Fractionation of O$_2$/N$_2$ and Ar/N$_2$ in the Antarctic ice sheet during bubble formation and bubble–clathrate hydrate transition from precise gas measurements of the Dome Fuji ice core

Ikumi Oyabu$^1$, Kenji Kawamura$^{1,2,3}$, Tsutomu Uchida$^4$, Shuji Fujita$^{1,2}$, Kyotaro Kitamura$^1$, Motohiro Hirabayashi$^1$, Shuji Aoki$^5$, Shinji Morimoto$^5$, Takakiyo Nakazawa$^5$, Jeffrey P. Severinghaus$^6$, and Jacob D. Morgan$^6$

$^1$National Institute of Polar Research, Tokyo 190-8518, Japan
$^2$Department of Polar Science, The Graduate University of Advanced Studies (SOKENDAI), Tokyo 190-8518, Japan
$^3$Japan Agency for Marine Science and Technology (JAMSTEC), Yokosuka 237-0061, Japan
$^4$Division of Applied Physics, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
$^5$Center for Atmospheric and Oceanic Studies, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
$^6$Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093, USA

Correspondence: Ikumi Oyabu (oyabu.ikumi@nipr.ac.jp)

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Abstract. The variations of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ in the Dome Fuji ice core were measured from 112 m (bubbly ice) to 2001 m (clathrate hydrate ice). Our method, combined with the low storage temperature of the samples ($\sim$−50$^\circ$C), successfully excludes post-coring gas-loss fractionation signals from our data. From the bubbly ice to the middle of the bubble–clathrate transition zone (BCTZ) (112–800 m) and below the BCTZ (>1200 m), the $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ data exhibit orbital-scale variations similar to local summer insolation. The data in the lower BCTZ (800–1200 m) have large scatter, which may be caused by millimeter-scale inhomogeneity of air composition combined with finite sample lengths. The insolation signal originally recorded at the bubble close-off remains through the BCTZ, and the insolation signal may be reconstructed by analyzing long ice samples (more than 50 cm for the Dome Fuji core). In the clathrate hydrate zone, the scatter around the orbital-scale variability decreases with depth, indicating diffusive smoothing of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$. A simple gas diffusion model was used to reproduce the smoothing and thus constrain their permeation coefficients. The relationship between $\delta$Ar/N$_2$ and $\delta$O$_2$/N$_2$ is markedly different for the datasets representing bubble close-off (slope $\sim$0.5), bubble–clathrate hydrate transformation ($\sim$1), and post-coring gas loss ($\sim$0.2), suggesting that the contributions of the mass-independent and mass-dependent fractionation processes are different for those cases. The method and data presented here may be useful for improving the orbital dating of deep ice cores over the multiple glacial cycles and further studying non-insolation-driven signals (e.g., atmospheric composition) of these gases.

1 Introduction

Air trapped in polar ice sheets provides information on past climate and atmosphere. Air is transported mainly by molecular diffusion from the surface to the bottom of firm (typically 50–100 m below the snow surface) and trapped as air bubbles. During the bubble close-off process, relatively small gas molecules such as He, Ne, O$_2$, and Ar are preferentially excluded from air bubbles to open pores (e.g., Bender et al., 1994a; Battle et al., 1996; Severinghaus and Battle, 2006; Huber et al., 2006). The size-dependent gas fractionation may be related to the size of channels within ice crystals (Huber et al., 2006) or the differences in the dominant diffusion mechanism (Ikeda-Fukazawa et al., 2004; Severinghaus and Battle, 2006). Deep ice cores from Antarctic inland show $\delta$O$_2$/N$_2$ of $-5\%_e$ to $-10\%_e$ relative to the atmosphere due to the close-off fractionation (Bender, 2002; Suwa and Bender, 2008a, b; Kawamura et al., 2007; Extier et al., 2018). $\delta$Ar/N$_2$
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has been rarely reported, and it is less depleted than $\delta$O$_2$/N$_2$ (Sowers et al., 1989; Bender et al., 1995; Severinghaus et al., 2009).

High correlations were found between local summer insolation and $\delta$O$_2$/N$_2$ records of the Vostok and Dome Fuji (DF) cores, which have been used for orbital dating of the cores (Bender, 2002; Suwa and Bender, 2008a; Kawamura et al., 2007). Summer insolation may influence the physical properties of snow, which later control the close-off fractionation (Bender, 2002; Kawamura et al., 2007; Fujita et al., 2009). The phasing between the local summer insolation and $\delta$O$_2$/N$_2$ signals and its variability are typically neglected in the dating practice. However, the $\delta$O$_2$/N$_2$ data from the European Project for Ice Coring in Antarctica (EPICA) Dome C (EDC), Vostok, and DF cores around the last glacial period show discrepancies and high-frequency variabilities, challenging the assumption of stable phasing (Bazin et al., 2016).

The current understanding of the gas fractionation and hence the assessment of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ as the local insolation proxy are hindered, at least partly, by the scarcestess of the data that are unaffected by post-coring gas loss (during ice-core drilling and storage), which also fractionates $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ (Bender et al., 1995; Kawamura et al., 2007; Kobashi et al., 2008; Severinghaus et al., 2009; Sowers et al., 1989). For example, configurational diffusion may occur in microcracks to produce size-dependent and weak mass-dependent fractionations (Bender et al., 1995; Huber et al., 2006). Molecular diffusion through ice matrix may also produce size-dependent fractionation (Ikeda-Fukazawa et al., 2004). The DF, Vostok, and GISP2 deep cores indeed showed gradual $\delta$O$_2$/N$_2$ depletion over several years at $-25$ to $-35$ °C (Kawamura et al., 2007; Suwa and Bender, 2008a, b).

Another obstacle to understanding the close-off fractionation lies in the transformation of bubbles to clathrate hydrates. In the bubble–clathrate hydrate transition zone (BCTZ: e.g., 450–1200 m at Dome Fuji (Narita et al., 1999), extreme gas fractionations on the order of several hundreds of $\%$ can occur between individual bubbles and clathrate hydrates due to lower dissociation pressure and larger permeation coefficient of O$_2$ relative to N$_2$ (e.g., Chazallon et al., 1998; Ikeda-Fukazawa et al., 2001). The microscopic gas fractionation, combined with the post-coring gas-loss fractionation, creates high variabilities of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ from gas measurements in the BCTZ (Bender, 2002; Kawamura et al., 2007; Kobashi et al., 2008; Lüthi et al., 2010; Shackleton et al., 2019). Below the BCTZ, the variabilities of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ decrease with depth over several hundred meters, possibly due to diffusive smoothing (Lüthi et al., 2010; Bereiter et al., 2014; Shackleton et al., 2019). The understanding of the smoothing process has been insufficient because of the lack of high-resolution gas data for a proper numerical simulation (Bereiter et al., 2014). Moreover, the fact that reliable $\delta$O$_2$/N$_2$ records have been available only from the clathrate hydrate ice (i.e., older than ~100 kyr) has hindered the discussion of how the original close-off fractionation signals are preserved through the BCTZ.

A better understanding of the gas fractionation associated with bubble close-off and clathrate hydrate formation is important for the ice-core dating and eventual reconstruction of the past atmospheric ratios. Bereiter et al. (2009) predicted that the original gas composition is preserved in the inner part of the cores for a few decades at low temperature (e.g., $-50$ °C), based on a numerical simulation of gas diffusion. The prediction was verified by analyzing the DF core, which has been stored at $-50$ °C for ~20 years, after sufficiently removing its fractionated outer part (Oyabu et al., 2020). In this work, we employ the method by Oyabu et al. (2020) and measure $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ from the bubbly ice to clathrate hydrate ice in the DF core. In addition to the discrete sampling, we obtain high-resolution, continuous gas and chemical data at selected depth intervals to understand the smoothing process of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ below the BCTZ. Moreover, the outer ice is also measured for discussing the artificial fractionation during storage. We analyze the data mainly based on the relationships between $\delta$O$_2$/N$_2$, $\delta$Ar/N$_2$, and $\delta^{18}$O of O$_2$ to distinguish the gas fractionation processes associated with the bubble close-off, transformation of bubbles to clathrate hydrates, and post-coring gas loss. A simple gas diffusion model is also employed to constrain the permeation coefficients of N$_2$, O$_2$, and Ar, and discuss the preservation of insolation signals in the gas records through the BCTZ.

2 Methods

2.1 Ice core

We use the first Dome Fuji ice core (DF1 core) drilled from 1993 to 1997 (Watanabe et al., 2003). After transporting to Japan, the samples had been stored at $-50$ °C at the Institute for Low Temperature Science, Hokkaido University (until 2009), and the National Institute of Polar Research (NIPR, 2009–present). Within the DF ice core, 105–450 m is bubbly ice, 450–1200 m is the BCTZ, and below 1200 m is bubble-free ice (Narita et al., 1999; Ohno et al., 2004).

2.2 Air extraction and measurements

A typical ice sample is ~60 g and ~110 mm long (corresponding to ~3 to 30 years) (Fig. 1a), which is cut out from a bulk section (~500 mm long). Because $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ near the sample surface are depleted by gas loss during storage, we removed the surface by more than 8 mm for clathrate ice (Oyabu et al., 2020) and 5 mm for bubbly ice (see below). For some samples in the BCTZ (1000–1200 m), we removed the surface by 20 mm (Fig. 1b) to minimize the signal of gas loss from high-pressure bubbles (Bender, 2002).
The thickness of surface removal (5 mm) for bubbly ice was determined as follows. Within a pair of samples with 3 mm removal, the sample with larger outer surface (“a2” in Fig. 1a) had generally lower $\delta^{18}O$/N$_2$ and $\delta$Ar/N$_2$, and slightly higher $\delta^{18}$O than the other sample (“a1” in Fig. 1a) (Fig. B1). No such tendency is observed with $>5$ mm surface removal (Fig. B1). We note that $\delta^{15}$N is insensitive to the removal thickness (Fig. B1c), confirming its immunity from gas loss (Severinghaus et al., 2009; Oyabu et al., 2020).

The experimental procedures at NIPR are described elsewhere (Oyabu et al., 2020). Briefly, ice sample was evacuated for 2 h and melted, and the released air was cryogenically collected into a sample tube. The air sample was split into two aliquots and measured with a mass spectrometer (Thermo Delta V, for $\delta$O$_2$/N$_2$, $\delta$Ar/N$_2$, $\delta^{15}$N and $\delta^{18}$O) and gas chromatographs (two Agilent 7890A, for CO$_2$, CH$_4$ and N$_2$O concentrations; not shown in this study). Corrections were made for non-linearity of the elemental and isotopic ratios upon sample pressure, and for the dependency of $\delta^{15}$N, $\delta^{18}$O and $\delta$Ar/N$_2$ upon $\delta$O$_2$/N$_2$ (Bender et al., 1994b). Then, the values were normalized to the modern atmosphere (Oyabu et al., 2020). The $\delta$O$_2$/N$_2$, $\delta$Ar/N$_2$, and $\delta^{18}$O values relative to the modern atmosphere were corrected for the gravitational enrichment in firm, which is nearly proportional to the mass difference between the gas pairs (Craig et al., 1988; Sowers et al., 1989). The gravitational correction can be estimated from $\delta^{15}$N of the same sample:

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

where $\delta_{\text{gravcorr}}$ is gravitationally corrected value, $\delta$ is measured value, and $\Delta m$ is mass difference (4 for $\delta$O$_2$/N$_2$, 12 for $\delta$Ar/N$_2$, and 2 for $\delta^{18}$O). We measured 522 and 162 depths with single and replicates, respectively, between 112.88 to 2001.12 m (3 to 173 kyr BP).

We tested the possibility of gas loss during the sample evacuation (Craig et al., 1988). For bubbly ice (446.4 m) and clathrate hydrate ice (2001.1 m), we split each sample into five thin pieces of 13–18 g (Fig. 1d) and evacuated them for different durations (two pieces for 20 min, one for 2 h, and two for 5 h). There is no dependence of $\delta$O$_2$/N$_2$, $\delta$Ar/N$_2$, $\delta^{15}$N, and $\delta^{18}$O on the pumping time (Fig. B2). The bubbly ice data show somewhat low $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ for the 20 min evacuation, but the result is opposite to the expectation from gas loss. Also, larger variabilities of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ are expected in the bubbly ice than in the clathrate hydrate ice (Sect. 4.1). Thus, our method and core quality do not significantly fractionate the gases.

In total, 11 samples from 179.69 to 2496.55 m, stored for 11 years at $-25^\circ$C, were measured for $\delta$O$_2$/N$_2$ and $\delta^{15}$N at Tohoku University. The analytical method was slightly mod-

![Figure 1](https://doi.org/10.5194/tc-15-5529-2021)
ified from the previous method by Kawamura et al. (2007) as follows. The typical sample size was 250 g, and the measurements were made with a Delta plus XP (Thermo Fisher Scientific) with 64 changeover cycles. Analytical precisions (1σ) were estimated to be 0.4 ‰ and 0.011 ‰ for δO2/N2 and δ15N, respectively.

2.3 High-resolution analyses

The air composition and ion concentrations were measured on five 50 cm segments at the resolutions of 1–2 cm. Three segments were measured for the air (1258.51–1258.99, 1389.79–1390.32, and 1893.51–1893.99 m) and two segments were measured for the air and ions (1292.29–1292.82 and 1399.03–1399.48 m). In Fig. 1c, the X and Y sections were divided into 25 and 12.5 mm pieces for air and ion measurements, respectively.

For the ion measurements, the ice was decontaminated by shaving off ∼3 mm and then chopped off with a ceramic knife and sampled in particle-free plastic bags. They were melted in a clean laboratory (class 10000) and analyzed for the concentrations of Cl−, SO42−, NO3−, F−, CH3SO3−, Na+, NH4+, K+, Mg2+, and Ca2+ using ion chromatography (Thermo Fisher Scientific Dionex ICS-5000+) (Goto-Azuma et al., 2019).

2.4 Diffusion model

We simulate diffusive smoothing of δO2/N2 and δAr/N2 in the clathrate hydrate ice with a one-dimensional diffusion model (Ikeda-Fukazawa et al., 2005; Bereiter et al., 2009, 2014) to test whether the observed reduction of variability below BCTZ (see Sect. 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 the molecular diffusion through ice lattice is driven by the concentration gradient of gas molecules dissolved in ice, which are in equilibrium with clathrate hydrates in respective layers of the model. The governing equation is

\[ \frac{\partial C_m^h}{\partial t} = \frac{\partial}{\partial z} \left( D_m \frac{\partial C_m^h}{\partial z} \right) , \]

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

\[ C_m^h = S_m P^d_m X_m , \]

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

\[ \log P_m^d = a_m - \frac{b_m}{T} , \]

where \( a_m \) and \( b_m \) are constant and shown in Table A2.

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, Tables A2 and A3).

There is no published permeability of Ar in ice; thus, we used two formulations proposed by Kobashi et al. (2015) (Fig. 2). The first permeability \( k_{\text{Ar(I)}} \) uses diffusion coefficients of \( \text{N}_2, \text{O}_2, \) and \( \text{Ar} \) 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 \( D_{\text{Ar}}^{270} = 4.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \)):

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

The second permeability \( k_{\text{Ar(II)}} \) is based on the observations that δAr/N2 is often depleted about half of δO2/N2 (e.g., Severinghaus et al., 2009) and is given by

\[ k_{\text{Ar(II)}} = \frac{(k_{\text{N}_2} + k_{\text{O}_2})}{2} . \]

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 δO2/N2 and δAr/N2 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 time step of ∼12 d to simulate the diffusive relaxation of the
3 Results

3.1 $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ in bubbly ice, BCTZ ice, and clathrate hydrate ice

$\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ from the 11 cm samples are shown in Fig. 3b and c. Note that all $\delta^{18}O_2/N_2$, $\delta^{18}Ar/N_2$, and $\delta^{18}O$ data in this and the following sections are gravitationally corrected (see Sect. 2.2). As expected, most data are negative (i.e., lower than the atmosphere) because of preferential loss of O$_2$ and Ar relative to N$_2$ during bubble close-off (Bender et al., 1995; Severinghaus and Battle, 2006). The average values of $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ are about $-10\% e$ and $-5\% e$, with the overall ranges of $-14\% e$ to $-5\% e$ and $-7\% e$ to $-3\% e$, respectively.

Variations in $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ for the depths deeper than $\sim 1200$ m have similarity with local summer insolation curve, while little similarity is found for 800–1200 m with extremely large scatter (Fig. 4). For the depths shallower than $\sim 800$ m, the comparisons between the gas records and insolation are less robust than for the deeper depths because of the short length (in terms of age) and small insolation amplitudes (small signal-to-noise ratio). Nevertheless, we find similarity between $\delta^{18}O_2/N_2$ and local summer insolation in that both curves show the two peaks at $\sim 350$ m (12 kyr BP) and $\sim 700$ m (32 kyr BP) and that the second peak (at $\sim 700$ m) is larger than the first one. We assess the scatter in the data by taking residuals of $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ from their low-pass-filtered curves (Fig. 3d and e). The low-pass filter (cut-off period: 16.7 kyr) and its usage are the same as in Kawamura et al. (2007). Briefly, we put the $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ data on the DFO-2006 timescale, linearly interpolated them at 0.1 kyr intervals, and applied the filter to extract their orbital-scale variations. The average residuals of $\delta^{18}O_2/N_2$ are $1.1\% e$ in the bubbly ice zone ($\sim 112–450$ m), $0.7\% e$ in the upper BCTZ ($\sim 450–800$ m), $4.6\% e$ in the lower BCTZ ($800–1200$ m), $2.3\% e$ just below BCTZ ($\sim 1200–1480$ m), and $0.4\% e$ in the deeper depths ($\sim 1480–2000$ m). The average residuals of $\delta^{18}Ar/N_2$ also show a similar pattern ($0.5\% e$ for 112–450 m, $0.5\% e$ for 450–800 m, $2.8\% e$ for 800–1200 m, $1.3\% e$ for 1200–1480 m, and $0.3\% e$ for $\sim 1480–2000$ m). Below, we divide our dataset into four depth ranges guided by the scatter as well as the classic boundaries between the bubbly ice zone, BCTZ, and clathrate ice zone (Narita et al., 1999; Ohno et al., 2004).

3.1.1 112–450 m (bubblly ice)

The average $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ are $-10.9\% e$ and $-5.6\% e$, with the overall ranges of $-13.0\% e$ to $-7.0\% e$ and $-7.2\% e$ to $-3.4\% e$, respectively. Figure 2f and g show differences of $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ between ice samples cut from the same depth (Fig. 1a) (hereafter referred to as the pair difference or $\Delta\delta^{18}O_2/N_2$ and $\Delta\delta^{18}Ar/N_2$). Ranges of $\Delta\delta^{18}O_2/N_2$ and $\Delta\delta^{18}Ar/N_2$ are $\sim 0.02\% e$ to 0.97$\% e$ and 0.01$\% e$ to 0.96$\% e$, respectively. Pair differences are usually used to calculate the pooled standard deviation, a metric of analytical precision. Instead, we use it to evaluate spatial variability in air composition for a given depth in the ice sheet (pair differences of $\delta^{15}N$ and $\delta^{18}O$ are plotted in Fig. B3 and pooled standard deviations are summarized in Table C1).

Our new $\delta^{18}O_2/N_2$ data are compared with previously obtained data at Tohoku University using the samples stored at $-25^\circ C$ for various durations (Fig. 5). As expected, the samples stored at $-25^\circ C$ generally show lower $\delta^{18}O_2/N_2$ than those stored at $-50^\circ C$, with dependency on the storage duration. Also, while the data from the $-50^\circ C$ samples slightly increase with depth in the bubbly ice zone as expected from the insolation variation, the data from the $-25^\circ C$ samples tend to decrease with depth possibly due to the increase in bubble pressure (leading to larger gas loss) (Ikeda-Fukazawa et al., 2005; Kawamura et al., 2007).

3.1.2 450–800 m (upper BCTZ)

The number and size of clathrate hydrates gradually increase with depth, but air bubbles are still the dominant form of air inclusion (Fig. 3i and j) (Ohno et al., 2004). In the lowermost part of this range (below 720 m), individual clathrate hydrates with extremely enriched $\delta^{18}O_2/N_2$ ($\sim 1000\% e$) 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. The $\delta^{18}O_2/N_2$ and $\delta^{18}Ar/N_2$ values from the gas analyses smoothly connect with those in the bubbly ice zone, with a slightly increasing trend with depth.
Figure 3. $\delta^{18}O_2/N_2^{gravcorr}$ and $\delta Ar/N_2^{gravcorr}$ records from the Dome Fuji ice core. Published data of water isotopes and air inclusions are also shown. (a) Stable water isotope record (Uemura et al., 2018), (b, c) $\delta^{18}O_2/N_2^{gravcorr}$ and $\delta Ar/N_2^{gravcorr}$ after gravitational corrections, (d, e) absolute residuals of $\delta^{18}O_2/N_2^{gravcorr}$ and $\delta Ar/N_2^{gravcorr}$ from their low-pass-filtered curves, (f, g) absolute pair differences of $\delta^{18}O_2/N_2^{gravcorr}$ and $\delta Ar/N_2^{gravcorr}$, (h) $\delta^{18}O_2/N_2$ in bubbles and clathrate hydrates observed by Raman spectroscopy (Ikeda-Fukazawa et al., 2001), and (i, j) number concentrations and radius of bubbles and clathrate hydrates (Ohno et al., 2004).
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Figure 4. δO$_2$/N$_2$gravcorr and δAr/N$_2$gravcorr with published records plotted against the age of ice. (a) Stable water isotope record (Uemura et al., 2018), (b) summer solstice insolation at Dome Fuji (Laskar et al., 2004), and (c) δO$_2$/N$_2$gravcorr and δAr/N$_2$gravcorr with low-pass-filtered curves (cut-off at 16.7 kyr; the filter was designed by Kawamura et al., 2007) (red lines).

Figure 5. Comparison of the new and previous δO$_2$/N$_2$gravcorr data from the Dome Fuji ice core. Solid circles (blue) are the new data (this study), and open circles (red) are the previous data corrected for gas loss during storage at −25 °C (Kawamura et al., 2007). Open triangles (orange), open diamonds (black), and the solid square (light blue) are the uncorrected previous data for the storage period of 29–167, 453–885 d (Kawamura, 2001) and ~4000 d (11 years) (this study), respectively.

differences of δO$_2$/N$_2$ and δAr/N$_2$ are smaller than 1 ‰ until ~650 m, below which they show high values (> 3 ‰, Fig. 3f and g).

3.1.3 800–1200 m (lower BCTZ)

Major transitions from air bubbles to clathrate hydrates occur in this depth range (Fig. 3i and j) (Ohno et al., 2004). The δO$_2$/N$_2$ values of clathrate hydrates decrease from extremely high values towards the atmospheric value, and those of remaining air bubbles decrease to extremely negative values (~ −500 ‰) (Ikeda-Fukazawa et al., 2001).

In contrast to the upper BCTZ, the bulk δO$_2$/N$_2$ and δAr/N$_2$ in the lower BCTZ show elevated scatter (Fig. 3b–e). Very high δO$_2$/N$_2$ scatter has also been reported from the Vostok (Suwa and Bender, 2008a), GISP2 (Kobashi et al., 2008), and West Antarctic Ice Sheet (WAIS) Divide (Shackleton et al., 2019) ice cores, with numerous positive values (higher than the atmosphere). The previous data were affected by the post-coring gas loss; thus, they were interpreted only as artifacts created by the preferential gas loss from extremely N$_2$-rich air bubbles (Bender, 2002; Ikeda-Fukazawa et al., 2001; Kobashi et al., 2008; Shackleton et al., 2019). In our data, relatively few samples (six and 10 samples for δO$_2$/N$_2$ and δAr/N$_2$, respectively) show positive values, and

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even the samples with twice the surface removal (20 mm) show large scatter. Thus, the large $\delta O_2/N_2$ and $\delta Ar/N_2$ variabilities naturally occur in this zone. The pair differences of $\delta O_2/N_2$ and $\delta Ar/N_2$ are also large (up to $\sim 10\%e$, Fig. 3g and h; Table C1), indicating large inhomogeneities also in the horizontal direction.

3.1.4 1200–1980 m (clathrate hydrate ice)

Between 1200 and 1480 m, the $\delta O_2/N_2$ and $\delta Ar/N_2$ data show smaller scatter than those in the lower BCTZ (Fig. 3b–e), and their low-pass-filtered curves (corresponding to $\sim 80$ to $100$ kyr BP) show similarity to the local summer insolation (Fig. 4). The residuals of the data from the filtered curves are up to $\sim 5\%e$ and $\sim 3\%e$ for $\delta O_2/N_2$ and $\delta Ar/N_2$, respectively. The large scatter below the BCTZ has also been found in the W AIS Divide (Shackleton et al., 2019), EPICA Dronning Maud Land (EDML), and EDC (Lüthi et al., 2010) ice cores. The pair differences of $\delta O_2/N_2$ and $\delta Ar/N_2$ values from the outer ice are positive (Fig. B4a and b), possibly due to the preferential gas loss from N$_2$-rich bubbles (Bender et al., 1995). We do not find significant differences between the outer and inner pieces for $\delta^{15}N$, CH$_4$ concentration and N$_2$O concentration (Fig. B4d–f). The results are consistent with the earlier notion that only the molecules smaller than 3.6 Å in collision diameter (O$_2$ and Ar among the above species) significantly fractionate (Huber et al., 2006; Severinghaus and Battle, 2006).

3.2 Outer ice

In almost all outer ice samples, $\delta O_2/N_2$ and $\delta Ar/N_2$ are significantly lower and $\delta^{18}O$ is significantly higher than those in the inner ice, as expected for gas loss (Ikeda-Fukazawa et al., 2005; Severinghaus et al., 2009). The outer ice stored at $\sim 30$°C for $\sim 1$ year shows larger gas-loss signals than those stored at $\sim 50$°C (Fig. B4), indicating that the gas-loss fractionation strongly depends on the storage temperature and duration. In the lower BCTZ, some $\delta O_2/N_2$ and $\delta Ar/N_2$ values from the outer ice are positive (Fig. B4a and b), possibly due to the preferential gas loss from N$_2$-rich bubbles (Bender et al., 1995). We do not find significant differences between the outer and inner pieces for $\delta^{15}N$, CH$_4$ concentration and N$_2$O concentration (Fig. B4d–f). The results are consistent with the earlier notion that only the molecules smaller than 3.6 Å in collision diameter (O$_2$ and Ar among the above species) significantly fractionate (Huber et al., 2006; Severinghaus and Battle, 2006).

3.3 High-resolution data

The high-resolution data ($\sim 1258, 1292, 1390, 1399$, and 1894 m) are shown in Fig. 6. For the upper four depths,
Figure 7. High-resolution data of δO₂/N₂gravcorr and δAr/N₂gravcorr (2.5 cm resolution) and ion concentrations (1.25 cm resolution). Dotted blue lines are the interpolated ion data to match with the resolution of the gas data. The Ca²⁺ data for 1258.51–1258.75 m are excluded (high contamination due to sample handling error).

δO₂/N₂ and δAr/N₂ fluctuate with very large amplitudes (peak to peak: 10 ‰–30 ‰) and the cycles of 10–15 cm. In the deepest sample (1894 m), the values are quite stable. The standard deviations of δO₂/N₂ are 8.4 ‰, 5.9 ‰, 5.8 ‰, 3.1 ‰, and 0.2 ‰, and those of δAr/N₂ are 12.5 ‰, 6.4 ‰, 5.6 ‰, 3.4 ‰, and 0.2 ‰ for 1258, 1292, 1390, 1399, and 1894 m, respectively.

The data are averaged over four to five consecutive samples and compared with the data from the normal (11 cm) samples (Fig. 6). Two normal samples at ∼1293 and 1390 m are taken from the same depths as the high-resolution measurements, and they agree with the averages of the high-resolution data. The standard deviations of the averaged data (blue curves in Fig. 6) for the upper four depths are 1.4 ‰ to 2.8 ‰ for δO₂/N₂ and 0.8 ‰ to 1.5 ‰ for δAr/N₂, which are significantly higher than that for the deepest sample (0.1 ‰ and 0.2 ‰). High variabilities at 10 cm scales have also been found in the continuous measurements of the GRIP core (in the BCTZ, Huber and Leuenberger, 2004) and EDML core (just below the BCTZ, Lüthi et al., 2010). Also, in the GRIP data, the variabilities of δO₂/N₂ well below the BCTZ (∼2500 m depth) are much smaller than those in the lower BCTZ (∼1100–1400 m) (Huber and Leuenberger, 2004).

Major ion concentrations (Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, and NO₃⁻) at 12.5 mm resolution from the two depths (1258 and 1399 m) are shown in Fig. 7. The Na⁺, Mg²⁺, and Ca²⁺ concentrations show similar variations, and they appear to be correlated with the gas records. For example, narrow dips in the ion concentrations at 1258.88–1258.89 and 1258.94–1258.95 m possibly correspond to the dips in the gas records. Another example is common dips in the Na⁺, Mg²⁺, Ca²⁺, Cl⁻, and SO₄²⁻ concentrations and the gas data for 1399.17–1399.18 m. On the other hand, the Cl⁻, SO₄²⁻, and NO₃⁻ concentrations show smooth variations possibly due to their higher mobility in firn and ice. The correlation coefficients between the ion concentrations and gas ratios are summarized in Table 1. For calculating the correlation coefficients, the ion data are resampled to the depths of the gas data. Significant correlations with the gas data are found for the Na⁺, Mg²⁺, and Ca²⁺ concentrations.

### 3.4 Diffusion model

The results of the diffusion model for 2.9, 13.7, 14.5, and 67.5 kyr (at 1292, 1390, 1399, and 1894 m, respectively) after the initial state (81.7 kyr BP at 1258 m, Fig. 6) are resampled at 2.5 cm intervals and compared with the data (Fig. 8). The IkFk05 permeation parameters give the smoothest δO₂/N₂ profiles with a poor agreement with the data (Fig. 8c). The IkFk01 parameters produce the profiles similar to the data at 1292 m, but the model results are too smooth at 1390 and 1399 m (Fig. 8b). The results with the Salm01 parameters agree well with the data, including rapid changes (> 10 ‰) within a few consecutive samples and the standard deviation (∼3 ‰) at 1399 m (Fig. 8a). We note that the data at 1390 and 1399 m show rather different standard deviations (5.8 ‰ and 3.1 ‰) probably reflecting the original fraction-
ations in the BCTZ. Thus, the model–data comparison is inadequate with the small number of cases. For Ar, the model results with the scaling function Ar(II) are closer to the data than those with Ar(I) (Fig. 9).

4 Discussion

4.1 Fractionation in firn

The $\delta O_2/N_2$ and $\delta Ar/N_2$ data below BCTZ show variations similar to the local summer insolation (Fig. 4). In addition, we find the possible insolation signals in the bubbly ice zone and upper BCTZ (see Sect. 3.1), as expected from the proposed link between the local summer insolation and close-off fractionation through the effects on the snow metamorphism (Bender, 2002; Fujita et al., 2009).

In the bubbly ice zone, the scatter of the data is significantly larger than that of the pair differences, probably reflecting high variabilities of natural close-off fractionation in the vertical direction. In the Dome Fuji region, firn layerings of several 10 cm are found in $^{18}$O of ice, ion concentrations, and density (Hoshina et al., 2014; Fujita et al., 2016). The layers closed off deeper may be less depleted in $O_2$ and Ar because (1) air bubbles spend a shorter time in the close-off zone, and (2) $\delta O_2/N_2$ and $\delta Ar/N_2$ are enriched deeper in the open pores (e.g., Severinghaus and Battle, 2006). Also, microbubbles may form near the surface (Lipenkov, 2000) and become extremely depleted in $O_2$ and Ar (Ohno et al., 2021), also causing the $\delta O_2/N_2$ and $\delta Ar/N_2$ variations (Kobashi et al., 2015). Hereafter, we collectively call the natural fractionation during the firn densification and bubble formation as “close-off fractionation”.

As discussed above, the relationship between $\delta Ar/N_2$ and $\delta O_2/N_2$ in our data is expected only to reflect natural fractionations. For bubbly ice, we find a high correlation between $\delta Ar/N_2$ and $\delta O_2/N_2$ with the slope of 0.50 ± 0.01 (Fig. 10c, Table C2), which agrees with that of pair differences (0.53 ± 0.04) (Fig. 10d, Table C2). The smaller fractionation for $\delta Ar/N_2$ is consistent with the size-dependent fractionation. We find similar slopes in the upper BCTZ, lower BCTZ, and below the BCTZ (0.45 ± 0.01, 0.61 ± 0.01, and 0.42 ± 0.02, respectively, Fig. 10e, g, and i, Table C2), despite large scatter in the lower BCTZ and just below the BCTZ (∼800–1480 m). We interpret the similarity of the slopes as preservation of the close-off fractionation signals through the BCTZ. The slight differences between the slopes
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Figure 8. Comparison of the diffusion model outputs for $\delta\text{O}_2/\text{N}_2$ with different permeation parameters (red lines) and high-resolution data (dotted blue lines), at 1292, 1390, 1399, and 1894 m. The data at 1258 m were given to the diffusion model as the initial condition. Solid lines (red) are the model outputs at the elapsed time of 2.9, 13.7, 14.5, and 67.5 kyr, resampled at 2.5 cm intervals, to compare with the corresponding high-resolution data. SDs of the model results are shown in each panel.

Figure 9. Same as Fig. 8 but for $\delta\text{Ar}/\text{N}_2$.

last interglacial period, Bazin et al. (2016) discussed the possibility of non-orbital-scale variabilities of close-off fractionation. In our data, the residuals of $\delta\text{O}_2/\text{N}_2$ from the low-pass-filtered curve are small ($1\sigma \approx 0.5\,\%$) below $\approx 1480$ m (Fig. 3d), whereas the previous data (after gas-loss correction) show the variability of $1.3\,\%$ for the similar depth range (Kawamura et al., 2007) (Fig. 5). Thus, the large short-term variabilities in the previous datasets may be mostly attributed to the poor ice-core quality, and the actual short-term variability of close-off fractionation may be rather small, at least for the DF core.

4.2 Bubble–clathrate transformation fractionation

In the upper BCTZ, the residuals of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ from the low-pass-filtered curves exhibit scatter of $\approx 3\,\%$ and $\approx 2\,\%$ (peak to peak), respectively, which is much smaller than that in the lower BCTZ (Fig. 4). Pair differences are similar to those at the bottom of the bubbly ice zone, suggesting insignificant effects of the clathrate hydrate formation on the measured $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ until $\approx 40\,$% of air bubbles are transformed to clathrate hydrates. This may be reasonably explained by the dominance of direct conversion of air bubbles to clathrate hydrates (thus little displacements of molecules) in the early stages of bubble–clathrate transformation (Lipenkov, 2000). It may also be the case that the distance of gas diffusion from the bubbles to clathrate hydrates, even if it occurs, is too short to create scatter in the bulk $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$.

in the different zones might arise from different temperature or accumulation rate in the past (affecting the close-off fractionation) or natural variations of $\text{O}_2$ in the atmosphere.

A firn–air study at WAIS Divide (Battle et al., 2011) provided the evidence of mass-dependent fractionation associated with the close-off process with the slope of $\delta^{18}\text{O}$ vs. $\delta\text{O}_2/\text{N}_2$ of $-0.0090\,\%_{\text{o}}\text{e}^{-1}$. For the DF ice-core data, the pair differences in the bubbly ice zone (Fig. B5), as well as the data for the last 2000 years (Oyabu et al., 2020), do not show significant correlations between $\delta^{18}\text{O}$ and $\delta\text{O}_2/\text{N}_2$. Thus, our data cannot verify the mass-dependent fractionation, and much higher precision is required to detect the $\delta^{18}\text{O}$ change of $\approx 0.01\,\%$ expected for the range of DF $\delta\text{O}_2/\text{N}_2$.

From the comparison of three Antarctic inland cores (EDC, Vostok, DF) that showed large short-term $\delta\text{O}_2/\text{N}_2$ variabilities and discrepancies between the cores around the
Figure 10. Scatter plot of $\delta O_2/N_2^{\text{grav corr}}$ vs. $\delta Ar/N_2^{\text{grav corr}}$ (a, c, e, g, i, k) and that of pair differences of $\delta O_2/N_2^{\text{grav corr}}$ and $\delta Ar/N_2^{\text{grav corr}}$ (b, d, f, h, j, l). (a, b) All data, (c, d) bubbly ice zone (112–450 m), (e, f) upper BCTZ (450–800 m), (g, h) lower BCTZ (800–1200 m), (i, j) clathrate hydrate ice zone (1200–2000 m), and (k, l) outer ice (bubbly ice and clathrate hydrate ice).
In the lower BCTZ, the scatter around the orbital-scale variations dramatically increases for δO\textsubscript{2}/N\textsubscript{2} and δAr/N\textsubscript{2} despite the sufficient removal of the outer ice (Figs. 3 and 4). Microscopic observations by Ohno et al. (2004) found layered distributions of air bubbles and clathrate hydrates in the lower BCTZ, as well as high spatial variability of total number of air inclusions on scales of a few millimeters, possibly due to diminishing bubbles by transferring their molecules to nearby clathrates. Using their number concentrations of air bubbles and clathrate hydrates, the average distance between air inclusions is estimated to be 1.1 mm. Thus, the distance of air migration associated with the bubble–clathrate transformation should be on this order. Ikeda-Fukazawa et al. (2001) observed extremely fractionated bubbles and clathrate hydrates in the lower BCTZ, up to about +1000‰ for clathrate hydrates and −740‰ for bubbles for δO\textsubscript{2}/N\textsubscript{2}. From these observations, we suggest that the highly fractionated bubbles and clathrate hydrates may be stratified in millimeter-scale layers, and that the scatter 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 100 mm long ice sample coincidentally includes a 1 mm thick anomalous layer with δO\textsubscript{2}/N\textsubscript{2} of +1000‰, the δO\textsubscript{2}/N\textsubscript{2} of the bulk sample should be elevated by ~10‰ relative to the value without the anomalous layer. We indeed observe the residual δO\textsubscript{2}/N\textsubscript{2} of up to ~10‰ in the lower BCTZ around the orbital-scale fitting curve. Thus, by simply analyzing longer samples, the scatter created by the thin anomalous layers should be reduced. We suggest that a sufficient sample length would produce anomalies of up to ~2‰. With this noise level in the δO\textsubscript{2}/N\textsubscript{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 δO\textsubscript{2}/N\textsubscript{2} in the ice sheet.

The slopes of δAr/N\textsubscript{2} vs. δO\textsubscript{2}/N\textsubscript{2} from the pair differences are close to 1 for both the upper and lower BCTZ (Fig. 10f and h, Table C2). They are strikingly different from the known correlation by the bubble–clathrate transformation is not mass dependent. This is clearly different from the known correlations between Δδ\textsuperscript{18}O and ΔδO\textsubscript{2}/N\textsubscript{2} for bubble close-off (Battle et al., 2011) and post-coring gas loss (Severinghaus et al., 2009). Thus, we suggest that the net fractionation associated with the bubble–clathrate transformation and molecular diffusion between air inclusions within the ice sheet is mass independent, and that the bubble close-off and post-coring gas-loss fractionations include mass-dependent processes for molecules smaller than 3.6 Å such as He, O\textsubscript{2}, and Ar (Craig and Scarsi, 1997; Severinghaus et al., 2009) (Fig. 11). 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\textsubscript{2}, the lower permeation coefficient of Ar than that of O\textsubscript{2} (2 × 10\textsuperscript{-20} and 3 × 10\textsuperscript{-20} m\textsuperscript{2} s\textsuperscript{-1} MPa\textsuperscript{-1} at 240 K, respectively) may be counteracted by the lower dissociation pressure of Ar than O\textsubscript{2} (3.5 and 4.9 MPa at 240 K, respectively), to result in similar relative fractionation between bubbles and clathrates with respect to N\textsubscript{2}. This hypothesis may explain the observed similarity of ΔδAr/N\textsubscript{2} and ΔδO\textsubscript{2}/N\textsubscript{2} enrichment in clathrates. For the bubble close-off, such a cancellation cannot occur, explaining the observed ΔδAr/N\textsubscript{2} that is only half as enriched as ΔδO\textsubscript{2}/N\textsubscript{2}. The bubble close-off fractionation of small molecules (< 3.6 Å molecular diameter) appears to be caused by permeation through the thin ice wall of freshly formed bubbles, which create both size-dependent and mass-dependent fractionations; Ikeda-Fukazawa et al., 2004; Severinghaus and Battle, 2006; Battle et al., 2011).

We find similar slopes (~1) of ΔΔδAr/N\textsubscript{2} vs. ΔδO\textsubscript{2}/N\textsubscript{2} in the BCTZ of the WAIS Divide (Seltzer et al., 2017) and South Pole (Severinghaus, 2019) ice cores, although the samples have possibly experienced post-coring gas loss to some extent (Table C2). The fact that the different cores from a wide range of temperature show similar relationships between ΔδAr/N\textsubscript{2} and ΔδO\textsubscript{2}/N\textsubscript{2} may suggest that the permeation coefficients of O\textsubscript{2} and Ar in ice have similar dependence on temperature.

### 4.3 Preservation of insolation signal through BCTZ

Below the BCTZ, the low-pass-filtered δO\textsubscript{2}/N\textsubscript{2} and δAr/N\textsubscript{2} show close resemblance to the variations of local summer insolation, although the residuals are rather scattered until 1480 m (Figs. 3 and 4). The large scatter probably originates in the extreme layered fractionation in the lower BCTZ. Until the conversion of bubbles to clathrate hydrates complete (at ~1200 m), gas flux from the remaining (extremely fractionated) bubbles to clathrate hydrates should continue and enhance the inhomogeneity of gas composition. Once all bubbles disappear, the gas flux occurs only between clathrate hydrates; thus, their compositions become gradually homogenized. The major homogenization finishes within 300 m (~25 kyr) below the BCTZ, and further homogenization continues to ~500 m (~50 kyr) below the BCTZ where the scatter becomes small and stable (~0.2‰) (Figs. 3d, e and 12).

In contrast to the scatter from the 11 cm samples discussed above, the pair differences decrease sharply at the bottom of BCTZ (Fig. 3f and g), suggesting smaller spatial vari-
Figure 11. Schematic of fractionations of O$_2$ 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$_2$gravcorr and $\delta$Ar/N$_2$gravcorr, respectively (see Fig. 10). The descriptions of “yes” indicate the observed results (this study; Severinghaus and Battle, 2006; Huber et al., 2006; Battle et al., 2011).
and δ

We also suggest that the original insolation signal on

than by centimeter-scale bulk migration of gas molecules.

by millimeter-scale inhomogeneity of the compositions of

δ

−

gration is on the order of 0.1 mm per 10 kyr (10

240 K (temperature at DF for the simulated depths).

the Salm01 and Ar(II) permeation parameters at around

scatter in comparison with the data. Therefore, our datasets

(11 cm resampled outputs) with the best permeation parameters are

may be explained by viscous flow for N2 (Severinghaus et al.,

1995). Thus, there may have been microcracks in the outer

ice, although we did not observe visible cracks. The insen-

sitivity of δ15N to gas loss, consistent with earlier findings,

may be explained by viscous flow for N2 or molecular-size-

limited diffusion through ice matrix (Severinghaus et al.,

2009).

4.4 Gas-loss fractionation

In the outer ice, the δO2/N2 and δAr/N2 are significantly
depleted and δ18O is enriched due to post-coring gas loss, with

higher storage temperature leading to larger fractiona-

tion (Fig. B4). The slope of ΔδAr/N2 vs. ΔδO2/N2 is 0.22

(Fig. 10l, Table C2), which is significantly smaller than those

from the pairs of inner ice, suggesting that the process for gas

loss is different from natural fractionation processes within

the ice sheet. The slope of Δδ18O vs. ΔδO2/N2 is −0.0083

(Fig. B5), which is similar to those previously reported for ar-

tificial gas loss from the Siple Dome (Severinghaus et al.,

2009), WAIS Divide (Seltzer et al., 2017), and EDC (Extier

et al., 2018) ice cores.

Severinghaus et al. (2009) extensively measured the Siple

Dome ice core and found a tight relationship between

ΔδAr/N2 and ΔδO2/N2 with the slope of ~0.5, which was

also typical for other ice cores that experienced large gas

loss (Sowers et al., 1989; Bender et al., 1995). The slope

of ~0.5 may be the combination of size-dependent frac-

tionation (e.g., 1 : 1 for δO2/N2 and δAr/N2) and mass-
dependent fractionation (1 : 3 for δO2/N2 and δAr/N2) (Sev-

eringhaus et al., 2009). The slope for the DF gas-loss frac-

tionation (~0.2) is significantly smaller than most of the

previous values, implying that mass-dependent fractionation

may be more important for the storage condition of the

DF core (Fig. 11). Significant mass-dependent fractionation

is expected for gas loss through microcracks (Bender et al.,

1995). Thus, there may have been microcracks in the outer

ice, although we did not observe visible cracks. The insen-

sitivity of δ15N to gas loss, consistent with earlier findings,

may be explained by viscous flow for N2 or molecular-size-

limited diffusion through ice matrix (Severinghaus et al.,

2009).

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°C after 20 years), a square cross section

of 3 × 3 cm seems sufficient in a −50°C storage, for sam-

pling a central part (cross section of 1 × 1 cm or more) that

is unaffected by the post-coring gas loss. The temperature

of −50°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 δO2/N2 and δAr/N2 data, it is recommended to
test the real ice-core samples to find sufficient removal thick-

ness. The removal thickness can be determined by examining


Figure 12. Diffusive smoothing of (a) δO2/N2 and (b) δAr/N2 below the BCTZ. Open markers with dashed lines (gray) are the residuals from the low-pass-filtered data. Black lines are exponential fits through the residuals for > 5600 years (corresponding to the model’s initial age). The model results (standard deviations of 11 cm resampled outputs) with the best permeation parameters are shown by solid red lines. Blue and green lines are the other model results.

(IkFk01, IkFk05 and Ar(I)) show a too-rapid decrease of scatter in comparison with the data. Therefore, our datasets (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 mi-

gration is on the order of 0.1 mm per 10 kyr (10−10 m s−1).

Therefore, we favor the interpretation that the extreme scatter of δO2/N2 and δAr/N2 in the BCTZ in our datasets is caused by millimeter-scale inhomogeneity of the compositions of air inclusions combined with the finite sample length, rather than by centimeter-scale bulk migration of gas molecules. We also suggest that the original insolation signal on δO2/N2 and δAr/N2 in the BCTZ may be reconstructed by analyzing long ice samples (> 50 cm) to average out the inhomogeneity (see Sect. 4.2).
the pair differences of $\delta$O$_2$/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 scatter 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 et al., 2019). To find a reasonable sample length for a core, it is advisable to continuously measure a $\sim$ 1 m long section with a $\sim$ 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).

5 Conclusions

The variations of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ within the ice sheet from bubbly ice to clathrate hydrate ice at Dome Fuji are reconstructed without post-coring gas-loss signals. Their variations in the bubbly ice zone, upper BCTZ, and below the BCTZ show close similarity to the local summer insolation. Our $\delta$O$_2$/N$_2$ data from the clathrate hydrate ice zone agree with the previous data after the gas-loss correction (Kawamura et al., 2007), with much less scatter, demonstrating that the original air composition is preserved in the ice core stored at $-50^\circ$C.

The large scatter in the lower BCTZ may be created by millimeter-scale vertical inhomogeneity of air composition combined with finite sample length. The insolation signal originally recorded at the bubble close-off remains through the BCTZ, and the insolation signal may be reconstructed by analyzing long ice samples (> 50 cm).

Below the BCTZ, the scatter around the orbital-scale variability decreases with depth. The high-resolution analyses of five 50 cm segments show decreasing centimeter-scale variability of $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ with depth, suggesting diffusive smoothing. A one-dimensional gas diffusion model reproduces the smoothing in this zone with the permeation coefficients of Salamatin et al. (2001).

The slope of the pair differences of $\delta$Ar/N$_2$ to $\delta$O$_2$/N$_2$ is about 1 in the BCTZ, and no correlation is found between those of $\delta$^{18}O and $\delta$O$_2$/N$_2$, suggesting that the O$_2$ and Ar fractionations associated with the bubble–clathrate transition are mostly mass independent (Fig. 11). On the other hand, the slope for the bubble close-off process is around 0.5, suggesting a combination of mass-independent and mass-dependent fractionation for O$_2$ and Ar. For the BCTZ, the slower molecular diffusion of Ar than O$_2$ may be canceled by the lower dissociation pressure of Ar than O$_2$, which should produce a steeper Ar partial pressure gradient from the bubbles to the growing clathrate. For the bubble close-off of small molecules, such a cancellation cannot occur, and both the bond-breaking mechanism and the interstitial mechanism may play roles for the molecular diffusion through the thin ice wall of fresh bubbles. The slope is small (0.2) in ice that experienced large gas loss, suggesting that mass-dependent fractionation may be important for the storage condition of the DF core.

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 work is 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}O of O$_2$ and $\delta^{40}$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}O during bubble close-off was evidenced by the WAIS Divide firm–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 $\delta$O$_2$/N$_2$ and $\delta$Ar/N$_2$ in different zones. Finally, the International Partnership for Ice Core Sciences regards the retrieval of an ice core containing ice older than 1 million years as highest priority (Fisher et al., 2013; Tsutaki et al., 2021). 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 such an ice core.

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.

A1 Parameters for Ar dissociation pressure

Because there are no published values for $a_{\text{Ar}}$ and $b_{\text{Ar}}$, we found them by fitting the dissociation pressures of argon hydrate vs. temperature measured by Nagashima et al. (2018) with Eq. (4) (Fig. A1). The $a_{\text{Ar}}$ and $b_{\text{Ar}}$ are 3.63 and 739.5, respectively.
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Figure A1. Relationship between temperature and dissociation pressure for N\textsubscript{2}, O\textsubscript{2} (Miller, 1969; Kuhs et al., 2000), and Ar hydrates (Nagashima et al., 2018). The data for Ar hydrate (solid circles) are fitted with an exponential function: log \( P^d = 3.63 - 739.5/T \).

A2 Molar fraction of the \( m \) molecule in clathrate hydrate

The molar fraction of the \( m \) molecule in the clathrate hydrate is given by

\[
X_m = \frac{U_m}{U_{N_2} + U_{O_2} + U_{Ar} + U^0_{\text{others}}},
\]

where \( U_m \) is the concentration of the \( m \) molecule in total air content, \( U^0_{\text{others}} \) is the concentration of minor gases, which is assumed to be constant and given by

\[
U^0_{\text{others}} = U^0 - U^0_{N_2} - U^0_{O_2} - U^0_{Ar} = \frac{TAC \cdot M_{H_2O}}{V_{STP}} (1 - R_{N_2} - R_{O_2} - R_{Ar}),
\]

where \( U^0 \) is concentration of total air content in ice, \( U^0_m \) is concentration of the \( m \) molecule with the atmospheric ratio in the total air content, TAC is total air content, \( M_{H_2O} \) is molar mass of ice (H\textsubscript{2}O), \( V_{STP} \) is molar volume of a gas at standard temperature and pressure, and \( R_m \) is the atmospheric ratio of the \( m \) molecule.

A3 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, 2005; Salamatin et al., 2001). Ikeda-Fukazawa et al. (2001) and Salamatin et al. (2001) estimated permeability of N\textsubscript{2} and O\textsubscript{2}, which were constrained by observed SO\textsubscript{2}/N\textsubscript{2} of individual air inclusions in BCTZ. Ikeda-Fukazawa et al. (2005) estimated solubility and diffusivity of N\textsubscript{2} and O\textsubscript{2} based on molecular dynamics simulations, and the results were consistent with gas-loss fractionation for the Dome Fuji core. The permeability (m\textsuperscript{2} s\textsuperscript{-1}) at

\[
T \text{ (K)} \text{ and 1 MPa of Ikeda-Fukazawa et al. (2001) (hereafter IkFk01) is given by} \k_i = k^0_m P_m^d \exp \left( -\frac{E_m^k}{RT} \right),
\]

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

\[
k_m = k^0_m P_m^d \exp \left[ \frac{E_m^k}{RT} \left( \frac{1}{220} - \frac{1}{T} \right) \right],
\]

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

\[
D_m = D^0_m \exp \left( -\frac{E_m^D}{RT} \right),
\]

Figure A2. Thinning function (red, Nakano et al., 2016), temperature (blue, Buizert et al., 2021) and age (black, Kawamura et al., 2007) in the ice sheet at Dome Fuji used for the diffusion model. Gray shading indicates the depth range of the model run.
The solubility at 1 MPa of Ikeda-Fukazawa et al. (2005) is given by

\[ S_m = S_m^0 \exp \left( -\frac{E_m^S}{RT} \right), \]  

(A6)

where \( S_m^0 \) is a constant for the \( m \) molecule, and \( E_m^S \) is activation energy of solubility for the \( m \) 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) (\( D_{270}^{N_2} \): \( 2.1 \times 10^{-11} \) m² s⁻¹, \( D_{270}^{O_2} \): \( 4.7 \times 10^{-11} \) m² s⁻¹ and \( D_{270}^{Ar} \): \( 4.0 \times 10^{-11} \) m² s⁻¹):

\[ k_{Ar(I)} = k_{O_2} - \left( \frac{D_{270}^{N_2} - D_{270}^{Ar}}{D_{270}^{O_2} - D_{270}^{N_2}} \right) (k_{O_2} - k_{N_2}). \]  

(A7)

The second permeability, \( k_{Ar(II)} \), is based on the observations that \( \delta Ar/N_2 \) is often depleted by about half of \( \delta O_2/N_2 \) (e.g., Severinghaus et al., 2009). The permeability of \( Ar(II) \) is expressed as

\[ k_{Ar(II)} = \frac{(k_{N_2} + k_{O_2})}{2}. \]  

(A8)

### A4 Discretization

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

\[ f_m(i) = D_m \frac{C_{m(i-1)}^h - C_{m(i)}^h}{\Delta z \tau_r}, \]  

(A9)

where \( \Delta z \) is the initial box height (0.5 mm) and \( \tau_r \) is the 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

\[ f_m(i) = \frac{D_m S_m P_m^d}{\Delta z \tau_r} (X_{m(i-1)} - X_{m(i)}). \]  

(A10)

The net flux of the \( m \) molecule for \( i \)th box is

\[ F_m(i) = \frac{f_m(i) - f_m(i+1)}{\Delta z \tau_r}, \]  

(A11)

and the concentration change of the \( m \) molecule in total air content becomes

\[ \Delta U_{m(i)} = F_m(i) \Delta t, \]  

(A12)

where \( \Delta t \) is time step (~11.6 d).
Table A1. List of symbols.

| Symbol | Meaning | Unit |
|--------|---------|------|
| m | molecule species ($m = N_2, O_2$ or $Ar$) | |
| $c_{m}^{i}$ | concentration of the $m$ molecule | mol mol$^{-1}$ ice |
| $p_{m}^{d}$ | dissociation pressure of the $m$ molecule | MPa |
| $X_{m}$ | molar fraction of the $m$ molecule in the clathrate hydrate | |
| $a_{m}$ | constant of dissociation pressure for the $m$ molecule | |
| $b_{m}$ | constant of dissociation pressure for the $m$ molecule | K |
| $T$ | temperature | K |
| $U_{m}$ | concentration of the $m$ molecule in total air content | mol mol$^{-1}$ ice |
| $U_{0}^{m}$ | concentration of total air content in ice | mol mol$^{-1}$ ice |
| $U_{0}^{m}$ | concentration of the $m$ molecule with the atmospheric ratio in the total air content | mol mol$^{-1}$ ice |
| $U_{0}^{m}$ | concentration of minor gases | mol mol$^{-1}$ ice |
| TAC | total air content | m$^3$ g$^{-1}$ |
| $M_{H_{2}O}$ | molar mass of ice ($H_2O$) (18.05128) | g mol$^{-1}$ |
| $V_{STP}$ | molar volume of a gas at 273.15 K and 100 kPa (0.022711) | m$^3$ mol$^{-1}$ |
| $R$ | atmospheric ratio of the $m$ molecule | |
| $k_{m}$ | permeation coefficient of the $m$ molecule in ice | m$^2$ s$^{-1}$ |
| $k_{m}^{0}$ | constant of permeation for the $m$ molecule in ice, | m$^2$ s$^{-1}$ |
| $D_{m}$ | diffusion coefficient of the $m$ molecule in ice | m$^2$ s$^{-1}$ |
| $D_{m}^{0}$ | constant of diffusion for the $m$ molecule in ice, | m$^2$ s$^{-1}$ |
| $S_{m}$ | solubility of the $m$ molecule in ice | mol mol$^{-1}$ MPa$^{-1}$ |
| $c_{m}^{0}$ | constant of solution for the $m$ molecule in ice | mol mol$^{-1}$ MPa$^{-1}$ |
| $E_{p}^{m}$ | activation energy of permeation for the $m$ molecule in ice | kJ mol$^{-1}$ |
| $E_{D}^{m}$ | activation energy of diffusion for the $m$ molecule in ice | kJ mol$^{-1}$ |
| $E_{S}^{m}$ | activation energy of solubility for the $m$ molecule in ice | kJ mol$^{-1}$ |
| $R$ | gas constant (8.314) | j mol$^{-1}$ K$^{-1}$ |
| $f_{m}$ | diffusive flux of the $m$ molecule | mol m$^{-2}$ s$^{-1}$ |
| $F_{m}$ | net flux of the $m$ molecule dissolved in ice | mol s$^{-1}$ |
| $\Delta z$ | grid size | m |
| $\tau_{r}$ | relative thinning function | |
| $\Delta t$ | time step | s |
Table A2. Model parameters.

|                         | IkkFk01 | Salm01 | IkkFk05 |
|-------------------------|---------|--------|---------|
| Constant of dissociation pressure for N\(_2\) | \(a_{N_2}\) | 3.6905\(^a\) | 3.6905\(^a\) | 3.77\(^b\) |
| Constant of dissociation pressure for O\(_2\) | \(b_{O_2}\) | 688.9\(^a\) | 688.9\(^a\) | 4.17\(^b\) |
| Constant of dissociation pressure for N\(_2\) (K) | \(a_{N_2}\) | 3.679\(^a\) | 3.67\(^a\) | 710\(^b\) |
| Constant of dissociation pressure for O\(_2\) (K) | \(b_{O_2}\) | 717\(^a\) | 717\(^a\) | 850\(^b\) |
| Constant of diffusion or permeation for N\(_2\) in ice (m\(^2\) s\(^{-1}\)) | \(k^0_{N_2}\) | \(2.4 \times 10^{-9}\),\(^{c}\) | \(5.7 \times 10^{-22}\),\(^{d}\) | – |
| Constant of diffusion or permeation for O\(_2\) in ice (m\(^2\) s\(^{-1}\)) | \(k^0_{O_2}\) | \(2.4 \times 10^{-8}\),\(^{e}\) | \(1.7 \times 10^{-21}\),\(^{d}\) | – |
| Constant of solution for N\(_2\) in ice (mol mol\(^{-1}\) ice MPa\(^{-1}\)) | \(g^0_{N_2}\) | – | – | \(4.5 \times 10^{-7}\),\(^{e}\) |
| Constant of solution for O\(_2\) in ice (mol mol\(^{-1}\) ice MPa\(^{-1}\)) | \(g^0_{O_2}\) | – | – | \(3.7 \times 10^{-7}\),\(^e\) |
| Constant of diffusion for N\(_2\) in ice (m\(^2\) s\(^{-1}\)) | \(D^0_{N_2}\) | – | – | \(2.0 \times 10^{-10}\),\(^e\) |
| Constant of diffusion for O\(_2\) in ice (m\(^2\) s\(^{-1}\)) | \(D^0_{O_2}\) | – | – | \(3.5 \times 10^{-9}\),\(^e\) |
| Activation energy of permeation for N\(_2\) in ice (kJ mol\(^{-1}\)) | \(E^k_{N_2}\) | 55.57\(^e\) | 50\(^d\) | – |
| Activation energy of permeation for O\(_2\) in ice (kJ mol\(^{-1}\)) | \(E^k_{O_2}\) | 55.57\(^e\) | 50\(^d\) | – |
| Activation energy of solution for N\(_2\) in ice (kJ mol\(^{-1}\)) | \(E^s_{N_2}\) | – | – | 9.2\(^e\) |
| Activation energy of solution for O\(_2\) in ice (kJ mol\(^{-1}\)) | \(E^s_{O_2}\) | – | – | 7.9\(^e\) |
| Activation energy of diffusion for N\(_2\) in ice (kJ mol\(^{-1}\)) | \(E^D_{N_2}\) | – | – | 5.1\(^e\) |
| Activation energy of diffusion for O\(_2\) in ice (kJ mol\(^{-1}\)) | \(E^D_{O_2}\) | – | – | 9.7\(^e\) |

\(^a\) Miller (1969). \(^b\) Kuhs et al. (2000). \(^c\) Ikeda-Fukazawa et al. (2001). \(^d\) Salamatin et al. (2001). \(^e\) Ikeda-Fukazawa et al. (2005).

Table A3. Examples of dissociation pressure, diffusivity, solubility, and permeability (at 240 K).

|                         | IkkFk01 | Salm01 | IkkFk05 | Ar(I) | Ar(II) |
|-------------------------|---------|--------|---------|-------|--------|
| Dissociation pressure of N\(_2\) (MPa) | \(p^d_{N_2}\) | 6.48\(^a\) | 6.61\(^b\) | 6.48\(^a\) | – |
| Dissociation pressure of O\(_2\) (MPa) | \(p^d_{O_2}\) | 4.25\(^a\) | 4.92\(^b\) | 4.25\(^a\) | – |
| Dissociation pressure of Ar (MPa) | \(p^d_{Ar}\) | – | – | 3.54 | 3.54 |
| Diffusivity of N\(_2\) (m\(^2\) s\(^{-1}\)) | \(D_{N_2}\) | 1.55 \times 10^{-11} | – | – | – |
| Diffusivity of O\(_2\) (m\(^2\) s\(^{-1}\)) | \(D_{O_2}\) | 2.71 \times 10^{-11} | – | – | – |
| Solubility of N\(_2\) (mol mol\(^{-1}\) ice MPa\(^{-1}\)) | \(S^k_{N_2}\) | 4.48 \times 10^{-9} | – | – | – |
| Solubility of O\(_2\) (mol mol\(^{-1}\) ice MPa\(^{-1}\)) | \(S^k_{O_2}\) | 7.06 \times 10^{-9} | – | – | – |
| Permeability of N\(_2\) (m\(^2\) s\(^{-1}\) MPa\(^{-1}\)) | \(k_{N_2}\) | \(1.27 \times 10^{-20}\) | \(1.02 \times 10^{-20}\) | \(6.95 \times 10^{-20}\) | – |
| Permeability of O\(_2\) (m\(^2\) s\(^{-1}\) MPa\(^{-1}\)) | \(k_{O_2}\) | \(9.49 \times 10^{-20}\) | \(3.12 \times 10^{-20}\) | \(1.91 \times 10^{-19}\) | – |
| Permeability of Ar (m\(^2\) s\(^{-1}\) MPa\(^{-1}\)) | \(k_{Ar}\) | – | – | 2.55 \times 10^{-20} | 2.07 \times 10^{-20} |

\(^a\) Miller (1969). \(^b\) Kuhs et al. (2000).
Appendix B: Supplementary figures

Figure B1. Pair difference (“a2” piece minus “a1” piece, Fig. 1) in the bubbly ice for (a) $\delta^{18}O_2/N_2$, (b) $\delta_{Ar}/N_2$, (c) $\delta^{18}O$, and (d) $\delta^{15}N$. Solid circles show the data from the samples after removing the outer ice by $>5$ mm thickness, and open circles show the data with $\sim3$ mm removal. Gray shadings are estimated 2σ uncertainty (twice the pooled standard deviations of the pair differences for clathrate hydrate ice below 1480 m).

Figure B2. Results of the evacuation experiment for $\delta^{18}O_2/N_2$, $\delta_{Ar}/N_2$, $\delta^{15}N$, and $\delta^{18}O$ in (a) bubbly ice (446.4 m) and (b) clathrate hydrate ice (2001.1 m). Dashed lines are the average of all five values.
Figure B3. Absolute pair differences of (a) $\delta O_2/N_{2_{\text{gravcorr}}}$, (b) $\delta Ar/N_{2_{\text{gravcorr}}}$, (c) $\delta^{15}N$, and (d) $\delta^{18}O_{\text{gravcorr}}$. Gray shadings indicate 2σ uncertainty (same as Fig. B1).
Figure B4. Differences of the values in the outer and inner pieces (outer minus inner) for (a) $\delta$O$_2$/N$_2$gravcorr, (b) $\delta$Ar/N$_2$gravcorr, (c) $\delta^{18}$O$_{\text{gravcorr}}$, (d) $\delta^{15}$N, (e) CH$_4$ concentration, and (f) N$_2$O concentration. Gray shadings indicate 2σ uncertainty (same as Fig. B1). Black and red markers show the data using the outer samples stored at −50 and −30°C, respectively.

Figure B5. Relationship between $\delta$O$_2$/N$_2$gravcorr and $\delta^{18}$O$_{\text{gravcorr}}$ for (a) the last 2000 years for bubbly ice, (b) pair differences in bubbly ice zone, (c) pair differences in BCTZ, (d) pair differences in clathrate hydrate ice zone, and (e) differences between the outer ice and inner ice (bubbly ice and clathrate hydrate ice). The dashed line represents linear fit to the data ($\Delta \delta^{18}$O$_{\text{gravcorr}} = -0.0083 \Delta \delta$O$_2$/N$_2$gravcorr + 0.0018).
Appendix C: Supplementary tables

Table C1. Pooled standard deviations for $\delta^{15}N$, $\delta O_2/N_2^{gravcorr}$, and $\delta Ar/N_2^{gravcorr}$ (%).

| Zone | $\delta^{15}N$ | $\delta O_2/N_2^{gravcorr}$ | $\delta Ar/N_2^{gravcorr}$ | n  |
|------|----------------|-----------------------------|-----------------------------|----|
| 112–450 m (bubbly ice) | 0.006 | 0.305 | 0.154 | 20 |
| 450–800 m (upper BCTZ) | 0.004 | 0.862 | 0.776 | 24 |
| 800–1200 m (lower BCTZ) | 0.005 | 2.662 | 2.555 | 46 |
| 1200–1480 m (clathrate hydrate ice) | 0.004 | 0.599 | 0.565 | 13 |
| 1480–1980 m (clathrate hydrate ice) | 0.007 | 0.184 | 0.112 | 26 |

Table C2. Slopes for $\delta Ar/N_2^{gravcorr}$ vs. $\delta O_2/N_2^{gravcorr}$ and for $\Delta \delta Ar/N_2^{gravcorr}$ vs. $\Delta \delta O_2/N_2^{gravcorr}$.

| Site name | Zone | Remarks | Slope | 1σ  | Reference for the original data |
|-----------|------|---------|-------|-----|---------------------------------|
| Dome Fuji | All (112–1980 m) | well preserved | 0.51 | 0.01 | This study                       |
| Dome Fuji | Bubbly ice (112–450 m) | well preserved | 0.50 | 0.01 | This study                       |
| Dome Fuji | Upper BCTZ (450–800 m) | well preserved | 0.45 | 0.01 | This study                       |
| Dome Fuji | Lower BCTZ (800–1200 m) | well preserved | 0.61 | 0.01 | This study                       |
| Dome Fuji | Clathrate hydrate (1200–1980 m) | well preserved | 0.42 | 0.02 | This study                       |
| Dome Fuji | Outer ice | significantly affected by gas loss | 0.25 | 0.01 | This study                       |
| Nine sites* | Bubbly ice | | 0.46 | 0.03 | Sowers et al. (1989)            |
| Byrd | All (145–2100 m) | extremely negative below 1800 m | 0.42 | 0.01 | Bender et al. (1995)            |
| Vostok-3G | All (140–2058 m) | thermally drilled | 0.70 | 0.01 | Bender et al. (1995)            |
| Dome C | Bubbly ice (180–625 m) | poor quality | 0.26 | 0.01 | Bender et al. (1995)            |
| GISP2 | Bubbly ice (73–213 m) | | 0.54 | 0.03 | Bender et al. (1995)            |
| Siple Dome | Bubbly ice (75–973 m) | highly fractured | 0.58 | 0.01 | Severinghaus et al. (2009)      |
| WAIS Divide | All (80–2625 m) | slightly affected by gas loss | 0.93 | 0.01 | Seltzer et al. (2017)           |
| WAIS Divide | Bubbly ice (80–2625 m) | slightly affected by gas loss | 0.64 | 0.01 | Seltzer et al. (2017)           |
| WAIS Divide | BCTZ (650–1600 m) | slightly affected by gas loss | 1.00 | 0.01 | Seltzer et al. (2017)           |
| WAIS Divide | Clathrate hydrate (1600–2625 m) | slightly affected by gas loss | 0.97 | 0.01 | Seltzer et al. (2017)           |
| SPICE | Bubbly ice (125–700 m) | slightly affected by gas loss | 0.60 | 0.05 | Severinghaus (2019)             |
| SPICE | BCTZ (700–1140 m) | slightly affected by gas loss | 1.47 | 0.07 | Severinghaus (2019)             |
| SPICE | Clathrate hydrate (1140–1751 m) | slightly affected by gas loss | 0.54 | 0.01 | Severinghaus (2019)             |
| NEEM | Bubbly ice (112–460 m) | slightly affected by gas loss | 0.45 | 0.01 | Oyabu et al. (2020)             |

$\Delta \delta Ar/N_2^{gravcorr}$/$\Delta \delta O_2/N_2^{gravcorr}$ (pair difference)

| Site name | Zone | Remarks | Slope | 1σ  | Reference for the original data |
|-----------|------|---------|-------|-----|---------------------------------|
| Dome Fuji | Bubbly ice (112–450 m) | well preserved | 0.53 | 0.08 | This study                       |
| Dome Fuji | Upper BCTZ (450–800 m) | well preserved | 0.92 | 0.03 | This study                       |
| Dome Fuji | Lower BCTZ (800–1200 m) | well preserved | 1.01 | 0.03 | This study                       |
| Dome Fuji | Clathrate hydrate (1200–1980 m) | well preserved | not detectable | | This study                       |
| Dome Fuji | Outer piece vs. inner piece | | 0.22 | 0.01 | This study                       |
| Byrd | All (145–2100 m) | extremely negative below 1800 m | 0.47 | 0.01 | Bender et al. (1995)            |
| Vostok-3G | All (140–2058 m) | thermally drilled | 0.54 | 0.03 | Bender et al. (1995)            |
| Dome C | Bubbly ice (180–625 m) | poor quality | 0.24 | 0.03 | Bender et al. (1995)            |
| Siple Dome | Bubbly ice (75–973 m) | highly fractured | 0.67 | 0.01 | Severinghaus et al. (2009)      |
| WAIS Divide | Bubbly ice (80–650 m) | slightly affected by gas loss | 0.72 | 0.01 | Seltzer et al. (2017)           |
| WAIS Divide | BCTZ (650–1600 m) | slightly affected by gas loss | 1.19 | 0.01 | Seltzer et al. (2017)           |
| SPICE | BCTZ (700–1140 m) | slightly affected by gas loss | 0.84 | 0.06 | Severinghaus (2019)             |
| SPICE | Clathrate hydrate (1140–1751 m) | slightly affected by gas loss | 1.60 | 0.08 | Severinghaus (2019)             |
| NEEM | Bubbly ice (112–460 m) | slightly affected by gas loss | 0.62 | 0.01 | Oyabu et al. (2020)             |

* Byrd, Camp Century, Cite, Dominion Range, Dye 3, D10, D57, and Dome C ice cores.
Data availability. All data presented in this study are available at the NIPR ADS data repository (https://ads.nipr.ac.jp/dataset/A20210430-001, last access: 7 December 2021; https://doi.org/10.17592/001.2021043001, Oyabu et al., 2021) and will be available on the NOAA paleoclimate database.

Author contributions. IO and KeK designed and led the study. IO, KeK, KyK, MH, SA, SM, and TN developed the methodologies and carried out the measurements. IO, KeK, and JDM worked directly with the data. IO, KeK, TU, SF, JPS, and JDM discussed the gas fractionation processes. IO and KeK wrote the manuscript with contributions from all co-authors. IO, KeK, and SF acquired funding.

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