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Air clathrate hydrates in the EDML ice core, Antarctica

Referee report #2

The authors present a new method for analyzing clathrate hydrates using a mosaic-style automated image processing method in "thick sections" of ice-core ice...specifically in their study using the EDML core. They note that this technique allows for more automation and analysis of multiple clathrates while reducing (often tedious and time-consuming) manual counting. The authors used images that were taken almost immediately after core recovery, thereby reducing the risk of clathrate decomposition as a factor in their measurements/analyses.

We thank the reviewer for the encouraging evaluation of our manuscript. The comments and questions will help us to improve the clarity and quality of the manuscript. We reply to the specific comments below.

One of the biggest questions I had was regarding the interpretation of calthrate number-density from a 2D image. The authors do note that they used the recorded thicknesses of the "thick sections" to calculate appropriate volumes for each sample, but that they also used mosaic images from a specific 2D plane in the samples (1.5 mm). This would seem to present some stereological considerations. For example, once clathrate counts are completed for a sample, when determining the appropriate volume for that sample, are cut corrections factored in? Should it be assumed that, similar with ice core bubbles in "thick sections", when sections are planed (or microtomed) for imaging, that some of the clathrates are cut at the surfaces? Given this, an additional amount of "volume" needs to be added back in to account for the portion of the clathrate (or bubble) that was removed. Martinerie and others (1999) as well as Saltykov (1976) note this and base the correction on both the shape of the sample as well as the mean size of the feature being measured in that sample. The end result usually means slightly lower number-densities than first measured. This interpretation of thick sections also leads to considerations when looking at shapes or other orientation data on features as it's not always clear which axis the observer is looking down. Fegyveresi and others (2019) note this to some extent, and made some notable assumptions.

Air hydrates cut at the surface of the ice sample decompose within hours. They leave behind a void that can be seen in the images as black objects (similar to air bubbles). We take care of this by filtering objects with a low mean gray value (i.e. dark objects). Therefore, we conclude that we do not need to consider an additional amount of volume to correct for cut air hydrates.

Fegyveresi and others (2019) correctly note that the maximum elongation is only represented for bubbles elongated in the plane of section. This is also true for air hydrate measurements. Similar to Fegyveresi and others (2019), our technique did not allow us to measure, or identify, the full air hydrate elongation.

Fegyveresi and others (2019) partially overcome this problem by measuring bubble elongation in grains with c-axes close to the plane of section. Provided that air hydrates preferentially elongate along the basal plane of ice, which has yet to be confirmed, this could be an approach to estimate maximum air hydrate elongations in the future.

Because the number of clathrates is ostensibly determined by the number of bubbles, which in turn are determined by the number of grains, and ultimately the site temperature and accumulation rate, it may be beneficial to show a comparison of Nah to bubble number-density with depth. Visually it would also be interesting to see the crossover of bubble decrease and clathrate increase in the transition zone. It would also give some preliminary estimates of bubble-to-clathrate ratios.

We agree that it would be great to show the evolution of Nab before- and in the BHTZ and compare it the with increase in Nah in the transition zone. However, or manuscript focusses on air hydrates below the BHTZ. Assessing of air hydrate properties in the BHTZ could be addressed in future work.

In the calculations/estimations of Total Air content, (ln ~260-275), are there any possible surface elevation implications that could be interpreted from changes in TAC, or perhaps changes in impurity content?

The TACh (Total air content included in air hydrates) obtained with our method should be primarily regarded as a control parameter for the accuracy of the method. We thereby use a similar approach to Lipenkov (2000). Our estimates are currently too uncertain to draw physical conclusions on surface elevation, etc.

We understand that our decision to place paragraph 4.2. in the Discussion can lead to a misinterpretation. We will follow the suggestions by reviewer #1 and move sections 4.1 and 4.2 from Discussion to Results, and merge them with sections 3.1 and 3.2, respectively. I.e. we move section 4.1 to 3.1.1 and the first paragraph of 4.2. to 3.2.1. However, L263 – L273 should not be merged with section 3.2. We propose to merge these lines with section 4.3.1 and add them after L301.

This should improve the clarity of the manuscript.

Are there any other ice-flow or deformational considerations that need to be made with respect to the site and observed measurements? Has the ice divide migrated over time? has the ice flow direction changed? What about borehole inclination or azimuth uncertainty of thick sections with respect to ice flow? Was ice-flow azimuth of the cores even recorded during recovery?

It is currently unclear whether and how the ice divide(s) migrated and if the ice flow direction changed through time. Generally, the ice at EDML most likely originates from further upstream around the Dome Fuji region (e.g. Huybrechts et al., 2007; https://doi.org/10.5194/cp-3-577-2007). This can cause non-climatic biases, e.g. in the interpretation of the d18O record (temperature). For this work, we decided to use measured d18O data rather than reconstructed values, especially since reconstructed values are not available for samples deeper than 2415m.

The borehole inclination was measured in the year 2005 and is roughly between +/- 3° (Weikusat et al., 2017; https://doi.org/10.1098/rsta.2015.0347). We will add this information to the manuscript in the Introduction.

Unfortunately, the absolute orientation of the samples with respect to ice flow could not have been obtained.

We thank the reviewer for the additional interesting questions. However, further interpretation of our data are beyond the scope of this manuscript.

Figure 5, panel 1, are the d18O data different colors because they come from two sources? (Also, the caption the Meyer et al. has no date.) While they are referenced in the text, the shaded bands should also be noted in caption. It's also not entirely clear what "a pronounced deviation of climatic influence" means here. Is this specific to the d18O data?

1) The blue data correspond to published record (EPICA Community Members, 2010) for the dated part of the EDML ice core (down to 2415m depth). Below 2415m depth, due to large scale disturbances in the ice stratigraphy, the integrity of the d18O record is lost. The different coloring should emphasize this.

They gray data were first mentioned by Weikusat et al. (2017) (personal communication with H. Meyer and H. Oerter 2016). They will be made publicly available via the open-access repositories PANGAEA by Meyer et al..

We will modify the figure caption for Fig. 5,7 as follows: "a) Paleo-climatic information as δ18Oice values. Blue corresponds to the dated- (EPICA Community Members, 2010), gray to the non-dated part of the ice core (Meyer et al.),

2) Yes. We use the d18O data as a proxy for past climate to compare it with measured air hydrate number and size. We will change L291 – 294 to make this clearer. "For samples from 2025 - 2115 m depth (region 1 in Fig. 5), encompassing MIS 5b and parts of MIS 5c, we observe an evident deviation of the climatic influence on the air hydrate ensemble. We measure a low Nah and a relatively large mean diameter (c.f. section 4.4.1), whereas the colder climate during MIS 5b (Fig. 5a) should result in a relatively high Nah and a small average size of air hydrates."

Figure 6 - I had some issues with the two colors being so similar...maybe just swap for something different? Perhaps noting in the graphs that the green dots are "Scaled values" instead of "adjusted". ...or maybe Nah-derived values (w 1.4 scaling applied). Either way, it should be clearer which color goes with which axis.

Thank you for this suggestion, we will change the coloring for this figure and replace "adjusted" with "scaled".

In this case, both colors correspond to both axis as the volume concentration can be directly converted to the TACh. We wanted to make this clear with the sentence on L226: "Naturally, the TACh and Vc signals show the same pattern (Fig. 6b)."

Figure 7 the eigenvalue lambda label should also be labeled on the axis or identified in the caption for the reader. Also, what are the shaded bands 1 and 2?

We will add the lambda label to the caption and add the explanation for the shaded bands Fig.5 and Fig. 7.

Figure 7 also shows a single max c-axis at ~2230, yet the text says it happens at 2030m.

For this Figure, the change in ice CPO via depth at EDML is indicated with the change in the second eigenvalue (lambda 2) of the orientation tensor of the ice crystals c-axis distribution. Lambda 2 shows the development of a single maximum at 2030m, which holds down to about 2500m. The insets of the schematic stereographic projections are only meant to visualize the change in CPO corresponding to the three "terraces" visible for the lambda 2 parameter. We think that using all 3 lambda values would overload the Figure, but the complete CPO evolution at EDML is given by Weikusat et al. (2017).

Weikusat et al., 2017: https://doi.org/10.1098/rsta.2015.0347

We will make this clearer in the Figure caption.

Figure 8 - can you re-identify the stars? I know they are noted in previous plots, but it would be helpful to identify here as they are so noteworthy.

We agree and will reidentify the stars.

250 Is there a physical significance to the 1.4 scaling, or was it simply the number that allowed for the Nah values to correlated with measured TAC? Also why was this not shown in the graphs?

There is no direct physical meaning for the scaling factor. It was used to match the mean TACh with the mean TAC measured by Ruth et al. (2004) and to estimate the measurement accuracy. We decided not to include the scaling factor in the other graphs because we want to stay close to the actual measured values.

The improvement of the structure of the text should provide additional clarity (see answer to L260-275).

330 Authors note: For the EDML ice core, the age of the ice deeper than 2415 m is not known. However, the sudden increase in ice grain size by one to two magnitudes to up to 0.5 - 1 m for the deepest samples (Faria et al., 2010a; Weikusat et al., 2017) and the relatively warm in-situ ice temperature of at about 2550 m (Figure 7d) indicate favorable conditions for air hydrate crystal growth. Thus we interpret our data to mean that from this depth, the climate signal is dampened by considerable air hydrate crystal growth." - So should it be assumed then that there is a trend that would need to be accounted for at any depths being influenced by warming from the bed?

Salamatin et al. (2003) report that the temperature dependent activation energy of air diffusion does not change their simulations of air hydrate properties for the Vostok ice core down to a depth of 3300m (temperatures below -13°C). For the GRIP ice core, where the ice temperature increases above -13°C close to the bed, their model fits the data by assuming the air diffusion rate activation energy increases near the bottom.

This means we can assume that there is no or negligible influence on air hydrate growth for ice temperatures colder than at least -13°C. Thus, we mention the possible temperature effect only for the depth region from 2550 m to the bottom.

196 - "No air hydrates were found in lowermost sample". Is this related to the proximity of the bed? Basal temperatures? etc.?

This question is related to a question asked by reviewer#1 (L196). We will provide identical answers to the two related questions:

The lowermost sample is from 2773.91 m depth. This means that it is about 25 cm above the bottom of the ice core. To the best of our knowledge there are no air content measurements for this sample. However, it was reported that, from 2760 m, the concentration of micro inclusions gradually decreases with depth (Faria et al., 2010). The bottom of the core reaches the pressure melting point (-2°C; Faria et al., 2010) and ice core drilling was terminated because subglacial water was entering the borehole (Wilhelms et al., 2014).

Therefore, it could either be accreted ice with no, or very little impurity inclusions (at least in the 10cm sample!). Or meteoric ice that underwent processes which resulted in the expulsion of impurities and gases, i.e. the segregation of impurities to the grain boundary network and the subsequent drainage to the bedrock driven by the hydraulic gradient (Rempel 2002,2005). These processes are considered to alter the basal ice at EDC, Dome Fuji and NEEM (Tison et al., 2015; Ohno et al., 2016; Goossens et al., 2016).

While we currently cannot explain its origin, we believe that the information about the air hydrate content in the deepest sample is an interesting detail that deserves mentioning. Further investigations of the deepest ice at EDML are necessary to determine its origin and explain the absence of air hydrates.

We will add this discussion about the last sample to the end of paragraph 4.3.2

Rempel et al., 2002: https://doi.org/10.1029/2002JB001857

Rempel 2005: https://doi.org/10.3189/172756405781813564

Faria et al., 2010: https://doi.org/10.1016/j.quascirev.2009.10.016

Tison et al., 2015: https://doi.org/10.5194/tc-9-1633-2015

Goossens et al., 2016: https://doi.org/10.5194/tc-10-553-2016

Ohno et al., 2016: https://doi.org/10.1002/2015JF003777

Best regards,

Florian Painer et al.