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Effects of molecular diffusion on trapped gas composition in polar ice cores

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Abstract

Enrichment of nitrogen gas has been found from gas analyses of ice cores retrieved from deep parts of Antarctica. Neither climate change nor gas loss through ice cracks explain the enrichment. In order to investigate the mechanism of the gas composition change, we develop a model of gas loss caused by molecular diffusion from clathrate hydrates toward the ice-core surface through ice crystal. We apply the model to interpret the data on the gas composition change in the Dome Fuji ice core during the storage for 3 years at 248 K. The mass transfer coefficients determined using the model are 1.4×10^{-9} and 4.3×10^{-9} $m \cdot s^{-1}$ at 248 K for N_2 and O_2, respectively. The difference in the coefficient between N_2 and O_2 causes the change in the O_2/N_2 ratio of the trapped gas in the ice core during the storage. During the storage period of 1000 days at 248 K, the O_2/N_2 ratio changes from −9.9‰ to −20.5‰. The effect of the gas loss decreases as the storage temperature decreases. The results have important implications for the accurate reconstructions of the paleo-atmosphere from polar ice cores.

Keywords: ice cores; gas analysis; gas fractionation; molecular diffusion; paleo-atmosphere

1. Introduction

Ancient atmospheric gases are trapped in polar ice sheets. Reconstruction of the paleo-atmosphere from the ice recovered from the ice sheets is one of the main topics of the environmental research [1–6]. The paleoclimate and paleoenvironmental records for 300,000–740,000 years have been provided from

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continuous long ice cores recovered from the Antarctic ice-sheet [7–10]. Atmospheric gases are trapped as air bubbles in ice when firn is transformed into ice by the sedimentation near the surface of the ice sheet. The air bubbles are compressed with depth and gradually transformed into clathrate hydrates below a certain depth at which the hydrostatic pressure becomes greater than the dissociation pressure of the clathrate hydrate phase [11]. Since the firn-ice transition and the formation of clathrate hydrates cause a change in the gas composition, these processes have been studied to reconstruct the accurate paleo-atmosphere [12–22].

Raynaud and Delmas [14] first measured the O_2/N_2 ratios of the total air contents in the ice core and found the O_2/N_2 ratio is 1% lower than the modern atmospheric value. The enrichment of N_2 was confirmed by Craig et al. [15], Sowers et al. [16] and Bender et al. [17] using ice cores from a wide range of depths. Fig. 1 shows the depth profile of O_2/N_2 ratio of total air contents in the 3 G Vostok ice core measured by Bender et al. [17]. The O_2/N_2 ratios are generally lower than the atmospheric value except some samples from the depths between 500 and 1200 m, which corresponds to the transition zone of clathrate hydrates from air bubbles. The O_2/N_2 ratio averaged over the all samples is 14.6‰ lower than the modern atmospheric value (i.e., 0.27). The past changes of atmosphere cannot explain the enrichment [16]. Although the O_2/N_2 ratio in atmospheric air seasonally varies [18], the amplitude is too small to be recorded in ice cores.

The fractionation during the firn-ice transition was suggested as the cause of the enrichment of N_2. Bender [19] interpreted the enrichment as gas effusion through air-channels during the pore closure. The gas molecules in forming air bubbles escape to the atmosphere through the channels of air, which are open to the surface of the ice sheet. He explained the variation of O_2/N_2 ratio by the difference in the molecular size between N_2 and O_2. The O_2/N_2 ratio of total air contents varies with variation of summertime insolation, because the velocity of the effusion depends on firn property, which is influenced by insolation affecting snow metamorphism in the near-surface layer of ice sheet [19]. On the other hand, Craig et al. [15] and Schwander [20] found that the atmospheric gases at the layer of the firn-ice transition are enriched in heavy isotopes (e.g., ^{15}N and ^{18}O) and in heavy gases (e.g., O_2 compared with N_2) in comparison with the atmosphere. These fractionations

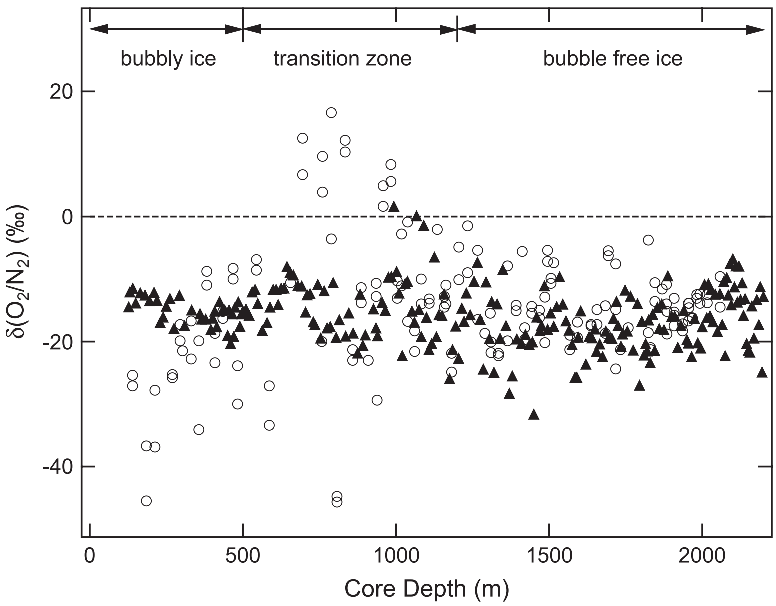

Fig. 1. Depth profile of O_2/N_2 ratio of air contents. The open circles and the solid triangles show the data of the 3 G Vostok ice core [17] and the Dome Fuji ice core [38], respectively. The dashed line shows the atmospheric value (i.e., $\delta(O_2/N_2)=0$).