Reply to referee's comments

Interactive comment on "Very old firn air linked to strong density layering at Styx Glacier, coastal Victoria Land, East Antarctica" by Youngjoon Jang et al.

We thank the reviewers and editor for valuable comments. We present our point-by-point responses to all of the comments below. The original comments from the reviewer is shown in black, while our responses are presented in blue.

Referee 1: Mauro Rubino

General comments

The manuscript by Jang et al. describes a study performed on the firn, the upper part made of partially compacted snow/ice, of Styx Glacier (near the coast of East Antarctica). The authors report older than usual firn air for a coastal site in Antarctica, where snow accumulation rate and temperature are relatively high. They suggest that firn layering, possibly produced by blizzards, creates a thick lock-in zone, which, in turn, causes the age of firn air to grow quickly before close-off.

Interactive comment

The paper is decently well written and clear enough (though I suggest some changes to improve clarity in the attached document). The methodology is adequate and the results are discussed in a balanced way. However, the conclusions are somewhat overstated because the authors generalise their findings without showing that the correlation between lock-in zone thickness and firn air age holds for all sites in Antarctica.

- ⇨ The high resolution (cm-scale) density measurements needed to generalize our analysis to all Antarctic firn sites are not available, unfortunately. Firn air data show very clearly that within the lock-in zone air ages much faster (in units of years/m). Therefore it is clear that all else being equal, a thicker lock-in zone will always lead to older air.
- ⇨ To address this comment we reworded the last sentence in the abstracts as follows: "Our study demonstrates that all else being equal, sites where weather conditions are favourable 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."

The results seem to be relevant to the journal's readers and, more in general, to the scientific community working on ice core science. However, the major novelty is the finding of the relatively old firn air for a coastal site. There is no major advancement in understanding the mechanisms of firn formation and air bubble sealing. I believe the article can be published in a technical, specialist journal (after some revisions as suggested in the attached document), but I leave it to the Editor to decide whether the manuscript is suitable for The Cryosphere.

- ⇨ The Cryosphere has a long history of publishing articles on firn air, gas diffusion, and snow layering. We clearly demonstrate a link between strong density layering and a thicker lock-in zone, which provides new insights into the nature of the lock-in zone (which is not completely understood). We now also discuss age distributions at various sites with old firn air, showing that the Styx age distribution is very narrow, allowing for higher resolution atmospheric reconstructions. We believe all these contributions make the article suitable for The Cryosphere.

Specific comments and technical corrections See notes in the attached document.

⇨ We appreciate the reviewer's comments. We have responded to each comment below.

Specific comments from Referee #1

Line 27: Maybe better "more rapidly than in the diffusive zone"

⇨ We reworded the sentence as follows:
"We hypothesize that the large density variations in the firn increase the thickness of the lock-in zone and, consequently, increase the firn air ages because the age of firn air increases more rapidly with depth in the lock-in zone than in the diffusive zone.

Line 35: What do you mean by "those"? Which ones? I would delete "those"

⇨ Deleted.

Line 37: It is not clear why you have decided to cite Etheridge et al. (1996 and 1998) to support your statements about obtaining records of atmospheric history from firn air. I understand Etheridge et al. have been among the first to show overlap of ice core. firn and atmospheric gas measurements, but, here I would rather cite the early articles on firn air from Schwander et al. (1989 and 1993)

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

Line 39: "trace" => and ultra-trace

⇨ "trace" is a more general term and may help readers understand better. Therefore, we decided to retain the word "trace"

Line 42: You need to cite the relevant articles for Southe Pole and Megadunes here

⇨ We added Battle et al. (1996) and Severinghaus et al. (2010)

Line 46: "The firn air"=> Delete "the"

⇨ Deleted.

Line 52: "diffusive and lock-in zones"=>Delete "zones"

⇨ Deleted.

Line 55: "d15N of N2" => Why do you mention d15N of N2 only and not other species? Given that you mention it again below, for non-experts, it could be worth explaining here why d15N of N2 is a powerful tracer of firn processes.

=> We added the following line to help the non-expert readers:

"The gravitational enrichment in $\delta^{15}N$ of N_2 is traditionally used to define the boundaries between these zones."

Line 59: "stagnant" => I would remove "stagnant"

⇨ Deleted.

Line 64: "mature" => Maybe "sealed" is a better word than "mature"?

⇨ "mature" was replaced with "sealed."

Line 65: "occurs the density" => Add "when": "... occurs when the density..."

⇨ "when" was added.

Line 77: "-" =>Delete dash; "The firn air models..." => Delete "the"

⇨ Deleted.

Line 78: "the layering" => Delete "the"

⇨ Deleted.

Line 79: "movement the firn air" => Delete "the"

⇨ Deleted.

Line 101: Replace "that was" with a comma

⇨ Replaced.

Line 103: Replace "two-year" with "two years"

⇨ Replaced.

Line 115: Delete "being inflated in", and maybe add something like "providing no risk of sample contamination" at the end of the sentence

⇨ Corrected.

Line 125: "4 types of..." => Is this the model version containing the parametrization of bubble trapping described in Mitchell et al. (2015)? Please, specify.

⇨ Yes, it is. We added:

"The model uses the stochastic bubble trapping formulation described by Mitchell et al. (2015)."

Line 127: Replace "A velocity of the air" with "Air velocity". Also, it is not very clear to me why you have decided to show this equation here. Is the mathematical formulation of air velocity important for your interpretation? Please, explain your choice.

⇨ We deleted the equation as the reviewer suggested. We also deleted “A velocity of the air” because the words are used to introduce the equation.

Line 129: Should "Wair" actually be "Wair(z)"?

⇨ Yes. We replaced “Wair” with “Wair(z).”

Line 134: “total air content measurements” => I do not see any description of the measurements of total air content in this section

⇨ We newly added a few sentences to describe the methods.

Line 139: Please explain why removing surface ice is needed.

⇨ “to remove the surface ice” was changed to “to remove contaminants on the surface ice.”

Line 140: “in the cooled” => Replace "the" with "a"

⇨ Replaced.

Line 142: “air in the bubbles were extracted” => Replace "were" with "was"

⇨ Corrected.

Line 149: “After the measurement” => After completing the measurements of...

⇨ Corrected.

Line 152: “Wrap text for the equations, as done for equation 1

⇨ Done.

Line 171: (Fig 2a) => It is not clear to me why in the figure caption you state that the pit is 220 cm deep, but you only show 180 cm in figure 2b. I would make them the same for consistency.

⇨ We measured only the top 180 cm because that is sufficient for the purpose of the research.

Line 172: “hoarse” => I have never heard this term (hoarse) used in this way. Could you explain what that means?

⇨ We revised the word “hoarse” to “depth hoar”

Line 173: (Fig. 2b) => I cannot really see the difference between low-density and high-density layers from the red line and the blue layers in figure 2b. First of all, you should explain what the blue and light-blue layers represent. Most importantly, what is the relationship between changes in density (as shown by the red line) and changes in the blue/light-blue layering?

⇨ We added a few words in the figure caption as follows:

“(b) Illustration of qualitatively defined hard (high-density, dark blue) and soft (low-density, pale blue) layers observed in the top 180-cm-depth interval. Progressive blue color changes indicate a gradual density decreases with depth. The red line is a 10-cm-resolution density profile."

Line 177: Fig. 2b-d => It would be good to explain how you have obtained the pictures in figures 2c-d in the Method section.

⇨ 2b. Method for obtaining the 10-cm-resolution density measurements is described in Section 3.1.

⇨ 2c-d photographs. We added scale bars in the figures and words in the figure caption, so that the readers can better understand how the figure was obtained.

Line 182: "Etheridge et al. (1996, 1998)" => Are you saying that you have used Law Dome firn air for calibration? If so, please specify it. Also, Etheridge et al. might not be the best references to cite here. There are two articles with Law Dome firn air records published more recently: MacFarling Meure et al. (2006) and Rubino et al. (2019)

⇨ We revised the references. The history was basded on MacFarling Meure et al (2006)

Line 183: "The simulated mole fraction profiles match well with observations" => It would be good to comment on by how much and why the model seems to overestimate CO2 and especially CH4 at the bottom of the firn column.

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

Line 191: "(MacFarling Meure et al., 2006)" => A new version of the Law Dome greenhouse gas records has just been published in Earth System Science Data: Rubino et al. (2019). Consider replacing MacFarling Meure et al. (2006) with Rubino et al. (2019)

⇨ We reworded this sentence as follows:
"The lowest CO_2 mole fraction of 305.18 ppm at depth of 64.8 m (304 ppm after correcting for gravitational enrichment) corresponds to the year of 1922 and and effective age of 93 years (relative to sampling year 2014) on the Law Dome ice core record (MacFarling Meure et al., 2006; Rubino et al., 2019)."

Line 195: "(Severinghause et al., 2001; Fig. 4)" => This is confusing: are you referring to figure 4 of your manuscript or figure 4 in Severinghaus et al. (2001)? If you refer to your figure 4, then in might be better to move "Fig. 4" before, maybe where the colon is.

⇨ We deleted "Fig. 4" to avoid the confusion.

Line 197: I wonder why you have not included Law Dome in Table 1, given that you have used Law Dome firn air records for calibration purposes (if I have understood) and you have cited the main publications of Law Dome records.

⇨ We added the Law Dome data in Table 1.

Line 197: “therefore the firn air” => Delete "the"

⇨ Deleted.

Line 204: Replace "and therefore" with "because"

⇨ Replaced.

Lines 207-208: CO2 has increased as well during the last century. Why have you not used CO2 too? Please explain

⇨ Only CH_4 is sufficient for qualitative data interpretation in this study. Additional measurements for other gas species would not change the main conclusions of the article. CH4 is more easily measured in ice than CO2 is, because a melt extraction can be used.

⇨ We slightly changed the words as follows:
“Because the mole fractions of atmospheric greenhouse gases (CO_2, CH_4, N_2O) have increased during the last century, we may obtain information on the timing of the closure of the bubbles from the greenhouse gas mole fractions of the air trapped in closed bubbles. In this study, we used the CH_4 concentration in closed bubbles ($[CH_4]_{cl}$) and the total air content of the firn ice as indicators of the close-off process.”

Line 210: “density and [CH4]cl show an anti-correlation (Fig. 5)” => Please, specify that you have measured it near the COD. Also, it is not clear to me what shows the anticorrelation you mention. Could you include an inset showing the density vs CH4cl anticorrelation in a scatter plot?

⇨ As the 2nd reviewer suggested, we expanded the depth axis in Fig. 5a-5d such that the anti-correlation may be easily seen.

Line 211: “low-density layers do” => Delete "do"

⇨ Deleted.

Line 213: Delete "Meanwhile"

⇨ Deleted.

Line 214: Cite Aydin et al. (2010), "Post-coring entrapment of modern air in some shallow ice cores collected near the firn-ice transition: evidence from CFC-12 measurements in Antarctic firn air and ice cores", Atmos. Chem. Phys., 10, 5135-5144

⇨ Citation was added.

Line 218: Maybe better something like: "cm-scale variability becomes lower with depth", if this is what you mean by "variations are stabilized at deeper layer"

⇨ “the variations are stabilized at a deep layer” was changed to “the cm-scale variability is reduced in deep layers”

Line 222: "snow fit likewise showed..." => Keep on using present tense for consistency: replace "showed" with "shows"

⇨ Changed.

Line 227: "www.clim-past..." =>I do not think this is needed

⇨ Deleted.

Line 237: "defined by the firn air d15N-N2" => I would say: "defined by the modelled d15N-N2 firn air profile".

⇨ Revised as suggested.

Line 237: Delete "Meanwhile"

⇨ We think that it would be better to retain this word.

Line 240: "thickness of LIZ from density data" => Worth specifying "(between the two orange lines in Fig. 6a)"

⇨ We added "(between the two orange lines in Fig. 6)".

Line 240: "comparable" => Please, provide numbers. How thick is the LIZ from density data and from firn air analysis?

⇨ We added "(15.6 vs. 12.4 m)"

Line 244: "in spite of the possibilities of error" => I suggest you delete this sentence, as there is always the possibilities of error

⇨ We deleted the words.

Line 244-246: "similarity in the LIZ thicknesses..." => This reasoning is not clear to me. Please rephrase

=> We added the following explanation of our procedure: "We test the idea that the lock-in zone corresponds to the depth range bounded by the first closed layer (porosity below 0.1) on the shallow side, and the last open layer (porosity above 0.1) on the deep side."

⇨ We reworded the sentence as follows:

⇨ "The similarity in the LIZ thicknesses from the two methods support the idea that..."

Line 246-247: "We demonstrate here that..." => I do not think you have demonstrated this. Rather, it is something known from past studies (Mitchell et al., 2015 and Horohold et al., 2011) that your study is just confirming at one more site (Stix Glacier). I suggest you replace "demonstrate" with "confirm". To generalise your results, you sh ould show that they hold for all firn sites in Antarctica. For example, in the Introduction you mention Dome C as an exception of site with low accumulation and temperature, but relatively young firn air. Can the characteristic layering at Dome C explain why firn air does not get very old at that site? If you can show this, then your results are valid more in general.

⇨ We changed “demonstrated” to “confirm.”
With regard to the generalization, unfortunately, the high-resolution density data are limited only a few ice cores. Our main goal is not to generalize, but rather report on the old firn air in the coastal site and discuss its causes.

Line 262: “Horhold et al. (2011) did (Table 2)” => "as Horhold et al. (2011) did for the other sites listed in Table 2."

⇨ Changed as suggested.

Line 267: Why have you not plotted the correlation between sigma density and LIZ thickness for all sites in table 2 (or even more, if data exist)?

⇨ High-resolution density data are required to calculate the sigma density, but they are not available for the other sites.

Line 273-281: All this section could go in section 3.1, whereas here you just comment on it.

⇨ We think the paragraph is better located here because the d18O data support the idea that non-seasonal events (e.g., blizzards) are the main control of snow layering.

Line 282-283: Are you suggesting that blizzards can be the main factor controlling snow density variability in firn? If so, you should write it clearly.

⇨ We added the following sentence at the end of the paragraph to clarify the possibility:
“In summary, blizzard events may have played a major role in forming snow density layers.”

Line 330: The surname of the third coauthor appears to be missing

⇨ Corrected.

Fig. 1b: What is the black object in fig 1b? A pen? What is its size? It would be good to provide some indications of the size of each element shown in fig 1b.

⇨ We added the following sentence in the figure caption:
“The length of the black sharp pencil in (b) is 14.3 cm.”

Fig. 4: Eight (8) figures are definitely too many for such a short paper. This figure (fig 4), and also figure 8, could go in a Supplement.

⇨ We deleted Fig. 4 because the firn air ages are presented in Tab. 1. and moved the Fig. 8 to *Supplement Materials*.

Fig. 5a: Please, include Total air content and CH4cl in the legend. Also, explain in the figure caption what the "b" above the blue line represents.
⇨ As the 2nd referee suggested we extended the depth axes and separated the previous Fig. 5a into Fig. 5a-5d. We also made a box in Fig. 5d where the Fig. 5e is located (previous Fig 5b is now Fig 5e).

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 δ15N 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 d15N 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 CO2 and CH4 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 Zcod (as p5 l130).

⇨ "close-off depth (COD)" was reviese to "full close-off depth (z_{COD})"

l64-72: this section uses a common term "COD" for different evaluation methods of different firn 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 δ15N 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 δ18O results shown (Fig. 2) are near surface measurements (surface to 1.6 meters depth) rather than deep firn 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 CH_4 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 CH_4 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 ρcrit 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 σp/A is a good indicator of air ages because the site having the second highest σp/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 ρcrit 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 CO_2 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 polaced 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.

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Editor Decision: Publish subject to minor revisions (review by editor) (26 Jun 2019) by Joel Savarino

Comments to the Author:

Dear authors

after reading the reviewer's comments and your replies, I'm accepting your revised manuscript for publication. However as mentioned in my original message I would like to see the label of the figure axis to conform with IUPAC standard (see below). Also considering that the reviewers greatly improved your manuscript and even suggested new idea (STDV of the age distribution), please acknowledge the reviewers.

⇨ We changed the axis labels as suggested. Now the two reviewers were acknowledged.

equation 1: use larger font so subscribes can be clearly differentiated from product

⇨ The previous equation 1 was deleted by the reviewer #1's suggestion. However, we increased all the font sizes in the other equations.

Use IUPAC nomenclature as much as possible; for instance remove (‰) and x1000 in the deltas definition (Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, Rapid Commun. Mass Spectrom., 25, 2538-2560, 10.1002/rcm.5129, 2011.) Identically, in figure unit should not be put in bracket. In science, a physical quantity is always the product of a scalar by a unit 3 kg, 5 m.s-1 etc. Since on axis are reported only scalar, the physical parameter reported should be divided by the unit to give the scalar. For instance you should not write depth (cm) but depth/cm, not d18O (‰) but d18O /‰ or 1000 d18O etc. (see IUPAC greenbook)

- ⇨ We changed the unit presentations in equations and figure labels as suggested by the editor.

Very old firn air linked to strong density layering at Styx Glacier, coastal Victoria Land, East Antarctica

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Abstract

Firn air provides plenty of old air from the near past, and can therefore be useful for understanding human impact on the recent history of the atmospheric composition. Most of the existing firn air records cover only the last several decades (typically 40 to 55 years) and are insufficient to understand the early part of anthropogenic impacts on atmosphere. In contrast, a few firn air records from inland sites, where temperatures and snow accumulation rates are very low, go back in time about a century. In this study, we report an unusually old firn air effective CO_2 age of ~~89~~ 93 years from Styx Glacier, near the Ross Sea coast in Antarctica. This is the first report of such an old firn air age (> 55 years) from a warm coastal site. The lock-in zone thickness of 12.4 m is larger than at other sites where snow accumulation rates and air temperature are similar. High-resolution X-ray density measurements demonstrate a high variability of the vertical snow density at Styx Glacier. The CH_4 mole fraction and total air content of the closed pores also indicate large variations in cm-scale depth intervals, indicative of layering. We hypothesize that the large density variations in the firn increase the thickness of the lock-in zone and, consequently, increase the firn air ages because the age of firn air increases more rapidly

~~increases~~ with depth in the lock-in zone than in the diffusive zone. Our study demonstrates that all else being equal, sites where weather conditions are favourable for the formation of large density variations at the lock-in zone ~~preserve very old~~preserve older air within their open porosity, making them ideal places for firn air sampling.

1 Introduction

Bubbles trapped in ice cores preserve ancient air and allow direct measurements of the atmospheric composition in the past (e.g., Petit et al., 1999). However, it is difficult to obtain air samples over the past several decades from ~~those~~ ice cores since the more recent air has not yet been completely captured into bubbles closed off from the atmosphere. In contrast, we can obtain the recent records from the interstitial air in the porous, unconsolidated snow layer (firn) on top of glaciers and ice sheets (Schwander et al., ~~Etheridge et al.,~~ 1989~~96~~, 1993~~8~~). In addition, we can take advantage of the very large amount of firn air because it allows us to accurately analyze isotopic ratios of greenhouse gases and many trace gases such as man-made CFCs, HCFCs and SF_6 (Buizert et al., 2012a; Laube et al., 2012). However, reported firn air ages date back only several decades at the sites where snow accumulation rates are relatively high (Table 1). Old firn air (> 55 years) was observed only at sites where surface temperatures and snow accumulation rates are low such as South Pole (Battle et al., 1996) and inland Antarctic Megadunes (Severinghaus et al., 2010) (Table 1); however, even under such circumstances very old firn air is not guaranteed, as demonstrated by Dome C (Table 1).

In the firn layer, air moves through the open pores and is occluded into the adjacent ice at at total porosity of ~0.1 ~~the typical close-off density~~ (Schaller et al., 2017~~wander, 1989~~). ~~The f~~Firn air moves downward with the adjacent ice (advection), but is furthermore mixed by diffusion, and affected by thermal and gravitational fractionation (Craig et al., 1988; Johnsen et al., 2000; Severinghaus et al., 2001; Goujon et al., 2003). In addition, the gradual bubble trapping in the firn affects the movement of the air. As a result, at each depth there is a gas age distribution (Schwander et al. 1993; Trudinger et al., 1997), rather than a single gas age. Therefore, studying firn air is also important for interpreting the record of ancient air trapped in ice cores.

The firn column is generally divided into three zones:~~;~~ convective, diffusive and lock-in~~ zones~~, depending on the mechanisms of firn air movement (Sowers et al., 1992). The gravitational enrichment in —^{15}N of N_2 is traditionally used to define the boundaries between these zones. The convective zone is the upper part of the firn where the air can ventilate with the overlying atmosphere. With stronger wind pumping, there can be a deeper convective zone (Kawamura et al., 2013). This zone has the same $\delta^{15}N$ of N_2 value as that of the atmosphere. The diffusive zone is located under the convective zone, where molecular diffusion is~~of~~ the ~~firn air~~ dominant~~es~~ ~~transport~~ mechanism of trace gas transport in interstitial ~~the firn~~ air (Blunier and Schwander, 2000). The age of the firn air increases slowly with depth in the diffusive zone because of continued gas exchange with atmospheric air via diffusion. Heavier isotopes are enriched with depth due to the gravitational fractionation in the ~~stagnant~~ diffusive layer. Thus, $\delta^{15}N$ of N_2 gradually increases with depth in the diffusive zone. In the lock-in zone (LIZ) below the diffusive zone, gas diffusion is strongly impeded although the bubbles are not entirely closed. The top of the lock-in zone is called lock-in depth (LID), where the gravitational fractionation ceases, so that the $\delta^{15}N$ of N_2 becomes constant. The bottom of the LIZ is defined as the full close-off depth (z_{COD}), where all air bubbles are closed off and firn becomes sealed~~mature~~ ice. The z_{COD}~~COD~~ can be estimated in two different ways. First, we can calculate the z_{COD}~~COD~~ from firn densification models. Typically, the close-off occurs when the density of ice reaches about 830 kg m^{-3} (Blunier and Schwander, 2000),~~.—~~ equivalent to a critical porosity of around 0.1 (Schaller et al., 2017). Also, if temperature is known, the average density at close-off can be estimated from empirical relations (Martinerie et al., 1992). Second, the deepest position where air can be sampled from the firn column is commonly considered as (just above) the z_{COD}~~COD~~. In theory, the z_{COD}~~COD~~ is the depth at which all pores are closed, but it can be ambiguous to specify the z_{COD}~~COD~~ in the field because firn air can be sampled at a slightly deeper depth than that of the shallowest impermeable snow layer due to the existence of permeable layers at deeper depths – this effect is due to density layering (Mitchell et al., 2015).

The gas ages in the LIZ increase with depth faster than in the diffusive zone. In the LIZ, firn air moves downward at ~~(~~nearly~~)~~ the same ~~imilar ame~~ rate as the surrounding ice, and therefore the age of the air increases with depth at nearly the same rate as the age of ice increases.

The age of the firn air is directly related to the movement of the firn air.~~We define the oldest firn air age as the mean age at the deepest sampling depth –. The f~~Firn air models help calculate the firn air age using some parameters such as temperature and accumulation rate. However, several studies found that ~~the~~ layering also affects the movement of ~~the~~ firn air (e.g., Mitchell et al., 2015; Schaller et al., 2017). This implies that physical properties of the ice may affect the age of the firn air as well.

With regard to the lock-in and close-off processes, recent studies have focused on snow layers and microstructure of the firn (Hörhold et al., 2011; Gregory et al., 2014; Mitchell et al., 2015; Schaller et al., 2017). Density variability on millimeter to tens of cm scales is observed in all polar sites. Hörhold et al. (2011) demonstrate that density variability is caused by physical snow properties in the firn column. Several studies have dealt with how snow density variations affect the transport of firn air (Hörhold et al., 2011; Mitchell et al., 2015). Mitchell et al. (2015) showed that the firn layering can affect the closure of pores and the thickness of LIZ, but the relation between snow density variations and range of firn air ages was not quantitatively examined.

In this study, we present firn air composition~~s~~ and $\delta^{15}N$-N_2 from Styx Glacier, East Antarctica to better understand the role of snow density variations on the age of firn air. We also present X-ray density data with millimeter resolution~~s~~ and compare them with $\delta^{18}O_{ice}$ and the closed-pore air composition~~s~~ in the LIZ.

We hypothesize that large snow density variations make the LIZ thicker and facilitate preservation of old firn air at the Styx Glacier. This study will help us better understand how the snow density layers of firn column affects movement and preservation of firn air, and provide guidance on selecting good sites for future firn air studies.

2 Materials and Methods

2.1 Firn air sampling and gas mole fractions analysis

The firn air and ice core were ~~sampled~~ collected at the Styx Glacier, East Antarctica (73° 51.10' S, 163° 41.22' E, 1623 m asl) in December of 2014 (Fig. 1). This site is located 85 km north of the Korean Jang Bogo Station in the Southern Cross Mountains near the Ross Sea (Han et al., 2015). The snow accumulation rate is ~10 cm ice year^{-1} ~~, that was~~ calculated from the Styx16b ice chronology based on methane correlation and tephra age tie-point and thinning functions (Yang et al., 2018). The mean annual surface temperature was measured as -31.7℃ by borehole temperature logging at 15 m depth, two ~~-~~years after the ice core drilling (Yang et al., 2018). Table 1 lists the characteristics of the Styx Glacier and other firn air sampling sites. A total of 13 samples from the surface to 64.8 m depth were collected. The firn air sampling device was constructed, following the design of ~~that of~~ the University of Bern, Switzerland (Schwander et al., 1993). Three vacuum pumps (two diaphragm pumps and one metal bellows pump), several pressure gauges, stainless steel lines, and vacuum valves were housed in an aluminum case to transfer to the polar site. The pump system plays four major roles: (1) purging modern air from the bottom of a borehole, (2) inflating the bladder to block the deep firn layers from the atmosphere, (3) removing the contaminated air and extracting the firn air, (4) transporting firn air to a CO_2 analyzer for measurements of gas mole fractions and store it in firn air containers. The bladder system is designed to be lowered into the borehole to seal the deep firn layer(s) being sampled from the atmosphere. The bladder consists of a 4 m-long rubber tube and metal caps on top and bottom of the rubber tube. The bladder's external diameter is 119.5 mm and internal diameter is 114.5 mm. The material of the tube is butyl rubber (BIIR) which can endure ~~being inflated in~~ low temperatures, providing no risk of sample contamination.

The firn air samples were collected in 3-liter glass flasks at all collection depths. However, to test preservation ability of the sample air containers, Silcocan canisters were also used at 4 depths (0, 35.36, 43.42, 53.95 m). Accurate mole fractions of CO_2, CH_4, and SF_6 were measured at US National Oceanic and Atmospheric Administration (NOAA; https://www.esrl.noaa.gov/). The results for the two types of containers show good agreements. $\delta^{15}N$ of N_2 was analyzed at Scripps Institution of Oceanography for correcting gravitational fractionation effect (Severinghaus et al., 2010).

2.2 Firn air transport model

We used the Center for Ice and Climate (CIC) firn air model which is a 1-dimensional advection-diffusion model to simulate how the air moves in Styx firn column. In this model, there are four~~4~~ types of air transport in the open porosity: (1) molecular diffusion, (2) vigorous mixing in the convective zone, (3) advection, and (4) dispersion in the deep firn (Buizert, 2012b, Buizert and Severinghaus, 2016). The model uses the stochastic bubble trapping formulation described by Mitchell et al. (2015).

~~Air velocity of the air is represented as w_{air} in open pores.~~

$$\cancel{w_{air}(z) = \frac{A\rho_{ice}}{s_{op}^{*}P_{0}}\left(\frac{s_{cl}(z_{COD})P_{cl}(z_{COD})}{\rho_{COD}} - \frac{s_{cl}(z)P_{cl}(z)}{\rho(z)}\right)}\ \text{~~(1), where~~}$$

~~A is the accumulation rate (0.10 m ice yr^{-1}), z_{COD} is the full close-off depth, ρ_{ice} is the density of ice (0.921 g cm^{-3}), s_{op}^{*} is the effective open porosity, s_{cl} is the closed porosity, and P_0 and P_{cl} is the enhanced pressure due to firn compaction in closed bubbles. Other variables are expressed in Table 1.~~

2.3 CH_4 in closed bubbles and total air content measurements

CH_4 mole fraction in the (closed) air bubbles in the firn~~ ice~~ was measured at Seoul National University ~~by a wet extraction method which extracts air from the ice by~~using a ~~thawing and refreezing~~melt-refreeze air extraction method (Yang et al., 2017). 124 discrete firn ~~ice~~ samples (cross section of 8.5 cm × 3 cm, length of 3 cm, ~35 g) were prepared from 4 different depth intervals in the lock-in zone (54.59-55.34, 58.11-59.05, 59.86-60.55, 64.02-65.25 m). All ice samples were cut and trimmed by ~2.5 mm with a band saw to remove contaminants on the surface ice. Then, the ice samples were inserted into the glass flasks attached to the gas extraction line. The pump system evacuated air in the flask placed in a~~the~~ cooled ethanol bath at -70 °C for 20 min. The evacuation time was limited to 20 minutes to prevent from gas loss due to pore openings by sublimation. After the pressure dropped below 0.2 mTorr, the ice samples in the glass flask were melted and air in the bubbles was~~ere~~ extracted. After the melting was finished, we refroze the ice using a cooled ethanol bath to release the gas dissolved in the ice melt. Finally, the extracted air was injected into the sample loop of the gas chromatograph equipped with a flame ionization detector (FID). The calibration curve of the GC-FID was calculated by the standard air prepared at NOAA with a~~the~~ CH_4 mole fraction of 895 ppb~~v~~ on the NOAA04 scale (Dlugokencky et al., 2005).

Total air content of the firn ice samples was analyzed simultaneously with CH_4 mole fraction using the wet extraction system at SNU. The total air content was expressed as the volume of air trapped in the closed pores of unit mass of firn ice sample (in unit of ml per gram ice at STP conditions). The volume of air extracted from a firn ice sample was calculated by the ideal gas law with the internal pressure, volume~~,~~ and temperatures of the sample flasks and vacuum lines. The pressure of extracted air was measured by a pressure manometer connected to the sample loop of the GC-FID. As no direct measure of temperature was available, the temperature of extracted air was assumed to be identical to the surrounding temperatures; the ethanol temperature was used for the sample flasks, room temperature for vacuum lines, and valve box temperature (50°C) for the sample loop. In this study, the corrections for bubble-cut effect and thermal gradient within vacuum line were not considered. More detailed description of the protocols of total air content measurements is described in Yang (2019).

2.4 Analysis for stable isotopes of ice

After completing the measurements of the CH_4 mole fraction in air, the melt water was put into cleaned 125 ml bottles and analyzed for water stable isotope ratios at Korea Polar Research Institute (KOPRI) using a Cavity Ring-Down Spectroscopy (CRDS, L1102-i, Picarro, USA) system. We performed the same analysis for the snow pit samples, but without CH_4 analysis. The data are here presented as δ-notations:

~~(~~$\delta^{18}O$ ~~(‰)~~$=((^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{VSMOW}-1)$~~$\times1000$~~ ~~, δD(‰)$=((^{2}H/^{1}H)_{sample}/(^{2}H/^{1}H)_{SMOW}-1)\times1000))$~~(1)

~~.~~The firn ice melt was filled into a 400 μl insert in a 2 ml glass vial using a syringe filter. The auto sampler transported the ice melt samples in the insert to the vaporizer about 180 nl at a time. The samples with the liquid state were transferred to the cavity after being converted into the water vapor in a vaporizer at 110 °C. The measurement precision evaluated by measuring an in-house standard repeatedly (n=12) was 0.08‰ ~~for $\delta^{18}O$ and 0.3‰ for δD~~ (1 sigma standard deviation~~s~~).

2.5 X-ray firn density measurement

We obtained high-resolution density data using the X-ray transmission method reported by Hori et al. (1999) for the firn ice at various depth intervals. This method is advantageous because it can measure continuously and non-destructively. The X-ray beam penetrates the ice samples and the detector on the opposite side analyzes the intensity of the beam. To make equal thickness for each core section, upper and side parts of the half circle-shape core were shaved by a microtome. After putting the precut ice core on a rack, we set the rate of measurement at 50 mm min^{-1}, and finally obtained 1mm-resolution density data.

3 Results

3.1 Layered stratigraphy

We examined a snow pit, located 10 m away from the main ice core borehole, 2 years after drilling to understand the physical properties such as layers, density, and ice grain size of the upper firn at Styx site. We scratched the snow wall by hand to remove soft layers and enhance the visibility of hard layers (Fig. 2a). The soft layers ~~have low density and~~ are presumed to be depth hoar~~se~~, and the hard ones are wind crusts ~~with high~~

~~density~~ (Fig. 2b). The alternating layers repeat with intervals of few centimeters to 20 centimeters. The top boundaries of the hard layers are sharp and extend horizontally about a meter, but the bottom boundaries are not well defined due to gradual density changes. 10 cm-resolution density data were obtained by a density cutter (Proksch et al., 2016). The soft layers are ~~density is low in~~ coarse-grained~~ layers~~, while the hard ones are ~~it is high in~~ fine-grained~~ layers~~ (Fig. 2b-d).

3.2 Firn gas sampling and the age of firn air

We calibrate the depth-diffusivity profile in the model using trace gases with a well-known atmospheric history (Buizert et al., 2012a; Trudinger et al., ~~1997~~2013; ~~Rommelaere~~ Witrant et al., 2012~~1997~~). The atmospheric time series from well-dated firn air (MacFarling Meure et al., 2006~~Etheridge et al. 1996, 1998~~) and instrument measurement records (NOAA; https://www.esrl.noaa.gov/) were used for calibration. The simulated mole fraction profiles match well with the observations (Fig. 3). CO_2, CH_4, SF_6 and $\delta^{15}N$-N_2 distributions in firn air were modeled. The model does not include thermal fractionation, and therefore provides a poor fit to the $\delta^{15}N$-N_2 data in the upper firn where seasonal temperature gradients fractionate the gases. Fitting the barometric equation to the $\delta^{15}N$ 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). The firn air age (black curves in Fig. 3) slowly increases with depth at the diffusive zone because it mixes with fresh atmospheric air on the surface mostly by molecular diffusion (Blunier and Schwander, 2000). In contrast, the firn air age rapidly increases within the LIZ at a rate ~~the~~ similar ~~same rate of the surrounded~~to that of the ice age~~ in the LIZ~~. The gas age distribution of Styx ice at z_{COD} is narrower than the other sites where old firn air ~~were~~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.

We estimate the age of samples in two ways. First, after calibrating the firn air model, we can derive the mean sample age from the simulated gas age distribution. At the deepest Styx sampling depth (64.8 m) we simulate a mean CO_2 age of 102 years, and a mean CH_4 age of 97 years; the CH_4 age is younger than the CO_2 age due to the higher diffusivity of CH_4. Second, we can estimate the sample ages by comparing the measured trace gas concentrations directly to the atmospheric histories of these gases – this age has been called the “effective age” (Trudinger et al. 20~~0~~13). The lowest CO_2 mole fraction of 305.18 ppm~~v~~ at depth of 64.8 m (304 ppm after correcting for gravitational enrichment) corresponds to the year 1921 ~~the year of 1926~~7 ~~or mean~~ an effective age of 93 ~~89~~years (relative to sampling year 2014) on the Law Dome ice core record (MacFarling Meure et al., 2006; Rubino et al., 2019). ~~We also obtained t~~The CH_4 mole fraction of 943.36 ppb~~v~~ at the same depth (946.5 after gravitational correction)~~, which~~ corresponds to an effective age of ~~88~~ 96 years (MacFarling Meure et al., 2006) (Figs. 3a, 3b).~~ Each gas has different modeled ages because their diffusivities are different~~. The second method provides younger ages because the growth rate in the atmospheric mixing ratios of these gases has increased over time, biasing the effective ages towards younger values (Trudinger et al. 2002). Table 1 lists effective CO_2 ages in the deepest firn air sample for several sites; we here compare the effective CO_2 age between sites rather than the modeled mean age, as it is purely empirical and does not rely on model assumptions.

Only few ~~studies have reported~~firn air sites have effective ~~firn air~~CO_2 ages~~ older than 89~~ around– 93 years or older: ~~93~~ 91 years from the South Pole (Battle et al., 1996~~Severinghaus et al., 2001~~) and ~~121~~ 129 years from Megadunes (Severinghaus et al., ~~2001~~2010; ~~Fig. S14~~Table 1). These sites are located~~ inland~~ in interior Antarctica and have low annual mean temperatures and low snow accumulation rates (Table 1). Firn densification takes a long time if snow accumulation ~~is~~ and/or temperature are low, therefore ~~the~~ firn air can be preserved for a long time without being trapped. In contrast, the Styx site is located near the coast and has relatively high snowfall, and therefore the age of ~~89~~ 93 years is very unusual. Sites of comparable climate characteristics typically have an oldest firn air age of around 40 years. This indicates that there may be other factors that can permit preservation of the old firn air at Styx Glacier.

3.3 Density layering and its influence on bubble trapping

Firn density is the primary control on the bubble close-off process.~~, becauseand therefore~~ ~~density~~ Density layering leads to staggered bubble trapping, with high-density layers closing off before low-density ones (Stauffer et al., 1985; Etheridge et al. 1992, Mitchell et al. 2015, Rhodes et al. 2016).

Because the mole fractions of atmospheric greenhouse gases (CO_2, CH_4, N_2O) ~~mole fractions~~ have~~s~~ increased during the last century, we may obtain information on the timing of the closure of the bubbles ~~close-off~~ from the greenhouse gas~~CH_4~~ mole fractions of the air trapped in closed bubbles. ~~($[CH_4]_{cl}$).~~ In this study, we used the CH_4 concentration in closed bubbles ($[CH_4]_{cl}$~~-~~) and the total air content of the firn ice as indicators of the close-off process. The density and $[CH_4]_{cl}$ show an anti-correlation (Fig. 5). Our results confirm the CH_4 concentration-total air content relation observed in West Antarctic Ice Sheet (WAIS) Divide firn ice (Mitchell et al., 2015). High-density layers reach the lock-in and close-off densities at shallower depths than low-density layers~~ do~~. Thus, air bubbles are trapped at shallower depths in high-density layers. Early trapped bubbles preserve older air with lower greenhouse gas mole fractions. ~~Meanwhile, h~~Higher air content is expected in the high-density layers, in which open porosity is small and closed porosity is large (Fig. 5). However, we cannot entirely exclude the possibility of some post-coring bubble close-off (Aydin et al., 2010). High open porosity in low-density layers may have more chances to trap modern ice storage air, which has higher mole fraction of CH_4 than atmospheric background levels.

Figure 5a shows $[CH_4]_{cl}$ and total air content~~s~~ in the LIZ of the Styx firn. $[CH_4]_{cl}$ generally decreases with depth and the cm-scale variability is reduced in the deep layers~~variations are stabilized at a deeper layer~~, while the total air content generally increases with depth. The $[CH_4]_{cl}$ greater than CH_4 mole fraction in neighboring firn air (green line in Fig. 5a-d) indicates part of bubbles formed after coring and increased the $[CH_4]_{cl}$, as previous studies also observed (Mitchell et al., 2015; Rhodes et al., 2013). Most of $[CH_4]_{cl}$ data show large cm-scale variations (Fig. 5). The highs and lows of $[CH_4]_{cl}$ repeat with cycles of 6 ~~cm~~ to 24 cm (Fig. 5e~~b~~). Note that the layering observed in the snow pit likewise shows~~ed~~ irregular intervals (Fig. 2b). From the layer spacing, we conclude that bubble trapping at Styx is not controlled by annual layers (Section 4), as was observed at Law Dome (Etheridge et al. 1992).

The evolution of CH_4 in the closed porosity may give information on how the snow layers can ~~make~~ induce inhomogenous records and help constraining~~ how~~ the gas age distribution ~~is determined~~ in ice~~ core studies~~ (Fourteau et al. 2017~~, www.clim-past.net/13/1815/2017/~~). However, the details are beyond the scope of this study and we will focus on the firn air age in the open porosity.

3.4 High-resolution firn density measurements

The X-ray measurements show highly variable density on cm scales. We converted the high-resolution density to total porosity using the following equation:

$$\Phi_{total} = 1 - \frac{\rho}{\rho_{ice}} \qquad (2\cancel{3})$$

where ρ = density of porous ice; ρ_{ice} = density of bubble-free ice (919 kg m^{-3}); and Φ = porosity. We test the idea that the lock-in zone corresponds to the depth range bounded by the first closed layer (porosity below 0.1) on the shallow side, and the last open layer (porosity above 0.1) on the deep side.

At Styx Glacier, the shallowest depth~~,~~ where the running mean of total porosity with a 1 cm-thick window reaches below 0.1, is 48.1 m (Figs. 6a and 6b). It is approximately 4.3 m shallower than the LID of 52.4 m defined by the modelled firn air $\delta^{15}N$-N_2 profile. Meanwhile, the deepest point, where the running mean (with a 1 cm-thick window) ~~becomes less than~~exceeds 0.1, is at 63.7 m (Figs. 6a and 6c), which is shallower than the z_{COD}~~COD~~ of 64.8 m defined by the deepest successful firn pumping depth. Although the LID and z_{COD}~~COD~~ from the density data are different from those defined by firn air data, the thickness of LIZ from density data (between the two orange lines in Fig. 6a) is comparable to that from firn air analysis (between two blue lines in Fig. 6) (15.6 vs. 12.4 m). The offsets of the LIZ about 1-4 m between those from total porosity and the firn air measurement may be due to for example small calibration offsets in the density data set, the fact that actual critical porosity may be variable and depend on the study site~~s,~~ ~~perhaps depending~~ or on horizontal snow density variations and the horizontal extent of diffusion-impeding layers. ~~In spite of the disagreementpossibilities of error, t~~The similarity in the LIZ thicknesses from the two methods support the idea that the large variations of density can increase the LIZ thickness by shallowing LID and/or deepening the z_{COD}~~COD~~. The thick LIZ eventually permits storing old firn air at Styx (Table 1). 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). ~~but firn air age would not increase if the density variability is not sufficient~~Refrozen melt layers may also act as high density, diffusion-impeding layers allowing for older firn air to be sampled ~~increase snow heterogeneities and reduce diffusivity and firn air age~~ as observed in Devon Island (Witrant et al., 2012)~~, but the age increase appears smaller than the case of Styx Glacier.~~ We demonstrate here that the snow density variability is an important factor in determining the firn air age. We suggest that sites with higher density variations at the LIZ have a high possibility of a thick LIZ and therefore old firn air, even in warm, relatively high-precipitation coastal climates.

4 Discussions

To quantitatively compare density variability of Styx snow with those at other glacier sites, we may use the standard deviation of densities (σ_ρ) near the mean air-isolation density (Hörhold et al., 2011; Martinerie et al., 1992). The mean density at the mean air-isolation depth (ρ_{crit}) can be related to mean annual temperature (T in Kelvin) using the following equation, which is empirically obtained from air content measurements (Martinerie et al., 1992):

$$\rho_{crit} = \left(\frac{1}{\rho_{ice}} + 7.6 \times 10^{-4} \times T - 0.057\right)^{-1} \quad (3\cancel{4}),$$

where ρ_{ice} is the density of bubble-free pure ice.

Although this equation cannot provide exact ρ_{crit}, we can take advantage in estimating the density at LIZ without gas chemistry data (Hörhold et al., 2011). 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. 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. Using the Styx high-resolution X-ray density data at depth interval of 43.13-66.97 m, we calculated the standard deviation of densities (σ_ρ). For each σ_ρ, we used 1000 density data points (Fig. 7) as Hörhold et al. (2011) did for the other sites listed in ~~(~~Table 2~~)~~. At Styx, ρ_{crit} is 821.68 kg m^{-3} according to equation (4), and the standard deviation of densities at ρ_{crit} (σ_ρ, ρ_{crit}) is 19.33 ± 1.87 kg m^{-3}, which is greater than those in the other previously studied sites (Hörhold et al., 2011; Fig. 7, Table 2). The high σ_ρ, ρ_{crit} at Styx likely facilitates the thick LIZ and old firn air. ~~A high snow accumulation rate may not allow old firn air ages for a certain LIZ thickness. Thus, σ_ρ, ρ_{crit} divided by a snow accumulation rate (A) can be a better indicator of the range of air ages. The Styx (σ_ρ, ρ_{crit} / A) is also greater than other studied~~

~~sites (Table 2).~~

A high-density (low-density) layer at surface may become a low-density (high-density) layer (Freitag et al., 2004; Fujita et al., 2009) at density of 600-650 kg m^{-3}, which occurs at shallower depths than LIZ (Hörhold et al., 2011). Thus, vertical snow layering at surface may not directly give information about density variability at LIZ (Hörhold et al., 2011). However, conditions for snow layering at the surface still may give us clues on the density variability at LIZ. The conditions may include redistribution of snow by wind and formation of wind and/or radiation crusts (Martinerie et al., 1992; Hörhold et al., 2011). To test the possibility of seasonal causes, we analyzed stable isotopes of surface snow (δ^{18}O) because the surface δ^{18}O generally follows seasonal variation (depleted in winter and enriched in summer). Figures 2e and 2f show the stable isotope profiles of snow (δ^{18}O) at Styx Glacier, which are apart by ~100 m; one is from a snow pit made in 2014 and the other is from the main ice core drilled in 2014. The δ^{18}O profiles commonly show cycles with intervals of ~40 cm per year, given that local maxima of δ^{18}O indicate summer, and minima winter layers. Meanwhile, the repetition of the density layers has twenty cycles (high and low density layer pairs) in the top 180 cm depth at the snow pit (Fig. 2b). Using~~Applying~~ a~~the~~ snow accumulation rate of ~40 cm y^{-1} in recent years, the density layers have 4~5 cycles y^{-1}, indicating that the formation of snow density layers is mainly controlled by non-seasonal factors.

A blizzard occurred during the ice coring campaign in December of 2014. We observed that the blizzard strongly reworked the surface snow. The Automatic Weather System (AWS) installed within 10 m from the borehole site show that blizzard events (wind speed > 15 m s^{-1}) took place on December 29 in 2015, May 23, June 26, August 17, and September 7 in 2016 (Fig. S1~~8~~). The number of blizzard events in a year is similar to the mean density layer cycle of 4~5 y^{-1}. Although Blizzards occur~~s~~ more frequently in winter, the frequency of 5 yr^{-1} is comparable to the number of the density layer cycles of 4~5 yr^{-1}. During ~~At~~ the blizzard events~~time intervals~~, westerly wind prevailed, and ~~. When redeposited by a blizzard event,~~ ~~–~~snow particles may have been redeposited with a sorted–size distribution (large grains in the bottom and small grains on the top)~~of snow can be sorted~~ similar to winnowing seen in sedimentary records (Sepp Kipfstuhl, personal communication~~s~~). ~~and~~ Between the blizzards, ~~following~~ the solar radiation and temperature gradient may have facilitated the diagenesis of the snow layers (Alley, 1988; Fegyveresi et al., 2018). During the diagenesis processes, fine and coarse flake layers may form high-density and low-density layers, respectively. In summary, blizzard events may have played a major role in forming snow density layers

5 Conclusions and implications

About ~~89~~93-year-old firn air (effective CO_2 age) was found at Styx Glacier, East Antarctica, located near the Ross Sea coast. This is of great scientific interest because such old firn air is commonly only found in the inland sites such as the South Pole and Megadunes. The thickness of Styx LIZ is relatively greater than those in other sites where snow accumulation and temperature are similar. The thicker LIZ made the Styx firn layer preserve old firn air because the age of stagnant firn air rapidly increases with depth in the LIZ as air exchange with the atmosphere has stopped. We hypothesized that the high snow density variations in~~at~~ the LIZ of Styx Glacier made the thick LIZ and old firn air. To test the hypothesis, we conducted high-resolution X-ray density measurements. We argue that the thick LIZ is related to the high density variations at Styx Glacier. We also examined why high snow density variability developed at Styx site. The effect of strong wind (e.g., blizzards) may facilitate the density layer formation. It is likely that old firn air (>55 years) can be found in areas where climatological conditions are favorable for high snow density variations at LIZ even when the sites are located near the coast. We may take advantage in sampling and transportation from the coastal sites, because logistics is easier for those sites. Theoretically, the oldest firn air should be available in a site that has both strong layering and a low accumulation rates. Older firn air, perhaps as old as 150 years, may still be found under such suitable conditions on the Antarctic continent.

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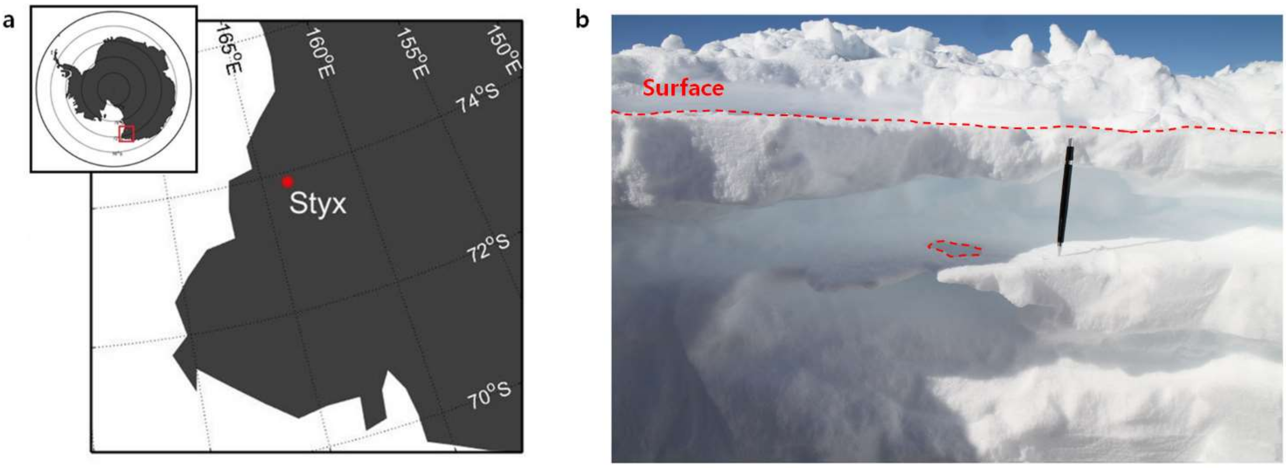
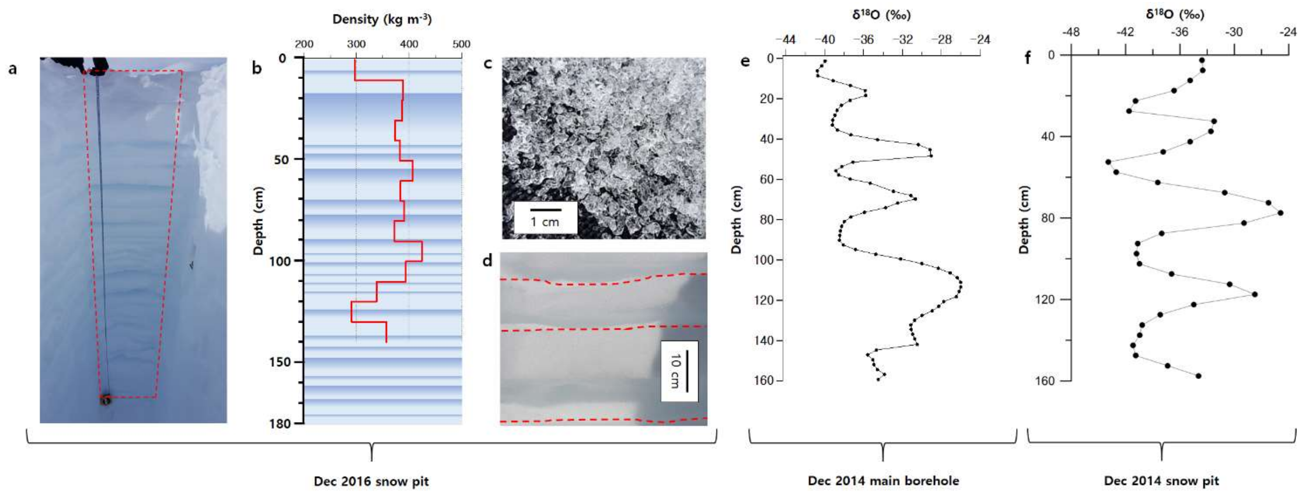


Figure 1. (a) Location map of study site, Styx Glacier, Antarctica ~~(a)~~ and (b) a photo of surface snow density layers ~~(b)~~. The thickness of the snow density layers varies~~y~~ horizontally. The top boundaries of the high-density layers are sharp (horizontal red-dashed line). A hole on a high-density layer surface is indicated by a red-dashed circle. The length of the black sharp pencil in (b) is 14.3 cm.



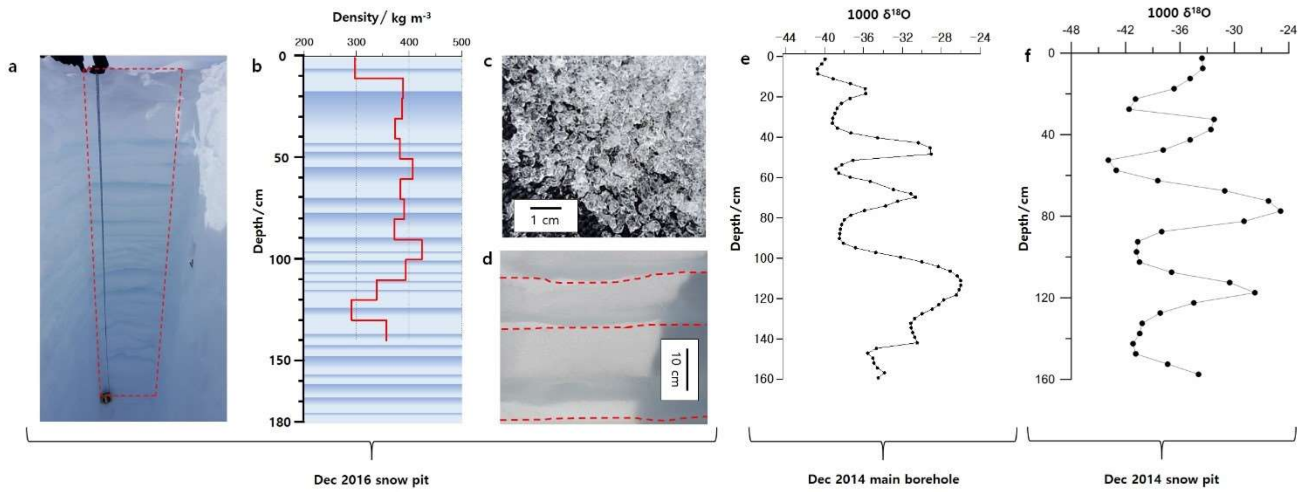
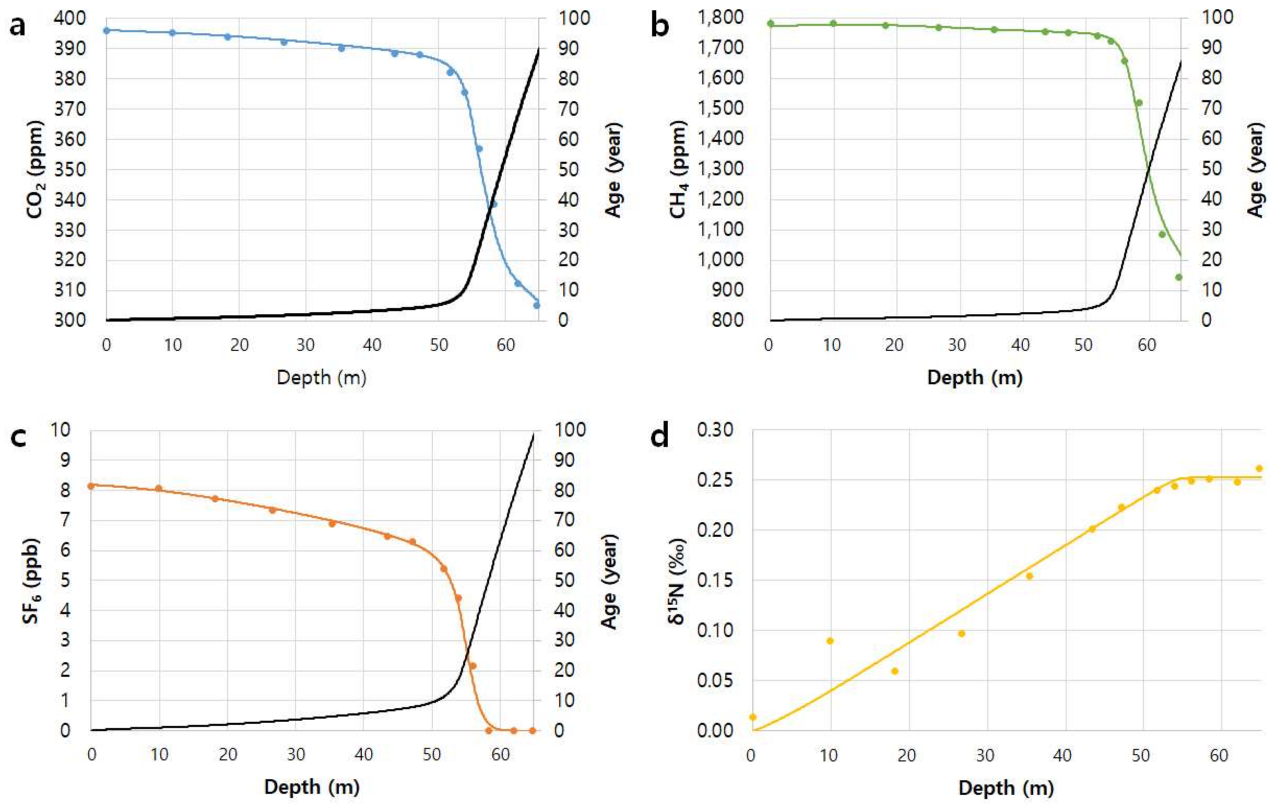
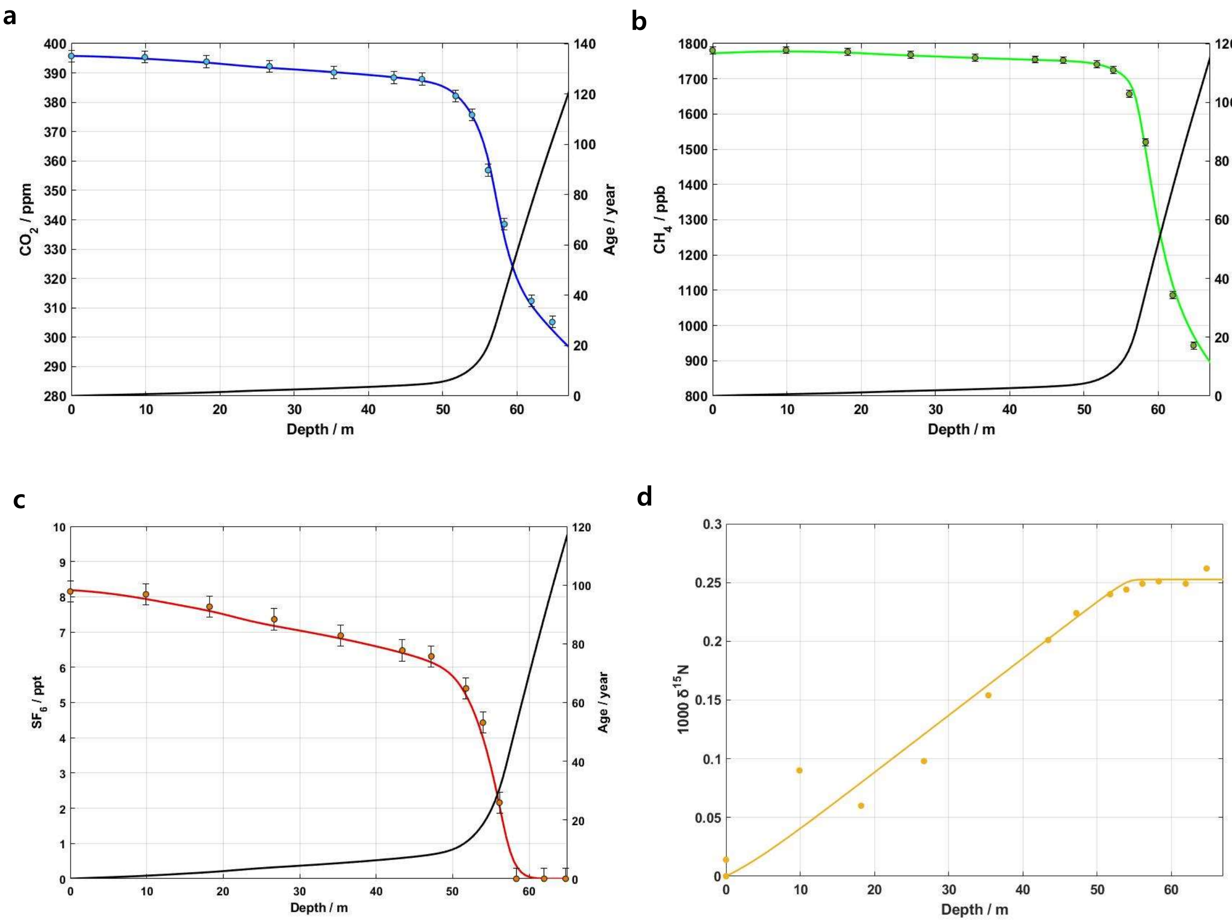


Figure 2. S~~The s~~now-pit photos at Styx Glacier. (a) The snow ~~-~~pit with dimensions of 280 × 65 × 220 cm (length × width × height). (b) The illustration of qualitatively ~~-~~defined hard (~~high-density,~~ dark blue) and soft (~~low-density,~~ pale blue) layers observed in the top 180-cm-depth interval. Progressive blue color changes indicate a gradual density decreases with depth. Red line is ~~with~~ a 10-cm-resolution density profile. (c) Coarse grains observed in a soft layer. The grains were placed on a black glove. (d) Enlarged snow layers. Dashed red lines indicate top boundaries of fine-grained hard layers~~Fine grains observed in a hard layer~~. (e) and (f) Stable isotope ratio ($\delta^{18}O$) of snow profiles at the main core ~~(e)~~ and a snow ~~-~~pit 100 m away from the main ice core borehole, respectively ~~(f)~~.

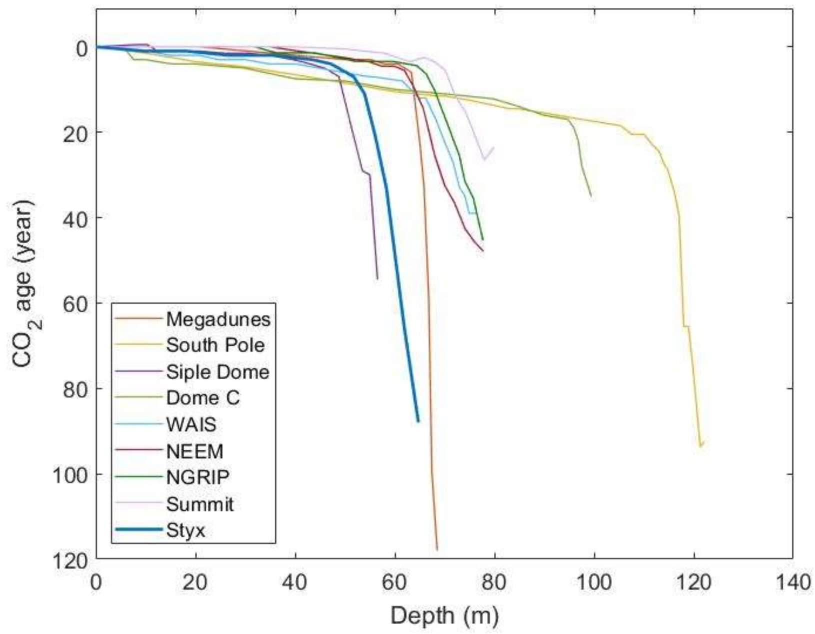


a
CO$_2$ (ppm)
Age (year)
Depth (m)
b
CH$_4$ (ppm)
Age (year)
Depth (m)
c
SF$_6$ (ppb)
Age (year)
Depth (m)
d
δ^{15}N (‰)
Depth (m)



a
CO$_2$ / ppm
Age / year
Depth / m
b
CH$_4$ / ppb
Age / year
Depth / m
c
SF$_6$ / ppt
Age / year
Depth / m
d
1000 δ^{15}N
Depth / m

Figure 3. CO_2, CH_4, SF_6 mole fractions and $\delta^{15}N$ of N_2 measurements (circles), and model results (solid line) for the Styx firn air (air in open porosity). Black lines are modeled ages for the gas species.



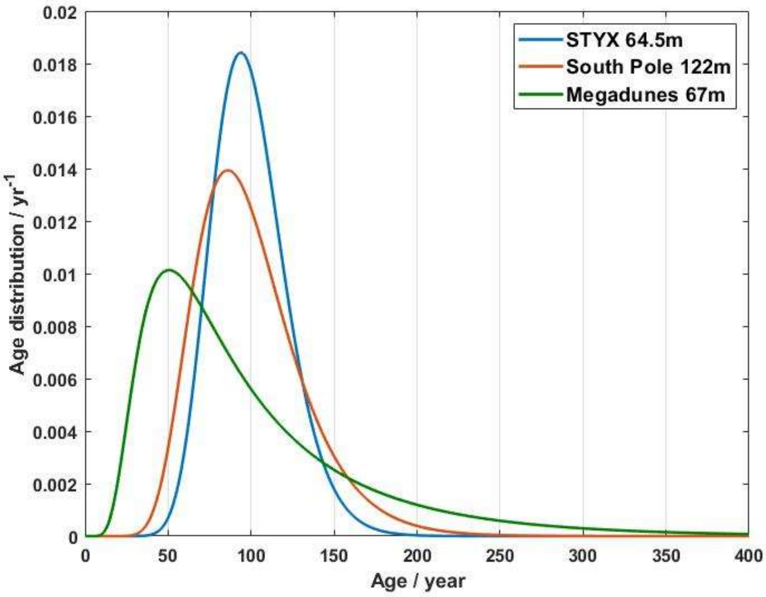
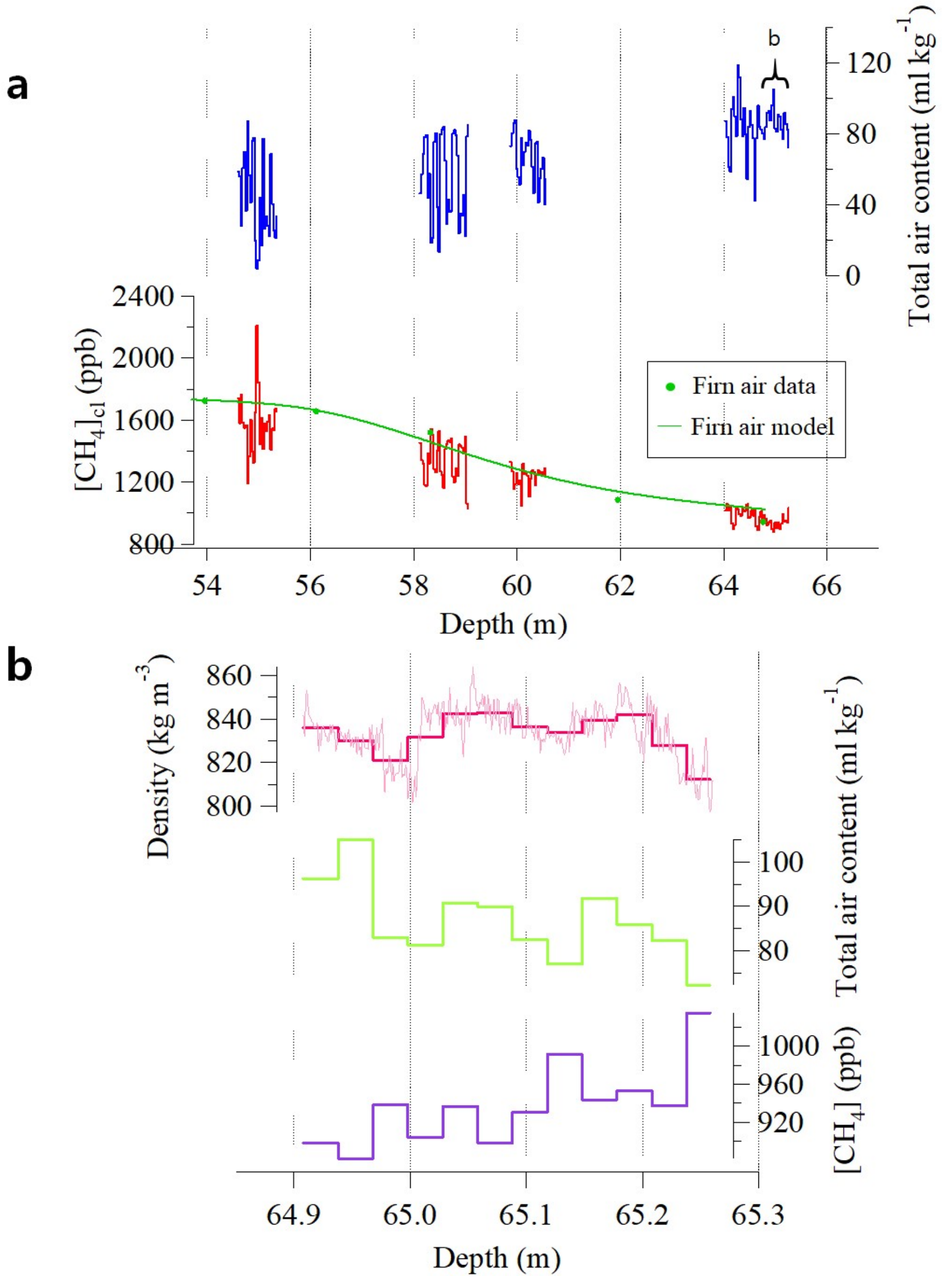


Figure 4. Comparison of model-simulated CO_2 age distributions at Styx (this study), South Pole (Battle et al., 1996), and Megadunes (Severinghaus et al., 2010).



a
b
Total air content (ml kg^{-1})
120
80
40
0
2400
2000
1600
1200
800
$[CH_4]_{cl}$ (ppb)
Firn air data
Firn air model
54
56
58
60
62
64
66
Depth (m)
b
Density (kg m^{-3})
860
840
820
800
Total air content (ml kg^{-1})
100
90
80
$[CH_4]$ (ppb)
1000
960
920
64.9
65.0
65.1
65.2
65.3
Depth (m)

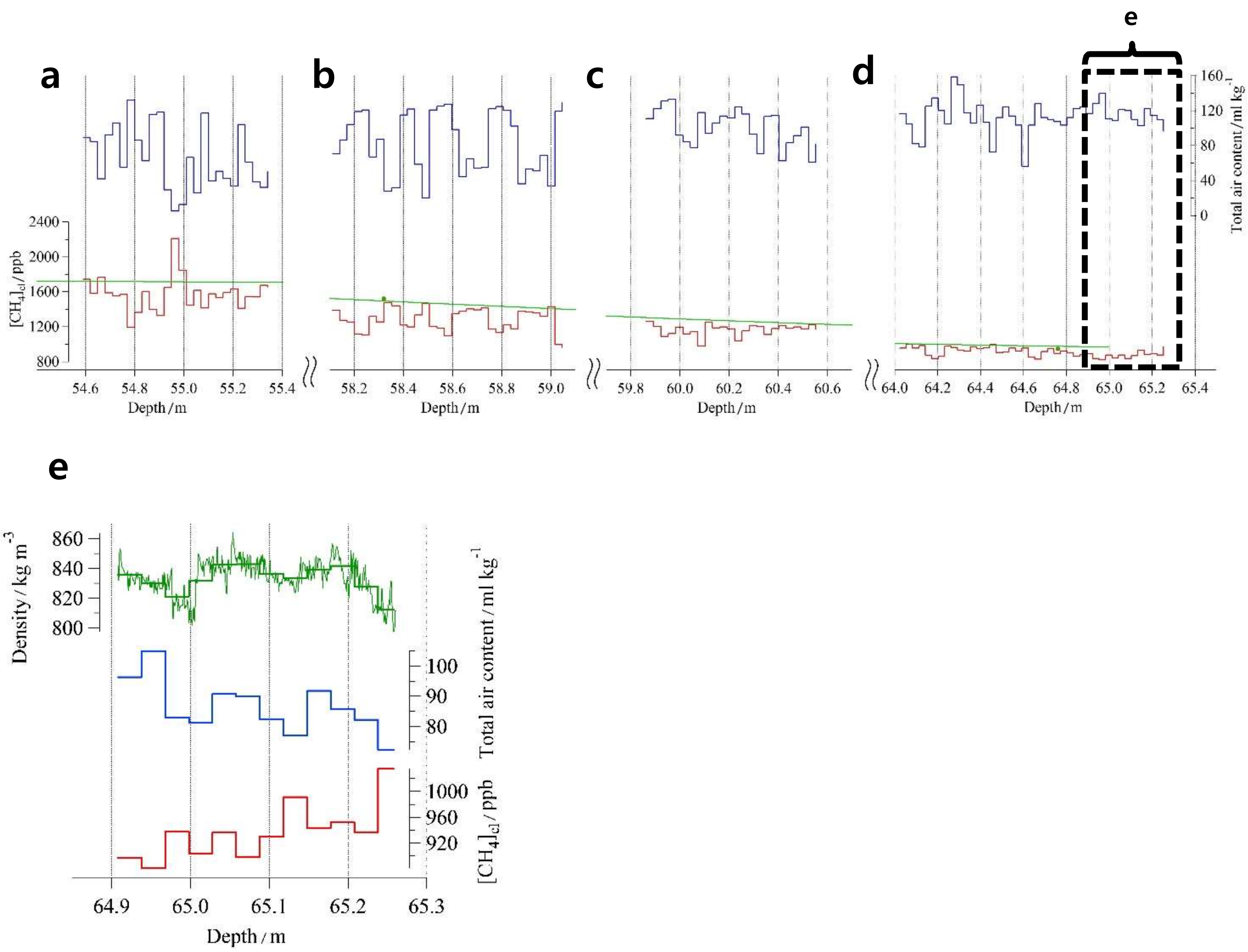
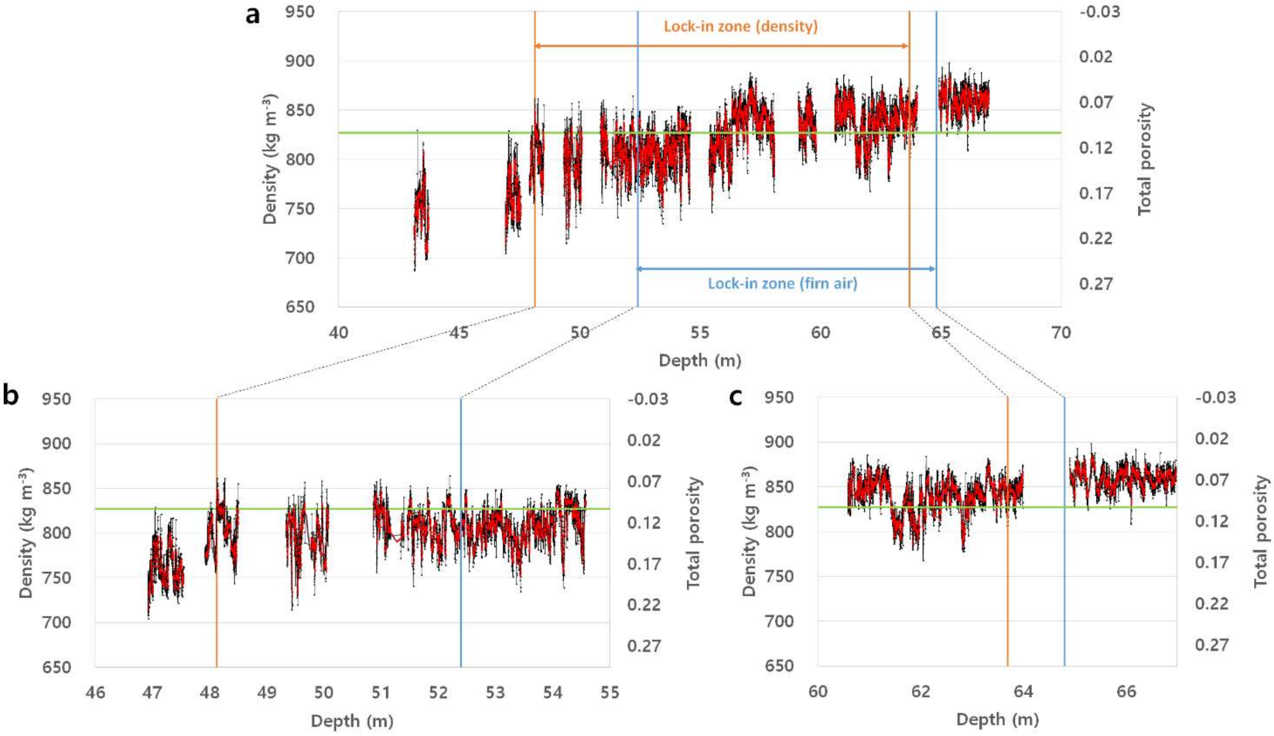


Figure 5. (a-d) CH_4 mole fraction in closed pores ($[CH_4]_{cl}$) (red line) and total air content (air volume per ice weight) (blue line) in the lock-in zone of Styx Glacier. (e~~b~~) Comparison of density with $[CH_4]_{cl}$ and total air content near z_{COD}. ~~(f) Demagnified figure of (a-d).~~ A small dashed-box in ~~figure 5~~(d) indicates the depth interval of F~~f~~ig.~~ure~~ 5e.



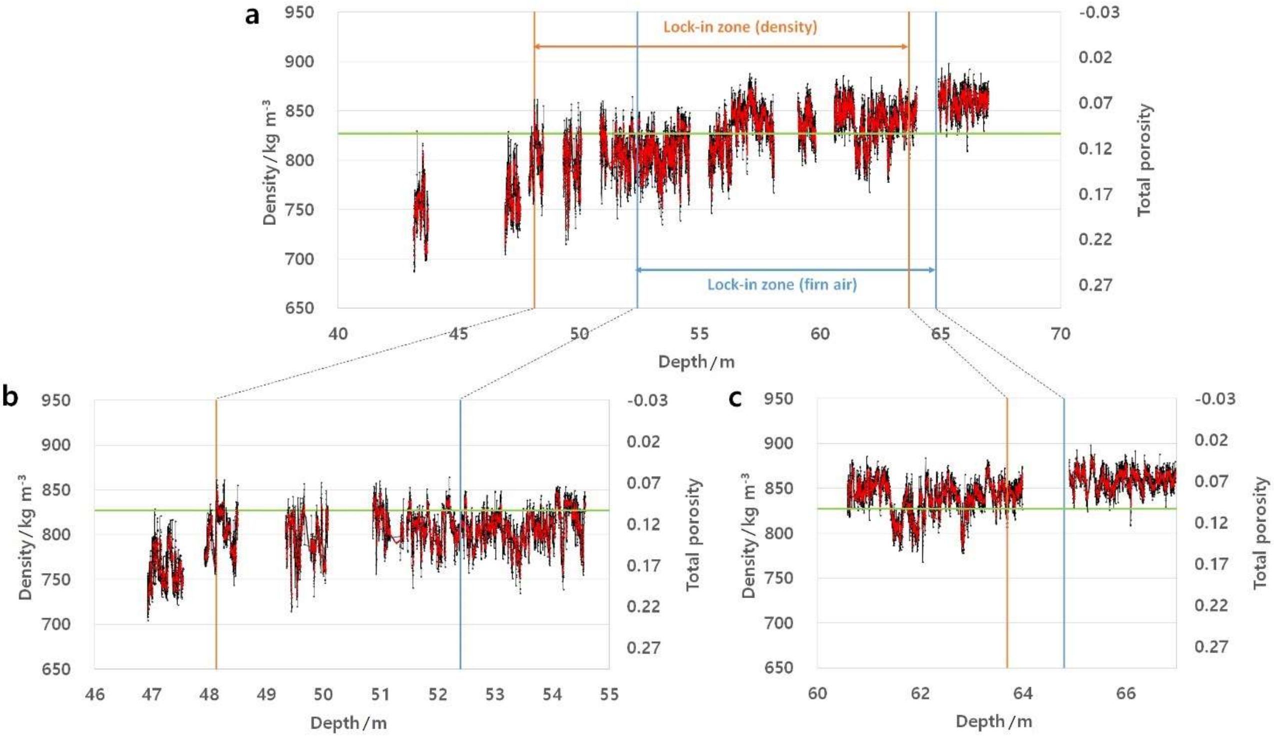
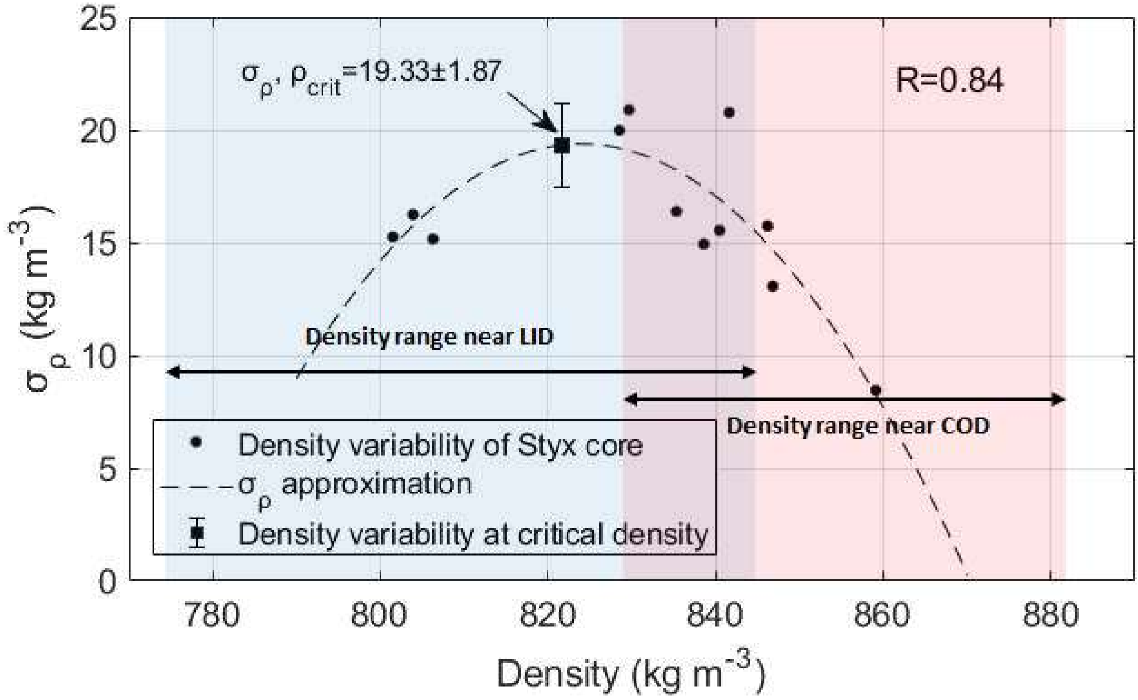


Figure 6. X-ray high-resolution density data obtained from the lock-in zone. (b) and (c) are enlarged portion of (a). Black lines show individual density data, while the red lines are 1-cm running means. Blue and orange lines represent the boundaries of the LIZ estimated from the gas compositions (between two

vertical blue lines) and the critical porosity thresholds~~measurements~~ (between two orange vertical lines), respectively (see section 3.4).



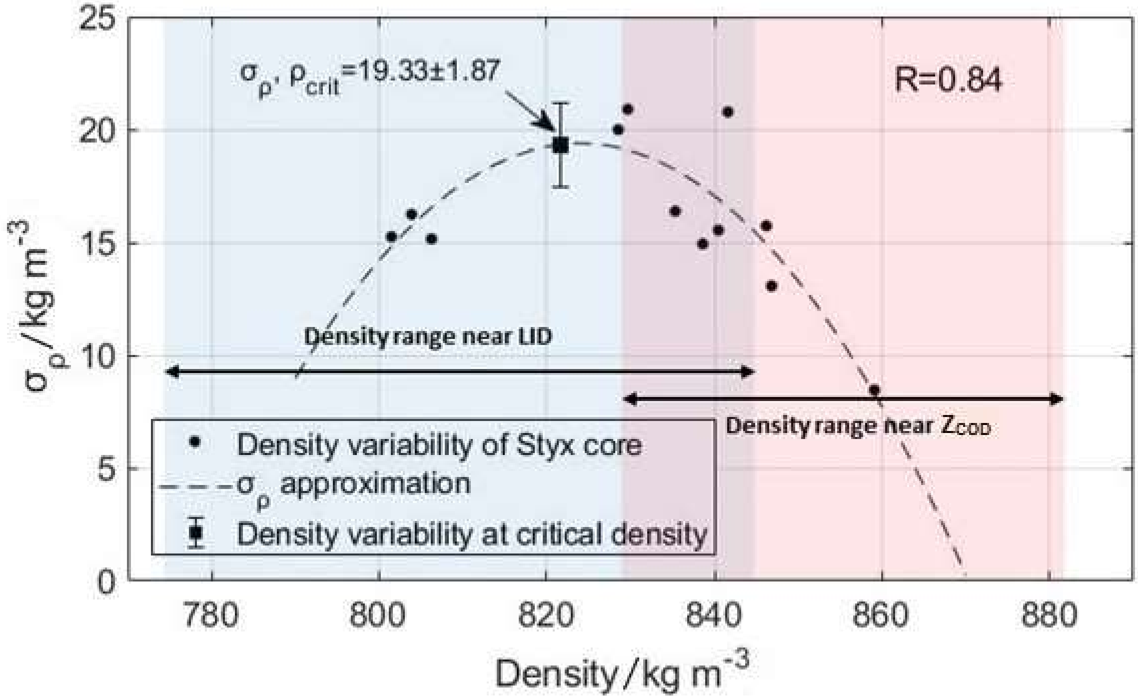
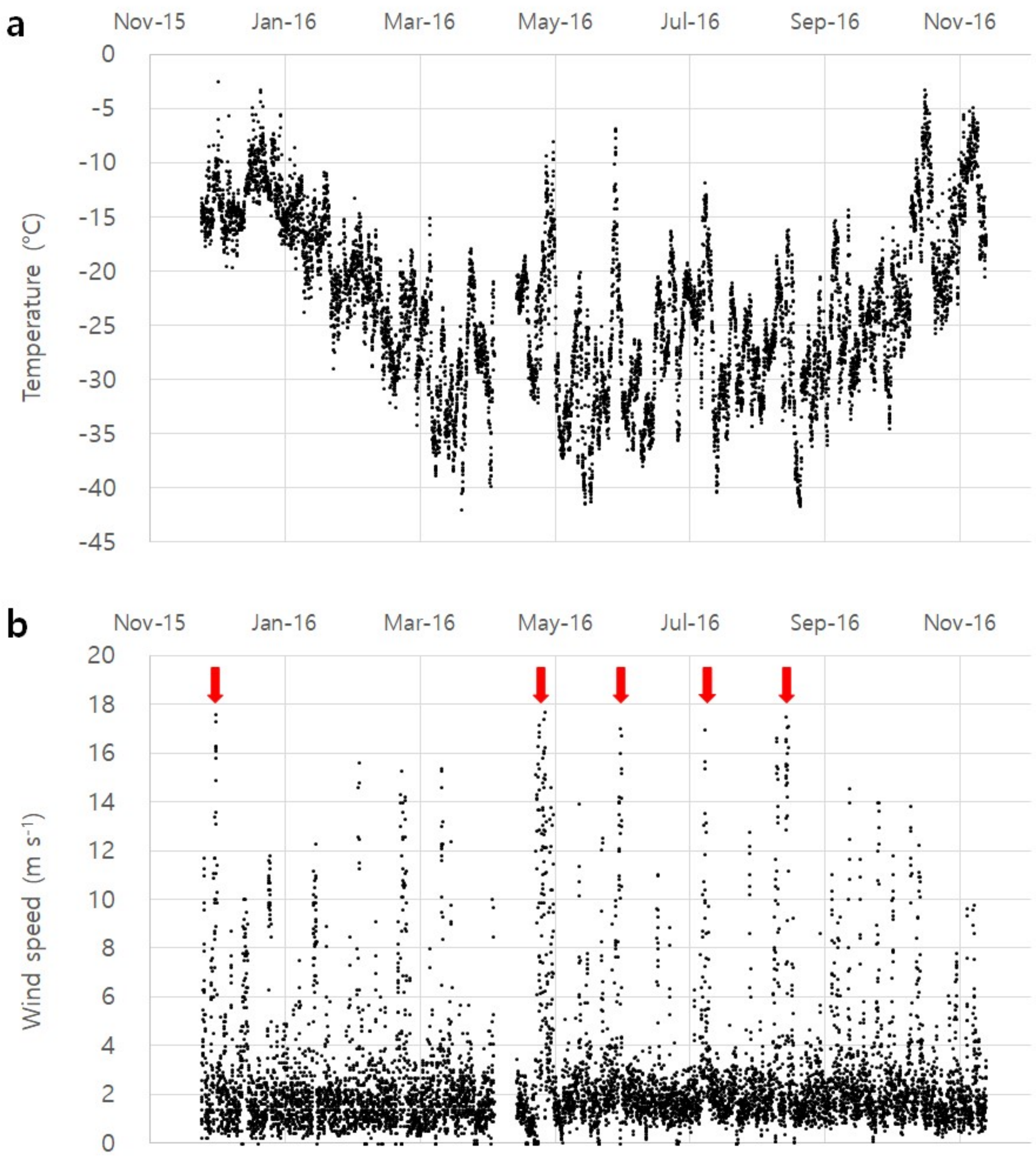


Figure 7. Density variability calculated from 1000 depth points and their average density. The standard deviation at the critical density (821.68 kg m^{-3}) calculated from the approximate ~~secondary~~

~~equation~~second order polynomial (R = 0.84) is 19.33 ± 1.87 kg m^{-3}. The blue and red areas are the density ranges near the LID (52.38 - 52.48 m) and the z_{COD} (64.91 - 65.01 m), respectively.



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~~**Figure 8. Surface air temperature (a) and wind speed (b) data from AWS (Automatic Weather System) at Styx Glacier during December 2015 to December 2016. Red arrows indicate blizzard events.**~~

Table 1. Glaciological characteristics of Styx Glacier and other firn air sampling sites.

Site	T (°C)	A (cm ice yr^{-1})	~~Firn~~ Effective CO_2 ~~air~~ age (year)	LID (m)	COD (m)	LIZ thickness (m)	References
Styx	-31.7	10	~~89~~ 93	52.4	64.8	12.4	This study, Yang et al. (2018)
Megadunes	-49	~0	129~~1~~	64.5	68.5	4	Severinghaus et al. (2010)
South Pole	-51.0	8	~~93~~91	115	125	10	Severinghaus et al. (2001)
Siple Dome	-25.4	13	~~55~~59	49	58	9	Severinghaus et al. (2001)
Dome C	-54.5	2.7	~~30~~33	97	100	3	Landais et al. (2006)
WAIS Divide	-31	22	~~38~~39	~67	76.5	9.5	Battle et al. (2011)
NEEM	-28.9	22	~~48~~50	63	78	15	Buizert et al. (2012a)
NGRIP	-31.1	19	45	67.5	78	11.5	Kawamura et al. (2006)
Summit	-32	23	~~27~~26	70	80.8	10.8	Witrant et al. (2012)
~~Law Dome~~DE-08	-19	120	13	71.8	88.5	16.8	Etheridge et al. (1996)

Table 2. Comparison of standard deviation of density (σ_ρ) at critical density (ρ_{crit}). For data from all other sites, except the Styx, refer to Hörhold et al. (2011).

Campaign/Region	Core name	ρ_{crit} (kg m^{-3})	σ_ρ, ρ_{crit} (kg m^{-3})	T (°C)	A(cm ice yr^{-1})	~~σ_ρ, ρ_{crit} / A~~
Styx	Styx	821.68	19.33±1.87	-31.7	10	~~1.93±0.19~~
NGT	B16	819.27	12.26	-27	15.5	~~0.79~~
NGT	B18	820.81	12.81	-30	11.3	~~1.13~~
NGT	B21	820.81	12.91	-30	11.8	~~1.09~~
NGT	B26	820.85	13.23	-30.6	20	~~0.66~~
NGT	B29	821.32	10.50	-31.6	16.7	~~0.63~~
Berkner Island	B25	819.16	14.57	-27	15	~~0.97~~
DML	B31	827.00	10.27	-42	6.9	~~1.49~~
DML	B32	827.00	11.28	-42	6.7	~~1.68~~
DML	B36/37	827.50	8.12	-44.6	7.3	~~1.11~~
Pre-IPICS	B38	815.00	16.59	-18.1	136	~~0.12~~
Pre-IPICS	B39	814.91	17.11	-17.9	84	~~0.20~~
Pre-IPICS	DML95	815.51	13.42	-19.2	60	~~0.22~~
Pre-IPICS	DML97	816.07	10.03	-20.4	53	~~0.19~~
Dome C	EDC2	832.02	4.59	-53	2.7	~~1.70~~
WAIS Divide	WDC06A	820.81	10.35	-31	22	~~0.47~~

Supplement Materials

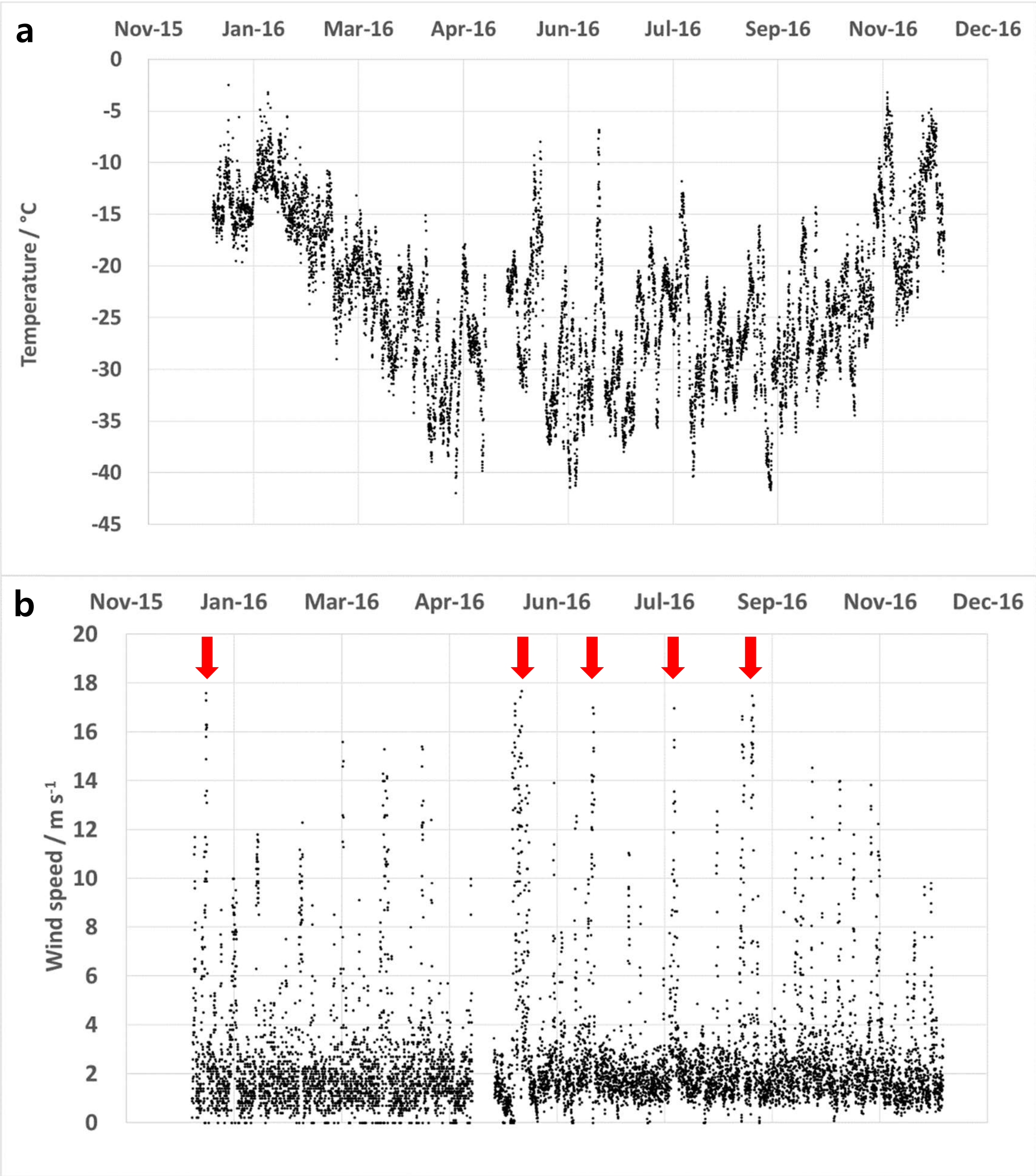

Figure S1. (a) Surface air temperature and (b) wind speed data from AWS (Automatic Weather System) at Styx Glacier during December 2015 to December 2016. Red arrows indicate blizzard events.