

## GROWTH PROCESS OF AIR-HYDRATES AND DIFFUSION OF AIR MOLECULES IN DEEP ICE SHEET

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**Abstract:** Geometrical parameters of air-hydrate crystals in Vostok ice cores revealed that air-hydrate crystals were growing in the deep ice sheet. Air-hydrate crystals with radius of 65 to 100 $\mu\text{m}$  grew while smaller crystals disappeared. Moreover, the smaller the crystal was, the quicker its number concentration decreased. A growth model of air-hydrate crystals in ice sheets was developed by assuming the spherical diffusion field of gas molecules and their steady state diffusions. The model with the given geometrical parameters gave an estimate that the product of the diffusion coefficient and equilibrium concentration of gas molecules in ice is of order  $10^{-19} \text{ m}^2 \text{ s}^{-1}$  under the conditions of the deep ice sheet. This estimate is reasonable if the concentration of gas molecules in ice is assumed to be the same as that of self-interstitial of ice. The results indicate that gas molecules could diffuse several tens of centimeters during 100 kyr.

### 1. Introduction

Polar ice cores provide direct evidence of past changes in greenhouse gas concentrations. Results obtained from deep ice cores highlight the correlation between greenhouse gas concentrations and atmospheric temperature throughout climatic cycles.

These gas molecules are stored in air bubbles at shallower depths of ice sheets, and in deeper regions, in air-hydrate crystals. In Vostok ice cores, Antarctica, air-hydrate crystals are transformed from air bubbles at depths between about 500 m and 1250 m (LIPENKOV, 1989). Therefore, in ice cores deeper than 1250 m, most ancient atmospheric gases older than the early Wisconsin glacial age are considered to be stored in air-hydrate crystals.

UCHIDA *et al.* (1994a) observed air-hydrate crystals included in Vostok ice cores of 1050 to 2542 m with an optical microscope, and measured geometrical parameters of the crystals. The dating of Vostok ice (JOUZEL *et al.*, 1993) has

indicated that the observed ice samples are aged between about 60 and 220 kyr. They revealed that the number concentration  $N$ , volume concentration  $V$  and mean volume  $V_m$  of air-hydrate crystals vary with depth, and change drastically with climatic changes. In the interglacial ice cores, for example,  $N$  is about half and  $V_m$  three times larger than in cold age ice cores.

They also revealed that  $N$  gradually decreases and  $V_m$  increases with depth below 1250 m, where no air bubbles were observed. This result suggests that air-hydrate crystals may grow slowly in the ice sheet. If so, the crystal growth of air-hydrates in the ice sheet is possibly caused by diffusion of both water and air molecules in ice, because an air-hydrate crystal contains both water molecules and air molecules. Diffusion of air molecules in the ice sheet is very important for studying the relation between greenhouse gases concentrations and climatic changes.

In the present study, we will develop a crystal growth model of air-hydrates in the ice sheet below the depth of air bubble disappearance, where the source of air molecules for crystal growth should be the air-hydrates themselves. Then we estimate the diffusion coefficient of air molecules in the ice lattice by applying the model to the geometric parameters of air-hydrate crystals obtained by UCHIDA *et al.* (1994a).

## 2. Crystal Growth of Air-Hydrates in Vostok Ice

The mean radius  $R$  of air-hydrate crystals is calculated from  $V_m$  (UCHIDA *et al.*, 1994a). The variation of  $R$  is plotted against ice ages obtained by JOUZEL *et al.* (1993) in Fig. 1. This figure shows that  $R$  gradually increases with age, except for ranging between about 110 and 140 kyr which corresponds to the interglacial age. The size of an air-hydrate crystal just after transformation is similar to that

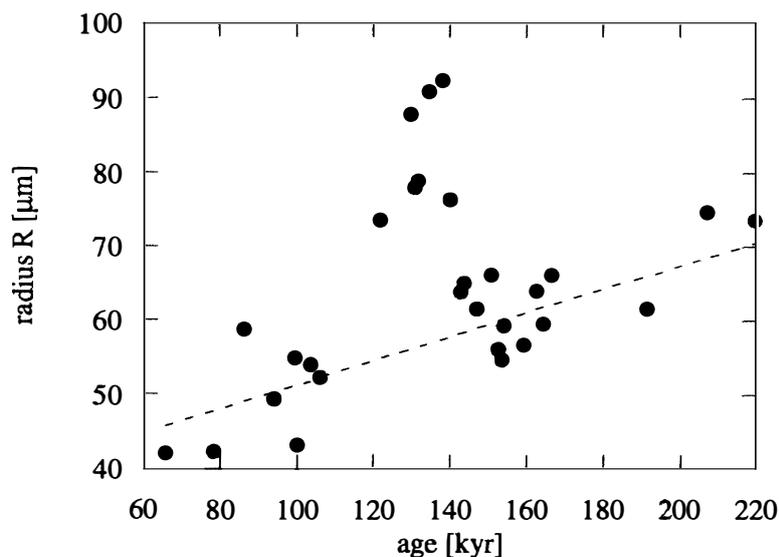


Fig. 1. Mean radius of air-hydrate crystal ( $R$ ) against core dating of the ice age (JOUZEL *et al.*, 1993). The dotted line indicates the mean growth rate of air-hydrate crystals in cold age ice.

of original air bubbles (UCHIDA *et al.*, 1992), and the size of air bubbles is determined by climatic conditions (LIPENKOV, 1989). Therefore, the sizes of air-hydrate crystals just after transformation in the interglacial age ice are assumed to be different from those in a cold age ice, which is caused by climatic changes. In order to prevent the effects of climatic changes, we use geometrical parameters of cold age ice only for estimations and modeling in the present study.

It is also assumed that air-hydrate crystals in cold age ice are almost the same size at all depths. Then the dotted line in Fig. 1 shows that air-hydrate crystals grow slowly, and linearly with time. The mean crystal growth rate of air-hydrates,  $dR/dt$ , in cold age ice is estimated as about  $0.16 \mu\text{m kyr}^{-1}$  by the least square method (the correlation coefficient is 0.77). This crystal growth rate is two orders of magnitude smaller than the transformation rate from an air bubble to an air-hydrate crystal obtained in the laboratory (UCHIDA *et al.*, 1994b).

In order to make sure that air-hydrate crystals grow in ice, we have classified air-hydrate crystals with size at intervals of  $10 \mu\text{m}$  in radius (smaller than  $10 \mu\text{m}$ ,  $10\text{--}20 \mu\text{m}$ ,  $20\text{--}30 \mu\text{m}$ , etc.). Figure 2 shows some variations of the number concentration included in each size range,  $n$ , against the ice age. The figure indicates that the number concentration of small crystals decreases with time (dashed line for  $10\text{--}20 \mu\text{m}$ , for example) whereas that of large crystals increases (dotted line for  $70\text{--}80 \mu\text{m}$ ).

Figure 2 also shows that  $n$  increases or decreases exponentially with time.

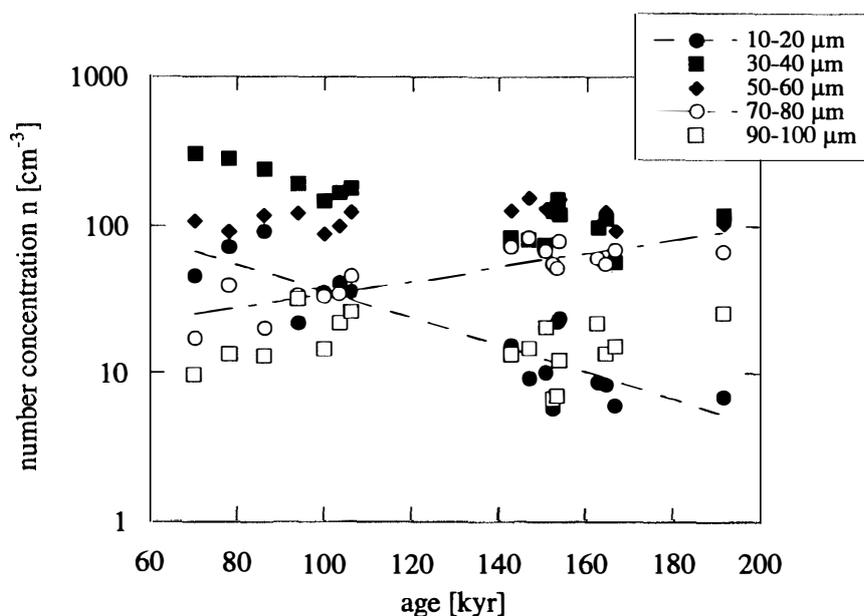


Fig. 2. Number concentration of air-hydrate crystals in cold age classified by size ( $n$ ) against core dating of the ice age. The dotted line shows the mean decreasing rate of  $n$  ( $10\text{--}20 \mu\text{m}$  in radius; solid circle). The broken line shows the mean increasing rate of  $n$  ( $70\text{--}80 \mu\text{m}$ ; open circle).

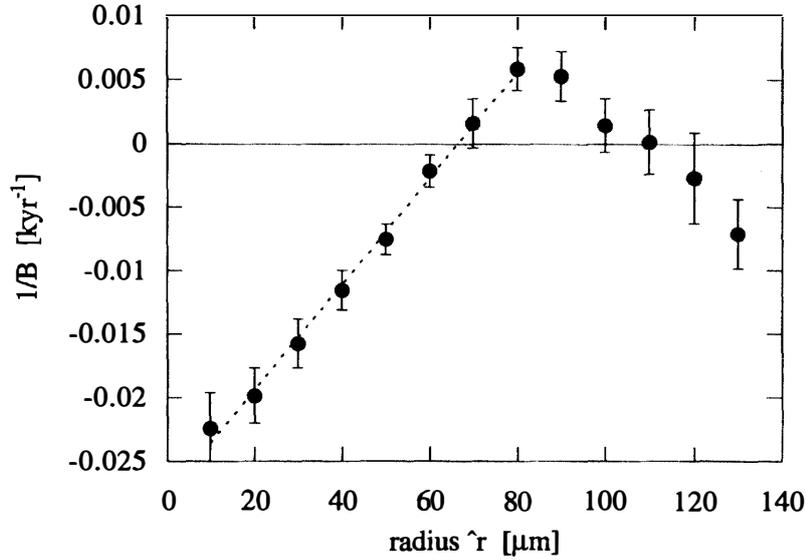


Fig. 3. Size dependence of mean rate of increase coefficient of  $n$ ;  $B$  (see eq. (1)). If  $B$  is negative, number concentrations of air-hydrate crystals decrease with time at a time constant  $B$ . The dotted line indicates the dependence of  $1/B$  on  $\hat{r}$  ranging between 10 and 80  $\mu\text{m}$ , which is estimated by the least square method.

Then we estimate the rate of increase of  $n$ , assuming the time dependence of  $n$  as follows:

$$\frac{n}{n_0} = \exp\left(\frac{t}{B}\right), \quad (1)$$

where  $n_0$  [ $\text{cm}^{-3}$ ] and  $B$  [kyr] are constants, and  $t$  is time. If  $B$  is negative, it indicates that air-hydrate crystals of such sizes will decrease with time at a time constant  $B$ .

Figure 3 shows the variation of  $1/B$  with the median of each size range,  $\hat{r}$  [ $\mu\text{m}$ ]. It indicates that the smaller the crystal is, the quicker its number concentration decreases. The dependence of  $B$  on  $\hat{r}$  between 10 and 80  $\mu\text{m}$  (shown by the dotted line in Fig. 3) is estimated by the least square method as follows:

$$B = \frac{2.4 \times 10^3}{\hat{r} - 67}. \quad (10 < \hat{r} < 80 \mu\text{m}) \quad (2)$$

Figure 3 also shows that the crystals whose radii are larger than 100  $\mu\text{m}$  will not grow effectively. It is, therefore, concluded that air-hydrate crystals whose radii are between 67 and 100  $\mu\text{m}$  grow in the ice sheet while smaller crystals disappear.

### 3. Crystal Growth of Air-Hydrates and Diffusion of Air Molecules in Ice

Normally air molecules are assumed to neither dissolve nor to diffuse in ice considerably. However, the result of the crystal growth of air-hydrates in ice suggested that air molecules can dissolve and diffuse in ice. As the source of air

molecules is air-hydrate crystals themselves below the depth of air bubble disappearance, an air-hydrate crystal in ice should grow with the supplement of air molecules from neighboring small air-hydrate crystals. Then the driving force of the air molecule diffusion in ice should be the difference of air molecule concentrations around each air-hydrate crystal.

The concentration of air molecules,  $C_{gi}$ , around an air-hydrate crystal with radius  $r_i$  is explained by Gibbs-Thomson's formula as follows:

$$C_{gi} = C_{ge} \exp\left(\frac{2\Omega_{ah}\gamma_{ah}}{kTr_i}\right), \quad (3)$$

where  $C_{ge}$  is the equilibrium concentration of air molecules in ice, which is written as the mole fraction, at temperature  $T$  and pressure  $P$ .  $\Omega_{ah}$  is the mean volume of an air molecule in the air-hydrate crystal,  $\gamma_{ah}$  is the boundary energy of the air-hydrate crystal with ice (UCHIDA *et al.*, 1993) and  $k$  is the constant. The suffix  $i$  identifies the individual crystal. According to this equation, the concentration of air molecules around a small air-hydrate crystal is larger than that around a large one. Thus, a difference of air molecule concentration appears, and drives the air molecule diffusion from small crystals to large ones in ice (Fig. 4).

We propose a crystal growth model of air-hydrates in ice taking the air molecules dissolved in ice into consideration. We derive this model from the following four assumptions. First, spherical air-hydrate crystals are distributed uniformly in ice. There are only two sizes of crystals whose radii are described as follows:

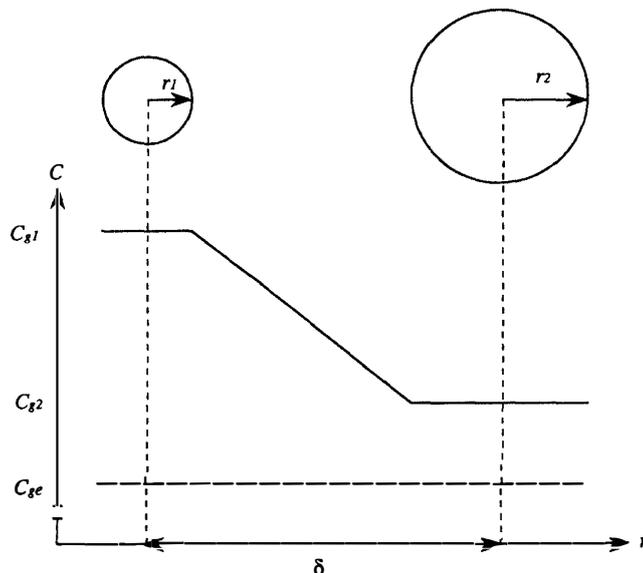


Fig. 4. Schematic diagram of air molecule concentrations in ice around two sized air-hydrate crystals. The distance between these crystals is  $\delta$ . The concentration of air molecules around each crystal is obtained by eq. (3). Both concentrations are considered to be higher than the equilibrium concentration in ice ( $C_{ge}$ ). The concentration difference is the driving force of the air molecule diffusion in ice.

$$r_1 = \left(\frac{d-s}{2}\right), \quad (4-1)$$

$$r_2 = \left(\frac{d-s}{2}\right), \quad (4-2)$$

where  $d$  is the mean diameter of air-hydrate crystals and  $s$  is its standard deviation (UCHIDA *et al.*, 1994a). Second, the diffusion field of air molecules is spherical. The radius of the field,  $\delta$ , is equal to the mean distance of each air-hydrate crystal, that is  $\delta = N^{-1/3}$ . There is a large air-hydrate crystal (radius  $r_2$ ) at the center of the spherical diffusion field, and the air molecule concentration at the shell of the field is uniform, which equals that around the small air-hydrate crystal (radius  $r_1$ ),  $C_{g1}$ . Third, the diffusion of air molecules is in a steady state in the field. This is because the mean growth rate of air-hydrate crystals,  $dR/dt$ , is almost constant (see Appendix). Fourth, the supplied air molecules will crystallize soon after they reach the surface of the large air-hydrate crystal.

This model allows us to estimate the diffusion coefficient of the air molecule through ice,  $D_g$ . As the value of  $C_{ge}$  is not known yet, the product of  $D_g$  and  $C_{ge}$  is useful for the evaluation. The product  $D_g C_{ge}$  is obtained from the following equation as described in the Appendix.

$$D_g C_{ge} = \frac{dr_2}{dt} \frac{(\delta - r_2)}{\delta} \frac{\delta_2}{\Omega_{ah}} \frac{\Omega_i}{\Omega_{ah}} \left[ \exp\left(\frac{2\Omega_{ah}\gamma_{ah}}{kTr_1}\right) - \exp\left(\frac{2\Omega_{ah}\gamma_{ah}}{kTr_2}\right) \right]^{-1}. \quad (5)$$

If air molecules diffuse in the interstitial mechanism,  $D_g C_{ge}$  gives the diffusion coefficient of air molecules in the ice lattice under atmospheric pressure and thermal equilibrium.

The value of  $D_g C_{ge}$  calculated from eq. (5) with geometric parameters of air-hydrate crystals in Vostok ice cores (UCHIDA *et al.*, 1994a) at depths of 1350

Table 1. Estimations of  $D_g C_{ge}$  from geometric parameters of air-hydrate crystals in cold age ice at Vostok ranging from 1350 to 2050 m.  $r_1$  and  $r_2$  are calculated from eqs. (4-1) and (4-2), respectively.  $\delta$  is the mean distance of air-hydrate crystals.

Depth m	$r_1$ $\mu\text{m}$	$r_2$ $\mu\text{m}$	$\delta$ $\times 10^{-3}\text{m}$	$D_g C_{ge}$ $\times 10^{-19}\text{m}^2\text{s}^{-1}$
1350	26.9	59.6	1.05	2.5
1421	20.4	65.6	1.05	1.3
1430	22.9	56.5	1.08	1.9
1470	13.0	62.5	1.02	0.53
1501	2.61	63.1	1.05	2.2
1980	36.5	73.9	1.15	4.3
2001	35.5	79.8	1.21	4.0
2011	31.6	67.5	1.15	3.5
2031	30.3	65.9	1.11	3.2
2041	30.6	71.5	1.09	3.0

to 2050 m (only cold age ice) are listed in Table 1. This indicates that  $D_g C_{ge}$  is of order  $10^{-19} \text{ m}^2 \text{ s}^{-1}$  under the conditions of the deep ice sheet ( $T$  is about  $-40^\circ\text{C}$  and  $P$  is about 10 MPa).

#### 4. Air Molecules in Ice Sheets

As neither values of  $D_g$  nor  $C_{ge}$  are known, we will compare the value of the product of  $D_g$  and  $C_{ge}$  of air molecules with those of water molecules. GOTO *et al.* (1986) obtained the equilibrium concentration,  $C_{we}$ , and the diffusion coefficient,  $D_w$ , of water molecules in ice using the X-ray diffraction method. They also revealed that the diffusion mechanism of water molecules in ice (self-diffusion) is interstitial. The product of  $D_w$  and  $C_{we}$  under conditions of the deep ice sheet can be calculated to be of order  $10^{-17} \text{ m}^2 \text{ s}^{-1}$ . This value is two orders larger than that of air molecules. If we assume  $C_{we} \approx C_{ge}$ , then we obtain the value of  $D_g$  to be  $0.01 D_w \approx 10^{-14} \text{ m}^2 \text{ s}^{-1}$  under deep ice sheet conditions.

If the diffusion mechanism of air molecules in ice is the interstitial type, it is more difficult for air molecules (mainly  $\text{N}_2$  and  $\text{O}_2$  molecules) to diffuse through the ice lattice than water molecules, because their molecular size is larger than that of water (HONDOH and UCHIDA, 1992). Then the diffusion coefficient of air molecules under the conditions of deep ice sheets should be larger than that of water molecules. The result  $D_g < D_w$  agrees with this prediction qualitatively.

SATOH *et al.* (1994) measured the diffusion coefficient of  $\text{N}_2$  molecules,  $D_{\text{N}_2}$ , in ice. They obtained  $D_{\text{N}_2} \approx 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in polycrystalline ice at about  $-10^\circ\text{C}$  and atmospheric pressure. However,  $D_{\text{N}_2}$  in a single ice crystal is considered to be smaller than  $10^{-10} \text{ m}^2 \text{ s}^{-1}$  under the same conditions. They hypothesized that  $D_{\text{N}_2} \approx 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  is the value of the grain boundary diffusion of  $\text{N}_2$  molecules. Considering the analogy that the diffusion coefficient of water molecules in an ice lattice is  $10^{-4}$  times as much as that in grain boundaries (ALLEY *et al.*, 1986), the diffusion coefficient of  $\text{N}_2$  molecules in an ice lattice should be of order  $10^{-4} D_{\text{N}_2}$ . This value coincides well with that estimated in the previous section,  $D_g \approx 10^{-14} \text{ m}^2 \text{ s}^{-1}$ .

$D_g$  allows us to estimate the distance of air molecule diffusion,  $x$ , in ice sheets as  $x = (D_g t)^{1/2}$ . If  $D_g \approx 10^{-14} \text{ m}^2 \text{ s}^{-1}$  and the same conditions have been maintained for 100 kyr ( $t \approx 3 \times 10^{12} \text{ s}$ ),  $x$  is several tens of centimeters. As  $\delta$  is much smaller than  $x$ , air molecules in ice sheets can diffuse enough to grow air-hydrate crystals. However, since annual layers in deeper regions of ice sheets become thinner, the diffusion of air-molecules becomes a serious problem.

UCHIDA *et al.* (1994a) related the volume concentration of air-hydrate crystals,  $V$ , to the total gas content, on the assumption that air molecules do not dissolve in ice. However, we consider the air molecule concentration in ice to be  $C_{ge} \approx C_{we}$ . Then we should discuss how much  $C_{ge}$  affects  $V$ . By assuming that the equation for  $C_{we}$  (eq. (1) in GOTO *et al.*, 1986) can be applied to  $C_{ge}$ , we estimate  $C_{ge}$  under conditions of the deep ice sheet to be of order  $10^{-5}$  in volume fraction. This value is equivalent to the order of  $10^{-8}$  in the volume concentration of air-hydrate crystals. As  $V$  is of order  $10^{-4}$  (UCHIDA *et al.*,

1994a),  $C_{ge}$  becomes about  $10^{-4}$  times as much as  $V$ . This value is sufficiently smaller than experimental error. Therefore,  $C_{ge}$  is so small that the relation between  $V$  and total gas content is significant. However, if the assumption of  $C_{ge} \approx C_{we}$  is correct, the problem of air molecules dissolved in ice becomes more serious in deeper regions because  $C_{ge}$  increases with temperature and pressure.

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### Appendix: The diffusion model of air molecules in ice

In the spherical diffusion field, a large crystal (radius  $r_2$ ) exists at the center and a small one is distributed uniformly on the shell at a distance  $\delta$  from the center. As shown in Fig. 4, the concentration difference between  $C_{g1}$  and  $C_{g2}$  drives air molecule diffusion from the shell to the center, where  $C_{g1}$  and  $C_{g2}$  are the gas concentration around small and large crystals, respectively.

The additional number of air molecules driven by this concentration difference in unit time,  $dQ_s/dt$ , passing across the spherical area of  $4\pi r^2$  is:

$$\frac{dQ_s}{dt} = 4\pi r^2 \frac{J}{\Omega_i}, \quad (\text{A1})$$

where  $J$  is the flux of air molecules and  $\Omega_i$  is the free volume of an air molecule in ice. On the other hand, the quantity of air molecules used for crystal growth per unit time,  $dQ_r/dt$ , is:

$$\frac{dQ_r}{dt} = 4\pi r_2^2 \frac{dr_2}{dt} \frac{1}{\Omega_{ah}}, \quad (\text{A2})$$

where  $\Omega_{ah}$  is the free volume of an air molecule in the air-hydrate crystal. If we assume that the supplied air molecules crystallize soon after they reach the surface of the large crystal,  $dQ_s/dt$  should equal  $dQ_r/dt$ . Then the growth rate of air-hydrate crystals becomes the following equation:

$$\frac{dr_2}{dt} = \frac{\Omega_{ah}}{\Omega_i} J \left(\frac{r}{r_2}\right)^2. \quad (\text{A3})$$

Fick's law describes the flux of air molecules  $J$  as  $-D_g (dc/dr)$ , where  $D_g$  is the diffusion coefficient of air molecules in ice. If the diffusion of air molecules is steady state in this spherical field, the differential equation becomes

$$\frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) = 0. \quad (\text{A4})$$

Then  $dc/dr$  is obtained from the following equation using the parameters in Fig. 4:

$$\frac{dc}{dr} = \frac{\delta r_2}{\delta - r_2} - (C_{g2} - C_{g1}) \frac{1}{r^2}. \quad (\text{A5})$$

The growth rate of air-hydrate crystals is obtained by substituting Fick's law and eq. (A5) into eq. (A3) as follows:

$$\frac{dr_2}{dt} = D_g \frac{\Omega_{ah}}{\Omega_i} \frac{\delta r_2}{\delta - r_2} (C_{g1} - C_{g2}) \frac{1}{r_2^2}. \quad (\text{A6})$$

Since the mean growth rate of air-hydrate crystals,  $dR/dt$ , is almost constant (Fig. 1), eq. (A5) indicates that the flux of air molecules in the ice sheet can be considered to be the steady state. The product of the diffusion coefficient and the equilibrium concentration of air molecules in ice,  $D_g C_{ge}$ , is obtained by substituting eq. (3) into (A5), which becomes eq. (5).