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.

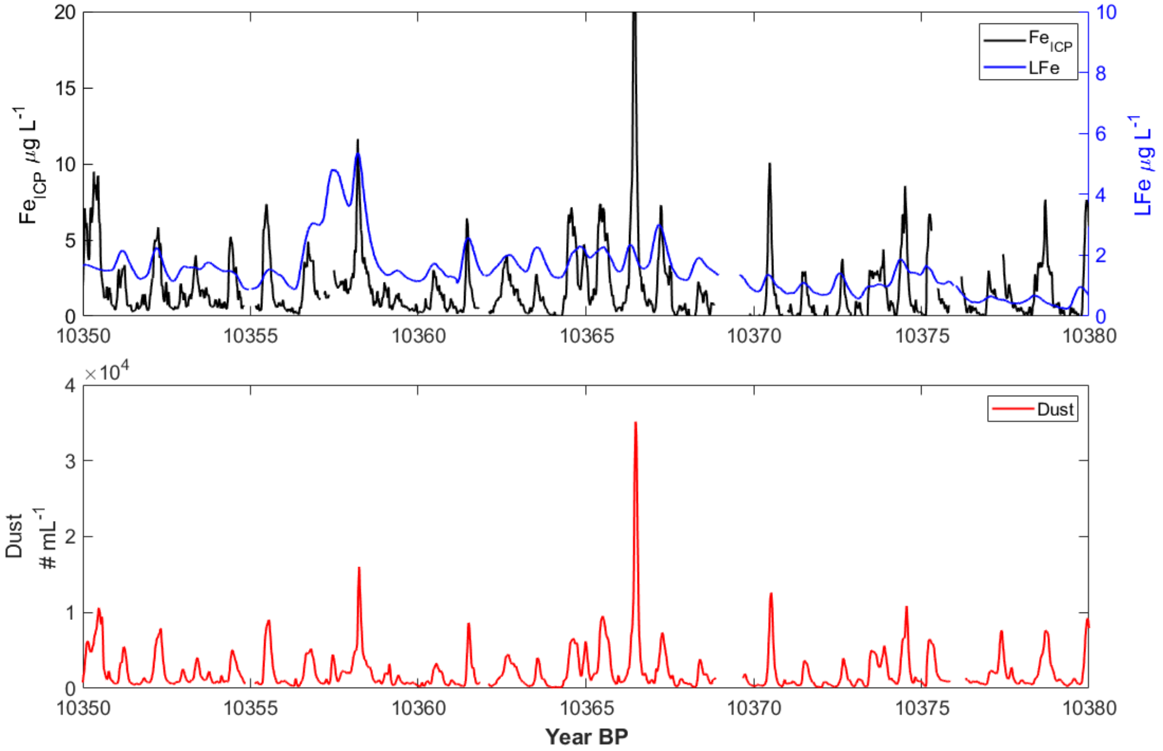

Figure S3– Seasonal signal of Fe_{ICP}, LFe and dust. Please note that sometime the LFe and Fe_{ICP} signals seem to be not perfectly aligned. This is due to the response factor of the LFe line (see main text for more details -L238).

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?