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Kinetics of Conversion of Air Bubbles to Air Hydrate Crystals in Antarctic Ice

P. B. Price

The depth dependence of bubble concentration at pressures above the transition to the air hydrate phase and the optical scattering length due to bubbles in deep ice at the South Pole are modeled with diffusion-growth data from the laboratory, taking into account the dependence of age and temperature on depth in the ice. The model fits the available data on bubbles in cores from Vostok and Byrd and on scattering length in deep ice at the South Pole. It explains why bubbles and air hydrate crystals coexist in deep ice over a range of depths as great as 800 meters and predicts that at depths below ~1400 meters the AMANDA neutrino observatory at the South Pole will operate unimpaired by light scattering from bubbles.

Ancient air is known to be trapped in polar ice at depths below the layer of firn (that is, porous) ice. Early investigations showed that the air was trapped in bubbles that decreased in size and concentration with increasing depth. To account for the disappearance of bubbles at great depth, Miller (1) predicted that the bubbles would convert into a clathrate hydrate phase at depths corresponding to a pressure greater than that for formation of that phase. He showed that the phase consists of a cubic crystal structure in which O₂ and N₂ molecules from air are trapped in clathrate cages. If O₂ and N₂ occur in atmospheric proportions, the crystals are usually referred to as air hydrate crystals. The hatched region in Fig. 1 shows Miller’s calculated curves for the temperature dependence of the formation pressure for nitrogen hydrate and for air hydrate, displayed on a scale in which pressure has been converted to depth in ice. The curves labeled for ice at four Antarctic sites and two Greenland sites show temperature as a function of depth (2–6). Koci (6) modeled the temperature versus depth at South Pole, using the known surface temperature of ~5°C and fixing the temperature at bedrock at the pressure melting temperature. In situ measurements (7) by AMANDA at depths from 800 to 1000 m gave temperatures that agreed with Koci’s model to within 0.3°C.

Over a wide range of depths, bubbles and air hydrate crystals are seen to coexist (Fig. 1). For Vostok and Byrd cores, quantitative measurements have been made of concentrations and sizes of bubbles (8, 9) and air hydrate crystals (10, 11). For Dome C, Dye 3, and Camp Century cores, Shoji and Langway (12, 13) reported only qualitative data on air hydrates. For the South Pole, no deep core has yet been obtained.

This paper poses solutions to several puzzles. Why do bubbles and air hydrate crystals coexist over a range of depths as great as 800 m? In particular, why does it take so long for bubbles to disappear at pressures at which they are unstable against the phase transition? Why do the depths of disappearance of bubbles in various cores not show some systematic dependence on depth or temperature? Based on the measurements on bubbles at Vostok and Byrd, can we predict the concentration of bubbles as a function of depth in ice at the South Pole? The last question is of great importance to the AMANDA project (14, 15), which involves implanting long strings of large photomultiplier tubes at great depths in South Pole ice in order to detect Cherenkov light from muons produced in high-energy neutrino interactions. Only if the array is located in bubble-free ice can the direction of a muon be precisely determined by measurement of the arrival times of the Cherenkov wave front at each of the phototubes.

Several studies of the transformation of air bubbles into air hydrate crystals have been done in pressure cells on time scales up to a few days at temperatures from ~20°C to ~2°C and at pressures up to ~8 MPa. Using a high-pressure cell on a microscope stage, Uchida et al. (16) studied the growth of air hydrate crystals on the walls of bubbles in a sample of Vostok core taken from a depth of 1514 m. Because of relaxation after recovery of the core, the original air hydrate crystals had converted back into bubbles before Uchida et al. started the experiment. They observed the growth rate of air hydrate crystals as a function of supersaturation, dP/dt, at temperatures just below the melting point of ice (where P is the hydrostatic pressure on the system and dP/dt is the equilibrium pressure at the phase boundary). They found that for dP/dt > 0.35, the crystals grew as spherical shells coating the bubble walls.

Continuing this line of research, Uchida et al. (17) showed that two activation energies were involved. Before a thin shell of air hydrate crystal had completely coated

Fig. 1. Temperature as a function of depth in ice, compared with equilibrium pressures (conventional to depths) for coexistence of the (bubble + ice) phase and the air hydrate phase. Upper boundary of the hatched region is for nitrogen-clathrate hydrate; lower boundary is for air-clathrate hydrate. Squares indicate the depths in cores below which air bubbles are not observed. The arrow on the square for Dome C indicates that air hydrate crystals were present to the bottom of the core. Triangles indicate the depths below which air hydrate crystals are observed.
the wall of a bubble, they found that \( E_v = 0.52 \pm 0.17 \text{ eV} \). After it had fully coated the bubble wall, they found a higher value, \( E_v = 0.9 \pm 0.1 \text{ eV} \), for thickening of the shell. In the early growth stage, it seemed clear that the process occurred by diffusion of water molecules through the normal ice to uncoated sites on the bubble wall, because their activation energy was consistent with that for self-diffusion, \( 0.57 \pm 0.1 \text{ eV} \) \( (18) \). The higher value, for the later growth stage, applied to diffusion through the air hydrate itself. With the assumption of a linear radial growth rate, they concluded that air hydrate crystals would form far too quickly to account for the broad range of depths over which bubbles and air hydrate crystals coexist in polar ice cores. They suggested that the rate-limiting process is nucleation, not diffusion.

Ikeda et al. \( (19) \) subjected artificial ice to various hydrostatic pressures at 270 K and measured the fraction of bubbles converted to air hydrate crystals in 16 days. They assumed that the rate-limiting step in the transformation is nucleation. After failing to account for the observed rates by homogeneous nucleation theory, they concluded that the mechanism must be heterogeneous nucleation, but with a different parameter for each data point [see figure 7 in \( (19) \)].

After examining the various models of nucleation, I concluded that none of them provides a satisfactory explanation for the data presented in Fig. 1. Homogeneous nucleation requires such an enormous supersaturation, defined as \( dP/P_o \), that it almost never occurs in nature. Heterogeneous nucleation on a foreign surface at low supersaturation is far more likely. The presence of a bubble wall serves as a suitable nucleation site. Fletcher \( (20) \) calculated nucleation rates as functions of supersaturation, size of the substrate on which nucleation occurs, and surface energies of the substrate and the nucleated phase. For typical bubble sizes and reasonable values of surface energies, his results show that nucleation would be rapid at supersaturations below 0.2, whereas for the data in Fig. 1, bubbles are still present at values of \( dP/P_o \) as large as 2. Further, the presence of one or more screw dislocations in the ice Ending at a bubble surface would reduce the needed supersaturation to a value less than 0.01 \( (21) \). Typical dislocation densities in even well-annealed crystals are high enough \( (>10^{16} \text{ cm}^{-2}) \) to ensure their presence at bubble walls.

To show that the rate-limiting step in the phase transition is diffusion rather than nucleation, I carried out a diffusion calculation that takes into account the time and temperature as a function of depth for the Vostok and Byrd sites. I converted depth to time for each core using age versus depth data in \( (7) \). I assumed that there is no nucleation barrier and that long-term scale for the disappearance of bubbles is due to slow diffusion. I assumed two diffusion steps: The first step consists of diffusion of water molecules through ice to a bubble wall, in which \( D(T) \) is taken to be \( D_o \exp(-E_v/kT) \), where \( E_v = 0.57 \text{ eV} \), the diffusion coefficient \( D_o = 1.2 \text{ cm}^2 \text{s}^{-1} \) as measured \( (18) \) for self-diffusion in ice \( (22) \), and \( T \) is the temperature.

The second step consists of diffusion of water molecules through a spherical shell of air hydrate coating the bubble wall and growing in thickness. For the activation energy for diffusion in air hydrate I adopted the value \( E_v = 0.9 \pm 0.1 \text{ eV} \) measured for the growth of the air hydrate layer \( (17) \). The authors in \( (17) \) did not measure \( D_o \).

After reaching the inner radius of the hollow air hydrate shell, water combines with air molecules and causes the crystal to thicken, with negligible activation barrier \( (23) \). At \( P \sim 10^5 \text{ atm}, T \sim 230 \text{ K} \), the concentration of air in the bubble, \( \sim 4 \times 10^{10} \text{ molecules per cubic centimeter} \), is comparable to that in an air hydrate crystal of the same volume (eight cages per unit cell, \( \sim 80\% \) occupancy, cubic structure, cube edge of 1.7 nm). Thus, the supply of air is adequate for full conversion from (air + ice) to the hydrate phase.

The first step, diffusion of water molecules in ice to the bubble wall, occurs so rapidly that one can apply the boundary condition that \( C(r > a) = C_o \) for all time, where \( a \) is the bubble radius and \( C_o \) is the initial concentration of interstitial \( \text{H}_2\text{O} \) molecules everywhere outside the bubble. The problem is that of spherically symmetric diffusion with \( C = 0 \) at time \( t = 0 \) inside the bubble and \( C = C_o \) at the wall \( (24) \). The justification for taking \( C = 0 \) at \( t = 0 \) inside the bubble is that all of the water vapor inside the bubble \( (\sim 10^{10}) \text{ molecules per cubic centimeter} \) at \( -40^\circ \text{C} \) is exhaustible in creating an infinitesimally thin shell of air hydrate, after which additional water must diffuse through the air hydrate shell \( (25) \).

As a function of time, the amount of mass \( M \) transported through the bubble due to diffusion grows, as given by eq. 6.21 of \( (24) \) (with the running index \( n \) replaced by \( j \) to avoid ambiguity with my symbol for bubble concentration)

\[
M(t)/M(\infty) = 1 - \frac{6}{\pi} \sum_{j=1}^{\infty} \frac{1}{\pi^{1/2}} \exp(-j^{1/2}D(T)t/a^2) \tag{1}
\]

Equating this value to the probability of disappearance per bubble yields for the fractional concentration remaining after time \( t \)

\[
n(t)/n_o = 6/\pi \exp(-\pi^2 t/a^2) + \frac{1}{4} \exp(-4\pi^2 t/a^2) + \ldots \tag{2}
\]

with

\[
L(t) = \int_{t_o}^{t} D_o \exp(-E_v/kT) dt' \tag{3}
\]

The integral \( L(t) \) takes into account the fact that \( D(T) \) and \( t \) change with depth. Its lower limit corresponds to the age of the ice at the transition pressure. The second term in Eq. 2 contributes only at short times, and higher order terms can be neglected.

I fitted Eq. 2 to the extensive Vostok data \( (8) \) on bubble concentrations at depths greater than 500 m, the depth corresponding to the transition pressure, at which air

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**Fig. 2.** Reciprocal of bubble-to-bubble scattering length, \( 1/\lambda_{bb} \propto \pi n r^2 \), as a function of depth. Data for Vostok \( (8) \) and Byrd \( (9) \) were obtained with microscopic examination of core samples in a cold laboratory; data for South Pole were obtained by in situ measurement of optical scattering \( (15) \). Upper triangles assume forward scattering from smooth-walled bubbles; lower triangles assume isotropic scattering from rough-walled bubbles. Hydrostatic pressure curve shows effect of shrinkage of bubble size without change of concentration. Calculated curves for the three sites show the effect of a decrease in bubble concentration as a function of time due to diffusion of \( \text{H}_2\text{O} \) molecules through air hydrate crystal walls.
hydrate crystals are first observed. With $D_0 = 2100 \text{ cm}^2 \text{s}^{-1}$, $D_c$, as a fitting parameter, I found that $D_c = 2100 \text{ cm}^2 \text{s}^{-1}$ gave acceptable fits to both the Vostok data and the Byrd data (9) on bubble concentration as a function of depth.

Figure 2 displays values of $1/A_{bub} \approx m \tau$, the reciprocal of the bubble-to-bubble scattering length, as a function of depth, $z$, for Vostok, Byrd, and South Pole. The experimental points use data on bubble concentration, $n(z)$, and radius, $r(z)$, for Vostok and Byrd. The data for South Pole are from in situ light scattering at depths of 800 to 1000 m (15). The curves show the results of applying the diffusion model to the three sets of data. The value for $n(t)$ is calculated from Eq. 2, taking $a = a_0$, the mean radius at the dissociation pressure. The observed values are $a_0 = 68 \mu$m for Vostok and $130 \mu$m for Byrd. In the absence of data on $a_0$, for the South Pole, I assumed the same value as for Vostok, because those two sites have similar elevations, surface temperatures, atmospheric pressures, and hydrate dissociation pressures (see Fig. 1), which are rather different from those at Byrd. To compute the curve for $1/A_{bub}$, I assumed that $r = a_0 (P/P_f)^{1/3}$ due to hydrostatic pressure. The fits to the South Pole and Byrd are quite good and lend confidence to the predicted dependence of $1/A_{bub}$ on depth for the South Pole (26).

The diffusion-growth model provides a solution to the puzzles listed in the introduction. The reason that bubbles do not all convert into air hydrate crystals at the phase transition pressure, and the reason for the great range of depths at which both air hydrate crystals and bubbles coexist, is that the time required for water molecules to diffuse through a growing shell of air hydrate at ambient ice temperature is extremely long. The diffusion coefficient for water in air hydrate, $D(T) = D_0 \exp(-0.9/kT)$, with $D_0 = 2100 \text{ cm}^2 \text{s}^{-1}$, is orders of magnitude smaller than for self-diffusion in hexagonal ice. For example, at $-46^\circ \text{C}$, the temperature of South Pole ice at a depth of 1 km, $D = 2.2 \times 10^{-17} \text{ cm}^2 \text{s}^{-1}$ for water in air hydrate, whereas $D = 2.65 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$ for water in hexagonal ice. The reason for the apparent lack of organization of the data on bubble disappearance in Fig. 1 is that the depth is the wrong variable to use. Because of large variations in snow accumulation rate from one polar site to another, depth is not universally related to time. Only when data are plotted on a graph of time versus reciprocal of temperature does the correlation become clear. When applied to laboratory data on the rate of decrease of concentration of bubbles in ice near the melting point (19), the model gives results consistent with the data.

The model predicts that in deep ice at the South Pole, the bubble-to-bubble scattering length is $\approx 6 \text{ m}$ at a depth of 1300 m, 20 m at 1400 m, and 130 m at 1500 m. For an AMANDA phototube spacing of 20 m, bubbles will cease to degrade imaging at depths greater than $\approx 1400 \text{ m}$.

REFERENCES AND NOTES

6. A model for temperature versus depth at the South Pole was developed by B. Koci (unpublished material).
15. AMANDA collaboration, Science, in press.
17. T. Uchida et al., in Fifth International Symposium on Antarctic Glaciology, in press.
23. An alternative possibility, that air molecules diffuse through the air hydrate shell and convert ice to air hydrate at the bubble boundary, is ruled out experimentally. Uchida et al. (16, 17) observed that air hydrate crystals grow inwardly, causing bubbles to shrink in size and eventually disappear.
25. This assumes that the vapor pressure of water at the surface of an air hydrate crystal is much smaller than at the surface of an ice crystal.
26. An alternative procedure is to fix $D_c$, at 1.2 cm$^2$ s$^{-1}$, the same value for diffusion of water in air hydrate as in ice, and to treat $E_c$ as a fitting parameter. Doing this leads to acceptable fits to the Vostok and Byrd data but with $E_c = 0.75 \text{ eV}$, which is outside the standard error claimed in (17). The resulting curves for $1/A_{bub}$ for Vostok, Byrd, and South Pole are similar to those calculated with $D_c = 2100 \text{ cm}^2 \text{s}^{-1}$, $E_c = 0.9 \text{ eV}$. The conclusion is that the present data do not permit determination of both $D_c$ and $E_c$ independent of laboratory data.
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Dike Injection and the Formation of Megaplumes at Ocean Ridges

Robert P. Lowell and Leonid N. Germanovich

A simple hydrologic model of seawater circulation at ocean ridge axes implies that the transient occurrence of large volumes of buoyant, heated water in the oceanic water column (megaplumes) can be attributed to the emplacement of dikes in oceanic crust. For dikes to generate megaplume flow, the permeability of both the recharge areas and the upflow zone must be greater than that required for ordinary black smokers. An increase in permeability in the upflow zone by several orders of magnitude results from dike emplacement, and megaplume discharge ceases as the dike cools. Vigorous black smoker venting may not persist very long at a megaplume site after the event occurs.

Megaplumes (or event plumes) appear to be sudden, short-lived hydrothermal events on the sea floor (Fig. 1). Even though the temperature of the water in megaplumes is only slightly higher than in the ambient ocean (by up to 0.25°C), their large volume indicates the liberation of $\sim 10^{11}$ J of heat (1, 2). Baker et al. (2) argued that the geometry of the plume and its particular content are indicative of an event lasting 2 to 20 days. The heat and mass fluxes are thus two to three orders of magnitude greater than typical, quasi-steady black smoker venting. A simple heat balance shows that roughly 0.01 km$^3$ of magma can provide the heat content of a megaplume; however, the chemical constituents of megaplumes (2, 3) and the rise height of the plume appear to make direct interaction between seawater and an extrusive lava flow an unlikely mechanism for megaplume generation (2). Nevertheless, observations of recent lava flows in the vicinity of the megaplumes observed