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EFFECTS OF AIR-HYDRATE CRYSTALS ON ICE GRAIN GROWTH

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Abstract: Microscopic observations of air-hydrate crystals in Vostok ice cores, Antarctica, revealed that air-hydrate crystals acted as obstacles to the grain boundary migration. About half of the air-hydrate crystals were observed to be located on the grain boundaries; their volume concentrations were more than 10^3 times larger than dust concentration (J. R. PETIT *et al.*, Nature, **326**, 62, 1990). The presence of air-hydrate crystals on grain boundary was considered to reduce effectively the ice grain growth rate. However, air-hydrate crystals did not result in marked changes in grain size associated with climate transitions.

1. Introduction

Grain growth in polar ice occurs in such a way that small grains shrink and disappear while large grains grow. The ice grain size as a function of depth has been investigated in ice sheets. Marked changes in grain size have been observed in deep ice cores, such as that of Dome C (PETIT *et al.*, 1987), or that of Vostok (LIPENKOV *et al.*, 1989), Antarctica. These changes appear to be associated with the climatic transitions.

ALLEY *et al.* (1986a) showed that the rate of grain growth depended on the intrinsic nature and geometry of grain boundaries in ice, and on the effects of extrinsic materials (microparticles, bubbles, and dissolved impurities). From these studies, it is clear that the microparticles exert a significant effect on grain growth only if present in high concentration. For Antarctic ice, the drag forces due to microparticles do not contribute significantly to the reduced grain growth rate of glacial ice as compared to ice in the interglacial stages. Grain growth is also nearly unaffected by porosity in firn and in ice (DUVAL, 1985). On the other hand, PETIT *et al.* (1987) proposed that grain growth rate was mainly driven by a built-in 'memory' of the surface temperature conditions at the time of deposition. The depth profiles of grain size do not seem to have been explained clearly by any theories yet.

The microscopic observations of air-hydrate crystals located on the grain boundary showed that the crystals preventd grain boundaries from migrating (Uchida *et al.*, 1993b, hereafter identified as paper I). This indicates that air-hydrate crystals act as obstacles to the grain boundary migration. The existence of air-hydrate crystals in ice is expected to affect the determination of the ice grain size.

In the present study, microscopic observations of air-hydrate crystals were carried out to determine how many air-hydrate crystals are located on the grain boundary. Subsequently, we estimated the effects of air-hydrate crystals on the depth profile of ice grain size.

2. Experimental Methods

The procedures for preparing the thin sections for microscopic observations of air-hydrate crystals on the grain boundary were the same as explained in paper I, except that the thickness of the thin sections was about 5 mm. The ice core samples used for the observations were 29 Vostok ice cores, whose depths ranged from 1050 to 2542 m. These cores were described in detail in the previous paper (Uchida *et al.*, 1993a).

Both air-hydrate crystals and grain boundaries in the sample were observed under a polarizing microscope. The number ratio of air-hydrate crystals on the grain boundary, B/N, was measured, where B is the number concentration of the air-hydrate crystal located on the grain boundary and N is the total number concentration obtained by Uchida *et al.* (1993a).

Subsequently, the thin section samples were made thinner, about 0.5 mm, for taking photographs of the thin sections under polarizing light. The average ice grain size was determined by the number concentration grains within a given area of each photograph.

3. Results

The typical air-hydrate crystals on grain boundary are the same as those observed in paper I (see Fig. 1 in paper I).

The depth profile of B/N, the number ratio of air-hydrate crystals on the grain boundary, is illustrated in Fig. 1. The ends of the error bars are given by the extreme values measured. This figure shows that the values of B/N decrease gradually with depth from 0.7 to 0.3, with some fluctuations. The average value of B/N is about 0.46 over this depth region. It is, therefore, considered that air-hydrate crystals are mainly located on the grain boundaries.

The volume concentration of air-hydrate crystals on the grain boundary, f, can be calculated as the product of B/N and V, where V is the total volume concentration of air-hydrate crystals in ice sample obtained by Uchida *et al.* (1993a). The value of f calculated in each sample is listed in Table 1. They are of order 10^{-4}, which is more than 10^3 times larger than the dust concentration in the Vostok ice core (Petit *et al.*, 1990).

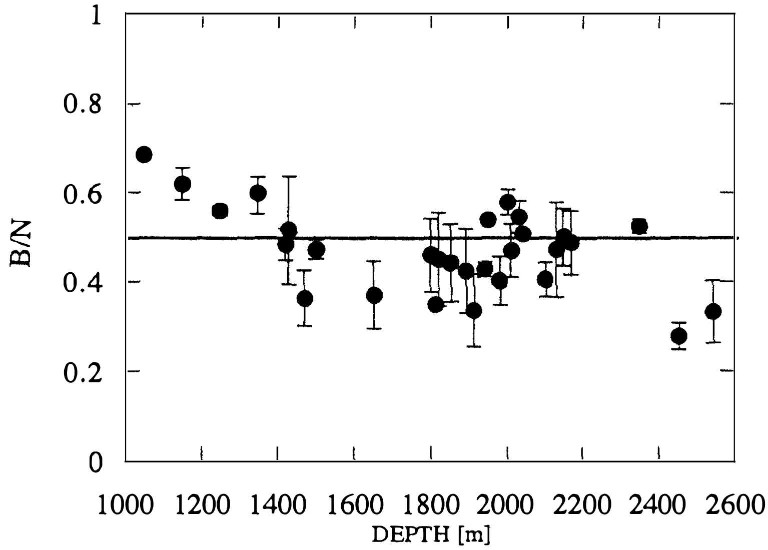

Fig. 1. Depth profile of number ratio of air-hydrate crystals on grain boundary to total number, B/N, where B and N are the number concentrations of air-hydrate crystals on grain boundary and total, respectively. Error bars represent the deviation of each measurement.

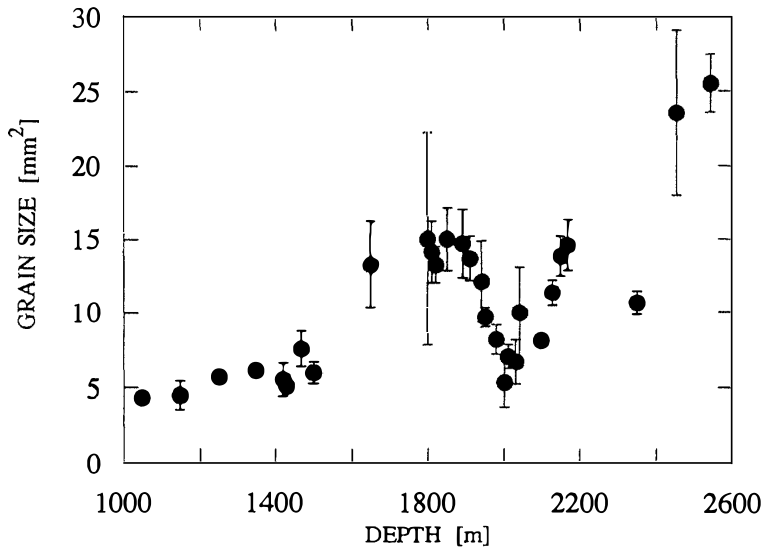

Fig. 2. Depth profile of average ice grain size, R_{obs}^2. Error bars represent the extreme values measured.

The depth profile of the average ice grain size, R_{obs}^2, is shown in Fig. 2. The ends of the error bars are given by the extreme values measured. This indicates that R_{obs}^2 increases with depth, and that the value of R_{obs}^2 in the depth range from 1650 to 1900 m are relatively large. The ice in this depth range accumulated in the interglacial period (LORIUS *et al.*, 1985). The variation of R_{obs}^2 seems to correspond to the profile measured by LIPENKOV *et al.* (1989) on the fresh ice cores of Vostok, but the values of R_{obs}^2 for the same depth are

Table 1. Effects of air-hydrate crystals on driving force for ice grain growth in Vostok ice.

Depth m	d μm	f $\times 10^{-4}$	R mm	Pe/Pi %
1050	76.4	2.51	2.07	5.04
1150	75.6	2.40	2.11	
1251	67.8	5.69	2.38	14.1
1350	86.5	2.61	2.46	
1421	86.0	2.94	2.34	
1430	79.4	1.75	2.25	
1470	75.5	2.22	2.75	5.52
1501	89.2	2.45	2.43	
1651	124.3	2.97	3.65	
1800	140.1	3.57	3.87	
1811	137.4	2.50	3.76	
1821	102.5	3.32	3.65	
1851	160.8	3.71	3.87	5.86
1891	165.9	3.30	3.83	
1910	132.5	2.34	3.70	
1941	113.4	2.68	3.49	
1950	115.2	3.13	3.11	
1980	110.4	2.55	2.86	
2001	115.3	3.99	2.30	
2011	99.1	2.28	2.65	
2031	96.2	2.74	2.59	
2041	102.2	3.42	3.16	
2101	100.2	2.23	2.84	
2131	107.9	1.45	3.38	2.98
2151	101.4	2.65	3.73	6.73
2170	116.3	2.82	3.82	
2351	101.5	2.97	3.27	
2452	126.8	1.51	4.85	
2542	125.6	1.59	5.05	4.41

The mean diameter of air-hydrate crystals is d (UCHIDA *et al.*, 1993a), the volume concentration of the crystal on grain boundary, f, the average grain radius, R, and the ratio of air-hydrate drag force to driving force for grain growth rate, Pe/Pi.

smaller. The discrepancy probably comes from the difference of the orientations of thin sections between our investigation and the previous study in which only thin sections oriented along the ice grain elongation were used.

4. Discussions

Comparison between Figs. 1 and 2 indicates that large values of R_{obs}^2 are observed in samples having low B/N values, that is, samples between 1650 and 1900 m and those below 2400 m. This is in agreement with the fact that air-hydrate crystals prevent the ice grain boundary from migrating, as is described in paper I. In addition, the depth regions having large R_{obs}^2 correspond to those of low N (UCHIDA *et al.*, 1993a). Then air-hydrate crystals are assumed to reduce effectively the rate of ice grain growth because of their pinning effects on the ice grain boundary. Here we estimate the effect of air-hydrate crystals on the grain growth rate by using the analysis model developed by ALLEY *et al.* (1986a).

Air-hydrate crystals are assumed to be spherical, uniformly distributed, of only one size d, which is small compared to grains, and to have zero mobility. The relative fractional reduction in driving force for grain growth is explained by the ratio Pe/Pi, where Pe is a drag force for grain boundary migration from air-hydrates, and Pi is the intrinsic driving force for grain growth. The ratio represents the relative fractional reduction in grain growth rate caused by air-hydrate crystals. These forces are given by the following equations (ALLEY *et al.*, 1986a):

$$Pe = \frac{8\gamma_{gb}}{9}(1+\cos\alpha)\frac{f\cdot\beta}{d}, \tag{1}$$

$$Pi = \frac{16\gamma_{gb}}{81R}, \tag{2}$$

where γ_{gb} is the grain boundary energy of ice, α is the contact angle between grain boundary and air-hydrate crystal, f is the volume concentration of the air-hydrate crystal on the grain boundary, β is the correction factor for the drag of widely spaced particles, and R is the average grain radius. Then the ratio of the drag force to the intrinsic driving force is:

$$\frac{Pe}{Pi} = \frac{9}{2}(1+\cos\alpha)\frac{f\cdot R}{d}. \tag{3}$$

Here we assume that β is identically unity.

The mean diameter of air-hydrate crystals obtained by UCHIDA *et al.* (1993a) is taken as d in eq. (3). The values of α were measured on seven samples which were shown in paper I. The calculated values of Pe/Pi for these samples are listed in Table 1. They show that the relative fractional reductions in grain growth rate caused by air-hydrate crystals range between 3 and 14%. The diagrams proposed by ALLEY *et al.* (1986b) indicate that almost all of these samples belong to the "slow growth" region, such as the ash bands of the Byrd ice core, Antarctica. In Vostok ice core, the maximum dust concentration was about 7×10^{-7} cm^3 g^{-1} (PETIT *et al.*, 1990). If we assume the radius of the dust to be about 1×10^{-4} cm, the maximum ratio of the dust drag force to the intrinsic driving force can be estimated to be a few percent. These values are similar to the minimum ratio of Pe/Pi obtained in the present study. It is, therefore, considered that air-hydrate crystals reduce the grain growth rate effectively.

As shown in Table 1, the value of Pe/Pi in the ice of a warm period, the 1851 m ice core, was not different significantly from those in the ice of cold periods. In addition, the volume concentration of the air-hydrate crystals on the grain boundary f in Vostok ice cores was almost the same magnitude in all depth ranges below the air bubble disappearance, which was more than 10^3 times larger than that of dust. The reduction in grain growth rate caused by air-hydrate crystals is, then, considered to occur over the depth range where the air-hydrate crystals exist. Therefore, it can be said that air-hydrate crystals reduce ice grain growth rate effectively, but that they do not result in the marked changes in grain size, as shown in Fig. 2, associated with climatic transitions.

The almost constant values of Pe/Pi and f below the depth of air bubble disappearance show that the mean diameter of air-hydrate crystals d is large where the average grain radius R is large (the correlation coefficient is about 0.73 for the 29 values listed in Table 1). This relation between d and R can be explained as follows. The large grain radius at the depth of pore close-off causes number concentration of air bubbles to be small (GOW, 1968). If the total gas content is almost the same, the mean volume of air bubbles becomes large in the ice containing a small number concentration air bubbles. The variation of mean volume of air bubbles may precede that of air-hydrate crystal.

This relation between d and R is observed by the comparison between the mean volume of air-hydrate crystals (UCHIDA *et al.*, 1993a) and the ice grain size (LIPENKOV *et al.*, 1989) in Vostok ice cores. Both the larger mean volume of air-hydrate crystals and larger ice grain size were observed in ice of warm periods compared with ice formed in cold periods. The variation of the mean volume of air-hydrate crystals is considered to be caused by the original variation of the mean volume of air bubbles (UCHIDA *et al.*, 1993a).

On the other hand, the observation of air-hydrate crystals in Vostok ice revealed that the air-hydrate crystals grew, while small crystals disappeared (UCHIDA *et al.*, 1993a). This requires the diffusion of both water and air molecules through ice. The measurements of ice grain size showed that ice grains had larger growth rate in warm periods (LIPENKOV *et al.*, 1989). When the ice grains grow actively, the water molecules may diffuse through the grain boundary (PETIT *et al.*, 1987). In such circumstances, the crystal growth rate of air-hydrate may be enhanced. It is, therefore, considered that the relation between d and R results from the relation between the mean diameter of air bubbles and the average ice grain size at the depth of pore close-off. Subsequently, in deeper ice, the relation may be emphasized by the diffusion of water molecules through the ice.

If water and air molecules diffuse actively, accompanied by the large crystal growth rate of air-hydrates, the mobility of air-hydrate crystals might not be zero. In the present study, however, the diffusion of water molecules is considered to be not so active that air-hydrate crystals can move. In addition, neither diffusion coefficients of air molecules in ice nor in air-hydrate crystals have been obtained. It is, therefore, assumed here that the air-hydrate crystals have zero mobility.

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References

ALLEY, R. B., PEREPEZKO, J. H. and BENTLEY, C. R. (1986a): Grain growth in polar ice: I. Theory. J. Glaciol., **32**, 415–424.

ALLEY, R. B., PEREPEZKO, J. H. and BENTLEY, C. R. (1986b): Grain growth in polar ice: II. Application. J. Glaciol., **32**, 425–433.

DUVAL, P. (1985): Grain growth and mechanical behavior of polar ice. Ann. Glaciol., **6**, 79–82.

GOW, A. J. (1968): Bubbles and bubble pressures in Antarctic glacier ice. J. Glaciol., **7**, 167–182.

LIPENKOV, V. Ya., BARKOV, N. I., DUVAL, P. and PIMIENTA, P. (1989): Crystalline texture of the 2083 m ice core at Vostok station. J. Glaciol., **35**, 392–398.

LORIUS, C., JOUZEL, 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.

PETIT, J. R., DUVAL, P. and LORIUS, C. (1987): Long-term climatic changes indicated by crystal growth in polar ice. Nature, **326**, 62–64.

PETIT, J. R., MOUNIER, L., JOUZEL, J., KOROTKEVICH, Y. S., KOTLYAKOV, V. I. and LORIUS, C. (1990): Palaeoclimatological and chronological implications of the Vostok core dust record. Nature, **343**, 56–58.

UCHIDA, T., HONDOH, T., MAE, S., LIPENKOV, V. Ya. and DUVAL, P. (1993a) : Air-hydrate crystals in deep ice core samples from Vostok station, Antarctica. J. Glaciol. (in press).

UCHIDA, T., MAE, S., HONDOH, T., DUVAL, P. and LIPENKOV, V. Ya. (1993b): 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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