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MICROSCOPIC OBSERVATIONS OF THE AIR HYDRATE-BUBBLE. TRANSFORMATION PROCESS IN GLACIER ICE

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Résumé - Des examens microscopiques des inclusions d'hydrates d'air ont été faits sur des échantillons provenant de forages profonds à Dye-3 et Camp-Century, Groënland et Byrd Station en Antarctique. Les plus faibles profondeurs pour lesquelles les hydrates d'air sont observés à Dye-3 Camp Century et Byrd Station correspondent respectivement à 1092 m, 1099 m et 727 m.

Pour les forages à Dye-3 et Camp Century, les profondeurs observées pour l'apparition des hydrates d'air sont en accord avec les calculs de Miller (1). Pour le forage à Byrd Station cette apparition a lieu environ 100 m moins profond que prévu par les calculs de Miller. Cette différence apparente peut être attribuée au flux ascendant de glace qui provient d'environ 5 km en amont de Byrd Station. Les observations de joints de grains et de phase et les expériences de déformation révèlent que l'énergie de joint de phases est supérieure à celle de joint de grains et que le processus de transformation de l'hydrate d'air en bulle est clairement lié à un mécanisme de nucléation induite par déformation. Ces résultats suggèrent que le processus de transformation hydrate d'air/bulle est étroitement contrôlé par un processus de restauration se produisant à la fois *in situ* et postérieurement à l'extraction.

Abstract: Microscopic examinations for air hydrate inclusions were made on specimens of the Dye-3 and Camp Century, Greenland and Byrd Station, Antarctica deep ice cores. The shallowest depths at which air hydrates are observed in the Dye-3, Camp Century and Byrd Station cores are at 1092 m, 1099 m and 727 m depths respectively. For the Dye-3 and Camp Century cores, the observed depths for air hydrate appearance agree with Miller's calculation [1]. For the Byrd Station core, the observed depth for the appearance is about 100 m shallower than the calculation result by Miller. This apparent difference at Byrd Station may be attributed to the general upward ice flow trajectory which begins about 5 km upstream from the Byrd Station location.

The phase/grain boundary observations and deformation experiments revealed that phase boundary energy is much higher than grain boundary energy and that the transformation process from air hydrate to bubble is clearly related to the strain-induced nucleation process. These findings suggest that the air hydrate/bubble transformation process is strongly controlled by both *in situ* and post ice core recovery nucleation activation process.

INTRODUCTION

Air hydrate inclusions were first observed in the deep ice core samples recovered at Dye-3, Greenland during an optical microscopic examination of the recovered ice core conducted in the field trench laboratory [2]. A thermal needle method was developed and used to microscopically observe the release of a large amount of air from the air hydrate inclusions. The shallowest depth at which air hydrates were observed in the Dye-3 specimens was at 1200 m [3]. The experimental results generally support the analysis and calculations given by Miller [1] but reveal that hydrates exist at slightly deeper depths. According to Miller, the transition zone from starting depth to completion depth for the air bubble/hydrate transformation

is 990-1040 m for Dye-3, 980-1050 m for Camp Century, and 800-850 m for Byrd Station. The deepest depth at which pre-existing air bubbles were observed in the Dye-3 core was 1537 m, which is about 500 m deeper than expected from Miller's equation. A Raman spectroscopy study of the air hydrate inclusions from the Dye-3 core specimens revealed the existence of N_2 and O_2 molecules in the inclusion [Nakahara et al., unpublished]. Neutron diffraction analyses made on artificial air hydrates [Davidson et al., unpublished] and x-ray analyses made on the air hydrates from Dye-3, Greenland [Hondoh et al., unpublished] both show the crystal structure of air hydrate is clathrate of structure II.

The original air hydrate tests made on selected sections of the 2037 m Dye-3, Greenland ice core, were subsequently expanded to include a systematic study of the air hydrate inclusions in the Camp Century (1387 m deep), Greenland and Byrd Station (2191 m deep), Antarctica ice cores. These three cores represent the only ice cores that have been recovered from substantial thicknesses from the surface to the bottom of the Greenland and Antarctica Ice Sheets.

SAMPLES AND EXPERIMENTS

Twenty-five new ice core samples were selected from systematic depths of the Dye-3 and Camp Century, Greenland and the Byrd Station, Antarctica deep ice cores. Table 1 lists the samples and their relationship to previous studies [2, 3, 4]. Test samples from the general fracture zones at each site (800 to 1200 m at Dye-3, 600 to 1150 m at Camp Century and 400 to 900 m at Byrd Station) were preferentially selected from unfractured core portions large enough to satisfy test requirements (more than 20 cm long). Planar faces for each sample were rough cut by a band-saw and finished with a surface microtome. All experiments were made in the cold laboratory at -15°C .

Optical examinations of air hydrates were made on specimens (1 x 2 x 2 cm) cut from the central part of each larger sample. The specimens were frozen onto a transparent Petri Dish and observed under a microscope. Alcohol was used as the dissolution medium. The air hydrate was identified by using the Becke test [2] with an optical microscope and to observe the escape of the large amount of air (about 100 times the hydrate volume) which evolved from the hydrate inclusion during the dissolving process.

Dye-3 core specimens from the 1930 m depth were used for the phase and grain boundary measurements. Ice crystal grain size ranged from 0.5 to 1.5 mm dia. The mounted hydrate section was partly dissolved by using a low-concentration solution of alcohol (less than 5% in volume). When half dissolved, a thin cover glass was placed on the surface of the specimen. The thin film of alcohol solution between the cover glass and the specimen surface affected a low dissolving rate by self-adjusting the alcohol/water concentration level close to the equilibrium point. This procedure permitted enough time (about 30 seconds) to take a micro-photograph of the process. When the air hydrate inclusions were located at intragranular positions the triple junctions of phase and grain boundaries were examined. The ratio of surface energies is obtained by the following equation under symmetrical conditions and isotropic assumptions:

$$\gamma_{ah}/\gamma_{gb} = 1/[2 \cos(\theta_{ah}/2)] \quad (1)$$

where θ_{ah} is equilibrium angle between ice-hydrate phase boundaries, γ_{ah} is the phase boundary energy between the ice crystal and air hydrate inclusion and γ_{gb} is the grain boundary energy between ice crystals. The ice-hydrate phase boundary energy was calculated from the measured angle, θ_{ah} from each micro-photograph by using the above equation (1).

Uniaxial compression tests were made on specimens from the 2183 m depth of the Byrd Station ice core. Grain size in these specimens averaged about 5 cm dia. The large grain size permitted careful examination of the single ice crystals to be made. Included in the single crystals were many air hydrate inclusions, air bubbles and pressure cracks. Specimens were cut in reference to the c-axis direction so as to have the uniaxial compression stress direction parallel (PARA specimen), perpendicular (PERP), and 45 degrees inclined (INCL) to the c-axis

direction of each specimen. Specimen sizes are shown in Table 2. Uniaxial stress was applied parallel to the maximum length direction of each specimen. PARA and PERP specimens were stressed by static loading and INCL specimens were deformed by using a laboratory designed and constructed apparatus as is shown in Fig. 1. The spring constant is 0.12 kgf/mm. With this apparatus the compressive stress decreases with the specimen deformation (the spring relaxation). The temperature control was held to better than $\pm 1^{\circ}\text{C}$.

RESULTS

The optical examinations revealed that significant amounts of air hydrate inclusions still exist in the deep ice cores up to 20 years after initial ice core recovery. The shallowest depths at which air hydrate inclusions were observed in the Dye-3, Camp Century and Byrd Station cores were at 1092, 1099 and 727 m depths respectively. These and other results are shown in Table 1.

From the phase boundary angle measurements the ratio of γ_{ah}/γ_{gb} was calculated as 4, 5, 5, 6 and 7 by using equation (1). An example of a phase and grain boundary triple junction is given in Fig. 2.

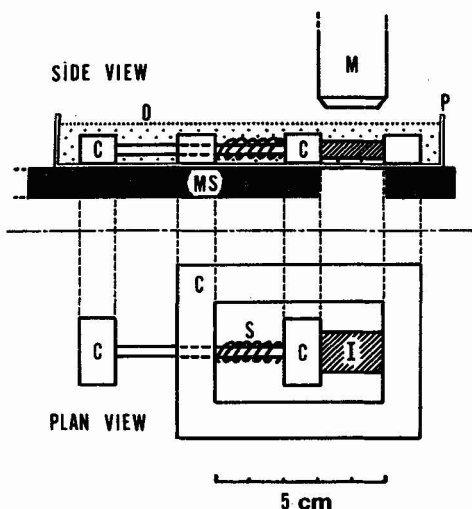


Fig. 1. Uniaxial compression apparatus: Specimen (I), Compression Frame (C), Spring (S), Silicone Oil (O), Petri Dish (P), Microscope Lens (M) and Microscope Stage (MS).

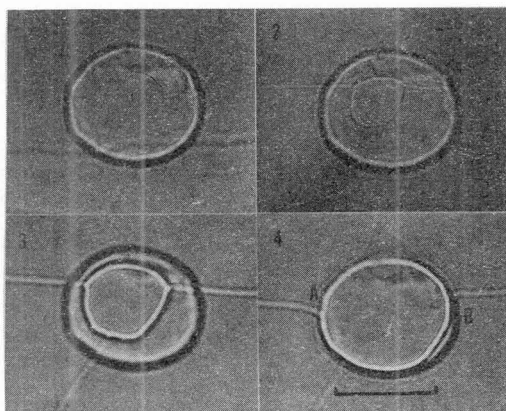


Fig. 2. The dissolving process of an air hydrate inclusion by alcohol dissolution. 0.1 mm bar is given for scale in Photo 4: Air hydrate exists below the specimen surface. Surface groove of grain boundary is shown in (1); Top portion of hydrate is dissolved. Circular groove of phase boundary is connected with grain boundary grooves (2); Dissolving progressed (3); Half dissolved. Triple junctions of phase/grain boundary at A and B are used for angle measurement.

The results of the uniaxial compression tests (Table 2) revealed that the air hydrate/bubble transformation process is strongly related to the plastic deformation of the surrounding ice matrix. Total strain on PARA and PERP specimens (hard glide orientation) was less than 1%. No physical change was observed before, during or after the uniaxial testing on these specimens.

Total strain on INCL specimens (easy glide orientation) was more than 17%. Significant physical changes were observed in the air hydrate inclusions before and after the INCL tests (Fig. 3). Most of the air hydrate inclusions in the INCL specimens nucleated air bubbles during specimen deformation. The nucleation site was clearly related to the strain field and always appeared at the local region of the air hydrate surface where basal plane glides away from the hydrate surface.

Table 1. Examinations of air hydrate inclusions in deep ice core samples.

<u>Drill Site</u>	<u>Sample Depth</u> m	<u>Year of Recovery</u>	<u>Air Hydrate observed (O) or none (N)</u>	<u>Examination Years after Recovery</u>	<u>References</u>
Dye-3 (65°11'N, 43°49'W) Greenland	235	1980	N	<0.25	[2]
	504	1980	N	<0.25	[2]
	708	1980	N	<0.25	[2]
	896	1980	N	<0.25	[2]
	939	1981	N	<0.25	[2]
	994	1981	N	<0.25	[2]
	1092	1981	O	4	this work
	1100	1981	N	1	this work
	1150	1981	O	4	this work
	1200	1981	O	1	[3]
	1280	1981	O	<0.25	[2]
	1293	1981	O	<0.25	[2]
	1537	1981	O	<0.25	[2]
	1642	1981	O	<0.25	[2]
	1711	1981	O	<0.25	[2]
	1814	1981	O	<0.25	[2]
	1930	1981	O	5	this work
1944	1981	O	4	this work	
1992	1981	O	<0.25	[2]	
Camp Century (77°10'N, 61°08'W) Greenland	953	1965	N	20	this work
	983	1965	N	20	this work
	1073	1966	N	19	this work
	1099	1966	O	19	this work
	1161	1966	O	19	this work
	1248	1966	O	19	this work
	1375	1966	N	17	[4]
	1377	1966	O	17	[4]
	1379	1966	O	17	[4]
Byrd Station (80°01'S, 199°31'W) Antarctica	599	1967/68	N	18	this work
	648	1967/68	N	18	this work
	699	1967/68	N	17	this work
	727	1967/68	O	17	this work
	752	1967/68	O	17	this work
	775	1967/68	O	17	this work
	801	1967/68	O	17	this work
	849	1967/68	O	17	this work
	886	1967/68	O	17	this work
	923	1967/68	O	17	this work
	1012	1967/68	O	17	this work
	1401	1967/68	O	17	this work
	1699	1967/68	O	17	this work
2183	1967/68	O	17	this work	

Figure 3 shows this phenomena. Once small bubbles nucleated, the transformation process was completed within one week as was observed by Shoji and Langway [5].

The phase diagram for air bubble/hydrate transformation given by Miller [1] is shown in Fig. 4. N_2 and O_2 hydrate lines are the dissociation pressure values of pure N_2 and O_2 hydrates respectively. The air hydrate line is obtained by approximating the air constituents as N_2 and O_2 mole fractions. Theoretically, as shown in Fig. 4, the air hydrate should begin to form at the depth of the air hydrate curve and all of the air should have formed hydrates by a depth of the N_2 hydrate curve, leaving no air bubbles. The results of the Dye-3 and Camp Century ice core examinations indicate that the shallowest depth at which air hydrates

Table 2. Specimens of ice single crystal for uniaxial compression tests. All specimens were prepared from a 2183 m depth ice core sample obtained at Byrd Station, Antarctica.

<u>Specimen Number</u>	<u>Specimen Size</u> mm	<u>Test Temperature</u> °C	<u>Uniaxial Stress</u> bar	<u>Test Duration</u> days	<u>Total Strain</u> %	<u>Bubble Nucleation during test</u>
PARA-1	8 x 9 x 24	-14	3.0	3	<1	None
2	8 x 11 x 24	-14	9.1	1	<1	None
PERP-1	8 x 10 x 23	-14	10	2	<1	None
2	8 x 10 x 27	-14	11	3	<1	None
INCL-1	7 x 12 x 17	-14	2.7 to 1.9	2	17	Nucleated
2	4 x 12 x 19	-17	4.3 to 3.0	1	18	Nucleated
3	5 x 12 x 19	-17	3.9 to 0.7	7	34	Nucleated

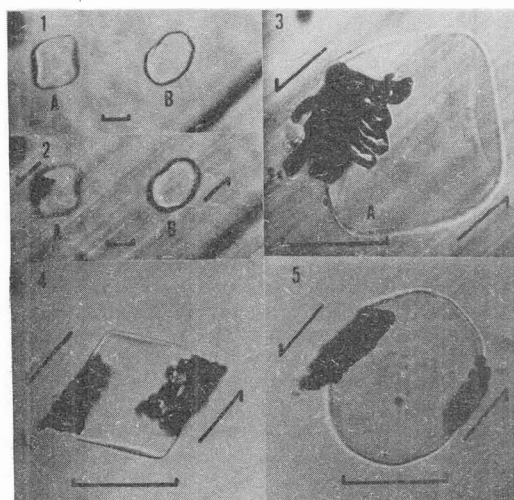


Fig. 3. Air bubble nucleation from hydrate inclusion during basal glide deformation tests (INCL-3). Arrows show the direction of basal glide. Scale bar in each photo is 0.1 mm; air hydrate before (1) and after (2) the deformation. Hydrate A nucleates a bubble, but hydrate B shows no change; close-up photo of 2-A is given in (3); other examples of bubble nucleation (4 and 5).

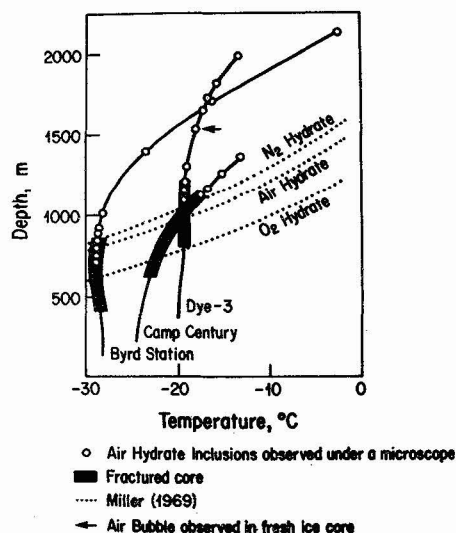


Fig. 4. Composite diagram of air hydrate experiment on the deep ice core samples.

appear is close to the N₂ hydrate line at each drill site. Only a few specimens were examined from depths between N₂ and the air hydrate curves due to the difficulty of sampling from the fracture zones. If an air inclusion did exist in the form of a combined air hydrate/bubble between these curves, the inclusion would be too unstable to exist under the surface ambient atmospheric pressure conditions [2, 5]. For the Byrd Station ice core, the shallowest depth at which air hydrate inclusions were observed was about 100 m less than calculated using Miller's equation. This apparent discrepancy may be explained by taking into consideration the upstream flow trajectory passing through the Byrd Station drill site. From about 5 km upstream toward Byrd Station, the bed level rises about 500 m resulting

in an upward ice flow of about 100 to 150 m around the 800 m depth [6]. In this analysis the ice at a depth of 727 m in the Byrd Station core was located at about a 827 to 877 m depth some 5 km upstream, a location at which the air hydrate is in a stable phase according to Miller's diagram. Due to the flow deformation upstream of Byrd Station most of air hydrate inclusions may nucleate small bubbles and transform into ice I_h and air bubbles. However, the laboratory test results show that some air hydrate inclusions can survive the glacier movement without the transformation. This survival may result from the non-uniform deformation of an ice mass on a microscopic scale. This concept of nucleation-controlled transformation process from air hydrate to air bubble might be also applicable for the transformation process from air bubble to air hydrate inclusions occurring in large ice sheets. The deepest depth at which pre-existing air bubbles were observed in the Dye-3 deep ice core was at 1537 m [2], which is about 500 m deeper than the completion depth for the transformation calculated by Miller (Fig. 4). The observed high energy value of phase boundary compared with ice crystal grain boundary may act as a threshold in the transformation of air bubbles to hydrates and extend to greater depths the transition interval in large ice sheets. Further study of the deformation behavior of the air hydrate/ice matrix interface or boundary will shed more light on the nucleation transformation process.

SUMMARY AND CONCLUSIONS

The systematic examination of three deep ice cores from Dye-3, Camp Century and Byrd Station revealed that significant amounts of air hydrate inclusions still exist in deep ice core samples several years after they were removed from their confined *in situ* environment. The shallowest depth at which air hydrates were observed agrees quite well with N_2 hydrate line calculated by Miller for conditions existing at Dye-3 and Camp Century, Greenland. For the Byrd Station, Antarctica ice core, a difference of 100 m exists between the direct observations and Miller's calculation for the depth of air hydrate appearance. This situation may be attributed to the upstream ice flow patterns at Byrd Station.

The transformation process between air hydrate and bubble formation is strongly controlled by the nucleation activation process. The observed high phase-boundary energy may be responsible for a later shift in the transition interval from air bubble to air hydrate in large ice sheets. Small air bubbles were nucleated from air hydrate inclusion by easy glide deformation of the ice matrix. These findings suggest that the transformation process from air hydrates to bubbles observed in a deep ice core (deeper than transition depth intervals) is mainly caused by deformation during core drilling; the subsequent core handling procedures as well as a volume expansion/relaxation process. The transformation of disturbed air hydrates to bubbles is complete after a few years, but non-disturbed hydrates still remain within the polycrystalline ice matrix for at least 20 years.

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