

Ref: I have read the revised version of “Microstructure, Micro-inclusions and Mineralogy along the EGRIP ice core - Part 2: Implications for paleo-mineralogy” and find it to be improved. Particularly, the more complete analysis of the mineralogy that is now found in the discussion is welcome. There are still a few points where I think further improvement can be made, which I detail below. I use the line numbers that appear in the track-changes version of the manuscript.

Ref: Line 74: I would strike “taken at arbitrary depths”, sampling design is usually carefully thought out and very seldom “arbitrary”.

Answer: “Arbitrary” was deleted.

Ref: Lines 78-91: This is a great amount of detail on a topic that is not directly relevant to this manuscript. It is good to give broader context, but the link between mineralogy and deformation structure is not subsequently addressed in this manuscript.

Answer: We keep this short part due to its importance for the general motivation and the linkage to part 1.

Ref: Line 101: “a profound understanding on...”: reword

Answer: Changed to: However, to develop a deep understanding of the mineralogy and localisation of impurities in polar ice, a combination of both approaches is required.”

Ref: Lines 108-111: In my previous review, I said that the introduction needed clearer research questions. But that doesn't mean these need to be literally posed as questions. An introduction needs to identify a key gap in knowledge and outline how the current effort will address that gap. This can usually be accomplished without directly using a question mark.

Answer: Changed to “We further investigate whether the mineralogy of the deposited impurities was stable over the last 14 ka or whether there were changes as a result of the evolution of the Greenland Ice Sheet. Deriving a mineralogy record of inclusions might also enable a better understanding of the aerosol content of the past. Finally, we investigate whether the location of the inclusion in the ice microstructure is related to its mineralogy.”

Ref: Line 122: This is a weak ending to the introduction. Why put something that is not the main focus as your final introductory remark? End with the main thing you hope to accomplish. If you don't think mineral formation is highly relevant, bury it mid paragraph and say something like: “these analyses also offer limited insights into mineral formation pathways”. But tell us what you are actually trying to discover.

Answer: Good point, we deleted the last sentence and edited a sentence in the paragraph:

“In this study we investigate the mineralogy of these visible micro-inclusions, which also offer a limited insight into mineral formation pathways.”

Ref: Line 127: Replacing unique with exclusive doesn't really solve the problem. In the rebuttal, you said these were the first measurements in a deforming ice stream. Say that. Let us know that these are new in part because they have never before been done in ice that was actively deforming to this degree.

Answer: We changed it to: At the drill site the ice flows with a velocity of 55 m a⁻¹

(Hvidberg et al., 2020) offering a novel possibility to study ice rheology and physical parameters contributing to deformation, such as crystal preferred orientation and impurity content, in an active deformation regime, i.e. an ice stream.

Ref: Line 148: I still don't understand why the data from the soluble section are not included in this paper. I know the authors are planning another manuscript. But several outstanding questions about mineral formation pathways could be efficiently resolved by appeal to the to composition of the dissolved fraction. I.e. did the sulphates gain their cations from sea water or from dust, etc.

Answer: CFA - chemistry data are not available yet, as the processing, synchronization and dating is still in progress. Further, sulfate was not measured online, but is currently measured on high-resolution discrete samples - also work in progress.

The analysis and interpretation of CFA chemistry and ion chemistry is beyond the scope of this paper.

To clarify this we changed the wording throughout the manuscript and now emphasise the use of micro-particle data instead of CFA data.

Ref: Table 2: Make it clear that “sulphates” and “mica” are the sum of all sulphate and mica species, respectively. At first, I thought they could be unidentified sulphates.

Answer: We changed it to “all sulphates” and “all mica”.

Ref: Line 342: Maybe: “Because the EGRIP is uniquely located on an ice stream, and ...”

Answer: Changed to: Because the EGRIP drilling site is uniquely located on an ice stream, and the assumed high impact of high-impurity layers on the deformation of the ice...

Line 344: I am still not too keen on these vague commands about what sort of future research is needed.

Answer: The addressed paragraph does not mention future research (in the new and track changes document), but summarises the advantages of our presented method.

This might refer to section 4.2.4 where we deleted the last sentence, which is indeed rather vague.

Ref: Line 363: The authors don't seem to appreciate just how rare. Kröhnkite is only known in 31 locations globally; most of these are copper ore bodies. A brief search reveals that it has been attested in one instance as a fumarolic mineral in Icelandic volcanism, but it is described as very rare in that setting too. 27 out of 386 sulphate minerals is 7%. The global abundance of kröhnkite as a fraction of sulphate minerals is many orders of magnitude below 7%. My first inclination is to assume that the authors have misidentified a more common mineral, but I am not enough of a Ramen expert to know how likely this is. If the authors are confident that their spectroscopy is correct, this is in fact a major mineralogical discovery. Given the mineral's rareness, it is very unlikely to be detrital and almost certainly formed in the snow or ice. But the authors need to think through how that could be possible. What is the total mass of copper implied? Is that even plausible? Etc.

Answer: The structure and general properties of Kröhnkite are very similar to bloedite, their main peak is thus also very similar ($\sim 1\text{cm}^{-1}$ difference). The valid concern about the scarcity of Kröhnkite in general and the fact that it has not been observed in ice cores, make it very likely that these inclusions are also bloedite. As explained in more details in the answer to referee 2 we thus choose a conservative approach and classify the 27 kröhnkite inclusions as bloedite. Bloedite is much more common and has been observed before with Raman spectroscopy (Eichler et al., 2019). We appreciate the consistent input of the referee regarding this matter.

Ref: Line 378: “As displayed in...”, just write “(Fig. 6.)”.

Answer: Adapted.

Ref: Line 382: What does “partially high” mean?

Answer: This indicated that gypsum, at some depths, is one of the most abundant minerals. We changed the text to “We have observed a pronounced change in mineralogy from a sulphate-diverse, while terrestrial dust rich, regime in the upper 900 m to a terrestrial dust-dominated regime with comparably large numbers of gypsum at some depths (e.g., S8 and S11)”.

Ref: Line 384: “other minerals”, you mean new minerals or minerals not found higher in the core, right?

Answer: Yes correct, we changed this to: The lack of a variety of sulphate minerals below 900 m is shown in our diversity index, which decreases with depth even though some minerals, such as dolomite, only occur below 900 m.

Ref: Line 385: “Varying numbers” is an incredibly vague way of putting it.

Answer: Defining the numbers more precisely is almost impossible here since we refer to three studies (with different absolute amounts of identified inclusions) and the two main mineral groups, i.e. sulphates and mineral dust, consisting of several minerals. Describing the exact amounts of these minerals results in a lengthy and confusing description of the work of others, which is not needed here.

Ref: Line 388: By rare, you mean uncommon in your ice core, not globally rare. I wouldn't even call hematite rare at $n=33$.

Answer: True, we changed it to “comparably rare minerals, such as...”

Ref: Line 389: maybe, “Hematite ... abundance does not detectably vary with depth”

Answer: Changed to: The abundance of comparably rare minerals, such as hematite, anatase and titanite, does not detectably vary with depth.

Ref: Line 395: Maybe, “Though previous data is scarce, Sakurai...”

Answer: Adapted.

Ref: Line 397: The topic sentence doesn't match well with the rest of the paragraph. If your differences don't correspond to glacial-interglacial transitions, why go on about other workers who do? You can discuss both, but it needs to be more clearly framed. Something like, "the changes we see at 900 m are similar to that observed in other settings at a glacial-interglacial transition".

Answer: Changed to: „The changes in mineralogy that we observe at 900 m depth are similar to observations made in other settings at a transition between Glacial and Interglacial. Eichler et al. (2019) found a strong difference in mineralogy...“

Ref: Line 452: Carbonate can also form in situ, as a chemical weathering product of carbonic acid interactions with mineral dust.

Answer: Thanks for noticing, we deleted carbonates here.

Ref: Line 461: Delete "it is suggested that"

Answer: Deleted.

Ref: Line 465: This is where the rest of the CFA data would be extremely helpful. And you apparently do have CFA data for H⁺ (figure 1), suggesting quite a bit what is very likely HCl (though probably other anions too) in most of the ice core. And indeed the portion with the dolomite (S10) is the one the part that is not acidic. This suggests either that carbonate is dissolving in the other portions of the core or that it precipitated in the part where acidity was low. In other instances, do the changes in sulphate abundance and mineralogy correlate with these changes in acidity? It is well worth doing some more analysis here.

Answer: The presented H⁺ acidity data is from published ECM measurements (Mojtabavi et al., 2020). The major feature in the acidity record is the drop in the Younger Dryas, variations in acidity are much smaller during the Holocene and Bolling Allerod. Acidity is slightly lower between 350 and 925 m, but a significant change in mineralogy in this depth regime was not observed (compared to above 350 m and below 925 m). We provided a high-resolution analysis of the acidity at the exact sample depths in the first review round and did not find any correlations regarding the mineralogy content.

We extend section 4.3.4 rare minerals with a brief summary on dolomite:

"Dolomite was only observed in S10 originating from the Younger Dryas, which is the only section of the ice core that is not acidic (Fig. 1). This indicates either that the carbonate is dissolving in the other parts of the core or that it has precipitated in the part where the acidity was low."

Ref: Line 480: Do your results really show this? There is a major outlier with the Younger Dryas. Though I suppose the word "often" accounts for this. I think the diversity in sulphate mineralogy requires both acidity and dust. Perhaps a multiple regression (or another similar statistical test) is in order here.

Answer: Our results show, that the only sulphate in the mentioned sample is gypsum (Fig. 5b) while dust values are very high (Fig. 1). This supports our statement that gypsum dominates over other sulphate minerals when dust values are high. We agree that more parameters are needed for a diverse mineralogy than dust alone, but we cannot discuss the impact of acidity or conductivity in detail here. A multiple regression, or a similar test, is indeed an interesting approach and will be especially useful when it is possible to implement data from the Glacial. Analysing the relationship between different environmental parameters is beyond the scope of this manuscript.

Ref: Line 483: Nitrate salts are a not common terrestrial mineral, being found mostly in extremely arid environments. I think it is a mistake to presume detrital origin here. Nitric acid (as N₂O₅ or HNO₃) is known to be a component of atmospheric fallout and therefore of ice cores. It is far more likely that the nitrate salts formed in some sort of competition with the sulphosalts, particularly since they are found where sulphate abundance is low.

Answer: We discuss this process a few lines further down, but adapted the paragraph in the following way: "Nitrates are well soluble in water and a major impurity component in polar ice as obtained from CFA (Röthlisberger et al., 2000b) and IC (Eichler et al., 2019) analyses, but there is a lack of understanding in which form they are present in ice. Nitric acid (N₂O₅ or HNO₃) is a component of atmospheric fallout, and thus of ice cores, and could compete with other acids, such as sulphuric acids. Sulphuric acid competes with other acids to react with the relative rare cations, replaces other acids in their salts and thus forms a variety of sulphate salts (Iizuka et al., 2008). The relative abundance of nitrates at a certain depth (Fig. 5A) indicates that similar processes occur with nitrates. However, nitrate ions seem to be more likely to exist in dissolved forms than in particle forms due to their good solubility in water."

Ref: Line 490: Epidote and prehnite are both fairly common metamorphic minerals, so I don't think they are overrepresented in your core. Pyromorphite is genuinely rare, but as you observe, only shows up once.

Answer: No changes.

Ref: Line 501: Jacobsite is the tricky one as there is now a "body of literature" suggesting that could actually form in ice cores, but I think you handle this fine.

Answer: No changes

Ref: Line 506: I would delete this final sentence. I think you've said enough given the data you have.

Answer: Adapted, we deleted the sentence.

Ref: Line 509: I think now that you've added all this additional analysis of the mineral formation pathways above, this no longer needs to be framed as "another possibility".

Answer: Changed to: "Chemical reactions occurring inside the ice could explain the diversity in chemical compounds as summarised for snow by Bartels-Rausch et al. (2014), and further discussed for ice by Steffensen (1997); de Angelis et al. (2013); Baccolo et al. (2018) and Eichler et al. (2019)."

Ref: Line 529: This is very intriguing. The notion that the formation of clathrates juggles around the salt chemistry is, as far as I know, novel and certainly a possible explanation of why you lose sulphates and gain nitrates.

Answer: No changes.

Ref: Line 530: What is a "prominent diversity"?

Answer: We deleted "prominent", this is indeed confusing wording: "We observed a diverse mineralogy of micro-inclusions in EGRIP ice across all scales."

Ref: Line 547: This should use the standard terminology of non-seasalt-sulphate that is used elsewhere in the ice core literature. It should also be clearly explained what climatic factors would drive changes in the ratio of sea salt to non-seasalt-sulphate. Again, if they included the CFA data, the authors would be able to calculate non-seasalt-sulphate abundance exactly and see if this mineralogical shift really is driven by changes in sulphate source.

Answer: Changed to "...impacting the input of sea salt (ss), a major source of sulphates ($ss-SO_4^{-2}$). The variability in sulphate diversity and number could display the variety in blown-in sea salt aerosols (ssa) carrying sulphate compounds, such as gypsum."

A more detailed description of the processes is not possible yet, because the data is still being processed while samples are still being measured (see answer above).

Ref: Line 566: Aerosols are not the same thing as dust. The dust is mostly from Asia, but the aerosols have far more diverse and complex origins.

Answer: True, we misused aerosols here and changed it to "Dust particles deposited in the Holocene are...".

Ref: Line 618: You might as well add the bubble-clathrate transition, since you are listing a number of other speculative possibilities.

Answer: Changed to: "the varying sea-ice cover impacting the availability of sulphates in the air during deposition or processes taking place at the bubble-clathrate transition."

This work investigates mineralogy of micro-inclusions in the EGRIP ice core with multiple methods, including Continuous Flow Analysis, optical microscopy and micro Raman spectroscopy.

As far as I know, this is one of the most detailed studies on the microstructural distribution of impurities in polar ice.

Because impurities are not only important climate proxies but also considered to be factors controlling various physical properties of polar ice such as ice deformation, results of the work will be interesting for many potential readers.

However, in the present state, it is not clear whether the main findings of this study (the diversity in mineralogy) is correct or not, due to the critical lack of information (results and discussion of Raman spectra).

Ref: Figure 3:

Raman shifts of the three spectra shown in the figure are considerably (about 5 cm^{-1}) larger than those reported in previous studies: for example, the position of the main peak for feldspar is 508 cm^{-1} (e.g. Sakurai and others, 2011), that for gypsum is 1008 cm^{-1} (e.g. Ohno and others, 2005; Sakurai and others, 2011), that for quartz is 465 cm^{-1} (Sakurai and others, 2011). Although a small difference in Raman shift (a few cm^{-1}) between reports may be caused by differences in apparatus and/or calibration method, this discrepancy is too large. Information about how the apparatus was calibrated and the accuracy of Raman shift (spectral resolution) must be shown in the paper.

Answer: We used the same system as Weikusat et al. (2012, 2015) and Eichler et al. (2019) and calibrated it using the standard procedure deployed by the manufacturer WITec. Thus, a Hg/Ar spectral calibration lamp was connected to the spectrograph with a $25\text{ }\mu\text{m}$ fiber cable enabling the automatic detection of known sharp peaks followed by an automated calibration. The applied grating of 600 enables a spectral range of $>3700\text{ cm}^{-1}$ with a pixel resolution of $<3\text{ cm}^{-1}/<0.025\text{ nm}$. We implement this information in the paper now: "Spectroscopy analysis was performed at the Alfred Wegener Institute Helmholtz Centre for Polar- and Marine Research, Bremerhaven with a WITec alpha 300 M+ combined with a NdYAG laser ($\lambda = 532\text{nm}$) and a UHts 300 spectrometer with a 600 grooves mm^{-1} grating resulting in a spectral range of $>3700\text{ cm}^{-1}$ and a pixel resolution of $<3\text{ cm}^{-1}$."

The identification of the minerals was done by comparing our spectra with data from the largest open-access data base for Raman spectroscopy: the RRUFF data base. Depending on the exact chemical composition of the mineral spectra can differ slightly even though the mineral is the same. Our Raman shifts are indeed slightly larger than the ones shown by Ohno et al. (2005) and Sakurai et al., (2011), both used the same Raman system. Our spectra are similar to the ones measured by Eichler et al. (2019), which used the same system as we did. However, since several peaks are usually used for the identification of a spectrum, small differences in Raman shift are tolerable (and normal) between different systems and/or mineral composition. Unfortunately, the spectra in Fig. 3 were chosen too hastily, the observed Raman shifts are usually lower than the values in Fig. 3 (more accurate are e.g., quartz = 466 cm^{-1} , gypsum = 1012 cm^{-1} and 1140 cm^{-1}). The spectra are thus within the variety range between different instruments and boundary conditions. We chose more accurate spectra for Fig. 3 and implement a figure showing an overview of all spectra in the appendix.

Ref: Figure 3:

My understanding is that one of the highlights of this work is to investigate the variety of minerals, including previously unreported species. However, Raman spectra being the key in analyzing the chemical forms of micro-inclusions are shown only for the three minerals in the paper. To verify the statements about the diversity in mineralogy, spectral information about the other minerals are needed.

Answer : This figure is provided in the appendix now.

Ref: Lines 205-206: "Sulphates can be difficult to distinguish due to tiny differences in Raman spectra, but most sulphates were identified (Fig. 4B)."

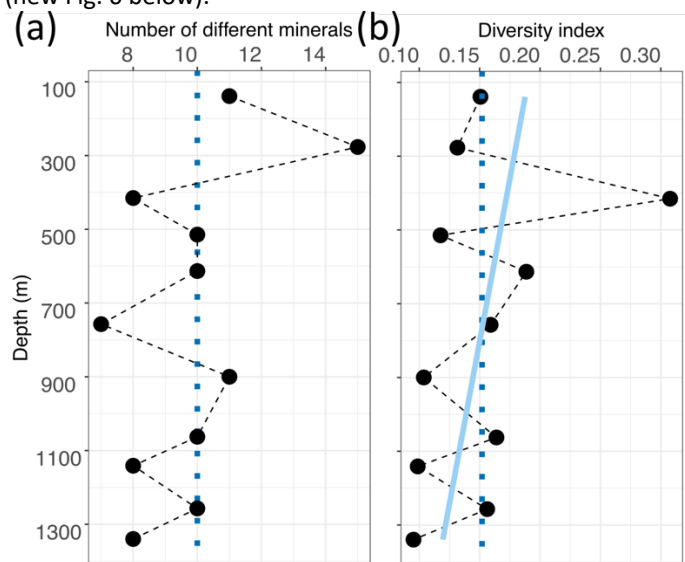
Indeed, it is difficult to distinguish some sulphates, especially between Mg-sulphate and Na-sulphates due to tiny (about 1cm^{-1}) differences in the position of the main peaks (Ohno and others, 2005). Therefore, many earlier works (e.g. Ohno and others, 2006; Sakurai and others, 2011) hesitated to distinguish the two sulphates, and reported peaks around $989\text{-}990\text{ cm}^{-1}$ as Mg-sulphates and /or Na-sulphates. I want to know

how the authors told Mg-sulphates from Na-sulphates using the “compact” spectrometer (the spectra must be shown). As a rule, focal Length of a compact spectrometer is short, resulting in low spectral resolution.

Answer:

This was indeed a point of major discussion throughout the entire process. We now decided to follow the more conservative approach and refrain from differentiating between these two sulphates in such detail. In the results we now classify them (following Ohno et al. (2005), Sakurai et al. (2011)) as Mg- and/or Na-sulphates. We now also apply the same approach to kröhnkite and bloedite (see also answer to referee 1), because these two minerals have similar lattices and thus Raman spectra peaks. Especially when measuring inclusions in ice, i.e. having an overlaying ice spectra, this is the safer approach.

This lowers the absolute number of identified minerals to 24 and has a slight influence on the diversity index (new Fig. 6 below).



Ref: Lines 207-208:” Spectra with a strong peak at 1050 cm⁻¹ probably indicate K-nitrates while a strong peak around 1070 cm⁻¹ might indicate Na-nitrates (Ohno et al., 2005).” The direct comparison with the spectra by Ohno and others (2005) is not inappropriate. As mentioned above, for some reason, Raman spectra in the present work are shifted by approximately 5 cm⁻¹ compared with those of the previous study.

Answer: Our wording here is unprecise und thus confusing. We observed pronounced peaks at 1051-1052 cm⁻¹ and 1070 cm⁻¹. Considering our slight shift in wavenumber compared to Ohno et al. (2005), their values of 1050 cm⁻¹ and 1068 cm⁻¹ for Na-nitrates and K-nitrates, respectively, are thus appropriate to use.

We changed the text to:

Spectra with a peak at 1051-1052 cm⁻¹ indicate K-nitrates while a peak at 1070 cm⁻¹ indicates Na-nitrates (slightly shifted compared to Ohno et al., 2005).

Ref: Figure 4:

It is difficult to distinguish some minerals because of similar colors. In addition to different colors, the use of different patterns will be helpful to differentiate mineral species.

Answer: We tried different approaches and several patterns turned out to be more confusing, especially when inclusions are very close to each other. We thus decided to keep the (colour-blind friendly) colours. Since we now differentiate between two less sulphates it should be easier to distinguish them (see Fig. 5, 7, 8, 9).

Ref: Line 233:”below a depth of” Above?

Answer: In the latest version this was already changed to “above”.

Ref: Lines 304-305:” We identified most sulphates as gypsum or Na-sulphates, which agrees with e.g., Ohno et al. (2005); Eichler et al. (2019) (Fig. 4B).”

The statement of this sentence inconsistent with the Fig. 4B. The figure shows that Na-sulphates (yellow) is a minor species.

Answer: Thanks for noticing, Mg-sulphates were meant and the text was changed according to the reply above to “Na- and Mg-sulphates”.

Ref: Line 479: "26 different spectra were identified"

All 26 spectra should be shown in the paper. Also, Raman peak assignment by comparing those with reference spectra must be done. First, the spectral information is essential to validate the identifications. Second, if the identifications are correct, the spectral information will be very valuable for potential readers.

Answer: A figure in the appendix provides the Raman spectra. Reference spectra are openly accessible in e.g., the RRUFF database or commercial databases.