Dear Editor,

Thank you for your decision of "accepted with corrections". We made corrections on the manuscript according to the reviewer's comments. Our replies were written after triangles below. The manuscript with a track-change-mode-on is attached at the end of this document.

Best regards,

Takuro Kobashi, corresponding author

First, my apologies to the authors of this paper for my slow reply to their changes. This revised manuscript now reads much more clearly and I appreciate the work done by the authors to address the reviewers' comments. I find it greatly improved and the authors have addressed most of my concerns. I read the insightful comments of reviewer #2 with interest, as well as the reply by the authors. I'll leave it to the reviewer to do decide if their concerns have been addressed and focus on my own.

It may be that I am simply benefitting from a second close reading, but I found the manuscript significantly less laborious to understand after revision. Nonetheless, there are some aspects that remain opaque or bothersome for me. I do think this paper should be published, pretty much in its present form. The results are interesting and important and are now presented in a comprehensible fashion. However, the interpretation of the data is very strongly driven by one site (GISP2). NGRIP seems to have an intrinsically small signal-to-noise ratio and Dome Fuji simply doesn't have a sufficiently rich dataset for subtle interpretation. Furthermore, the only way to explain the GISP2 data requires that a fractionation mechanism expected to apply to microbubbles must also apply to some other form of trapped air (whatever that may be). All of these concerns leave me very cautious about the robustness of these results. Nonetheless, they should be published so that other investigators can try to replicate or expand on this work. I do not need to see this manuscript again before it is published (or isn't).

> Thank you for your comments. We made corrections or clarifications according to the comments.

Below are several substantive comments, followed by some very minor corrections.

Throughout, I would like to see a different designation for the two processes that are defined here. As the work is presented, it gradually becomes clear that the "microbubble/pressure-sensitive" process is not limited to microbubbles and the "normal bubble" process is very similar mechanistically and is also pressure sensitive. The big difference is really where the bubbles form. The "normal" bubbles form deep in the firn, so they experience only modest pressure increases before being isolated from open porosity. The microbubbles form in the shallow part of the firn column, and thus many of them become very highly pressurized (and in turn, highly depleted in the small, mobile species). That said, it seems unlikely that there is enough air in genuine microbubbles to explain the signals seen in the cores, so the authors invoke "other air" to explain the strong correlations to accumulation and temperature seen at GISP2. I suggest the two processes be renamed throughout the paper. Something like "shallow-trapped" and "deep-trapped" would be more generally correct and less confusing. It's fine to point out that normal bubbles are deep-trapped and microbubbles are shallow-trapped, but in the end, shallow-trapped applies to much more air than we would expect to find in microbubbles alone.

The findings from various data indicates that trapped bubbles are more sensitive to overloading pressure than previously thought. The trapped bubbles can be either formed in shallow or deep firn, although microbubbles likely played a major role as discussed in the text. We think that even bubbles formed in deeper firn should be affected by changes in overloading pressure as indicated by changes in air contents. Therefore, we believe it is better to use current form of definition of "pressure sensitive process" and "normal bubble process", rather than the depth-related definition.

I'm still unhappy with Figure 9 (formerly Figure 8), panel C but at least I understand it now. The left axis should be labeled "fraction of air retained in microbubbles (%)" or something like that. The existing label is very confusing.

> The caption is changed accordingly as suggested by the reviewer.

Page 22 lines 8-11 are very confusing and I wonder if the problem is deeper than just language. In these lines, you claim that normal bubbles are compressed (i.e. their volume is reduced) as they move deeper. This is a clear statement, but it's true for any bubble (normal or micro-) unless clathrates are being formed (which is not what you're discussing here). You then say this leads to "generally smaller pressure build-up". Smaller than what? Isn't it all just governed by the ideal gas law? If the normal bubbles aren't at high pressure, it's only because they were formed close to the firn-ice transition. Or is there something more here that I'm missing?

This is a good point. In a real world, bubble pressure changes should be associated with density change on average except the rearrangements of air within the bulk ice. In the model, the density changes are described by prescribed functions with an assumption that firn is a homogeneous medium. In the present study, we use two different processes. One is a model-density driven process in bubble pressures. The other is a "pressure sensitive process", which is linearly controlled by overloading pressure. It is plausible as the firn is inhomogeneous medium in the real world, and so certain bubbles could reach near overloading pressure according to the micro-environments of bubbles in any depths. The sentence is revised for the clarification.

Page 11, line 9: Your reference to datasets is a bit vague. When you say "we consider the Ar/N2 as the original values before coring" do you mean "we treat Bender's data (all points averaged together for each depth) as the true Ar/N2 values before coring." Please make this clearer.

> The sentence is revised accordingly.

Various minor corrections I stumbled across while reading: On p3 line 21, should read "depletions of these smaller gases in the…" I think.

➢ Corrected.

Page 5, line 7 should read "Dome Fuji data are new"

 \succ Corrected.

Page 5, line 16 should read "less than that of GISP2 (0.24m ice/year) over the..."

 \succ Corrected.

Page 10, line 20 should read "in ice is often depleted..."

➢ Corrected.

Page 13, line 3: For clarity, please begin the paragraph "The subset of the GISP2 data covering the past 4000 years..."

➢ Corrected.

Page 14, line 14 should read "are time, lag for temperature and lag for accumulation rate, respectively (all in years)."

➢ Corrected.

Page 14, line 18-19 should read "Temperature records derived from d18O_ice can be quite noisy but stacking several d18O_ice records can substantially improve the derived temperature histories (White et al., 1997; Kobashi et al., 2011). Thus, we stacked..."

 \succ Corrected.

Page 15, line 4 should read "...as the one with the temperature and accumulation rate records for the last 4000 year based on Ar & N2 isotope values, but does slightly..."

 \succ Corrected.

Page 15, line 13-14 should read "The observed dAr/N2 variations..."

➢ Corrected.

Page 23, lines 20-12 should read "...have higher correlation with temperature (r = 0.97) than with accumulation rates (r = 0.57) in the model (Table 3)."

 \succ Corrected.

Page 26, line 15 should read "is the carrier of the"

 \succ Corrected.

Page 27 line 6 should read "...changes. We note that dAr/N2..."

 \succ Corrected.

Page 29, line 2 should read "in each parameter in ice cores"

 \succ Corrected.

Page 31, line 3 should read "Several lines of evidence indicate"

 \succ Corrected.

Page 31, line 16 should read "We are grateful to G. Hargreaves..."

 \succ Corrected.

Page 31, line 18 should read "Polar Research for supplying ice core information

 \succ Corrected.

1 Post bubble close-off fractionation of gases in polar firm

- 2 and ice cores: Effects of accumulation rate on permeation
- 3 through overloading pressure
- 4
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17 Abstract

18 Gases in ice cores are invaluable archives of past environmental changes (e.g., the past 19 atmosphere). However, gas fractionation processes after bubble closure in the firn are poorly 20 understood, although increasing evidence indicates preferential leakages of smaller molecules 21 (e.g., neon, oxygen, and argon) from the closed bubbles through the ice matrix. These 22 fractionation processes are believed to be responsible for the observed millennial $\delta O_2/N_2$ 23 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 24 few thousand years. We find that $\delta Ar/N_2$ at multi-decadal resolution on the gas age scale in the 25 GISP2 ice core has a significant negative correlation with accumulation rate and a positive 26 27 correlation with air contents over the past 6000 years, indicating that changes in overloading

pressure induced $\delta Ar/N_2$ fractionation in the firn. Furthermore, GISP2 temperature and 1 2 accumulation rate for the last 4000 years have nearly equal effects on $\delta Ar/N_2$ with sensitivities of $0.72 \pm 0.1 \text{ }$ °C⁻¹ and $-0.58 \pm 0.09 \text{ }$ (0.01 m ice yr⁻¹)⁻¹, respectively. To understand the 3 4 fractionation processes, we applied a permeation model for two different processes of bubble 5 pressure build-up in the firn, "pressure sensitive process (e.g., microbubbles: 0.3 to 3 % of air contents)" with a greater sensitivity to overloading pressures and "normal bubble process". The 6 7 model indicates that $\delta Ar/N_2$ in the bubbles under the pressure sensitive process are negatively correlated with the accumulation rate due to changes in overloading pressure. On the other hand, 8 9 the normal bubbles experience only limited depletion (< 0.5%) in the firn. Colder temperatures 10 in the firn induce more depletion in $\delta Ar/N_2$ through thicker firn. The pressure sensitive bubbles 11 are so depleted in $\delta Ar/N_2$ at the bubble close-off depth that they dominate the total $\delta Ar/N_2$ 12 changes in spite of their smaller air contents. The model also indicates that $\delta Ar/N_2$ of ice cores 13 should have experienced several permil of depletion during the storage 14 to 18 years after 14 coring. Further understanding of the $\delta Ar/N_2$ fractionation processes in the firn, combining with 15 nitrogen and argon isotope data, may lead to a new proxy for the past temperature and 16 accumulation rate.

17

18 1 Introduction

19 Atmospheric gases trapped in the firn layer (unconsolidated snow layer; ~70 m at the 20 Greenland Summit) and preserved in the underlying ice sheets provide precious and continuous 21 records of the past atmosphere and environments (Petit et al., 1999;Spahni et al., 2005;Ahn and 22 Brook, 2008;Kobashi et al., 2008a). However, to reconstruct the original environmental records, 23 it is important to understand the processes of air trapping in the firn, and how the air is retained 24 in the ice until it is analysed in laboratories. Two processes are well-known that change air 25 composition before the air is trapped within bubbles in the firn. First, gravitational fractionation 26 separates gases according to their mass differences and diffusive column height of the firn layer 27 (Craig et al., 1988;Schwander, 1989). Second, a temperature gradient (ΔT) between the top and 28 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 a third process that 1 2 occurs after the bubbles are closed (post bubble close-off fractionation) and that preferentially 3 affects gases with smaller molecular sizes (< 3.6 Å; for example, helium, neon, oxygen, and 4 argon), but also gases with larger molecular sizes in smaller magnitudes (Ikeda-Fukazawa et 5 al., 2005; Huber et al., 2006; Ikeda-Fukazawa and Kawamura, 2006; Severinghaus and Battle, 6 2006; Ahn et al., 2008). This fractionation continues deep in ice sheets smoothing signals (Ahn 7 et al., 2008;Bereiter et al., 2014), and the process continues during/after coring (Ikeda-8 Fukazawa et al., 2005;Kobashi et al., 2008b;Suwa and Bender, 2008b;Bereiter et al., 9 2009; Vinther et al., 2009).

10 Clear evidence of the diffusive gas loss from ice cores through ice crystals has been 11 observed in the oxygen content in ice cores as a depletion of oxygen relative to nitrogen (Bender 12 et al., 1995; Ikeda-Fukazawa et al., 2005; Suwa and Bender, 2008b). Depletion of air content by 13 ~ 10 % was observed for the Camp Century ice core after storage for 35 years, although possible 14 analytical differences between early and late measurements cannot be rejected (Vinther et al., 15 2009). The process is highly temperature dependent, and the gas loss is induced by the pressure 16 gradients between the bubbles and the atmosphere (Ikeda-Fukazawa et al., 2005). In ice sheets, 17 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 18 19 such as helium, neon, oxygen, and argon preferentially leak out from the closed bubbles, leading 20 to enrichments of these gases in open pores near the bubble-close-off depth, which leads to 21 depletions of lighter these smaller gases in the closed bubbles (Huber et al., 2006;Severinghaus 22 and Battle, 2006;Battle et al., 2011). However, the mechanisms creating $\delta Ar/N_2$ or $\delta O_2/N_2$ 23 variations in the time domain (i.e., ice cores) are still poorly understood.

On a longer time scale (i.e, orbital), variations in $\delta O_2/N_2$ closely follow local insolation 1 2 changes (Bender, 2002;Kawamura et al., 2007;Suwa and Bender, 2008a;Landais et al., 2012). 3 As a possible mechanism, it has been hypothesized that changes in local insolation affect 4 physical properties of the snow at the surface that persist into the bubble close-off depth, 5 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 $\delta O_2/N_2$ on the orbital time 6 7 scale, indicating common causes (Raynaud et al., 2007;Lipenkov et al., 2011). According to 8 this hypothesis, the orbital signals in $\delta O_2/N_2$ in ice cores are linked to the ice chronology rather 9 than to the gas chronology, which differ by up to a few thousand years. Therefore, the precise 10 understanding of the gas loss process in the firn is essential to determine how climate signals 11in the bubbles are placed between the ice-ages and gas-ages on the orbital time scale.

12 In this paper, encouraged by the observation of a significant negative correlation between 13 $\delta Ar/N_2$ and accumulation rate over the past 6000 years in GISP2 ice core (Fig. 1), we 14 investigated the processes of multi-decadal to centennial $\delta Ar/N_2$ variability in three ice cores 15 (GISP2, NGRIP, and Dome Fuji) as well as gas loss processes during storage. $\delta Ar/N_2$ variations 16 are generally highly correlated with $\delta O_2/N_2$ in ice cores, suggesting similar processes driving 17 these variations (Bender et al., 1995). As $\delta Ar/N_2$ is nearly constant in the atmosphere over the 18 relevant period (Kobashi et al., 2010), it is better suited to assess the permeation processes in 19 the firn and ice cores than $\delta O_2/N_2$ that varied in the atmosphere by ~1.5 ‰ during the glacial-20 interglacial cycles (Bender et al., 1995). In the following sections, we first describe the data and 21 investigate the relationships between $\delta Ar/N_2$ and changes in accumulation rates and surface 22 temperatures. Then, the fractionation processes are examined by applying a permeation model 23 to the ice cores and the firn under two processes, "pressure sensitive processes (e.g,

1 microbubbles)", and "normal bubble process". Finally, we discuss our findings, draw2 conclusions and mention implications.

3

4 2 Data description

5 $\delta Ar/N_2$ 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 6 (Kobashi et al., 2008b, 2015), and Dome Fuji data is are new. Importantly, storage histories of 7 8 these cores (i.e., temperatures) are known and methods for measuring $\delta Ar/N_2$ are all comparable. 9 GISP2 and NGRIP ice cores were drilled from the Greenland ice sheet, and Dome Fuji was 10 drilled from the Antarctic ice sheet (Table 1). For GISP2, sample resolution varies from 10 to 11 20 years with high resolution analyses covering the past 1000 years (Kobashi et al., 2008b, 12 2010) and around the 8.2ka event (8100 ± 500 years Before Present [B.P., "Present" is defined 13 as 1950]) (Kobashi et al., 2007). For NGRIP, sample resolution is about 10 years throughout the past 2100 years (Kobashi et al., 2015). Both GISP2 and NGRIP have similar annual average 14 15 temperatures of approximately -30 °C (Table 1). However, accumulation rate of NGRIP (~0.19 16 m ice/year) is 20 % less than that of GISP2 (0.024 m ice/year) of GISP2 over the past 2100 17 years, and importantly its variation (standard deviation after 21-year Running Means; RMs) is 18 lower by 40 % than that of GISP2 (see later discussion). Dome Fuji has a radically different 19 environment from Greenland with the current annual average air temperature of -54.3 °C and a 20 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 obtain gas ages, we applied a firn densification-heat diffusion model (Goujon et al., 2003) that calculates firn density structure, close-off depth, and delta age. The 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 used 1 reconstructed temperature records from argon and nitrogen isotopes in the trapped air within 2 3 the GISP2 ice core for the past 4000 years (Kobashi et al., 2011) and NGRIP for the past 2100 4 years (Kobashi et al., 2015), and layer-counted accumulation rate data for the Holocene (Alley 5 et al., 1997;Cuffey and Clow, 1997;Gkinis et al., 2014). Dome Fuji have neither precise temperatures nor accumulation rates over the past 2100 years. The annual resolution 6 7 accumulation rate data were smoothed with 21-year running means (RMs) to correspond to gas 8 diffusion and the bubble close-off process in the firn (Kobashi et al., 2015). A spline fit (Enting, 9 1987) was applied to gas data (e.g., $\delta Ar/N_2$) with a 21-year cut off period to be consist with 21 10 RMs of other parameters, and used for the following analyses to investigate signals longer than 11 the decadal time scale.

12 GISP2 and NGRIP ice cores were analysed for $\delta Ar/N_2 \sim 14$ years after coring, however, 13 with different temperature histories. GISP2 (82.4 m -540 m) was drilled in summer 1991. After 14 shipment, they were stored at -29 °C in a commercial freezer until they were moved to a freezer 15 (-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 16 17 Oceanography, where $\delta Ar/N_2$ was measured in 2005 (Kobashi et al., 2008b). One the other 18 hand, NGRIP2 ice cores (one of the two NGRIP ice cores; 64.6m to 445.2m) were drilled in 19 summer 1999 (Dahl-Jensen et al., 2002). Shallower parts (64.6m to 254.4m) were stored in a 20 freezer at the University of Copenhagen around -24 °C (J. P. Steffensen, pers. comm., 2015), 21 and deeper parts (255.5m to 445.2m) were in a freezer of a commercial facility rented by the 22 Alfred Wegener Institute (AWI) at -30 °C (S. Kipfstuhl, pers. comm., 2015). In fall 2011, we 23 cut the ice samples, and shipped them to a freezer at the National Institute of Polar Research at 24 -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 δAr/N₂ as follows:

6

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

7

8 where the subscript "sample" indicates ice core values, and "standard" is the present 9 atmospheric composition. For GISP2, mass 40 of argon and 29 of nitrogen, and for NGRIP and 10 Dome Fuji, mass 40 of argon and 28 of nitrogen were used to calculate $\delta Ar/N_2$. All $\delta Ar/N_2$ data 11 presented in this study were corrected for gravitational and thermal fractionations in the firn 12 using the conventional method based on $\delta^{15}N$ (Bender et al., 1995; Severinghaus and Battle, 13 2006; Severinghaus et al., 2009) as follows:

14

15

$$\delta Ar/N_{2corr} = \delta Ar/N_2 - 11\delta^{15}N \tag{2}$$

16

The coefficient 11 arises because the mass difference of $\delta Ar/N_2$ (⁴⁰Ar and ²⁹N₂) is 11 times larger than that of the nitrogen isotopes (²⁹N₂ and ²⁸N₂). This coefficient is replaced with 12 for the calculation of $\delta Ar/N_{2corr}$ for NGRIP and Dome Fuji because the mass difference between ⁴⁰Ar and ²⁸N₂ is 12. As the temperature sensitivities of $\delta^{15}N$ and $\delta Ar/N_2$ 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. After these

1 corrections, the $\delta Ar/N_{2corr}$ variations in the ice cores can be attributed only to gas loss. $\delta Ar/N_{2corr}$ of the GISP2 data using the mass 28 or 29 leads to negligible differences (an average difference 2 is 0.4×10^{-3} ‰ and the standard deviation is 0.94×10^{-3} ‰), which is much smaller than the 3 measurement uncertainty of $\delta Ar/N_2$ (1 σ < 0.7 ‰). We also note that standard deviation (0.07‰) 4 5 of $\delta^{15}N \times 11$ in GISP2 is much smaller than standard deviation of raw $\delta Ar/N_2$ (1.33‰) over the 6 past 6000 years, indicating that the variations of $\delta Ar/N_{2corr}$ mostly originate from the raw 7 $\delta Ar/N_2$ 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 8 sections.

9 The significance of correlations were calculated considering the autocorrelation of time 10 series (Ito and Minobe, 2010;Kobashi et al., 2013). We consider > 95% confidence as 11 significant, unless otherwise noted. All error bounds in figures and texts are 2σ .

12

13 **3** Post-coring fractionation

14 Before evaluating $\delta Ar/N_2$ in ice cores for the changes that have occurred in the firm, it is 15 necessary to consider the post-coring fractionation (Ikeda-Fukazawa et al., 2005). For this 16 purpose, we applied a molecular diffusion model (permeation model) through ice crystals 17 (Ikeda-Fukazawa et al., 2005). It has been applied to observed depletions of oxygen in the Dome 18 Fuji and GISP2 ice cores by ~10 ‰ with respect to nitrogen (Ikeda-Fukazawa et al., 2005;Suwa 19 and Bender, 2008b). The model was also implemented with modifications for gas permeation 20 processes in the firn (Severinghaus and Battle, 2006) and in ice cores (Bereiter et al., 2009). 21 The gas permeation in ice cores is driven by the pressure gradients between two spaces isolated 22 by ice walls (e.g., between bubbles or between bubbles and the atmosphere). The concentration 23 $(U_m; \text{mol} \cdot \text{mol}_{ice}^{-1})$ of species *m* (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): 24

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

3

where U_m^0 (mol · mol_{ice}) is the original concentration of species *m*. k_m (m·s⁻¹) is the mass 4 transfer coefficient and equals to $D_m/\Delta l$, where D_m (m²·s⁻¹) is the diffusion coefficient of the 5 species *m*, and Δl (m) is the thickness of the surface layer of ice (Ikeda-Fukazawa et al., 2005). 6 $X_m (\text{mol} \cdot \text{mol}_{ice}^{-1} \cdot \text{MPa}^{-1})$ is the solubility of species *m* in ice. P^i and P^a are the pressures in the 7 bubbles and in the atmosphere, respectively. Z_m^i and Z_m^s are molar fractions of species m in the 8 bubbles and in the atmosphere, respectively. $S(m^2)$ and $V(m^3)$ represent the surface area and 9 10 the volume of an ice sample such that S/V can be understood as specific surface area (m⁻¹), an 11 important variable for the gas exchange between the atmosphere and the ice (Matzl and 12 Schneebeli, 2006).

13 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 14 multiplied by the atmospheric molar ratio of each gas. In this case, Z_m^i and Z_m^s are set to the 15 atmospheric partial pressures for each molecule. Another factor that affects the gas loss is the 16 17 specific surface area. GISP2 ice core has a larger diameter (0.132 m) and longer length (1 m) 18 during the storage than that for NGRIP core (diameter 0.098 m and length 0.55m). Dome Fuji 19 core has a diameter of 0.093 m and length of 0.50 m. Therefore, the specific surface areas (S/V)20 were calculated to be 32.3 m⁻¹, 44.5 m⁻¹, and 47.0 m⁻¹ for GISP2, NGRIP, and Dome Fuji, 21 respectively. It is noted that these specific surface areas are approximations as ice cores during 22 the storage often have different shapes, and we shaved the ice surface by ~5 mm before the 23 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 $\Delta l = 12$ 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 m² s⁻¹) of argon at 270 10 K calculated from molecular dynamic simulations with those of nitrogen (D_{N2} ; 2.1 × 10⁻¹¹ m² 11 12 s⁻¹) and oxygen $(D_{02}; 4.7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})$ (Ikeda-Fukazawa et al., 2004). Owing to the molecular-13 size dependent fractionation, argon permeation occurs slower than oxygen but faster than 14 nitrogen (Fig. 2), which cannot be explained by their mass differences (Huber et al., 2006; 15 Severinghaus and Battle et al., 2006). Then, temperature-dependent k_{Ar} and X_{Ar} were estimated 16 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: 17

18
$$k_{Ar} = k_{02} - (D_{02at270K} - D_{Ar at270K}) / (D_{02} at270K - D_{N2} at270K) (k_{02} - k_{N2})$$
 (4)

19
$$X_{Ar} = X_{O2} - (D_{O2 \ at270K} - D_{Ar \ at270K}) / (D_{O2 \ at270K} - D_{N2 \ at270K}) (X_{O2} - X_{N2})$$
(5)

Second, we estimated Ar (II) from an observation that $\delta Ar/N_2$ in ice <u>are-is</u> 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:

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

23

10

(6)

1 Estimated $k_{Ar}X_{Ar}$ for Ar (I) and Ar (II) are higher than $k_{N2}X_{N2}$ and increase with temperatures, 2 resulting in a general depletion of δ Ar/N₂ in ice compared to the atmospheric composition, and 3 the depletion is faster in warmer temperatures (Fig. 2). The use of Ar (I) induces faster depletion 4 of δ Ar/N₂ than that of Ar (II) owing to faster permeation of argon. With the two estimates of 5 $k_{Ar}X_{Ar}$, we explore the range of uncertainties associated with argon permeation.

6 In a pioneering study by Bender et al. (1995), $\delta Ar/N_2$ in a shallow core of GISP2 was 7 analysed after one week, three months, and seven months of drilling in 1989 to study the time 8 dependent gas loss process (Fig. 3). As the data from three different periods are not significantly 9 different, we treat Bender's data as the true Ar/N_2 values before coring we consider the $\delta Ar/N_2$ 10 as the original values before the coring. By comparing the data (Bender et al., 1995) with our 11 dataset analysed 14 years after the coring (Kobashi et al., 2008b), we estimated the post-coring 12 fractionation of $\delta Ar/N_2$ in GISP2 to be -1.5 \pm 0.6 ‰, a difference of the two datasets for 13 common depths (124 to 214 m) (Fig. 3). Using this value, we derived an unknown parameter 14 (i.e., bubble pressure) in Eq. (3). The bubble pressures are calculated as 0.6 ± 0.2 MPa and 0.815 \pm 0.3 MP for two different estimates of $k_{Ar}X_{Ar}$ of Ar(I) and Ar(II), respectively, which agree 16 with the normal bubble pressure at 150-200 m deep in Vostok (Lipenkov, 2000). Using the 17 estimated bubble air pressure and aforementioned parameters, the amounts of depletion in 18 δ Ar/N₂ after coring are estimated as -3.0 ± 1.2 ‰, -2.5 ± 1.0 ‰, and 1.5 ± 0.7 ‰ for NGRIP 19 shallow, and NGRIP deep, and Dome Fuji, respectively (Table 2). As a result, it is possible to 20 derive the original δAr/N₂ values before coring for GISP2, NGRIP shallow, and NGRIP deep, 21 and Dome Fuji as -2.4 ± 0.6 ‰, -3.3 ± 1.2 ‰, -3.4 ± 1.0 , and 6.3 ± 0.8 , respectively (Table 2).

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1 4 Post bubble close-off fractionation in firn: Empirical evidence

2 4.1 GISP2 $\delta Ar/N_2$ variation over the Holocene

3 The $\delta Ar/N_2$ record over the Holocene in the GISP2 ice core exhibit relatively constant 4 values around -3 ‰, except for a prominent rise of up to 10 ‰ around 7000 B.P. (Fig. 4). The 5 rise is located within the depths of the brittle zone (650 to 1400 m), where air in the bubbles 6 changes to clathrate inducing anomalously high pressure (Gow et al., 1997). The dissociation 7 pressure of nitrogen in the clathrate phase is higher than that of argon (or oxygen) so that 8 nitrogen is enriched in the gas phase in relation to the clathrate (more stable state), resulting in 9 a preferential leakage of nitrogen, and thus argon (or oxygen) enrichments in these depths 10 (Ikeda et al., 1999;Ikeda-Fukazawa et al., 2001;Kobashi et al., 2008b). As the dissociation of 11 gases from the clathrate depends on various factors, $\delta Ar/N_2$ in these depths are highly variable (Fig. 4). It is noted that $\delta^{15}N$ and $\delta^{40}Ar$ exhibit little influences from the anomalous $\delta Ar/N_2$ 12 13 fractionation, indicating that the processes are mass independent in first order (Huber et al., 14 2006;Severinghaus and Battle, 2006) (Fig. 4).

15 Changes in the surface temperatures and accumulation rates are the dominant controlling factors for the state of firn layers (e.g., density profile, bubble close-off depth, and firn 16 17 thickness) (Herron and Langway, 1980;Schwander et al., 1997;Goujon et al., 2003). Therefore, 18 we investigated if changes in surface temperature or accumulation rate have any controls on the 19 $\delta Ar/N_2$ variations. We found a significant negative correlation (r = -0.35, p = 0.03) between 20 $\delta Ar/N_2$ on the gas age scale and the accumulation rate for the past 6000 years, a time interval 21 in which the abnormal $\delta Ar/N_2$ fractionation is not observed (Fig. 1 and 4). This negative 22 correlation is opposite of what an earlier study (Severinghaus and Battle, 2006) suggested for 23 the permeation fractionation in the firn (positive correlation). In addition, the significant 24 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 firm.

3 The subset of the GISP2 GISP2 data covering for over the past 4000 years provides a unique opportunity to investigate δAr/N2 variations because precise temperature (Kobashi et al., 2011) 4 5 and accumulation rate by layer counting (Alley et al., 1997;Cuffey and Clow, 1997) are 6 available. Using these data, we applied a linear regression and lag analysis on $\delta Ar/N_2$. It is found that the surface temperature is positively correlated with $\delta Ar/N_2$ on the gas ages (r = 0.47, 7 8 p = 0.04; r = 0.28, p = 0.001 after linear detrending) with a 68-year lag (Fig. 5a), indicating that 9 cooler (warmer) temperatures induced more (less) depletions in $\delta Ar/N_2$ with a multidecadal lag. 10 On the other hand, the accumulation rate is negatively correlated with $\delta Ar/N_2$ on the gas ages 11 (r = -0.47, p = 0.12; r = -0.26, p = 0.01 after linear detrending) with a 38-year lag (Fig. 5b), 12 indicating that high (low) accumulation rates induced more (less) depletions in $\delta Ar/N_2$ over the 13 past 4000 years. We note that the surface temperature and accumulation rate have a negative 14 but insignificant correlation (r = -0.32, p = 0.13; after linear detrending r = -0.11, p = 0.2) over 15 the past 4000 years.

16 To estimate the relative contribution of the accumulation rate and the surface temperature 17 changes on $\delta Ar/N_2$, we applied a multiple linear regression, which finds the best linear 18 combination of variables (i.e., temperature and accumulation rate) for a response variable (i.e., 19 δAr/N₂). Before the regression is applied, the temperature and accumulation records were 20 shifted toward younger ages to account for the lags (38 years and 68 years for accumulation 21 rate and temperature, respectively), and $\delta Ar/N_2$ is corrected for the post-coring fractionation 22 (1.5 ‰ added). As ordinary least squares including the multiple linear regression underestimate 23 the variance of target time series when the data is noisy (Von Storch et al., 2004), we used 24 "variance matching" by linearly scaling regression coefficients according to the ratio between

1	the variance of the target and model time series. Figure 5c shows the original and modeled
2	results of $\delta Ar/N_2$ over the past 4000 years. As expected, the model of the multiple linear
3	regression captures the $\delta Ar/N_2$ variations better than the individual variables do (Figs. 5a-c)
4	with a correlation coefficient of $r = 0.58$, $p = 0.09$ ($r = 0.36$, $p < 0.001$ after linear detrending).
5	For the centennial variations, the model captures nearly half of the total variance of the observed
6	δ Ar/N ₂ variations with a 95% confidence ($r = 0.71$, $p = 0.05$ after linear detrending with 200-
7	year RMs). The high and significant correlation between the model and observed $\delta Ar/N_2$
8	indicates that changes in the surface temperature and accumulation rate play important roles in
9	controlling the $\delta Ar/N_2$ variations. From the multiple linear regression, $\delta Ar/N_2$ on the gas ages
10	in GISP2 can be expressed by temperature (°C) and accumulation rate (m ice/year) as a function
11	of time after adjusting for the lags:
12	
13	$\delta Ar/N_2(t) = A \times temperature (t + t_{temp}) + B \times accumulation (t + t_{accm}) + C$ (7)
14	where $A = 0.72 \pm 0.06$ ‰ °C ⁻¹ , $B = -58.8 \pm 4.3$ ‰ (m yr ⁻¹) ⁻¹ , $C = 32.7 \pm 1.8$ ‰, and t , t_{temp} ,
15	and t_{accm} are time, (years), $lags$ (years) for temperature and <u>lag for</u> accumulation rate,
16	respectively <u>(all in years)</u> .
17	
18	Next, we attempted to use oxygen isotopes of ice ($\delta^{18}O_{ice}$) as a temperature proxy for the
19	same regression analyses of $\delta Ar/N_2$ since we do not have the N ₂ -Ar isotope based temperature
20	information before 4000 years B.P. Temperature records derived from $\delta^{18}O_{ice}$ can be quite noisy
21	
21	but stacking several $\delta^{18}O_{ice}$ records can improve the derived temperature histories (White et al.,
21	but stacking several $\delta^{18}O_{ice}$ records can improve the derived temperature histories (White et al., 1997; Kobashi et al., 2011). Thus, we stacked Although a $\delta^{18}O_{ice}$ record from an ice core

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1	several $\delta^{18}\Theta_{iee}$ -records contains substantial noise and provides a better temperature record
2	(White et al., 1997;Kobashi et al., 2011). Thus, we stacked three oxygen isotope records (GISP2,
3	GRIP, and NGRIP) over the Holocene in the 20-year RMs (Stuiver et al., 1995; Vinther et al.,
4	2006). The stacked record was calibrated to temperatures using the relation obtained from
5	borehole temperature profiles (Cuffey and Clow, 1997). Using the regression coefficients
6	obtained in Fig. 5c, a $\delta Ar/N_2$ model was calculated from the oxygen-isotope-based temperature
7	and the accumulation rate (Fig. 5d). We found that the correlation between the model and the
8	observed $\delta Ar/N_2$ performs not as well as the one with the temperature and accumulation rate
9	records for the past-last 4000 years based on Ar-N2 isotope values (Fig. 5c), but does slightly
10	better than the correlations with the temperature or accumulation rate individually (Figs. 5a,b).
11	The $\delta Ar/N_2$ regression model with the $\delta^{18}O_{ice}\text{-}based$ temperatures and accumulation rates
11 12	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
11 12 13	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
11 12 13 14	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., the model and observed $\delta Ar/N_2$ exhibit rather constant values of -1 to
 11 12 13 14 15 	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., the model and observed $\delta Ar/N_2$ exhibit rather constant values of -1 to -3 ‰ during the Holocene (Fig. 6). Interestingly, the model indicates that the constant $\delta Ar/N_2$
 11 12 13 14 15 16 	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., the model and observed $\delta Ar/N_2$ exhibit rather constant values of -1 to -3 ‰ during the Holocene (Fig. 6). 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
 11 12 13 14 15 16 17 	The δ Ar/N ₂ regression model with the δ^{18} O _{ice} -based temperatures and accumulation rates can span the entire Holocene, including the periods when the observed δ Ar/N ₂ are highly variable owing to the post coring fractionation as discussed earlier. Except the time interval around 7000 years B.P., the model and observed δ Ar/N ₂ exhibit rather constant values of -1 to -3 ‰ during the Holocene (Fig. 6). Interestingly, the model indicates that the constant δ 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. 6). The
 11 12 13 14 15 16 17 18 	The δ Ar/N ₂ regression model with the δ^{18} O _{ice} -based temperatures and accumulation rates can span the entire Holocene, including the periods when the observed δ Ar/N ₂ are highly variable owing to the post coring fractionation as discussed earlier. Except the time interval around 7000 years B.P., the model and observed δ Ar/N ₂ exhibit rather constant values of -1 to -3 ‰ during the Holocene (Fig. 6). Interestingly, the model indicates that the constant δ 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. 6). The observed δ Ar/N ₂ variations remained higher or noisier from the early Holocene to ~6000 B.P.
 11 12 13 14 15 16 17 18 19 	The δ Ar/N ₂ regression model with the δ^{18} O _{ice} -based temperatures and accumulation rates can span the entire Holocene, including the periods when the observed δ Ar/N ₂ are highly variable owing to the post coring fractionation as discussed earlier. Except the time interval around 7000 years B.P., the model and observed δ Ar/N ₂ exhibit rather constant values of -1 to -3 ‰ during the Holocene (Fig. 6). Interestingly, the model indicates that the constant δ 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. 6). The observed δ Ar/N ₂ variations remained higher or noisier from the early Holocene to ~6000 B.P. than that for the later period, which probably make it difficult to decipher the original

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1 4.2 NGRIP and Dome Fuji $\delta Ar/N_2$ variation over the past 2100 years

2 $\delta Ar/N_2$ of NGRIP ice cores provides a good comparative dataset with the GISP2 data 3 (Fig. 7). Average $\delta Ar/N_2$ for the past 2100 years are -3.36 ‰ and -2.40 ‰ for NGRIP and GISP2, respectively (Fig. 7). The $\delta Ar/N_2$ variability in NGRIP (1 σ = 0.91 ‰) over the past 4 5 2100 years is 24% smaller than that of GISP2 ($1\sigma = 1.19$ ‰) after correcting for the post-coring 6 fractionation (Table 2), likely owing to the smaller variations of the accumulation rate at NGRIP 7 than that of GISP2 (Fig. 7). The pooled standard deviations of replicated samples are 0.94 ‰ 8 for NGRIP over the past 2100 years, and 0.66‰ for GISP2 over the past 1000 years (replicates 9 are available only for the past 1000 years in GISP2) (Kobashi et al., 2008b). The noisier data 10 for NGRIP than that for GISP2 should not be analytical as the mass spectrometer used for the 11 NGRIP had better precision on $\delta Ar/N_2$ than the one used for GISP2 (Kobashi et al., 12 2008b;Kobashi et al., 2015). $\delta Ar/N_2$ for GISP2 and NGRIP are weakly but significantly 13 correlated with a correlation coefficient of r = 0.24, p = 0.02 (after linear detrending) for the 14 past 1000 years of the high resolution part of GISP2, but not for the deeper part likely owing to 15 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 16 17 (r = 0.20, p = 0.06 after linear detrending) and were uncorrelated in the shallower part. No 18 significant correlations were found between $\delta Ar/N_2$ and the accumulation rate for NGRIP, 19 probably due to the lower variation of the accumulation rate at NGRIP than that of GISP2. It is 20 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 21 22 NGRIP signals from Eq. (7).

23 From the relationship between $\delta Ar/N_2$ and the temperature or accumulation rate of 24 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 1 observation (Table 1) for Dome Fuji, expected $\delta Ar/N_2$ from Eq. (7) were calculated as 0.3 ± 2 3 1.3 % and -6.4 \pm 1.2 %, respectively. The value for NGRIP is significantly higher than the 4 observed value of -3.3 ± 1.2 % corrected for the post-coring fractionation (Table 2). For Dome 5 Fuji, the value is similar to the observed -6.3 \pm 0.8 ‰ corrected for the post-coring fractionation 6 (Fig. 7 and Table 2). This may indicate that the relationship of $\delta Ar/N_2$ with the temperature and 7 accumulation rate becomes non-linear when the firn thickness becomes thinner than that of 8 GISP2 as $\delta Ar/N_2$ is not expected to be positive without the existence of clathrate (see later 9 discussion).

10 δ Ar/N₂ ice core data of NGRIP from the depth range 64.6-80 m exhibit some interesting 11 features (Fig. 8). The depth from ~60 to 78 m corresponds to the lock-in zone in NGRIP, where 12 vertical mixing of gas is limited so that δ^{15} N stays nearly constant in these depths (Huber et al., 13 2006; Kawamura et al., 2006). Therefore, the shallowest data at 64.6 m are located in the lock-14 in zone. Generally, gas data from the lock-in zone are not used owing to possible contamination 15 (Aydin et al., 2010). However, a recent study (Mitchell et al., 2015) demonstrated that δ^{15} N can 16 be used to estimate the amount of ambient air contamination using ice samples in the lock-in 17 zone, and the original methane concentration in the firn was reconstructed with a range of uncertainties. Therefore, we interpret the observed rapid decreases of $\delta^{15}N$ and $\delta^{40}Ar$ toward 18 19 shallower depths in the lock-in-zone as the result of mixing with ambient air (Fig. 8d). Based 20 on isotope mass balance, we calculated the original $\delta Ar/N_2$ values, which exhibited highly 21 depleted values as low as -50 ‰ (Fig. 8e). The depleted $\delta Ar/N_2$ in the lock-in-zone provides a 22 clue to the processes of gas loss in the firn (see later discussion).

23

1 5 Post bubble-close-off fractionation in firn: Process study

2 Air bubbles in the polar firn or ice can be categorized into two types (Lipenkov, 2000): 3 normal bubbles and microbubbles (< 50 μ m). They can be distinguished as a bimodal distribution in ice cores (Lipenkov, 2000;Ueltzhöffer et al., 2010;Bendel et al., 2013). The air 4 5 volume contribution of the microbubbles to the total air content is estimated to be 0.3% in the 6 Vostok ice core (Lipenkov, 2000), but the value is not known for Greenland ice cores. 7 Importantly, the two types of bubbles have significantly different bubble pressure histories in 8 the firn. The normal bubbles form at the bubble close-off depth. Most of the air in ice cores is 9 captured as normal bubbles, and the air-trapping processes are relatively well known 10 (Schwander et al., 1997;Goujon et al., 2003;Mitchell et al., 2015). Normal bubble pressures 11 build up according to increasing density (normal bubble process; Severinghaus and Battle, 12 2006). On the other hand, the microbubbles are believed to form near the surface (Lipenkov, 13 2000). So, they are highly pressurized and have rounded shape by the time when the bubbles reach the bubble close-off depth (Lipenkov, 2000;Ueltzhöffer et al., 2010). As a result, the 14 15 microbubbles are more sensitive to changes in the overloading pressure at the bubble close-off 16 depth (pressure sensitive process).

17 Owing to the different bubble pressure histories in the firn, $\delta Ar/N_2$ or $\delta O_2/N_2$ in the 18 microbubbles and normal bubbles are expected to be different due to the differential permeation 19 of each molecule. In this study, we attempted to quantify two types of the gas loss processes, 20 "pressure sensitive process (microbubble)" and "normal bubble process", in the firn using a 21 permeation model (Ikeda-Fukazawa et al., 2005) combined with the inputs from firm-22 densification heat-diffusion models (Schwander et al., 1993; Spani et al., 2003; Goujon et al., 2003).

24

1 5.1 Pressure sensitive process (microbubbles)

2 We first look into the pressure sensitive process as exemplified by the microbubbles. 3 Microbubbles are believed to form in the shallow firn by sublimation-condensation processes 4 (Lipenkov, 2000). These bubbles have smaller sizes, smoothed spherical surfaces, and can 5 generally be found in the interior of the ice crystals (Lipenkov, 2000). The bubble pressure 6 reaches near overloading pressure at the bubble close-off depth, and so it is sensitive to changes 7 in the overloading pressure. As the actual contribution of microbubbles and air content involved 8 in the pressure sensitive processes is not known, we consider a 2% contribution of air to the 9 total air. As it will be discussed later, more air fraction than simply from microbubbles (0.3 % 10 in Vostok) are likely involved in the pressure sensitive process. Therefore, we conducted 11 additional calculations with 0.3 %, 1 %, and 3 % microbubble contributions, and assessed the 12 impacts to the total $\delta Ar/N_2$.

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., 1993; Spahni et al., 2003). Then, they are interpolated for annual layers in the firn for the following calculation.

18 Changes in the concentrations of species *m* were calculated according to the following19 Eq. (8) similar to Eq. (3).

20

21
$$U_m(l+1) = U_m(l) - k_m X_m \left(P^i(l) Z_m^i(l) - P^a Z_m^s \right) \left(\frac{s}{v}(l) \right) s_o/s(l) t C(l)$$
(8)

22
$$Z_m^i(l) = \frac{U_m(l)}{U_{Ar}(l) + U_{02}(l) + U_{N2}(l)}$$

23

1	where <i>l</i> is an annual layer from the surface to below the firn layer (e.g., $l = 1$ to 2000),
2	and s_o/s (l) in a layer l is the open porosity ratio. s, s_c , and s_o are the total, closed, and open
3	porosities ($s_o = s - s_c$), respectively (Spahni et al., 2003; see also the next section "normal bubble
4	process"). In a steady state, l can be considered as a time variable. At $l = 1$, the microbubbles
5	in an annual layer are at surface, although they are not active in terms of permeation at these
6	depths (Fig. 9). With l increasing in a one year step, the microbubbles move deeper in the firm
7	with l annual layers overlying. $C(l)$ is a coefficient defining the gas concentration in annual
8	layer l relative to the total air in ice. It is assumed that the pressure $P^{i}(l)$ in the microbubbles
9	starts increasing with overloading pressure from the depth of which the normal bubbles
10	generation initiates (firn density of around 0.7 g/cm ³) (Fig. 9c), and that pressure changes were
11	considered to be negligible above that depth (Lipenkov, 2000). Initial $P^i(0)$ was set at 0.065
12	MPa similar to the atmospheric pressure at the Greenland Summit (Schwander et al., 1993) with
13	a 0.3 MPa lag from overloading pressure as in Fig. 9 (Lipenkov, 2000). We estimated the
14	specific surface area $(S/V(l))$ in a layer l from the linear relationship between the specific surface
15	areas (m ⁻¹) and densities ρ from the Greenland Summit (Lomonaco et al., 2011) with an
16	equation: S/V (l) (m ⁻¹) = -16799 $\rho(l)$ (g cm ⁻³) + 14957. The initial gas content in the
17	microbubbles was set at 0.3 to 3% of the air content (6.53226 \times 10 ⁻⁵ mole \times 0.01) per 1 mole
18	of ice, and it is composed of nitrogen (78.084%), oxygen (20.9476%), and argon (0.934%). The
19	specific surface area S/V was multiplied by the open porosity ratio $s_o / s(l)$ (Spahni et al., 2003;
20	Fig. 9a) as the gas loss occurs toward open pores. $k_m X_m$ was calculated as for the post coring
21	fractionation, and we used the estimate, Ar (II) for argon.

Figure 9 shows model results with a temperature of -31 °C, an accumulation rate of 0.25 m ice/year (similar to GISP2 condition), and 2% microbubble contribution. It shows that the gas permeation from the microbubbles starts soon after the pressure was applied in the microbubbles (Figs. 9c,d). As oxygen has a larger permeability than that of argon, $\delta O_2/N_2$ 20 1 depletion is larger than $\delta Ar/N_2$ (Fig. 9b). At the temperature of -30 °C and accumulation rate of 2 0.25 m ice yr⁻¹, the depletion reaches up to 133 ‰ for $\delta Ar/N_2$, and 243 ‰ for $\delta O_2/N_2$ in the 3 model, which corresponds to 12 % gas loss from the original air content of the microbubbles 4 (Fig. 9c).

5

6 5.2 Normal bubble process

7 Most of the air in ice cores is trapped as normal bubbles near the lock-in depth. As a 8 result, bulk air pressure in the normal bubbles does not build up as high as the microbubbles in 9 the lock-in zone (Lipenkov, 2000). We used Eq. (8) to model the permeation process for the 10 normal bubbles. As for the microbubbles, we assumed steady state with the given temperatures 11 and accumulation rates. The general characters of the firn in various depths (ages, densities, 12 porosities, loading pressures, bubble close-off depths) were calculated using the firn-13 densification heat diffusion model (Schwander et al., 1993; Spahni et al., 2003), and they were 14 interpolated for annual layers as for the microbubbles. We first calculated how much bubble air 15 is generated in each annual layer according to the increase in the closed porosity (s_c) with depth 16 as the following equation.

17

18
$$V_0(l+1) = a\{(s_c(l+1) - s_c(l)(\rho_{\text{tce}} - \rho(l+1))/(\rho_{\text{tce}} - \rho(l))\} / \rho(l+1)$$
 (9)

19

where $V_0(l)$ is newly trapped air in an annual layer l, ρ_{lce} is the density of ice, and $\rho(l)$ is the density at depth l. $s_c(l)$ 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):

23

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

1

3 where ρ_{co} is the density at the depth in which the air is totally enclosed in bubbles. The sum of 4 all the newly generated air $(\sum_{l=1}^{2000} V_0(l))$ are set to have the air content of 6.53×10^{-5} mole per 5 mole of ice. Then, $V_0(l)$ was scaled accordingly using the coefficient *a*, and converted to the 6 volume (m³) with the atmospheric pressure (0.065 MPa) as in Fig. 10a.

7 The normal bubbles start forming at approximately 40 m depth and the formation is 8 maximum around the bubble close-off depth of 60 to 75 m at -31 °C and 0.24 m ice yr⁻¹ in the 9 model (Fig. 10a). Then, the permeation from each annual layer was calculated according to Eq. 10 (8). The difference from the microbubble permeation process is that the volume of the normal 11 bubbles decreases according to increasing modelled-density towards deeper depth, leading to 12 generally smaller pressure build-up and total permeation from the bubbles in the firn than that 13 of the pressure sensitive process for the microbubbles (Fig. 10a). C(l) in Eq. (8) was calculated 14 from $V_0(l)$ for each annual layer l by setting the sum of C(l) as 1 - 0.02 = 0.98 (if microbubble 15 contribution is 2 %) (Fig. 10e). Other parameters in Eq. (8) were set to be the same as for the 16 microbubbles.

Figure 10 shows the evolution of the normal bubble volumes, the nitrogen and argon concentrations, the δ Ar/N₂ in each annual layer, and the air content and bulk δ Ar/N₂ with depth at a temperature of -31 °C and an accumulation rate of 0.24 m ice yr⁻¹ as for the microbubbles for Fig. 9. A new generation of closed pore volumes in annual layers generally increases towards deeper depths (Fig. 10a). When open pore space disappears completely, we assume the gas permeation to the open pore stops. As argon (oxygen) permeation in ice is faster than nitrogen by 289 (479) % at -31 °C (Ar (II), Fig. 2), δ Ar/N₂ (δ O₂/N₂) within the bubbles

decreases when the permeation proceeds. At the temperature of -31 °C and accumulation rate 1 of 0.24 m ice yr⁻¹, the $\delta Ar/N_2$ depletion can reach about -5 ‰ for those bubbles formed at 2 3 shallow depths (Fig. 10d). However, the amount of air contained in these bubbles is so small 4 (Fig. 10a) that the influence on the total $\delta Ar/N_2$ is limited (Fig. 10e). The depth vs. $\delta Ar/N_2$ 5 relationship of the total air from the normal bubbles (Fig. 10e) indicates that the total $\delta Ar/N_2$ reaches the minimum of -0.39 ‰ at the middle of the bubble close-off depth of 73.2 m. Then, 6 7 the total $\delta Ar/N_2$ increases to -0.29 ‰ as a large amount of ambient air with $\delta Ar/N_2 = 0$ is 8 trapped in these depths (Fig. 10a,d,e).

9

10 5.3 Total air in bubbles

11 The permeation models for the normal and microbubbles were run for various firn 12 conditions with different surface temperatures, accumulation rates, and microbubble 13 contributions to investigate their effects on the $\delta Ar/N_2$ in the bubbles (Figs. 11 and Table 3). 14 Resultant air content (i.e., nitrogen, argon, and oxygen) for each annual layer from the micro-15 and normal bubbles were added to calculate the combined effects of the accumulation rates and 16 temperatures on total $\delta Ar/N_2$ (Fig. 11). Results show that the normal bubbles experience only 17 limited $\delta Ar/N_2$ depletion (> -0.5‰) by the different temperatures or accumulation rates we 18 considered (Table 3). On the other hand, $\delta Ar/N_2$ in the microbubbles varies with temperatures 19 through thickening of the firn, leading to higher pressures in the bubbles and longer duration 20 exposed to the gas loss in the firn (Table 3). Higher accumulation rate with the same 21 temperatures induces more depletion as it is primarily controlled by the changes in loading 22 pressure (Figs. 11c and Table 3). As a result, -the total $\delta Ar/N_2$ generally reflects the variation 23 of $\delta Ar/N_2$ in the microbubbles (r = 0.95; Table 3). Overall, the total $\delta Ar/N_2$ have high<u>er</u>

1 correlation with temperatures (r = 0.97) than <u>with accumulation rates</u> that (r = 0.57) with 2 accumulation rates in the model (Table 3).

3 The modeled $\delta Ar/N_2$ agrees with the observed $\delta Ar/N_2$ corrected for the post-coring 4 fractionation within their uncertainty ranges (Table 2). Extremely cold temperature in Dome 5 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 6 7 the total air (Table 3). The variations of $\delta Ar/N_2$ in normal bubbles are limited, and clearly 8 microbubbles (or the pressure sensitive process) play a critical role for the variation of $\delta Ar/N_2$ 9 in ice cores. The $\delta Ar/N_2$ minima in the firm ranges from -14 % to -83 % depending on the 10 temperatures and accumulation rates. The most depleted $\delta Ar/N_2$ with a temperature of -30 °C and accumulation rate of 0.2 m ice yr⁻¹ in Fig. 11c capture the highly depleted observation-11 12 based estimates of $\delta Ar/N_2$ in NGRIP ice core (Fig. 8e). As the normal bubble process alone 13 does not produce such depleted values in the firn (Fig. 11a), the observed highly-depleted 14 $\delta Ar/N_2$ (Fig. 8e) is an evidence for the involvement of the microbubble process (or pressure 15 sensitive process). The total $\delta Ar/N_2$ at the bubble close-off depth increases to less depleted 16 values from the minimum owing to the rapid inclusion of the ambient air (Fig. 11c).

17 The calculated dependencies of the $\delta Ar/N_2$ variations on the temperature (0.24 ‰ °C-18 ¹ for an accumulation rate of 0.25 m ice yr⁻¹) and accumulation rate (-0.05 ‰ (0.01 m ice yr⁻¹)⁻ 19 ¹ at -30 °C) with the 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), 20 21 respectively. Considering a possibility of larger volume contributions on the pressure sensitive process, we calculated the permeation model with microbubbles volume contributions from 22 23 0.3 % to 3 % to the total air. The 3 % microbubble contribution induces more depletion in the 24 total δAr/N2 (Fig. 11d). Also, the dependencies of δAr/N2 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, indicates the involvements of larger air contents as microbubbles
and/or normal bubbles influenced by the pressure sensitive process. This is plausible
considering the inhomogeneity of firn (Hörhold et al., 2012) and resultant differential
pressurization of bubbles.

7 An evidence for the larger air involvement in the pressure sensitive process is the significantly positive correlation between $\delta Ar/N_2$ and air contents over the past 6000 years in 8 9 GIPS2 (Fig. 1). This correlation indicates that the bubble air was squeezed out before close-off 10 resulting in smaller air contents when overloading pressure was higher, eventually inducing 11 higher pressure in the bubbles and so enhanced $\delta Ar/N_2$ depletions. This observation is also 12 consistent with recent findings that abrupt increases of accumulation rate at abrupt warming 13 during the last glacial period induced reductions in air contents (Eicher et al., Climate of the 14 Past, submitted, 2015). In addition, artificial sintering of snow with higher pressure has been 15 shown to contain much smaller air content than ice cores owing to the lack of time to develop 16 spherical cavities by vapour transport (B. Stauffer, pers. comm., 2015). These lines of evidence 17 indicate that higher overloading pressure at the lock-in-zone have impacts on normal as well as 18 microbubbles. The inclusion of this process in the model is beyond the scope of the current 19 paper, and we leave it for future studies.

We also investigated the observed lags of the $\delta Ar/N_2$ variations in GISP2 from the changes in the surface temperatures and accumulation rates by 68 and 38 years, respectively (Fig. 5). Presumably, the lags are introduced during the process of transferring surface temperature and accumulation rate signals into overloading pressure at the bubble close-off depths. Therefore, two transient simulations were conducted using a firn densification and heat

1 diffusion model (Goujon et al., 2003). First, the model was run with a constant temperature (-2 30 °C) and accumulation rate (0.2 m ice yr⁻¹) over thousands of years to reach an equilibrium 3 state. Then, surface temperature and accumulation rate anomalies of -35 °C and 0.26 m ice yr⁻¹ 4 ¹ for 20 years were introduced, separately (Fig. 12a). The surface anomalies of the temperature 5 and accumulation rate were set to induce similar $\delta Ar/N_2$ changes by 3.5 ‰ from the relationship 6 obtained by the multiple linear regressions on the $\delta Ar/N_2$ of GISP2.

7 We found that the surface temperature anomaly takes 20 years to reach the minimum 8 temperature at the bubble close-off depth (Fig. 12b). The cooling induces maximum firn 9 thickening after 56 years. The accumulation rate anomaly also induces firn thickening with an 10 11-year lag (Fig. 12c). Overloading pressures at the bubble close-off depth reach similar 11 maximum values with 85- and 21-year lags from the surface temperature and accumulation rate 12 anomalies, respectively (Fig. 12d). Apparently, the surface temperature anomaly takes longer 13 to reach the maximum increase in the overloading pressure than that of the accumulation rate 14 anomaly, which is consistent with the observation (68 and 38 years, respectively). The 15 accumulation rate anomaly is almost instantaneously but increasingly felt by the bubble close-16 off depth through overloading pressure, compared to the temperature anomaly that takes 17 decades to reach the bubble close-off depth. In addition, we note that similar magnitudes of the 18 overloading pressure anomalies were induced by the temperature and accumulation rate 19 anomalies (Fig. 12d). Therefore, we conclude that the overloading pressure is the carriers of the 20 surface temperature and accumulation rate signals, linking the $\delta Ar/N_2$ variations through the 21 permeation.

22

1 6 Discussions

2 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 3 4 of oxygen (Bender et al., 1995;Huber et al., 2006;Severinghaus and Battle, 2006;Battle et al., 5 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). 6 7 The altered snow properties remain until the snow reaches the bubble close-off depth and affects 8 the preferential oxygen loss (Bender, 2002). Our work demonstrates that the permeation 9 processes in the firn can be induced by changes in the surface temperature and the accumulation 10 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 11 12 changes. It is We noted that $\delta Ar/N_2$ in GISP2 also shows a significant positive correlation (r =13 0.38, p < 0.001 after linear detrending) with the air content (Kobashi et al., 2008b) over the past 14 6000 years, indicating a similar link between $\delta O_2/N_2$ and air content in the orbital time scale 15 (Raynaud et al., 2007;Lipenkov et al., 2011). As the time scale we considered in this study is 16 different from the orbital scale variation, other mechanisms may play a role in controlling the 17 $\delta O_2/N_2$ variations in ice cores. However, the mechanisms discussed here must be considered in 18 future studies.

Although the gas permeation from ice is generally believed to be a mass independent process (no effects on isotopes), there is some evidence 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). In particular, poor quality ice cores often exhibit isotope fractionation (e.g, δ^{18} O and δ^{40} Ar) with highly depleted δ O₂/N₂ or δ Ar/N₂ (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 1 2 flow. On the other hand, slowly occurring gas permeations through ice crystals in good quality 3 ice cores (e.g, NGRIP, GISP2, and Dome Fuji) appear to have small or non-existent effects on isotopes (Kobashi et al., 2008b;Suwa and Bender, 2008b). As small mass dependent 4 5 fractionation of δ^{15} N and δ^{40} Ar during the gas loss are similar to the gravitational fractionation (Kobashi et al., 2008b), the removal of the gravitational components also cancels the post-6 coring isotopic fractionation. As a result, the estimated temperature gradients in the firn are 7 8 little affected by the gas loss (Kobashi et al., 2008b).

Another sign of isotopic fractionation during the gas loss is δ^{40} Ar enrichment in ice cores, 9 10 which produces calculated temperature gradients in the firn to be lower than expected from firn 11 modeling (Kobashi et al., 2010;Kobashi et al., 2011;Kobashi et al., 2015). The systematically 12 higher δ^{40} Ar is believed to be caused by processes during the bubble close-off, but so far no 13 clear evidence has been found in firn air studies (Huber et al., 2006;Severinghaus and Battle, 2006) except δ^{18} O of O₂ (Battle et al., 2011). If the enrichment of δ^{40} Ar occurs in the firn, it 14 15 should be correlated with $\delta Ar/N_2$. Therefore, the corrections for the $\delta^{40}Ar$ enrichment have been 16 applied using $\delta Ar/N_2$ (Kobashi et al., 2010;Kobashi et al., 2011;Kobashi et al., 2015) or $\delta Kr/Ar$ 17 (Severinghaus et al., 2003)), or a constant value (Orsi, 2013;Kobashi et al., 2015). All these 18 methods of correction generate similar surface temperature histories (Kobashi et al., 19 2010;Kobashi et al., 2015). Another possible causes for the systematic offset are related to the 20 standardizations to the atmosphere (in this case both nitrogen and argon isotopes can be 21 affected.), or methodological differences during the extraction from ice samples (Kobashi et al., 22 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

1 deeper depth through the increase of ice loads, which should have induced a decrease in $\delta Ar/N_2$ 2 toward deeper depth. However, the $\delta Ar/N_2$ data do not exhibit any trends with depth (Fig. 7), 3 indicating that some other processes (e.g. changes in bubble diameters, S/V, and relaxation of 4 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 5 6 pressure between ice and clathrate boundaries can be estimated from the dissociation pressures 7 of clathrates, and it should be independent of depth (Ikeda-Fukazawa et al., 2005). In the future 8 studies, it would be necessary to consider changes in each parameters in ice cores and 9 investigate post-coring fractionation. Second, we identified that overloading pressure at the 10 bubble close-off depth plays an important role in the post bubble close-off fractionation in the 11 firn. These pressure anomalies should also remain in ice cores, and play some roles for the post 12 coring fractionation. For example, the relationship of $\delta Ar/N_2$ with temperatures and accumulate 13 rates in GISP2 may have overestimated by the imprints of differential post coring fractionations 14 owing to the different bubble pressures induced by temperatures and accumulation rates at the 15 time of the bubble close-off. Of course, the imprints of the post-coring fractionation increase if 16 the duration of storage is longer at warmer temperatures, emphasizing the need for colder 17 storage temperatures and the timing of measurements to recover the original signals.

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 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., 1 2005;Bereiter et al., 2009;Landais et al., 2012), and/or to be analysed soon after the coring. 2 3 Third, we also found that the use of large ice samples (600-700 g) for each analysis reduced the noise in $\delta O_2/N_2$ and $\delta Ar/N_2$ substantially (Headly, 2008), compared to the data from smaller 4 5 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 6 microbubbles (e.g., numbers, volume contributions, pressure, and gas composition) are lacking, 7 8 which are critical for further advances in understanding of permeation in the firn and ice cores. 9 Fifth, we have shown that $\delta Ar/N_2$ could be estimated from local temperatures and accumulation 10 rates. Therefore, combined with nitrogen and argon isotopes, it may be possible to retrieve the 11 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 12 13 accumulation rates and temperatures on the permeation, which warrants further similar studies 14 along with surface temperature reconstructions.

15

16 7 Conclusions

17 Gas fractionation after bubble close-off in the firn is complex and associated processes 18 are poorly understood, especially in ice cores. In this study, we investigated the gas permeation 19 processes in the firn and ice cores using high resolution δAr/N₂ data from GISP2, NGRIP, and 20 Dome Fuji ice cores for the past few millennia. We found that $\delta Ar/N_2$ on the gas-age in the 21 GISP2 ice core is significantly negatively correlated with the accumulation rate and positively 22 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 23 24 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 (‰ °C⁻¹) and -0.58 (‰ (0.01 m ice yr⁻¹)⁻¹). To 1 2 understand the processes of the $\delta Ar/N_2$ fractionation, we applied a permeation model (Ikeda-3 Fukazawa et al., 2005), in which air in the bubbles leak out by steric diffusion through ice 4 crystals, driven by the pressure gradients between the bubbles and the atmosphere. The 5 permeation model in the firn was applied considering two processes on the bubbles, "pressure sensitive process (e.g., microbubbles)" and "normal bubble process". Microbubbles are 6 believed to form near the surface. Therefore, by the time when the microbubbles reach the 7 8 bubble close-off depth, they develop pressures as high as overloading ice pressure that are 9 strongly associated with changes in the accumulation rates at surface. Several lines of evidences 10 indicate that the pressure sensitive process occur on a larger air fraction than that only from the 11 microbubbles. On the other hand, the normal bubbles develop slightly higher pressures than 12 that of the atmosphere at the bubble close-off depth such that the permeation in the firn is limited 13 (> -0.5 ‰). The model also indicates that $\delta Ar/N_2$ of the microbubbles is negatively correlated 14 with changes in accumulation rates through increases in the overloading pressures, although it 15 underestimates the magnitude observed in GISP2 ice core. Colder temperatures are found to 16 induce more depletions in $\delta Ar/N_2$ through higher overloading pressure (thicker firn) and longer 17 exposure time to the permeation, which explains a larger depletion in Dome Fuji ice core. 18 Further understanding of the gas permeation processes in the firn may lead to a new tool to 19 estimate the past accumulation rates and/or surface temperature.

20

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1 Tables

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).

_		Latitude	Longitude	Altitude m a.s.l.	Average temperature (°C)	Accumulatio n 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	

 $1 \qquad Table \ 2.1 \ Estimated \ post-coring \ fractionation \ on \ \delta Ar/N_2. \ The \ original \ values \ are \ averages \ over$

2 the past 2100 years for GISP2 and Dome Fuji. NGRIP shallow and deep are averages of the

Period 1 Period 2 $\delta Ar/N_2$ (‰) Duration Temp. Duration Temp. Est. post-Observation Est. Average coring in values before (°C) (years) (°C) (years) depletion coring ice cores GISP2 12 $\mathbf{2}$ -29 -36 1.5 ± 0.6 -3.9 ± 0.2 $\textbf{-}2.4\pm0.6$ NGRIP 12-24 $\mathbf{2}$ -30 3.0 ± 1.2 -6.3 ± 0.1 -3.3 ± 1.2 shallow NGRIP 14-30 -- 2.5 ± 1.0 -5.9 ± 0.2 -3.4 ± 1.0 deep Dome 0.2-25 18-50 1.5 ± 0.7 -7.8 ± 0.3 -6.3 ± 0.8 Fuji

3 corresponding depths defined in the text.

4

5 Table 2.2 $k_{N2}X_{N2}$ and $k_{Ar}X_{Ar}$ (m·s⁻¹·mol·mol_{ice}⁻¹·MPa⁻¹) in various temperatures. See also Figure

6

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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}
(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
<i>kArXAr</i> (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 1 2 of 2 %. In the first left column, T: indicates temperature (°C) and A: indicates accumulation 3 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 4 5 overloading pressure between the depths of the 20 % bubble-closure and complete bubble closeoff. The average depth is the middle depth between the 20 % bubble-closure and complete 6 7 bubble close-off. Depth width is the depth range from 20 % to 100 % bubble closed. 8 Microbubbles, normal bubbles, and total $\delta Ar/N_2$ are the values after all the bubbles are closed 9 (i.e., in ice cores). Observed $\delta Ar/N_2$ is the values corrected for the post-coring fractionation in 10 Table 2.

	Surface	condition.			Model						
	Temp. (°C)	Accm. (m ice/yr.)	Duration (yr.)	Ave. press. (MPa)	Avg. depth (m)	Depth width (m)	Micro- Bubb. δAr/N ₂ (‰)	Normal - Bubb. δAr/N ₂ (‰)	Total δAr/N ₂ (‰)	δAr/N2 (‰)	
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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1 Figure Captions

Figure 1. $\delta Ar/N_2$ vs. accumulation rates or air contents in GISP2 over the past 6000 years. Note 2 3 that $\delta Ar/N_2$ is corrected values for the post coring fractionation (1.5‰ added). A spline with a 4 21-year cut off period (blue line) was applied to the $\delta Ar/N_2$ data. Two σ error bounds are shown, 5 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 6 7 reversed. $\delta Ar/N_2$ vs. accumulation rates are significantly negatively correlated over the past 8 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 9 10 contents around 3700 B.P. is probably due to the analytical changes that occurred between two 11 different periods of measurements (Kobashi et al., 2008b). The correlations between $\delta Ar/N_2$ 12 and air contents before and after 3700 B.P. are similar and significant (r = 0.30, p = 0.002 and 13 r = 0.26, p = 0.008, respectively). Therefore, the $\delta Ar/N_2$ variation can explain 7 to 14 % of the 14 total variance of the air contents.

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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).

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Figure 3. Comparison of δ Ar/N₂ 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.

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Figure 4. δ¹⁵N, δ⁴⁰Ar/4, and δAr/N₂ from GISP2 ice core over the Holocene (Kobashi et al.,
2008b). The grey arrow indicates the brittle zone (Gow et al., 1997).

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9 Figure 5. Observed, modeled $\delta Ar/N_2$, surface temperatures, and accumulation rates from GISP2 10 ice core over the past 4000 years. Note that the observed $\delta Ar/N_2$ is corrected for the post coring 11 fractionation (1.5‰ added). (a) $\delta Ar/N_2$ and surface temperatures (Kobashi et al., 2011). Ages 12 of the temperatures were adjusted for the lag (68 years). (b) $\delta Ar/N_2$ and accumulation rates in 13 21-year RMs (Alley et al., 1997;Cuffey and Clow, 1997). Ages of the accumulation rates were 14 adjusted for the lag (38 years) (c) Observed and modeled $\delta Ar/N_2$ from multiple linear regression 15 (see text). (d) Observed and modeled $\delta Ar/N_2$ of multiple linear regression using $\delta^{18}O_{ice}$ as a 16 temperature proxy (see text). 17 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).

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Figure 7. Surface temperatures, accumulation rates, $\delta^{15}N$, $\delta Ar/N_2$ for GISP2, NGRIP, and 1 2 Dome Fuji over the past 2100 years. (a) Surface temperatures for GISP2 (black) and NGRIP 3 (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 δ^{15} N and 4 5 spline for NGRIP and GISP2 (Kobashi et al., 2010, 2015). (d-f) $\delta Ar/N_2$ and the values corrected 6 for the post-coring fractionation for GISP2, NGRIP, and Dome Fuji. Blue and black lines are 7 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). 8

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10 Figure 8. δ^{15} N, δ^{40} Ar/4, and δ Ar/N₂ in the NGRIP ice core from shallower depths (60-100 m). 11 (a) $\delta^{15}N$, (b) $\delta^{40}Ar/4$, (c) $\delta Ar/N_2$, (d) estimated original air fractions, (e) estimated original 12 δAr/N₂. The estimated original air fractions relative to the value at 75.6 m was calculated with 13 a mass balance calculation, assuming that δ^{15} N in the lock-in zone is constant with the value of 14 0.289 ‰ at 75.6 m and δ^{15} N of the ambient air is 0.0 ‰. From the calculated original air fraction, 15 the original $\delta Ar/N_2$ were estimated again by the mass balance calculation, assuming that the 16 ambient $\delta Ar/N_2$ is 0.0 ‰. Green shaded area indicates the lock-in zone. Black dotted lines in 17 δ^{15} N, δ^{40} Ar, and estimated original air fraction are the values at 75.6 m (red dotted line).

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Figure 9. Simulated $\delta Ar/N_2$ vs. depth relationship in the microbubbles with a temperature of -31 °C, accumulation rate of 0.24 m ice yr⁻¹, and microbubble contribution of 2 %. (a) Density and closed porosity (*s_c*). (b) $\delta Ar/N_2$ and $\delta O_2/N_2$. (c) Air content and air pressure in the microbubbles. (d) Nitrogen and argon concentrations.

23

Figure 10. Traces of simulated $\delta Ar/N_2$ changes for each annual layer for the normal bubbles. 1 2 The model calculates bubble generation for each annual layer, gas permeation into open air, 3 and finally trapping into ice (see text). The model is calculated assuming an equilibrium state with a temperature of -31 °C and accumulation rate of 0.24 m ice yr⁻¹, and microbubble 4 5 contribution of 2 % (same as for Fig. 9). (a) Changes in the volumes of the normal bubbles for each annual layer induced by density changes with depth. (b) Nitrogen concentrations as in (a). 6 7 (c) Argon concentrations as in (a). (d) $\delta Ar/N_2$ as in (a). (e) Air contents with depth, $\delta Ar/N_2$, and 8 C(l) for the bulk normal bubbles (sum of the values in annual layers for each depth) for the 9 normal bubbles. Different colours (a to d) indicate values for each annual layer, showing how 10 the bubbles that generated in different annual layers evolve with time.

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Figure 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 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 (changes in the sum of the micro- and normal bubbles). (d) Total $\delta Ar/N_2$ changes as in (c), but with different microbubble contributions (0.3 to 3 %) with a temperature of -30 °C and accumulation rate of 0.25 m ice yr⁻¹.

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Figure 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 accumulation rate (0.2 m ice yr⁻¹) and surface temperature (-30 °C) with 20-year anomalies (+0.06 m yr⁻¹ and -5 °C) for the 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 46

- 1 year 990 B.P.) of the anomalies. (b) Temperatures at the bubble close-off depth. (c) Firn
- 2 thickness. (d) Overloading pressures at the bubble close-off depth. The orange line is the
- 3 accumulation rate experiment, and the blue line is the temperature experiment. Numbers on
- 4 peaks in (b)-(d) are lags in years from the central year of the initial anomalies in the panel (a).