two penal into one figure, which can better compare the correspondence across the different periods.

Ok, we produced a single 2x2 picture merging both LFe and acidity data (see below).



Comment 4: Add one figure superimposing the volcanic LFe and acidity data onto the records of the 8 selected periods, to provide further supporting evidence for the limiting effects of aerosol alkalinity on Fe solubility.

We believe that the effect of acidity in enhancing LFe is already quite clear from Figure S5 (now in the main text) and the Figure above (now Figure 4).

REVIEWER 3

Burgay et al. present new high-resolution soluble iron data from the EGRIP ice core over the Younger Dryas-Holocene transition. The authors employ two continuous methods to measure soluble iron in the ice core. Consistent with previous studies, the authors show that soluble iron concentrations were higher in the dusty Younger Dryas period relative to the Holocene. They attribute this change to alkaline conditions. In addition, the authors suggest that volcanic eruptions caused episodic increases in the deposition of soluble iron to the Greenland ice sheet. As there is a complex interplay of sources and processes that drive the solubility of atmospheric iron, these new data from Greenland provide valuable insight into the relationship between soluble iron and mineral dust. Thank you for the valuable contribution to the literature.

Outlined below are three areas that would benefit from further clarification and discussion.

Some aspects of this review are drawn on my earlier work in this area. References to this work provide an example of how the present-day understanding of the controls on iron solubility can be applied to paleorecords, thereby providing a framework for interpreting the soluble iron data presented in this manuscript. They are intended solely to support constructive suggestions for strengthening the manuscript.

We thank Dr. Holly Winton for her feedback and valuable suggestions.

Methods

1. Operational definition of dFe

Within the marine biogeochemistry community (aerosol and ocean chemistry), the standard operational definition of dissolved iron (dFe) is Fe <0.2 or 0.4 um. This is typically determined by filtering the sample through a 0.2 um or 0.4 um filter and the iron concentration in the leachate analysed. In addition, total dissolvable iron (TDFe) is the fraction of iron that is leached with weak acid in an unfiltered sample. Further information on these definitions can be found in the GEOTRACES programme https://www.geotraces.org/. These standard methods have been adopted in iron solubility studies of snow and ice, first by Edwards and Sedwick [2001] for TDFe and by Winton et al. [2016] for dFe, and subsequently by other studies e.g., Du et al. [2019]; Du et al. [2020]; Liu et al. [2019]; Liu et al. [2021]; Winton et al. [2022]. The 'dFe' method employed by Burgay et al. does not access the <0.2 or 0.4 um fraction of Fe and thus the term 'dFe' is misleading. Please rename with a different term such as 'labile iron' or other. Consistency of terms will avoid confusion especially for the marine biogeochemistry community who will be highly interested in this work. See Berger et al. [2008] for a background on labile iron methods. There are various methods in the literature that assess a different pool of soluble iron in snow/ice/aerosols. These were developed to mimic certain processes of iron dissolution upon deposition to the ocean. Please clearly explain the rational for the two methods of soluble iron employed in this study and include what fraction of soluble iron each method assesses.

We agree with the reviewer and will replace 'DFe' with 'labile iron' (LFe) throughout the manuscript, defined as the fraction solubilized after a short acidification step using HCl at pH ≈ 1.6. We explicitly state that the iron investigated in this study should not be associated with DFe as defined by GEOTRACES.

Assessment of bioavailable iron typically requires both the dFe <0.2 um and labile phases. I'm assuming this is why Burgay et al. have used two methods of soluble iron in this manuscript with 'FeICP' representing instantaneous soluble iron and 'dFe' representing a fraction of labile iron where iron continues to leach from particles over days after deposition to surface waters. Although this is currently unclear in the manuscript (to me at least). Have I understood this correctly? If I understand the intention of the methods, then please reframe the manuscript around instantaneous soluble iron and labile iron.

We acknowledge that the first version of the manuscript suffered from a bit of confusion in the different iron definitions. We reworked completely this part in the introduction and we now provide a more detailed and clearer definition of FeICP and LFe.

In the manuscript, LFe is defined as the fraction solubilized following a short acidification step and detected by absorption techniques. The quantified fraction includes iron associated with colloidal phases and iron-binding ligands (Lohan et al., 2006), as well as iron released from Fe-hydroxides and Fe-complexes (Hiscock et al., 2013). For these reasons, LFe represents an operationally defined, easily leachable and labile fraction, i.e., the form of iron most prone to become available for complexation by phytoplankton siderophores once deposited in seawater (Yoshida et al., 2002). Accordingly, in this work we interpret LFe as a proxy for the potentially bioavailable iron pool (Hiscock et al., 2013). We report this new sentence in the manuscript:

LFe corresponds to an easily leachable and labile fraction, which accounts for 20-30% of FeICP (Erhardt et al., 2019). Due to methodological differences, however, this fraction cannot be directly compared with the standard operational definition of DFe discussed above and used in many oceanographic studies by the GEOTRACES community (www.geotraces.org). To make this distinction, we refer to this fraction as labile iron (LFe). We interpret LFe as a proxy for the potentially bioavailable iron fraction (Hiscock et al., 2013), i.e., the iron fraction that is most prone to become available for complexation by phytoplankton siderophores once deposited in seawater (Yoshida et al., 2002). From this perspective, LFe should be interpreted as an upper bound on the pool of potentially bioavailable iron, rather than a direct measure of iron available for phytoplankton uptake.

FeICP is defined as the total iron fraction, excluding the fraction structurally bound with the exception of the fraction bound with silicates. This attribution is largely supported by the good agreement between TDFe (NEEM) and FeICP (EGRIP). This is now explicitly reported in the manuscript:

FeICP captures most of the atmospheric Fe pool, but, as TDFe also does, excludes the fraction structurally bound with refractory silicates, which would require HF-based microwave-assisted digestion for complete dissolution (Gaspari et al., 2006).

It would be helpful to include a discussion on how these two continuous methods compare to dFe <0.2 um. Has a study been carried out to compare dFe <0.2 um or TDFe with the two continuous soluble iron methods used here? What consideration was made for an in-line filter in the CFA to assess the dFe <0.2 um fraction?

Yes, we discuss the differences between TDFe (from NEEM) and FeICP/labile iron in the manuscript (L239–253). Unfortunately, due to the limited availability of ice material, TDFe measurements could not be performed on the EGRIP samples. However, the similarity between

TDFe values from NEEM and FeICP measurements from EGRIP suggests that the two measurements refer to the same iron fraction.

Simonsen MF, Baccolo G, Blunier T, Borunda A, Delmonte B, Frei R, Goldstein S, Grinsted A, Kjær HA, Sowers T, Svensson A. East Greenland ice core dust record reveals timing of Greenland ice sheet advance and retreat. Nature communications. 2019 Oct 3;10(1):4494.

2. Lack of total or TDFe concentration and fractional iron solubility data

A limitation of this study is that total or total dissolvable iron (TDFe) data are not reported and thus there is no information on the fractional iron solubility. While soluble iron provides an idea of the concentration, fractional iron solubility identifies the efficiency of the conversion from total to soluble. This is important information as it helps understand what factors are controlling the solubility. Total iron with a low fractional iron solubility often comes from mineral dust, while high fractional iron solubility is derived from other sources, such as combustion, or indicates processing in the atmosphere that enhances the solubility. Thus, fractional iron solubility is an important metric for assessing changes in iron bioavailability across a significant climate and dust transition. In core cores studies, there is a trade-off between high resolution continuous data and discrete sampling - both having advantages and disadvantages. Please acknowledge this limitation in the manuscript.

As noted above, and especially considering the remarkably good agreement between TDFe (NEEM) and FeICP (EGRIP), FeICP includes not only the soluble fraction, but also the fraction bound to sub- and micrometer particles which are ionized and atomized in the plasma. This means that, as we do with TDFe, we can use FeICP to describe fractional iron solubility (see also answer below).

3. Trace metal protocols and figures of merit

Measuring trace metals at low concentration levels in ice cores is not a trivial task. Please include additional information on the steps taken to minimise trace metal contamination.

As reported at L91-93 (see below), to minimize trace metal contamination, only the inner part of the ice core was used for CFA analysis. Furthermore, from each stick prepared for melting, only the central portion was analyzed, while the outer layers, i.e., those potentially exposed to gloves or other surfaces, were excluded through the geometry of the melter. This is one of the key advantages of continuous flow analysis systems, that minimize sample handling and, therefore, contamination.

***To remove contamination of the ice due to handling or drilling fluid, only the meltwater from the innermost 26x26 mm of the ice is used for analysis*.**

To ensure the quality of the data, please report figures of merit for both types of soluble iron measurements including blank concentrations, accuracy and reproducibility.

Many details regarding blanks, detection limits and calibration curves are reported in 2.2.1. Other details regarding accuracy and reproducibility are reported in Erhardt et al., 2019 (for Fe_{ICP}) and Burgay et al., 2018 (for LFe).

Drivers of iron solubility

The current manuscript considers a single explanation (aerosol alkalinity) for the change in soluble iron concentrations between climate states. Yet iron solubility is driven by a complex interplay of sources and processes.

There is a well-established non-linear relationship between total/TDFe and soluble iron in the literature. The Sholkovitz et al. [2012] global compilation of aerosol iron data showed that fractional iron solubility is a function of total iron. The non-linear relationship is described by a simple two-component mixing model, whereby the fractional iron solubility of iron reflects the mixing of mineral dust (high total/TDFe Fe and low fractional iron solubility) and non-mineral combustion aerosols (low total/TDFe Fe and high fractional iron solubility). This model was applied to Antarctic ice cores over the last glacial transition. See Winton et al. [2022] and Supplementary Figure 5. In the Holocene, dFe concentrations decreased and fractional iron solubility increased which is best explained by greater biomass burning and/or changes in the chemical processing of iron in the atmosphere that make it more soluble e.g., cloud processing. Burgay et al. present a strong argument for changes in aerosol alkalinity driving the soluble iron concentration. However, there are a range of other factors (sources and processes) that are currently overlooked. The manuscript would benefit from a discussion of these.

We thank the reviewer for this suggestion and we added here an additional explanation on how aerosol acidity has influenced iron solubility through enhanced cloud processing.

We acknowledge that the acidity released in the ice cores after melting may not be quantitatively the same as the one experienced by mineral dust aerosol in the atmosphere. However, it is reasonable to assume that changes in the acidity in the atmosphere (as reconstructed from our ice-core meltwater analysis) have also influenced iron solubility through cloud processing (Winton et al., 2022). Cloud processing refers to the repeated condensation–evaporation cycles that aerosol particles experience during atmospheric transport before their removal by wet or dry deposition. These cycles strongly modify the chemical environment surrounding the particles, potentially enhancing the fractional solubility of iron in the affected air masses. During repeated cycling, iron in both nanoparticles and mineral dust can continue to dissolve, with longer or more frequent acidic wet-aerosol stages leading to higher atmospheric iron solubility. Leaching experiments and model simulations of iron-bearing dust cycling between wet aerosols and cloud droplets show that mineral dust iron dissolves efficiently under acidic conditions typical of wet aerosols, whereas dissolution is reduced under the higher-pH conditions characteristic of cloud droplets.

Winton VH, Bowie AR, Curran MA, Moy AD. Enhanced deposition of atmospheric soluble iron by intrusions of marine air masses to East Antarctica. Journal of Geophysical Research: Atmospheres. 2022 Jul 16;127(13):e2022JD036586.

Even better if the authors can measure TDFe in Younger Dryas and Holocene samples to investigate the relationship between TDFe and fractional iron solubility. This does not necessarily need to be a continuous record. Some constraint on the fractional iron solubility would be highly valuable and allows the authors to frame their discussion around the model described above. If there is no sample material available or additional analyses are out of scope, the authors could apply assumptions to estimate the total iron content of the dust which would help their interpretation of the soluble iron data over the Younger Dryas-Holocene transition. It would be a valuable exercise to compare Greenland vs Antarctica where the dust loading and atmospheric composition are different. Other

datasets to support the discussion could include black carbon or other biomass burning proxies, mineral dust particle size, soluble iron fluxes.

Unfortunately, we cannot provide TDFe data for EGRIP, however we report TDFe values from NEEM which are very similar to FeICP indicating both describe the same iron fraction (see our answers above). This means that the fractional solubility reported in this paper (LFe/FeICP) is expected to be very similar to a LFe/TDFe one (i.e., fractional solubility decreased due to higher pH values, which decreased Fe solubility and reduced cloud processing efficiency).

The study assumes soluble iron in EGRIP comes from mineral dust. Please acknowledge this assumption. What about a changing dust source over the last deglaciation transition?

We added this sentence in the introduction. Also, Figure S3 (see comment below) helps in supporting this assumption.

Given that iron is a key component of mineral dust, its quantification in ice cores represents a valuable approach for assessing changes in atmospheric iron concentrations and solubility during past climatic transitions.

Volcanic sources of soluble iron

There is an emerging body of literature on this topic. I agree with the authors that volcanic eruptions are an important source of episodic soluble iron. There is an opportunity to strengthen the argument by:

1. Including a brief introduction to aerosol iron sources, including volcanic eruptions, as a source of soluble iron in the introduction.

After the description of the limited role of iron fertilization during glacial-interglacial periods in explaining changes in atmospheric CO2, we added this paragraph with additional references (also considering the following comment):

Besides aeolian mineral dust, volcanic ash emissions represent an additional source of iron to surface waters. Although acting on shorter time scales (i.e., months to maximum a few years), it was first hypothesized (Spirakis, 1991), and subsequently demonstrated, that iron contained in volcanic ash can stimulate phytoplankton blooms in HNLC ocean areas (Langmann et al., 2010; Frogner et al., 2001). Observed decreases in atmospheric CO2 following major eruptions such Agung (1963) and Pinatubo (1991) have been interpreted as evidence of the fertilizing effect of ash-derived Fe on ocean productivity (Watson, 1997).

Spirakis, C. S.: Iron fertilization with volcanic ash?, Eos, Transactions American Geophysical Union, 72, 525–525, 1991.

Langmann, B., Zakšek, K., Hort, M., and Duggen, S.: Volcanic ash as fertiliser for the surface ocean, Atmos. Chem. Phys., 10, 3891–3899, 10.5194/acp-10-3891-2010, 2010.

Frogner, P., Gíslason, S. R., and Óskarsson, N.: Fertilizing potential of volcanic ash in ocean surface water, Geology, 29, 487–490, 2001.

Watson, A. J.: Volcanic iron, CO2, ocean productivity and climate, Nature, 385, 587–588, 1997.

2. Citing references relevant to enhanced aerosol iron solubility via volcanic eruptions and atmospheric processing in section 3.3. The emerging body of literature does support this interpretation, but they are currently not cited.

In 3.4 (ex 3.3), we added a sentence: *meaning that volcanic eruptions can sustain short-term phytoplankton blooms and productivity when their timing coincides with periods of active biological growth (Rogan et al., 2016).*

Rogan N, Achterberg EP, Le Moigne FA, Marsay CM, Tagliabue A, Williams RG. Volcanic ash as an oceanic iron source and sink. Geophysical Research Letters. 2016 Mar 28;43(6):2732-40.

Other citations have been included in the Introduction (see related comment above)

3. Supporting the argument by reporting values of soluble iron concentrations in volcanic vs background dust samples. A figure in the main manuscript could support this as well.

We moved Figure S5 from the supplementary to the main text. In this way it is clear how identified volcanic eruptions (See Table S2), have a distinct fingerprint compared to the background. Also, we added a sentence to better show how volcanic eruptions enhance labile iron concentration in the ice compared to median background values: *During these events, labile iron increased up to 17 µg L-1, compared to median background values of 0.60 and 0.66 µg L-1 observed during the Holocene and the YD, respectively. Enhanced labile iron concentrations may have triggered local phytoplankton blooms in the HNLC North Pacific Ocean, in line with modern satellite observations (Olgun et al., 2011; Langmann et al., 2010).*

Specific comments

L10 'Total iron' mentioned here but not reported.

L10 dissolved iron 'concentration'.

Referred to both comments:

We change in: "iron as determined by Inductively-Coupled Plasma Mass Spectrometry"

L30-32 Large number of studies that support this statement. Please include additional references.

To further support our statements we added, at L30:

Boyd PW, Jickells T, Law CS, Blain S, Boyle EA, Buesseler KO, Coale KH, Cullen JJ, De Baar HJ, Follows M, Harvey M. Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions. science. 2007 Feb 2;315(5812):612-7.

at L32:

Saini H, Meissner KJ, Menviel L, Kvale K. Impact of iron fertilisation on atmospheric CO 2 during the last glaciation. Climate of the Past. 2023 Jul 28;19(7):1559-84.

And at L33:

Weber ME, Bailey I, Hemming SR, Martos YM, Reilly BT, Ronge TA, Brachfeld S, Williams T, Raymo M, Belt ST, Smik L. Antiphased dust deposition and productivity in the Antarctic Zone over 1.5 million years. Nature Communications. 2022 Apr 19;13(1):2044.

Schmitt, J., Schneider, R., Elsig, J., Leuenberger, D., Lourantou, A., Chappellaz, J., Köhler, P., Joos, F., Stocker, T. F., Leuenberger, M., & Fischer, H. (2012). Carbon isotope constraints on the deglacial CO2 rise from ice cores. Science, 336, 711-714. https://doi.org/10.1126/science.1217161

Bauska, T.K., Baggenstos, D., Brook, E.J., Mix, A.C., Marcott, S.A., Petrenko, V.V., Schaefer, H., Severinghaus, J.P., Lee, J.E., 2016. Carbon isotopes characterize rapid changes in atmospheric carbon dioxide during the last deglaciation. Proceedings of the National Academy of Sciences 113(13), 3465-3470.

L46-70 This would benefit from restructuring to clearly show the difference between soluble vs total/TDFe fractions.

The paragraph was revised by including additional explanations on FeICP and LFe, as reported in our previous answers.

L58-59 Note that dFe method in snow/ice was employed by Winton et al. [2016] and uses HCl.

We modified accordingly

L134-137 Helpful to provide a bit more information on conductivity and particle measurements.

At L134, we define the acronym Electrolytic Meltwater Conductivity (ECM). Below L137, we added: ***ECM is sensitive to changes in ice acidity, i.e., variations in H^+concentration, with higher values corresponding to higher acidity. Glacial periods, which have a high concentration of alkaline dust, present a significantly reduced conductivity compared to interglacials (Taylor et al., 1993). Insoluble particle concentration and size distribution are measured using an Abakus laser sensor, which determines the optical extinction cross section of particles in the 1–15 µm size range (Simonsen et al., 2018).***

Simonsen MF, Cremonesi L, Baccolo G, Bosch S, Delmonte B, Erhardt T, Kjær HA, Potenza M, Svensson A, Vallelonga P. Particle shape accounts for instrumental discrepancy in ice core dust size distributions. Climate of the Past. 2018 May 3;14(5):601-8.

Taylor KC, Hammer CU, Alley RB, Clausen HB, Dahl-Jensen D, Gow AJ, Gundestrup NS, Kipfstuh J, Moore JC, Waddington ED. Electrical conductivity measurements from the GISP2 and GRIP Greenland ice cores. Nature. 1993 Dec 9;366(6455):549-52.

L154 Ca proxy may need a quick introduction.

We specify, that calcium is a commonly used proxy for mineral dust by adding an additional citation: ***[…] as extensively demonstrated by the higher dust, Ca2+ (i.e., a commonly used ice-core proxy for mineral dust (Ruth et al., 2008)), and TDFe concentration compared to the Holocene […]***

Ruth U, Barbante C, Bigler M, Delmonte B, Fischer H, Gabrielli P, Gaspari V, Kaufmann P, Lambert F, Maggi V, Marino F. Proxies and measurement techniques for mineral dust in Antarctic ice cores. Environmental science & technology. 2008 Aug 1;42(15):5675-81.

L174-176 Helpful to explain data gaps in the caption.

We added the following sentence*: Data gaps for dust and acidity are caused by incorrect data acquisition during the corresponding runs*.

L200-201 Could an in-line filter be added to the CFA?

Unfortunately not, as it would add many problems associated with back-pressure. We added a sentence:

These methods are incompatible with continuous measurements due to the filtering step, which would introduce in the CFA system back-pressure issues.

L206 Support statement by showing seasonality data.

We added a Figure in the Supplementary (Figure S3) showing for a specific section (representative of the entire dataset) the alignment between dust, labile iron and Fe_ICP. It is well known that dust in Greenland follows seasonal patterns (see Steffensen, 1988) due to the position of the polar front. In the text we added this sentence:

In Greenland, dust follows seasonal patterns due to the position of the polar front, which enables a more efficient transport of dust from lower latitudes in spring (Steffensen et al., 1988)

Steffensen JP. Analysis of the seasonal variation in dust, Cl−, NO3−, and SO4 2− in two central Greenland firn cores. Annals of Glaciology. 1988 Jan;10:171-7.

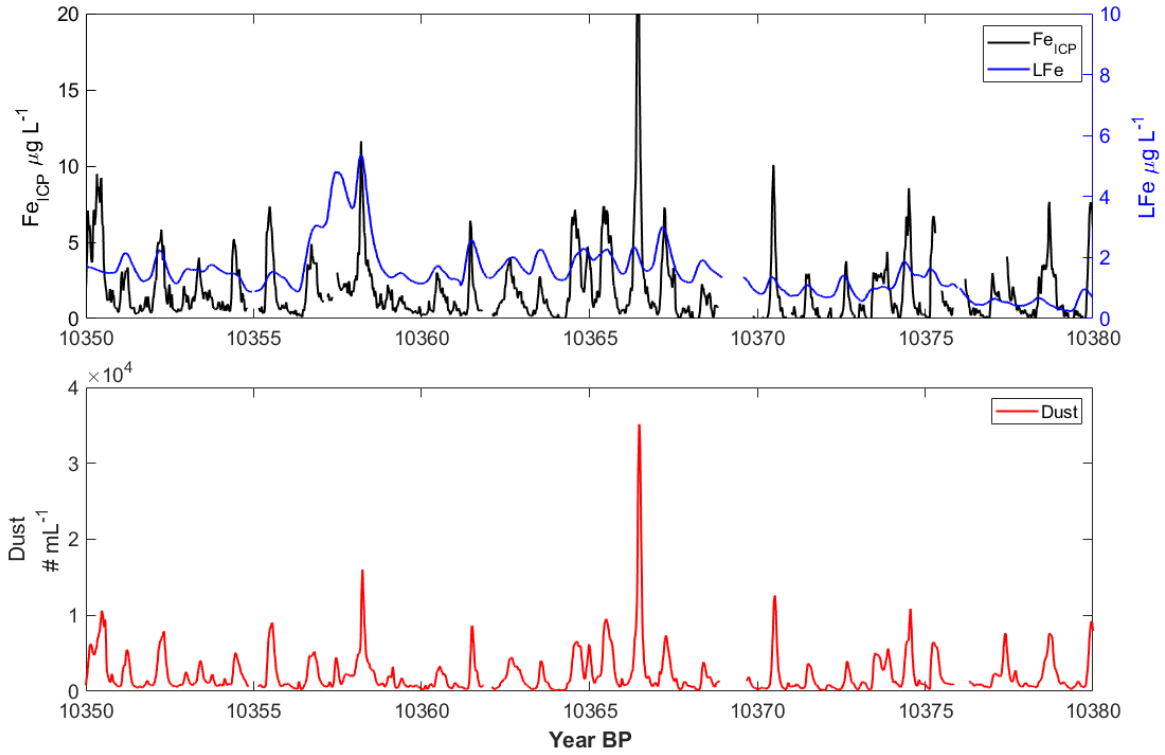


Figure S3– Seasonal signal of Fe_{ICP}, LFe and dust. Please note that sometime the LFe and Fe_{ICP} signals seem to be not perfectly aligned. This is due to the response factor of the LFe line (see main text for more details -L238).

L317 Do you mean “increased dust deposition”? The measurements represent iron deposition to the ice sheet.

Yes, we modified accordingly

Figure 2 ECM and acidity y-axis is small compared to Fe.

We are not sure what the reviewer means: should we scale conductivity and acidity differently?