Review of: Deep ice as a geochemical reactor: insights from iron speciation and mineralogy of dust in the Talos Dome ice core (East Antarctica)
Submitted to: The Cryosphere Discussions
Reviewer: Nicolas Stoll

General comments:

The manuscript tackles the important question of chemical reactions occurring in deep polar ice and the discussed, but so far not observed, option of ice as a chemical reactor. Impurities in polar ice are of importance for several reasons, but dedicated studies on the processes taking place in the ice are rare. Thus, this manuscript is of interest for the cryo-community and offers new exciting results worthy of publication. The current "re-birth" of detailed impurity studies with new or improved techniques (e.g., Synchrotron radiation spectroscopy, LA-ICP-MS) will hopefully help to tackle the challenges ahead regarding Beyond EPICA Oldest Ice.

The presented manuscript, figures and data are of good quality and I mainly have suggestions regarding details. Unfortunately, there are several small issues regarding language, I would thus recommend a dedicated language check. However, the manuscript content is of high quality and I recommend it for publication with minor revisions.

Specific comments:

1) TALDICE should be explained earlier in the introduction or methods. The varying use of "TALDICE" or "Talos Dome ice" can be confusing, I would suggest to stay consistence in wording and to check for the proper use. Throughout the text TALDICE sometimes misses specific affixes such as "TALDICE ice" or "TALDICE dust", the acronym describes the entire ice core and not the described section or parameter in detail. Adding TALDICE ice or TALDICE dust would be enough to increase readability. Furthermore, I suggest to merge the (very short) section on TALDICE with the Materials and methods section.
2) P. 2 l. 24 "growing numbers of studies", please give some examples.
3) In general, the methods are very short and largely refer to other publications. This is a neat way to minimize word count, but 1-2 more sentences for each method, explaining the basics, would enable the broad audience of *The Cryosphere* to follow the manuscript directly. Especially more details on Synchrotron radiation spectroscopic measurements and XANES will be useful since it is relatively new to the cryo-community. One or two examples of the "many additional precautions" taken would be helpful on P. 4 l. 105.
4) P. 4 methods: It is described that 54 samples were prepared, the samples per climate period however add up to 55 (l. 93ff). What is the correct number of samples or did I miss something?
5) A table (possibly in the appendix) providing the formulas of the minerals introduced in 3.3.3. would enhance readability and make it easier to follow the interpretations and weathering effects etc. (4.4.1-4.5). It could even make sense to display the

chemical formula of the weathering processes resulting in jarosite, but I leave that to the authors.

6) P. 6 l. 162: I agree that the observed increase in dust size can be due to aggregation. However, “deep ice” is always relative and it would be good to mention that De Angelis et al. (2013) studied much deeper (~2900 m) and older (>400 ky) ice. Furthermore, Simoes et al. (2002) described something similar for Vostok (3450-3540 m / > 400ky).
7) P. 6 l 168 ff. It´s a very strong statement and other references for other Antarctic ice cores might be needed in addition to Delmonte et al. (2002). Additionally, it is difficult to argue that no post-depositional alteration occurred in EPICA ice since this was not the main objective of Delmonte et al. (2002) (Maybe I missed this explicit statement in the paper though).
   I suggest to mitigate and rephrase the sentence to something like “high abundance of coarse particles is probably a result from in situ…”
8) P. 8 l. 181f link Fig. 3 here.
9) P. 9 l. 200: Define what is detected for the first time.
10) Check wording for “concern”, “appreciate”, xxxx m deep
11) P. 11 l. 221f The cited papers did not analyse Talos Dome ice and it should be stated clearly that only the processes are addressed here. You could add ”…reactive species as proposed for Dome Fuji (Ohno et al., 2005) and EDML (Eichler et al., 2019).” Furthermore, the modelled pinning process by Durand et al, 2006 hasn’t been observed yet in polar ice (e.g., Faria et al, 2010, Eichler et al, 2017, Stoll et al, 2021). Pinning is likely to play a role in the grain size evolution, but without a dedicated study on the microstructure of MIS 2 from TALDICE we can´t say for sure. Rephrasing to e.g., “probably related to pinning of grain boundaries by insoluble particles as suggested by Durand et al 2006.” Could solve this issue.
    What do you mean with “ice metamorphism is too advanced”? Do you refer to the dynamic recrystallization at 1141 m mentioned in Fig. 2 from Montagnat et al., (2012)?
12) I suggest to go through the structure of 4.4. and 4.5 again, the mixture of results and discussion is sometimes difficult to follow. Ways to structure it are e.g., from most abundant (absolute) to least abundant or relative occurrence with depth. Discussing one mineral per subsection and always starting in the same way could enhance readability, e.g., either first presenting the original origin/process leading to the formation of the mineral or describing your data i.e. how much you observed (I would start with your data first and then discuss the origins and other issues).

    I would briefly describe Jarosite in 4.4.X (abundance with depth) which can then lead to the “weathering” subsection explaining the origin. I think this link is one of the main strengths of the manuscript and should thus be presented clearly. I support the idea of the weathering index, but would describe it earlier in the text and also briefly in the figure caption (see comment on Fig. 6).
    Jarosite is not found in the 3 youngest climate periods displayed in Fig. 5, so please restructure the sentence in P.12 l 233. (e.g., Hornblende and Jarosite are found throughout large parts of the core, Hornblende dominates the young/shallow

samples while Jarosite becomes more dominant with depth.)
4.4.2 starts with several sentences which could also be part of the introduction of 4.4. It would be easier to follow by keeping the structure, i.e. first stating the results and then discuss them. Are the 3% pyrite and siderite really "relatively common"?

13) Some statements are made and the used reference are mentioned a sentence or two later (e.g., P. 13 l. 275 "..it has been proposed that additional…"). Naming your references first or connecting the sentences would back up your arguments better.
14) On p. 14 l. 282 it is stated that hematite is not stable in deep ice. However, Hematite was observed e.g., at 2390 m (transition MIS 5.1 to 6) by Eichler et al. (2019) with Raman spectroscopy. To clarify this issue you could simply add "in our analysed TALDICE ice samples" and briefly describe other findings of hematite in deep ice. To explore the processes in deep ice further it would be interesting to know if there is a pH record for TALDICE which could back-up the hypothesis of acidic conditions?
15) Think about adding Kuiper et al. (2020b) to the section on pre-melting.
16) P. 15 l. 320ff. To my knowledge the processes acting on impurities, microstructure and grain growth are not fully understood yet (e.g., Eichler et al. 2019, Stoll et al., 2021). There might be more processes in the ice resulting in the concentration of impurities in addition to large deposition events as suggested for cloudy bands. Which process are you addressing here?
17) P. 16 l. 328 I suggest to explicitly link Fig. 2 from Baccolo et al. (2021) to the microscopic observations.
18) P. 16 Give some specific examples if possible, e.g., l. 341 "The trend of some elements…", l. 349 "TALDICE presents a number of peculiarities, such as…, if compared to…". Later you can explain them in detail, but a brief overview helps to follow.
19) I know it is very difficult to define (and to prove) but I would be interested in your thoughts on the exact processes involving high ice-temperature and ice metamorphism altering the dust record. This goes beyond the scope of this study, but is somehow crucial to understand (deep) ice better.
20) Sect. 5 Conclusions and perspectives:
The results of this study shine new light on the area of impurities in polar ice. Thus, I suggest so include more details regarding the results/discussion in the conclusions and to shift the perspectives part to a dedicated subsection of the discussion (e.g., which other elements/minerals would be interesting to investigate deep ice as a geochemical reactor).

References:

Delmonte, B., Petit, J., and Maggi, V.: Glacial to Holocene implications of the new 27000-year dust record from the EPICA Dome C (East Antarctica) ice core, Climate Dynamics, 18, 647–660, 2002.

de Angelis, M., Tison, J. L., Morel-Fourcade, M. C., and Susini, J. (2013). Micro-investigation of EPICA Dome C bottom ice: evidence of long term in situ processes involving acid-salt interactions, mineral dust, and organic matter. *Quat. Sci. Rev.* **78**, 248–265. doi:10.1016/j.quascirev.2013.08.012

Simoes, J.C., Petit, J.-R., Soichez, R., Lipenkov, V. Y., de Angelis, M., Liu, L., Jouzel, J., Duval,

P., 2002. Evidence of glacial flour in the deepest 89 m oft he Vostok ice core. *Ann. Glaciol*. 35, 340-346
Eichler, J., Weikusat, C., Wegner, A., Twarloh, B., Behrens, M., Fischer, H., et al. (2019). Impurity Analysis and Microstructure Along the Climatic Transition From MIS 6 Into 5e in the EDML Ice Core Using Cryo-Raman Microscopy. *Front. Earth Sci.* **7**, 1–16. doi:10.3389/feart.2019.00020
Kuiper, E.-J. N., de Bresser, J. H. P., Drury, M. R., Eichler, J., Pennock, G. M., and Weikusat, I. (2020a). Using a composite flow law to model deformation in the NEEM deep ice core, Greenland – Part 2: the role of grain size and premelting on ice deformation at high homologous temperature. *Cryosphere* **14**, 2449–2467. doi:10.5194/tc-14-2449-2020
Stoll, N, Eichler, J., Hörhold, M., Shigeyama, W. and Weikusat, I. (2021) A Review of the Microstructural Location of Impurities in Polar Ice and Their Impacts on Deformation. *Front. Earth Sci.,* doi: 10.3389/feart.2020.615613
Baccolo, G., Delmonte, B., Niles, P.B. *et al.* Jarosite formation in deep Antarctic ice provides a window into acidic, water-limited weathering on Mars. *Nat Commun* **12,** 436 (2021). https://doi.org/10.1038/s41467-020-20705-z

Figures

Figure 1 caption: The red bands highlight the Holocene and marine isotopic stages 5.5, 7.5 and 9.5.

Figure 2: The plots are rather busy and the use of the Holocene 95% confidence interval in 2b-d is not trivial to understand with the current legend. It might help to have the same legend in each panel and highlighting that the Holocene is always the reference.
Caption: Consider adding (arrows from shallow to deep) for the trajectories as done in Fig. 4, “with time” can be interpreted both ways.
Out of curiosity: why the jump in displaying the dust size distribution from MIS2 to MIS6?

Figure 3 caption: PAAS reference seems to be missing.

Figure 4: Minor, but the depth axis is the other way around compared to other figures. Having it always the same way would enhance understandability.

Figure 6: Please describe the weathering index briefly in the caption, for more details you can then refer to the section in the main text.

Technical corrections:

P. 1 l. 12 “allowed” change to “allow”

P. 2 l. 22 to clarify between dust and physical properties of ice consider changing “grain size” to “dust grain size”

P. 2 l. 26 sentence is difficult to understand, please rephrase “the older the ice”

P. 2 l. 30 a brief definition of “metamorphism of ice” would be good

P. 2 l. 35 pressure, stress and strain-rate

P. 2 l. the bottom of polar ice cores, true for Greenland too

P. 2 l. 38 check sentence, "…stable and its concentration"

P. 2 l. 39 "untouched" consider using "unaltered" throughout the manuscript

P. 2 l.41 consider restructuring the sentence

P. 2 l. 50 "to take place in ice are"

P. 3 l. 53 define very deep englacial environments

P. 3 l. 56 "secondary Fe-bearing minerals", maybe give 1 or 2 examples

P. 3 l. 58 first use of TALDICE – please define acronym here

P. 3 l. 61 "considerable attention" might need more references than Wolff et al., 2006

P. 3 l. 62 "the effects of… have been only…"

P. 3 l. 64 define your objectives with some more details

P. 3 section 2 consider merging with Materials and methods

Own paragraph on dust in TALDICE, define studies of "extensive research"

p.3 l. 72 "…what was observed at…"

P. 3 l. 74 sites of the Victoria Land region

P. 3 l. 78 consider rephrasing for clarity: 191 25 cm long section of TALDICE ice. Or in brackets (25 x 3 x 2 cm)
They consist of insoluble mineral…

P. 3 l. 81 "until completely melted" or "melting was completed"

p.4 l. 90 Consider changing the sentence to "Filtration was done with a micro-pipette to concentrate the particles on the membrane in the smallest possible area."

P. 4 l. 109 "600 s"

P. 4 l. 111 "…100% following an…"

P. 5 l. 138 "Antarctic climate visible"

P. 5 l 139 please refer again to figure 1 for the dust concentration (Stenni et al., 2011)
P. 5 l 144 Consider a new paragraph on dust size

P. 6 l. 144 consider spelling FPP and CLPP in full first and then in brackets

P. 6 l. 148 "relatively small compared to"

P. 6 l 149f give examples and references for other sites
…allowing the efficient removal of coarse particles".

P. 6 l. 160 consider changing "appreciated" to "it is visible/ Fig. 1 and Table 1 show that below"

P.7 l. 170 "in TALDICE ice"

P. 8 l. 185 "The latter is richer in residual oxides while lacking labile soluble oxides.

P. 8 l. 188ff "from Fig. 3 is the change…", deep part of the core, respectively. Also check for consistency of the spacing of "%".

P. 9 l. 197 “…the deepest sample lack MGO and CaO, indicating carbonate dissolution,…”

Fig. 4 caption: “the arrow indicates the observed but not quantified ice crystals…”

P. 10 subsection 4.3 I suggest to extent the title to “coordination symmetry”

P. 10 l. 105 “...core consists of a mixture of…”

P. 10 l. 213 “…confirmed by the similarity of the oxidation trend…” The overall pattern is comparable, but consider rephrasing. Also, grain growth is impacted by several processes (impurities, recrystallization, temperature) and the sentence should be rephrased.

P. 11. l. 217 “…during glacials is….”

P. 11 l. 218 “…fresh and only partially oxidized due to limited atmospheric exposure”

P. 11 l. 230 “…have been considered in the discussion.”

P. 12 l. 235 “Fe-mineral in Holocene ice...”

P. 12 l. 241 “…regarded as evidence of…”

P.12 l. 242 “…seems to be the principal mineral”

P. 13 l. 252 “Minerals, which… Patagonian dust, are… or “Minerals enabling to distinguish between…”

P. 13 l. 259f. Rephrase to “In the Holocene siderite and pyrite did not undergo chemical reactions during transport because of proximal dust sources are

P. 13 l. 265 “…main reason…”

P. 13 l. 270 Muscovite is completely absent below 1300 m indicating that this mineral is affected by weathering in deep ice, similar to hornblende. Muscovite, an Al-K silicate, probably supplies a fraction of the K required for…”

P. 15 l. 295 “…the mean value…”

P. 15 l. 308 “These features, …,support…”

P. 15 l. 320 “…of deep ice are responsible for”

P. 15 l. 321 “…local lowering of the pressure melting point.”

P. 15 l.326 “…observed in deep ice…”?

P. 16 l. 331 “Another anomaly is the oxidation…”

P. 16 l. 333 “…which, among others, leads to…”

P. 17 l. 371ff “…making it difficult to isolate…”. This stidy demonstrated that also dust-related signals are altered/impacted by post-depositional transformations.

The Cryosphere guidelines: The abbreviation "Fig." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence, e.g.: "The results are depicted in Fig. 5. Figure 9 reveals that...".