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