

Reply to referee1

Thank you for your valuable comments. Our responses and the changes we plan to make in the revised manuscript are explained below. Our replies are in blue, the changes we plan to make in red and reviewer comments are written in black italic letters.

This paper reviews all of the non climatic mechanisms responsible for dO_2/N_2 fractionation in ice cores, and includes a compilation of most existing measurements, in addition to a large dataset of new measurement from the Dome F ice core, with a variety of sampling strategies.

It is an extremely useful and valuable paper, that clearly identifies optimal strategies for sampling ice cores to retrieve a valuable dO_2/N_2 signal. In particular, the authors did a great effort in cutting the ice in various ways to identify where and how dO_2/N_2 fractionation was happening, both between outer and inner ice samples, and with high resolution vertical sampling. Their new datasets shed new light on processes affecting gas loss in ice cores. The paper is very well written, the scientific quality of the analyses is excellent, and the figures are also very clear. Although I have a few important comments on the presentation of the results, I recommend its rapid publication.

Major comments:

1. *Section 4, called “Discussion” actually has results in it, and I am missing a “discussion” section that would include perspectives. I think it would be valuable to add a small “perspective” section, devoted to next steps: Do you think that everything is known about the different mechanisms of fractionation? What could/should be done next to improve either our understanding and isolation of the various processes, or improve the corrections? In particular, a summary on how your data could be picked up by ice physicists to test hypotheses about the mechanisms that you talk about in the paper would be an important addition, to make sure that your results are re-used.*

We will move the results of the diffusion model (L368 – 376) to the Results chapter.

For the perspective, we will add the following paragraph in the Conclusion chapter (and delete the last part of the first paragraph of Conclusion, which has some perspectives).

“The primary application of the $\delta O_2/N_2$ record has been the orbital tuning of the ice-core age scales. In the future, high-precision $\delta O_2/N_2$ and $\delta Ar/N_2$ data of the Dome Fuji core may be obtained with our technique for precise orbital tuning of the ice core. The high-precision data may also provide non-insolation signals on the gases and eventually be useful for reconstructing past atmospheric oxygen and argon concentrations.

More observational and theoretical works are still needed for advancing our understanding of the mechanisms of gas movements in different zones in the ice sheet. For example, the current precisions

of ice-core measurements of $\delta^{18}\text{O}$ of O_2 and $\delta^{40}\text{Ar}$ are insufficient for detecting mass-dependent fractionation during bubble close-off and bubble-clathrate transformation processes (note that the mass-dependent fractionation of $\delta^{18}\text{O}$ during bubble close-off was evidenced by the WAIS Divide firn-air data, Battle et al., 2011). Theoretical works including molecular dynamics simulations for different gases and ice conditions may shed light on the different relationships between $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in different zones. Finally, our constraints on the permeation coefficients of the gases in ice might be useful for predicting the magnitude of diffusive smoothing of air composition in the ice sheet more than 1 million years old to be drilled in the future.”

2. *Related to my first comment, I am missing a summary at the end of the paper of the optimal sampling strategy. I think it would be great, either to add it to the conclusion, or to have a “sampling strategy” summary section, separated for each of the zones that you added. This section could summarize for each zone, the mechanisms controlling non gravitational $d\text{O}_2/\text{N}_2$ signal, and how to mitigate these.*

The magnitude of the post-coring gas loss depends on the ice-core quality, sample size and dimensions, and storage temperature and period. The frequency and magnitude of the natural fractionation in the BCTZ might be related to the annual layer thickness and impurity concentrations. Therefore, an optimal sampling strategy for the Dome Fuji ice core should not be readily applicable to other ice cores. Instead, we will add our recommendations for finding the optimal sampling strategy for other cores. We will add the following section at the last part of Discussion.

“4.5 Optimal storage and sampling strategy

We discuss here the recommended practices for the storage and measurement of a newly drilled ice core based on our data. For long-term storage, it is more advantageous to have a larger ice-core cross-section and lower temperature. Based on our Dome Fuji data (~1 cm from the surface is affected by the gas loss at $-50\text{ }^\circ\text{C}$ after 20 years), a square cross-section of 3×3 cm seems sufficient in a $-50\text{ }^\circ\text{C}$ storage, for sampling a central part (cross-section of 1×1 cm or more) that is unaffected by the post-coring gas loss. The temperature of $-50\text{ }^\circ\text{C}$ was originally selected for inhibiting the clathrate hydrate dissociation due to the relaxation of ice matrix during long-term ice-core storage (Uchida et al., 1994). To obtain high-quality $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ data, it is recommended to test the real ice-core samples to find sufficient removal thickness. The removal thickness can be determined by examining the pair differences of $\delta\text{O}_2/\text{N}_2$ with different surface removal thicknesses (e.g., 5 and 8 mm or 3 and 5 mm; Oyabu et al., 2020), which should be within the measurement uncertainty. Five pairs or more for a given combination of removal thicknesses would be required to make the assessment.

The length of a sample is also an important ice-core-specific factor, especially for reasonably averaging the high scatters in the BCTZ. We speculate that the reasonable sample length in the BCTZ to obtain

a clear insolation signal may be more than 50 cm for the Dome Fuji ice core. We note that this length should be different for different ice cores because the thicknesses of the alternating layers of high and low clathrate concentrations should be different at different sites (Lüthi et al., 2010; Shackleton, 2019). To find a reasonable sample length for a core, it is advisable to continuously measure a ~1-m-long section with a ~2 cm resolution and examine various averaging lengths. The sample length should also be larger than one annual layer thickness to average out the seasonal layering (especially important for the cores with high accumulation rates).”

Uchida, T., Hondoh, T., Mae, S., Shoji, H., and Azuma, N.: Optimized Storage Condition of Deep Ice Core Samples from a View Point of Air-Hydrate Analysis, Mem. Nat. Inst. Polar Res., Special Issue, 49, 320-327, 1994.

3. For someone who is not close to the literature of O₂/N₂, it would be good to have, maybe in the introduction, or in your discussion section, a schematics of the fractionation mechanisms. You may have to have 3 or 4 of them, for each of your zones, and maybe one more for post-coring. Generally speaking, all of the mechanisms are discussed in a hand-wavy matter, and it’s a bit difficult, through the reading of your paper, to understand what hypotheses about what mechanisms are actually testable or tested in your presentation.

We will add a schematic in the revised manuscript.

Fractionation of O₂ and Ar (Dome Fuji)

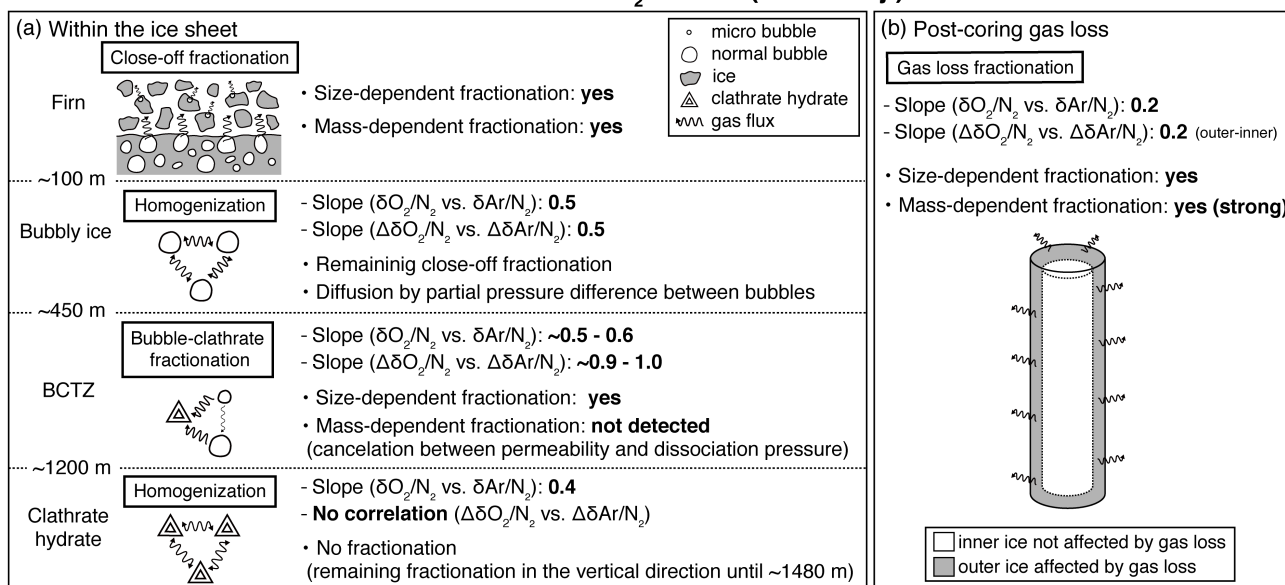


Figure caption: Schematic of fractionations of O₂ and Ar (a) within the ice sheet at Dome Fuji and (b) for the post-coring gas loss. The slopes were taken by the bulk data and the pair difference of $\delta O_2/N_{2\text{gravcorr}}$ and $\delta Ar/N_{2\text{gravcorr}}$, respectively (see Fig. x). The descriptions of “yes” indicate the observed results (this study; Severinghaus and Battle, 2006; Huber et al., 2006; Battle et al., 2011).

4. In the conclusion, in addition to specific recommendations for sample handling and storage to avoid fractionation in the first place, I am missing an optimal strategy for correcting for gas loss. You find different slopes of O₂/N₂ vs Ar/N₂ and for d180 vs O₂/N₂. I wonder if you could separate out the different mechanisms involved in “gas loss” fractionation, and provide several sequential correction strategies that could account for these differences, valid across different zones and different cores, to make it less heuristic.

We did not propose a universal method of correction for all ice cores, because there are many determining factors on the post-coring gas loss (e.g., drilling quality, storage condition just after coring, and size, dimensions, temperature and period during the storage, etc.), which cannot be separately and quantitatively evaluated. Thus, we think it is sufficient to propose the method for excluding the gas-loss fractionation from the ice-core dataset, as we describe in the original manuscript.

For reference, empirical correction methods for δO₂/N₂ and δ¹⁸O have been successfully established from fractionated datasets (e.g., if there is a clear relationship between δO₂/N₂ and the storage period, or between δ¹⁸O and δO₂/N₂) (Kawamura et al., 2007; Severinghaus et al., 2009).

Detailed comments:

1. You don't explain clearly what you mean in the figures by dO₂/N₂_grav. It's only explained in Figure 8, but you use it already in Fig 4. You should briefly explain in Section 2 how (and why) you correct for gravitational fractionation, and introduce your notation.

We will add the following sentences and equations in the third paragraph of section 2.2, and denote the gravitationally corrected ratios by adding subscripts “gravcorr” (δO₂/N₂_{gravcorr}, δAr/N₂_{gravcorr} and δ¹⁸O_{gravcorr}).

“The δO₂/N₂, δAr/N₂ and δ¹⁸O values relative to the modern atmosphere were corrected for the gravitational enrichment in firn, which is nearly proportional to the mass difference between the gas pairs (Craig et al., 1988). The gravitational correction can be estimated from δ¹⁵N of the same sample (Sowers et al., 1989):

$$\delta_{\text{gravcorr}} = \delta - \Delta m \times \delta^{15}\text{N} \quad (1),$$

where δ_{gravcorr} is gravitationally corrected value, δ is measured value, and Δm is the mass difference (4 for δO₂/N₂, 12 for δAr/N₂, and 2 for δ¹⁸O).”

2. The section on your diffusion model is a bit difficult to understand. In the main text, you should start by saying what you want to do with this model, what you want to test. Do you want to validate the effective diffusivity? Do you want to predict how much diffusion there will be in newly drilled deep ice cores, to inform the sampling strategy?

We aimed at testing with the model whether the observed homogeneity of the gas composition below BCTZ is quantitatively consistent with molecular diffusion in the ice sheet, with the independently proposed permeabilities of N₂, O₂ and Ar by previous authors. The prediction of gas diffusion for future ice corings is beyond the scope of this study, because it requires more advanced model setups (for significantly thinned ice near bedrock) and evaluation of temperature dependence of diffusivity.

Then you might consider including the main equation, it does not take too much space, but helps the reader. It's maybe more useful than the Argon diffusivity (which is also described in the appendix), since O₂ is the focus of your paper.

We will add the main equation and a few associated equations that would help the readers.

- $\frac{\partial c_m^h}{\partial t} = \frac{\partial}{\partial z} \left(D_m \frac{\partial c_m^h}{\partial z} \right)$ (diffusion equation)
- $C_m^h = S_m P_m^d X_m$ (concentration of m -molecule ($m = \text{N}_2, \text{O}_2$ or Ar) dissolved in ice in equilibrium with clathrate hydrate)
- $\log P_m^d = a_m - \frac{b_m}{T}$ (dissociation pressure)

Finally, you need to describe better what you use for inputs, what you use for outputs, what are the tunable versus known parameters. In the main text, you need to have a sentence or 2 that have enough details that the reader understands what you are trying to do, and in the appendix, you need to add more details. As it is now, there is not enough information to reproduce your results. Can you describe more the model set up? How deep, the discretisation scheme you used, how long you ran it for, the input that you used, the outputs that came out.

According to the comment, we will modify section 2.4 and Appendix A as follows (original sentences are in black and our changes are in red) to better describe the model.

(section 2.4)

We simulate diffusive smoothing of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in the clathrate hydrate ice with a one-dimensional diffusion model (Ikeda-Fukazawa et al., 2005; Bereiter et al., 2009; Bereiter et al., 2014) to test whether the observed reduction of variability below BCTZ (see 3.1.4) is consistent with molecular diffusion in ice as previously hypothesized. Because both diffusion coefficients and solubilities of O₂, N₂ and Ar in ice are poorly known, we run the model with different sets of previously proposed permeabilities (the product of diffusion coefficient and solubility).

The model assumes that molecular diffusion through ice lattice is driven by the concentration gradient

of gas molecules dissolved in ice, which are in equilibrium with clathrate hydrates. The governing equation is

$$\frac{\partial C_m^h}{\partial t} = \frac{\partial}{\partial z} \left(D_m \frac{\partial C_m^h}{\partial z} \right), \quad (2)$$

where D_m is the diffusivity of m -molecule in ice at 1 MPa and C_m^h is the concentration of m -molecule ($m = \text{N}_2, \text{O}_2$ or Ar) dissolved in ice in equilibrium with clathrate hydrate (see Table A1 for the full list of symbols). C_m^h is expressed as

$$C_m^h = S_m P_m^d X_m, \quad (3)$$

where S_m is the solubility of m -molecule in ice at 1 MPa, X_m is the mean molar fraction of m -molecule in the clathrate hydrates, and P_m^d is the dissociation pressure of the m -molecule. The dissociation pressure (MPa) of m -molecule at temperature T (K) is given by (Miller, 1969; Kuhs et al., 2000) (Fig. A1)

$$\log P_m^d = a_m - \frac{b_m}{T}, \quad (4)$$

where a_m and b_m are constant and shown in Table 2.

We tested three sets of model-based permeabilities estimated by Ikeda-Fukazawa et al. (2001) (hereafter IkFk01), Salamatin et al. (2001) (hereafter Salm01), and Ikeda-Fukazawa et al. (2005) (hereafter IkFk05) (Fig. 2, Table A2, A3). There are no published permeability of Ar in ice, thus we used two formulations proposed by Kobashi et al. (2015) (Fig. 2). The first permeability $k_{Ar(I)}$ uses diffusion coefficients of N_2 , O_2 and Ar at 270 K from the molecular dynamics simulations by Ikeda-Fukazawa et al. (2004) ($D_{\text{N}_2}^{270}$: $2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{O}_2}^{270}$: $4.7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and D_{Ar}^{270} : $4.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$):

$$k_{Ar(I)} = k_{\text{O}_2} - \left(\frac{D_{\text{O}_2}^{270} - D_{\text{Ar}}^{270}}{D_{\text{O}_2}^{270} - D_{\text{N}_2}^{270}} \right) (k_{\text{O}_2} - k_{\text{N}_2}). \quad (5)$$

The second permeability $k_{Ar(II)}$ is based on the observations that $\delta\text{Ar}/\text{N}_2$ is often depleted about half of $\delta\text{O}_2/\text{N}_2$ (e.g., Severinghaus et al., 2009), and is given by:

$$k_{Ar(II)} = \frac{(k_{\text{N}_2} + k_{\text{O}_2})}{2}. \quad (6)$$

The model has the initial depth domain of 20 m, consisting of 0.5-mm-thick boxes. The initial depth profiles of the gas concentrations are given by repeating the shallowest high-resolution $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ data (1258.51 – 1258.99 m, 81.7 kyr BP) normalized to zero-mean, converted with total air content. The model is run for 100 kyr with the timestep of ~ 12 days to simulate the diffusive relaxation of the initial concentration variations and thus the composition of clathrate hydrates. To account for the actual ice sheet conditions, the box heights are gradually reduced according to the thinning function (Nakano et al., 2016) and age scale of the ice core (Kawamura et al., 2007). The temperature in the model is also changed according to the observed depth profile of borehole temperature (Buizert et al., 2021). We assume that the depth profiles of thinning and temperature are constant through time. The modeled $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ at 2.9, 13.7, 14.5 and 67.5 kyr (modeled age) are compared with the

corresponding high-resolution data at 1292, 1390, 1399 and 1894 m, respectively. Because we do not know the initial concentration profiles at the top of the clathrate-hydrate zone for each high-resolution data, it is reasonable only to compare the amplitudes and frequencies of the $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ variations between the data and model outputs. Additional details of the model and simulation method are described in Appendix A.

(Appendix A)

Appendix A: Diffusion model

The time-varying inputs for the model are temperature and thinning function. The temperature is used to calculate dissociation pressure and diffusion constants, and the thinning function is used to determine box size. There is no tunable parameter in the model.

Parameters for Ar dissociation pressure

Because there are no published values for a_{Ar} and b_{Ar} , we constructed them by fitting the dissociation pressures of argon hydrate vs. temperature measured by Nagashima et al. (2018) with eq. (4) (Fig. A1). The a_{Ar} and b_{Ar} are 3.63 and 739.5, respectively.

Molar fraction of m -molecule in clathrate hydrate

The molar fraction of m -molecule in clathrate hydrate is given by

$$X_m = \frac{U_m}{U_{\text{N}_2} + U_{\text{O}_2} + U_{\text{Ar}} + U_{\text{others}}^0}, \quad (\text{A1})$$

where U_m is the concentration of m -molecule in total air content. U_{others}^0 is the concentration of minor gases, which is assumed to be constant and given by

$$U_{\text{others}}^0 = U^0 - U_{\text{N}_2}^0 - U_{\text{O}_2}^0 - U_{\text{Ar}}^0 = \frac{TAC \cdot M_{\text{H}_2\text{O}}}{V_{\text{STP}}} (1 - R_{\text{N}_2} - R_{\text{O}_2} - R_{\text{Ar}}), \quad (\text{A2})$$

where U^0 is concentration of total air content in ice, U_m^0 is concentration of m -molecule with the atmospheric ratio in the total air content, TAC is total air content, $M_{\text{H}_2\text{O}}$ is molar mass of ice (H_2O), V_{STP} is molar volume of a gas at standard temperature and pressure, and R_m is the atmospheric ratio of m -molecule.

Permeability

The diffusivity D_m , solubility S_m , or their product (permeability, k_m) for air molecules are taken from the literature (Ikeda-Fukazawa et al., 2001; Salamatin et al., 2001; Ikeda-Fukazawa et al., 2005). Ikeda-Fukazawa et al. (2001) and Salamatin et al. (2001) estimated permeability of N_2 and O_2 , which were constrained by observed $\delta\text{O}_2/\text{N}_2$ of individual air inclusions in BCTZ. Ikeda-Fukazawa et al. (2005) estimated solubility and diffusivity of N_2 and O_2 based on molecular dynamics simulations, and the results were consistent with gas-loss fractionation for the Dome Fuji core. The permeability ($\text{m}^2 \text{s}^{-1}$) at T (K) and 1 MPa of Ikeda-Fukazawa et al. (2001) (hereafter IkFk01) is given by

$$k_m = k_m^0 P_m^d \exp\left(-\frac{E_m^k}{RT}\right), \quad (\text{A3})$$

where k_m^0 is a constant, P_m^d is dissociation pressure of m -molecule, E_m^k is activation energy of permeation for m -molecule, R is the gas constant. The permeability ($\text{m}^2 \text{s}^{-1}$) at temperature T (K) and 1MPa of Salamatin et al. (2001) (hereafter Salm01) is given by

$$k_m = k_m^0 \frac{P_m^d}{P_m^{220}} \exp\left[\frac{E_m^k}{R} \left(\frac{1}{220} - \frac{1}{T}\right)\right], \quad (\text{A4})$$

where P_m^{220} is dissociation pressure of m -molecule at 220 K. The diffusivity D_m or permeability k_m ($\text{m}^2 \text{s}^{-1}$) at temperature T (K) of Ikeda-Fukazawa et al. (2005) (hereafter IkFk05) is given by

$$D_m = D_m^0 \exp\left(-\frac{E_m^D}{RT}\right). \quad (\text{A5})$$

The solubility at 1MPa of Ikeda-Fukazawa et al. (2005) is given by

$$S_m = S_m^0 \exp\left(-\frac{E_m^S}{RT}\right), \quad (\text{A6})$$

where S_m^0 is a constant for m -molecule, E_m^S is activation energy of solubility for m -molecule. We used those permeation parameters for our model (parameters are summarized in Table A2 and each permeability is shown in Fig. 2 and Table A3).

There are no published values of k_{Ar} , thus we estimated it from k_{N_2} and k_{O_2} in Salamatin et al. (2001) with two formulations by Kobashi et al. (2015). The first one $k_{Ar(I)}$ uses diffusion coefficients of N_2 , O_2 and Ar at 270 K from the molecular dynamic simulations by Ikeda-Fukazawa et al. (2004) ($D_{N_2}^{270}: 2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $D_{O_2}^{270}: 4.7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $D_{Ar}^{270}: 4.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$):

$$k_{Ar(I)} = k_{O_2} - \left(\frac{D_{O_2}^{270} - D_{Ar}^{270}}{D_{O_2}^{270} - D_{N_2}^{270}}\right) (k_{O_2} - k_{N_2}) \quad (\text{A7})$$

The second permeability $k_{Ar(II)}$ is based on the observations that $\delta\text{Ar}/\text{N}_2$ is often depleted about half of $\delta\text{O}_2/\text{N}_2$ (e.g., Severinghaus et al., 2009). The permeability of Ar(II) is expressed as

$$k_{Ar(II)} = \frac{(k_{N_2} + k_{O_2})}{2}. \quad (\text{A8})$$

Discretization

The model uses the central differencing scheme. The downward diffusive flux (f_m) of m -molecule per unit area at the top boundary of i -th box is the product of the diffusivity and concentration gradient:

$$f_{m(i)} = D_m \frac{c_{m(i-1)}^h - c_{m(i)}^h}{\Delta z \tau_r}. \quad (\text{A9})$$

where Δz is initial box height (0.5 mm) and τ_r is relative thinning function (thinning function divided by the initial value at 1258 m). By substituting eq. 3 into eq. A9, f_m is expressed as

$$f_{m(i)} = \frac{D_m S_m P_m^d}{\Delta z \tau_r} (X_{m(i-1)} - X_{m(i)}). \quad (\text{A10})$$

The net flux of m -molecule for i -th box is

$$F_{m(i)} = \frac{f_{m(i)} - f_{m(i+1)}}{\Delta z \tau_r}, \quad (\text{A11})$$

and the concentration change of m -molecule in total air content becomes

$$\Delta U_{m(i)} = F_{m(i)} \Delta t, \quad (\text{A12})$$

where Δt is the time step ($10^6 \text{ s} \approx 11.6 \text{ days}$).

3. *Regarding the input of the diffusion model, have you considered using a tuned version of the Ca record, since the O₂/N₂ seems well correlated with Ca, rather than reproducing a shallow segment of data? There is a funny offset in your figures, that I presume cannot be interpreted, but it would be interesting to see if we could use Ca²⁺ your diffusion model as a predictor (and then, maybe, as a correction factor).*

Following the suggestion, we conducted simulations with the scaled Ca²⁺ data as the model's initial states. As we have two depths with detailed chemistry data along with the gas data (1258 m and 1399 m), we used the 1258 m data to establish the Ca- $\delta\text{O}_2/\text{N}_2$ and Ca- $\delta\text{Ar}/\text{N}_2$ relationship. We converted the 1399-m Ca record to $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$, and used them as the initial state at 1258 m (we also considered the ice thinning). The model results with the permeability of Salm01 and Ar(II) are shown below. For both $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$, the model results agree with the data rather well in terms of the number of wiggles and their positions, as the reviewer speculated. However, the amplitudes are both overestimated and underestimated by the model (e.g., the model overestimates the amplitude at 1399.1 m and underestimates at 1399.25 m for both $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$). As the initial states of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ would not be perfectly reconstructed by scaling the Ca record, some mismatches would be expected (some other impurities such as Na and Mg might also be related because they are also highly correlated with $\delta\text{O}_2/\text{N}_2$).

This modeling exercise has the advantage that it doesn't have the arbitrariness of the relative phases in comparing the model results and data. However, the application of this alternative input is limited to only one case (1399 m) with a few wiggles. Thus, we would rather refrain from adding it to the manuscript.

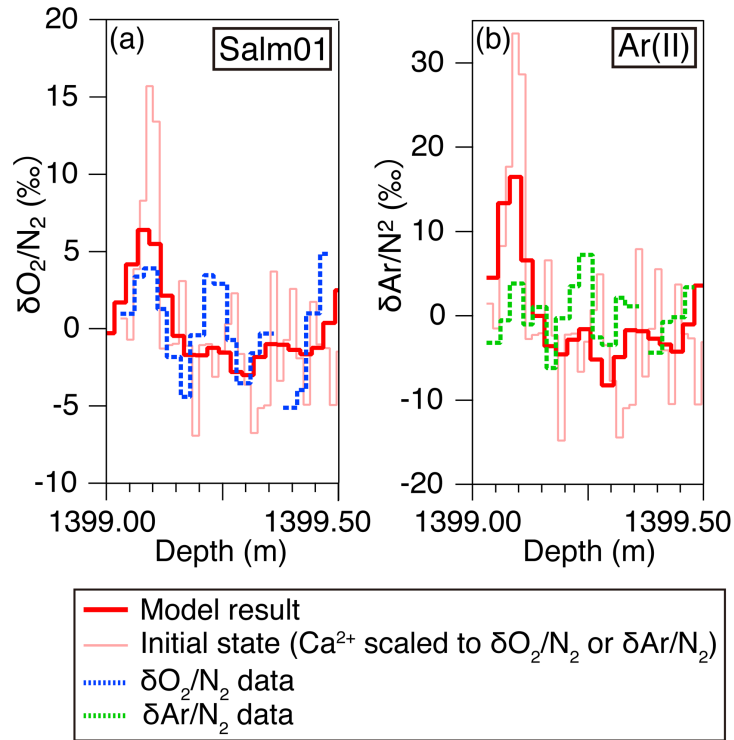


Figure caption: Comparison of the diffusion model outputs for (a) $\delta O_2/N_2$ and (b) $\delta Ar/N_2$ with Salm01 and Ar(II) permeation parameters (red lines) and high-resolution data (blue and green dotted lines) at 1399 m. For this simulation, the initial states were constructed from the measured $[Ca^{2+}]$ profile with linear equations established from the data at 1258 m; $\delta O_2/N_2 = 2.8033 [Ca^{2+}] - 33.55$ and $\delta Ar/N_2 = 5.9868 [Ca^{2+}] - 61.467$.

4. Raman spectroscopy is not described at all (line 186). You could add a sentence or 2 describing how this technique does, what it shows. I expect your readership will have a lot of ice core scientist who may not be too familiar with it. Just 1-2 sentences would help them understand (even if of course, they could read the cited paper).

We will add the following descriptions (original sentences are in black and our changes are in red).
 “In the lowermost part of this range (below 720 m), individual clathrate hydrates with extremely enriched $\delta O_2/N_2$ ($> \sim 1000$ ‰) are found by Raman spectroscopy (Fig. 3h) (Ikeda-Fukazawa et al., 2001), in which laser light is focused on individual bubbles or clathrate hydrates, and the shift of wavelength and intensity of scattered light (Raman spectra) are measured for quantifying O_2 and N_2 . The compositional ratio of O_2 and N_2 is assumed to be equal to the ratio of their Raman peak intensities.”

Line 270 : precise before/after gravitational correction.

In the revised manuscript, we will denote them as $\delta O_2/N_{2\text{gravcorr}}$ and $\delta Ar/N_{2\text{gravcorr}}$ to indicate they are after gravitational correction.

Line 310 : You say that highly fractionated bubbles and clathrates are stratified in mm scale samples. Then, if you average over a certain depth, do you retrieve a better signal? Later on, you say 50cm, but here, you could go into a bit more detail, and justify this number. I also wonder if averaging is enough, or if, in addition to this layering, you have selective fractionation (perhaps post coring, or diffusion) that creates a bias.

The reviewer is right that if we average over a certain length, we should be able to retrieve a better signal. We agree that we can explain the idea and justify the acceptable length here.

The justification of the 50 cm is as follows. On the one hand, the acceptable scatter of $\delta\text{O}_2/\text{N}_2$ around the orbital-scale low-pass filtered curve is $\sim 2\text{‰}$ (one standard deviation), as seen for the depths just below the BCTZ (1200 – 1480 m) where the similarity to local summer insolation is observed. Also, the dataset of Kawamura et al. (2007) has scatters of 1.2 – 1.3 ‰ around the orbital-scale $\delta\text{O}_2/\text{N}_2$ variations. On the other hand, if we add a thin (e.g., 1-mm-thick) layer with extremely fractionated $\delta\text{O}_2/\text{N}_2$ of +1000 ‰ at one end of a 50-cm-long sample, it creates an anomaly of +2 ‰ ($1000\text{‰} \times 0.1\text{ cm} / 50\text{ cm}$) to the original $\delta\text{O}_2/\text{N}_2$ of the 50-cm sample. The exact thickness and $\delta\text{O}_2/\text{N}_2$ of anomalous layers can vary in real situations, but the above assumption is quite extreme (assuming all air inclusions in the thin layer has the maximum $\delta\text{O}_2/\text{N}_2$ observed by Raman spectroscopy), thus we expect that the length of 50 cm is sufficient for “diluting” the effect of anomalous layers.

The reviewer is also correct that the averaging would only work if we can eliminate the selective fractionations such as by post-coring gas loss. As we indeed excluded the gas-loss-fractionated outer ice from our dataset, we believe that the averaging is enough with our data. We will emphasize in the revision that the removal of gas-loss fractionated outer ice is a prerequisite.

We will add the following sentences at the end of the second paragraph of section 4.2.

“..... From these observations, we suggest that the highly fractionated bubbles and clathrate hydrates may be stratified in mm-scale layers, and that the scatters in our dataset may be produced by random inclusion of such fractionated layers at the top and/or bottom of the ice samples. **For example, if a sample coincidentally includes a thin (e.g., 1-mm-thick) layer with $\delta\text{O}_2/\text{N}_2$ of +1000 ‰ at the top or bottom of a 10-cm-long ice, an anomaly of $\sim 10\text{‰}$ from the average $\delta\text{O}_2/\text{N}_2$ (excluding the anomalous layer) should result. We indeed observe the residual $\delta\text{O}_2/\text{N}_2$ of up to $\sim 10\text{‰}$ in the lower BCTZ around the orbital-scale fitting curve. Thus, by simply analyzing longer samples, the scatters created by the thin anomalous layers should be reduced. We suggest that a sufficient sample length to reduce the scatter to an acceptable level is $\sim 50\text{ cm}$, which would produce anomalies of up to $\sim 2\text{‰}$. With this noise level in the $\delta\text{O}_2/\text{N}_2$ data, the insolation signal should be reconstructed in the BCTZ, as seen in the somewhat scattered depths just below the BCTZ (1200 – 1480 m). We also emphasize that**

the removal of the gas-loss fractionated outer ice is a prerequisite for the practice of averaging longer samples, for better reconstruction of average $\delta\text{O}_2/\text{N}_2$ in the ice sheet.”

Line 325: lower dissociation pressure should produce a steeper Ar partial pressure of gradient from bubbles to clathrate. Why? Can you explain a bit more ? (it's maybe obvious to you, but not to me)

The description in the original manuscript was too brief and imprecise, thus we modify this sentence as follows. The basic idea is that the gas flux from bubbles to clathrates depends on permeation coefficient and dissociation pressure (Salamatin et al., 2001), with higher permeation coefficient and lower dissociation pressure leading to larger flux. For the case of O_2 and Ar, the former has a *higher* permeation coefficient and *higher* dissociation pressure, thus their effects on the flux should cancel to each other.

“For the BCTZ, the mass fluxes of gases from bubbles to clathrates through ice may depend on permeation coefficient and dissociation pressure (Eq. 8 in Salamatin et al., 2001), with larger permeation coefficient and lower dissociation pressure leading to larger flux. Thus, for the case of Ar and O_2 , the lower permeation coefficient of Ar than that of O_2 (2×10^{-20} and $3 \times 10^{-20} \text{ m}^2 \text{ s}^{-1} \text{ MPa}^{-1}$ at 240K, respectively) may be counteracted by the lower dissociation pressure of Ar than O_2 (3.5 and 4.9 Mpa at 240K, respectively), to result in similar relative fractionation between bubbles and clathrates with respect to N_2 . This hypothesis may explain ...”

Paragraph near line 355 : Add that nucleation increases $\delta\text{O}_2/\text{N}_2$. If you average over two annual cycles of Ca, do you get back a good value or is it also biased? Is there a selective loss for some layers?

We will add that nucleation increases $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ as the following.

It appears that the averaging over two cycles of Ca, which seems to roughly correspond to red lines (25-cm average) in Fig. 6, may be sufficient for obtaining a good value, with slight biases in some cases (1292 m in Fig. 6).

“Thus, the high-micro-inclusion layers may create early clathrate nucleation, which attract O_2 and Ar from air bubbles in the adjacent layers with fewer micro-inclusions, and increase their $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$.”

Could the correlation to Ca also be due to different bubble sizes for different densification rates in the firm, like in Freitag's papers?

We do not think that the correlation to Ca is related to the densification rate of firm. If Ca or some impurities (see below for a supplementary note) make smaller pores and enhance firm densification, the high-impurity layers close off earlier than the low-impurity layers in the close-off region in firm. This would promote bubble compression and thus O₂ depletion in the high-impurity layers. Thus, the correlation between Ca²⁺ and δO₂/N₂ from this mechanism is expected to be negative, which is opposite to the observation.

As a supplementary note, on the link between impurities and firm densification rate, Fujita et al. (2014, 2016) suggested that, based on the observations of firm at Dome Fuji in Antarctica and NEEM in Greenland, the actual active agent for the layered firm densification rates are ions such as Cl⁻, F⁻ and NH₄⁺, and the correlation with Ca²⁺ is possibly superficial (as Ca is a major element to form salts). In our high-resolution ion data, the correlation between the ions (Cl⁻, F⁻ and NH₄⁺) and Ca²⁺ are generally low because they are mobile in ice so that they are lost during firm densification or smoothed in ice. In any case, the layered firm densification rate is probably irrelevant to the observed correlation between Ca²⁺ and δO₂/N₂, as explained above.

Fujita, S. et al. (2014). Densification of layered firm of the ice sheet at NEEM, Greenland. *Journal of Glaciology*, 60, 905–921. <http://doi.org/10.3189/2014JoG14J006>

Fujita, S et al. (2016). Densification of layered firm in the ice sheet at Dome Fuji, Antarctica. *Journal of Glaciology*, 62(231), 103–123. <http://doi.org/10.1017/jog.2016.16>.

Line 368: Here, it's difficult to understand the hypothesis, the inputs and the results. What mechanisms are you taking into account? Do you start with very high bubble/clathrate layered concentrations?

We test whether the decreasing scatters below BCTZ are due to diffusive homogenization of layered displacement of gas molecules originally created in the BCTZ (thus not due to disturbance of insolation signal on the gas fractionation at the firm-ice transition in the past). We also test different permeabilities proposed by several studies. The only mechanism in the model is the molecular diffusion through the ice lattice driven by the concentration gradient of dissolved gas in the ice, which is in equilibrium with clathrate hydrates. The initial conditions of the model are the actual δO₂/N₂ and δAr/N₂ profiles at 1258 m, which show highly layered values, and we let the model homogenize the layerings. The evolutions of temperature and thinning are incorporated in the model to mimic the real ice sheet condition (the depth profiles of thinning and temperature are assumed to be constant through time). We obtain the smoothed δO₂/N₂ and δAr/N₂ profiles according to the elapsed time, and compare the model results with the high-resolution continuous ice-core data to assess the model results with

different permeabilities. Please note that a similar simulation has been conducted by previous authors (Bereiter et al., 2014), but the study was limited without continuous high-resolution ice-core data to compare; thus, this is the first study that we can directly compare the model results with the detailed $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in the ice sheet.

In the revised manuscript, we will modify the descriptions about the model as the following: (1) Methods and Appendix will include the aim and setups of the model, and (2) the description at lines 368 – 376 will be moved to Results, and (3) the following text (in red letters) will be added to Discussion (before line 378 in the original manuscript). (black letters are unchanged from the original manuscript)

“This study, for the first time, directly compares the diffusion model results with the detailed $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in the ice sheet. The model could reproduce the smoothing of layered gas compositions as seen in the high-resolution continuous data (Fig. 10a and 11b). Also, the relationships between $\delta\text{Ar}/\text{N}_2$ and $\delta\text{O}_2/\text{N}_2$ in different zones (bubbles, BCTZ and clathrates) are similar to each other (slope of around 0.5). From these observations, we conclude that the large scatters just below the BCTZ originate in layered gas fractionations in the lower BCTZ, and that the subsequent decrease of scatters is due to diffusive homogenization. We thus disfavor the possibility that calls for a failure of the recording mechanism of insolation variations during the past firn-ice transition to generate the high scatters of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in and below the BCTZ.

We also analyze our data in a similar manner as the work by Bereiter et al. (2014). The standard deviations of the model results resampled at 11-cm intervals are compared with the residual $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ data from the low-pass filtered curves (Fig. 12). Exponential fitting curves through the residual data (black line) are in close agreements with the model results with the Salm01 and Ar(II) permeation parameters. On the other hand, the model results with the other parameters (IkFk01, IkFk05 and Ar(I)) show too rapid decrease of scatters in comparison with the data. Therefore, our datasets (both high-resolution and normal datasets) consistently support the Salm01 and Ar(II) permeation parameters at around 240 K (temperature at DF for the simulated depths).

From the Salm01 parameters, the rate of diffusive migration is on the order of 0.1 mm per 10 kyr (10⁻¹⁰ m s⁻¹). Therefore, we favor the interpretation that the extreme scatters of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in the BCTZ in our datasets are caused by mm-scale inhomogeneity of the compositions of air inclusions combined with the finite sample length, rather than by cm-scale bulk migration of gas molecules. We also suggest that the original insolation signal on $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ in the BCTZ may be reconstructed by analyzing long ice samples (>50 cm) to average out the inhomogeneity (see Section 4.2).”

Line 389 : explain where the 50cm nb comes from, maybe above.

See above.

Figure 7: add some vertical bars to help the reader.

We added vertical bars.

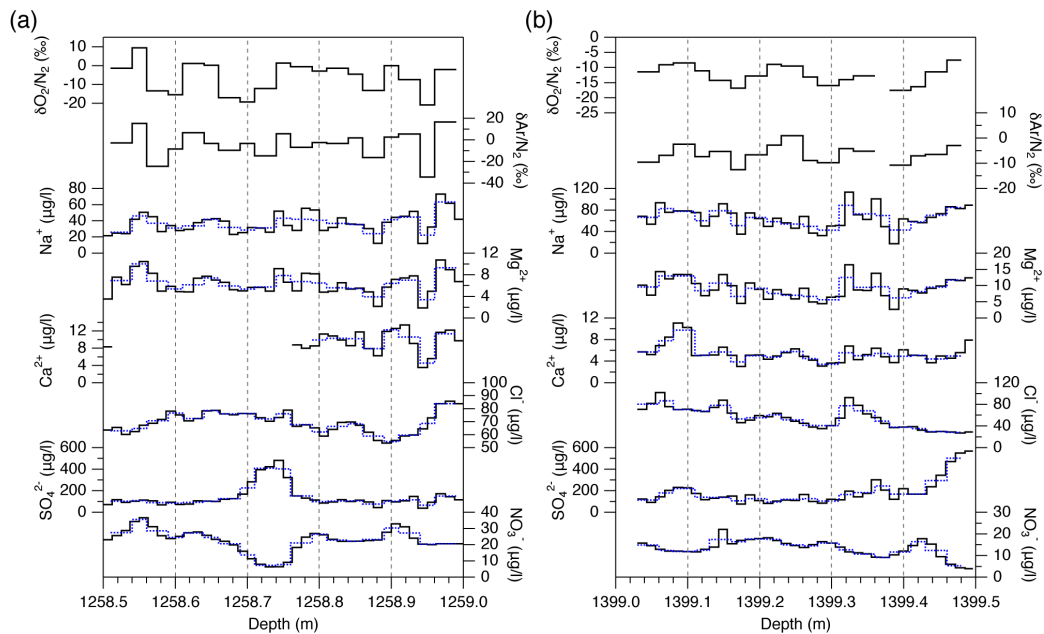


Figure 8 and 9 : it would be useful to put them on the same figure (except panel 1), to help the comparison.

Differences in axes ranges of bulk data and those of pair differences are too large to show in the same figure. Thus, we combined Figure 8 and Figure 9 in the same figure as shown below. The ratio of ranges of horizontal and vertical axes is 1:1 for each panel for easy comparisons of the slopes, except for panels (a) and (b).

