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Key Points:

- The gas pressure distribution in bubbly ice can be inferred by measuring velocities of bubbles migrating under a temperature gradient
- The bubble close-off history can be reconstructed from the pressure distribution
- Gas-trapping functions can be determined for different depths (climatic periods)

Supporting Information:

- Supporting Information S1
- Figure S1

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Temperature-Driven Bubble Migration as Proxy for Internal Bubble Pressures and Bubble Trapping Function in Ice Cores

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Abstract Ice core data record significant and abrupt past climate changes that are associated with large and rapid changes in atmospheric greenhouse gases, such as methane. Due to the gradual close-off of gas bubbles and the relatively fast diffusion of gases within the firn column, even a discrete or quick step increase in air composition may be smoothed or integrated in the data; current laboratory analyses of gases consider the mean gas content value across all bubbles in a sample, rather than the content of individual bubbles. The convolution of the distribution of trapping ages with the history of atmospheric composition thus smears the measured gas record in each sample. We developed a nondestructive method to determine pressure distribution in all bubbles in a sample and estimate the shape of the trapping function derived from that bubble pressure distribution and site characteristics. Our method works not only for present conditions but also through varying paleo-atmospheric conditions, while providing accurate measurements of morphological bubble properties. The method is based on using temperature-driven air bubble migration as a proxy for the pressure of individual bubbles, which we combine with a model for bubbly ice densification to obtain the gas trapping functions and constrain the age distribution of air bubbles for past conditions, which are preserved at different depths. The trapping functions will help us to obtain a more accurate gas signal in the future that is less attenuated through the age distribution of the gas during the close-off process.

1. Introduction

Ice cores have revolutionized our understanding of the relationship between greenhouse gases and global temperatures by providing unique archives of past atmospheric conditions. Gases trapped within bubbles provide high-fidelity records of past greenhouse gas levels (especially CO₂ and CH₄), which are vital for understanding the implications of past and present changes in atmospheric composition (e.g., Blunier et al., 2004; Dansgaard et al., 1969, 1993; Gow & Williamson, 1975; Johnsen et al., 1972; Jouzel et al., 1997; Petit et al., 1999; Schwander, 1989; Stauffer, Fischer, et al., 1985). Ice core records revealed large abrupt climate changes in the past that are associated with changes in atmospheric greenhouse gases, such as methane (e.g., Alley, 2000; Stauffer, Fischer, et al., 1985; Schwander et al., 1993). Large uncertainties remain, however, in the age distribution of gases as well as in the relative timing of temperature and greenhouse gas variations due to, in large part, age differences between the gas trapped in air bubbles and the surrounding ice from which air temperature is often reconstructed, leading to an ice age-gas age difference, or Δ Age (Schwander & Stauffer, 1984; Severinghaus et al., 2010). Most notably, the gas in air bubbles does not have a discrete age but rather an age distribution, caused by (a) convection (mainly in the top 5 m of the firn layer for most modern sites; Bender et al., 2006; Buizert, 2011; Kawamura et al., 2006), (b) diffusion within the firn column (Blunier et al., 2004; Buizert, 2011; Schwander et al., 1988), and (c) gradual and stochastic bubble close-off within the close-off zone (Mitchell et al., 2015; Schwander et al., 1993). The first two processes already lead to smoothing of the atmospheric signal prior to close-off and are often accounted for by existing models (see Buizert, 2011, for a review). In this study, we discuss the third smoothing process noted above that is usually not accounted for in existing models: specifically, how the close-off depth of individual bubbles can vary by

tens of meters, which leads to a distribution of pressures and sizes for bubbles at a given depth (Gow, 1970a; Schwander & Stauffer, 1984).

Due to the gradual close-off of gas bubbles and the relatively fast diffusion of gases within the firn column (Blunier et al., 2004), signals of fast changes in atmospheric greenhouse gases are smoothed and attenuated, thus broadening the age distribution in the measured gas record in each sample. The width of the age distribution, or the gas trapping function, determines the time resolution for detection of changes in atmospheric composition (Schwander & Stauffer, 1984; Spahni et al., 2003).

In addition, the chemical and/or isotopic indicators in ice that are used as temperature proxies are derived directly from the original precipitation that led to the formation of the specific layer being measured and thus reflects the age of that precipitation event (Dansgaard, 1964; Johnsen et al., 1972; Jouzel et al., 1997; Schwander et al., 1993). In contrast, the air enclosed in bubbles has a similar composition as the overlying atmosphere at the time of bubble close-off and is therefore younger than the surrounding ice. Bubble close-off depends on local temperature and precipitation (Schwander & Stauffer, 1984). This ice age-gas age difference can be substantial in East Antarctica, ranging from 35 years at the high accumulation site of Law Dome (i.e., ~100 cm; Etheridge et al., 1992) to 7,000 years at the low accumulation site at Vostok during the Last Glacial Maximum (i.e., ~1 cm; e.g., Bender et al., 2006; Ekaykin et al., 2004) and even up to 12,000 years at the low accumulation site of Taylor Dome during the Last Glacial Maximum (i.e., ~0.35 cm; e.g., Baggenstos, 2015; Baggenstos et al., 2018).

The age difference and distribution of gases decreases the resolution of the gas reconstructions from ice cores and limits our ability to determine the phase relationship between gas and ice and, thus, the impact of rapid changes of greenhouse gases on surface temperatures and vice versa (Blunier et al., 2004; Schwander & Stauffer, 1984; Spahni et al., 2003, 2005).

The attenuation is likely to be larger for colder sites with less accumulation (such as Vostok), as well as for shorter duration periods of atmospheric gas variations. Spahni et al. (2003) show that fast atmospheric variations of CH₄ (Alley et al., 1997; Alley, 2000; Blunier et al., 1995; Brook et al., 1996; Chappellaz et al., 1993), similar in magnitude to recent anthropogenic changes in greenhouse gases (Stauffer, Fischer, et al., 1985), are not erased in ice core records from low accumulation sites. The pore close-off depth, that is, the depth at which contemporary gas is sealed in the ice, depends on surface temperature and snow accumulation history, which leads to a distribution of pressures for air bubbles at a given depth (Gow, 1968; Schwander & Stauffer, 1984). Currently, the trapping functions of the bubbles can be directly estimated in present-day firn-to-ice transition zones by measuring the closed bubble volume as a function of depth (Mitchell et al., 2015; Schwander & Stauffer, 1984; Schaller et al., 2017; Stauffer, Schwander & Oeschger 1985) but cannot be determined for the past. The Δ age can be estimated empirically either using gas and ice synchronization (stratigraphic markers) for certain events (Parrenin et al., 2012) or by combining measurements of present bubble volumes, depths, and density with firn densification models (Salamatin et al., 2009; Schwander & Stauffer, 1984). The latter technique is only valid for present-day trapping functions. Firn densification models are, however, tuned and validated to present-day conditions, and uncertainties on the bubble close-off depth for cold and low accumulation intervals remain (Bender et al., 2006; Loulergue et al., 2007; Parrenin et al., 2012; Salamatina et al., 2009). To our knowledge, the only previous works to estimate pressure from individual air bubbles in ice were by Scholander and Nutt (1960) for icebergs in Greenland, by Gow and Williamson (1975) for the Antarctic Byrd ice core, and by Lipenkov et al. (1997) and Lipenkov (2000) for Vostok. None of the studies focused on the bubble pressure distribution at a given depth, however. Information on the depth distribution at which air trapped in the firn becomes disconnected from the overlying atmosphere (bubble trapping function) would improve the reconstructions of the age distribution of the gas that is extracted from ice cores (Schwander et al., 1997), as well as the estimates of the magnitude of greenhouse gas signals. Mitchell et al. (2015) recently highlighted that “the observed smoothing of the trapped gas records is less than expected from the gradual bubble closure ... because the vertical diffusion of gas is prevented by impermeable horizontal layers in the lock-in-zone.” The smoothing of the gas signal is thus also affected by the location of the lock-in zone (LIZ) and not by the gas trapping function alone. The LIZ is the zone below the first impermeable high-density layer, below which diffusion is minimal, and gases can generally not be exchanged with the firn above (Buizert et al., 2012). The bubbles in the LIZ are not all closed off, and air exchange through advection within the surrounding ice can take place (Mitchell et al., 2015).

While the impermeable horizontal layers might not be present for all sites (we currently have no measurements on whether they are present in the Roosevelt Island Climate Evolution [RICE]), we appreciate that the trapping function is obviously not the sole factor in determining the gas age distribution. The trapping function, however, will help toward improving the resolution of gas age measurements, and its theoretical prediction based on the continuous densification concepts will estimate the degree of maximum smoothing.

Here, we present a new method that will help constrain the gradual close-off functions of gas bubbles in ice cores. We used laboratory experiments on air bubble migration under a temperature gradient as a proxy to estimate bubble pressure distribution in the RICE ice core samples from different depths. The different depths represent different climatic conditions. In combining our experiment results with a bubbly-ice densification model (Lipenkov et al., 1997; Salamatin et al., 1997), we then determined the bubble trapping function for each depth, and we estimated whether those functions have changed for the different depths. We discuss the applications of our method to the RICE core and show an example of a possible climatic shift in the last 200 years.

In future work, we aim to estimate how changes in climatic conditions affect the gas trapping function. The gas trapping functions can be used to deconvolve the greenhouse gas signal in the ice core record and to more accurately estimate the magnitude of the greenhouse gas signal and determine the signal attenuation. In doing so, we will contribute to a better understanding of the relationship between rapid climatic shifts and greenhouse gas signals. Our method is limited to the depth range below bubble close-off depth and ~ 100 – 200 m (depending on ice core site characteristics and how soon after core recovery the experiments are made), which is discussed later in this paper.

2. Methods

2.1. Ice Cores

We used samples from two ice cores in this study: (1) the RICE project ice core (Bertler et al., 2018), which was drilled between 2011 and 2013 and (2) the Mount Erebus Saddle (MES) ice core, which was drilled in 2004/2005. Both cores were stored in the -35°C cold laboratory at the New Zealand Ice Core Laboratory (GNS Science, New Zealand) before shipping of the evaluated samples to the Institute for Snow and Avalanche Research cold laboratory in Davos, Switzerland. The ice core samples were shipped with sufficient dry ice and arrived in Davos in good condition.

The RICE core site (79.36°S , 161.71°W ; 550 m above sea level) is located on Roosevelt Island, a grounded ice rise at the northern edge of the Ross Ice Shelf. The total length of the recovered ice core is 764 m (Bertler et al., 2018). As a coastal core, it is characterized with relatively high accumulation of 20–30 cm/year water equivalent (Winstrup et al., 2017), and an average temperature of $\approx -25^{\circ}\text{C}$. We evaluated five samples from RICE at 50, 55, 60, 80, and 100 m, using micro computed tomography (micro-CT) data. Because the density of the 50-m sample ($\rho = 794 \text{ kg/m}^3$) was below the close-off density for ice (~ 810 – 830 kg/m^3 ; e.g., Hörhold et al., 2011), we did not use that sample for bubble migration experiments.

The MES core site is located on Mount Erebus Saddle (1,680 m above sea level, $77^{\circ}30.900\text{S}$, $167^{\circ}40.590\text{E}$), and is close to the edge of the Ross Ice Shelf in the southwestern Ross Sea sector (Rhodes et al., 2012). The total length of the recovered ice core was 168 m (depth of the ice at the location is 209 m). Due to the proximity of seasonally open water in the Ross Sea polynya, Mount Erebus Saddle is a local snow accumulation zone between Mount Erebus and Mount Terra Nova, with annual accumulation of 40 cm/year water equivalent (Rhodes et al., 2009) and average annual temperature of -19°C . We evaluated six samples from MES at 70, 75, 85, 90, 120, and 140 m. All samples were below pore close-off depth, as was observed in the micro-CT images. Mount Erebus Saddle can experience melt, which could in turn have affected the close-off process.

2.2. Bubble Migration Rates Under Temperature Gradients

When a temperature gradient is applied to gas bubbles in an ice sample, the bubbles migrate toward warmer ice (Shreve, 1967; Stehle, 1967). This motion is caused by sublimation from the warm wall and subsequent frost deposition on the cold wall of the bubble (Dadic et al., 2010; Nakaya, 1956; Shreve, 1967; Stehle, 1967). The migration rate depends on ice temperature and bubble pressure and is proportional to the temperature gradient (Shreve, 1967). While the migration rate equations have been developed for spherical bubbles, the additional increase in pressure through surface tension differences based on curvature inside the bubble is negligible (Dadic et al., 2010; Ketcham & Hobbs, 1969).

Dadic et al. (2010) observed substantial variability of migration rates at given temperatures, which were correlated with bubble size. The bubble size effects (through curvature) were shown to be too small to cause detectable changes in migration rates and they concluded that, while the bubble size does correlate with migration rates, it does so only because smaller bubbles have generally higher pressures (because they were likely closed off earlier) and not due to curvature effects. They concluded that the spread in migration rates reflect the variations in bubble pressures in the ice core samples. Thus, we propose here that air bubble migration can be used as a proxy to measure the pressure of individual bubbles and can help constrain the gradual close-off of gas bubbles and the resulting age distribution of gases in ice cores. At a given atmospheric pressure, the pressure in bubbles is a function of hydrostatic pressure in ice and the time since the close-off of that bubble. If the pressure distribution in a sample is relatively narrow, the close-off of bubbles must have occurred within a narrower depth range and/or time interval than if the pressure distribution is broader. The bubble lock-in and close-off depth depend on temperature, precipitation, and wind history: Higher accumulation favors a deeper close-off; lower temperature favors a deeper close-off. Wind speed affects the local accumulation, surface snow density, snow microstructure, and turbulent fluxes, which in turn affect the diffusivity and close-off density in the firn (Kaspers et al., 2004; van den Broeke, 2008). Across existing ice core sites, colder, lower-accumulation-rate sites have generally a deeper close-off depth than warmer, high accumulation sites (Herron & Langway Jr, 1980; Kaspers et al., 2004; van den Broeke, 2008). For very cold, low-accumulation conditions, the age distribution of gases is wider than for warmer sites with higher accumulation rates (Spahni et al., 2003).

The depth range where this method can be applied is below bubble close-off depth, down to ~100–200 m (depending on the location and site characteristics), for cores that have been recovered more than a year prior to the experiments. This limit comes from studies that show that bubbles with pressures >1.3–1.6 MPa (>100–200 m), with ~1.6 MPa being within the tensile strength of ice, can undergo significant decompression or fracturing during/after core recovery when the ice core is exposed to a much lower atmospheric pressure (Gow & Williamson, 1975; Langway, 1958; Neff, 2014). This decompression and fracturing thus fails to preserve the in situ bubble pressures at depth. For ice under pressures up to ~1.3–1.6 MPa, the pressure distribution of bubbles from a single depth provides a record of the trapping function of air bubbles in the firn column corresponding to a specific time in the past. Air bubbles with higher pressures would have been closed off higher in the firn column and thus have had time to equilibrate with the surrounding ice pressure, while air bubbles that have been closed off recently would have pressures that are closer to today's atmospheric pressure above the firn column (Stauffer, Schwander & Oeschger 1985). At a depth of $\approx$ 300 m (for Vostok conditions), the natural variability of bubble pressure becomes statistically negligible, as all bubbles have reached the asymptotic phase of the ice densification process. At this depth, slight pressure differences between individual bubbles that were closed off at varying depths in the firn column are indistinguishable (Lipenkov et al., 1997). The asymptotic phase for the warmer RICE site is likely shallower and we expect the natural variability of bubble pressure to disappear around 200-m depth. More accurate sampling of the natural variability in bubbles pressures might allow measurements over a broader depth scale in the future. If the experiments are done within a year of the core recovery, the core relaxation is minimal and the method can be applied until the depth where the bubbles reach the asymptotic phase (if that depth is shallower than the start of the brittle zone). Generally, all bubbles with pressure over atmospheric pressure will relax at a rate that depends on storage temperature and bubble pressure (Gow, 1970b; 1971; Neff, 2014). For this reason, our proposed method to estimate trapping functions of air bubbles in ice should be applied as soon as possible after core recovery.

We conducted two sets of experiments on temperature-driven air bubble migration rates. First, we used a temperature gradient stage mounted on a microscope, set within our cold-room laboratory (Dadic et al., 2010; Light et al., 2009), to measure migration rates of single air bubbles in the RICE ice core at three different depths (60, 80, and 100 m). The experiments were carried out using a Nikon Eclipse 50i microscope fitted with a camera head, and a 4X magnification objective lens, resulting in images with a resolution of 1 $\mu\text{m}/\text{pixel}$. The experiments were made following Light et al. (2009). This first set of experiments is only suited to measure pressure in single air bubbles and not feasible to use for determining an accurate pressure distribution in an entire sample. The second set of experiments, carried out at a much lower resolution of 18 μm , was conducted on the RICE core (at five different depths) and on the MES core (at six different depths) using micro-CT and a “snow breeder” (Pinzer & Schneebeli, 2009; Schneebeli & Sokratov, 2004; Wiese &

Schneebeli, 2017a). Micro-CT imagery produces a 3-D model of a physical snow or ice sample by combining (or stacking) sequential high energy, 2-D X-ray cross-sectional images (or “slices”). It can distinguish between the ice phase and the vapor phase in a sample by differentiating image brightness and is therefore a suitable tool to determine bubble migration rates (Figure A1). This, therefore, allows for calculations of the pressure distribution of all bubbles in a sample. Micro-CT has been shown to work for a range of snow and firn research applications (Hagenmuller et al., 2013; Haussener et al., 2012; Kaempfer et al., 2005; Keegan et al., 2014; Schneebeli & Sokratov, 2004; Wang & Baker, 2013) as well as for studying air bubbles in ice (Dadic et al., 2013). Additional to the migration rate measurements, we also determined porosity, bubble size distribution, and bubble number density (Supporting Information S1, Figure S1) for each sample (Spencer et al., 2006). The snow breeder is a custom-designed “sample holder that allows applying well-defined and stable thermal gradients to a snow/ice sample while it is scanned in an x-ray micro-tomograph” (Pinzer & Schneebeli, 2009; Wiese & Schneebeli, 2017a; 2017b).

After a first initial scan, the snow breeder was turned on for 42–72 hr, and subsequent scans were carried out every 6 hr. The height of the samples was ≈ 16 –20 mm, the x-y dimension between $\approx 12 \times 12 \text{ mm}^2$ and $\approx 14 \times 14 \text{ mm}^2$, respectively. The sample size has no effect on the measurements, because the migration velocity scales with the temperature gradient. The set temperature within the breeder instrumentation ranged from -6°C down to -10°C , resulting in temperature gradients ΔT of ≈ 2 –2.5 K/cm, depending on the height of the sample. We assumed a linear temperature profile through the sample to calculate the temperature at the position of individual bubbles during the experiment. Diffusive gas loss from closed bubbles could occur at -6°C , but lowering the experiment temperatures was not feasible because the experiments would take too long leading to substantial frost build up inside the bubbles. The resolution of the initial micro-CT images was $18 \mu\text{m}$ per voxel. To perform the image processing, the resolution of the images was downsampled to $54 \mu\text{m}$ per voxel. We compared the migration rates from the downsampled images to the migration rates from the first set of measurements (with the microscope) with $1\text{-}\mu\text{m}$ resolution and found that both sets of experiments show the same range of migration rates. This comparison gave us confidence that the results from the micro-CT are adequately resolved.

The migration rates were determined from the micro-CT images in the following way: First, the displacements of each voxel between the first and the last CT image of one experiment (Figure A1) were calculated using digital image correlation (Pinzer et al., 2012; Westerweel, 1997). The spatial correlation of the two displaced images was measured using particle image velocimetry (PIV), developed in the field of fluid dynamics (Westerweel, 1997). “For every CT image, a displacement vector $\Delta = (\Delta x, \Delta y, \Delta z)$ with respect to a subsequent image was assigned to each ice voxel by shifting one image until the local correlation within a three-dimensional window was maximized” (Pinzer et al., 2012). The correlation gives an estimate of the mean displacement with subpixel accuracy by fitting a Gaussian or similar function to the tallest correlation peak (Westerweel, 1997). Then the individual bubbles were identified by a connected-component labeling algorithm. The algorithm consists of assigning a unique label to all pixels of each connected object in a binary image (He et al., 2017). All partially open bubbles at cut surfaces during the image processing were removed before the calculations of the bubble migration rates.

Volumes for individual bubbles were determined by multiplying each bubble's total voxel count with the known metric volume of the voxel. Bubble radii were then calculated from the measured volumes, assuming spherical bubble shape.

Because the temperatures within our experiments were warmer than the storage temperatures, this could have allowed for faster relaxation of the bubbles. Due to the rather quick experimentation times (42–72 hr), in full agreement with estimates from Salamatov and Lipenkov (1993), we do not expect that bubble expansion or pressures were affected. We did not observe notable changes in bubble size during the experiments; for most samples, the decrease in pore size during the experiment, due to what we think is frost build up inside the bubbles, was less than 5%. The exceptions are samples MES120, MES140, and RICE55, where the decrease in pore size is up to 20%. The changes in pore size contribute to the uncertainty in our pressure calculations.

2.3. Modeling the Evolution of Bubble Pressure With Depth

To better resolve the climate signal with our pressure estimations, it is necessary to estimate the depth at which each bubble has been closed off. The close-off depth and the pressure increase after the close-off are dependent on the densification process both above as well as below the close-off, which is a function not only

of temperature and accumulation rate but also of the rheological behavior of ice and other factors such as layering, impurities, or porosity (Alley et al., 1982; Arnaud et al., 1998, 2000; Freitag et al., 2013; Gow, 1968; Gregory et al., 2014; Hörhold et al., 2011, 2012; Mitchell et al., 2015; Salamatin et al., 1997, 2009; Salamatin & Duval, 1997; Schaller et al., 2017; Wilkinson & Ashby, 1975). There is a reasonable number of bubbly-ice densification models, and here we followed the mechanistic approach that, in a more explicit and detailed way describes the pressure evolution in bubbles after close-off (Salamatin et al., 1997; Lipenkov et al., 1997). The mathematical model is based on previous work on creep flow of bubbly ice, pressure relaxation and kinematic interaction of ice sheet flow with compressibility effects by Glen (1955); Langway (1958); Gow (1968); Wilkinson and Ashby (1975); Pimienta and Duval (1987); Pimienta and Duval (1989); Salamatin (1991); Salamatin and Lipenkov (1993); Salamatin and Duval (1997). The model does not account for layering of the firn (Hörhold et al., 2011; Mitchell et al., 2015) and the LIZ, below which the effective diffusivity of gases ceases (Battle et al., 1996; Buizert et al., 2012; Mitchell et al., 2015; Schaller et al., 2017). We will discuss how this could affect our results later. The model is described in detail in Salamatin et al. (1997); Lipenkov et al. (1997) and uses the generalized polynomial form of the rheological relationship for ice.

The model predicts the densification process below the mean close-off level in terms of locally averaged characteristics, for the mean bubble-size, assuming that all bubbles are closed off at the same time and depth. Therefore, to solve the inverse problem and estimate possible differences in bubble pressures for groups of bubbles closed at different depths, we applied the model to the samples from the RICE core assuming different close-off depths in the range of 40–65 m (± 10 m each side from the density-estimated close-off depth for RICE of 50–55 m, where $\rho = 830 \text{ kg/m}^3$).

The above assumption that all bubbles are closed off simultaneously does not change the compression rates greatly in the upper part of the bubbly ice, in the proximity of the close-off zone (50–55 m), because the pressure in bubbles remains much lower than the load pressure in ice, which governs the densification process. At depths shallower (40–50 m) than the average close-off, however, the assumption that all bubbles are closed off at the same depth, instead of just a few closed bubbles with many open pores, slightly changes the compression rate of the ice at depth, which can affect the porosity evolution. The change is not large, and will be discussed in more detail later. Further down in the bubbly ice column (60–65 m), with the increase in bubble and ice pressures, the bubble volume decreases, and different bubbles compress independently, as single bubbles in an infinite ice bulk. Thus, the main influence of the assumption about simultaneous bubble closure on model predictions should be expected from possible inconsistencies in the total air mass captured by the bubbly ice. This impact could be compared to locking-in effects, but it seems to be negligible in our case of continuous/smooth density (as will also be discussed in detail later).

2.3.1. Model Parameters

We largely used the model in its original configuration, while tuning the modeled porosity to measured porosity. The rheological model parameters (μ_1 , μ_2 , α , Table 1) were optimized for measured porosities at the close-off depth of 55 m (density $\approx 830 \text{ kg/m}^3$). The optimized model parameters μ_1 , μ_2 were within the given boundaries in the original paper (Lipenkov et al., 1997), and we determined a value for α of 3.25, slightly lower than the 3.5 value from the original study. Those parameters were kept constant for all modeled close-off depths. The ice formation conditions (except accumulation rate) were adjusted for each depth separately (Table 1). Measured firn/ice density was used to calculate the load pressure at close-off p_{i0} and the porosity at close-off c_0 . A gradient in atmospheric pressure of 10 Pa/m was applied to calculate the initial bubble pressure at close-off (Martinerie et al., 1994).

3. Measurement Results

3.1. Ice Core Sample Properties

The density of the RICE samples, as measured by micro-CT, logarithmically increases from $\approx 790 \text{ kg/m}^3$ at 50 m to $\approx 900 \text{ kg/m}^3$ at 100 m. The micro-CT densities were systematically 15% smaller than the densities measured in the field, and we used the micro-CT densities in this manuscript. The calculated bubble radii are < 0.8 mm, with the bubble radius distribution generally showing larger bubbles in shallower samples and smaller bubbles in deeper samples (Figure 1a). The 80- and 100-m samples show a unimodal distribution of the bubble radii, with maxima around 0.3 and 0.25 mm, respectively. The 55-m sample, which is at the theoretical bubble close-off density of 830 kg/m^3 , does not show a unimodal distribution of bubble radii (average bubble radius is 0.4 mm). The 60-m sample ($\rho = 840 \text{ kg/m}^3$) has a maximum at 0.35 mm and a less pronounced maximum at 0.5 mm (average bubble radius is 0.41 mm).

Table 1
Parameters for the Bubbly-Ice Densification Model Application to RICE

Parameters	Value	Units
Rheophysical parameters		
Pure ice density (at 268K), ρ_0	919	kg/m ³
Linear viscosity coefficient, μ_1	3.2	MPa year
Nonlinear viscosity coefficient, μ_2	0.028	MPa ^{α} year
Creepancy index, α	3.25	—
Linear activation energy, Q_1	60	kJ/mole
Nonlinear activation energy, Q_2	60	kJ/mole
Flow interrelation coefficient, κ	5	—
Scale of averaging	0.7	—
Mean square Pb-c weight (0–1)	0.5	—
Ice formation conditions parameters		
Atmospheric pressure, p_0	0.091	MPa
Close-off depth, h_{c0}	40–65	m
Bubble pressure at close-off, p_{b0}	0.0826–0.1	MPa
Load pressure at close-off, p_{l0}	0.344–0.544	MPa
Ice porosity at close-off, c_0	0.17–0.075	
Ice mean temperature, T_0	248–245.5	K
Accumulation rate	24	cm/year ice equivalent

RICE = Roosevelt Island Climate Evolution.

The density of the MES samples, as measured by the micro-CT, logarithmically increases from ≈ 870 kg/m³ at 70 m to ≈ 900 kg/m³ at 140 m, with all samples clearly above the close-off density. The calculated bubble radii are <0.7 mm, with the bubble radius generally decreasing with depth (Figure 1b). The mode of the radius also decreases from 0.3 mm at 70-m depth, down to 0.2 mm at 140-m depth, as does the standard deviation of the bubble radius distribution.

3.2. Bubble Pressure Distribution From Migration Experiments

The temperature gradient experiments caused sublimation at the warm end of the bubble and deposition of the sublimated water molecules at the cold end of the bubble, leading to apparent migration of the bubble. We calculated the internal bubble pressure from this migration velocity. When a bubble gets compressed with depth, the diffusion distance that a molecule travels from warm end to the cold end decreases, but the reduced distance also causes a proportionally reduced temperature difference across the bubble, keeping the temperature gradient that is driving the diffusion unchanged. The bubble compression with depth also increases the pressure in the bubble and thus the number density of molecules in the bubble, reducing the mean free path of diffusing molecules and therefore the diffusion coefficient. The migration velocity

Figure 1. Relative frequency of the bubble radius distribution in each measured sample for the RICE (a) and the Mount Erebus Saddle (b) cores. Bin width is 0.02 mm. RICE = Roosevelt Island Climate Evolution.

Figure 2. Internal bubble pressure for the four RICE samples, calculated from migration rates. Black circles are the larger Vol1 and red circles are Vol2 (inner 1/8 of Vol1). The gray shaded pressure range is where 80% of estimated pressures occur. The range is placed so it is the narrowest possible distribution containing 80% of the bubbles. Std is the standard deviation representing the range of estimated pressures for each depth. The temperature on the x axis is used to spread the data for better readability of the figure. Circles are scaled to show relative bubble size. The dotted line is the overburden pressure. (a) 55 m, (b) 60 m, (c) 80 m, and (d) 100 m. RICE = Roosevelt Island Climate Evolution.

in temperature gradient experiments allows us to calculate the diffusivity, and thus the pressure for each bubble.

To calculate the bubble pressures from bubble migration rates for the experiments presented here, we used all voxels in the “warm” half of each bubble (i.e., the sublimating half) to avoid nonequilibrium deposition processes (Dadic et al., 2010). We then calculated the pressure in each bubble using the theoretical air bubble velocity equation for spherical bubbles under a unit temperature gradient (Nakaya, 1956; Stehle, 1967; Shreve, 1967):

$$\frac{1}{V} = \frac{1}{3} \frac{\rho \lambda}{K} + \frac{2}{3} \frac{\rho}{DC}, \quad (1)$$

where ρ is the measured ice density, λ is the latent heat of sublimation of H_2O over ice, K is the thermal conductivity of ice (Paterson, 1994), D is the diffusion constant at the temperature of the bubble, and C is the rate of change with temperature of the concentration of water in saturated air. V is the measured migration velocity from our temperature gradient experiments under a unit temperature gradient. C is calculated using the equation published by the National Research Council (1926, vol. 3, p. 210)

$$C = \frac{\Delta P_{\text{sat}}}{(0.4615 * T)} * 10^{-6}, \quad (2)$$

where ΔP_{sat} is the difference in saturation vapor pressure in a unit temperature gradient (Marti & Mauersberger, 1993), and T is temperature in K. D (cm^2/s) is calculated using the equation published by the National Research Council, 1926 (1926, vol. 3, p. 62)

$$D = D_0 * \frac{T k^m}{T_0} * \frac{P_0}{P}, \quad (3)$$

with $D_0 = 0.22 \text{ cm}^2/\text{s}$ for H_2O in air, $T_0 = 273.16 \text{ K}$, $P_0 = 1 \text{ atm}$, and $m = 1.75$. We solved the above equations (1)–(3) for internal bubble pressure P .

We evaluated two rectangular volumes (cuboids) for each sample; Vol1, the largest possible cuboid from each scanned sample (black circles in Figures 2 and 3) and Vol2, the inner 1/8 (after removing the outer 1/4 from every side of Vol1) of each sample to eliminate bubbles that have likely been affected by the sample

Figure 3. Internal bubble pressure for the six Mount Erebus Saddle (MES) samples, calculated from migration rates. Black circles are the larger Vol1 and red circles are Vol2 (inner 1/8 of Vol1). The gray shaded pressure range is where 80% of estimated pressures occur. The range is placed so it is the narrowest possible distribution containing 80% of the bubbles. Std (atm) is the standard deviation representing the range of estimated pressures for each depth. The temperature on the x axis is used to spread the data for better readability of the figure. Circles are scaled to show relative bubble size. (a) 70 m, (b) 75 m, (c) 85 m, (d) 90 m, (e) 120 m, and (f) 140 m.

preparation/cutting process (red circles in Figures 2 and 3). Figures 2 and 3 show the bubble pressures at different depths, calculated from the migration rate, as a function of temperature in each bubble during the experiments for the RICE and the MES core, respectively. The calculated pressure is independent of temperature and the temperature on the x axis is only used to spread the data for better readability of the figure.

Figure 4. Average Pressure for Vol1 and Vol2 in each sample, including error bars, which are based on the standard deviation of measurement errors. The dotted line is the overburden pressure for RICE. RICE = Roosevelt Island Climate Evolution; MES = Mount Erebus Saddle.

Figure 5. Pressure distribution for the four RICE samples. The dotted line is the pressure distribution for Vol1 and the solid line is the pressure distribution for Vol2. (a) 55 m, (b) 60 m, (c) 80 m, and (d) 100 m. RICE = Roosevelt Island Climate Evolution; MES = Mount Erebus Saddle.

There is generally a decrease of bubble size with increasing bubble pressure in both cores (Figure B1). The smaller, inner cuboid (Vol2) shows a narrower pressure range with higher average pressure than the larger volume (Vol1) (Figure 4).

For RICE and Vol2 (Figure 5, solid lines), most bubbles at 55 m ($\rho = 827 \text{ kg/m}^3$) and 60 m ($\rho = 840 \text{ kg/m}^3$) have a pressure of $\approx 1 \text{ atm}$, confirming them close to the theoretical close-off depth (50–55 m or $\rho = 830 \text{ kg/m}^3$). The most frequently occurring pressure increases to $\approx 3 \text{ atm}$ at 80 m and $\approx 5 \text{ atm}$ at 100 m. Maximum pressure at 80 m is $\approx 6 \text{ atm}$, which is $\approx$ the hydrostatic pressure (maximum possible pressure in bubbles) for the given depth.

For MES and Vol2 (solid lines), the shallowest sample at 70 m ($\rho = 870 \text{ kg/m}^3$) is significantly deeper than the close-off depth with most frequently occurring pressures at 2 atm. The pressure distribution is generally wider than in the RICE core, but the maximum pressure still largely reflects the hydrostatic pressure for sample depth: $\approx 5 \text{ atm}$ at 70 m, ≈ 6 –8 atm at 75–90 m, $\approx 10 \text{ atm}$ at 120 m, and ≈ 12 –14 atm at 140 m. The 120- and 140-m MES samples (Figures 6e and 6f) show a wide pressure distribution in Vol1 as well as in Vol2, indicating significant gas loss through volume expansion (Gow, 1970b; Salamatín & Lipenkov, 1993) from

Figure 6. Pressure distribution for the six Mount Erebus Saddle samples. The dotted line is the pressure distribution for Vol1 and the solid line is the pressure distribution for Vol2. (a) 70 m, (b) 75 m, (c) 85 m, (d) 90 m, (e) 120 m, and (f) 140 m.

the bubbles in those two samples. So not only were the bubbles at the edges affected by the gas loss through ice cracks possibly formed during cutting of the sample, but bubbles throughout the sample were affected. Such cracks would be too small to detect at the available resolution. The MES core chemistry was analyzed using continuous flow analysis to 120-m depth and discrete samples below due to internal fractures in the section 120–180 m. This fracturing could further explain the air loss from bubbles in the 120- and 140-m samples.

The standard deviation of the measurements errors (std_{err}) for the RICE pressure estimations, based on the migration measurements for warm half, “cold” half, and average velocity in each bubble, is 0.29 atm at 55 m, 0.30 atm at 60 m, 0.32 atm at 80 m, and 0.68 atm at 100 m. std_{err} describes the uncertainty that is associated with relatively large migration rates in the experiments, which can lead to nonequilibrium deposition of water vapor. Because of the large migration rates, the theoretical assumption that the vapor density near the bubble walls is at static equilibrium density (Shreve, 1967) is not valid, and the nonequilibrium can cause frost precipitation on the cold wall (Tiller, 1963). Dadic et al. (2010) discuss this effect in more detail, and Krol and Loewe (2016) also found that the purely diffusion limited equations are not strictly valid for all conditions. This effect increased with increasing bubble pressure, and therefore the standard deviation increased with depth, increasing bubble pressure and increasing migration rates (Figure 4, error bars). std_{err} for MES increases with depth, pressure and migration rate, 0.21 atm at 70 m to 1.1 atm at 140 m, except for an anomalous decrease in std_{err} at 120 m. The lower than expected standard deviation in pressure is accompanied by a lower average pressure across all bubbles in 120 m (Figure 4). The higher the internal pressure and the migration rate, the larger the probability for nonequilibrated deposition at the cold bubble wall. We suspect that this is the reason for increasing measurement uncertainties with depth and increasing bubble pressure. We did not calculate the errors based on the displacement of each individual voxel in a bubble, due to limitation with tracking individual voxels separately in time, with changing bubble shape. By assuming a linear temperature gradient across the sample, we neglected the changes of local temperature gradients in the vicinity of bubbles (Krol & Loewe, 2016), which contributes to our uncertainty.

The standard deviation for each sample around the mean pressure (std_{mean}), describing the pressure distribution of all bubbles in each sample for RICE, is 0.44 atm (55 m), 0.67 atm (60 m), 1.15 atm (80 m), and 1.44 atm (100 m). For the MES core, the values are 0.8 atm (70 m), 1.44 atm (75 m), 1.8 atm (85 m), 1.22 atm (90 m), 2.69 (120 m), and 2.95 (140 m; Figures 2–4).

4. Modeling Results: The Trapping Functions of Air Bubbles in the RICE Core

4.1. Bubble Close-Off Depth

We modeled the bubble pressure evolution for the RICE core below 40 m using a mathematical model and the software that was developed for simulating the densification of bubbly ice after bubble close-off (Lipenkov et al., 1997; Salamatin et al., 1997). Because the model assumes only one average close-off depth for the entire core, we have conducted six different runs (Figure 7), mimicking different close-off depths for all bubbles in each run (40–65 m, in 5-m intervals). We then calculated the changes in bubble pressures after close-off for each run/close-off depth. This meant that we effectively calculated the changes in bubble pressures of different bubble fractions closed at different depths. The better we can model the average porosity evolution with depth, the more accurate our estimates of internal bubble pressures increase should be, by taking into account the volumetric bubble interactions.

For the two runs where we assumed a shallow close-off depth (Figure 7, 40- to 45-m close-off depth), the modeled compression/densification rates at depth <70 m were lower than the measured densification rates, because the difference in pressure between the ice matrix (overburden pressure) and closed pores is smaller (leading to smaller densification rates) than for open pores. In reality, a few closed bubbles cannot interfere substantially with other open pores during the densification process, and at low bubble pressure (close to the atmospheric pressure), they behave similarly to the open pore ensemble. For our computation experiments here, all pores were closed off and therefore do affect the densification process. In contrast, for the model experiments where all bubbles were assumed to be closed off at a depth deeper than 50–55 m, the model generally overestimated the densification rates at depths <70–80 m (Figure 7, 60- to 65-m close-off depth),

Figure 7. Measured porosity from the RICE (Roosevelt Island Climate Evolution) core (plus symbols), and modeled porosity (for different experimental closed-off depths) with depth. rmse = root-mean-square error.

because the difference between the overburden pressure and the modeled pore pressure was on average greater than the actual values. To account for those shortcomings, caused by the assumption of a monodispersion of the bubbles, we applied a small correction to both the bubble pressure at close-off as well as the porosity at close-off (Table 1) to improve the fit between measured and modeled porosities. Specifically, we lowered the porosity at close-off for the 40- and 45-m close-off depths by 4% and 3% and increased them for the 60- and 65-m closed off depths by 19% and 13%, respectively. The close-off porosity for 50- and 55-m depth was not modified. We lowered the pressure at close-off for 40, 45, and 50 m by 9% (resulting in lower than atmospheric pressure (p_{bo})) and increased it for 55, 60, and 65 m by 2%, 7%, and 9%, respectively. Larger changes in bubble pressure at close-off could further improve the fit but were incompatible with the data in the upper part of the bubbly ice layer. As mentioned above, the predicted porosity profiles could be seen as the maximum porosity variations caused by possible lock-in scenarios and generally fall within the range of measured porosities. The ice temperatures were adjusted for a better fit with the the measured porosities and

decreased by 0.5 K for each subsequent model run (248 K at 40 m to 245.5 K at 65 m). While we acknowledge that the assumed temperature changes between the depths are higher than in reality, they were necessary to reproduce the observed porosities, which are important to accurately model the bubble pressure evolution with depth. The root-mean-square error between measured and modeled porosities ranges from 0.0059 at 50 m to 0.0085 at 40 m.

Figure 8 shows the pressure change inside bubbles with depth for the six calculated bubble close-off depths. Eighty percent of the estimated bubble pressures overlap with the chosen range of close-off depths. Additional to the estimated measurements errors in the RICE core (pressure std: 0.29–0.68 atm), some of our pressure estimates are clearly too high. All of the measured high pressures (Figure 8, red asterisks) are small bubbles with volumes less than 0.3 mm^3 . This agrees with the larger uncertainty for smaller bubbles and faster migration rates. Furthermore, smaller bubbles could originate much higher in the firn column and were previously identified by Lipenkov (2000) as well as by Ueltzhöffer et al. (2010) and Fegyveresi et al. (2016) as microbubbles. Their origin is attributed to sublimation/condensation in the shallow section of the firn column and they mostly occur inside ice grains. Microbubbles also have a higher pressure than the so-called “normal” bubbles that were closed off in the close-off zone. While the vapor pressure strongly depends on the curvature and size of the bubble, the effect ($\approx 0.04 \text{ atm}$ for a tenfold increase in bubble radius; Dadic et al., 2010) is too small to account for the large pressures we estimate in some small bubbles. Our

Figure 8. Pressure evolution for Roosevelt Island Climate Evolution with depth for different modeled bubble close-off depths. Dotted line is the overburden pressure. Black asterisks are estimated pressures of single bubbles; red are bubbles with volumes $< 0.3 \text{ mm}^3$. Over 80% of estimated bubbles pressures fall within the gray shaded pressure range (see Figure 2).

Figure 9. (a) Bubble (porosity) trapping functions for the four RICE samples, combining our bubble pressure estimates and bubble pressure evolution modeling. The gray bar is outside the modeled close-off depths. (b) Cumulative trapping functions for porosity for the four RICE samples. The dotted lines in both figures are the “depressurized” porosities to account for the extra air in bubbles with higher pressure. RICE = Roosevelt Island Climate Evolution.

only explanation at the moment is that smaller bubbles are associated with larger uncertainties (a) because any nonequilibrium effects of frost deposition are likely to have larger effects (e.g., change of shape and size), in smaller bubbles, and (b) because of the smaller number of voxels available to calculate the migration velocities. The pressure measurements below the modeled close-off ranges are potentially affected by gas loss through ice cracks from the bubbles.

4.2. Trapping Functions

We can estimate bubble close-off depths from the combination of measured bubble pressures and model experiments, as described above. If we know the depth and pressure of each bubble from the measurements (at 55, 60, 80, and 100 m), we can simply read the bubble close-off depth from the different modeled close-off curves (Figure 8). Thus, we can determine the depth range at which each bubble was closed off (trapping functions). We determined the fraction of bubble volume from each sample that has been closed off in the following modeled depth ranges: <40, 40–45, 45–50, 50–55, 55–60, 60–65, and >65 m (Figure 9), resulting in the trapping function for RICE porosity in the respective samples, at different time periods in the past. The grayed area in Figure 9a is outside of our close-off depth experimental range, and as we discussed above, those measurements could be affected by either gas loss through cracks caused by sample cutting at the low pressure end or uncertainty in measuring high pressures in very small bubbles or by the presence of microbubbles. Here, we only discuss the close-off depths from the bubble pressures within our experiment range (40–65 m). For all samples, most bubbles were closed off between 50 and 55 m. The only sample with a significant amount of bubbles closing off after 55 m was from 100-m depth (Figure 9b). The 80-m sample has a larger proportion of bubbles closed above 45 m than the other three samples.

The shape of the trapping function did not change significantly when we “depressurize” the bubbles (Figure 9a, dotted lines) and account for the different pressures at different depths.

5. Discussion

5.1. Bubble Pressure Distribution

We estimated internal bubble pressures using temperature-driven air bubble migration in ice core samples. The experiments were done (a) using a microscope with a temperature stage and camera and (b) in the micro-CT with a temperature-controlled snowbreeder. Both sets of experiments were done on samples from different depths. Experiment (a) was only used to test the method as well as to test if the resolution from Experiment (b) was sufficient for our purposes. We only discuss the micro-CT measurements in this paper.

Figure 10. Air content estimates for each sample (Vol1 and Vol2), calculated from estimated individual bubble pressures. The black squares are independently measured air contents for the RICE core (J. Lee and E. Brook, Oregon State University, personal communication). The top x axis shows the estimated ice ages from each core. Age data are from Bertler et al. (2018) and Rhodes et al. (2012). RICE = Roosevelt Island Climate Evolution; MES = Mount Erebus Saddle.

We evaluated two volumes out of each sample: the larger volume Vol1, which is the largest possible volume we could evaluate from each sample, and the smaller volume Vol2, which is the inner 1/8 of Vol1 (1/4 removed from each side of Vol1). Vol1 was likely affected by the cutting process, thereby leaking gas, and therefore having more bubbles close to atmospheric pressure. This is reflected in bubble pressure distributions (Figures 5 and 6), where we see a bimodal pressure distribution in Vol1 (dotted line) in Figures 5c and 5d as well as in Figures 6b–6d. The bubble cluster with lower pressure largely disappears when we limit our evaluation volume to the inner 1/8 of each sample (Vol2; Figures 2 and 3, red circles). The 120- and 140-m MES samples (Figure 6e and 6f) show a wide pressure distribution in Vol1 as well as in Vol2, likely reflecting the poor core recovery from below 120 m. Poor core recovery and microcracks would lead to air leakage and more bubbles with lower pressures than expected. The average estimated pressures increase with depth in both cores and their distribution (std_{mean}) widens, and would theoretically get narrower again, when all closed bubbles approach overburden pressure (or as close as they can get to overburden pressure). We did not observe the “narrowing in the pressure distribution” in the RICE core (increasing std_{mean} with depth), and need more experiments at greater depth to test at which depth the pressure distribution would get narrower.

5.2. Air Content

We estimated the air content (dry air volume in 1 g of ice at T_s and P_s) from the bubble pressure estimates (Martinerie et al., 1992, equation 1). The air content, being sensitive to pressure and thus to the elevation of the surface of the ice sheet, has previously been used to estimate the elevation changes of the ice sheet in time, although with considerable uncertainty (Martinerie et al., 1994). Mitchell et al. (2015) observed that the bubble close-off depth, governed by porosity of ice, atmospheric pressure, and the temperature at the close-off depth (Martinerie et al., 1992), is one of the primary controlling factors that determine the magnitude of the total air content in polar ice. And because the air content is dependent on the bubble closure, it is also dependent on firn layering, impurities and firn rheology.

We used the internal pressure, bubble volume in each individual bubble within a sample, as well as the measured temperature at depth (for volume expansion) to estimate the total air content in each sample, for both the larger Vol1 and the inner Vol2 (Figure 10). The difference in estimated air content between Vol1 and Vol2 was 10–40%. We only have two measurements for depths similar to our pressure estimate samples from the RICE core, at 80 and 100 m (J. Lee and E. Brook, Oregon State University, personal communication, 2017). There are no air content measurements from the MES core to which we could compare our air content estimates. The two measurements that we have on air content agree with our estimated air contents from individual bubble pressures (Figure 10, squares) and imply that, in the future, indirect measurements of bubble pressure could be used for independent air content estimates to constrain the uncertainties in air content estimates from conventional methods and to gain a better understanding as to what controls total air trapping.

5.3. Bubble Trapping Functions

We used the modeled bubble pressures, caused by different closed-off depths, together with the measured bubble pressures to estimate bubble trapping functions (Figure 9). The minor differences in close-off functions (trapping functions) between the four samples could reflect a slight change in climate, but we will require additional samples and data to discuss any changes in detail. The ages of the four samples at 55, 60, 80, and 100 m were estimated to be ≈ 1833 , 1815, 1722, and 1630 (CE), based on the age scale from Winstrup et al. (2017) and Bertler et al. (2018) (Figure 10, placing the 55- and 60-m samples after 1800 CE and the 80- and 100-m sample before 1800 CE, or the end of the Little Ice Age. A climatic shift around 1800 CE is discussed in previous reconstructions from West Antarctica, specifically from the West Antarctic Ice Sheet core (Fegyveresi et al., 2011; Orsi et al., 2012), Talos and Taylor Dome (Stenni et al., 2002), and the Ross Sea Region (Bertler et al., 2011), where data indicate a cooling associated with the Little Ice Age between

≈1300 and 1800 CE and a subsequent warming afterward. However, most recent data from the RICE core show a distinct Ross Sea Dipole, with RICE and Siple Dome experiencing warmer than average conditions during the Little Ice Age (Bertler et al., 2018), while West Antarctic Ice Sheet and MES record colder temperatures (Orsi et al., 2012; Rhodes et al., 2012). We obviously need more experiments to improve our results and to discuss possible changes in bubble trapping functions for RICE in the last 400 years. But our first results show the possible implications for ice core records.

5.4. Shortcomings and Limitations

In this study, we did not account for the layering and the density variability of the firn (Hörhold et al., 2011; Mitchell et al., 2015; Schaller et al., 2017). Layering can “broaden the depth range over which bubbles are trapped” (Mitchell et al., 2015) and widen the modeled gas age distribution. We did not use a forward model to estimate the bubble close-off depth, as previously done by Schwander et al. (1997) or Mitchell et al. (2015) but rather a combination of the modeled pressure evolution of an assumed bubble close-off depth and measured bubble pressures at different depths. While the layering can influence the density/porosity evolution of the firn/ice column, we think that the approximation by a smooth density evolution is justified for our application. We also neglected the effects of impurities on firn densification (Freitag et al., 2013; Hörhold et al., 2012) and the rheological properties and the geometry of firn (Freitag et al., 2013; Gregory et al., 2014), both of which can influence the porosity evolution in firn, and which we plan to address in the future.

The presented method is limited to the top ~200 m of the firn/ice. To extend the applicability of our method to a larger depth and improve the resolution of abrupt climate changes further back in the past, we need to determine trapping functions for a range of shallow ice cores that span many different climate conditions. Doing this with ice samples from today's different climate conditions will allow us to compile look-up tables of how bubble ensembles in different types of climates behave (e.g., size, clustering, and pressure distribution), which we can then use to improve the interpretation and resolution for ice deeper than our measurement range.

6. Conclusions

We introduce a new method, based on temperature-driven air bubble migration in ice core samples, to estimate pressure distribution in individual bubbles from ice core samples. The migration velocity in our temperature gradient experiments allowed us to calculate the diffusivity and subsequently the pressure for each bubble in a sample. We then combined the measured bubble pressure distributions with a model for the pressure evolution in bubbles after close-off to estimate a bubble trapping function for each depth. Our estimates from the RICE core revealed slight changes in the bubble trapping functions between ≈1630 and 1833 CE, consistent with other data from the RICE core, further validating our technique, but more measurements are needed to interpret these results. Future work involves combining the estimates of the bubble trapping functions at a higher spatial resolution, with gas measurements, and thus improving the resolution of the gas signal through deconvolution.

For times of rapid climate change in the past, and including the most recent 150 years, knowledge of the age distribution of the gases trapped in air bubbles will enable us to refine the interpretation of the composition of gases in ice cores and the precision of the age differences between the gas and surrounding ice. If the age distribution is broad, then a small and slow increase in trapped-gas composition may in fact record a large and rapid increase in atmospheric composition.

Our new technique presented here to estimate individual bubble pressures, combined with the modeling of changes in bubble pressure with depth, demonstrates the importance of the close-off bubble pressure convolution for paleoclimatic interpretations of ice core data. Additional studies are needed to extend the bubbly ice densification model to the spatially distributed close-off process in polar ice sheets. In addition, other factors need to be considered, such as impurity content, layering impacts on densification, and firn geometry. The development of a volumetrically evolved model, which includes real geometry of near-surface firn and physical changes of that geometry under an applied load (or an idealized individual bubble pressure model), could provide further insight into the densification rate, supplementing our approach.

Additional to our primary objective (estimating bubble trapping functions in ice core samples), the application of our method to estimate total air content in ice core samples could have broader impacts for ice core research, by providing a valuable tool for constraining what controls total air content trapping.

Appendix A: Micro-CT Images of RICE Samples

The main set of experiments for this research has been conducted using micro-CT. Micro-CT imagery produces a 3-D model (Figure A1) of a physical snow or ice sample by combining (or stacking) sequential high-energy, 2-D X-ray cross-sectional images (or “slices”). It can distinguish between the ice phase and the vapor phase in a sample by differentiating image brightness and is therefore a suitable tool to determine bubble migration rates. We determined migration rates by measuring voxel displacement between images before (Figure A1, top row), and after temperature-driven migration (Figure A1, bottom row).

Appendix B: Bubble Size and Pressure

We observe a decrease of bubble size with increasing bubble pressure in all samples (Figure B1). The bubble size correlates with migration rates because smaller bubbles have generally higher pressures, and therefore lower migration rates, because they were closed off earlier.

Figure A1. Reconstructed micro-CT images from RICE at 55, 60, 80, and 100 m; before (top row) and after (bottom row) the migration experiments. RICE = Roosevelt Island Climate Evolution.

Figure B1. Bubble diameter versus bubble pressure for RICE samples at 55, 60, 80, and 100 m. Note that the x scale is logarithmic. (RICE = Roosevelt Island Climate Evolution).

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