

## Behavior of air molecules in polar ice sheets

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**Abstract:** Ancient atmospheric gases are trapped in polar ice sheets. The gas molecules are stored in air bubbles at shallower depth. The air bubbles are gradually compressed with depth and begin to transform into clathrate hydrates below a level at which the hydrostatic pressure becomes greater than the formation pressure of the phase of air clathrate hydrate. Air bubbles and clathrate hydrates coexist in the deep ice over a long period of time. Significant gas fractionations during the transition process have been found from measurements of the depth profile of the N<sub>2</sub>/O<sub>2</sub> composition ratios in clathrate hydrates and air bubbles in the Dome-Fuji ice and the Vostok ice. Analyzing the molecular diffusion process in ice, the gas fractionation is attributed to a larger mass flux of O<sub>2</sub> molecules from air bubbles to clathrate hydrates through the ice matrix than that of N<sub>2</sub>. We review the process of gas fractionation caused by the formation of clathrate hydrates in polar ice sheets.

**key words:** clathrate hydrate, molecular diffusion, ice sheet, paleoatmosphere,

### 1. Introduction

Paleoatmospheric reconstruction is one of the main topics of research on ice cores (*e.g.*, Raynaud *et al.*, 1988; Neftel *et al.*, 1988; Stauffer *et al.*, 1988; Chappellaz *et al.*, 1990). The ancient gas molecules are stored in air bubbles at shallower depth and are incorporated into clathrate hydrates below a certain depth (Miller, 1969; Shoji and Langway, 1982). Since the processes of formation of clathrate hydrates may affect the composition and distribution of atmospheric gases in ice sheets, the processes have been studied in order to reconstruct accurate records of the paleoatmosphere from polar ice cores.

### 2. Formation of clathrate hydrates in polar ice sheets

Atmospheric gases are trapped in air bubbles when firn is transformed into ice by sedimentation near the surface of polar ice sheets. The air bubbles are compressed with depth and gradually transform into clathrate hydrates below a depth at which the hydrostatic pressure becomes greater than the formation pressure of the clathrate hydrate phase. Clathrate hydrate is a kind of inclusion compound, whose composition changes depending on temperature and pressure. Water molecules in clathrate hydrate are linked together by hydrogen bonds in the closest packing of polyhedral cage-like structures that can accommodate a variety of guest molecules. Most clathrate hydrates form one of two distinct crystallographic

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structures, Stackelberg's structure-I or II, depending on the size and shape of the guest molecules (Davidson, 1972). The crystallographic structure of natural clathrate hydrate in a polar ice sheet is structure-II (Hondoh *et al.*, 1990), since the major guest molecules,  $N_2$  and  $O_2$ , are preferentially accommodated in the dodecahedral cages of structure-II.

The formation pressure (*i.e.*, the dissociation pressure)  $P^d$  is a function of the composition of the gas mixture and the temperature. For air clathrate hydrate,  $P^d$  is given by

$$P^d = \frac{P_{N_2}^d P_{O_2}^d}{Z_{N_2} P_{O_2}^d + Z_{O_2} P_{N_2}^d}, \quad (1)$$

where  $P_{N_2}^d$  and  $P_{O_2}^d$  are the respective dissociation pressures of pure  $N_2$ - and  $O_2$ -clathrate hydrates, and  $Z_{N_2}$  and  $Z_{O_2}$  are the mole fractions of  $N_2$  and  $O_2$  in the gas phase, respectively.  $P_{N_2}^d$  and  $P_{O_2}^d$  (MPa) at temperature  $T$  (K) are given by (Miller, 1969)

$$\begin{aligned} \log P_{N_2}^d &= 3.6905 - 688.9/T, \\ \log P_{O_2}^d &= 3.679 - 717/T. \end{aligned} \quad (2)$$

Figure 1 shows the temperature dependence of  $P^d$  of air clathrate hydrate (Ikeda-Fukazawa *et al.*, 2001). The open and solid circles show the depths below which clathrate hydrates are observed and below which air bubbles are not observed in Dome Fuji, Vostok, GRIP, and Dye-3 ice cores, respectively. Clathrate hydrates and air bubbles coexist in the deep ice sheet within the depth range (transition zone) denoted by open and solid circles. For instance, the transition zone in Dome Fuji ice is 450–1200 m in depth, which corresponds to

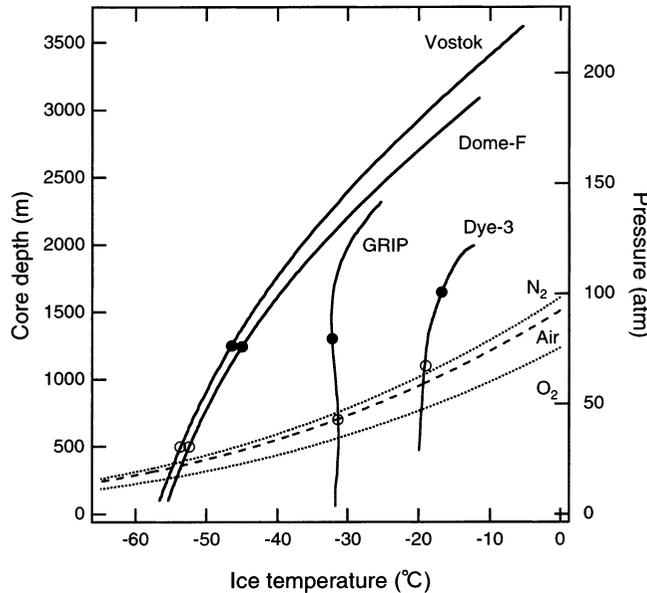


Fig. 1. Relationship between temperature and dissociation pressures of  $N_2$ -,  $O_2$ -, and air- ( $N_2/O_2 = 3.7$ ) clathrate hydrates (Ikeda-Fukazawa *et al.*, 2001). The solid lines are the depth profiles of the ice temperatures of Dome-Fuji, Vostok, GRIP, and Dye-3 ice cores. The open and solid circles show the depths below which clathrate hydrate crystals are observed and below which air bubbles are not observed, respectively.

a time period of about 30 kyr (Narita *et al.*, 1999).

### 3. Gas fractionation caused by formation of clathrate hydrate

When clathrate hydrate is formed in a ternary system (*i.e.*, a gas mixture and H<sub>2</sub>O), the gases are fractionated by selective enclathration (Barrer and Stuart, 1957). According to the theory of Van Der Waals and Platteeuw (1959), air clathrate hydrate transformed from air and ice (or water) is enriched in O<sub>2</sub> because of the lower dissociation pressure for pure O<sub>2</sub> clathrate hydrate than that for pure N<sub>2</sub> clathrate hydrate. This fractionation effect on air clathrate hydrate was confirmed from Raman spectroscopic study of artificial air clathrate hydrate by Chazallon *et al.* (1998). Thus, gas fractionation during the transition process from air bubbles to clathrate hydrates in polar ice sheets was predicted. Since the composition and distribution of the atmospheric gases in the ice sheets can be changed by gas fractionation during the formation of clathrate hydrate, the effects of gas fractionation have been studied in order to reconstruct accurate records of the paleoatmosphere from polar ice cores.

Nakahara *et al.* (1988) measured Raman spectra of 3 clathrate hydrates from a depth of 1501 m in the Dye-3 Greenland ice core. Since the frequencies of two peaks at 2322 and 1546 cm<sup>-1</sup> in the observed spectra were close to those of the stretching vibrational modes of N<sub>2</sub> and O<sub>2</sub> gases, they identified the major guest molecules in the clathrate hydrates as N<sub>2</sub> and O<sub>2</sub>. From the scattering intensities of the peaks of N<sub>2</sub> and O<sub>2</sub>, they found that the N<sub>2</sub>/O<sub>2</sub> composition ratio averaged over three clathrate hydrate crystals was 1.7. The value was much smaller than the present atmospheric ratio of 3.7. They concluded that this enrichment of O<sub>2</sub> is due to the gas fractionation caused by the difference in dissociation pressures between pure N<sub>2</sub>- and O<sub>2</sub>-clathrate hydrates.

In contrast, Pauer *et al.* (1995, 1997) showed there was no significant enrichment of gases in clathrate hydrates from measurements of Raman spectra of 144 clathrate hydrates from different depths between 1219 and 2923 m in the GRIP Greenland ice cores. The N<sub>2</sub>/O<sub>2</sub> ratio averaged over 144 clathrate hydrates was 3.6, which was close to the atmospheric ratio. They predicted that the difference in the dissociation pressures between the pure N<sub>2</sub>- and O<sub>2</sub>-clathrate hydrates causes an inhomogeneous distribution of N<sub>2</sub>/O<sub>2</sub> ratio within an individual clathrate hydrate crystal.

In order to investigate the fractionation effect on the air distribution within a crystal, Pauer *et al.* (1996) measured the focal plane dependence of the N<sub>2</sub>/O<sub>2</sub> ratio within a clathrate hydrate crystal from a depth of 1475.65 m in the GRIP ice core using Raman spectroscopy. However, they found no fractionation effect (*i.e.*, gradient) on the N<sub>2</sub>/O<sub>2</sub> composition within the clathrate hydrate crystal, which is in contrast to the different dissociation pressures for the pure N<sub>2</sub>- and O<sub>2</sub>-clathrate hydrates. They concluded that the gradient of the composition resulting from the initial fractionation may have been leveled out with time. This conclusion was later supported by the results of the measurements of the spatial distribution of N<sub>2</sub>/O<sub>2</sub> ratio in clathrate hydrates from Vostok ice (Ikeda *et al.*, 2000b). They showed that the pattern of the spatial distribution of N<sub>2</sub>/O<sub>2</sub> ratio depends on the depth at which the clathrate hydrate formed and thermodynamic conditions in the ice sheet.

Significant gas fractionations during the transition process were found in the Vostok ice and the Dome-Fuji ice (Ikeda *et al.*, 1999; Ikeda-Fukazawa *et al.*, 2001). They measured Raman spectra of clathrate hydrates and air bubbles over a wide range of depths, and found

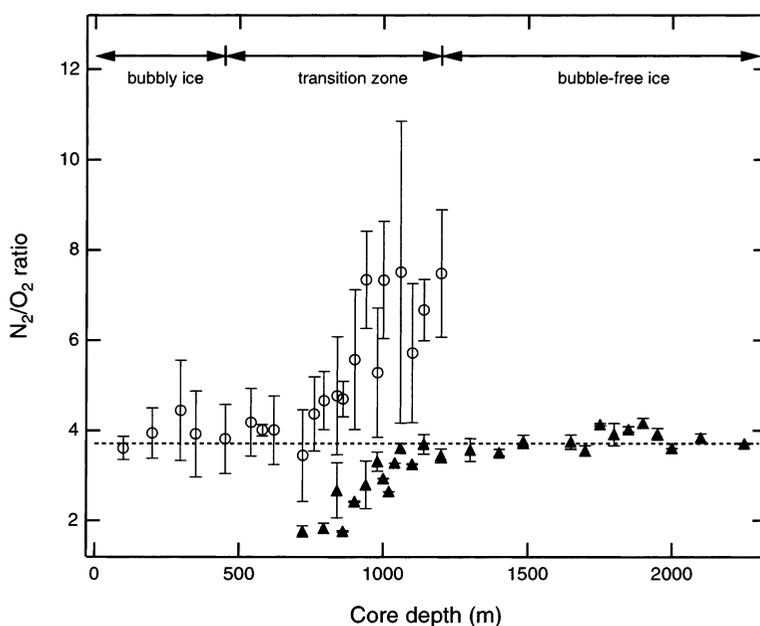


Fig. 2. Depth profiles of  $N_2/O_2$  ratios of clathrate hydrates and of air bubbles of Dome-Fuji ice (Ikeda-Fukazawa *et al.*, 2001). The solid triangles and the open circles are the average values for clathrate hydrates and air bubbles, respectively. The error bars are standard deviations for scattering of data at the same depth. The broken horizontal line shows the value of the atmospheric ratio (3.7).

remarkable variations in the  $N_2/O_2$  ratios in the clathrate hydrates and the air bubbles with depth in the transition zone (see Fig. 2). For air bubbles, the average  $N_2/O_2$  ratios increase from the atmospheric ratio at the beginning of the transition zone to 7.5 at the end. In contrast, the average  $N_2/O_2$  ratios in the clathrate hydrates are 1.8 at the beginning of the transition zone and approach the atmospheric ratio with increase in depth. Because the  $N_2/O_2$  ratio of the atmosphere has remained within  $\pm 0.2\%$  of the present value over the time period covered by the Vostok ice core (Bender *et al.*, 1995), the variations in the  $N_2/O_2$  ratios found in the Vostok ice and the Dome-Fuji ice are attributed to physical alterations within the ice sheet. They concluded that the gas fractionation is caused by a diffusive mass transfer of  $N_2$  and  $O_2$  molecules between clathrate hydrates and air bubbles, which coexist in the transition zone.

#### 4. Gas diffusion in ice crystals

We consider the diffusive mass transfer process of gas molecules dissolved in ice that alters the gas compositions in clathrate hydrates and air bubbles. When ice is in equilibrium with a gas phase of  $i$ -molecule at a partial pressure  $P_i$ , the concentration of  $i$ -molecules dissolved in ice, or the solubility of  $i$ -molecules,  $X_i^B$  in mole fraction can be expressed by Henry's law

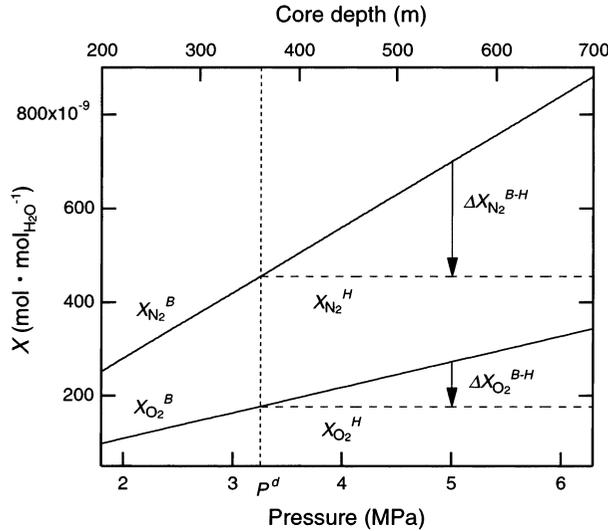


Fig. 3. Concentrations of  $N_2$  and  $O_2$  dissolved in ice (Ikeda et al., 1999).  $X_{N_2}^B$  and  $X_{O_2}^B$  are the equilibrium concentrations of  $N_2$  and  $O_2$  dissolved in ice at the interface with air bubble, respectively.  $X_{N_2}^H$  and  $X_{O_2}^H$  are the equilibrium concentrations of  $N_2$  and  $O_2$  dissolved in ice at the interface with clathrate hydrate, respectively.  $\Delta X_{N_2}^{B-H}$  and  $\Delta X_{O_2}^{B-H}$  are the concentration differences of  $N_2$  and  $O_2$  in ice between the air bubbles and the clathrate hydrates, respectively. The  $N_2/O_2$  ratios of the clathrate hydrate and the air bubble are kept equal to 3.7.

$$X_i^B = k_i P_i, \quad (3)$$

where  $k_i$  is the pressure sensitivity constant of the solubility, or Henry's constant, for  $i$ -molecules. The two solid lines in Fig. 3 show pressure dependence of the solubility for  $N_2$  and  $O_2$ ,  $X_{N_2}^B$  and  $X_{O_2}^B$  respectively when ice including air-bubbles with the same gas composition is compressed. The two horizontal lines indicate the equilibrium concentrations of  $N_2$  and  $O_2$ ,  $X_{N_2}^H$  and  $X_{O_2}^H$  respectively when the ice includes only clathrate hydrates. Since  $X_i^H$  ( $X_{N_2}^H$  or  $X_{O_2}^H$ ) varies proportionally with the composition ratio of  $i$ -molecules occluded in the cages of the clathrate structure  $Y_i$ , but does not depend on pressure and temperature significantly along the transition zone, it is given by

$$X_i^H = k_i P^d Y_i \quad (i = N_2, O_2). \quad (4)$$

In the transition zone, in which bubbles coexist with hydrates, a diffusive mass flux of  $i$ -molecules from bubbles to hydrates is driven by the concentration difference  $\Delta X_i^{B-H}$  as shown in Fig. 3. To solve the diffusive mass transfer equation, we assume that the concentrations of  $i$ -molecules dissolved in ice close to the bubble surface and hydrate surface are kept equal to  $X_i^B$  and  $X_i^H$ , respectively, during the whole process. Then, the boundary conditions for the concentration of  $i$ -molecules in ice matrix  $X_i$  are given by

$$\begin{cases} X_i = X_i^B = k_i P_i & \text{(at bubble surface),} \\ X_i = X_i^H = k_i P^d Y_i & \text{(at hydrate surface).} \end{cases} \quad (5)$$

$$(6)$$

Considering a simple case in which one hydrate crystal is surrounded by many bubbles with the same partial pressure  $P_i$ , the diffusive mass flux of  $i$ -molecule  $q_i$  can be expressed in terms of the pressure difference as

$$q_i \propto D_i k_i (P_i - P^d Y_i), \quad (7)$$

$$\propto D_i k_i P^d \left( \frac{P_i - P^d Y_i}{P^d} \right), \quad (8)$$

where  $D_i$  is the diffusion coefficient of  $i$ -molecules in ice, or it is defined by the time average of the square of the displacement. Since the mass flux driven by the pressure difference is proportional to the term  $D_i k_i$  in eq. (7), this term is referred to as the permeability constant in general. In the present case, however, we define the term  $D_i k_i P^d$  in eq. (8) as the permeation coefficient  $D_i^S$  because  $P^d$  is also a material constant and we prefer to use a non-dimensional expression for the pressure difference (Salamatin *et al.*, 2001), specifically:

$$D_i^S = D_i k_i P^d. \quad (9)$$

To understand the gas fractionation shown in Fig. 2, we have to know the difference between  $D_{N_2}^S$  and  $D_{O_2}^S$ . Although the diffusion coefficients of monatomic molecules and very small diatomic and polyatomic molecules such as  $H_2$  and  $H_2O$  in ice crystals have been measured (Goto *et al.*, 1986; Satoh *et al.*, 1996; Ikeda-Fukazawa *et al.*, 2002), no experimental data on  $N_2$  and  $O_2$  have been reported until now because of difficulty in the measurements for such a slowly diffusing species. Ikeda *et al.* (2000a) estimated both  $D_i$  and  $k_i$  by a semi empirical method. Rough estimation of  $k_i$  was made by extrapolating the relationship between the solubilities and the van der Waals radii obtained for smaller molecules. For  $D_i$ , the relationship between the diffusion coefficients measured for other molecules and the potential barriers for the interstitial diffusion of gas molecules in the ice lattice was extrapolated to those for  $N_2$  and  $O_2$ . Those estimated values are given in Table 1. In addition, Salamatin *et al.* (2001) also estimated the permeation coefficients of  $N_2$  and  $O_2$  by constraining their mass transfer model to the experimental data (Ikeda *et al.*, 1999; Lipenkov, 2000) as shown in Table 1. As a result,  $D_{O_2}^S$  is 2 to 4 times larger than  $D_{N_2}^S$  above 220K, and a higher diffusive flux for  $O_2$  is suggested by substituting typical values for  $P_i$  and  $Y_i$  into eq. (8).

In real ice sheets, however, we have to take into account much more complicated distributions of bubbles and hydrates with different gas compositions. Salamatin *et al.* (2001) developed an averaged model of the transformation process of clathrate hydrates from air bubbles along the transition zone in a polar ice sheet. The model tracks the time evolution of the coexisting ensembles of bubbles and hydrates in a unit volume of pure ice as it moves along the transition zone of the ice sheet. To drive the fractionation of gas molecules in the

Table 1. Diffusion coefficient  $D_i$ , pressure sensitivity constant of solubility  $k_i$ , and permeability coefficient  $D_i^S$  used for the calculation of mass transfer.

	Ikeda <i>et al.</i> , 2000a (263K)		Salamatin <i>et al.</i> , 2001 (220K)	
	$N_2$	$O_2$	$N_2$	$O_2$
$D_i$ (m <sup>2</sup> /s)	$1.6 \times 10^{-13}$	$5.5 \times 10^{-13}$	–	–
$k_i$ (1/MPa)	$1.8 \times 10^{-7}$	$2.6 \times 10^{-7}$	–	–
$P_i^d$ (MPa)	11.78	8.97	3.6	2.6
$D_i^S$ (m <sup>2</sup> /s)	$3.4 \times 10^{-19}$	$1.3 \times 10^{-18}$	$1.4 \times 10^{-21}$	$3.0 \times 10^{-21}$

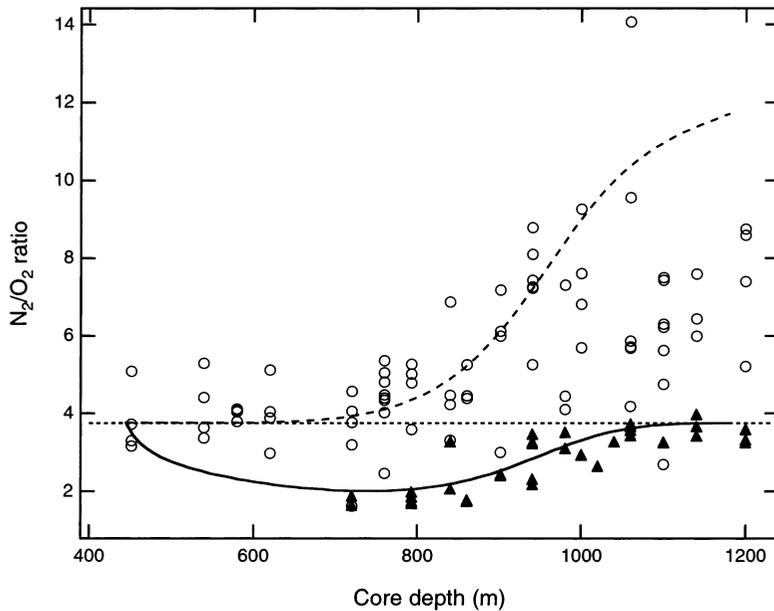


Fig. 4. The calculations of the  $N_2/O_2$  ratio of clathrate hydrate (solid line) and air bubble (broken line) of the Dome-Fuji ice (Ikeda-Fukazawa et al., 2001). The solid triangles and the open circles show the experimental data for clathrate hydrates and air bubbles, respectively.

transition zone, the conventional cell-model approximation for multiphase media with low volume concentration of dispersed particles was used.

Figure 4 shows the simulated results for the variation of the  $N_2/O_2$  ratios of hydrates (solid line) and bubbles (dashed line) in the Dome Fuji ice using the averaged model. The  $N_2/O_2$  ratio of hydrates decreases rapidly from the atmospheric value in the early half of the transition zone, and then increases back to the atmospheric value in the later half of the transition zone. In contrast, the  $N_2/O_2$  ratio of bubbles gradually increases with depth. This behavior of the  $N_2/O_2$  ratios can be understood if we consider the number densities of bubbles and hydrates as a function of depth as well as mass transfer between bubbles and hydrates. At the beginning of the transition zone, newly formed hydrates have the atmospheric  $N_2/O_2$  ratio, but the  $N_2/O_2$  ratio rapidly decreases because a small number of hydrates are surrounded by a large number of bubbles that supply  $O_2$  preferentially. Corresponding to this change for hydrates, the  $N_2/O_2$  ratio of bubbles gradually increases. As the transition proceeds, new hydrates are formed from bubbles with larger  $N_2/O_2$  ratios, and then the  $N_2/O_2$  ratio of hydrates increases on average. In addition to this effect, it also increases by a higher flux of  $N_2$  than  $O_2$  from bubbles with larger ratios. At the end of the zone, mass transfer occurs mainly between hydrates with different ratios so that the ratio approaches the atmospheric value.

## 5. Conclusions

Significant gas fractionation in the transition zone was found from measurements of the depth profiles of  $N_2/O_2$  composition ratios in clathrate hydrates and air bubbles in the Dome-Fuji ice and the Vostok ice, using Raman spectroscopy (Ikeda *et al.*, 1999; Ikeda-Fukazawa *et al.*, 2001). The gas fractionation is attributed to diffusion of air molecules between air bubbles and clathrate hydrates through the ice matrix. The fractionation process was established using a mathematical model of the transformation process of clathrate hydrates from air bubbles (Salamatin *et al.*, 2001). Similar fractionation occurs in the bubbly ice zone and the bubble-free ice zone (Ikeda-Fukazawa *et al.*, 2001). These fractionations might have important implications for the interpretation of gas distributions in ice sheets and paleoatmospheric reconstruction.

The fractionation process of atmospheric gases in polar ice sheets demonstrates a valuable micro-physical process that cannot be observed on a laboratory time scale. It is possible to observe the diffusion phenomena of such large molecules as  $N_2$  and  $O_2$ , because the polar ice sheets are maintained for a very long time.

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