Dear Editor,

We now revised the paper according to the reviewer's comments, which were very useful to improve the quality of the paper. In this revision, we included new $\delta Ar/N_2$ data from Dome Fuji ice core and air content data from GISP2 ice core, which supported our conclusions. We believe that now the conclusions are strongly argued, and the uncertainty in the arguments are more clearly stated. Therefore, we think it is ready for the final publication in ACP. In the following, we write our replies to reviewer's comments after triangles.

P.s., H. Motoyama at National Institute of Polar Research joined as a coauthor.

Best regards,

Takuro Kobashi, corresponding author

Anonymous Referee #1

In this paper, Kobashi et al. tackle the difficult question: What controls the Ar/N2 and O2/N2 ratios in ice cores? Ar/N2 is a particularly useful tool for investigation because the ratio is essentially constant in the atmosphere (on the relevant timescales and with attainable precision). The authors take two approaches: Using Holocene data from GISP2 and GRIP, they look for correlations between variations in Ar/N2 and temperature and/or accumulation rate. They also develop a model of size-dependent permeation that they apply to a) post-coring gas evasion and b) gas losses during bubble formation and air enclosure. Overall, I find this work is interesting, important, thoughtfully conceived and carefully executed. I have few suggestions or comments on the scientific content of the manuscript and none are major. However, primarily because the authors are not writing in their native languages, there is a definite need for correction and clarification in the writing. I have been extremely detailed in my comments below because these apparently minor grammatical errors and ambiguities made it much harder for me to absorb the substance of the work upon first reading.

- Thank you very much for your comments.

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First, my more substantive questions/comments:

Overall: When considering post-coring artifacts, you should acknowledge the possibility that, not only does there appear to be gas leaking out of recently closed pores, but there is also the possibility of open bubbles closing off and trapping ambient air. Compelling evidence of this was seen by Aydin et al (Atmos. Chem. Phys., 10, 5135–5144, 2010). Have you considered this in your analysis?

- We considered the inclusion of present air after the coring for the discussion of Figure 6. $\delta^{15}N$ provide a good mean to test if the bubbles are contaminated by modern air. We included the reference in the discussion of modern air contamination.

P15714 Lines 25-26: When you say "between the bubbles and the atmosphere", you're limiting yourself to either post-coring losses or permeation between very recently closed bubbles and the open porosity. However, you suggest the same process is responsible for smoothing records deep in ice cores. Please clarify.

- The words for "between the bubbles and the atmosphere" is aimed for the gas loss process, and "the same process" indicate "gas diffusion through ice crystals". We clarified it "in the text".

P15716 Line 13 (and later in the manuscript): This phrase "a firn densification-heat diffusion model" doesn't really describe these models correctly. They are primarily models of gas transport, influenced by firn densification and thermal gradients (due to heat diffusing through the system).

- We added a few words describing the model in more detail.

Line 20: How did you arrive at the number 21? You should explain where it comes from.

- We added a reference (Kobashi et al., 2015), in which we discussed gas smoothing in the firn and 21 running means.

P15718 First paragraph: It seems to me that you're claiming that Ar/N2 rises in the brittle ice zone because N2 is reluctant to go into clathrates so it escapes and Ar is left behind. Fair enough. But to where does the N2 escape? Presumably this is an example of post-coring loss so the N2 just enters the atmosphere at large. Also, if this picture is correct, shouldn't the problem persist at all depths below the onset of clathrates? Or is it only the fractures that allow the N2 to escape? Please clarify!

- Yes. Indeed, nitrogen should have escaped to the atmosphere more than argon in these depths after coring. This is a special phenomenon for the brittle zone, as in deeper depths clathrate are more stable owing to higher pressures.
- If both nitrogen and argon exist as clathrates, then argon leaks out more than nitrogen as argon with smaller molecular size has a higher permeation coefficient than nitrogen.
- According to the permeation theory, nitrogen and argon leak out from ice cores through the ice crystal from any depths (i.e., as long as pressure or concentration gradients persist).

P15724 Line 10: Is the diffusion coefficient for Argon from experiment? If so, cite the source. If not, change the sentence so it clearly states that the Argon value comes from the dynamics simulation too.

- The argon permeation coefficient is derived from the molecular dynamic simulation (Ikeda-Fukazawa et al., 2004) as now clearly stated in the text. In the revised manuscript, we also derive argon permeation from nitrogen and oxygen permeation coefficients.

P15727 Line 1 The value of 0.375MPa seems arbitrary. How did you choose this value?

- Now we set the value to the depth where the bubbles start forming in the model. The results are similar but it is more reasonable closely linked with density changes. The choice is supported by the observation by Lipenkov (2000).

Line 6 You say earlier that Vostok only has 0.3% of the air in microbubbles, yet you are exploring the range 1% -3%. Why? You should explain this choice.

- Now we included a simulation with 0.3 % contribution of microbubbles. A positive correlation between air content and dAr/N2 indicates that the pressure sensitive process including micro-bubbles is probably not limited on microbubbles. Therefore, we explored larger air content's involvements. Texts are changed accordingly.

Figure 9 is essentially incomprehensible. It is too small to read without 300% enlargement, but more importantly, the content is inadequately explained. For example, despite the statement on line 19, it's not at all clear that Fig. 9a is showing us that 99% of the air is trapped as normal bubbles near the lock-in zone.

- Each line in the panel (a) of Figure 9 shows how volumes generated in each annual layer has changed with time. If you integrate the volumes of the bubbles for each depth, you will get the red line (air content) in panel (e).
- ~99% was a bit confusing as Fig. 9 is only for normal bubbles only. In this case, 100% of the normal bubbles are trapped at the bubble close-off depth. Now the reference to Fig. 9a in p12727, line 9 is deleted.
- Caption of Fig 9 is now improved to explain better.

Is this statement based on output from the model (somehow derived from the multitude of curves shown in Fig 9a)?

- The ~99% is not a result of the model output, but it is a setting of the model.

Or does Fig. 9a show (somehow) that the model successfully reproduces a set of independent observations?

- The objective of the Fig. 9 is to show how the model for normal bubbles is derived in Fig. 10.

The other panels are similarly cryptic: Which are the 3 bottom layers in 9b and 9c and why don't they show the same shape as the three bottom layers in 9a?

- The volume change in an annual layer is induced by density change. On the other hand, panel (b), (c) are the moles of gases that are nearly flat over the depth because permeation is so little compared to the volume. Panel (d) shows the argon-nitrogen ratio from the values in the panel (b), (c), which clearly shows argon is more depleted owing to higher permeation.

Why does dAr/N2 in 9e look so different from every layer in 9d?
I'm sure this is a useful and potentially informative figure, but in its present form, it's merely confusing.

- dAr/N2 in 9e is integrated values calculated from moles of nitrogen and argon for each depth in the panel b, c.
- The bubbles formed in shallow depth experience a long-term permeation. So, it get depleted in a large magnitude. The bubbles formed deeper depth has a limited time for permeation so limited depletion. However, the bubbles trapped in deeper depth have much larger air contents than that of shallower ones. Therefore, the $\delta Ar/N_2$ of the total air contents are different from $\delta Ar/N_2$ of individual ones.

P15728 Lines 9-11: I can't really assess the statement beginning "The difference: : :" because I can't fully understand Fig. 9. However, the idea microbubbles would not be subject to the same compression and volume change that normal bubbles experience certainly begs for a sentence or two of explanation. Perhaps you mentioned this earlier in the paper and I missed it.

- We added a sentence "leading to smaller pressure build-up and total permeation from the bubbles" to clarify the difference between the microbubble and normal bubbles permeation processes.

P15729 This paragraph lays out an important result from this work. According to the model presented here, the behavior of Ar/N2 in microbubbles under cold conditions is the same as was anticipated by Severinghaus and Battle (2006). That is to say, longer bubble residence time in the firn leads to greater permeation and fractionation. On the other hand, the normal bubbles don't show much of any effect. Furthermore, higher accumulation rate leads to the more fractionation in the microbubbles (presumably again due to the longer residence time), but to less fractionation in the normal bubbles. Why is this? The fact that the model reproduces the results of the multiple linear regression doesn't do much good unless we can learn from the model which processes are causing this counterintuitive behavior.

- The depletion in dAr/N2 in microbubbles is opposite of what Severninghaus and Battle (2006) prescribed. Rather, depletion in normal bubbles are more consistent with their study. The effects of temperatures on the normal bubble in the model is interesting. Colder temperatures induce thicker firn, longer time for bubbles (more depletion) in the firn, increased bubble air pressures (more depletion), but also smaller permeation coefficients, which cancel each other.

- However, the magnitude of depletion is rather small in the normal bubbles in different environment. The different magnitudes of depletions are induced by the pressure sensitive process (e.g., microbubbles).

Figure 8c: Do you really mean to plot air content change? I would think you're actually plotting the percentage of original air remaining, but I'm not certain. As it stands I can't make sense of a 99% air content change that then falls with depth.

- This is actually air content change of "microbubbles". As the pressure is so high, and the volume is small for microbubbles, the permeation plays a rather big role on gas loss. But total air content change should be much smaller.

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Second, a long list of grammatical corrections/clarifications.
P15713 Line 8: change to "we find"

- Done.

Line 10-11 should read ": : :the precise records spanning the last 4000 years show temperature and accumulation rate have nearly equal effects: : :"

- Done.

Line 14: put the quotes around "microbubbles" only (not the parenthetical statement).

- Done.

Lines 16-17 should read ": : :the accumulation rate due to changes in overloading pressure, as seen in the observations. Colder (warmer) temperatures in the firn induce more (less) depletion in: : :"

- Done.

Lines 25 and following: The studies cited are not really firn studies. Instead, they are about much longer ice-core histories. My guess is that you really are trying to say is ": : :trapped in the firn layer (unconsolidated snow; _70m at the Greenland Summit) and preserved in the underlying ice sheets provide precious: : :"

- Yes. It is corrected.

P15714 Line 10 should read "we investigate a third process"

- Corrected.

Line 16 should read "the process continues during/after coring"

- Corrected.

Line 20 remove the word "rapid"

- Corrected.

Lines 21-22 should read "Depletion of the total air content by::"

- We intentionally do not use "total" air content in this context as "air content" is a sufficient word for this purpose.

Line 25 should read "and is induced"

- The sentence is revised.

Line 5: Should read "Variations in dO2/N2 on orbital timescales closely follow: : :"

- The sentence is revised.

Lines 5-16: This section is a bit confusing in its order. In the previous paragraph (on p15714), you should explicitly state the situations in which this single process operates: As bubbles close at the firn-ice transition, deep within the ice sheet, after coring.
Then address these in the same order on p15715.

- To clearly show the story changes in the paragraph, we inserted "In a longer time scale (i.e, orbital)" at the beginning of the paragraph.

Lines 17-19 should read “: : :using records from GISP2 for the entire Holocene and NGRIP for the past 2100 years, we investigate the multi-decadal to centennial variability of Ar/N2, as well as gas loss processes during storage.”

- Corrected.

Line 22: should read “over the relevant period”

- Corrected.

Line 25: remove the comma after “data”

- Corrected.

Line 29: should read “drawing conclusions”

- Corrected.

P15716
Line 2: should read “measured in the”

- Corrected.

Line 10: should read “obtain high analytic precision (Kobashi: : :”

- Corrected.

Line 14: “uncertainties” in what are _10%? Gas ages? Or the gas-age/ice-age difference? Please clarify.

- It is the gas-age/ice-age difference, and now it is clarified.

Line 15 -20 should read “To investigate the Ar/N2 fractionation, we used: : : : : :Gkinis et al., 2014). The annual resolution: : :: : :with 21-year running means: : :”

- Corrected.

Line 22-23: Should read “We also used new dAr/N2 data for the past 2100 years from the NGRIP ice core, providing a good : : :”

- Corrected.

P15717

Line 10 should read “The coefficient 11 arises because the: : :”

- Corrected.

Lines 13-14 should read “: : :temperature sentivities of d15N and dAr/N2 are slightly: : :”

- Corrected.

Line 16 Remove the whole sentence beginning “Therefore, these corrections: : :”

- Corrected.

Line 17-18 should read “attributed only to gas loss.

- Corrected.

Line 18-20: The sentence beginning “It is also noted: : :” is very unclear to me. You appear to say above that GISP2 only had data with mass 29.

- Of course, we had GISP2 data with mass 28 and 29. This is simply because of the laboratory difference of calculation of $\delta Ar/N_2$ using mass 28 or 29 As stated in the text, either methods of calculating dAr/N2 makes little difference within analytical uncertainties.

Last paragraph: Where does the number “21” come from? It appears to be a completely arbitrary choice, but I imagine it’s not.

- It is to be consistent with 21-year running means, which produces smoothing similar to gas diffusion in the firn column.

P15718 Line 8 should read “: : :preferential leakage of nitrogen, and thus argon: : :”

- Corrected.

Line 19 should read “: : :variations. We found a significant: : :”

- Corrected.

Lines 20-21 should read “: : :accumulation rate for the past 6000 years, a time interval in which the abnormal dAr/N2: : :”

- Corrected.

C4981P15719 Line 2 should read “: : :variations because precise: : :”

- Corrected.

Line 9: Shouldn’t the last r value (0.26) actually be negative?

- Yes! Corrected.

Line 10 should read “with a 38-year lag”

- Corrected.

Line 11: should read “We note that the surface: : :”

- Corrected.

Line 12 should read “rate have a negative: : :”

- Corrected.

Line 1: It would be very nice to see a figure of the centennial variations in model and data. Also, how are centennial variations determined? Is it a 100-year running mean or a spline or some other technique?

- We tried to put the line in the figure, but it was too crowded. Therefore we did not add the line.

Lines 8-9 should read “do not have Ar-isotope based temperature information before 4000 year BP. “

- Corrected.

Line 10 should read “: : :contains substantial noise”

- Corrected.

Line 21 Remove the comma after “rate”

- Corrected.

Line 22 should read “with the d18O_ice-based temperature proxy and: : :

- Corrected.

Lines 24-25 should read “: : :discussed earlier. Except for the time interval around _7000 BP, the model and observed dAr/N2 exhibit rather constant: : :”

- Corrected.

Line 13 should read “: : :better precision on dAr/N2 than the one used for GISP2”

- Corrected.

Line 19 should read “: : :detrending) and were uncorrelated in the shallower part.”

- Corrected.

Line 22 should read “dAr/N2 data from the depth range 64.6-80m exhibit some: : :”

- Corrected.

Line 1 should read “: : :of contamination, and”

- Corrected.

Line 3 should read “uncertainties using ice samples” and “: : :we interpret the”

- Corrected.

Line 4: In what sense do things “decrease”? Wth greater depth? As you approach the surface? As written, it’s not clear.

- Inserted “toward shallower depths”.

Line 5 should read “Fig 6). Based on isotope mass balance: : :”

- Corrected.

Line 7 should read “a clue to the processes”

- Corrected.

Lines 9-10 should read “and application to post-coring fractionation.”

- Corrected.

Line 11 should read “after coring”

- Corrected.

Line 13 should read “depletions of”

- Corrected.

Line 18 (and subsequent occurrences) should have “species m” instead of “m molecule”.

- Corrected.

Line25 ibid.

- Corrected.

Line 2 should read “are mole fractions of species m”

- Corrected.

Line 8 should read “during storage”

- Corrected.

Line 9 should read “14 years after coring, but with different temperature histories. GISP2: : :”

- Corrected.

Line 10 should read “After shipment,”

- Corrected.

Line 13 should read “2015). The ice samples were then cut: : :”

- Corrected.

Line 24 Remove the comma before “and”. Also, latter part should read “: : :to 1MPa; a normal bubble: : :”

- Corrected.

P15724 Line 4 should read “storage often have”

- Corrected.

Line 6 should read “surface areas imply the”

- Corrected.

Line 27 should read “respectively. We note that”

- Corrected.

P15725 Line 1 should read “that our estimated”

- Corrected.

Line 2 should read “several times larger than”

- Corrected.

Line 3 should read “introduced noise into”

- Corrected.

Line 9 should read “introduce more noise if the gas loss is greater”

- Corrected.

Lines 11-12 should read “2000): normal bubbles and so-called microbubbles”

- Corrected.

Line 16 should read “depth. Most of the air in cores is captured as normal bubbles”

- Corrected.

Line 6 should read “to the total air content”

- Corrected.

Line 8 should read “can approach ice load pressure at the bubble closeoff”

- Corrected.

Line 20 remove the word “concerned”

- Corrected.

Lines 21-22 should read “With l increasing in one-year steps, the microbubbles”

- Corrected.

Line 23 remove the words “a concerned”

- Corrected.

Line 25 should read “starts increasing”

- Corrected.

Line 16 should read “which corresponds to 5%”

- Corrected.

Line 27 should read “how much bubble volume is generated”

- Corrected.

Line 4 should read “newly trapped air”

- Corrected.

Line 20 should read “we assume the gas”

➢ Corrected.

Line 23 should read "O2/N2) within the bubbles decreases with"

➢ Corrected.

Lines 24-25 should read "However, the amount of air contained in these bubbles is so small that the influence on the total"

➢ Corrected.

Fig. 10: Change the color scheme so that cold temperatures are blue and warmer temperatures are red. In the paragraph beginning "The permeation: : :" please removal all of the parenthetical terms in the more/less, higher/lower, warmer/colder pairings. They're just distracting, and the converse of each term is clear.

➢ Corrected.

Line 12 should read "may indicate even larger"

➢ Corrected.

Line 25 should read "GISP2. We found that"

➢ Corrected.

Line 28 should read "with an 11-year lag"

➢ Corrected.

Line 3 remove the word "time"

➢ Corrected.

Line 18 should read “2002). Our work demonstrates that the”

- Corrected.

Line 5 should read “there is some evidence of”

- Corrected.

Line 7 should read “2011). In particular, poor quality”

- Corrected.

Lines 12-13 should read “appear to have small or non-existent effects on isotopes (Kobashi”

- Corrected.

Line 19 should read “Another sign of isotope fractionation”

- Corrected.

Line 20 should read “enrichment in ice cores”

- Corrected.

Line 22 should read “caused by processes”

- Corrected.

Line 23 should read “evidence has been found in firn air studies”

- Corrected.

Line 25 should read “it should be correlated with”

- Corrected.

Lines 27-28 should read “2015), dKr/Ar (Severinghaus et al., 2003), or a constant value (Orsi, 2013; Kobashi et al., 2015). All these methods of correction generate”

- Corrected.

Line 9 should read “stronger constraints”

- Corrected.

Line 11 should read “that ice core”

- Corrected.

Line 15 should read “use of large ice samples”

- Corrected.

Line 16 should read “the noise in”

- Corrected.

Line 21 should read “of permeation”

- Corrected.

Line 26 should read “after bubble closeoff”

- Corrected.

Line 27 should read “especially in ice cores. In this study, we investigated gas”

- Corrected.

Line 25 should read “surface temperature. It is also”

- Corrected.

Figure 2 caption: Was the spline really set to a 31 year cut-off period, or a 21 year? Similarly for the length of the RMs.

- We confirmed that it is 21-year RMs and 21-year cut-off period. It is corrected.

Figure 11 caption: The 4th line should read “Settings for”

- Corrected.

Anonymous Referee #2

Received and published: 21 July 2015

General comments :

The loss of small air molecule in ice cores is still a poorly known phenomenon. Ice core air samples have low dAr/N2 and d02/N2 due to the preferential loss of Ar and O2. This loss happens in the firn, in solid ice and during core storage. The principal mechanism is the permeation of small molecules through the ice lattice (Ikeda Fukasawa et al 2005), and this mechanism has been used to quantify gas loss at different temperatures, and to explain the enrichment in dAr/N2 and d02/N2 in steady state.
Here, the authors go one step further and try to identify a link between the amount of Ar loss and climate, such that dAr/N2 could be used as a climate (temperature and accumulation) proxy, rather than an indicator of the quality of the core storage. This subject is particularly interesting because of the observed correlation between d02/N2 and insolation, which is so far unexplained. The authors observe that there is a significant correlation between dAr/N2 and temperature and accumulation, and explore the potential mechanisms for such a relationship.
They build on existing ideas about permeation through the ice, and find that 1) microbubbles likely play an important role, and 2) firn thickness (controlled by temperature and accumulation) impacts the bubble pressure, and will lead to different amounts of post-coring fractionation. Although the motivation of the study is well justified, and the methods used appropriate, the logical links between the observations and models, and between different mechanistic hypotheses are not well articulated, and the conclusions are not well supported by the data and models presented here. I offer here a few suggestions to rewrite the paper in order to better highlight the actual conclusions, and make a stronger relationship between hypotheses, models, and observations.

- Thank you very much for your comments.

1. Are the dAR/N2 time series the best tool to test your hypotheses?

It is interesting that you find a correlation between dAr/N2 and temperature or accumulation, but this relationship is not consistent between the two cores, and even the raw data has little common variability, which leaves me to wonder whether the correlations you find are actually significant. I realize that it’s a difficult exercise to make, because the input time series of temperature and accumulation are not well known themselves, but the lack of consistency between GISP2 and NGRIP is a red flag for me, especially because they are consistent in terms of d15N and d40Ar. I would suggest that you would instead use the known and measured dAr/N2 (or d02/N2) from shallow ice cores all over Greenland and Antarctica, where we have a good constraint on present day temperature and accumulation. This would allow you to explore a larger parameter space in terms of T and acc, and perhaps find a stronger relationship between climate and gas loss (dAr/N2 grav corr).

- The relationships of GISP2 between dAr/N2 vs. the regression model (temperature and accumulation rate) are highly significant by itself. That is, it is extremely unlikely happened by chance ($p < 0.001$).
- We found that the signal to nose ratio is much lower (one fifth) in NGRIP than that of GISP2, which provides a reason why did not see the relation in NGRIP.
- Published dAr/N2 data with storage histories are very limited. However, now we included Dome Fuji dAr/N2 data with storage history.

2. Uncertainties in the permeation model

In Section 5, the authors use the permeation model of Ikeda-Fukasawa et al. (2005) to estimate gas loss. There are a number of unknown parameters in equation (3).

The authors make an honest attempt at finding reasonable values for them, but do not give uncertainty estimates in the parameters. A propagation of uncertainty would be necessary for us to understand what can conclusions can be drawn from this model.

- We now included two estimates of permeation coefficients, and included uncertainties if possible. We would like to note that the current study is a conceptual model to explain the variability of dAr/N2. We believe that we produced an important scientific advance on the variability of dAr/N2 in ice cores with the model. Future studies will take into account various uncertainties with more data.

- You do not comment on what you use for _l, the thickness of the ice layer, which is an essential parameter.

- ➢ We used the estimates of *l* from Ikeda-Fukazawa et al. (2005). It is now stated in the text.

- You use constant values for D and X, but it is very likely that they strongly depend on temperature, otherwise we would not witness that there is less gas loss at -50_C than at -10_C. You may not know what it should be (I don't know either), but it would be useful to include a range of possible permeabilities that would fit the data. The conclusion of Section 5 is that the model doesn't match the data, but perhaps, you could instead use the data to constrain the permeability used in the model, and see if you can learn something. (Here again, I would use data for many core sites, to have better constraints)

- ➢ We use variable D and X with temperatures for argon (Fig 2).
- ➢ Now, we used a different approach to find the post-coring fractionation, and we found a solution, which fit with the observation.

- You use for your S/V the geometric shape of the core, rather than the distance from one bubble to the next. This is very surprising. What's the reason for this ? I would have imagined that what matters for gas loss is how much the bubbles near the edges of the core can loose their gas, not have a model where all the air is in the middle, and has to go through solid ice of 9.8cm diameter.

- ➢ First, this is an established method for the gas loss from ice cores (Ikeda-Fukazawa et al., 2005), which found to be consistent with the observations (Suwa and Bender, 2008a, Bereiter et al., 2009).
- ➢ This is also consistent with the observations that near surface of ice is not preferentially depleted for dAr/N2 and dO2/N2 compared with more central part of the ice core (unpublished data). Rather, we assumed that air in ice crystals and bubble air are in equilibrium (Ikeda-Fukazawa et al., 2005). Therefore, gas loss from an ice piece can be approximated as a function of specific surface area (S/V). In other words, a large chunk of ice is less susceptible to gas loss than smaller pieces (Ikeda-Fukazawa et al., 2005). Of course, further studies are warranted in the point.

- In the end, I suspect that the uncertainty in the amount of post-coring fractionation (section 5) completely erases the possibility to detect any sign of microbubble fractionation, which has a much smaller amplitude, but it would be nice of you could quantify that.

- A significant correlation between air content and dAr/N2 indicates that larger air content is involved in the pressure sensitive process. Therefore, in the revised paper, we argue that the pressure sensitive process is not limited on the microbubbles but it likely involves larger air content, and provided several evidences.
- We now estimated the post coring fractionation in a new way, and now we take into account that for the analyses of the post bubble-close off fractionation.

3. Microbubble concentration You make an interesting point about microbubble concentration. As I understand, although the volume of gas is very small, the fractionation is so intense that they matter. This argument depends strongly on the microbubble concentration in a sample, but you make no attempt at quantifying it from observations. Only you quote a concentration of 0.3% from Vostok, which is a very different site from GISP2 and NGRIP, and I doubt that the bubble shapes are the same at a cold low accumulation like Vostok and at warmer Greenland sites. In addition, you use in your model a concentration of 1 to 3%, which is one order of magnitude higher than the 0.3% documented at Vostok without justification.
Since your argument depends very strongly on the presence of microbubbles, I think that a documentation/quantification of their presence is needed. You can do this by imaging a few thin sections from the core at these sites, or look at tomography data from Greenland firn cores. I'm sure that such data exists already, and including them would considerably strengthen your argument.

- See our new arguments for earlier comments. Now we think that the pressure sensitive process is not only limited on the microbubbles but likely involves larger air contents.
- Unfortunately, we did not find the image data for this. We stated in the text that it is important to obtain more information of microbubbles (volume and pressrues) for the advances of the permeation process.

4. Link between the two process studies
Your dominant mechanism for linking dAr/N2gravcor and (T, accum) is through bubble pressure, affecting permeation through the ice. I could imagine that for cores with different bubble pressure (perhaps because of different depths), the post-coring fractionation would be more or less important.

- Bubble air pressure data is very limited, but we showed in this paper that the bubble pressure is a critical observation to advance understanding of the permeation. We included discussion on the effects of pressure for the post-coring fractionation.
- Impacts of different bubble pressures on the post coring fractionation are interesting and important points. Although we did not have enough information to constrain this, we included these points in the discussion for further research.

- This study is complicated if we look at different depths because of clathrate formation, but you could look for a trend in the first 500m where there are few clathrates. Perhaps you could take a look at what we expect bubble pressure to be with depth, and run your gas loss model for an expected range of bubble pressures to see if we could see any change that would match your data

- The depth effect should induce increasing depletion in dAr/N2 with deeper depth by overloading press, which we did not observe in the ice core data. This is an interesting point and we included in the discussion. Future studies should look at this more in detail.
- We included a reference of an observation of bubble pressures by Gow and Williamson (1975), which showed that ice core relaxation produces stable bubble air pressure deeper than 300 m, which solve the problem for the deeper part.

- In your time series, you are looking at the fractionation of micro-bubbles due to different bubble pressure for different (T, accum), but what about the fact that if the bubble pressure is higher, you will also have more post-coring fractionation ? Perhaps you could make a plot of bubble pressure in the x axis, and expected dAr/N2 from postcoring fractionation after 15 years, with the parameters used in Section 5, to estimate whether this could have a significant impact on the correlation of dAr/N2 with temperature or accumulation. You could also use this graph to add the expected fractionation of dAr/N2 from the presence of microbubbles, since bubble pressure depends on firn thickness. This would be a way to put both studies together in a comparable framework, and estimate what can be said. If your model runs have error bars, even better.

- Now we derived bubble pressure from the post coring depletion of dAr/N2 in GISP2. Then, it was applied to other cores. The possibility of effects of gas pressures in ice cores are likely, but it is difficult to quantify from the data we have (see earlier replies). As it is important points, we included the point in the discussion section.

5. link between model and data

The link between the observed time series and the model could be made more clear. For instance, you could have run the model for the input temperature and accumulation time series shown in Fig 3, and do a model/data comparison. If you follow my advice #1 to show multiple sites, you could instead make a 2D plot of temperature, accumulation and dAR/N2, on which to compare data and model.

- The particular model we used (Schwander et al., 1997) in Fig 9-11 is an equilibrium model (run only for constant temperature and accumulation rate), and the Goujon model does not have all necessary parameters in outputs. Therefore, it was not possible to do the suggested run. An obvious future advance of this study would be to run the model with variable accumulation rate and temperatures in transient runs, but it is beyond the scope of the current study.

6. Conclusions

You emphasize in the abstract and conclusion the importance of process #2 (microbubbles), but you find that process #1 is responsible for -2.7 to -6.6 per mil of dAr/N2, whereas process #2 accounts for 0.38‰_C (and Holocene changes are on the order
of 1_C), or -0.11‰(cmice/yr), with Holocene changes on the order of 2-5cm/yr. It's hard for me to believe that, in the presence of noisy data, and with a moderately well-known amount of post-coring gas loss (process #1), you could identify the contribution of microbubbles (process #2). It does not make the modeling study any less valuable, but I believe that with such data, and uncertainty in the model, you cannot conclude that you have observed it, or that this process is significant. As it stands, the conclusions of the paper are not sufficiently strong, and the articulation between the observation and models not clear, but there is potential for making this a much stronger paper, or at least, clearly state the limits of current knowledge and offer suggestions for better observations. I hope that you will take this into account in rewriting the paper.

- As stated earlier, the correlation between air contents and dAr/N2 (new Fig. 1 bottom) indicate that pressure sensitive process involves not only microbubble but also larger air contents. Therefore, the use of the larger percent of "microbubbles" is legitimate, and support our conclusion. In the revised paper, we included discussions on remaining uncertainties and implications on the permeation processes.
- We believe that new data (Dome Fuji and total air content of GISP2) and new calculations now well support our conclusion.

Specific comments:
Page 15717 l 6-7: It’s confusing to use dAr/N2, and it would be more clear to keep the dAr/N2gravcor (or dAr/N2gc if you want to be more compact), during the remainder of the manuscript, like you did for equation (2).

- Because all dAr/N2 are dAr/N2gravcorr after the explanatory section, we used dAr/N2 throughout but clearly stated that dAr/N2 denote dAr/N2gravcorr later sections.

Pqge 15718 l 19 : it’s unclear now that dAr/N2 has been corrected for gravitation. If it has not, this is a trivial result, but I assume it is, and it would reduce confusion if you keep a clearer notation.

- See above.

P 15719 l l 7 : colder temperature induce more fractionation. This is opposite the conventional wisdom that colder ice has less gas loss. Can you comment on it? It would be good to add the plots of the stated correlations (scatter plots) in the online supplement.

- An important finding from this regression analyses is that gas loss is apparently caused by changes in the overloading pressure of the bubble air near the bubble-close off region. The colder temperature induces thicker firn layer, and so higher pressure in the bubble-close off region. Colder temperature induces less permeation from unit volume of ice in unit time, but the effects of higher pressure is apparently stronger.
- We now provide a table with data for various temperature and accumulation rate, which can be used to make plots.

P 15721 l17-19 : “not in the shallower part”, does it mean that it is better than “weakly correlated”, or not correlated at all? You commented on the fact that the accum rate is smaller at NGRIP, but you don’t comment on the lack of correlation with temperature.
Could you say something?

- NGRIP dAr/N2 had a weak correlation with temperature for the deeper part, where ice was stored in colder temperature.
- From the model exercise, it became clear that when the firn becomes thinner, dAr/N2 fractionation reduces. Therefore, the relation found in GISP2 will become less sensitive

when firn becomes thinner (e.g., NGRIP). This may be one of the reasons why we do not find a correlation between dAr/N2 and temperature in NGRIP.

Figure 5 : put the data points in (+), so that we can see the original scatter in the data

- Data points are added.

page 15724, line 23 : " using these values ", add a table with the values used for D, X, and KX.

- A table is added.

page 15724: impact on the uncertainty of the values for k, and X?

- Now we use two different sets for *kX*.

- why use S/V ice core rather than S/V bubbles?

- We are interested on the surface areas that are exposed to open air. In the case of ice cores, it corresponds to the S/V of ice cores.

- S/V bubbles changes with depth due to compression, does it affect your results?

- We take into account the effects of changing S/V with depth in firn, linked with density change.

P 15725, l 2 : " several orders of magnitude larger " : what impact on results?

- Now we use a different way to estimate post-coring fractionation.

l 16: close-off with dash, not one word (valid for the whole document)

- Corrected.

p 15726, l5 : vostok vs gisp2 ? is vostok data relevant for a very different firn?

- It could be expected that the environment like Vostok where accumulation rate is very low, the number of bubbles are smaller owing to the larger grain sizes. On the other hand, GISP2 with high accumulation rate, smaller grain size may have induced more microbubbles.

- ➢ Now we also use Dome Fuji data, and we found that our model is consistent with Dome Fuji data.

p 15727 : above the depth -> that depth

- ➢ Corrected.

fig 7 : would be a more efficient use of space in a table

- ➢ We believe that a plot will be useful to show the relationship between different molecules, but now we provided a table as well (Table 2.2).

p 15728 : equation 7 is wrong for 2 reasons :
- it's not homogeneous : P is unitless, V is a volume (m3) or maybe unitless like C(l)? (unclear), rho is a density (kg/m3), you probably want to divide the right hand side by rho_ice.
- you are neglecting the change in total porosity by multiplying by (rho_ice - rho(l)), and an equivalent term of (rho_ice - rho(l+1)) should appear, probably in the form of :
[p_open(l)*(rho_ice - rho(l))-p_open(l+1)*(rho_ice - rho(l+1))]
Actually, many equations loosely described in line 8-13 should be written explicitely, with a clear definition of variables to be understandable. I don't understand how you relate C(l) with v0(l)

- ➢ We now a provided more precise equation, although it did not change results much.

Page 15729, section 6.3, figure 11a Can you explain why the dAr/N2 in normal bubbles decreases and increases again before stabilising ? What are the competing effects ? You mention competing effects between micro and normal bubbles, but not in the normal bubbles themselves.

- ➢ To understand this, you need to think about the inclusion of larger air contents near the bubble-close off depth with dAr/N2 = 0, which induce an increase of dAr/N2 near stabilization.

page 15730 : You conclude that the micro-bubble effect is one order of magnitude too small, and you have likely overestimated the micro-bubble fraction by an order of magnitude (see my earlier comment). The reader can naturally conclude that microbubbles are not a dominant contributor to the fractionation. I believe that there is a lot

- We analyzed air content for GISP2 and found that dAr/N2 have a positive correlation with air contents, indicating that when air content is smaller dAr/n2 is more depleted. This indicates that the pressure sensitive process involves not only microbubbles but larger air content.

C5107 of value in quantifying the micro-bubble contribution, as you did, but I would not reach the conclusion that " they dominate the total _Ar/N2 changes in spite of their smaller volumes. " as you state in the abstract on line 18-19. Instead, perhaps you could hint at other processes, or highlight the limits of your model, due to unconstrained parameters that we could perhaps quantify experimentally, by doing an uncertainty estimation including a range of possible values for the permeation coefficients, the geometry of the bubbles, etc.

- See earlier replies.

Page 15730, lines 25-30. As you know, gases take some time to diffuse through the firn, and take about 10 years to reach the lock-in depth. You use a densification model (Goujon et al 2003) to infer dAr/N2, but neglect gas diffusion. The time-lags you find are 81 and 21 years for bubble pressure changes, which are the parameter you are most interested about, and these timelags are in the same ballpark as the timelag due to gas diffusion. Therefore, I wonder how including gas diffusion would change your time-lag estimates. In particular, gas diffusion does not affect bubble pressure, but it affects gravitational fractionation, and thus what time lag we include in the gas-age ice-age difference used for the chronology.

- Gravitational correction using d15N does not affect dAr/N2 variation as d15N variation is so small at least for the time interval we see. The time lag should not be constant if the firn thickness changes more radically by accumulation rate or temperatures, although in the late Holocene it worked as near constant lag.
- For a longer time scale and more variable firn, it would be necessary to use transient run of the firn and permeation model.

page 15730 : " Apparently, the surface temperature anomaly takes longer time to reach the maximum increase in the overloading pressure than that of the accumulation rate anomaly, which is consistent with the observation (68 and 38 years, respectively). "
Perhaps you could add that when you have an accumulation increase, you increase the

downward advection in the firn, so the propagation of the anomaly is quicker. (At least, that's how I interpret this difference)

- Yes, we did.

Pages 15731-33 : the discussion is great, and very thorough

- Thank you!

Page 15734 (conclusion) line 20: " Therefore, the observed negative correlation of _Ar/N2 and accumulation rate can be explained by the processes on the micro-bubbles through the changes in the overloading pressure. " I disagree. You are overstating your conclusions. You find that micro-bubbles have the right sign, but produce a much smaller (10x) fractionation than observed. This could be due to poor knowledge of the diffusivity/sorptivity, or to the fact that post-coring permeation is dominant, or to unknown additional processes. Also, you don't talk about post-coring fractionation, which you calculated to be highly significant. Why ?

- As we think the sentence before "Therefore, .." is enough, we deleted the sentence "Therefore, the observed negative correlation of _Ar/N2 and accumulation rate can be explained by the processes on the micro-bubbles through the changes in the overloading pressure. ".

Figure 2 (and also in the text). Did you plot dAr/N2 or dAr/N2gravcor ? Of course, we expect dAr/N2 to be subject to gravitational fractionation, which depends on T and accumulation. This is not new at all to find a correlation between gravitational fractionation and T or acc. I suspect that you meant to plot dAr/N2gravcor , and you should make it clear throughout the manuscript.

- Yes. I plot dAr/N2 gravitationally corrected.

Figure 3 : Can you be sure that the correlation you find between dAr/N2 and T or accumulation is not due to a remnant of gravitational fractionation that was not corrected well by d15N ? Is there a way that you can test that ?

- Standard deviation (0.07) of ($\delta^{15}N$ * 11) in GISP2 over the past 6000 years is much smaller than standard deviation (1.33) of raw $\delta Ar/N_2$. Therefore, gravitation correction using d15N does not introduce significant variability into dAr/N2.

- This is a good point. The sentence above is added in the text.

Figure 5 : Perhaps you could add to Fig 5 the comparison of d15N for both cores, which shows good agreement.

- $\delta^{15}N$ is plotted now in Fig. 7.

Figure 9 : I don't understand what all the colored lines show. What is your point in this figure ?

- Each line indicates air content and fractionation in annual layer. More explanation is added in the caption.
- You can see how each bubbles generated in different depth evolve with time in terms of permeation. Some of each annual layer is plotted on the bottom.

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Kobashi, T., Box, J., Vinther, B., Goto - Azuma, K., Blunier, T., White, J., Nakaegawa, T., and Andresen, C.: Modern solar maximum forced late twentieth century Greenland cooling, Geophys. Res. Lett., 42, 5992-5999, 2015.

Post bubble-close-off fractionation of gases in polar firn and ice cores: Effects of accumulation rate on permeation through overloading pressure

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Abstract

Gases in ice cores are invaluable archives of past environmental changes (e.g., the past atmosphere). However, gas fractionation processes after bubble closure in the firn are poorly understood, although increasing evidence indicates preferential leakages of smaller molecules (e.g., neon, oxygen, and argon) from the closed bubbles through the ice ~~crystals~~matrix. These fractionation processes are believed to be responsible for the observed millennial $\delta O_2/N_2$ variations in ice cores, linking ice core chronologies with orbital parameters. In this study, we investigated high-resolution $\delta Ar/N_2$ of GISP2, NGRIP, and Dome Fuji ice cores for the past few thousand years. ~~Herein~~W~~, w~~e ~~found~~ find that $\delta Ar/N_2$ at multi-decadal resolution on the gas age scale in the GISP2 ice core has a significant negative correlation with accumulation rate and a positive correlation with air contents over the past 6000 years, indicating that changes in

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overloading pressure induced $\delta Ar/N_2$ fractionation in the firn. Furthermore, ~~the precise~~ GISP2 temperature and accumulation rate ~~records over the past 4000 years are found to~~ for the last 4000 years have nearly equal effects on $\delta Ar/N_2$ with sensitivities of 0.72 ± 0.1 ‰ $^{o}C^{-1}$ and -0.58 ± 0.09 ‰ (0.01 m ice $yr^{-1})^{-1}$, respectively. To understand the fractionation processes, we applied a permeation model for two different processes of ~~to~~ bubble pressure build-up in the firn, "~~microbubbles (< 1 % of air content in the Vostok ice core)~~pressure sensitive process (e.g., microbubbles: 0.3 to 3 % of air contents)" with a greater sensitivity to overloading pressures and" ~~and~~ "normal bubble~~s~~ process" ~~in the firn~~. The model indicates that $\delta Ar/N_2$ in the ~~microbubbles~~ bubbles under the pressure sensitive process are negatively correlated with the accumulation rate due to changes in overloading pressure ~~as found in the observation, due to changes in overloading pressure~~. On the other hand, the normal bubbles experience only limited depletion (< 0.5‰) in the firn. Colder ~~(warmer)~~ temperatures in the firn induce more ~~(less)~~ depletion~~s~~ in $\delta Ar/N_2$ through thicker firn. ~~.~~The pressure sensitive bubbles~~microbubbles~~ are so depleted in $\delta Ar/N_2$ at the bubble ~~closeoff~~close-off depth that they dominate the total $\delta Ar/N_2$ changes in spite of their smaller ~~volumes~~air contents.~~.~~ The model also indicates that $\delta Ar/N_2$ of ~~GISP2 and NGRIP~~ice cores should have experienced several permil of depletion during the storage 14 to 18 years after coring. Further understanding of the $\delta Ar/N_2$ ~~and $\delta O_2/N_2$~~ fractionation processes in the firn, combining with nitrogen and argon isotope data, may lead to a new proxy for the past temperature and accumulation rate.

1 Introduction

Atmospheric gases trapped in the firn layer (unconsolidated snow layer; ~70 m at the Greenland Summit) and preserved in the underlying ice sheets provide precious and continuous records of the past atmosphere and environments (Petit et al., 1999;Spahni et al., 2005;Ahn and Brook, 2008;Kobashi et al., 2008a). However, to reconstruct the original environmental records, it is important to understand the processes of air trapping in the firn, and how the air is retained in the ice until it is analysed in laboratories. Two processes are well-known that change air composition before the air is trapped within bubbles in the firn. First, gravitational fractionation separates gases according to their mass differences and diffusive column height of the firn layer

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(Craig et al., 1988;Schwander, 1989). Second, a temperature gradient (ΔT) between the top and bottom of the firn layer induces thermal fractionation generally pulling heavier gases toward the colder end (Severinghaus et al., 1998). In this study, we investigate ~~the~~ a third process that occurs after the bubbles are closed (post bubble ~~closeoff~~close-off fractionation) and that preferentially affects gases with smaller molecular sizes (< 3.6 Å; for example, helium, neon, oxygen, and argon), but also gases with larger molecular sizes in smaller magnitudes (Ikeda-Fukazawa et al., 2005;Huber et al., 2006;Ikeda-Fukazawa and Kawamura, 2006;Severinghaus and Battle, 2006;Ahn et al., 2008). This fractionation continues deep in ice sheets smoothing signals (Ahn et al., 2008;Bereiter et al., 2014), and the process ~~further~~ continues during/after coring (Ikeda-Fukazawa et al., 2005;Kobashi et al., 2008b;Suwa and Bender, 2008b;Bereiter et al., 2009;Vinther et al., 2009).

Clear evidence of the diffusive gas loss from ice cores through ice crystals has been observed in the oxygen content in ice cores as a ~~rapid~~ depletion of oxygen relative to nitrogen (Bender et al., 1995;Ikeda-Fukazawa et al., 2005;Suwa and Bender, 2008b). Depletion of air content by ~10 % was ~~also~~ observed for the Camp Century ice core after storage for 35 years, although possible analytical differences between early and late measurements cannot be rejected (Vinther et al., 2009). The process is highly temperature dependent, and ~~it~~ the gas loss is induced by the pressure gradients between the bubbles and the atmosphere (Ikeda-Fukazawa et al., 2005). In ice sheets, the concentration gradients at different depths drive the gas diffusion through ice crystals, which smooth climate signals (Bereiter et al., 2014). Firn air studies showed that smaller molecules such as helium, neon, oxygen, and argon preferentially leak out from the closed bubbles, leading to enrichments of these gases in open pores near the bubble-~~closeoff~~close-off depth, which leads to depletions of lighter gases in the closed bubbles (Huber et al., 2006;Severinghaus and Battle, 2006;Battle et al., 2011). However, the mechanisms creating $\delta Ar/N_2$ or $\delta O_2/N_2$ variations in the time domain (i.e., ice cores) are still poorly understood.

On a longer time scale (i.e, orbital), v□~~O_2/N_2 variations~~ariations in $\delta O_2/N_2$~~ in the orbital scale~~ ~~are found to~~ closely follow local insolation changes (Bender, 2002;Kawamura et al., 2007;Suwa and Bender, 2008a;Landais et al., 2012). As a possible mechanism, it has been hypothesized that changes in local insolation affect physical properties of the snow at the surface that persist into the bubble ~~closeoff~~close-off depth, controlling the $\delta O_2/N_2$ fractionation (insolation hypothesis) (Bender, 2002;Fujita et al., 2009). In addition, air content in ice cores are also found to covary with $\delta O_2/N_2$ ~~in~~ on the orbital time scale, indicating common causes (Raynaud et al., 2007;Lipenkov et al., 2011). According to this hypothesis, the orbital signals in $\delta O_2/N_2$ in ice cores are ~~locked~~ linked ~~in~~ to the ice chronology rather than ~~in~~ to the gas chronology, which differ by up to a few thousand years. Therefore, the precise understanding of the gas loss process in the firn is essential to determine how climate signals in the bubbles are placed between the ice-ages and gas-ages on the orbital time scale.

In this paper, encouraged by the observation of a significant negative correlation between $\delta Ar/N_2$ and accumulation rate over the past 6000 years in GISP2 ice core (Fig. 1), ~~using $\delta Ar/N_2$ from GISP2 for the entire Holocene and from NGRIP for the past 2100 years,~~ we investigated the processes of ~~ir~~ multi-decadal to centennial $\delta Ar/N_2$ variability in three ice cores (GISP2, NGRIP, and Dome Fuji)~~,~~ as well as ~~the~~ gas loss processes during ~~the~~ storage. $\delta Ar/N_2$ variations are generally highly correlated with $\delta O_2/N_2$ in ice cores, suggesting ~~that~~ similar processes driving these ~~for $\delta O_2/N_2$ that drive the $\delta Ar/N_2$~~ variations (Bender et al., 1995). As $\delta Ar/N_2$ is nearly constant in the atmosphere over the ~~concerned~~ relevant period (Kobashi et al., 2010), it is better suited to assess the permeation processes in the firn and ice cores than $\delta O_2/N_2$ that varied in the atmosphere by ~1.5 ‰ during the glacial-interglacial cycles (Bender et al., 1995).

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In the following sections, we first describe the data~~,~~ and investigate the relationships between $\delta Ar/N_2$ and changes in accumulation rates and surface temperatures. Then, the fractionation processes are examined by applying a permeation model~~s~~ to the ice cores and the firn under two processes, “pressure sensitive processes (e.g., ~~and the~~ microbubbles)”, and “normal bubble~~s~~ process” ~~in the firn~~. Finally, we discuss our findings, draw conclusions and mention implications.

2 Data description

$\delta Ar/N_2$ data from three ice cores covering the past millennia (NGRIP, Dome Fuji, and GISP2) were used for the analyses. GISP2 and NGRIP data have been published earlier (Kobashi et al., 2008b, 2015), and Dome Fuji data is new. Importantly, storage histories of these cores (i.e., temperatures) are known and methods for measuring $\delta Ar/N_2$ are all comparable. GISP2 and NGRIP ice cores were drilled from the Greenland ice sheet, and Dome Fuji was drilled from the Antarctic ice sheet (Table 1). For GISP2, ~~□Ar/N$_2$ was measured from the GISP2 ice core over the entire Holocene in an attempt to reconstruct the past surface temperatures from □^{15}N and □^{40}Ar (Kobashi et al., 2008b). The~~ sample resolution varies from 10 to 20 years with high resolution analyses covering the past 1000 years (Kobashi et al., 2008b, 2010) and around the 8.2ka event (8100 ± 500 years Before Present [B.P., “Present” is defined as 1950]) (Kobashi et al., 2007). For NGRIP, sample resolution is about 10 years throughout the past 2100 years (Kobashi et al., 2015). ~~The sizes (50-100 g) of ice samples for this study (Kobashi et al., 2008b;Kobashi et al., Submitted) were bigger than that that (15-20 g) commonly used for δ^{15}N and $\delta O_2/N_2$ measurements (Bender et al., 1995;Suwa and Bender, 2008b). The larger sample size is important to obtain high precision for analytical purposes (Kobashi et al., 2008b) and to minimize the effect of the inhomogeneity in an ice sample (Headly, 2008).~~ Both

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GISP2 and NGRIP have similar annual average temperatures of approximately -30 °C (Table 1). However, accumulation rate of NGRIP (~0.19 m ice/year) is 20 % less than that (0.024 m ice/year) of GISP2 over the past 2100 years, and importantly its variation (standard deviation after 21-year Running Means; RMs) is lower by 40 % than that of GISP2 (see later discussion). Dome Fuji has a radically different environment from Greenland with the current annual average air temperature of -54.3 ºC and a mean accumulation rate of ~0.03 m ice/year (Watanabe et al., 2003).

For the time scale of GISP2 and NGRIP ice ages, we used the GICC05 (Vinther et al., 2006; Seierstad et al., 2014). To ~~calculate~~ obtain gas ages, we applied a firn densification-heat diffusion model (Goujon et al., 2003) that ~~was applied~~ calculates firn density structure, close-off depth, and delta age. ~~, and~~ T~~t~~he gas age uncertainties relative to ice age were estimated as ~10 % of the estimated gas age-ice age difference (Goujon et al., 2003). To investigate the $\delta Ar/N_2$ fractionation, ~~We~~ we used reconstructed temperature records from argon and nitrogen isotopes in the trapped air within the GISP2 ice core for the past 4000 years (Kobashi et al., 2011) and NGRIP for the past 2100 years (Kobashi et al., ~~2011~~2015), and layer-counted accumulation rate data for the ~~entire~~ Holocene (Alley et al., 1997;Cuffey and Clow, 1997;Gkinis et al., 2014) ~~to investigate the $\delta Ar/N_2$ fractionation,~~. Dome Fuji have neither precise temperatures nor accumulation rates over the past 2100 years. ~~and t~~The annual resolution accumulation rate data were smoothed with 21-year running means (RMs) to ~~mimic~~ correspond to gas diffusion and the bubble ~~closeoff~~close-off process in the firn (Kobashi et al., 2015). A spline fit (Enting, 1987) was applied to gas data (e.g., $\delta Ar/N_2$) with a 21-year cut off period to be consist with 21 RMs of other parameters, and used for the following analyses to investigate signals longer than the decadal time scale.

~~Similarly, new NGRIP $\delta Ar/N_2$ data for the past 2100 years from the NGRIP ice core were also investigated in this study, providing a good comparison with the GISP2 data. The current NGRIP site has a similar mean annual air temperature of around -30 °C with GISP2. However, the accumulation rate at NGRIP is 20 % lower than that of GISP2 over the past 2100 years, and importantly its variations (standard deviation after 21-year RMs) are lower by 40 % than that of GISP2 (see later discussion).~~GISP2 and NGRIP ice cores were analysed for $\delta Ar/N_2$ ~14 years after coring, however, with different temperature histories. GISP2 (82.4 m -540 m) was drilled in summer 1991. After shipment, they were stored at -29 °C in a commercial freezer until they were moved to a freezer (-36 °C) at the National Ice Core Laboratory (NICL) in February 1993 (G. Hargreaves, pers. comm., 2015). The ice samples were then cut and moved to the Scripps Institution of Oceanography, where $\delta Ar/N_2$ was measured in 2005 (Kobashi et al., 2008b). One the other hand, NGRIP2 ice cores (one of the two NGRIP ice cores; 64.6m to 445.2m) were drilled in summer 1999 (Dahl-Jensen et al., 2002). Shallower parts (64.6m to 254.4m) were stored in a freezer at the University of Copenhagen around -24 °C (J. P. Steffensen, pers. comm., 2015), and deeper parts (255.5m to 445.2m) were in a freezer of a commercial facility rented by the Alfred Wegener Institute (AWI) at -30 °C (S. Kipfstuhl, pers. comm., 2015). In fall 2011, we cut the ice samples, and shipped them to a freezer at the National Institute of Polar Research at -30 °C until 2013 when we analysed the ice cores (Kobashi et al., 2015). The ice cores from Dome Fuji were drilled in late 1995, and stored at -50 °C with a short period (2.5 months) at < -25 °C during shipment from Antarctica to Japan (S. Fujita, pers. comm., 2015). The ice core was analysed in early 2014.

The conventional delta notation is used to express $\delta Ar/N_2$ as follows:

$$\delta Ar/N_2 = [(Ar/N_2)_{sample} / (Ar/N_2)_{standard} - 1]10^3 \text{ (‰)} \qquad (1)$$

where the subscript "sample" indicates ice core values, and "standard" is the present atmospheric composition. For GISP2, mass 40 of argon and 29 of nitrogen, and for NGRIP and Dome Fuji, mass 40 of argon and 28 of nitrogen were used to calculate $\delta Ar/N_2$. All $\delta Ar/N_2$ data presented in this study were corrected for gravitational and thermal fractionations in the firn using ~~a~~ the conventional method~~ (Severinghaus and Battle, 2006;Severinghaus et al., 2009) with~~ based on $\delta^{15}N$ (Bender et al., 1995; Severinghaus and Battle, 2006; Severinghaus et al., 2009)~~for GISP2~~ as follows:

$$\delta Ar/N_{2\,\cancel{grav}corr} = \delta Ar/N_2 - 11\delta^{15}N \qquad (2)$$

The coefficient 11 ~~is~~ arises ~~derived as~~because the mass difference of $\delta Ar/N_2$ (^{40}Ar and $^{29}N_2$) is 11 times larger than that of the nitrogen isotopes ($^{29}N_2$ and $^{28}N_2$)~~ for GISP2~~. This coefficient is replaced with 12 for the calculation of $\delta Ar/N_{2\,\cancel{grav}corr}$ for NGRIP and Dome Fuji because the mass difference between ^{40}Ar and $^{28}N_2$ is 12. As the temperature ~~sensitivity~~ sensitivities of $\delta^{15}N$ and $\delta Ar/N_2$ ~~is~~ are slightly different, the correction is not perfect. However, the variability induced by the gas loss is much bigger than the uncertainties introduced by the differences of the thermal sensitivities. ~~Therefore, these corrections work well.~~ After these corrections, the $\delta Ar/N_{2\,corr}$ variations in the ice cores can be attributed only to ~~the process of the~~ gas loss. ~~It is also noted that~~ $\delta Ar/N_{2\,\cancel{grav}corr}$ of the GISP2 data using the mass 28 or 29 leads to negligible differences (an average difference is 0.4×10^{-3} ‰ and the standard deviation is 0.94×10^{-3} ‰), which is much smaller than the measurement uncertainty of $\delta Ar/N_2$ ($1\sigma < 0.7$ ‰). We also note

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that standard deviation (0.07‰) of $\delta^{15}N \times 11$ in GISP2 is much smaller than standard deviation of raw $\delta Ar/N_2$ (1.33‰) over the past 6000 years, indicating that the variations of $\delta Ar/N_{2corr}$ mostly originate from the raw $\delta Ar/N_2$ not from $\delta^{15}N$. For the sake of simplicity, we denote all the $\delta Ar/N_{2corr}$ as $\delta Ar/N_2$ in later sections.

The significance of correlations were calculated considering the autocorrelation of time series (Ito and Minobe, 2010;Kobashi et al., 2013). We consider > 95% confidence as significant, unless otherwise noted. All error bounds in figures and texts are 2σ.

~~A spline fit (Enting, 1987) was applied to the δAr/N2 data with a 21-year cut off period, and used for the following analyses to investigate signals longer than the multidecadal period. The significances of correlations were calculated considering the autocorrelation of time series (Ito and Minobe, 2010;Kobashi et al., 2013). We consider > 95% confidence as significant, unless otherwise noted.~~

3 Post-coring fractionation

Before evaluating $\delta Ar/N_2$ in ice cores for the changes that have occurred in the firn, it is necessary to consider the post-coring fractionation (Ikeda-Fukazawa et al., 2005)~~{Ikeda-Fukazawa, 2005 #128}~~. For this purpose, we applied a molecular diffusion model (permeation model) through ice crystals (Ikeda-Fukazawa et al., 2005). It has been applied to observed depletions of oxygen in the Dome Fuji and GISP2 ice cores by ~10 ‰ with respect to nitrogen (Ikeda-Fukazawa et al., 2005;Suwa and Bender, 2008b). The model was also implemented with modifications for gas permeation processes in the firn (Severinghaus and Battle, 2006) and in ice cores (Bereiter et al., 2009). The gas permeation in ice cores is driven by the pressure gradients between two spaces isolated by ice walls (e.g., between bubbles or between bubbles and the atmosphere). The concentration (U_m; $\mathrm{mol \cdot mol_{ice}^{-1}}$) of species *m* (i.e., nitrogen, oxygen,

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and argon) in bubbles in one mole of ice after a time t can be described as follows (Ikeda-Fukazawa et al., 2005):

$$U_m = U_m^0 - k_m X_m \left(P^i Z_m^i - P^a Z_m^s\right) S/Vt \qquad (3)$$

where U_m^0 $(\mathrm{mol} \cdot \mathrm{mol}_{\mathrm{ice}}^{-1})$ is the original concentration of species m. k_m ($\mathrm{m \cdot s^{-1}}$) is the mass transfer coefficient and equals to $D_m/\Delta l$, where D_m ($\mathrm{m^2 \cdot s^{-1}}$) is the diffusion coefficient of the species m, and Δl (m) is the thickness of the surface layer of ice (Ikeda-Fukazawa et al., 2005). X_m $(\mathrm{mol} \cdot \mathrm{mol}_{\mathrm{ice}}^{-1} \cdot \mathrm{MPa}^{-1})$ is the solubility of species m in ice. P^i and P^a are the pressures in the bubbles and in the atmosphere, respectively. Z_m^i and Z_m^s are molar fractions of species m in the bubbles and in the atmosphere, respectively. S ($\mathrm{m^2}$) and V ($\mathrm{m^3}$) represent the surface area and the volume of an ice sample such that S/V can be understood as specific surface area ($\mathrm{m^{-1}}$), an important variable for the gas exchange between the atmosphere and the ice (Matzl and Schneebeli, 2006).

For Eq. (3), we assumed an initial air content of 6.53×10^{-5} mole in one mole of ice (a typical air content in ice cores). U_m^0 for each gas is calculated from the total air content multiplied by the atmospheric molar ratio of each gas. In this case, Z_m^i and Z_m^s are set to the atmospheric partial pressures for each molecule. Another factor that affects the gas loss is the specific surface area. GISP2 ice core has a larger diameter (0.132 m) and longer length (1 m) during the storage than that for NGRIP core (diameter 0.098 m and length 0.55m). Dome Fuji core has a diameter of 0.093 m and length of 0.50 m. Therefore, the specific surface areas (S/V) were calculated to be 32.3 $\mathrm{m^{-1}}$, 44.5 $\mathrm{m^{-1}}$, and 47.0 $\mathrm{m^{-1}}$ for GISP2, NGRIP, and Dome Fuji, respectively. It is noted that these specific surface areas are approximations as ice cores during the storage often have different shapes, and we shaved the ice surface by ~5 mm before the analyses (Kobashi et al., 2008b;Kobashi et al., 2015). However, we also note that shallow late Holocene ice cores often had near intact shapes (no sampling) at the time of our sampling from ice cores.

Diffusivity (D_{Ar}) and solubility (X_{Ar}) for argon in ice are less known than those of nitrogen and oxygen. Therefore, we attempted to estimate two possible functions (Ar (I) and Ar (II)) for $k_{Ar}X_{Ar}$ (= $D_{Ar}/\Delta l \cdot X_{Ar}$) in relation to those for nitrogen and oxygen (Fig. 2). $K_{N2}X_{N2}$ and $k_{O2}X_{O2}$ in different temperatures can be estimated using Eqs. (4) and (8) with Δl = 12 mm and 7 mm for nitrogen and oxygen in Ikeda-Fukazawa et al. (2005) for the Dome Fuji core (Fig. 2), which were consistent with various observations (Ikeda-Fukazawa et al., 2005; Severinghaus and Battle, 2006; Suwa and Bender, 2008b; Bereiter et al., 2009).

First estimate of Ar (I) uses a diffusion coefficient (D_{Ar}; 4.0 × 10^{-11} m^2 s^{-1}) of argon at 270 K calculated from molecular dynamic simulations with those of nitrogen (D_{N2}; 2.1 × 10^{-11} m^2 s^{-1}) and oxygen (D_{O2}; 4.7 × 10^{-11} m^2 s^{-1}) (Ikeda-Fukazawa et al., 2004). Owing to the molecular-size dependent fractionation, argon permeation occurs slower than oxygen but faster than nitrogen (Fig. 2), which cannot be explained by their mass differences (Huber et al., 2006; Severinghaus and Battle et al., 2006). Then, temperature-dependent k_{Ar} and X_{Ar} were estimated assuming that the geometrical relationship between D_{N2}, D_{Ar}, and D_{O2} at 270 K from the molecular dynamics simulations holds for k_{Ar} and X_{Ar} at different temperatures as follows:

$$k_{Ar} = k_{O2} - (D_{O2\,at270K} - D_{Ar\,at270K}) / (D_{O2\,at270K} - D_{N2\,at270K})\,(k_{O2} - k_{N2}) \qquad (4)$$

$$X_{Ar} = X_{O2} - (D_{O2\,at270K} - D_{Ar\,at270K}) / (D_{O2\,at270K} - D_{N2\,at270K})\,(X_{O2} - X_{N2}) \qquad (5)$$

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Second, we estimated Ar (II) from an observation that $\delta Ar/N_2$ in ice are often depleted about half of $\delta O_2/N_2$ in ice cores (Bender et al., 1995). To satisfy this condition, $k_{Ar}X_{Ar}$ can be written as:

$$k_{Ar}X_{Ar} = (k_{N2}X_{N2} + k_{O2}X_{O2}) / 2 \qquad (6)$$

Estimated $k_{Ar}X_{Ar}$ for Ar (I) and Ar (II) are higher than $k_{N2}X_{N2}$ and increase with temperatures, resulting in a general depletion of $\delta Ar/N_2$ in ice compared to the atmospheric composition, and the depletion is faster in warmer temperatures (Fig. 2). The use of Ar (I) induces faster depletion of $\delta Ar/N_2$ than that of Ar (II) owing to faster permeation of argon. With the two estimates of $k_{Ar}X_{Ar}$, we explore the range of uncertainties associated with argon permeation.

In a pioneering study by Bender et al. (1995), $\delta Ar/N_2$ in a shallow core of GISP2 was analysed after one week, three months, and seven months of drilling in 1989 to study the time dependent gas loss process (Fig. 3). As the data from three different periods are not significantly different, we consider the $\delta Ar/N_2$ as the original values before the coring. By comparing the data (Bender et al., 1995) with our dataset analysed 14 years after the coring (Kobashi et al., 2008b), we estimated the post-coring fractionation of $\delta Ar/N_2$ in GISP2 to be -1.5 ± 0.6 ‰, a difference of the two datasets for common depths (124 to 214 m) (Fig. 3). Using this value, we derived an unknown parameter (i.e., bubble pressure) in Eq. (3). The bubble pressures are calculated as 0.6 ± 0.2 MPa and 0.8 ± 0.3 MP for two different estimates of $k_{Ar}X_{Ar}$ of Ar(I) and Ar(II), respectively, which agree with the normal bubble pressure at 150-200 m deep in Vostok (Lipenkov, 2000). Using the estimated bubble air pressure and aforementioned parameters, the amounts of depletion in $\delta Ar/N_2$ after coring are estimated as -3.0 ± 1.2 ‰, -2.5 ± 1.0 ‰, and 1.5 ± 0.7 ‰ for NGRIP shallow, and NGRIP deep, and Dome Fuji, respectively (Table 2). As a result, it is possible to derive the original $\delta Ar/N_2$ values before coring for GISP2, NGRIP

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shallow, and NGRIP deep, and Dome Fuji as -2.4 ± 0.6 ‰, -3.3 ± 1.2 ‰, -3.4 ± 1.0, and 6.3 ± 0.8, respectively (Table 2).

4 Post bubble close-off fractionation in firn: Empirical evidence

~~3~~4.1 GISP2 $\delta Ar/N_2$ variation over the Holocene

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The $\delta Ar/N_2$ record over the Holocene in the GISP2 ice core exhibit relatively constant values around -3 ‰, except for a prominent rise of up to 10 ‰ around 7000 B.P. (Fig. ~~1~~4). The rise is located within the depths of the brittle zone (650 ~~–~~to 1400 m), where air in the bubbles changes to clathrate inducing anomalously high pressure (Gow et al., 1997). The dissociation pressure of nitrogen in the clathrate phase is higher than that of argon (or oxygen) so that nitrogen is enriched in the gas phase in relation to the clathrate (more stable state), resulting in a preferential leakage of nitrogen, and thus ~~leading to~~ argon (or oxygen) enrichments in these depths (Ikeda et al., 1999;Ikeda-Fukazawa et al., 2001;Kobashi et al., 2008b). As the dissociation of gases from the clathrate depends on various factors, $\delta Ar/N_2$ in these depths are highly variable (Fig. ~~1~~4). It is noted that $\delta^{15}N$ and $\delta^{40}Ar$ ~~do not~~ exhibit little influences from the anomalous $\delta Ar/N_2$ fractionation, indicating that the processes are mass independent in first order (Huber et al., 2006;Severinghaus and Battle, 2006) (Fig. ~~1~~4).

Changes in the surface temperatures and accumulation rates are the dominant controlling factors for the state of firn layers (e.g., density profile, bubble ~~closeoff~~close-off depth, and firn thickness) (Herron and Langway, 1980;Schwander et al., 1997;Goujon et al., 2003). Therefore, we investigated if changes in surface temperature or accumulation rate have any controls on the $\delta Ar/N_2$ variations. ~~Then,~~We found a significant negative correlation (r = -0.~~29~~35, p = 0.03) between $\delta Ar/N_2$ on the gas age scale and the accumulation rate ~~was found~~ for the past 6000 years, a time interval in which ~~when~~ the abnormal $\delta Ar/N_2$ fractionation is not observed (Fig~~s~~. ~~1 and 2~~1 and 4). This negative correlation is opposite of what an earlier study (Severinghaus and Battle, 2006) suggested for the permeation fractionation in the firn (positive correlation). In addition, the significant correlation was found for $\delta Ar/N_2$ on the "gas ages" scale rather than the "ice ages" that the insolation hypothesis predicts; an indication that new processes need to be considered for the gas loss processes in the firn.

GISP2 data for over the past 4000 years provides a unique opportunity to investigate ~~$\delta Ar/N_2$~~$\delta Ar/N_2$ variations ~~as~~ because precise temperature (Kobashi et al., 2011) and accumulation rate ~~records~~ by layer counting (Alley et al., 1997;Cuffey and Clow, 1997) are available. Using these data, we applied a linear regression and lag analysis on $\delta Ar/N_2$~~$\delta Ar/N_2$~~. It is found that the surface temperature is positively correlated with $\delta Ar/N_2$~~$\delta Ar/N_2$~~ on the gas ages (r = 0.47, p = 0.04; r = 0.28, p = 0.001 after linear detrending) with a 68-year lag (Fig. ~~3a~~5a), indicating that cooler (warmer) temperatures induced more (less) depletions in $\delta Ar/N_2$ with a multidecadal lag. On the other hand, the accumulation rate is negatively correlated with $\delta Ar/N_2$ on the gas ages (r = -0.47, p = 0.12; r = -0.26, p = 0.01 after linear detrending) with a 38-year lag (Fig. ~~3b~~5b), indicating that high (low) accumulation rates induced more (less) depletions in $\delta Ar/N_2$ over the past 4000 years. ~~It is noted~~We note that the surface temperature and accumulation rate have a ~~weak~~ negative but insignificant correlation (r = -0.32, p = 0.13; after linear detrending r = -0.11, p = 0.2) over the past 4000 years.

To estimate the relative contribution of the accumulation rate and the surface temperature changes on $\delta Ar/N_2$, we applied a multiple linear regression, which finds the best linear combination of variables (i.e., temperature and accumulation rate) for a response variable (i.e., $\delta Ar/N_2$). Before the regression is applied, the temperature and accumulation records were

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shifted toward younger ages to account for the lags (38 years and 68 years for accumulation rate and temperature, respectively), and δAr/N_2 is corrected for the post-coring fractionation (1.5 ‰ added). As ordinary least squares including the multiple linear regression underestimate the variance of target time series when the data is noisy (Von Storch et al., 2004), we used "variance matching" by linearly scaling regression coefficients according to the ratio between the variance of the target and model time series. Figure ~~3c~~ 5c shows the original and modeled results of δAr/N_2 over the past 4000 years. As expected, the model of the multiple linear regression captures the δAr/N_2 variations better than the individual variables do (Figs. ~~3a~~5a-c) with a correlation coefficient of $r = 0.58$, $p = 0.09$ ($r = 0.36$, $p < 0.001$ after linear detrending). For the centennial variations, the model captures nearly half of the total variance of the observed δAr/N_2 variations with a 95% confidence ($r = 0.71$, $p = 0.05$ after linear detrending with 200-year RMs). The high and significant correlation between the model and observed δAr/N_2 indicates that changes in the surface temperature and accumulation rate play~~ed~~ important roles in controlling the δAr/N_2 variations. From the multiple linear regression, ~~The sensitivities of~~ δAr/N_2 on the gas ages in GISP2 can be expressed by temperature (ºC) and accumulation rate (m ice/year) as a function of time after adjusting for the lags:~~on the changes in the temperatures and the accumulation rates were estimated to be~~

$$\delta Ar/N_2\,(t) = A \times \text{temperature}\,(t + t_{temp}) + B \times \text{accumulation}\,(t + t_{accm}) + C \qquad (7)$$

where $A = 0.\cancel{72}\,72 \pm 0.\cancel{1}\,06$ ‰ $°C^{-1}$, ~~and~~ $B = -\cancel{0.}58.8 \pm \cancel{0.09}\,4.3$ ‰ $(\cancel{0.01}\ \text{m yr}^{-1})^{-1}$, $C = 32.7 \pm 1.8$ ‰, and t, t_{temp}, and t_{accm} are time (years), lags (years) for temperature and accumulation rate, respectively.~~1~~~~, respectively.~~

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Next, we attempted to use oxygen isotopes of ice ($\delta^{18}O_{ice}$) as a temperature proxy for the same regression analyses of $\delta Ar/N_2$ since we do not have the ~~the precise~~N_2-Ar isotope based temperature information before ~~the past~~ 4000 years~~s~~ B.P. Although a $\delta^{18}O_{ice}$ record from an ice core contains large noises that could be transferred to an estimated temperature record, stacking several $\delta^{18}O_{ice}$ records contains substantial~~reduces the~~ noise~~s~~ and provides a better temperature record (White et al., 1997;Kobashi et al., 2011). Thus, we stacked three oxygen isotope records (GISP2, GRIP, and NGRIP) over the Holocene in the 20-year RMs (Stuiver et al., 1995;Vinther et al., 2006). The stacked record was calibrated to temperatures using the relation obtained from borehole temperature profiles (Cuffey and Clow, 1997). Using the regression coefficients obtained ~~earlier~~ in ~~(~~Fig. ~~3c~~5c~~)~~, a $\delta Ar/N_2$ model was calculated from the oxygen-isotope-based temperature and the accumulation rate (Fig. ~~3d~~5d). We found that the correlation between the model and the observed $\delta Ar/N_2$ performs not as well as the one with the temperature and accumulation rate for the past 4000 years (Fig. ~~3c~~5c), but does slightly better than the correlations with the temperature or accumulation rate~~,~~ individually (Figs. ~~3a~~5a,b).

The $\delta Ar/N_2$ regression model with the $\delta^{18}O_{ice}$~~-~~-based temperatures and accumulation rates can span the entire Holocene, including the periods when the observed $\delta Ar/N_2$ are highly variable owing to the post coring fractionation as discussed earlier. Except the time interval around 7000 years B.P., ~~T~~the model and observed $\delta Ar/N_2$~~ except the time window around ~7000 B.P.~~ exhibit rather constant values of ~~-3~~1- to ~~-4~~ 3 ‰ ~~throughout~~ during the Holocene (Fig. ~~4~~6). ~~Interestingly~~Interestingly, the model indicates that the constant $\delta Ar/N_2$ during the early Holocene is the result of a cancellation between the effects of the accumulation rate and the temperature, both of which were rapidly rising in the early Holocene (Fig. ~~4~~6). The $\delta Ar/N_2$ variations remained higher or noisier from the early Holocene to ~6000 B.P. than that for the

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later period, which probably ~~made~~ make it difficult to decipher the original multidecadal to centennial signals in $\delta Ar/N_2$ (Fig. ~~4~~6).

~~4~~4.2 NGRIP and Dome Fuji $\delta Ar/N_2$ variation over the past 2100 years

$\delta Ar/N_2$ of ~~the~~ NGRIP ice cores provides a good comparative dataset with the GISP2 data (Fig. ~~5~~7). Average $\delta Ar/N_2$ for the past 2100 years are -~~6~~3.~~12~~36 ‰ and -~~3~~2.~~90~~40 ‰ for NGRIP and GISP2, respectively (Fig. ~~5~~7). The $\delta Ar/N_2$ variability in NGRIP (1σ = 0.~~75~~91 ‰) over the past 2100 years is ~~about 40~~24% smaller than that of GISP2 (1σ = 1.~~21~~19 ‰) after correcting for the post-coring fractionation (Table 2), likely owing to the smaller variations of the accumulation rate at NGRIP than that of GISP2 (Fig. ~~5~~7). The pooled standard deviations of replicated samples are 0.94 ‰ for NGRIP over the past 2100 years, and 0.66‰ for GISP2 over the past 1000 years (replicates are available only for the past 1000 years in GISP2) (Kobashi et al., 2008b). The noisier data for NGRIP than that for GISP2 should not be analytical as the mass spectrometer used for the NGRIP had better precision on $\delta Ar/N_2$ than the one~~that~~ used for ~~the~~ GISP2 (Kobashi et al., 2008b;Kobashi et al., ~~Submitted~~2015). $\delta Ar/N_2$ for GISP2 and NGRIP are ~~only marginally~~ weakly but significantly correlated with a correlation coefficient of r = 0.~~22~~24, ~~(~~p = 0.~~07~~02 (after linear detrending)~~)~~ for the ~~overlapping period~~past 1000 years of the high resolution part of GISP2, but ~~the centennial variations (with 100 year RMs) exhibit a more significant correlation (r = 0.44, p = 0.04 after linear detrending)~~not for the deeper part likely owing to the difference of sampling densities between the two periods (Kobashi et al., 2015). The surface temperatures at NGRIP were only weakly correlated with $\delta Ar/N_2$ in the deeper part of NGRIP (r = 0.20, p = 0.06 after linear detrending) and were uncorrelated in the ~~but not in the~~ shallower part. No significant correlations were found between $\delta Ar/N_2$ and the accumulation rate for ~~NGIRP~~NGRIP, probably due to the lower variation of the

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accumulation rate at NGRIP than that of GISP2. It is consistent with the fact that the signal to noise ratio (SNR = variance of signals/variance of analytical errors = 1.2) for NGRIP is about one fifth of that for GISP2 (6.1) estimating the NGRIP signals from Eq. (7).

From the relationship between $\delta Ar/N_2$ and the temperature or accumulation rate of GISP2 in Eq. (7), we can calculate expected $\delta Ar/N_2$ for NGRIP and Dome Fuji. Using the past 2100 years of temperatures and accumulation rates for NGRIP (Fig. 7a,b) and the current observation (Table 1) for Dome Fuji, expected $\delta Ar/N_2$ from Eq. (7) were calculated as 0.3 ± 1.3 ‰ and -6.4 ± 1.2 ‰, respectively. The value for NGRIP is significantly higher than the observed value of -3.3 ± 1.2 ‰ corrected for the post-coring fractionation (Table 2). For Dome Fuji, the value is similar to the observed -6.3 ± 0.8 ‰ corrected for the post-coring fractionation (Fig. 7 and Table 2). This may indicate that the relationship of $\delta Ar/N_2$ with the temperature and accumulation rate becomes non-linear when the firn thickness becomes thinner than that of GISP2 as $\delta Ar/N_2$ is not expected to be positive without the existence of clathrate (see later discussion).

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$\delta Ar/N_2$ ice core ~~record~~ data of NGRIP from the depth ~~of~~ range 64.6-80 m exhibit~~s~~ some interesting features (Fig. ~~6~~8). The depth from ~60 to 78 m corresponds to the lock-in zone in NGRIP, where vertical mixing of gas is limited so that $\delta^{15}N$ stays nearly constant in these depths (Huber et al., 2006; Kawamura et al., 2006). Therefore, the shallowest data at 64.6 m are located in the lock-in zone ~~(Fig. 6)~~. Generally, gas data from the lock-in zone are not used owing to possible contamination (Aydin et al., 2010). However, a recent study (Mitchell et al., 2015) demonstrated that $\delta^{15}N$ can be used to estimate the amount of ambient air contamination using ice samples in the lock-in zone~~s~~, and the original methane concentration in the firn was reconstructed with a range of uncertainties. ~~from ice samples in the lock-in zone.~~ Therefore, we interpret~~ed~~ the observed rapid decreases of $\delta^{15}N$ and $\delta^{40}Ar$ toward shallower depths in the lock-in-zone as the result of mixing with ambient air (Fig. ~~6~~8d). ~~Considering~~ Based on~~the~~ isotope mass balance, we calculated the original $\delta Ar/N_2$ values, which exhibited highly depleted values as low as -50 ‰ (Fig. 8~~6~~e). The depleted $\delta Ar/N_2$ in the lock-in-zone provides a clue ~~for~~ to the processes of gas loss in the firn (see later discussion).

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~~5 Process study I: δAr/N2 permeation model and application to the fractionation during the storage~~

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~~To quantitatively evaluate changes in gas composition after the coring, we applied a molecular diffusion model (permeation model) on the ice cores (Ikeda-Fukazawa et al., 2005). This model has been applied to observed oxygen depletions by ~10 ‰ in the Dome Fuji and GISP2 ice cores (Ikeda-Fukazawa et al., 2005;Suwa and Bender, 2008b). The model has also been implemented with modifications for gas permeation processes in the firn (Severinghaus and Battle, 2006) and in ice cores (Bereiter et al., 2009). The gas permeation from ice cores is driven by the pressure gradients in the bubbles and the atmosphere. The concentration (U_m; mol · mol$_{ice}^{-1}$) of m-molecule (i.e., nitrogen, oxygen, and argon) in bubbles in one mole of ice after a time t can be described as follows (Ikeda-Fukazawa et al., 2005):~~

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$$\cancel{U_m = U_m^0 - k_m X_m \left(P^i Z_m^i - P^a Z_m^s\right) S/Vt \qquad (3)}$$

~~where U_m^0 (mol · mol$_{ice}^{-1}$) is the original concentration of m-molecule. k_m (m·s^{-1}) is the mass transfer coefficient and equals to $D_m/\Delta l$, where D_m (m^2·s^{-1}) is the diffusion coefficient of the m-molecule, and Δl (m) is the thickness of the surface layer of ice (Ikeda-Fukazawa et al., 2005).~~

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~~X_m ($\mathrm{mol \cdot mol_{ice}^{-1} \cdot MPa^{-1}}$) is the solubility of *m* molecule in ice. P^i and P^a are the pressures in the bubbles and in the atmosphere, respectively. Z_m^i and Z_m^s are molar fractions of *m* molecule in the bubbles and in the atmosphere, respectively. *S* (m^2) and *V* (m^3) represent the surface area and the volume of an ice sample such that *S/V* can be understood as specific surface area (m^{-1}), an important variable for the gas exchange between the atmosphere and the ice (Matzl and Schneebeli, 2006).~~

~~In this study, we applied the model to estimate argon loss from the ice cores during the storage. Coincidentally, both GISP2 and NGRIP ice cores were analysed for $\delta Ar/N_2$ ~14 years after the coring, however, with different temperature histories. The GISP2 (82.4 m -540 m) was cored in summer 1991. After the shipment, they were stored at -29 °C in a commercial freezer until they were moved to a freezer (-36 °C) at the National Ice Core Laboratory (NICL) in February 1993 (G. Hargreaves, pers. comm., 2015). Then, the ice samples were cut and moved to the Scripps Institution of Oceanography where $\delta Ar/N_2$ was measured in 2005 (Kobashi et al., 2008b). One the other hand, the NGRIP2 ice cores (64.6m – 445.2m) were cored in summer 1999 (Dahl-Jensen et al., 2002). Shallower parts (64.6m – 254.4m) were stored in a freezer at the University of Copenhagen around -24 °C (J. P. Steffensen, Pers. Comn., 2015), and deeper parts (255.5m – 445.2m) were in a freezer of a commercial facility rented by the Alfred Wegener Institute (AWI) at -30 °C (S. Kipfstuhl, Pers. Comn., 2015). In fall 2011, we cut the ice samples, and shipped them to a freezer at the National Institute of Polar Research at -30 °C until 2013 when we analysed the ice cores (Kobashi et al., Submitted).~~

~~We assumed an initial air content of 6.53×10^{-5} mole in one mole of ice (a typical air content in ice cores), and bubble pressures P^i to 1 MPa that is a normal bubble pressure at 200 m depth for Vostok (Lipenkov, 2000). U_m^0 for each gas is calculated from the total gas content multiplied by the atmospheric molar ratio of each gas. In this case, Z_m^i and Z_m^s are set to the atmospheric~~

~~partial pressures for each molecule. Another factor that affects the gas loss is the specific surface area. GISP2 has a larger diameter (0.132 m) and longer length (1 m) during the storage than that (diameter 0.098 m and length 0.55m) for NGRIP. Therefore, the specific surface areas (*S/V*) were calculated to be 32.3 m^{-1} and 44.5 m^{-1} for GISP2 and NGRIP, respectively. It is noted that these specific surface areas are approximations as ice cores during the storage have often different shapes, and we shaved the ice surface by ~5 mm before the analyses (Kobashi et al., 2008b;Kobashi et al., Submitted). The temperature histories and the specific surface areas indicate that the NGRIP ice cores were more susceptible to the gas loss during storage.~~

~~To calculate argon diffusion from the ice cores, it is necessary to estimate the solubility and diffusivity of argon in ice at different temperatures. However, diffusion coefficients of argon is only available at 270 K (D_{Ar}; 4.0×10^{-11} m^2 s^{-1}) with those of nitrogen (D_{N2}; 2.1×10^{-11} m^2 s^{-1}) and oxygen (D_{O2}; 4.7×10^{-11} m^2 s^{-1}) from molecular dynamics simulations (Ikeda-Fukazawa et al., 2004). Therefore, we estimated k_{Ar} and X_{Ar} assuming that the geometrical relationship between D_{N2}, D_{Ar}, and D_{O2} at 270 K holds for k_m and X_m at different temperatures. This leads to the following equations (Fig. 7).~~

$$\cancel{k_{Ar} = k_{O2} - (4.7-4.0) / (4.7-2.1)\,(k_{O2} - k_{N2})} \qquad \cancel{(4)}$$

$$\cancel{X_{Ar} = X_{O2} - (4.7-4.0) / (4.7-2.1)\,(X_{O2} - X_{N2})} \qquad \cancel{(5)}$$

~~X_m and k_m for nitrogen and oxygen in different temperatures can be calculated through Eqs. (4) and (8) in Ikeda-Fukazawa et al. (2005). This leads to estimates of $k_{Ar}X_{Ar}$ (= permeability/Δl) (Fig. 7). Using these values, the gas loss of each gas was calculated from Eq. (3) with different temperature histories, and expressed by the standard delta notation relative to the atmospheric~~

~~values. Then, it is found that $\delta Ar/N_2$ should be depleted in relation to the original values by -2.7 ‰, -6.6 ‰, and -4.4 ‰ for GISP2, NGRIP shallow, and NGRIP deep, respectively. The observed average $\delta Ar/N_2$ of GISP2, NGRIP shallow, and NGRIP deep over the past 2100 years are -3.9‰, -6.3 ‰, and -6.0 ‰ (Fig. 5), indicating that $\delta Ar/N_2$ before the storage had the values of -1.2 ‰, 0.3 ‰, and -1.6 ‰, respectively. It is noted that a large gap in the calculated original $\delta Ar/N_2$ between the shallow and deep NGRIP ice cores and in particular the positive value for the NGRIP shallow, may indicate that the estimated permeability is possibly several fold larger than that in the real world.~~

~~The larger depletion in $\delta Ar/N_2$ from the NGRIP ice core likely introduced noises into the original $\delta Ar/N_2$ signals, causing poorer reproducibility in the NGRIP data than that of the GISP2 data, which likely made it difficult to attribute the NGRIP $\delta Ar/N_2$ variation to changes in surface temperature and/or accumulation rate. Ice cores during the storage often have different shapes from earlier samplings, and have different micro-environments in boxes or freezers. All of these factors induce differential permeations for different ice pieces, and so introduce larger noises if the gas loss are more intense.~~

5 ~~Process study II:~~ Post bubble-~~closeoff~~close-off fractionation in firn ~~for micro- and normal bubbles~~: Process study

~~6~~

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Air bubbles in the polar firn or ice can be categorized into two types (Lipenkov, 2000)~~.~~: ~~The first one are~~ normal bubbles and ~~the other are so called~~ microbubbles (< 50 μm). ~~.~~ They ~~can be~~ can be distinguished as a bimodal distribution in ice cores (Lipenkov, 2000;Ueltzhöffer et al., 2010;Bendel et al., 2013). The air volume contribution of the microbubbles to the total air content is estimated to be 0.3% in the Vostok ice core (Lipenkov, 2000), but the value is not known for Greenland ice cores. Importantly, the two types of bubbles have significantly different bubble pressure histories in the firn. ~~They can be distinguished as a bimodal distribution in ice cores (Lipenkov, 2000;Ueltzhöffer et al., 2010;Bendel et al., 2013).~~ The normal bubbles form at the bubble ~~closeoff~~close-off depth~~,~~. ~~and m~~Most of the air in ice cores is captured as ~~the~~ normal bubbles, ~~-~~and the air-trapping processes are relatively well known (Schwander et al., 1997;Goujon et al., 2003;Mitchell et al., 2015). Normal bubble pressures build up according to increasing density (normal bubble process; Severinghaus and Battle, 2006). On the other hand, the microbubbles are believed to form near the surface (Lipenkov, 2000)~~.~~. ~~Therefore,~~ So, they are highly pressurized and have rounded shape by the time when the bubbles reach the bubble ~~closeoff~~close-off depth (Lipenkov, 2000;Ueltzhöffer et al., 2010). As a result, the microbubbles are more sensitive to changes in the overloading pressure at the bubble close-off depth (pressure sensitive process).

Owing to the different bubble pressure histories in the firn, $\delta Ar/N_2$ or $\delta O_2/N_2$ in the microbubbles and normal bubbles are expected to be different due to the differential permeation of each molecule. In this study, we attempted to quantify two types of the gas loss processes, "pressure sensitive process (microbubble)" and "normal bubble process", in the firn using a permeation model (Ikeda-Fukazawa et al., 2005) combined with the inputs from firn-densification heat-diffusion models (Schwander et al., 1993; Spani et al., 2003; Goujon et al., 2003).

~~Owing to the different histories of the bubbles in the firn (i.e., air pressures and duration in the firn after the closure),~~ ~~$\delta Ar/N_2$ or $\delta O_2/N_2$~~ ~~in the microbubbles and normal bubbles should be different if the permeation theory is correct. Therefore, we attempted to quantify the processes of the gas loss from closed bubbles using a permeation model (Ikeda-Fukazawa et al.,~~

~~2005) combined with the inputs from firn-densification heat-diffusion models (Schwander et al., 1997;Goujon et al., 2003).~~

~~6.1~~5.1 Pressure sensitive process (microbubbles)~~Microbubbles~~

We first look~~ed~~ into the ~~microbubble~~ pressure sensitive process~~es~~ as exemplified by the microbubbles. Microbubbles are believed to form in the shallow firn by sublimation-condensation processes (Lipenkov, 2000). These bubbles have smaller sizes, smoothed spherical surfaces, and can generally be found in the interior of the ice crystals (Lipenkov, 2000). The bubble pressure reaches near overloading pressure at the bubble close-off depth, and so it is sensitive to changes in the overloading pressure. As the actual contribution of microbubbles and air content involved in the pressure sensitive processes is not known, we consider a 2% contribution of air to the total air. As it will be discussed later, more air fraction than simply from microbubbles (0.3 % in Vostok) are likely involved in the pressure sensitive process. Therefore, we conducted additional calculations with 0.3 %, 1 %, and 3 % microbubble contributions, and assessed the impacts to the total $\delta Ar/N_2$.

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~~The air volume contribution of the microbubbles to the air content is estimated to be 0.3% in the Vostok ice core (Lipenkov, 2000). Because microbubbles are formed in the shallow firn, air pressure in the microbubbles can reach as high as ice load pressure or slightly below at the bubble closeoff depth (Lipenkov, 2000).~~ To model the gas permeation process from the microbubbles, we assumed steady state with given surface temperatures and accumulation rates, and calculated the ages, firn densities, porosities, and overloading pressures at given depths, using a firn densification-heat diffusion model (Schwander et al., 199~~7~~3; Spahni et al., 2003). Then, they are interpolated for annual layers in the firn for the following calculation.

Changes in the concentrations of species *m*~~m molecule~~ were calculated according to the following Eq. (~~6~~8) similar to Eq. (3).

$$U_m(l+1) = U_m(l) - k_m X_m\left(P^i(l) Z_m^i(l) - P^a Z_m^s\right)\left(\frac{S}{V}(l)\right) s_o/s\cancel{P_{open}}(l)\, t\, C(l) \qquad (\cancel{6}8)$$

$$Z_m^i(l) = \frac{U_m(l)}{U_{Ar}(l) + U_{O2}(l) + U_{N2}(l)}$$

where *l* is an annual layer from the surface to below the firn layer~~to~~ (e.g., *l* = 1 to 2000)~~deeper firn~~, and ~~P_{open}~~ s_o/s *(l)* in a layer *l* is the open porosity ratio~~open pore ratio relative to the porosity (Fig. 8a)~~. *s*, s_c, and s_o are the total, closed, and open porosities ($s_o = s - s_c$), respectively (Spahni et al., 2003; see also the next section "normal bubble process"). In a steady state, *l* can be considered as a time variable. At *l* = ~~0~~1, the ~~concerned~~ microbubbles in an annual layer are at surface, although they are not active in terms of permeation at these depths (Fig. ~~8~~9). With *l* increasing~~*l*~~ in a one year step, the microbubbles move deeper in the firn with *l* annual layers overlying. *C(l)* is a coefficient defining the gas concentration in ~~a concerned~~ annual layer *l* relative to the total air in ice. ~~For the microbubbles, 0.01 to 0.03 (1 % to 3 %) were used according to the percentage of the microbubbles (see below) relative to the total air.~~ It is assumed that the pressure P^i *(l)* in the microbubbles starts increasing with overloading pressure from the depth of which the normal bubbles generation initiates ~~overloading pressure of~~ (firn density of around ~~0.375~~0.7 ~~MPa~~ g/cm^3) (Fig. ~~8c~~9c), and that pressure changes were considered to be negligible above ~~the~~ that depth (Lipenkov, 2000). Initial $P^i(0)$ was set at 0.065 MPa similar ~~-~~to the atmospheric pressure at the Greenland Summit (Schwander et al., 1993) with a 0.3 MPa lag from overloading pressure as in Fig. 9 (Lipenkov, 2000). We estimated the specific surface area (*S*/*V(l)*) in a layer *l* from the linear relationship between the specific surface

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areas (m^{-1}) and densities ρ from the Greenland Summit (Lomonaco et al., 2011) with an equation: S/V (l) (m^{-1}) = -16799 ρ(l) (g cm^{-3}) + 14957. The initial gas content in the microbubbles was set at ~~1~~0.3 ~~-~~ to 3% of the air content (6.53226 × 10^{-5} mole × 0.01) per 1 mole of ice, and it is composed of nitrogen (78.084%), oxygen (20.9476%), and argon (0.934%). The specific surface area S/V was multiplied by the open porosity ratio ~~P_{open}~~ s_o / s (l) (~~(~~Spahni et al., 2003; Fig. ~~8a~~9a) as the gas loss occurs toward open pores. $k_m X_m$ was calculated as for the post coring fractionation, and we used the estimate, Ar (II) for argon.

Figure ~~8~~ 9 shows model results with a temperature of -~~30~~ 31 ºC, an accumulation rate of 0.25 m ice/year (similar to GISP2 condition), and ~~1~~2% microbubble contribution. It shows that the gas permeation from the microbubbles starts soon after the pressure was applied in the microbubbles (Figs. ~~8c~~9c,d). As oxygen has a larger permeability than that of argon, $\delta O_2/N_2$ depletion is larger than $\delta Ar/N_2$ (Fig. ~~8b~~9b). At the temperature of -30 ºC and accumulation rate of 0.25 m ice yr^{-1}, the depletion reaches up to ~~~70~~ 133 ‰ for $\delta Ar/N_2$, and ~~~100~~ 243 ‰ for $\delta O_2/N_2$ in the model, which ~~leads~~ corresponds to ~~5~~ 12 % gas loss from the original air content of the microbubbles (Fig. ~~8c~~9c).

~~6.~~25.2 N~~Normal~~ ormal bubble~~s~~ process

Most of the air in ice cores ~~(~99%)~~ is trapped as normal bubbles near the lock-in depth ~~(Fig. 9a)~~. As a result, bulk air pressure in the normal bubbles does not build up as high as the microbubbles in the lock-in zone (Lipenkov, 2000). We used ~~the permeation model in the~~ Eq. (~~6~~8) to model the permeation process for the normal bubbles. As for the microbubbles, we assumed steady state with the given temperatures and accumulation rates. The general characters of the firn in various depths (ages, densities, porosities, loading pressures, bubble

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~~closeoff~~close-off depths) were calculated using the firn-densification heat diffusion model (Schwander et al., ~~1997~~1993; Spahni et al., 2003), and they were interpolated for annual layers as for the microbubbles. We first calculated how much bubble ~~volume~~air ~~of bubbles~~ is generated in each annual layer according to the ~~decreases~~ increase in the ~~open pore~~closed porosity (~~P_{open}~~s_c) with depth as the following equation.

$$V_0(l+1) = a\{(\cancel{(}s_c\cancel{P_{open}}(l+1) - s_c\cancel{P_{open}}(l\cancel{+1})(\rho_{ice} - \rho(l+1))/(\rho_{ice} - \rho(l))\cancel{)(\rho_{ice} - \rho(l))}\} / \rho(l+1)$$

(~~7~~9)

where $V_0(l)$ is newly ~~generated~~ trapped ~~bubbles~~ air in an ~~each~~ annual layer l, ρ_{ice} is the density of ice, and $\rho(l)$ is the density at depth l ~~(Fig. 9a).~~. $s_c(l)$ is the closed porosity in an annual layer l, and a is a scaling coefficient. s_c can be written as (Schwander, 1989; Spahni et al., 2003):

$$s_c = \begin{cases} s \cdot exp\left[75 \cdot \left(\frac{\rho(l)}{\rho_{co}} - 1\right)\right], & 0 < \rho(l) < \rho_{co} \\ s, & \rho(l) > \rho_{co} \end{cases} \qquad (10)$$

where ρ_{co} is the density at the depth in which the air is totally enclosed in bubbles. The sum of all the newly generated air $(\sum_{l=1}^{2000} V_0(l))$ ~~was~~ are set to have the air content of 6.53 × 10^{-5} mole per mole of ice~~,~~. ~~and t~~Then, $V_0(l)$ was scaled accordingly using the coefficient a, and converted to the volume (m^3) with the atmospheric pressure (0.065 MPa) as in Fig. ~~9a~~10a.

The normal bubbles start forming at ~~~~~approximately 40 m depth and the formation is maximum around the bubble ~~closeoff~~close-off depth of 60 to 75 m at -~~30~~ 31 °C and 0.2~~4~~ m ice yr^{-1} in the model (Fig. ~~9a~~10a). Then, the permeation from each annual layer was calculated

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according to Eq. (~~6~~8). The difference from the microbubble permeation process is that the volume of the normal bubbles~~ in each annual layer~~ decreases according to increasing density towards deeper depth, leading to generally smaller pressure build-up and total permeation from the bubbles in the firn (Fig. ~~9a~~10a). $C(l)$ in Eq. (~~6~~8) was calculated from $V_0(l)$ for each annual layer l by setting the sum of $C(l)$ as ~~-~~1 – 0.02 = 0.98 (if microbubble contribution is 2 %) (Fig. ~~9e~~10e). ~~-~~Other parameters in Eq. (~~6~~8) were set to be the same as for the microbubbles.

Figure ~~9~~ 10 shows the evolution of the normal bubble volumes, the nitrogen and argon concentrations, the $\delta Ar/N_2$ in each annual layer, and the air content and bulk $\delta Ar/N_2$ with depth at a temperature of -~~30~~ 31 ºC and an accumulation rate of 0.~~25~~ 24 m ice yr^{-1} as for the microbubbles for Fig. ~~8~~9. A new generation of ~~the~~ closed pore volumes in annual layers generally increases towards deeper depths~~ except the last three layers, showing decreasing trapped air volume~~ (~~small circles in~~ Fig. ~~9a~~10a). When open pore space disappears completely, we ~~consider~~ assume the gas permeation to the open pore stops. As argon (oxygen) permeation in ice is faster than nitrogen by ~~∼380~~289 (~~∼480~~479) % at -~~30~~ 31 °C (Ar (II), Fig. ~~7~~2), $\delta Ar/N_2$ ($\delta O_2/N_2$) within the bubbles decreases~~-~~ when the permeation proceeds. At the temperature of -~~30~~ 31 ºC and accumulation rate of 0.~~25~~ 24 m ice yr^{-1}, the $\delta Ar/N_2$ depletion can reach about -~~7~~ 5 ‰ for those bubbles formed at shallow depths (Fig. ~~9d~~10d). However, the amount of air ~~contents~~ contained ~~of~~ in these bubbles ~~are~~ is so small (Fig. 10a) that the influence~~s~~ on the total $\delta Ar/N_2$ is limited (Fig. ~~9e~~10e). The depth vs. $\delta Ar/N_2$ relationship of the total air from the normal bubbles (Fig. ~~9e~~10e) indicates that the total $\delta Ar/N_2$ reaches the minimum of -0.~~56~~ 39 ‰ at ~~the beginning of~~ the middle of the bubble ~~closeoff~~close-off depth of ~~∼68~~ 73.2 m. Then, the total $\delta Ar/N_2$ increases to -0.~~42~~ 29 ‰ as a large amount of ~~the total~~ambient air with $\delta Ar/N_2 = 0$ ~~(after the correction for gravitation)~~ is trapped in these depths (Fig. ~~9e~~10a,d,e).

~~6.3~~5.3 Total air in bubbles

The permeation models for the normal and microbubbles were run for various firn conditions with different surface temperatures, accumulation rates, and microbubble contributions to investigate their effects on the ~~total~~ δAr/N_2 in the bubbles (Figs. ~~10~~ 11 and ~~11~~Table 3). Resultant air content (i.e., nitrogen, argon, and oxygen) for each annual layer from the micro- and normal bubbles were added to calculate the combined effects of the accumulation rates and temperatures on total δAr/N_2 (Fig. ~~10~~11). ~~The r~~Results show that the normal bubbles experience only limited δAr/N_2 depletion (> -0.5‰) by the different temperatures or accumulation rates we considered (Table 3). On the other hand, δAr/N_2 in the microbubbles varies with ~~colder (warmer)~~ temperatures ~~induce more (less) depletions in δAr/N2 for the microbubbles~~ through thickening ~~(thinning)~~ of the firn, leading to higher ~~(lower)~~ pressures in the bubbles and longer ~~(shorter)~~ duration exposed to the gas loss in the firn (~~Figs. 10c and 11b~~Table 3). Higher accumulation rate with the same temperatures induces more depletion as it is primarily controlled by the changes in loading pressure (Figs. 11c and Table 3). As a result, ~~For the normal bubbles, the temperature changes do not appreciably influence the final δAr/N2~~ the total δAr/N_2 generally reflects the variation of δAr/N_2 in the microbubbles~~values~~ (*r* = 0.95; ~~Figs. 10b and 11a~~Table 3). ~~On the other hand, different accumulation rates induce contrasting effects on δAr/N2 between the normal bubbles and microbubbles. For the normal bubbles, higher (lower) accumulation rate leads to less (more) depletions in δAr/N2; however, for the microbubbles, higher (lower) accumulation rate induces more (less) depletions (Figs. 10c and 11b).~~ Overall, the total δAr/N_2 have high correlation with temperatures (*r* = 0.97) than that (*r* = 0.57) with accumulation rates in the model (Table 3).

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~~The sum of $\delta Ar/N_2$ in the microbubbles and normal bubbles with depth is plotted in Fig. 11c.~~ The modeled $\delta Ar/N_2$ agrees with the observed $\delta Ar/N_2$ corrected for the post-coring fractionation within their uncertainty ranges (Table 2). Extremely cold temperature in Dome Fuji with low accumulation rate induces a long duration (274 years) of the bubble exposed to the permeation in the firn, leading to a large depletion of $\delta Ar/N_2$ of the microbubbles and so in the total air (Table 3). The variations of $\delta Ar/N_2$ in normal bubbles are limited, and clearly microbubbles (or the pressure sensitive process) play a critical role for the variation of $\delta Ar/N_2$ in ice cores. The $\delta Ar/N_2$~~$\delta Ar/N_2$~~ minima in the firn ranges from -14 ‰ to -~~48~~ 83 ‰ depending on the temperatures and accumulation rates. The most depleted $\delta Ar/N_2$ with a temperature of -~~35~~ 30 °C and accumulation rate of 0.2~~5~~ m ice yr^{-1} in Fig. 11c capture ~~in Fig. 11c resembles~~ the highly depleted observation-based estimates of $\delta Ar/N_2$ ~~at 65 m~~ in NGRIP ice core (Fig. ~~6e~~8e). As the normal bubble~~s~~ process alone does not produce such depleted values in the firn~~have only limited depletions on $\delta Ar/N_2$ with depth~~ (Fig. ~~11a~~11a), the observed ~~-~~highly-depleted $\delta Ar/N_2$ (Fig. ~~6e~~8e) is an evidence for the involvement of the microbubble ~~permeation~~ process (or pressure sensitive process) ~~process~~. The total $\delta Ar/N_2$ at the bubble ~~closeoff~~close-off depth increases to less depleted values from the minimum owing to the rapid inclusion of the ambient air ~~-~~(~~-0.6 ‰ to -1.4 ‰;~~ Fig. ~~11c~~11c).

The calculated dependencies of the $\delta Ar/N_2$ variations on the temperature (0.~~13~~ 24 ‰ °C^{-1} for an accumulation rate of 0.25 m ice yr^{-1}) and accumulation rate (-0.~~03~~ 05 ‰ (0.01 m ice yr^{-1})$^{-1}$ at -30 °C) with ~~a~~ the ~~1~~ 2 % microbubble contribution (Table 3) is lower than that of the observed ones in GISP2 ice cores (0.72 ± 0.1 ‰ °C^{-1} and -0.58 ± 0.09 ‰ (0.01 m ice yr^{-1})$^{-1}$), respectively. Considering ~~the~~ a possibility of larger volume contributions ~~of the microbubbles~~on the pressure sensitive process ~~in GISP2~~, we calculated the ~~microbubble~~ permeation model with ~~the~~ microbubbles volume contributions from 0.3 % to ~~of 2 % and~~ 3 %

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to the total air. The 3 % microbubble contribution induces more depletion in the total δAr/N_2 (Fig. ~~11d~~11d). Also, the dependencies of δAr/N_2 on temperatures and accumulation rates linearly increase to 0.38 ‰ °C^{-1} with an accumulation rate of 0.25 m ice yr^{-1}, and -0.11 ‰ (0.01 m ice yr^{-1})$^{-1}$ with a temperature at -30 °C, respectively. The fact that they are still lower than those of the observations, ~~may~~ indicates the involvements of ~~even~~ larger air ~~volume contributions~~contents ~~from~~ as ~~the~~ microbubbles and/~~and~~or/~~or~~ normal bubbles influenced by the ~~additional amplifying processes~~pressure sensitive process. This is plausible considering the inhomogeneity of firn (Hörhold et al., 2012) and resultant differential pressurization of bubbles.

An evidence for the larger air involvement in the pressure sensitive process is~~-~~ the significantly positive correlation between δAr/N_2 and air contents over the past 6000 years in GIPS2 (Fig. 1). This correlation indicates that the bubble air was squeezed out before close-off resulting in smaller air contents when overloading pressure was higher, eventually inducing higher pressure in the bubbles and so enhanced δAr/N_2 depletions. This observation is also consistent with recent findings that abrupt increases of accumulation rate at abrupt warming during the last glacial period induced reductions in air contents (Eicher et al., Climate of the Past, submitted, 2015). In addition, artificial sintering of snow with higher pressure has been shown to contain much smaller air content than ice cores owing to the lack of time to develop spherical cavities by vapour transport (B. Stauffer, pers. comm., 2015). These lines of evidence indicate that higher overloading pressure at the lock-in-zone have impacts on normal as well as microbubbles. The inclusion of this process in the model is beyond the scope of the current paper, and we leave it for future studies.

We also investigated the observed lags of the δAr/N_2 variations in GISP2 from the changes in the surface temperatures and accumulation rates by 68 and 38 years, respectively (Fig. ~~3~~5). Presumably, the lags are introduced during the process of transferring surface

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temperature and accumulation rate signals into overloading pressure at the bubble ~~closeoff~~close-off depths. Therefore, two transient simulations were conducted using a firn densification and heat diffusion model (Goujon et al., 2003). First, the model was run with a constant temperature (-30 °C) and accumulation rate (0.2 m ice yr^{-1}) over thousands of years to reach an equilibrium state. Then, surface temperature and accumulation rate anomalies of -35 °C and 0.26 m ice yr^{-1} for 20 years were introduced, separately (Fig. ~~12a~~12a). The surface anomalies of the temperature and accumulation rate were set to induce similar δAr/N_2 changes by 3.5 ‰ from the relationship obtained by the multiple linear regressions on the δAr/N_2 of GISP2.

We found that~~Then, it is found that~~ the surface temperature anomaly takes 20 years to reach the minimum temperature at the bubble ~~closeoff~~close-off depth (Fig. ~~12b~~12b). The cooling induces maximum firn thickening after 56 years. The accumulation rate anomaly also induces firn thickening with an 11-year lag (Fig. ~~12c~~12c). Overloading pressures at the bubble ~~closeoff~~close-off depth reach similar maximum values with 85- and 21-year lags from the surface temperature and accumulation rate anomalies, respectively (Fig. ~~12d~~12d). Apparently, the surface temperature anomaly takes longer~~ time~~ to reach the maximum increase in the overloading pressure than that of the accumulation rate anomaly, which is consistent with the observation (68 and 38 years, respectively). The accumulation rate anomaly is almost instantaneously but increasingly felt by the bubble close-off depth through overloading pressure, compared to the temperature anomaly that takes decades to reach the bubble close-off depth. In addition, we note that similar magnitudes of the overloading pressure anomalies were induced by the temperature and accumulation rate anomalies (Fig. ~~12d~~12d). Therefore, we conclude that the overloading pressure is the carriers of the surface temperature and accumulation rate signals, linking the δAr/N_2 variations through the permeation.

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~~7~~6 Discussions

The processes responsible for the $\delta Ar/N_2$ variations should also play similar roles on the variations of $\delta O_2/N_2$ in ice cores but with larger magnitudes owing to the larger permeability of oxygen (Bender et al., 1995;Huber et al., 2006;Severinghaus and Battle, 2006;Battle et al., 2011). In earlier studies, causes of the $\delta O_2/N_2$ variation were attributed on the metamorphisms of surface snow induced by local insolation changes (Bender, 2002;Kawamura et al., 2007). The altered snow properties remain until the snow reaches the bubble ~~closeoff~~close-off depth and affects the preferential oxygen loss (Bender, 2002). ~~This~~ Our ~~study~~ work ~~demonstrated~~ demonstrates that the permeation processes in the firn can be induced by changes in the surface temperature and the accumulation rate through the changes in overloading pressure, indicating a possibility that the $\delta O_2/N_2$ variations in the orbital scale are also a result of the surface temperature and accumulation rate changes. It is noted that $\delta Ar/N_2$ in GISP2 also shows a significant positive correlation (r = 0.~~37~~38, p ~~=~~ $<$ 0.001 after linear detrending) with the air content (Kobashi et al., 2008b) over the past 6000 years, indicating a similar link between $\delta O_2/N_2$ and air content in the orbital time scale (Raynaud et al., 2007;Lipenkov et al., 2011). As the ~~environments of the interior of the Antarctic such as Vostok, Dome Fuji, and Dome C are radically different (very low temperatures and accumulation rates) from the Greenland Summit or NGRIP site~~time scale we considered in this study is different from the orbital scale variation, other mechanisms may play a role~~s~~ in controlling the $\delta O_2/N_2$ variations in ice cores. However, the mechanisms discussed here must be considered in future studies.

Although the gas permeation from ice is generally believed to be a mass independent process (no effects on isotopes), there ~~are~~ is some evidence~~s~~ of isotopic fractionation (Bender et al., 1995;Severinghaus et al., 2003;Severinghaus and Battle, 2006;Kobashi et al., 2008b;Severinghaus et al., 2009;Battle et al., 2011). ~~Especially~~In particular, poor quality ice cores often exhibit isotope fractionation (e.g, $\delta^{18}O$ and $\delta^{40}Ar$) with highly depleted $\delta O_2/N_2$ or $\delta Ar/N_2$ (Bender et al., 1995;Severinghaus et al., 2009). This mass dependent fractionation is explained by the existence of micro-cracks in poor quality ice samples that permit a relatively large air flow. On the other hand, slowly occurring gas permeations through ice crystals in good quality ice cores (e.g, NGRIP ~~and,~~ GISP2, and Dome Fuji) appear to have small or non-existent effects ~~no effects~~ on isotopes ~~or very small~~ (Kobashi et al., 2008b;Suwa and Bender, 2008b). As small mass dependent fractionation of $\delta^{15}N$ and $\delta^{40}Ar$ during the gas ~~permeation~~ loss are similar to the gravitational fractionation (Kobashi et al., 2008b), the removal of the gravitational components also cancels the post-coring isotopic fractionation. As a result, the estimated temperature gradients in the firn are little affected by the gas loss (Kobashi et al., 2008b).

Another ~~evidence~~ sign of~~of the~~ isotopic fractionation during the gas loss is $\delta^{40}Ar$ enrichment~~s~~ in ice cores, which produces calculated temperature gradients in the firn to be lower than expected from firn modeling (Kobashi et al., 2010;Kobashi et al., 2011;Kobashi et al., ~~Submitted~~2015). The systematically higher $\delta^{40}Ar$ is believed to be caused by ~~the~~ processes during the bubble ~~closeoff~~close-off, but so far no clear evidence ~~is~~ has been found in ~~the~~ firn air studies (Huber et al., 2006;Severinghaus and Battle, 2006) except $\delta^{18}O$ of O_2 (Battle et al., 2011). If the enrichment of $\delta^{40}Ar$ occurs in the firn, it should be correlated with $\delta Ar/N_2$. Therefore, the corrections for the $\delta^{40}Ar$ enrichment have been applied using $\delta Ar/N_2$ (Kobashi et al., 2010;Kobashi et al., 2011;Kobashi et al., ~~Submitted~~2015) or $\delta Kr/Ar$ (Severinghaus et al., 2003)), or ~~it was corrected by~~ a constant value (Orsi, 2013;Kobashi et al., ~~Submitted~~2015~~),~~). All these methods of correction ~~noting that both corrections~~ generate similar surface temperature histories (Kobashi et al., 2010;Kobashi et al., ~~Submitted~~2015). Another possible causes for the systematic offset are related to the standardizations to the atmosphere (in this case both nitrogen and argon isotopes can be affected.), or methodological differences during the extraction from ice samples (Kobashi et al., 2008b). In these cases, a constant shift should be a better solution.

Some uncertainties remain regarding the bubble air pressures for the modelling of post coring fractionation. First, Lipenkov (2000) reported that bubble air pressure increases toward deeper depth through the increase of ice loads, which should have induced a decrease in $\delta Ar/N_2$ toward deeper depth. However, the $\delta Ar/N_2$ data do not exhibit any trends with depth (Fig. 7), indicating that some other processes (e.g. changes in bubble diameters, *S/V*, and relaxation of ice after coring especially at depth deeper than 300 m (Gow and Williamson, 1975)) may have cancelled the depth effect. At even deeper depths where the bubbles exist as clathrate, the pressure between ice and clathrate boundaries can be estimated from the dissociation pressures of clathrates, and it should be independent of depth (Ikeda-Fukazawa et al., 2005). In the future studies, it would be necessary to consider changes in each parameters in ice cores and investigate post-coring fractionation. Second, we identified that overloading pressure at the bubble close-off depth plays an important role in the post bubble close-off fractionation in the firn. These pressure anomalies should also remain in ice cores, and play some roles for the post coring fractionation. For example, the relationship of $\delta Ar/N_2$ with temperatures and accumulate rates in GISP2 may have overestimated by the imprints of differential post coring fractionations owing to the different bubble pressures induced by temperatures and accumulation rates at the time of the bubble close-off. Of course, the imprints of the post-coring fractionation increase if the duration of storage is longer at warmer temperatures, emphasizing the need for colder storage temperatures and the timing of measurements to recover the original signals.

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For future studies on $\delta Ar/N_2$ or $\delta O_2/N_2$ in ice cores, the following suggestions should be taken into account. First, the solubility and diffusivity of argon, oxygen, and nitrogen in ice are not well constrained (Salamatin et al., 2001;Ikeda-Fukazawa et al., 2005;Bereiter et al., 2014). As precise $\delta Ar/N_2$ or $\delta O_2/N_2$ data from various ice cores are building up, the reanalyses from these cores could provide stronger constraints on the permeability. Second, although $\delta Ar/N_2$ is less susceptible to the post coring gas loss than $\delta O_2/N_2$, we have shown that ~~the~~ ice core preservation is critical to retrieve the original $\delta Ar/N_2$ signals. To preserve original signals, ice cores need to be stored in low temperatures (ideally < -50 °C) (Ikeda-Fukazawa et al., 2005;Bereiter et al., 2009;Landais et al., 2012), and/or to be analysed soon after the coring. Third, we also found that the use of ~~a~~ large ~~amount of~~ ice samples (600-700 g) for each analysis reduced the noise~~s~~ in $\delta O_2/N_2$ and $\delta Ar/N_2$ substantially (Headly, 2008), compared to the data from smaller samples in GISP2 (Suwa and Bender, 2008b). This observation emphasizes the importance of samples sizes. Fourth, observations on the bubbles in the firn and ice cores, especially on the microbubbles (e.g., numbers, volume contributions, pressure, and gas composition) are lacking, which are critical for further advances in understanding of ~~the~~ permeation in the firn and ice cores. Fifth, we have shown that $\delta Ar/N_2$ could be estimated from local temperatures and accumulation rates. Therefore, combined with nitrogen and argon isotopes, it may be possible to retrieve the information of past temperatures and accumulation rates from $\delta Ar/N_2$ in ice cores. Finally, the high resolution analyses (10-20 years) provided key observations for the effects of the accumulation rates and temperatures on the permeation, which warrants further similar studies along with surface temperature reconstructions.

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~~8~~7 Conclusions

Gas fractionation after ~~the~~ bubble ~~closeoff~~close-off in the firn is complex and associated ~~are poorly understood~~ processes are poorly understood, especially in ~~the time domain (i.e. in~~

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ice cores~~)~~. In this study, we investigated the gas permeation processes in the firn and ice cores using high resolution $\delta Ar/N_2$ data from GISP2, ~~and~~ NGRIP, and Dome Fuji ice cores for the ~~Holocene~~past few millennia. We found that $\delta Ar/N_2$ on the gas-age in the GISP2 ice core is significantly negatively correlated with the accumulation rate and positively with air contents over the past 6000 years. Further, the precise surface temperatures (Kobashi et al., 2011) and accumulation rates (Alley et al., 1997;Cuffey and Clow, 1997) over the past 4000 years from the GISP2 ice core have nearly equal controls on the $\delta Ar/N_2$ variations over the past 4000 years with the sensitivities of 0.72 (‰ ºC^{-1}) and -0.58 (‰ (0.01 m ice yr^{-1})$^{-1}$). To understand the processes of the $\delta Ar/N_2$ fractionation, we applied a permeation model (Ikeda-Fukazawa et al., 2005)~~.~~, in which air in the bubbles leak out by ~~molecular~~ steric diffusion through ice crystals, driven by the pressure gradients between the bubbles and the atmosphere.

The permeation model in the firn was applied considering two processes~~types~~ ~~of~~ on the bubbles, “pressure sensitive process ~~microbubbles~~(e.g., microbubbles)” and “normal bubble~~s~~ process”. Microbubbles ~~(0.3 % of air content in the Vostok ice cores)~~ are believed to form near the surface. Therefore, by the time when the microbubbles reach the bubble ~~closeoff~~close-off depth, they develop pressures as high as overloading ice pressure that are strongly associated with ~~the~~ changes in the accumulation rates at surface. Several evidences indicate that the pressure sensitive process occur on a larger air fraction than that only from the microbubbles. On the other hand, the normal bubbles develop slightly higher pressures than that of the atmosphere at the bubble ~~closeoff~~close-off depth ~~induced by density increases~~such that the permeation in the firn is limited (> -0.5 ‰). The model also indicates that $\delta Ar/N_2$ of the microbubbles is negatively correlated with ~~the~~ changes in accumulation rates through increases in the overloading pressures, although it underestimates the magnitude observed in GISP2 ice core. ~~Therefore, the observed negative correlation of $\delta Ar/N_2$ and accumulation rate can be~~

~~explained by the processes on the microbubbles through the changes in the overloading pressure.~~ Colder ~~(warmer)~~ temperatures are found to induce more ~~(less)~~ depletions in $\delta Ar/N_2$ through higher overloading pressure (thicker firn) and longer exposure time to the permeation, which explains a larger depletion in Dome Fuji ice core.~~.~~ Further understanding of the gas permeation processes in the firn may lead to a new tool to estimate the past accumulation rates and/or surface temperature~~s,~~ .~~and it is also important to precisely place ice core chronologies onto the orbital time scale, and to determine the timing of climate changes.~~

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Tables

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Table 1. Environmental parameters for GISP2, NGRIP and Dome Fuji. Temperatures for GISP2 and NGRIP are averages over the past 2100 years (Kobashi et al., 2015). Accumulation rates (Alley et al., 1997; Cuffey and Clow, 1997; Gkinis et al., 2014) for GISP2 and NGRIP are averages for the past 2100 years, and accumulation rate variations are calculated as standard deviations of accumulation rates in 21-year RMs. Annual average temperature and accumulation rate for Dome Fuji are from Watanabe et al. (2003).

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	Latitude	Longitude	Altitude m a.s.l.	Average temperature (°C)	Accumulation rate (m ice/yr)	Accumulation rate variation (m ice/yr)
GISP2	72.59 °N	38.46 °W	3203	-31.0	0.24	0.013
NGRIP	75.1 °N	42.32 °W	3230	-31.5	0.19	0.008
Dome Fuji	77.32 °S	39.67 °E	3810	-54.3	0.03	N/A

Table 2.1 Estimated post-coring fractionation on $\delta Ar/N_2$. The original values are averages over the past 2100 years for GISP2 and Dome Fuji. NGRIP shallow and deep are averages of the corresponding depths defined in the text.

	Period 1		Period 2		$\delta Ar/N_2$ (‰)		
	Duration (years)	Temp. (°C)	Duration (years)	Temp. (°C)	Est. post-coring depletion	Observation in ice cores	Est. Average values before coring
GISP2	2	-29	12	-36	1.5 ± 0.6	-3.9 ± 0.2	-2.4 ± 0.6
NGRIP shallow	12	-24	2	-30	3.0 ± 1.2	-6.3 ± 0.1	-3.3 ± 1.2
NGRIP deep	14	-30	-	-	2.5 ± 1.0	-5.9 ± 0.2	-3.4 ± 1.0
Dome Fuji	0.2	-25	18	-50	1.5 ± 0.7	-7.8 ± 0.3	-6.3 ± 0.8

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Table 2.2 $k_{N2}X_{N2}$ and $k_{Ar}X_{Ar}$ ($m \cdot s^{-1} \cdot mol \cdot mol_{ice}^{-1} \cdot MPa^{-1}$) in various temperatures. See also Figure 2.

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	-24 °C	-25 °C	-29 °C	-30 °C	-36 °C	-50 °C
$k_{N2}X_{N2}$	7.54×10^{-18}	7.33×10^{-18}	6.54×10^{-18}	6.36×10^{-18}	5.31×10^{-18}	3.37×10^{-18}
$k_{Ar}X_{Ar}$ (Ar I)	2.78×10^{-17}	2.69×10^{-17}	2.34×10^{-17}	2.26×10^{-17}	1.82×10^{-17}	1.05×10^{-17}
$k_{Ar}X_{Ar}$ (Ar II)	2.27×10^{-17}	2.19×10^{-17}	1.91×10^{-17}	1.84×10^{-17}	1.49×10^{-17}	8.71×10^{-18}

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Table 3. Modelled and observed $\delta Ar/N_2$ in various conditions with microbubble contribution of 2 %. In the first left column, T: indicates temperature (ºC) and A: indicates accumulation rate (m ice/year). Duration is the time, for which bubbles experience from the depth of 20 % bubble-closure to the depth of complete bubble close-off. Average pressure is the average overloading pressure between the depths of the 20 % bubble-closure and complete bubble close-off. The average depth is the middle depth between the 20 % bubble-closure and complete bubble close-off. Depth width is the depth range from 20 % to 100 % bubble closed. Microbubbles, normal bubbles, and total $\delta Ar/N_2$ are the values after all the bubbles are closed (i.e., in ice cores). Observed $\delta Ar/N_2$ is the values corrected for the post-coring fractionation in Table 2.

	Surface condition.		Model							Obser.
	Temp. (ºC)	Accm. (m ice/yr.)	Duration (yr.)	Ave. press. (MPa)	Avg. depth (m)	Depth width (m)	Micro-Bubb. $\delta Ar/N_2$ (‰)	Normal - Bubb. $\delta Ar/N_2$ (‰)	Total $\delta Ar/N_2$ (‰)	$\delta Ar/N_2$ (‰)
GISP2	-31	0.24	31	0.54	72.8	8.7	-133.2	-0.31	-2.74	-2.4± 0.6
NGRIP	-31.5	0.19	36	0.50	68.0	8.3	-120.8	-0.34	-2.56	-3.3± 1.2
Dome Fuji	-54.3	0.03	274	0.62	89.6	10.3	-599.8	-0.43	-6.43	-6.3± 0.8
T: -25 A: 0.2	-25	0.2	27	0.42	54.4	6.5	-41.8	-0.33	-1.13	–
T: -25 A: 0.25	-25	0.25	23	0.45	59.1	6.9	-60.6	-0.30	-1.45	–
T: -25 A: 0.3	-25	0.3	21	0.48	63.4	7.5	-74.4	-0.28	-1.68	–
T: -30 A: 0.2	-30	0.2	33	0.49	65.4	8.0	-103.3	-0.33	-2.25	–
T: -30 A: 0.25	-30	0.25	29	0.53	71.3	8.8	-121.7	-0.30	-2.54	–
T: -30 A: 0.3	-30	0.3	27	0.56	76.6	9.8	-135.4	-0.27	-2.75	–
T: -35 A: 0.2	-35	0.2	40	0.58	79.5	9.8	-184.2	-0.33	-3.58	–
T: -35 A:0.25	-35	0.25	36	0.63	86.9	10.9	-203.0	-0.30	-3.83	–
T: -35 A: 0.3	-35	0.3	34	0.67	93.5	12.4	-216.6	-0.27	-4.01	–

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Figure Captions

Figure 1. $\delta Ar/N_2$ vs. accumulation rates or air contents in GISP2 over the past 6000 years. Note that $\delta Ar/N_2$ is corrected values for the post coring fractionation (1.5‰ added). A spline with a 21-year cut off period (blue line) was applied to the $\delta Ar/N_2$ data. Two σ error bounds are shown, which were estimated by 1000 times of Monte Carlo simulation. Accumulation rates (m ice yr^{-1}) (black line) were filtered by 21-year RMs. Note that the y-axis for the accumulation rate is reversed. $\delta Ar/N_2$ vs. accumulation rates are significantly negatively correlated over the past 6000 years (r = -0.35, p = 0.03). $\delta Ar/N_2$ and air contents are significantly positively correlated over the past 6000 years (r = 0.38, p < 0.001 after linear detrending). A slight shift of the air contents around 3700 B.P. is probably due to the analytical changes that occurred between two different periods of measurements (Kobashi et al., 2008b). The correlations between $\delta Ar/N_2$ and air contents before and after 3700 B.P. are similar and significant (r = 0.30, p = 0.002 and r = 0.26, p = 0.008, respectively). Therefore, the $\delta Ar/N_2$ variation can explain 7 to 14 % of the total variance of the air contents.

Figure 2. $k_m \cdot X_m$ for oxygen, argon, and nitrogen for different temperatures. Ar (I) and Ar (II) were calculated from Eqs. (4) - (5) and (6), respectively (see text).

Figure 3. Comparison of $\delta Ar/N_2$ for shallow GISP2 cores (124- 214 m) measured in different periods. Colour data points (yellow triangles, orange squares, and grey diamonds) are individual data from Bender et al. (1995), and black data points with error bounds are from Kobashi et al. (2008b). We did not use shallower data of Bender et al. (1995) as they exhibit depletions similar

to our shallow NGIRP data (Fig. 8), and also an anomalous value (-16.91 ‰ at 145.4m) in the Bender dataset was excluded. Squares, diamonds, and triangles represent the data measured after one week, three months, and seven months of coring, respectively (Bender et al., 1995). The average difference between the Kobashi and Bender datasets is -1.51 ± 0.58 ‰, which we interpret as the post coring fractionation for GISP2.

f

Figure ~~1~~4. $\delta^{15}N$, $\delta^{40}Ar/4$, and $\delta Ar/N_2$ from ~~the~~ GISP2 ice core over the Holocene (Kobashi et al., 2008b). The grey ~~area~~ arrow indicates the brittle zone (Gow et al., 1997).

~~Figure 2. $\delta Ar/N_2$ and accumulation rate in GISP2 over the past 6000 years. A spline with a 31-year cut-off period (grey line) was applied to the $\delta Ar/N_2$ data, and a 1σ error bound (shown) was estimated by 1000 times of Monte Carlo simulation. Accumulation rate (m ice yr^{-1}) (red line) was filtered by 31-year RMs. Note that the y-axis for the accumulation rate is reversed.~~

Figure ~~3~~5. ~~The o~~Observed, ~~and~~ modeled $\delta Ar/N_2$~~,~~, surface temperatures, and accumulation rates from ~~the~~ GISP2 ice core over the past 4000 years~~, compared with the surface temperature and accumulation rate~~. Note that the observed $\delta Ar/N_2$ is corrected for the post coring fractionation (1.5‰ added). (a) $\delta Ar/N_2$ and ~~the~~ surface temperatures (Kobashi et al., 2011). Ages of the temperatures were adjusted for the lag (68 years). (b) $\delta Ar/N_2$ and ~~the~~ accumulation rates in 21-year RMs (Alley et al., 1997;Cuffey and Clow, 1997). Ages of the accumulation rates were adjusted for the lag (38 years) (c) Observed and modeled $\delta Ar/N_2$ from ~~the~~ multiple linear regression (see text). (~~c~~d) Observed and modeled $\delta Ar/N_2$ of ~~the~~ multiple linear regression using $\delta^{18}O_{ice}$ as a temperature proxy (see text). ~~Error bounds are 1σ.~~

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Figure 6. Observed and modeled $\delta Ar/N_2$ over the Holocene, and decomposition of $\delta Ar/N_2$ into the effects of accumulation rates and temperatures. Note that the observed $\delta Ar/N_2$ is corrected values for the post coring fractionation (1.5‰ added). (a) Observed and modelled $\delta Ar/N_2$. (b) Decomposition of $\delta Ar/N_2$ into the effects of temperatures and accumulation rates using multiple linear regression (see text).

Figure 7. Surface temperatures, accumulation rates, $\delta^{15}N$, $\delta Ar/N_2$ for GISP2, NGRIP, and Dome Fuji over the past 2100 years. (a) Surface temperatures for GISP2 (black) and NGRIP (blue) (Kobashi et al., 2015). (b) Accumulation rates in 21-year RMs for GISP2 (black: Alley et al., 1997; Cuffey and Clow, 1997) and NGRIP (blue: Gkinis et al., 2014). (c) Raw $\delta^{15}N$ and spline for NGRIP and GISP2 (Kobashi et al., 2010, 2015). (d-f) $\delta Ar/N_2$ and the values corrected for the post-coring fractionation for GISP2, NGRIP, and Dome Fuji. Blue and black lines are the raw and corrected values for the post coring fractionations, respectively. A red point with error bounds (2σ) indicates estimated $\delta Ar/N_2$ for Dome Fuji using Eq. (7).

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~~Figure 4. The observed and modeled $\delta Ar/N_2$ over the Holocene (a), and decomposition of $\delta Ar/N_2$ into the effects of the accumulation rates and temperatures (b).~~

~~Figure 5. The observed $\delta Ar/N_2$ for GISP2 and NGRIP over the past 2100 years. Spline fits (Enting, 1987) were applied with a 20 year cut off period, and 1σ uncertainties bounds (shown) were estimated by 1000 Monte Carlo simulations.~~

Figure ~~6~~8. $\delta^{15}N$, $\delta^{40}Ar/4$, and $\delta Ar/N_2$ in the NGRIP ice core from shallower depths (60-100 m). (a) $\delta^{15}N$, (b) $\delta^{40}Ar/4$, (c) $\delta Ar/N_2$, (d) estimated original air fractions, (e) estimated original $\delta Ar/N_2$. The estimated original air fractions relative to the value at 75.6 m was calculated with a mass balance calculation, assuming that $\delta^{15}N$ in the lock-in zone is constant with the value of 0.289 ‰ at 75.6 m and $\delta^{15}N$ of the ambient air is 0.0 ‰. From the calculated original air fraction, the original $\delta Ar/N_2$ were estimated again by the mass balance calculation, assuming that the ambient $\delta Ar/N_2$ is 0.0 ‰. Green shaded area indicates the lock-in zone. Black ~~D~~dotted lines in $\delta^{15}N$, $\delta^{40}Ar$, and estimated original air fraction are the values at 75.6 m (red dotted line). ~~Error bounds are 2σ.~~

~~Figure 7. k_m -X_m for oxygen, argon, and nitrogen at different temperatures.~~

Figure ~~8~~9. Simulated $\delta Ar/N_2$ vs. depth relationship in the microbubbles with a ~~a~~ temperature of -~~30~~ 31 ºC, accumulation rate of 0.~~25~~ 24 m ice yr^{-1}, and microbubble contribution of ~~1~~ 2 %. (a) Density and ~~open~~ closed ~~pore~~porosity (s_c). (b) $\delta Ar/N_2$ and $\delta O_2/N_2$. (c) Air content ~~change~~ and air pressure in the microbubbles. (d) Nitrogen and argon concentrations.

Figure ~~9~~10. Traces of s~~The s~~imulated $\delta Ar/N_2$ ~~changes~~ changes ~~in~~ for each annual layer~~s with depth~~ for the normal bubbles. The model calculates bubble generation for each annual layer, gas permeation into open air, and finally trapping into ice (see text). The model is calculated assuming an equilibrium state with a temperature of -~~30~~ 31 ºC and accumulation rate of 0.~~25~~ 24 m ice yr^{-1}, and microbubble contribution of 2 % (same as for Fig. 9).~~and parameters (volumes~~

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~~and *C(l)*) for the calculation.~~ (a) Changes in the volumes of the normal bubbles for each annual layer ~~in annual layers~~induced by density changes with depth. ~~Three circles show decreasing trapped air volumes with depth (see text).~~ (b) Nitrogen concentrations as in (a). (c) Argon concentrations as in (a). (d) $\delta Ar/N_2$ as in (a). (e) A~~A~~ir contents with depth, $\delta Ar/N_2$, and *C(l)* for the bulk normal bubbles (sum of the values in annual layers for each depth) for the normal bubbles. Different colours (a to d) indicate values for each annual layer, showing how the bubbles that generated in different annual layers evolve with time.

~~Figure 10. The simulated $\delta Ar/N_2$ fractionation in response to different temperatures and accumulation rates for the total, normal bubbles, and micro-bubbles after all the fractionations in the firn. Microbubble contribution was set to 1 %. (a) Total $\delta Ar/N_2$. (b) $\delta Ar/N_2$ in the normal bubbles. (c) $\delta Ar/N_2$ in the microbubbles. Circles, rectangles, and triangles indicate values at -25 °C, -30 °C, and -35 °C, respectively.~~

Figure ~~11~~11. The simulated $\delta Ar/N_2$ fractionation with depth in the firn for the normal and microbubbles with different temperatures and accumulation rates. Microbubble contribution was set to ~~1~~ 2 % except the panel (d). See also Table 3. (a) $\delta Ar/N_2$ changes in the normal bubbles. (b) $\delta Ar/N_2$ changes in the microbubbles. (c) Total $\delta Ar/N_2$ changes ~~in all the bubbles~~ (changes in the sum of the micro- and normal bubbles). ~~Setting for the temperatures and accumulation rates were defined in the panel (a).~~ (d) Total $\delta Ar/N_2$ changes as in (c), but with different~~Influences of variable~~ microbubble ~~volumes~~ contributions (~~1~~ 0.3 to 3 %) ~~to the total $\delta Ar/N_2$~~ with a temperature of -30 ºC and accumulation rate of 0.25 m ice yr^{-1}.

Figure ~~12~~12. Two model experiments for the effects of surface temperatures and accumulation rates on the overloading pressure at the bubble close-off depth. (a) Input data for the ~~A~~accumulation rate~~s~~ (0.22~~0~~ m ice yr^{-1}) and surface temperature~~s~~ (-30 °C) with 20-year anomalies (+0.06 m yr^{-1} and -5 ºC) for the ~~model~~ year 1000-981 B.P., respectively. When one input was used for an experiment, the other was set constant. Zero in the panel (a) indicates the central year (model year 990 B.P.) of the anomalies. (b) Temperature~~ changes~~s at the bubble ~~closeoff~~close-off depth. (c) ~~Changes in the f~~Firn thickness. (d) Overloading pressures at the bubble ~~closeoff~~close-off depth. The orange line is the accumulation rate experiment, and the blue line is the temperature experiment. Numbers on peaks in (b)-(d) are lags in years from the central year of the initial anomalies in the panel (a).

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