

THE EFFECT OF HYDROSTATIC PRESSURE ON THE FORMATION OF AIR-HYDRATE CRYSTALS

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Abstract: The transformation of air-hydrate crystals from air-bubbles in ice was observed by a microscope at 270 K under high hydrostatic pressure between 19.6 and 34.3 MPa during the period of 16 days. The number concentration of the air-hydrates formed by the pressurization was measured and was compared with the number concentration of the air-bubbles included. It was found that the transformation rates calculated from these number concentrations increased from 0 s^{-1} at 19.6 MPa to $5.4 \times 10^{-9} \text{ s}^{-1}$ at 34.3 MPa. The transformation process is discussed in terms of the nucleation theory of the crystal.

1. Introduction

SHOJI and LANGWAY (1982) first found air-hydrates in fresh ice cores from Dye-3, Greenland, using an optical microscope. Subsequently, SHOJI and LANGWAY (1987) reported that the shallowest depth at which air-hydrates were observed in the Dye-3 core was 1092 m, and at the depth of 1642 m, air-bubbles disappeared completely in the Dye-3. This means that air-hydrates and air-bubbles coexist in the zone between 1092 m and 1537 m, known as the transition zone. The zone corresponds to a time interval of about 6000 years (REEH *et al.*, 1985). According to MILLER (1969), air-hydrates form at the depth at which the pressure in the air-bubbles is equal to the dissociation pressure of the air-hydrate. This depth, approximately equal to the shallowest depth of the transition zone, is calculated to be 990 m at Dye-3. SHOJI and LANGWAY (1987) measured the phase boundary energy between ice and air-hydrate and reported that its value was very high compared with the grain boundary energy. They pointed out that the observed high phase boundary energy might act as a high threshold in the transformation from air-bubble to air-hydrate, thereby causing the very thick transition zone of about 450 m.

LIPENKOV (1989) observed air-bubbles and air-hydrates in ice cores from Vostok station, Antarctica. He revealed that air-hydrates formed at about 500 m depth and the transformation from air-bubble to air-hydrates was completed at about 1250 m depth. In this case as well, the shallowest depth that air-hydrates formed was similar to the depth obtained from the dissociation pressure of air-hydrates. The thickness of the transition zone is about 750 m, corresponding to a time interval of about 60000 years (LORIUS *et al.*, 1985).

UCHIDA observed the growth process of air-hydrate from air-bubbles in ice

under hydrostatic pressures ranging from 10 to 20 MPa and temperatures ranging from 265 to 270 K, and found that the transformation to air-hydrate from air-bubbles was completed in a few weeks (UCHIDA *et al.*, 1992 ; UCHIDA, 1993). Even if we take into consideration the temperature effect which reduces the transformation rate in Dye-3 and Vostok cores, This leads to the conclusion that the thick transition zone is not caused by the growth process but by the nucleation process. Contrary to the result of SHOJI and LANGWAY (1987), UCHIDA *et al.* (1993) precisely measured the phase boundary energy between air-hydrates and ice and reported that it was similar to the grain boundary energy. This implies that the phase boundary is not the cause of the thick transition zone.

While the ice temperature hardly varies in the transition zone of the Dye-3 (from 253 K at 1092 m to 256 K at 1537 m (MCINNES and RADOK, 1985)), pressure increases from 9.9 MPa to 13.9 MPa. Even in the transition zone of the Vostok core, the ice temperature is almost constant (from 220 K to 227 K (RITZ, 1989)) but the pressure increases from 4.5 MPa to 11.3 MPa. The fact that the pressure difference is larger than the temperature difference in both cases implies that the transformation from air-bubbles to air-hydrate is affected by the pressure. Therefore, it is important to investigate the pressure dependence of air-hydrate formation in the study of the thick transition zone.

In order to investigate the pressure dependence of the nucleation rate of air-hydrates, we carried out ice pressurization tests including air-bubbles and observed air-bubbles before pressurization and air-hydrates after pressurization using an optical microscope. The transformation rate of air-hydrate was calculated from the number ratio of air-hydrate to air-bubbles at several pressures, and the pressure dependence of the transformation rate was obtained. In the following, we discuss the transformation rate based on crystal nucleation theory.

2. Experiments

For the preparation of ice samples including uniformly distributed air-bubbles, small ice particles were soaked into distilled and deionized water at 273 K, and the mixture was frozen rapidly. A cubic specimen with dimensions of about $30 \times 30 \times 30 \text{ mm}^3$ was cut from the central part of the frozen ice using a band saw for the pressurization tests. Sizes and number of air-bubbles included were measured in a thin section of the specimen with a thickness of 1 mm prepared before the experiments. Figure 1a shows a photograph of such a thin section. The measurements were made on a specimen volume of 30 mm^3 ; the number concentrations of the air-bubbles measured were in the range of 6 and 25 mm^{-3} . For easy comparison of the data, spherical shape was assumed for all of the air-bubbles, and then the sizes of the air-bubbles can be expressed by sphere diameters.

The specimen was encapsulated in a polyethylene bag to prevent the permeation of the pressure transmitting liquid (silicone oil Toray silicone SH200) into the specimen. Specimens were pressurized and annealed in a high pressure vessel of which detail was given in the literature (HIGASHI and SHOJI, 1979). In the

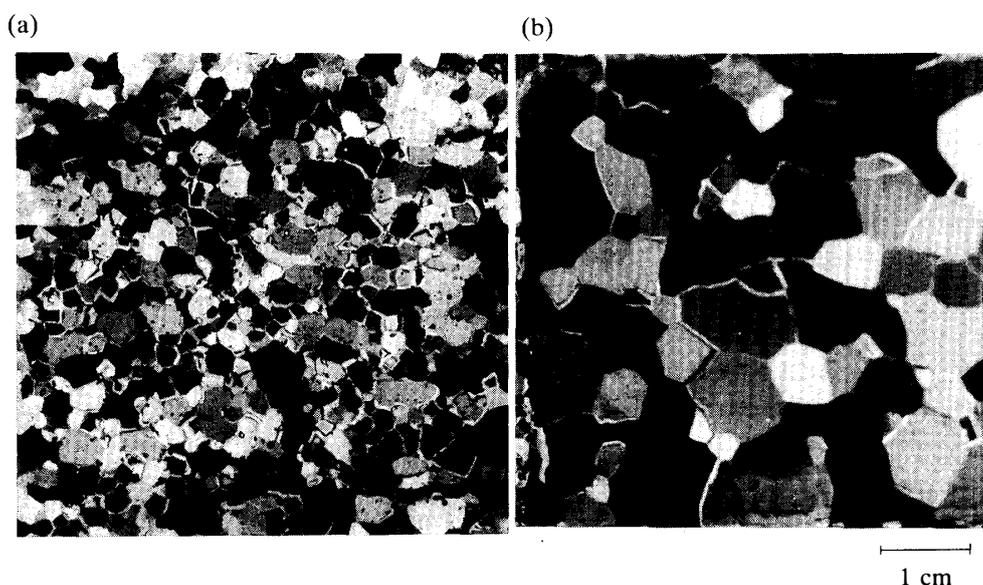


Fig. 1. Photographs of thin sections. (a) before pressurization (b) after pressurization. Photographs are taken between crossed polaroids.

present experiments, annealing period and temperature were fixed for 16 days and 270 ± 0.3 K, respectively. The applied pressure was varied among 19.6, 24.5, 29.4 and 34.3 MPa, above the dissociation pressure of air-hydrate ($P_d = 13.0$ MPa at 270 K) calculated by MILLER (1969). The pressure was kept constant within ± 0.5 MPa during the annealing.

For microscopic observations of air-hydrates after pressurization tests, a thin section of about 5 mm in thickness was cut from the central part of the cubic specimen to avoid the surface effect. Optical conditions for the observations were obtained by using silicone oil sandwiched between the thin specimen and the glass plate and by polishing the upper surface of the specimen by ethyl-alcohol. This polishing diminished the light scattering and yielded a clear image of the air-hydrate under an optical microscope. The polished upper surface was covered with a thin layer of silicone oil to prevent sublimation.

The number and sizes of air-hydrates were measured by the same method as for the air-bubbles described above, although a larger volume of the specimen ($50\text{--}150$ mm³) was observed because of the lower density of the air-hydrates.

3. Results

3.1. Transformation of air-bubbles into air-hydrates

The number concentration, N_b , of air-bubbles was measured for 12 specimens; 3 specimens for each pressure. The average number concentrations of air-bubbles for each pressure classified into the diameter range at an interval of 100 μm (from 10 to 110 μm , from 110 to 210 μm , etc.) are presented in Fig. 2. The data at pressures of 19.6, 24.5 and 34.3 MPa were almost the same, but the data at pressure 29.4 MPa was different from the others because of different microscope magnification.

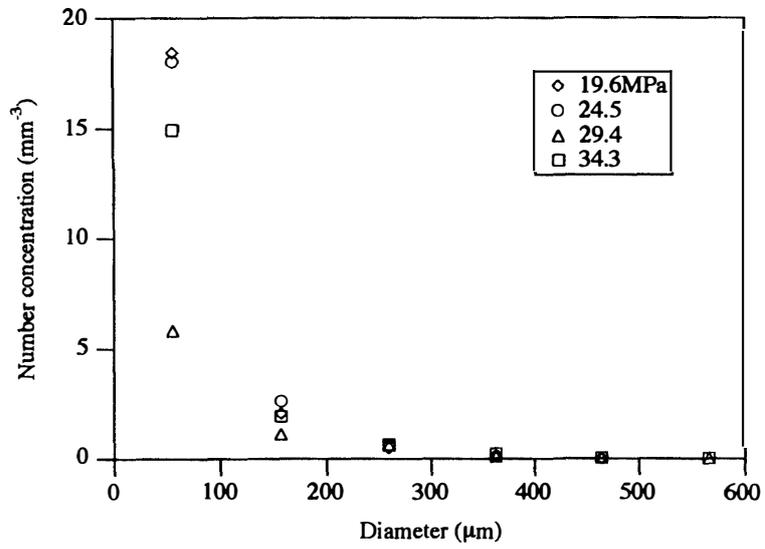


Fig. 2. Distribution of diameters of air-bubbles in the specimen before pressurization.

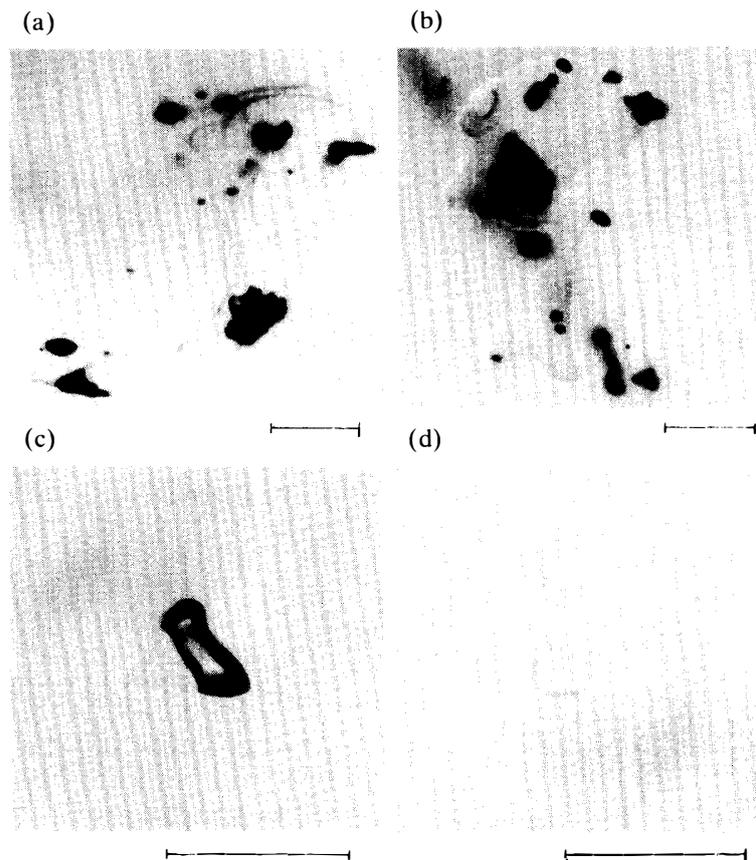


Fig. 3. Photographs of air-hydrates in the specimen after pressurization. (a)(b) irregular shape (c)(d) polyhedral shape. 100 μm bar is given for scale in each photograph.

Figure 3 is a photograph of air-hydrates under the microscope. Most of the air-hydrates were of irregular shapes, as shown in Figs. 3a and b, but about 10% of them were of a polyhedral shape, as shown in Figs. 3c and d. No significant relation between the polyhedral shape ratio and the pressure was detected.

The mean grain diameter of ice in the specimen was in the range between 1.4 and 2.2 mm before pressurization and between 2.4 and 3.3 mm after pressurization, indicating that grains grow during the pressurization tests. Since the observation shows that the mean grain diameter after the pressurization tests does not depend on the applied hydrostatic pressure, we neglect the effect of grain growth on the transformation of air-bubbles into air-hydrates.

3.2. Transformation rate of air-hydrates

Air-hydrates were observed in all specimens annealed under 24.5, 29.4 and 34.3 MPa but not in the specimens annealed under 19.6 MPa. Figure 4 shows the number concentration, N_h , of air-hydrates formed during the annealing. Since the number concentration N_h depends on the number concentration, N_b , of the air-bubbles included in the specimen, N_h was plotted against N_b in this figure. From the linear relationship between N_h and N_b found in this figure, we define the transformation rate of air-hydrates, K , as the slope of this plot divided by the annealing period. The values of K obtained were $1.1 \times 10^{-9} \text{ s}^{-1}$ at 24.5 MPa, $2.9 \times 10^{-9} \text{ s}^{-1}$ at 29.4 MPa and $5.4 \times 10^{-9} \text{ s}^{-1}$ at 34.3 MPa.

Figure 5 shows the transformation rate K as a function of pressure P . If we assume a linear relationship between K and P , then we obtain

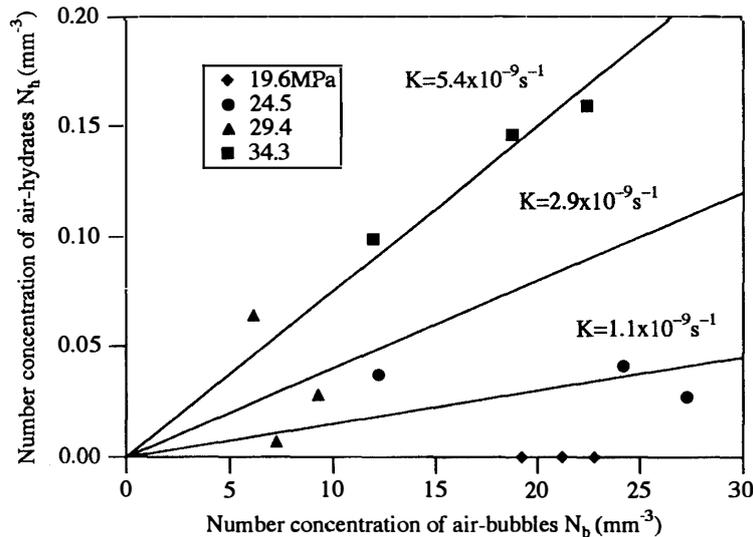


Fig. 4. The relation between the number concentration of air-hydrate (N_h) in the specimen after pressurization and the number concentration of air-bubbles (N_b) in the specimen before pressurization at 270 K. Solid lines are obtained using the method of least squares for each pressure. K is the transformation rate of air-hydrates obtained from the slope of the line divided by the annealing period.

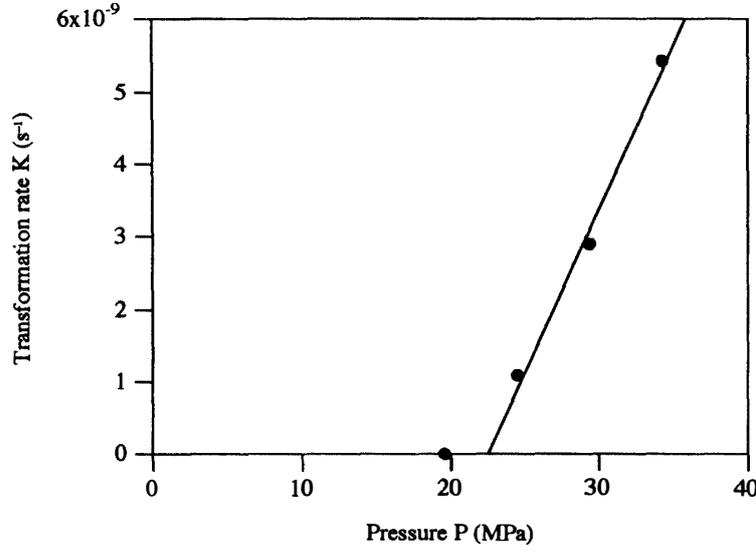


Fig. 5. Pressure dependence of transformation rate of air-hydrates (K) at 270 K. The solid line was obtained using the method of least square for 24.5, 29.4 and 34.3 MPa data.

$$K = K_0 + \alpha P, \quad (1)$$

where $K_0 = -0.014 \text{ s}^{-1}$, $\alpha = 6.1 \times 10^{-10} \text{ s}^{-1} \text{ MPa}^{-1}$.

3.3. Growth rate of air-hydrates

We define a growth rate of air-hydrates, V , as the mean radius of air-hydrates divided by the annealing period. Figure 6 shows the growth rate V as a function of excess pressure $P - P_d$. If we assume a linear relationship between V and $P - P_d$, then we obtain

$$V = \beta(P - P_d), \quad (2)$$

where $\beta = 2.2 \times 10^{-6} \text{ mmh}^{-1} \text{ MPa}^{-1}$. It is smaller than that extrapolated from UCHIDA'S experiments ($\beta = 8.4 \times 10^{-5} \text{ mmh}^{-1} \text{ MPa}^{-1}$ UCHIDA, 1993).

4. Discussion

The transformation rate, K_n , can be expressed by the following simple equation.

$$K_n = Js, \quad (3)$$

where J is the nucleation rate of air-hydrates per unit surface area of ice and s is the average surface area of air-bubble under hydrostatic pressure. Applying the rate of nucleation in condensed systems (TURNBULL and FISHER, 1949), we express J as follows

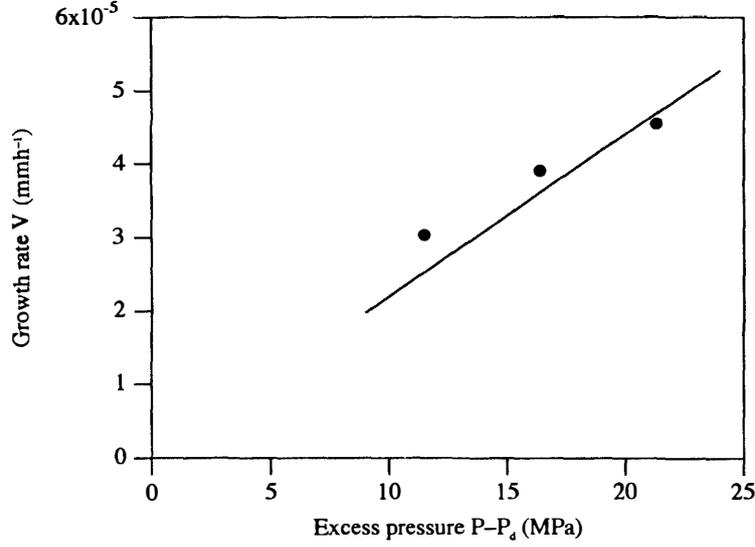


Fig. 6. Growth rate of air-hydrates (V) at 270 K against excess pressure over dissociation pressure of air-hydrate ($P-P_d$). The solid line was obtained using the method of least square.

$$J = \frac{n_l r^* kT}{h} \exp\left(-\frac{\Delta g}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right), \quad (4)$$

where n_l is the number of water molecules per unit volume of ice ($3.07 \times 10^{28} \text{ m}^{-3}$), k is the Boltzmann constant, T is temperature and h is Planck's constant. Δg is the activation energy for a water molecule to join a nucleus, assumed to be the activation energy for self diffusion in ice (0.56 eV GOTO *et al.*, 1986). ΔG^* is the activation energy of critical nucleus of which radius is r^* . To derive the expression, we assume the reaction region to be a shell of thickness r^* around an air-bubble.

HONDOH (1989) estimated ΔG^* as the maximum of the free energy change caused by the formation of an air-hydrate nucleus under pressure higher than that of air-hydrate dissociation. HONDOH assumed the nucleus to be a half spherical air-hydrate on the flat surface of an air-bubble. Using this nucleus model, r^* and ΔG^* are expressed by:

$$r^* = \frac{2 \Omega_H \gamma_{I-H}}{\Delta \mu_{I-H}}, \quad (5)$$

$$\Delta G^* = \frac{8\pi \Omega_H^2 \gamma_{I-H}^3}{3 \Delta \mu_{I-H}^2}, \quad (6)$$

where Ω_H is the molecular volume of water in air-hydrate ($3.75 \times 10^{-29} \text{ m}^3$), γ_{I-H} is the phase boundary energy between ice and air-hydrate ($\gamma_{I-H} = 0.97 \gamma_{gb}$ UCHIDA *et al.*, 1993; γ_{gb} is the grain boundary energy of ice, $\gamma_{gb} = 0.065 \text{ J/m}^2$ HOBBS, 1974) and $\Delta \mu_{I-H}$ is the difference of the chemical potentials of water molecules between ice (μ_I) and hydrate (μ_H) as

$$\Delta\mu_{I-H} = \mu_I - \mu_H = kT v_H \ln\left(\frac{P}{P_d}\right), \quad (7)$$

where v_H is the number of cages per water molecule ($v_H=3/17$ in air-hydrate). The surface area s under pressure P can be expressed by

$$s = \frac{s_0}{P^{2/3}}, \quad (8)$$

where s_0 is average surface area of an air-bubble obtained from the mean diameter of the air-bubbles in the specimen before pressurization.

According to eqs. (3), (4), (5), (6), (7) and (8), K_n is less than 10^{-10} in the pressure range between P_d and 40 GPa. This means that the formation of air-hydrates is not detectable in the pressure range of this experiment. The disagreement between K and K_n implies that the nucleation of air-hydrate is not homogeneous because the theory described above is based on the homogeneous nucleation. Then, we introduce the heterogeneous factor f which reduces ΔG^* according to:

$$\Delta G^* = \Delta G^* \cdot f. \quad (9)$$

J' denotes J using $\Delta G^{*'}$ and K'_n denotes K_n using J' below. Because of the difference of pressure dependence between K'_n and K as shown in Fig. 7, f cannot be suitable for all values of K . We calculate f by fitting K'_n for an individual K . As a result f is 0.009 at 24.5 MPa, 0.015 at 29.4 MPa, 0.020 at 34.3 MPa.

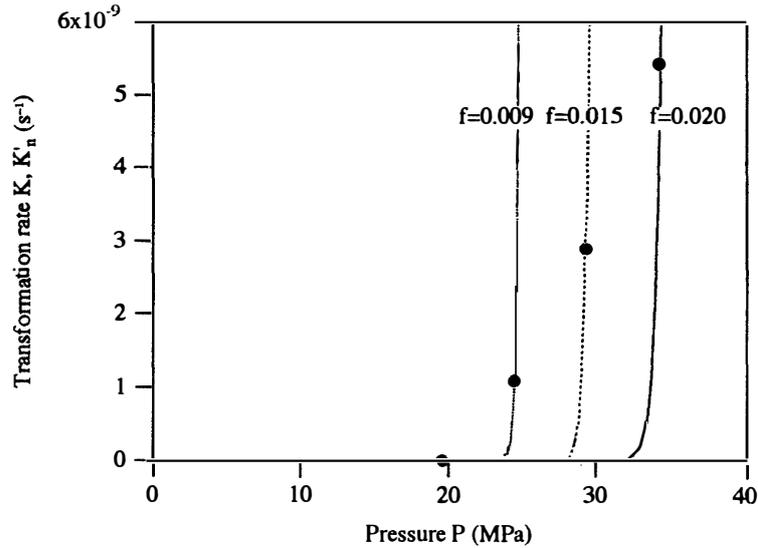


Fig. 7. Pressure dependence of transformation rate of air-hydrate at 270 K. Filled circles show observed transformation rate (K). Three curves show calculated transformation rate (K'_n) for various value of f , the heterogeneous factor for the nucleation of air-hydrate.

Although it is difficult to explain the pressure dependent factor f at present, we propose a plausible mechanism as follows: The air-bubble surface is not smooth but with many grooves. Then, application of hydrostatic pressure causes stress concentration at the grooves. Since the magnitude of the stress concentration increases with the applied pressure, a higher factor f can be expected for higher pressure. This might be the reason for the pressure dependence of the heterogeneous factor f .

We consider two possibilities for the reason why the magnitude of β in this study is smaller than that of UCHIDA (1993). One of them is the difference of definition of the growth rate V . While we calculate V as the mean radius of air-hydrates divided by the annealing period, UCHIDA calculated V from the change of the radius of air-hydrate with time. If the annealing period is longer than the growth period, then the magnitude of V in our calculation is smaller than that of UCHIDA.

Another possibility is the different specimens. Our specimen is artificial ice, but UCHIDA prepared specimens from Vostok ice core at the depth of 1514 m. Since no air-bubble was observed in the Vostok ice core deeper than 1250 m as described above, air-bubbles included in UCHIDA's specimen were presumed to have been formed by the air-hydrate dissociation after recovery from the ice sheet.

This study is a preliminary investigation of the effect of hydrostatic pressure to the air-hydrate formation. Although we cannot entirely explain the thickness of the transition zone in a polar ice sheet using the nucleation theory of air-hydrates, we can point out that pressure is the most important factor for the formation of air-hydrate.

Acknowledgments

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References

- GOTO, K., HONDOH, T. and HIGASHI, A. (1986): Determination of diffusion coefficients of self-interstitials in ice with a new method of observing climb of dislocations by X-ray topography. *Jpn. J. Appl. Phys.*, **25**, 351–357.
- HIGASHI, A. and SHOJI, H. (1979): *Renzoku kaatsu tanku nai ichiziku shikenki ni yoru nankyoku hyôshôshinbugori no seisuiatsuka ni okeru rikigaku shiken* (Mechanical tests of Antarctic deep core ice under hydrostatic pressure). *Oyo Butsuri*, **48**, 41–47.
- HOBBS, P. V. (1974): *Ice Physics*. Oxford, Clarendon Press, 837 p.
- HONDOH, T. (1989): *Hyôshôshinbu ni okeru kurasurêto suiwabutsu tankesshō no seicho katei* (Growth process of clathrate-hydrate crystals in deep ice sheet). *Nihon Kessho Seicho Gakkai Shi*, **16**, 149–161.
- LIPENKOV, V. Ya. (1989): *Obrazvaniye i razlozheniye gidratav v lednikovom l'du* (Formation and dissociation of air hydrate in ice). *Mater. Glyatsiol. Issled.*, **65**, 58–64.
- LORIUS, C., JOUSEL, J., RITZ, C., MERLIVAT, L., BARKOV, N. I., KOROTKEVICH, Y. S. and KOTLYAKOV, V. M. (1985): A 150,000-year climatic record from Antarctic ice. *Nature*, **316**, 591–596.
- MCINNES, B. and RADOK, U. (1985): A steady-state prediction of Dye 3 core features. *Geophys. Monogr.*, **33**, 111–117.

- MILLER, S. L. (1969): Clathrate hydrates of air in Antarctic ice. *Science*, **165**, 489–490.
- REEH, N., JOHNSEN, S. J. and DAHL-JENSEN, D. (1985): Dating the Dye 3 deep ice core by flow model calculations. *Geophys. Monogr.*, **33**, 57–65.
- RITZ, C. (1989): Interpretation of the temperature profile measured at Vostok, East Antarctica. *Ann. Glaciol.*, **12**, 138–144.
- SHOJI, H. and LANGWAY, C. C., Jr. (1982): Air hydrate inclusions in fresh ice core. *Nature*, **298**, 548–550.
- SHOJI, H. and LANGWAY, C. C., Jr. (1987): Microscopic observations of the air hydrate-bubble transformation process in glacier ice. *J. Phys.*, **48**, C1-551–556.
- TURNBULL, D. and FISHER, J. C. (1949): Rate of nucleation in condensed systems. *J. Chem. Phys.*, **17**, 71–73.
- UCHIDA, T. (1993): *Kyokuchi hyôshô-chu ni sonzai suru kûki hôsetsu suiwabutsu kesshô no seisei katei ni kansuru kenkyû*. Ph.D.Thesis, Hokkaido University.
- UCHIDA, T., HONDOH, T., MAE, S., DUVAL, P. and LIPENKOV, V. Ya. (1992): *In-situ* observations of growth process of clathrate air-hydrates under hydrostatic pressure. *Physics and Chemistry of Ice*, ed. by N. MAENO and T. HONDOH. Sapporo, Hokkaido University Press, 121–125.
- UCHIDA, T., MAE, S., HONDOH, T., DUVAL, P. and LIPENKOV, V. Ya. (1993): Measurements of surface energy of air-hydrate crystal in Vostok ice core, Antarctica. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **7**, 1–6.

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