

MEASUREMENTS OF SURFACE ENERGY OF AIR-HYDRATE CRYSTALS IN VOSTOK ICE CORE, ANTARCTICA

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Abstract: Microscopic observations of thin sections of Vostok ice cores, Antarctica, showed that various shapes and sizes of air-hydrate crystals are located on the grain boundaries. The surface energy of air-hydrate crystal was measured on 41 crystals in 7 different depth ice cores. These measurements revealed that the surface energy of air-hydrate was almost constant at all depths below 1050 m, and that the average ratio between the surface energy of air-hydrate and ice grain boundary energy was 0.97 ± 0.19 . The observations also showed that air-hydrate crystals acted as obstacles for ice grain boundary migration.

1. Introduction

Clathrate air-hydrate crystals exist in the deep parts of the ice sheets of both Antarctica and Greenland. They are transformed from air bubbles, and can be stable molecular compounds only at high pressure and low temperature conditions.

Microscopic observations (SHOJI and LANGWAY, 1982) have revealed that air-hydrate crystals were transparent, and that their index of refraction was slightly higher than that of the surrounding ice matrix. X-ray diffraction analysis of the air-hydrates from Dye-3 ice core, Greenland (HONDOH *et al.*, 1990), revealed that the crystallographic structure of air-hydrate crystals is Stackelberg's structure II. It also revealed that the cage occupancy of air molecules (mainly O₂ and N₂) is about 0.8.

The depth profiles of air-hydrate crystals in the deep ice cores retrieved from Vostok station, Antarctica (UCHIDA *et al.*, 1993), showed that the crystals grew in compensation for disappearance of small crystals below the depth of air bubble disappearance. The driving force of this growth process is considered to be the gradients of either air or water molecule concentrations in the ice lattice. The molecule concentrations around an air-hydrate crystal depend on the surface

energy of the crystal, γ_{ah} . The ratio of surface energies γ_{ah}/γ_{gb} , where γ_{gb} is the grain boundary energy of ice, was obtained by measurement of the contact angles between the air-hydrate crystal and the ice grain boundary. SHOJI and LANGWAY (1987) found that γ_{ah}/γ_{gb} was between 4 and 7. They measured the contact angles by partly dissolving the ice surrounding the air-hydrate crystal with a low-concentration solution of alcohol. HONDOH (1989) pointed out, however, that their results were overestimated, and assumed that γ_{ah} was the order of the surface energy of ice.

In the present study, microscopic observations of air-hydrate crystals in Vostok ice cores were carried out to determine what kinds of air-hydrate are located on the grain boundary. Subsequently, the values of γ_{ah}/γ_{gb} were measured in several ice cores of different depths by using micro-photographs of the air-hydrate crystals on the grain boundary.

2. Experimental Methods

For observations of air-hydrate crystals on the grain boundary, high quality ice cores, which contain neither cracks nor air bubbles formed by the volume relaxation of the ice core, are required. This is because air-hydrate crystals on the grain boundary are considered to dissociate easily with the volume relaxation of the core. In the present study, 7 Vostok ice cores were used, whose depths were 1050, 1251, 1471, 1851, 2131, 2151 and 2542 m. These cores were taken by the Soviet Antarctic Expedition at Vostok station, Antarctica (78°28'S, 106°48'E), during 1987 and 1989. They were stored in a field trench at about -55°C , and were sent to Sapporo in 1992. Neither cracks formed from the volume relaxation of the core nor air bubbles formed from the dissociation of the air-hydrate were observed in any of the samples. More details of these cores were described in a previous paper (UCHIDA *et al.*, 1993). The ice cores were stored in a cold room at about -50°C and all these experiments were carried out in a cold room at -20°C .

Thin section samples were cut roughly from the ice cores by a band saw and were made thinner to about 0.5 mm. The samples were prepared along the vertical direction of the ice core. The upper surface of the sample was polished chemically by ethyl alcohol to make it flat. This polishing diminished light scattering and gave clear images both for observation under the polarizing microscope and for taking photographs of the air-hydrate crystals on the grain boundary. Air-hydrate crystals were identified by the Becke test which was used by SHOJI and LANGWAY (1982).

When an air-hydrate crystal is located on the grain boundary, the triple junction of the air-hydrate and grain boundaries can be examined. The ratio of surface energies γ_{ah}/γ_{gb} is obtained by the following equation under symmetrical conditions and the isotropic assumption (SHOJI and LANGWAY, 1987):

$$\frac{\gamma_{ah}}{\gamma_{gb}} = \frac{1}{2 \cos \alpha}, \quad (1)$$

where α is half of the equilibrium dihedral angle between ice and air-hydrate phase boundaries, or the contact angle (ALLEY *et al.*, 1986). α for each air-hydrate crystal was measured on the micro-photograph. This procedure, which was different from the partly dissolved method used by SHOJI and LANGWAY (1987), gives α between air-hydrate and ice phases under thermal equilibrium conditions.

3. Results

Typical air-hydrate crystals on the grain boundaries are shown in Fig. 1. A 100 μm bar is given for scale in each photograph. Various shapes of air-hydrate crystals on the grain boundary were observed, such as spherical, irregular and faceted ones. Crystal size ranged from several decades to several hundreds of μm . It is, therefore, considered that air-hydrate crystals on the grain boundary have neither special shape nor special size.

The air-hydrate crystals on the straight grain boundary (Fig. 1a) had the symmetrical and isotropic equilibrium dihedral angles at the triple junctions of the air-hydrate and grain boundary. The equilibrium dihedral angles, 2α , were measured on 41 air-hydrate crystals by using micro-photography shown in Fig. 1a. Each surface energy ratio was obtained from eq. (1). The depth profile of the surface energy ratio of air-hydrate crystals is shown in Fig. 2. This shows that the ratios are almost constant, about unity, but those of shallower depths are slightly smaller. The average value of all surface energy ratios was calculated as follows:

$$\frac{\gamma_{\text{ah}}}{\gamma_{\text{gb}}} = 0.97 \pm 0.19. \quad (2)$$

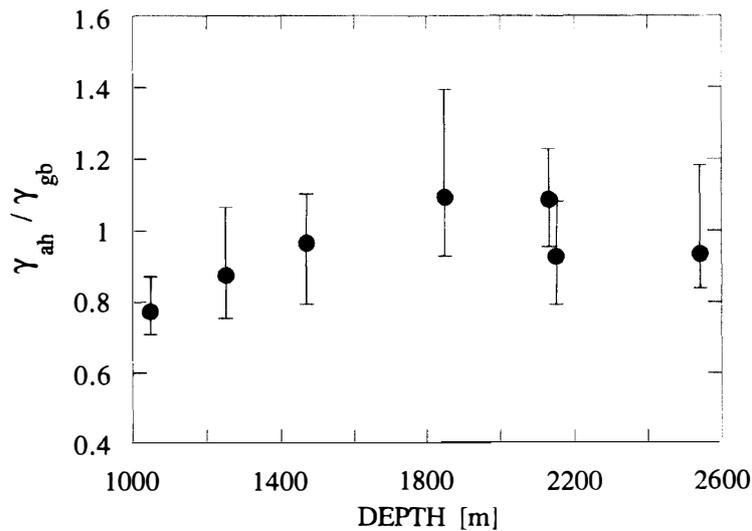


Fig. 2. Depth profile of surface energy ratio $\gamma_{\text{ah}}/\gamma_{\text{gb}}$, where γ_{ah} is surface energy of air-hydrate crystal and γ_{gb} is ice grain boundary energy. Error bars represent the deviation of each measurement.

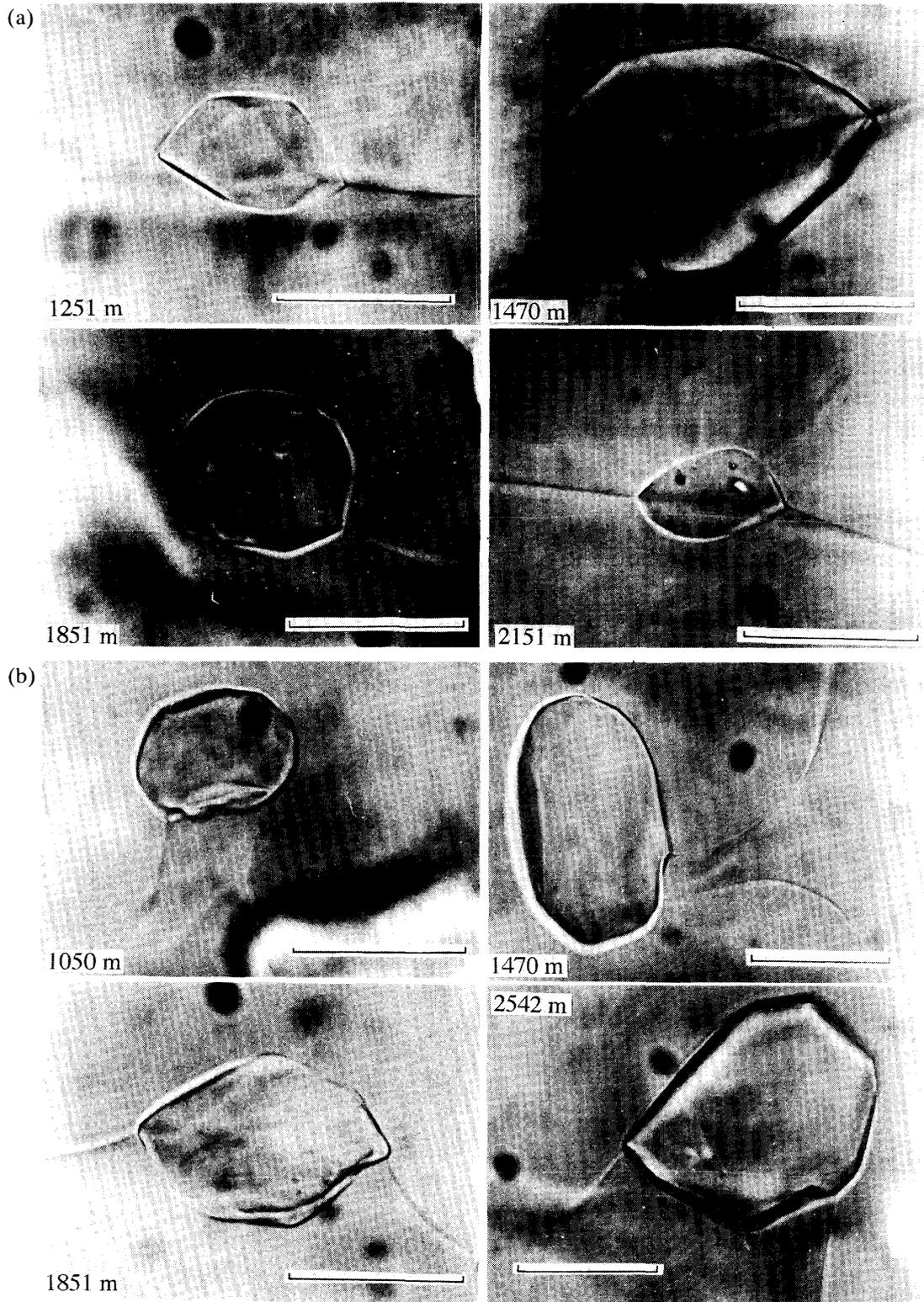


Fig. 1. Polarizing micro-photographs of air-hydrate crystals on grain boundaries. (a) A crystal located on a straight grain boundary with symmetrical equilibrium angles. (b) A crystal bending the grain boundary remarkably. A 100 μm bar is given for scale in each photograph.

This result is smaller than the values obtained by SHOJI and LANGWAY (1987), that is, between 4 and 7, and is about half of the value assumed by HONDOH (1989).

Some air-hydrate crystals were observed to bend the grain boundaries remarkably (Fig. 1b). This result indicates that the air-hydrate crystals act as an obstacle to grain boundary migration. The pinning effect on grain boundary migration seems larger when the direction of the migration is perpendicular to the long axis of oval or rod-like crystals.

4. Discussions

The surface energy of air-hydrate crystals in ice was estimated to be about the same as the grain boundary energy. This may be caused by the fact that the physical properties, such as the index of refraction or the density, of the air-hydrate crystals are similar to those of the ice lattice.

The index of refraction of air-hydrate crystals was revealed to be slightly higher than that of the surrounding ice matrix by microscopic observation (SHOJI and LANGWAY, 1982). This was supported by model calculation of the refractive index for air-hydrate by DAVIDSON *et al.* (1986). They calculated that the index of refraction of air-hydrate crystal is about 0.6% larger than that of ice.

The density of air-hydrate crystals is also considered to be similar to ice. The density of air-hydrate crystals can be calculated by using crystal structure data obtained by X-ray diffraction study (HONDOH *et al.*, 1990). When the site occupancy of air molecules for the cages is assumed to be 0.8, which was obtained by the X-ray diffraction study, the density of air-hydrate crystals is estimated to be about 0.98 g cm^{-3} at about -30°C . On the other hand, the crystal structure of the ice lattice is calculated by data measured by X-ray diffraction study (GOTO *et al.*, 1990). Then the density of air-hydrate crystals is estimated to be only about 7% larger than that of the ice lattice.

Observations of the air-hydrate crystal on the grain boundary showed that the crystal had neither special shape nor special size. This result indicates that there is no remarkable interaction between the air-hydrate crystals and the ice matrix surrounding them. It is considered that the physical properties of air-hydrate crystals are similar to those of ice lattice. The surface energy of air-hydrate crystals in ice is, therefore, almost the same as the grain boundary energy.

The surface energy ratios obtained in the present study are much smaller than those obtained by SHOJI and LANGWAY (1987). They measured contact angles by partly dissolving the ice surrounding the air-hydrate by a low-concentration solution of alcohol. This procedure permitted some time (about 30 s) to take a micro-photograph of the triple junctions of the air-hydrate and grain boundary. However, the triple junction was in contact with three phases, that is, the air-hydrate, ice and water phases. The observed contact angles were different from those between air-hydrate and ice. In addition to this, the air-hydrate could survive about 30 s only. This period appears to be not enough for the triple

junction to establish thermal equilibrium. The discrepancy between the values of γ_{ah}/γ_{gb} obtained in the previous measurements and in the present study may be caused by this problem.

As shown in Fig. 2, the values of γ_{ah}/γ_{gb} are about 20% smaller than the average value in the samples from 1050 m depth, and the value increases gradually to the average with depth. This may indicate that considerable time is necessary for the triple junction to establish thermal equilibrium. However, the depth variations are small compared to the reduction of the surface energy associated with the phase transition. When air bubbles transform to air-hydrate crystals, the boundary energy between the air bubble and ice matrix will be changed to that between the air-hydrate crystal and ice, that is, the surface energy becomes about half. It is, therefore, considered that the values of γ_{ah}/γ_{gb} are almost constant in the present study.

The microscopic observations of air-hydrate crystals on the grain boundary in Vostok ice cores revealed that various shaped air-hydrate crystals were located on grain boundaries, and that they were preventing the grain boundary from migrating. It is concluded that the surface energy of air-hydrate crystals is similar to the grain boundary energy, and that it is almost constant over the depth range below 1050 m.

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