

Reply to referee's comments

Anonymous Referee #2

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The manuscript presents a fairly large new dataset allowing to characterize the gas transport and trapping at a new firn air pumping site: Styx glacier. It is a very interesting site, with very old air (~90 years) in the open porosity of the deep firn. The few previously documented sites with similarly old air undergo lower accumulation rates. The manuscript provides an overall convincing interpretation relating the older than usual ages to a wider than usual lock-in zone with a larger density variability possibly related to a wind effect on snow metamorphism.

General comments

I am surprised to see no convective zone in $\delta^{15}\text{N}$ data of this windy site (Figure 3d). A check with the barometric equation (Equation 3 in Sowers et al. (1992), cited by the authors) confirmed it.

⇒ Yes, the data clearly confirm that the convective zone (CZ) is small. Fitting the barometric equation suggests a CZ of approximately 3m, which is, in fact rather small for a windy site.

Could the authors comment the absence of a large convective zone?

⇒ We have no clear explanation for this observation, but the data is clear in this regard. We added the following statement to the manuscript.
"Fitting the barometric equation to the $\delta^{15}\text{N}$ data of the upper diffusive zone suggests a convective zone thickness of approximately 3 m. This is within the typical range of observed convective zones, but perhaps lower than expected for a very windy site (Kawamura et al. 2006)."

An overestimation by the firn model of both CO_2 and CH_4 data at the two deepest levels suggests that the diffusivity and/or dispersion used may not be optimal, and the resulting gas ages too young (see also comment on line 183), this point should be checked and the adjustment method for diffusivity and dispersion should be described.

⇒ We updated the tuning of diffusivity and dispersion using the automated method described in Buizert et al. (2012) and Buizert (2011) to improve the fit to the deepest data, and the calculated gas ages are indeed older now, as suggested by the reviewer.

The gas age distribution width in deep firn should be shown and commented (see also comment on l197-199).

- ⇒ We included a figure (Fig. 4) that compares the model-simulated gas age distribution at Styx, South Pole and Megadunes. In each case, we showed the distribution for air with a 100-yr mean age; this occurs at depths near 64.5, 122, and 67 m for Styx, South Pole, and Megadunes, respectively. We added the following sentence:
“The gas age distribution of Styx ice at z_{COD} is narrower than the other sites where old firn air is reported (Fig. 4); we simulate a spectral width of 15.9, 22.8 and 45.5 years at Styx, South Pole, and Megadunes, respectively. This means that the past atmospheric history of trace gases can in principle be reconstructed with higher resolution at Styx than at the other old-air firn sites.”

The authors sometimes used ancient but not the oldest bibliographic references or recent but not the most recent in a somewhat surprising way (see suggestions below).

- ⇒ We added new references as the two reviewers suggested.

There are instances of clumsy drafting (see technical corrections) sometimes making the text difficult to understand (see for example comments on lines 145, 225-226, 287-288), a careful reading by a native English speaker should help improving the manuscript.

- ⇒ We improved English with the help of reviewers' comments and a professional writer.

Specific comments

l28-30: This sentence could apply to DE08 which shows distinct layering (Martinerie et al., 1992, cited in the manuscript) but very young air in the open porosity due to its high accumulation, please reformulate.

- ⇒ We reworded the above-mentioned sentence as follows:
“Our study demonstrates that, all else being equal, sites where weather conditions are favorable for the formation of large density variations at the lock-in zone preserve older air within their open porosity, making them ideal places for firn air sampling.”

l37: I would also quote Schwander et al., 1993 (cited elsewhere in the manuscript) that reports the first firn air pumping operation.

- ⇒ Etheridge et al. (1996, 1998) was replaced with Schwander et al. (1989 and 1993)

l45-46: gas trapping in ice is still an active area of research (e.g. Schaller et al., 2017, cited by the authors), thus the expression “the typical close-off density” without a clear definition should be

avoided. Here the authors could simply quote a range of density values for example.

⇒ We reworded the above-mentioned phrase as follows:
"at a total porosity of ~0.1 (Schaller et al., 2017)"

l49-50: age distributions are also shown in Schwander et al. (1993).

⇒ We added Schwander et al. (1993) in the references.

l63: use consistent terminology: the full close-off depth Z_{cod} (as p5 l130).

⇒ "close-off depth (COD)" was revised to "full close-off depth (Z_{COD})"

l64-72: this section uses a common term "COD" for different evaluation methods of different firm properties. For example, some concepts refer to a mean bubble closure level, and other to complete bubble closure. It should be clarified and/or shortened.

⇒ All "COD"s in the text were revised to " Z_{COD} "s

l73-75: this is not entirely true. Buizert et al. (2012a, cited by the authors) showed that all models in the intercomparison study need a non-zero diffusivity in the lock-in zone to simulate the reference gas profiles at NEEM (see for example the abstract or conclusion), which means that the gas transport speed remains different from the surrounding ice advection.

⇒ We changed "same rate" to "similar rate."

l120-121: I am surprised to see that no co-author is affiliated to SCRIPPS and SCRIPPS personnel is not mentioned in the acknowledgements although the manuscript includes new $\delta^{15}N$ data measured at SCRIPPS (Fig. 3d).

⇒ Thanks for reminding us of this issue. We added several persons in the acknowledgement. The data were measured at a fee for service.

l132: I did not understand which other variables are presented in Table 1.

⇒ We erased "Other variables are expressed in Table 1."

l145: does the standard air used for calibration originate from NOAA?

⇒ Yes, we used the standard air calibrated in NOAA. We changed the sentence as follows:
"The calibration curve of the GC-FID was calculated by the standard air prepared at NOAA, with a CH_4 mole fraction of 895 ppb on the NOAA04 scale (Dlugokencky et al., 2005)."

l149: the $\delta^{18}O$ results shown (Fig. 2) are near surface measurements (surface to 1.6 meters depth) rather than deep firm data, thus this introductory sentence should be modified.

⇒ We added the following sentence:

"We performed the same analysis for the snow pit samples, but without CH₄ analysis."

l152 and 156: δD data are not shown or commented, thus the corresponding equation and precision should be suppressed.

⇒ We deleted the equation and corresponding words as suggested.

l172-173: I don't see a clear correlation between hardness and density in Figure 2b. However, the processes producing snow layering are complex and these parameters are not necessarily correlated. For example, a recent study of a wind event concludes that sintering is not the dominating hardening process and that hardness variability could not be adequately explained (Sommer et al., 2018).

⇒ We agree that the low-resolution (10 cm-resolution) density data for the snow pit do not indicate the relation; however, we qualitatively describe the relation in the text. To make it clear, we added the following sentence:

"The soft layers are presumed to be depth hoar, and the hard ones are wind crust (Fig. 2b)"

We also change the last sentence in the same paragraph as follows:

"The soft layers are coarse-grained, while the hard ones are fine-grained (Fig. 2b-d)"

l181: the references of the up-to-date Australian and French models should be preferred to ancient versions in this context (Trudinger et al., 2013; Witrant et al., 2012).

⇒ "(Buizert et al., 2012a; Trudinger 1997; Rommelaere 1997) was changed to "(Buizert et al., 2012a; Trudinger et al., 2013; Witrant et al., 2012)."

l183: at the two deepest firn sampling levels, the model overestimates both the CO₂ and CH₄ concentrations while SF₆ has already dropped to zero. It thus seems that reduced diffusivity and/or dispersion in deep firn would improve the results and increase gas ages, the effect of using a slightly different accumulation rate could also be investigated. As gas age in deep firn is a major conclusion of the manuscript, this discrepancy should be investigated.

⇒ We retuned the diffusivity and dispersion of the firn to obtain an improved fit of the deepest points (indeed by reducing the mixing). The model fits the SF₆ data almost within the uncertainty; however, we agree that the SF₆ measurements go to zero before the model does. It could be that the low SF₆ concentrations in deep firn are below the detection limit of the SF₆ analysis. In response to this comment we experimented by slightly increasing the accumulation rate to see if it could improve the fit to the SF₆ data, but this was not the case. Thus, we prefer to use the 10 cm/yr accumulation rate that was estimated independently.

l197-199: a high accumulation also tends to reduce the gas age distribution widths, and thus provide stronger constraints for atmospheric trend reconstructions. Therefore age distributions in Styx glacier deep firn should be shown and the comparison with Megadunes (Severinghaus et al., 2010, Supplementary Figure A3) and South Pole (Trudinger et al., 2013, Figure 13) commented.

⇒ We included a figure (Fig. 4) that compares the model-simulated gas age distribution at Styx, South Pole, and Megadunes. In each case, we showed the distribution for air with an 100-yr mean age; this occurs at depths near 64.5, 122, and 67 m for Styx, South Pole, and Megadunes, respectively. We also reported the spectral width of the distributions, which are 15.9, 22.8, and 45.5 years, respectively. Confirming the intuition of the reviewer, Styx indeed has the narrowest distribution, associated with its higher accumulation rate. This means that Styx can potentially provide higher-resolution reconstructions of past atmospheric composition compared to the other sites. We noted this fact in the manuscript.

l205: the density layering effect was already shown by Stauffer et al. (1985).

⇒ The reference was added.

l209-210 and Section 3.3: the importance heterogeneities in gas records at Styx compared to other sites is difficult to appreciate as no quantitative comparison is performed. This could be improved for example by comparing the Styx results with WAISD (Figure 2 in Mitchell et al., 2015), where a very similar methodology was used.

⇒ Mitchell et al. (2015) performed the analysis for WAIS Divide ice with the same depth resolution of 3 cm. We added the following sentence:

“Our results confirm the CH₄ concentration-total air content relation observed in West Antarctic Ice Sheet (WAIS) Divide firn ice (Mitchell et al., 2015).”

l214 and Figure 5: the scale of Figure 5a is inappropriate to properly appreciate the correlation between CH₄ and air content, it could be enlarged in order to use the full page width.

⇒ We expanded the width of the x-axis and separated the figure into four parts (fig. 5a-d) to clearly show correlations.

l239 and elsewhere: replace “COD” with full COD or FCOD each time it refers to the approximate level of complete bubble closure.

⇒ As the reviewer suggested for lines 64-72, we replaced the “COD”s with “z_{COD}”s.

l248-249: Witrant et al., 2012 (cited in the manuscript) also reported LIZ thicknesses at different sites (see their Figure 9), this should be mentioned. Moreover, they report reduced diffusivities (and thus older air ages) at a site with another kind of heterogeneities: numerous refrozen melt layers, this Devon Island site could be mentioned too.

⇒ We added the following sentences:

“Usually, the LIZ thickness increases with a snow accumulation rate (Witrant et al., 2012), presumably because at high accumulation sites density variability in the lock-in zone tends to increase (Horhold et al. 2011).”

“Refrozen melt layers may also act as high density, diffusion-impeding layers allowing for older firn air to be sampled as observed in Devon Island (Witrant et al., 2012).”

l255-257: this relationship was updated in Martinerie et al. (1994), it should be mentioned although I expect the impact on the pcrit estimates to be small.

⇒ We added the following sentence:

“We note that Martinerie et al. (1994) suggested slightly different coefficients for the equation based on a different set of data; however, the results do not significantly change our conclusions.”

l259-260: a parameterization of the lock-in density was proposed by Bréant et al., 2018 (Equation 10).

⇒ We added the following sentence:

“We also note that Bréant et al. (2018) used an equation relating ice density at LID to snow accumulation rate; however, but we prefer to use the relation of temperature- ice density at LIZ by Martinerie et al. (1992) because the latter is more relevant to the ice density at LIZ.”

l265-267: I am not convinced that σ_p/A is a good indicator of air ages because the site having the second highest σ_p/A after Styx is Dome C which undergoes a narrow LIZ, small accumulation and young air ages (Table 1). Thus I suggest to suppress the last column in Table 2 and related comments.

⇒ We deleted the last column as per the reviewer’s suggestion.

l287-288: I did not understand if westerly winds prevail during or between blizzard events, and what is meant by “particles of snow can be sorted”.

⇒ We reworded the sentences as follows:

“During the blizzard events, westerly wind prevailed, and snow particles may have been redeposited with a sorted-size distribution (large grains in the bottom and small grains on the top) similar to winnowing seen in sedimentary records (Sepp Kipfstuhl, personal

communication). Between the blizzards, the solar radiation and temperature gradient may have facilitated the diagenesis of the snow layers..."

l475: critical porosity thresholds (see Section 3.4).

⇒ The Fig. 6 caption was reworded as suggested.

Figures 2c and 2d: a scale should be provided on the pictures.

⇒ We added new scales on Fig. 2c and 2d.

Figure 4 shows CO₂ age data versus depth at 8 other sites than Styx without methodological indications or references. Either references or a methodological description (for new data) should be provided (possibly in a Supplement).

⇒ Now, Figure 4 became Figure S1 in "*Supplement Materials*", and we added a reference for each data set.

Figure 7: it is obvious in this figure that p_{crit} and the air content related definition of the COD is different from the full COD where all the porosity is closed. This is why it would be less ambiguous to use the term full COD or FCOD than COD in the manuscript when it refers to complete porosity closure.

⇒ We replaced "COD" with " z_{COD} "

Table 1 column 4: indicate which gas is used for the age estimation.

⇒ We changed the column title from "Firn air age" to "Firn CO₂ age".

Technical corrections

l35: suppress "those"

⇒ Deleted.

l52: into three zones:

⇒ The semicolon was replaced by a colon.

l56-57: molecular diffusion is the dominant mechanism of trace gas transport in interstitial air

⇒ Corrected as suggested.

l77: remove "-"

⇒ Removed.

l88: composition

⇒ "Compositions" was revised to "composition"

l90: resolution, composition

⇒ Corrected.

l105: suppress "that of"

⇒ Deleted

l135: in the firn was measured

⇒ "firn ice" was changed to "firn"

l135-136: University using a thawing and refreezing air extraction method

⇒ Corrected as suggested.

l136-137: discrete firn samples

⇒ "firn ice" was changed to "firn"

l140-141: in the flask placed in a cooled

⇒ "air in the flask in the cooled ethanol bath" was changed to "air in the flask placed in a cooled ethanol bath"

l172: depth hoar

⇒ We revised "hoarse" to "depth hoar"

l217: content

⇒ "contents" was revised to "content"

l218: and the variability is reduced in deeper layers

⇒ "the variations are stabilized in a deep layer" was revised to "the cm-scale variability is reduced in the deep layers"

l225-226: can induce inhomogeneous records and help constraining the gas age distribution in ice

⇒ "can make inhomogeneous records and how the gas age distribution is determined in ice core studies" was revised to "can induce inhomogeneous records and help constrain the gas age distribution in ice"

l227: Fourteau et al. (2017) is not in the list of references

⇒ The reference was added.

l235: shallowest depth where

⇒ "shallowest depth, where" was revised to "shallowest depth where"

l264: (Hörhold et al., 2011; Fig. 7 and Table 2)

⇒ "(Fig. 7 and Table 2)" was revised to "(Hörhold et al., 2011; Fig. 7 and Table 2)"

l280: Using a snow accumulation rate of

⇒ "Applying the snow accumulation rate of" was revised to "Using a snow accumulation rate of"

l286: blizzards occur

⇒ "blizzard occurs" was revised to "blizzards occur"

l299 and 304: variations in the LIZ

⇒ "variations at the LIZ" was revised to "variations in the LIZ"

l433-435: incomplete reference

⇒ Page numbers were added.

References not cited in the manuscript

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Martinerie, P., Lipenkov, V. Y., Raynaud, D., Chappellaz, J., Barkov, N. I., and Lorius, C. (1994), Air content paleo record in the Vostok ice core (Antarctica): A mixed record of climatic and glaciological parameters, *J. Geophys. Res.*, 99(D5), 10565– 10576, doi:10.1029/93JD03223.

Sommer, C. G., Wever, N., Fierz, C., and Lehning, M.: Investigation of a wind packing event in Queen Maud Land, Antarctica, *The Cryosphere*, 12, 2923-2939, <https://doi.org/10.5194/tc-12-2923-2018>, 2018.

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Trudinger, C. M., Enting, I. G., Rayner, P. J., Etheridge, D. M., Buizert, C., Rubino, M., Krummel, P. B.,

and Blunier, T.: How well do different tracers constrain the firn diffusivity profile?, *Atmos. Chem. Phys.*, 13, 1485-1510, <https://doi.org/10.5194/acp13-1485-2013>, 2013.