



HOKKAIDO UNIVERSITY

Title	Microscopic observations of air hydrate inclusions in deep ice core samples
Author(s)	Shoji, Hitoshi; Miyamoto, Atsushi; Kipfstuhl, Josef et al.
Description	International Symposium on Physics of Ice Core Records. Shikotsukohan, Hokkaido, Japan, September 14-17, 1998.
Citation	Physics of Ice Core Records, 363-371
Issue Date	2000
Doc URL	https://hdl.handle.net/2115/32475
Type	conference paper
File Information	P363-371.pdf



Microscopic observations of air hydrate inclusions in deep ice core samples

Hitoshi Shoji*, Atsushi Miyamoto**, Josef Kipfstuhl*** and Chester C. Langway, Jr.****

*Kitami Institute of Technology, Koencho 165, Kitami 090-0015, JAPAN

**ILTS, Hokkaido University, N19W8, Sapporo 060-0819, JAPAN

***Alfred-Wegener-Institut, D-27515 Bremerhaven, GERMANY

****State University of New York at Buffalo, Amherst, New York 14260, USA

Abstract: Since the first observation of air hydrate particles under an optical microscope at Dye 3, Greenland in 1981, there have been many field and laboratory measurements on their physical properties as they occur in both Greenland and Antarctic deep-ice-core samples. Microscopic observations provide the distribution of sizes and shapes in the ice sheets, information that is important for understanding the characteristics of ice sheets. Although Miller's equation gives the approximate depth in ice sheets that air bubbles transform to hydrates, the transformation process is not fully understood. We studied this transformation process in terms of molecular diffusion and ice matrix deformation to understand the observed delay of the transformation depth in ice sheets. Some comparisons are made in this paper and we find areas where core observations and theoretical examinations of laboratory experiments are lacking.

1. Introduction

The possibility of air hydrate inclusions in polar ice sheets was first discussed by Miller [1969] to account for the disappearance of air bubbles in the Byrd Station deep ice core [Gow and Ueda, 1968]. He obtained the following equations for the dissociation pressures P_{N_2} and P_{O_2} at temperature T for pure N_2 and O_2 hydrates, respectively.

$$\log P_{N_2} = 4.6849 - 688.9/T \quad (1)$$

$$\log P_{O_2} = 4.673 - 717/T \quad (2)$$

The pressure at which an air hydrate can start forming from an air bubble is given approximately by

$$P_{\text{air}} = P_{N_2}X_{N_2} + P_{O_2}X_{O_2} \quad (3)$$

where X_{N_2} and X_{O_2} are the mole fractions in the air hydrate of N_2 and O_2 , respectively [Salamatin et al., 1998]. The complete transformation into hydrate should occur at the dissociation pressure of pure N_2 hydrate [Miller, 1969]. Shoji and Langway [1982], using an optical microscope, were the first to directly observe air hydrate inclusions in ice core samples. Thereafter, experimental studies [Uchida et al., 1992, 1994; Ikeda, 1997] and theoretical studies [Price, 1995;

Hondoh, 1996; Salamatin et al., 1998] of air hydrates have been done.

In this paper, we suggest new ways to understand discrepancies between previously published theory and observations.

2. Transformation depth from air bubble to hydrate

Microscopic observations on ice core samples show that the transformation of air bubbles into air hydrates needs a much longer time period than that predicted by Miller [1969]; in an ice sheet, this amounts to a transition depth interval of several hundred meters. Within the transient zone of an ice sheet, both air bubbles and hydrate particles are observed, although it is very rare to observe a hydrate particle only partly transformed (i.e., with an air bubble attached to it). Recently, several partly-transformed hydrate particles were

observed on fresh ice core samples at North GRIP, Greenland [Kipfstuhl, unpublished]. Microscopic images showed growth process type B only: no image showed type A growth [Uchida et al., 1992]. In Type A, a hydrate particle grows from the boundary between bubble and ice, and progresses to grow along the boundary. Then the boundary is covered with the hydrate and bubble is located inside of the hydrate particle. On the other hand, the boundary between bubble and ice is never covered completely with hydrate until the completion of bubble/hydrate transformation in Type B. The shallowest depths that hydrates were observed are summarized in Table 1 along with the calculated depth for the transformation from the above equation (3) and the depth where approximately half of the air bubbles disappeared or transformed into air hydrate (the middle depth of the transformation).

Except for the Byrd Station core, all

Table 1: The shallowest depth for the appearance of air hydrate inclusions.

Site	Approximate depth by eq.(3) (m)	The shallowest depth observed (m)	Middle depth for the transformation (m)	Reference
Dye 3	990	1092	1300	Azuma, unpublished Shoji and Langway, 1987
Camp Century	980	1099	---	Shoji and Langway, 1987
Summit	790	1022	1300	this work Pauer et al, 1999
Byrd	820	727	900	Gow, 1971 Shoji and Langway, 1987
Vostok	400	500	850	Uchida et al., 1994 Salamatin et al., 1998

depths calculated by eq. (3) are 100 or more meters shallower than those observed. The exception is attributed to the upwelling flow of ice caused by the bottom topography upstream from the Byrd Station [Shoji and Langway, 1987]. In general, the observed depths for the transformations easily exceeds that for pure N_2 hydrate formation. These findings show that hydrate nucleation should be quite difficult deep in the ice sheets [Shoji and Langway, 1987; Salamatin et al., 1998]. Then, what determines the hydrate nucleation rate in ice sheets? Although crystal nucleation can be strongly influenced by impurity type and content, previous studies of bubble-hydrate transformation have not considered impurity effects.

3. Time duration for the transformation

Bubble concentrations remain essentially constant in Holocene ice at Byrd Station [Gow and Ueda, 1968], but the mean bubble diameter decreases with depth according to the gas law under the hydrostatic pressure in the ice sheet. When a bubble starts to transform into a hydrate, either hydrate nucleation or bubble shrinkage (post-nucleation hydrate growth) should determine the transformation rate. If the hydrate nucleation rate is fast enough, the bubble shrinkage rate will control the transformation rate by deforming the ice matrix and hydrate particle. However, microscopic observations of hydrate to bubble transformation revealed that hydrate particles are too rigid to show any deformation as air bubbles grow at the calculated dissociation pressures of 98 and 72 bar [Shoji and Langway, 1983]. The rheological parameters of air hydrates were

estimated by Salamatin et al. [1998]. Moreover, the transformation from hydrate to bubble starts with bubble nucleation in a few places along the phase boundary, and these bubbles are observed to grow without additional bubble nucleation. This shows that bubble nucleation is not rapid in the phase boundary between hydrate and the ice matrix even when hydrates transform to bubbles at ambient pressure.

After a small hydrate nucleates on the surface of an air bubble in the ice sheet, the ice matrix surrounding the bubble might deform and penetrate into the bubble as the hydrate crystal grows. If the hydrate particle does not deform at all during the ice deformation as assumed, the just-nucleated, small hydrate crystal may rotate thus slightly changing the position of the bubble surface. This might occur during formation of hydrates termed graupel-like (because of their shape) by Shoji and Langway [1982].

Once an air bubble starts to transform into hydrate at a depth required for the dissociation pressure by eq. (3), the gas pressure in the bubble decreases leading to hydrate decomposition unless pressure rebuilds by ice deformation. However, the gas pressure decrease should be fast enough to prevent the latter. Therefore, some delay in the transformation depth (i.e., a super-cooling) is needed for the stable growth of a hydrate particle.

Assuming that one air bubble with diameter $\phi_0 = 300 \mu\text{m}$ transforms into hydrate at $T = -30^\circ\text{C}$ (a condition approximating that at Summit, Greenland), the dissociation pressure P_c equals 70 bar by eq. (3). Assume also that the nucleation rate of air hydrate is fast. If the nucleation of hydrate on the bubble occurs at a depth of 1200 m ($P = 106$ bar), the air and water molecules continue to transform into

hydrate until the internal pressure in the bubble decreases to 70 bar. Then the pressure difference, $\Delta P = 36$ bar, between the gas pressure in the bubble and the hydrostatic pressure around the bubble causes bubble shrinkage thus rebuilding the internal pressure of the bubble for further transformation. This condition corresponds to air hydrate growth type B, which was observed in situ during an experiment [Uchida et al., 1992]. The time duration t (sec) required for the bubble to shrink to $\phi = 1 \mu\text{m}$ can be used to estimate the transformation duration. Using a bubble deformation equation [Shoji and Langway, 1983] and an activation energy $Q = 78.1$ kJ/mol for ice deformation [Barnes, Tabor and Walker, 1971], this time is

$$\phi = \phi_0 \exp[(\Delta P/B)^n \exp\{(Q/R) \cdot (1/T_1 - 1/T_2)\}]t$$

where R is gas constant, $T_1 = 243$ K, and $T_2 = 261$ K for the condition at Summit. Constants n and B are 2.7 and 7.8×10^3 , respectively. The result gives about 5 years for the complete transformation to hydrate. Calculated transformation times for various pressure differences are plotted as Fig. 1. The plot suggests that air hydrates in the middle of their transformation (with air bubble attached) should be observed only near the top of the transient zone in ice sheets if many hydrates nucleate. Assuming the nucleation rate is constant with depth, we estimate that in the Summit core the number density of hydrate particles in the middle of their transformation is about 10 particles/cm³ for the top 30 m of the transient zone and decreases rapidly with depth to a few particles/cm³. If the nucleation rate instead increases with depth (ΔP), which might be the case, the number

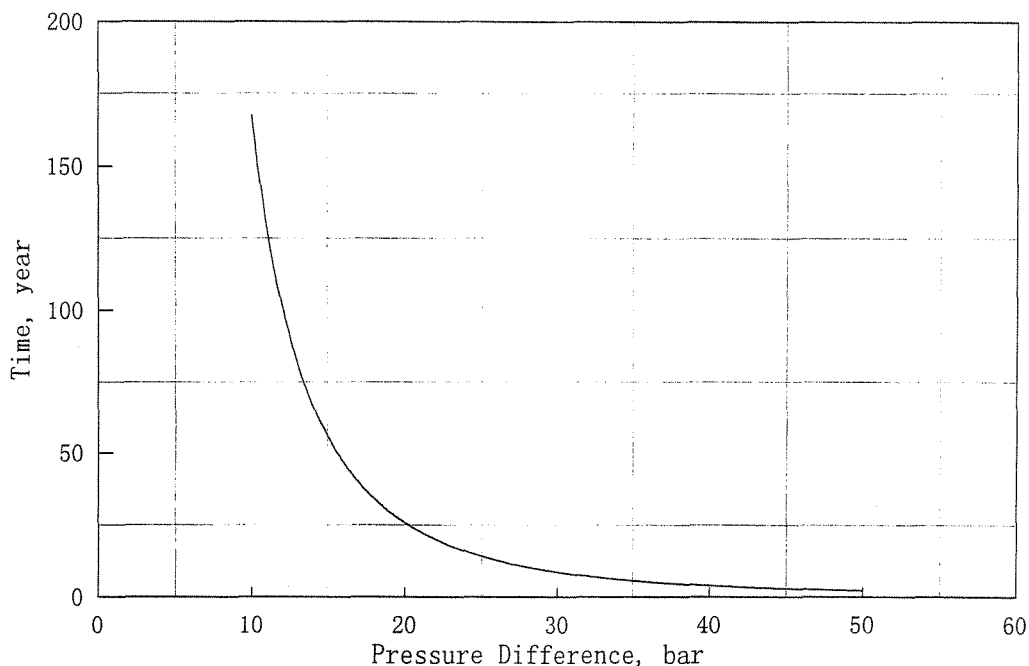


Figure 1: Calculated time duration required for the bubble-hydrate transformation.

density should be much lower in the top 30 m.

This result agrees with field observations of air inclusions.

4. Elongated shape of air bubbles and hydrates

Elongated air hydrate particles are observed in deep ice core samples, although the fraction with this shape is low (Fig. 2). It is possible that each elongated hydrate grew along a triple junction of grain boundaries that later migrated away after the transformation was complete. Elongated air bubbles are also observed (Fig. 3). This shape could result from bubble expansion through a triple junction of grain boundaries during post-drilling relaxation of the ice core. Another possibility is the dissociation of an elongated air hydrate crystal along a

triple junction into an air bubble after core recovery.

The cloudy band is a milky-colored zone with clear ice above and below, and easily seen by the unaided eye; the prime source for this light scattering is a high density of small bubbles (micro-bubbles). These micro-bubbles are sometimes distributed in a line or plane (Fig. 4). Their occurrence suggests that air molecules might diffuse into a triple junction of one or more sub-boundaries and then form micro-bubbles. The role of grain boundaries in the bubble to hydrate transformation and in the relaxation of deep cores after recovery are not known in detail, but are certainly important. X-ray diffraction topography studies on ice core samples revealed highly strained regions around cleavage cracks [Shoji and Higashi, 1978]. Bubble growth (relaxation after core recovery) and shrinkage (in situ in the ice sheet) occur

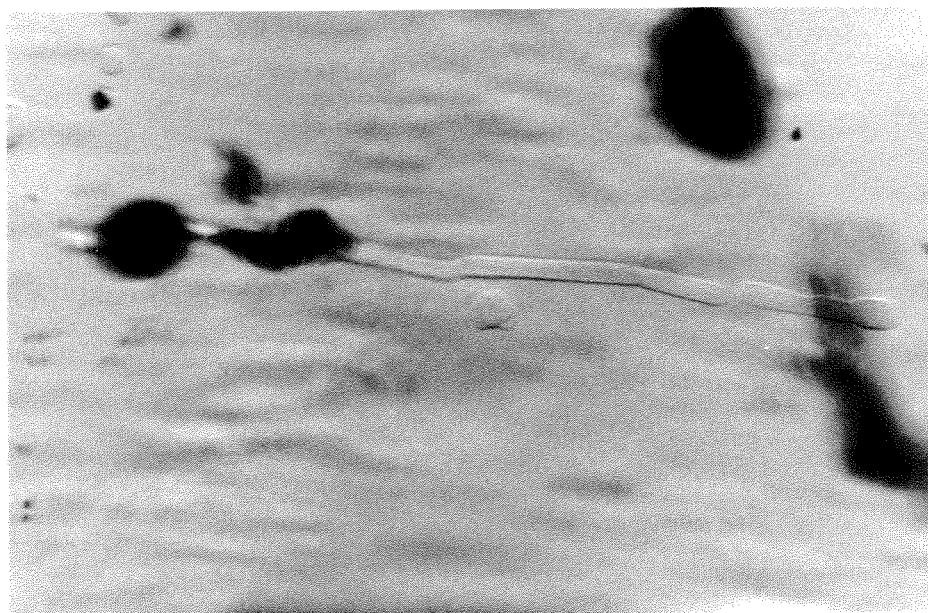


Figure 2: Elongated air hydrate crystal 1327-m deep in the Summit ice core. The width of the picture is 2.6 mm.

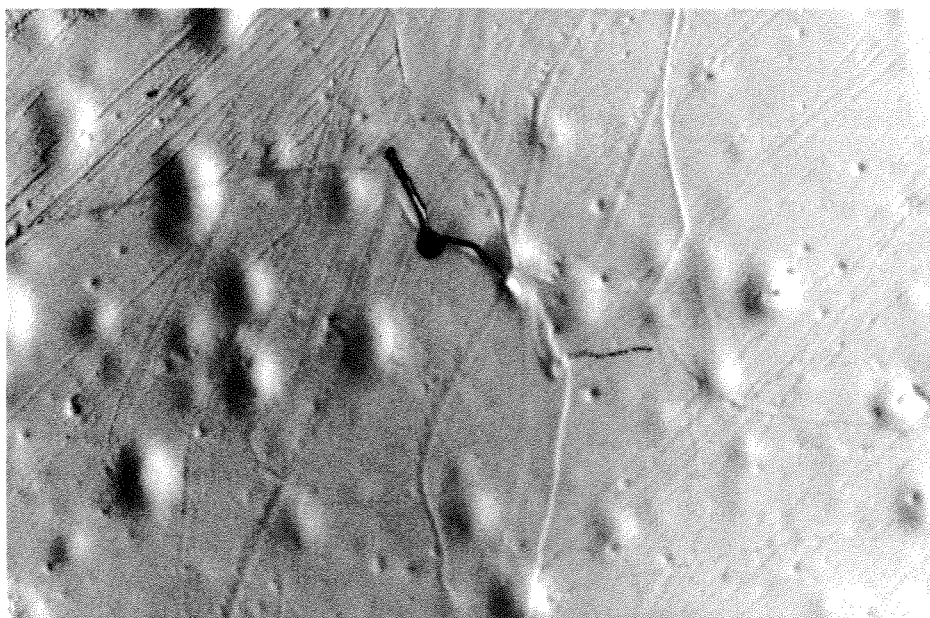


Figure 3: Elongated air bubble 1465-m deep in the Summit ice core. The width of the picture is 2.6 mm.

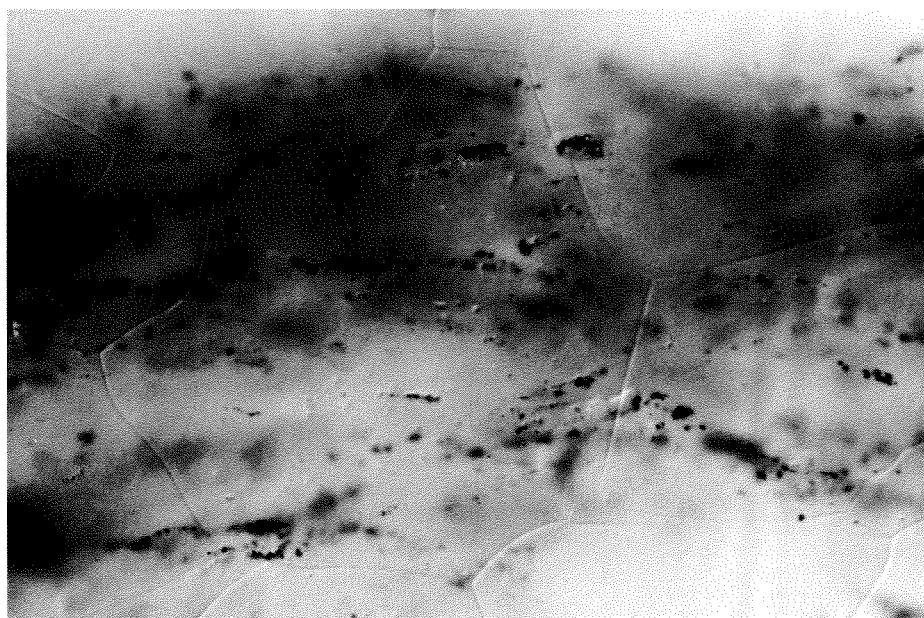


Figure 4: Micro-bubble arrays in a cloudy band 1465-m deep in the Summit ice core. The width of the picture is 2.6 mm.

through ice-matrix deformation near the bubble. Sub-boundaries likely exist around the bubble and into which air molecules could diffuse while the ice deforms. This is because grain boundary grooves are observed on the surface of air bubbles during relaxation (Fig. 5).

Small hydrate sections are sometimes observed sticking out from the mother hydrate particle in a fresh core. Air molecules might have diffused out from a shrinking bubble to surrounding sub-boundaries in the ice sheet and transformed to a small hydrate. Another possibility is that ice deformation during bubble shrinkage leads to rotation of a small hydrate that then sticks out.

Small bubbles have been observed surrounding a larger bubble during volume relaxation. When a high-pressure bubble expands, or a hydrate particle transforms

into a high-pressure bubble after the core retrieval, ice deformation caused by the bubble growth might generate sub-boundaries around the bubble. Air molecules could then diffuse into these boundaries and form the small bubbles (Fig. 5).

Testing these possibilities require more field and laboratory studies; in particular, studies of fresh ice cores in the field are needed to do more realistic modeling.

5. Conclusions

The following three subjects should be emphasized in a future study of air bubble/hydrate transformation process in polar ice sheets.

(1) The shallowest depth for the trans-



Figure 5: Micro-bubbles surrounding a larger bubble that has grain boundary grooves on its surface. The sample is prepared from a section 1327-m deep in the Summit core. The width of the picture is 2.6 mm.

formation from air bubble to hydrate is about one hundred meter deeper and the transient depth zone several times thicker compared with Miller's diagram [1969]. This means that nucleation is quite difficult in site in ice sheets. What causes the nucleation so difficult? We should note that almost no discussion is made for the effect of impurity in ice sheets so far.

- (2) Recent observation on fresh ice core by Kipfstuhl [unpublished] shows hydrate growth type is B [Uchida et al., 1992]. A simple calculation made shows that a single air bubble may complete the transformation within about one hundred year, which coincides well with field results that the number of air hydrate particle in the middle of transformation is quite rare to be observed. Growth process type A for bubble-hydrate transformation can really occur in ice sheets?
- (3) Grain and sub- boundary is high speed path for air molecular diffusion. If air diffusion is a key-factor, how grain/sub- boundaries affect bubble-hydrate transformation process?

References

- Azuma, N., *unpublished (Master's Thesis in Hokkaido University, Sapporo, Japan, 1983).*
- Barnes, P., Tabor, D. and Walker, J.C.F., 1971, The friction and creep of polycrystalline ice, *Proc. Roy. Soc. London*, A324, 127-155.
- Gow, A.J., Ueda, H.T. and Garfield, D.E., 1968, Antarctic ice sheet: Preliminary results of first core hole to bedrock, *Science*, 161, 1011-1013.
- Gow, A.J., 1971, Relaxation of ice in deep drill cores from Antarctica, *J. Geophys. Res.*, 76, 11, 2533-2541.
- Hondoh, T., 1996, *Proc. of 2nd Int. Conf. on Gas Hydrate*, Toulouse, France, 2-6 June 1996, 131-138.
- Ikeda, T., Fukazawa, H., Mae, S., Hondoh, T. and Langway, C.C., Jr., 1997, Crystal orientation dependence of Raman spectra of natural air hydrate single crystal, *J. Phys. Chem. B*, 101, 32, 6180-6183.
- Miller, S.L., 1969, Clathrate hydrates of air in Antarctic ice, *Science*, 165, 3892, 489-490.
- Pauer, F., Kipfstuhl, J., Kuhs, W.F. and Shoji, H., 1999, Air clathrate crystals from the GRIP ice core - a number, size, and shape distribution study, *J. Glaciol.*, 45, 149, 22-30.
- Price, P.B., 1995, Kinetics of conversion of air bubbles to air hydrate crystals in Antarctica ice, *Science*, 267, 1802-1804.
- Salamatin, A.N., Hondoh, T., Uchida, T. and Lipenkov, V.Ya., 1998, Post-nucleation conversion of an air bubble to clathrate air-hydrate crystal in ice, *J. Cryst. Growth*, 193, 197-218.
- Shoji, H. and Higashi, A., 1978, X-ray diffraction topographic studies of Antarctic deep core ice, *Jpn. J. Appl. Phys.*, 17, 6, 993-1001.

- Shoji, H. and Langway, C.C. Jr., 1982, Air Hydrate inclusions in fresh ice core, *Nature*, 298, 5874, 548-550.
- Shoji, H. and Langway, C.C. Jr., 1983, Volume relaxation of air inclusions in a fresh ice core, *J. Phys. Chem.*, 87, 4111-4114.
- Shoji, H. and Langway, C.C. Jr., 1987, Microscopic observations of the air hydrate-bubble transformation process in glacier ice, *J. Phys. (Paris), Colloq. C1*, 48, 551-556.
- Uchida, T., Hondoh, T., Mae, S., Duval, P., Lipenkov, V.Ya., 1992, In-situ observations of growth process of clathrate air-hydrates under hydrostatic pressure, *Physics and Chemistry of Ice*, eds. N. Maeno and T. Hondoh, Hokkaido Univ. Press, Sapporo, 121-125.
- Uchida, T., Hondoh, T., Mae, S., Duval, P., Lipenkov, V.Ya., 1994, Effects of temperature and pressure on the transformation rate from air bubbles to air-hydrate crystals in ice sheets, *Ann. Glaciol.*, 20, 143-147.
- Uchida, T., Duval, P., Lipenkov, V.Ya., Hondoh, T., Mae, S. and Shoji, S., 1994, Brittle zone and air-hydrate formation in polar ice sheets, *Mem. Natl. Inst. Polar Res., Spec. Issue*, 49, 298-305.