Available online at www.sciencedirect.com
SCIENCE DIRECT®
Earth and Planetary Science Letters 244 (2006) 474–500
EPSL
www.elsevier.com/locate/epsl

Fractionation of gases in polar ice during bubble close-off: New constraints from firn air Ne, Kr and Xe observations

Jeffrey P. Severinghaus [a,*], Mark O. Battle [b]

[a] Scripps Institution of Oceanography, University of California, 9500 Gilman Dr., San Diego, CA 92093-0244, USA
[b] Department of Physics and Astronomy, Bowdoin College, 8800 College Station, Brunswick, ME 04011-8488, USA

Received 12 June 2005; received in revised form 14 January 2006; accepted 16 January 2006
Available online 28 February 2006
Editor: E. Boyle

Abstract

Gas ratios in air withdrawn from polar firn (snowpack) show systematic enrichments of Ne/N_2, O_2/N_2 and Ar/N_2, in the firn–ice transition region where bubbles are closing off. Air from the bubbles in polar ice is correspondingly depleted in these ratios, after accounting for gravitational effects. Gas in the bubbles becomes fractionated during the process of bubble close-off and fractionation may continue as ice cores are stored prior to analysis. We present results from firn air studies at South Pole and Siple Dome, Antarctica, which add Ne, Kr and Xe measurements to the suite of observations. Ne, O_2 and Ar appear to be preferentially excluded from the shrinking and occluding bubbles, and these gases therefore accumulate in the residual firn air, creating a progressive enrichment with time (and depth) in firn air. Early sealing of gases by thin horizontal impermeable layers into a non-diffusive zone or "lock-in zone" greatly enhances this enrichment. A simple model of the bubble close-off fractionation and lock-in zone enrichment fits the data adequately. The model presumes that fractionation is caused by selective permeation of gas through the ice lattice from slightly overpressured bubbles. The effect appears to be size-dependent, because Ne, O_2 and Ar have smaller effective molecular diameters than N_2, and fractionation increases strongly with decreasing size. Ne is fractionated 34 ± 2 times more than O_2 in South Pole firn air and reaches an enrichment of 90‰ in the deepest sample. The large atoms Kr and Xe do not appear to be fractionated by this process, despite the large size difference between the two gases, suggesting a threshold atomic diameter of ~ 3.6 Å above which the probability becomes very small that the gas will escape from the bubble. These findings have implications for ice core and firn air studies that use gas ratios to infer paleotemperature, chronology and past atmospheric composition.

Keywords: ice cores; trapped gases; air bubbles; noble gases; fractionation; molecular size

1. Introduction

1.1. Background

Snow accumulating on a polar ice sheet gradually compacts and sinters under its own weight to form first firn, and then ice. The firn, a layer of recrystallized and partially compacted snow, is porous and permeable to

* Corresponding author. Tel.: +1 858 822 2483; fax: +1 858 822 3310.
E-mail address: jseveringhaus@ucsd.edu (J.P. Severinghaus).

0012-821X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2006.01.032

air. The air contained within the firn mixes with the atmosphere through molecular diffusion and in some circumstances, through convection [1,2]. At the base of the firn layer, which is typically 50–100 m thick in polar settings, firn air is occluded in bubbles as the firn becomes impermeable ice. Air trapped in bubbles in polar ice has been used for a wide variety of paleoenvironmental studies, principally to reconstruct the composition of past atmospheres [3,4].

Atmospheric constituents that are nearly constant in time (during the 10^6-yr period spanned by ice cores), such as the noble gases and the isotopes of N_2, have also been used to infer the local histories of climate-related processes occurring within the firn layer that overlies polar ice sheets. The most important of these processes is gravitational settling [5–7], in which heavier gas molecules are enriched towards the bottom of a column of gas in diffusive equilibrium. Gravitational enrichment increases with depth in the firn air column and with the absolute mass difference Δm between a pair of gas species, as given by the barometric equation [5]. For example, the enrichment of the $^{132}Xe/^{28}N_2$ ratio, with $\Delta m = 104$, is 104 times greater than the enrichment of $^{15}N/^{14}N$ with $\Delta m = 1$. Prior studies have used the observed enrichments of $^{15}N/^{14}N$ in air bubbles to infer past firn diffusive column thickness. This thickness is related to climatic variables of interest such as temperature and accumulation rate [8–11].

A second process that alters firn air and hence bubble air composition is thermal fractionation. A gas mixture subjected to a temperature gradient will tend to unmix, with heavier components generally migrating towards colder regions [12]. Thermal fractionation of air in the firn is driven by transient temperature gradients that arise from seasonal temperature change [13] or during the several hundred years following rapid climate changes [14–16]. The resulting isotopic signal is captured in bubbles in ice and permits reconstruction of the magnitude and rapidity of past climate change [17].

Here we concentrate on a third process that alters firn and bubble air composition: the preferential exclusion of Ne, Ar and O_2 during bubble close-off. Ice core bubble air is typically depleted in Ar/N_2 and O_2/N_2 relative to atmospheric values, with the Ar depletion typically half that of the O_2 depletion [2,6,8,18]. The fact that Ar is heavier than N_2 and O_2, yet has intermediate depletion, argues against a mass-dependent fractionation process, but is consistent with the ordering of molecular sizes [5]. Typical values for $\delta O_2/N_2$ in well-preserved ice samples are −4‰ to −8‰ [18]. Some very large depletions with this size-dependent signature observed in certain ice cores can probably be attributed to artifactual gas loss during core retrieval or handling (e.g., the deep Byrd core, with $\delta O_2/N_2 = -200‰$ and $\delta Ar/N_2 = -100‰$) [18]. Poor core quality is often associated with low O_2/N_2 [19] and long storage of samples in freezers at −25 °C has been shown to cause depleted O_2/N_2 [20,21]. However, firn air studies show that some in situ (natural) size-dependent fractionation process must also occur [2]. Furthermore, Bender [19] has recently shown that Vostok ice core O_2/N_2 correlates strongly with local insolation, a relationship confirmed by Dome Fuji O_2/N_2 [20]. These latter studies clearly imply a natural O_2/N_2 fractionation at bubble close-off.

In support of this conclusion, we report measurements of noble gas ratios, O_2 and isotopes of N_2 in air withdrawn from the firn at Siple Dome and South Pole, Antarctica. The data show large enrichments of O_2/N_2 (up to 10‰), Ne/N_2 (up to 90‰) and Ar/N_2 (up to 3‰) in the transitional region where firn becomes ice. Kr/N_2 and Xe/N_2 show no such enrichment, providing an important constraint on fractionation mechanisms. Bubble air composition is depleted in O_2/N_2 in a complementary fashion, as would be expected by mass balance if the segregation process occurred during bubble close-off [2]. However, the magnitude of the observed depletion in ice samples is often a factor of 2–4 greater than predicted by mass balance; we discuss this discrepancy further below. We also show that the Ne/N_2 and O_2/N_2 enrichments are well correlated and discuss implications for paleoenvironmental studies of gas ratios in polar firn and ice.

1.2. The firn–ice transition and "lock-in" zone

Initial density differences in snow deposited at the surface in summer and winter appear to be preserved through the entire densification process in the firn [22]. Thus, higher-density winter layers become impermeable before lower-density summer layers as the firn turns to ice. These layers allow horizontal movement within each summer layer while preventing most vertical movement [1,2,7,9,22–24]. The result is a vertical region in the firn, referred to as the "lock-in zone", at the transition between firn and ice (Fig. 1). While some authors [2] originally thought that vertical movement was completely blocked in this zone, we suggest in this paper that widely spaced leaks permit some gas to escape upward. The zone is defined above by the onset of impermeable winter layers and below by the complete absence of open pores (the firn–ice transition). Large volumes of air can be drawn from the open summer layers within the lock-in zone.