

OPTIMIZED STORAGE CONDITION OF DEEP ICE CORE SAMPLES FROM  
THE VIEWPOINT OF AIR-HYDRATE ANALYSISTsutomu UCHIDA<sup>1</sup>, Takeo HONDOH<sup>2</sup>, Shinji MAE<sup>3</sup>,  
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**Abstract:** Experimental data on the dissociation rate of air-hydrate crystals in Vostok cores, Antarctica, and Dye-3 cores, Greenland, during their long term storage revealed that dissociation of the crystals affected the volume expansion of deep ice cores. The temperature dependence of the dissociation rate of the air-hydrate crystals determines the optimized storage temperature and the time period for both the transportation of ice cores and their long storage plans. The results also suggest that deep ice cores should be stored in the shape of bulk samples to prevent the from dissociating, including the air-hydrate crystals.

## 1. Introduction

Deep-ice cores drilled from the Greenland and Antarctic ice sheets undergo volume relaxation because the pressurized air bubbles expand with time after core recovery. Since the volume relaxation process affects the physical properties of ice core samples, such as decrease in bulk density, it is important to investigate the relaxation of ice cores. Below a few hundred meters depth, however, all air bubbles have transformed into air-hydrate crystals in the ice sheet. Bubble free ice relaxation can be attributed to the formation of cracks and air bubbles resulting mainly from the dissociation of air-hydrate crystals.

Some relaxation characteristics of deep ice cores have been reported, for example the decrease in density of the Byrd ice core, Antarctica (Gow, 1971). This profile indicated that the bulk density of each ice core decreased with time. The volume relaxation rate of the ice core samples varied with depth, and the largest measurable relaxation had occurred in bubbly ice from the brittle zone, where ice core samples fractured seriously soon after their recovery from the borehole.

LIPENKOV and SALAMATIN (1989) measured the porosity of Vostok ice cores, Antarctica, changing during their storage. They suggested that the relaxation processes of ice cores could be classified into three modes. The relaxation mode of an ice aggregate was determined by its initial phase condition. A-mode expansion occurred in a system containing two phases, that is, ice and air bubbles. C-mode expansion occurred in the system containing ice and air-hydrate crystals. B-mode expansion was observed in a three-phase system consisting of ice, air bubbles and air-hydrate crystals. A-mode expansion was observed to be due to the volume expansion of pre-existing bubbles. On the other hand, C-mode expansion is thought to result from the dissociation of air-hydrate crystals

and from secondary air bubble appearance. B-mode expansion resulted from the expansion of both pre-existing and secondary air bubbles. Therefore it is important to explain the effects of air-hydrate dissociation on the volume relaxation of deep ice cores as a function of storage temperature and time period. These investigations will give us good suggestions for the transformation method and the storage plan for deep ice cores.

In the present study, we examine the dissociation rate of air-hydrate crystals in Vostok ice cores from Antarctica, and Dye-3 ice cores from Greenland. On the basis of the experimental data, we have taken into account the temperature dependence of the dissociation rate of air-hydrate crystals in the deep ice cores. These dissociation rates affect both B and C-mode volume expansions of deep ice cores. We suggest, then, the optimized storage conditions of deep ice cores for preventing the dissociation of air-hydrate crystals in the ice cores.

## 2. Experimental Procedures and Results

### 2.1. Microscopic observations of air-hydrate crystals in Vostok ice cores from Antarctica

Three series of Vostok ice cores were used for microscopic observation (see Table 1). Series 1 ice cores were drilled during 1987 and 1988. They were stored in a field trench (approximately  $-55^{\circ}\text{C}$ ) for about four years and then sent to Japan. Series 2 ice cores were drilled during 1980 and 1982, and sent to France. They had been stored in a cold room at approximately  $-20^{\circ}\text{C}$  for about six years, and then transported to Japan in 1989. The experimental procedures and the results on these two ice cores have been published elsewhere (UCHIDA *et al.*, 1994a). The storage temperature and time histories of series 3 ice cores are the same as those of series 2, but the observations of series 2 ice cores were carried out in France. Results of observations were presented in a previous paper (UCHIDA *et al.*, 1994b).

Table 1. Storage temperatures and time periods of three series of Vostok ice cores.

Series*	Depth (m)	Storage condition		
		Period (month)	Temperature ( $^{\circ}\text{C}$ )	
1	1000-2100	47	$-55$	excellent
2	1200-2100	73	$-20$	bubble formation
3	1000-1300	99	$-20$	bubble, crack formation

\*1, 2: UCHIDA *et al.* (1994a), 3: UCHIDA *et al.* (1994b).

Microscopic observation revealed that neither cracks nor secondary bubbles were observed in series 1 ice cores. Some secondary bubbles due to the dissociation of air-hydrate crystals were found in both series 2 and 3 ice cores. When air-hydrate dissociation occurs, a transparent crystal changes to an opaque object, that is, a secondary air bubble (Fig. 1a). The gas pressure of the secondary bubbles is the same as the dissociation pressure. Sometimes cracks were formed around a dissociating air-hydrate crystal (Fig. 1b). As shown in UCHIDA *et al.* (1994b), the formation of air-hydrate crystals stabilized the ice core. The dissociation of air-hydrates, therefore, makes the quality of the ice core lower.

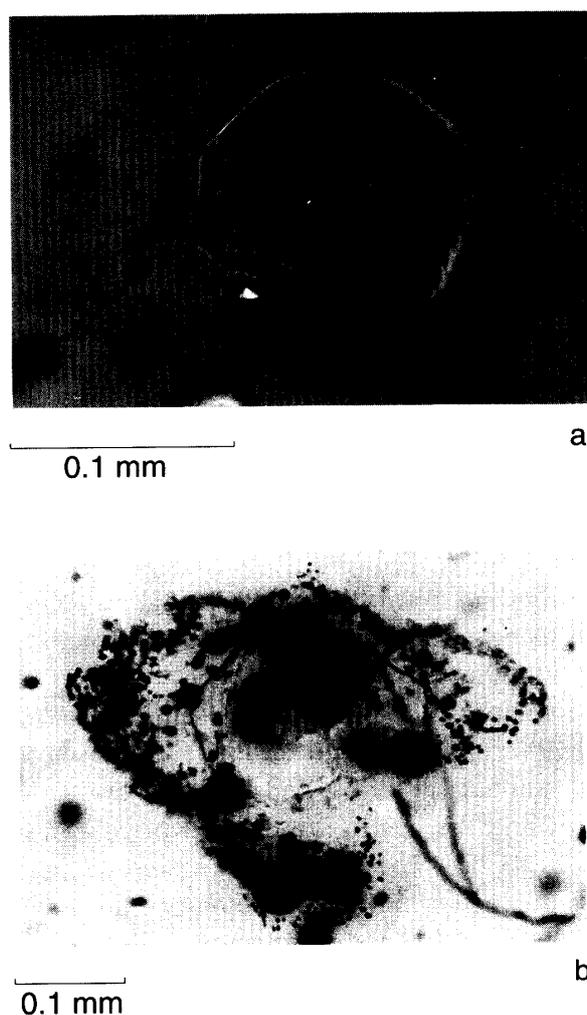


Fig. 1. Dissociation patterns of an air-hydrate crystal.  
 (a) Partly dissociated crystal (transparent) and secondary bubble (opaque).  
 (b) Dissociation of the crystal with cracks forming around it.  
 Significant amounts of small air bubbles were formed along the cracks.

Here we compare the number concentration change of air-hydrate crystals under different ice core storage conditions. We use the series 1 ice core for the reference number concentration  $N_0$  [ $\text{m}^{-3}$ ] in each depth because of its excellent quality. The change of the number concentration of air-hydrate crystals with time is, then, explained by the following equation:

$$\frac{N}{N_0} = \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

where  $N$  [ $\text{m}^{-3}$ ] is the number concentration of air-hydrate crystals in each ice core,  $t$  [day] is the storage time period and  $\tau$  [day] is the time constant.  $\tau$  indicates the time period that the number concentration of air-hydrate crystals decreases to  $N_0/e$ . The depth profile of  $\tau$  for the Vostok ice core is shown by solid marks in Fig. 2 ( $\bullet$  is for series 2, and  $\blacklozenge$ , for series 3).

Figure 2 shows that values of  $\tau$  above the depth of 1600 m are smaller than those of

deeper ice cores. This means that air-hydrate crystals in a deeper ice core are more stable than those in a shallower one. The ice cores above 1250 m included pre-existing air bubbles, so their volume expansion was in B-mode. The difference between the shallower and deeper ice cores, therefore, mainly results from the difference of the expansion mode. The depth variation of  $\tau$  corresponds qualitatively to the results obtained in UCHIDA *et al.* (1994b).

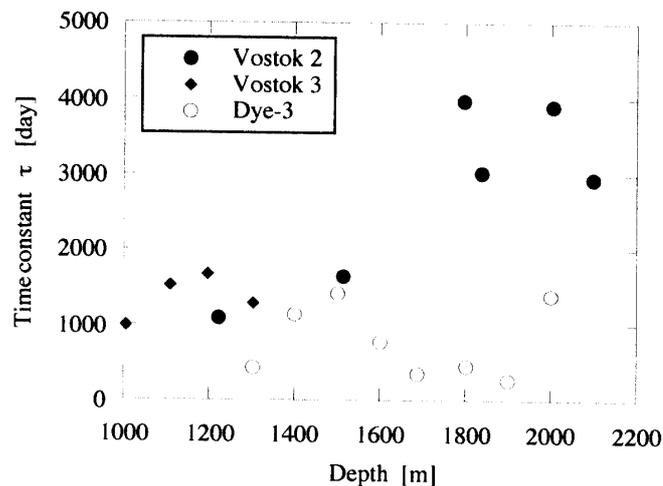


Fig. 2. Depth profiles of time constant  $t$  of series 2 (●) and series 3 (◆) of Vostok ice cores, and of Dye-3 ice cores (○).

## 2.2. Decreasing rate of the number concentration of air-hydrate crystals in Dye-3 ice core, Greenland

The measurements of the number concentration of air-hydrate crystals in the Dye-3 ice core, Greenland, were carried out by SHIGESATO (1985). The depth range of these ice cores was below 1300 m, which included both the Holocene-Wisconsin glacial period boundary at about 1800 m (DANSGAARD *et al.*, 1985), and the bottom of the brittle zone at 1300 m (UCHIDA *et al.*, 1994b).

SHIGESATO also observed the air-hydrate crystals with a microscope on thin section samples of the Dye-3 ice (about 3 to 4 mm thick). He measured their number concentration several times during one to two years after their recovery. During the time period, the thin sections were stored in the silicone oil bath at approximately  $-12^{\circ}\text{C}$ .

The measurement of the number concentration of air-hydrate crystals revealed that the number concentration of air-hydrate crystals in each sample decreased with time (Fig. 3). This figure also shows that the decreasing rate was different in each sample. To compare the decreasing rates of the Dye-3 ice core with those of the Vostok ice core, we calculated the time constant  $\tau$  by using eq. (1).

The variation of  $\tau$  of the Dye-3 ice core with depth is also represented by the open circles in Fig. 2. The error of the calculation of  $\tau$  is about 20%. The value of  $\tau$  varies ranged between 200 and 1500 days with depth. The ice cores above 1600 m underwent B-mode expansion, but their values of  $\tau$  are not much different from those of C-mode expansion except for the 1300 m ice core. The 1300 m ice core was in the brittle zone

(UCHIDA *et al.*, 1994b). The ice core fracture may have been the cause for the small  $\tau$  of the 1300 m ice core. The reason for the small  $\tau$  value of the 2000 m Dye-3 ice core is not clear, but it may be affected by the strong deformation of ice on the bed rock (2037 m depth).

Figure 2 shows that the values of  $\tau$  of the Vostok ice cores are larger than those of the Dye-3, especially at depths below 1600 m. This means that the volume expansion of the Dye-3 ice cores occurs more easily than that of the Vostok. Different storage conditions, that is, the higher storage temperature and thinner samples of Dye-3, may result in the lower value of  $\tau$ .

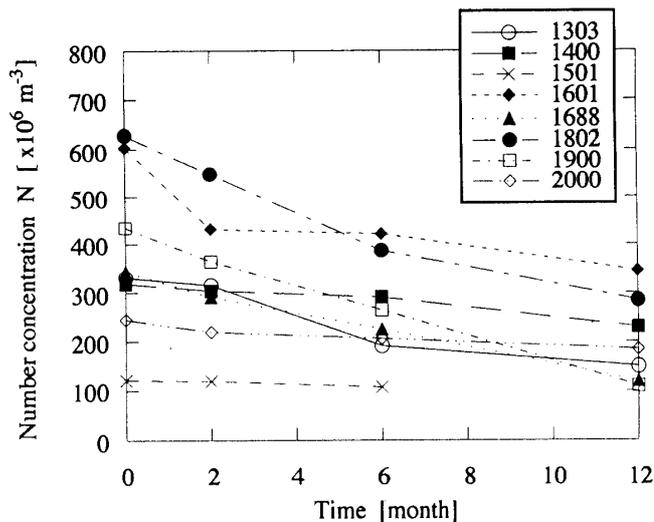


Fig. 3. Change of the number concentration of air-hydrate crystals in Dye-3 ice cores with time period at  $-12^{\circ}\text{C}$  (SHIGESATO, 1985).

SHIGESATO also measured the change of ice core density with time. Comparing the decreasing rate profile of the ice core density with the depth variation of  $\tau$ , large decreasing rate of density is observed in ice cores with small  $\tau$  values. This indicates that the volume expansion of the ice core is enhanced by dissociation of air-hydrate crystals.

### 3. Discussion

#### 3.1. Temperature dependence on air-hydrate dissociation

Air-hydrate crystals cannot exist at atmospheric pressure due to their high dissociation pressure predicted by MILLER (1969); they only exist in ice, which acts as a high pressure vessel. The existence of air-hydrate crystals in ice cores, therefore, depends on the ice storage temperature.

The driving force of air-hydrate dissociation is mainly the difference between the atmospheric pressure and the dissociation pressure of an air-hydrate crystal. The temperature and pressure phase diagram of air-hydrate (MILLER, 1969) shows that the pressure difference increases with increasing temperature. Subsequently, the higher storage temperature will result in a larger driving force of the dissociation. Moreover, the deformation of surrounding ice becomes easier at higher temperature. These temperature effects may, therefore, cause lower  $\tau$ .

The other important process in air-hydrate dissociation is the molecular diffusion of air through the ice. If the diffusion is sufficient, the air-hydrate crystal becomes unstable in ice. Here we assume a spherical air-hydrate crystal (diameter  $d$ ) in ice under a confined hydrostatic environment (pressure  $P$  and temperature  $T$ ). This crystal is stable when the air molecule concentration around it,  $C_H$ , is explained by Gibbs-Thomson's formula as follows:

$$C_H = C_e \exp \left( \frac{4 \Omega \gamma_{ah}}{d k T} \right), \quad (2)$$

where  $C_e$  is the equilibrium air concentration in ice at  $T$  and  $P$ ,  $\Omega$  is the volume of a water molecule,  $\gamma_{ah}$  is the boundary energy between air-hydrate and ice and  $k$  is Boltzmann's constant. When the ice core including this crystal is recovered from a depth in the glacier to the surface,  $C_e$  decreases to  $C_e/P$ . The excess air molecules in ice will, then, diffuse out of the ice sample. The subsequent decrease of  $C_H$  induces dissociation of the air-hydrate crystal.

The diffusion depends not only on temperature but also on the sample thickness. If the ice core is stored as a bulk sample, the gas diffusion effect will be important only in the surface region of the bulk sample. This diffusion process can also explain the lower value of  $\tau$  of the Dye-3 ice cores as compared to those of Vostok.

Microscopic observations of air-hydrate dissociation (Fig. 1) indicate that, even if the dissociation has occurred only partly, the air-hydrate will transform into an air bubble completely. The air pressure in a secondary bubble is the same as the dissociation pressure. If the temperature is high, the bubble pressure becomes high. The high bubble pressure may enhance deformation of the surrounding ice. Then volume expansion of the ice core will cause subsequent dissociation of other air-hydrate crystals around it. This idea is supported by the good agreement between the depth profile of  $\tau$  and that of the decreasing rates of Dye-3 ice core density.

### 3.2. Optimized storage conditions of ice core samples

As discussed in the previous section, the time constant of the dissociation rate of an air-hydrate crystal,  $\tau$ , depends mainly on the ice core storage temperature. Although each  $\tau$  includes some error, we will apply the experimental results to the storage condition of ice core samples, for a qualitative discussion of optimized conditions.

Average values of  $\tau$  for Vostok and Dye-3 ice cores are approximately 2380 days at a storage temperature of  $-20^\circ\text{C}$ , and 770 days at  $-12^\circ\text{C}$ , respectively. We assume the temperature dependence of  $\tau$  as:

$$\tau = \tau_0 \exp \left( \frac{a}{T} \right), \quad (3)$$

where  $\tau_0$  and  $a$  are constants. Substituting average values into eq. (3), we obtain the constant values  $\tau_0 = 3 \times 10^{-12}$  days and  $a = 9 \times 10^3$  K.

Now, we can calculate the value of  $\tau$  at an arbitrary temperature. At a temperature of  $-55^\circ\text{C}$ , which corresponds to that of the Vostok station, the value of  $\tau$  becomes approximately  $5 \times 10^3$  days. The series 1 Vostok ice cores had been stored at this condition for about 1500 days. The dissociation ratio of air-hydrate crystals in these ice cores is calculated from eqs. (1) and (3) to be only 0.3%. This estimation is supported by the fact that the quality of the series 1 ice cores was excellent. This allows us to estimate the

optimized storage condition of ice core qualitatively, although the  $\tau$ ,  $\tau_0$  and  $a$  values include experimental errors. Further measurements of air-hydrate crystals in deep ice cores will establish these parameters more accurately.

The above result allows us to estimate the optimized storage condition of ice core samples to keep air-hydrate crystals unchanged. Figure 4 illustrates the storage temperature and time period dependence of the dissociation ratio of air-hydrate crystals in ice cores. Each line represents a dissociation ratio from 1 to 50%. Using this diagram, we can suggest the optimized temperature and time period conditions for the deep ice core samples. For example, in ice core transportation at  $-20^\circ\text{C}$  for 90 days, about 4% of air-hydrate crystals will dissociate. In long term storage of ice cores, 10 years for instance, the temperature which keeps the dissociation ratio of air-hydrate crystal to be less than 1% is below  $-53^\circ\text{C}$ .

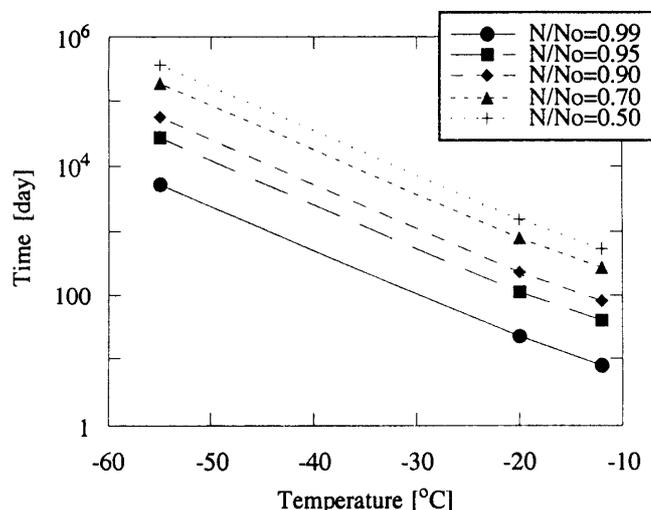


Fig. 4. Storage temperature and time period diagram of air-hydrate dissociation in ice. Each line represents a dissociation ratio of air-hydrate crystals from 1 to 50%. If a deep ice core, which includes air-hydrate crystals, is stored at  $-20^\circ\text{C}$  for 90 days, this diagram says that about 4% of the crystal will dissociate.

As a conclusion, we suggest that the most important factor in the storage of ice cores is temperature. Higher temperature enhances not only the dissociation of air-hydrate crystals but also the volume expansion of ice cores. Besides these conditions, it is also important to store ice cores as a bulk sample.

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## References

- DANSGAARD, W., CLAUSEN, H. B., GUNDESTRUP, N., JOHNSEN, S. J. and RYGNER, C. (1985): Dating and climatic interpretation of two deep Greenland ice cores. *Greenland Ice Core: Geophysics, Geochemistry and the Environment*, ed. by C.C. LANGWAY, Jr. *et al.* Washington, D.C., Am. Geophys. Union, 71–76 (Geophysical Monograph 33).
- GOW, A. J. (1971): Relaxation of ice in deep drill cores from Antarctica., *J. Geophys. Res.*, **76**, 2533–2541.
- HERRON, S. L., LANGWAY, C. C., Jr. and BRUGGER, K. A. (1985): Ultrasonic velocities and crystalline anisotropy in the ice core from Dye-3, Greenland. *Greenland Ice Core: Geophysics, Geochemistry and the Environment*, ed. by C.C. LANGWAY, Jr. *et al.* Washington, D.C., Am. Geophys. Union, 23–31 (Geophysical Monograph 33).
- LIPENKOV, V. Ya. and SALAMATIN, A. N. (1989): Relacsacionnoe rastshirenje ledyanogo kerna iz burovoy skvagyny na st. Vostok (Volume relaxation of the core from the bore hole at Vostok station). *Antarktika (The Antarctica)*, **28**, 59–72.
- MILLER, S. L. (1969): Clathrate Hydrate of Air in Antarctic Ice. *Science*, **165**, 489–490.
- SHIGESATO, Y. (1985): Raman sanran ni yoru Greenland sinsô kôrichû no air-hydrate no kenkyû (Raman spectroscopic study of air-hydrates in Greenland deep ice core), Master Thesis of Faculty of Engineering, Hokkaido University (unpublished).
- SHOJI, H. and LANGWAY, C. C., Jr. (1987): Microscopic Observation of The Air Hydrate-Bubble. Transformation Process in Glacier Ice. *J. Phys. (Paris), Colloq. C1*, **48**, 551–556.
- UCHIDA, T., HONDOH, T., MAE, S., LIPENKOV, V. Ya. and DUVAL, P. (1994a) : Air-hydrate crystals in deep ice core samples from Vostok Station, Antarctica. *J. Glaciol.*, **40**, 79–86.
- UCHIDA, T., DUVAL, P., LIPENKOV, V. Ya., HONDOH, T., MAE, S. and SHOJI, H. (1994b): Brittle zone and air-hydrate formation in polar ice sheets. *Mem. Natl Inst. Polar Res., Spec. Issue*, **49**, 298–305.

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