Optical-Cell Evidence for Superheated Ice under Gas-Hydrate-Forming Conditions

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We previously reported indirect but compelling evidence that fine-grained H₂O ice under elevated CH₄ gas pressure can persist to temperatures well above its ordinary melting point while slowly reacting to form methane clathrate hydrate. This phenomenon has now been visually verified by duplicating these experiments in an optical cell while observing the very slow hydrate-forming process as the reactants were warmed from 250 to 290 K at methane pressures of 23 to 30 MPa. Limited hydrate growth occurred rapidly after initial exposure of the methane gas to the ice grains at temperatures well within the ice subsolidus region. No evidence for continued growth of the hydrate phase was observed until samples were warmed above the equilibrium H₂O melting curve. With continued heating, no bulk melting of the ice grains or free liquid water was detected anywhere within the optical cell until hydrate dissociation conditions were reached (292 K at 30 MPa), even though full conversion of the ice grains to hydrate requires 6-8 h at temperatures approaching 290 K. In a separate experimental sequence, unreacted portions of H₂O ice grains that had persisted to temperatures above their ordinary melting point were successfully induced to melt, without dissociating the coexisting hydrate in the sample tube, by reducing the pressure overstep of the equilibrium phase boundary and thereby reducing the rate of hydrate growth at the ice-hydrate interface. Results from similar tests using CO_2 as the hydrate-forming species demonstrated that this superheating effect is not unique to the CH_4 – H_2O system.

Introduction

Methane clathrate hydrate (CH₄·nH₂O, $n \ge 5.75$) is a nonstoichiometric compound consisting of a network of H₂O

molecules that are hydrogen-bonded in a manner similar to ice and interstitially encage CH_4 gas molecules. In addition to its possible widespread occurrence on the icy moons of the outer solar system at Saturn and beyond,¹ methane hydrate occurs on Earth in a variety of geologic settings where methane and water are in chemical contact at low temperatures and elevated pressures and may harbor the largest untapped reservoir of natural gas on Earth.^{2,3}

In an earlier study, we developed a new technique for laboratory synthesis of large-volume methane hydrate samples suitable for physical and material properties testing.⁴ We reported evidence suggesting that under hydrate-forming condi-

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tions, metastable water ice can persist to at least 276 K and possibly as high as 290 K. Nearly pure aggregates of polycrystalline methane hydrate (CH₄·6.1H₂O \pm 0.1 H₂O) were grown under undisturbed conditions from granular H₂O ice (~200 μ m grain size) with porosity suffused with cold, pressurized CH₄ gas, by the reaction $CH_4(g) + 6H_2O_2$ $(s \rightarrow l) \rightarrow CH_4 \cdot 6H_2O(s)$ (Figure 1). The reactants were slowly warmed from 250 to 290 K at methane gas pressures (P_{CH4}) that increased from 23 to 30 MPa⁵ (Figure 1B) in a constantvolume reactor [see Figure 2 in Stern et al.⁴]. Full conversion of ice to hydrate required 6 to 8 h near these peak conditions (Figure 1B, inset), yet the lack of evidence for diagnostic melting in the sample pressure-temperature (P-T) histories indicated that macroscopic melting of ice grains during reaction did not occur.⁶ Instead, the run histories suggested that ice grain melting was suppressed or its rate slowed such that hydrate formation essentially kept pace with incipient melting, and macroscopic water was not produced in the system.^{4,7,8}

We have now confirmed these hypotheses by direct observation, using a small high-pressure optical cell in which we duplicated the hydrate-synthesis procedure of our previous study while observing the progress of the reaction under a microscope. We observed details of surface reaction processes that had not been previously detected or measured in our large, constantvolume reactor, including rapid formation of hydrate films on ice grain surfaces at temperatures well below the ice point, the systematic development and growth of hydrate mantles around original ice grains at supersolidus temperatures, and the pervasive sublimation and recrystallization processes that accompany the hydrate-forming reaction. Our in situ technique permits direct observation of these hydrate growth processes on a stable ice substrate with controlled geometry, conditions that are difficult to achieve during hydrate formation by conventional methods involving vigorous agitation of gas + H₂O mixtures9 or that are only partially met during reaction along liquid water or gas bubble interfaces.¹⁰

Experimental Section

The basic optical cell used for these experiments has been previously described,¹¹ and simply incorporates a closed-ended, fused-silica tube (1.0 mm i.d., 3.0 mm o.d.) housed within a conventional, stainless steel, high-pressure valve body with a cut-away window for viewing. We initially chilled the cell to 250 K and loosely filled the silica tube with 200 μ m ice grains prepared identically to those used in our large-volume samples (Figure 1A, point A; Figure 2A, inset).⁴ This "seed" ice was prepared from gas-free, coarsely crystalline ice grown from frozen, triply distilled water, ground and sieved to a 180-250 μ m grain-size fraction.^{4,8} After filling the tube with this material, the remaining pore volume was evacuated and then flooded with cold CH₄ gas at 23 MPa and 255 K (Figure 1A, point B), or CO₂ gas at 2.2 MPa (or CO₂ liquid at 4.5 MPa) and 260 K. The cell was then immersed in an insulated dish of cold ethanol, placed under an optical microscope, and then slowly warmed from 255 to 290 K (Figure 1A, points B-G) at a rate similar to that used in our earlier large-volume experiments (Figure 1B, inset). Temperature was measured with a chromel-alumel thermocouple emplaced within the valve body and in contact with the outer wall of the silica tube, and pressure was monitored with a pressure transducer attached to one of the valve-body ports. Commercially available UHP-grade gases were used for these experiments, and CH₄ pressures were



Figure 1. (A) Phase diagram for the CH₄-H₂O system. Shaded region shows field of methane hydrate stability; at low pressures or high temperatures, hydrate dissociates to H2O plus CH4 gas. The metastable extension of the H₂O melting curve is traced by the gray curve. Heavy dotted lines mark the reaction path established previously⁴ for producing large-volume samples of pure methane hydrate from H2O ice plus CH4 gas mixtures, by the reaction $CH_4(g) + H_2O(ice) \rightarrow CH_4 \cdot 6H_2O$ (detailed in Figure 1B). Points A through G, A through C₂, and A through E₂ show pressure and temperature conditions of optical cell tests described in the text and shown in Figures 2 and 3. (B) Detail of temperaturepressure history during synthesis of large-volume samples of methane hydrate as discussed in earlier work.^{4,6,8} Warming the ice + gas mixture above the H₂O liquidus (dot-dashed line) initiates macroscopic reaction. Increasing temperature slowly to 290 K over an 8 h span promotes full reaction. Complete reaction is marked by a 1.8 MPa pressure drop (ΔP_r) from start to finish, relative to the extrapolated subsolidus pressure-temperature curve.⁵ Squares correspond to peak pressure-temperature conditions of individual samples that were quenched at specific intervals during hydrate formation to determine hydrate content (given as vol %) as a function of ΔP_r and time [see Stern et al.⁴ for further detail]. Solid circles labeled C, E, and F designate the pressure-temperature conditions corresponding to optical cell tests C-F shown in Figure 1A and to A-F shown in Figure 2. Inset: Temperature-time profile during hyrate formation. Hydrate content (vol %) of partial reaction tests is given on the top scale bar, and shows how the rate of hydrate formation decays with time under static growth conditions.

boosted from tank pressure to the desired testing conditions by means of a gas intensifier.



Figure 2. H_2O ice grains (180–250 μ m grain size) and CH₄ gas reacting to form methane hydrate, shown in two series of photo micrographs of grains near the wall of the optical cell tube (A–C) and at the center of the tube (D–F). (A, inset) H_2O ice grains (180–250 μ m grain size) in air and throughout the 2-minute evacuation process remain smooth and glassy in appearance (Figure 1A, point A). (A and D) T = 261 K, $P_{CH4} = 25$ MPa (Figure 1, point C). After first exposure to pressurized CH₄ gas (or to CO₂ gas or liquid), the ice grains took on the mottled appearance shown here due to growth of a very thin surface layer of hydrate. (B and E) T = 275 K, $P_{CH4} = 27.6$ MPa (Figure 1, point E). Same grains as shown above. Grains have now been warmed over 3 K above the H₂O liquidus for 0.5 h. (C and F) T = 283 K, $P_{CH4} = 28.7$ MPa (Figure 1, point F). Grains have been above the H₂O liquidus for 1.5 h, but are still approximately 4 h from complete conversion to hydrate. Ice is approximately 60% reacted to hydrate, based on X-ray analyses and pressure-temperature-time relationships determined in Stern et al.⁴ and shown in Figure 1B. Grains throughout the tube retained their original shapes and sizes, and there is no optical evidence for accumulation of liquid water despite lengthy exposure to temperatures well above the H₂O liquidus. Hydrate growth along the tube wall (visible in central portion of B and C) increasingly obscured viewing of grains located in the center of the tube (E and F),¹³ but diagnostic grain shapes are still easily identifiable. (C inset) Complete conversion of an ice grain to methane hydrate after slow heating to the conditions designated by Figure 1, point G. Compare to A, inset.

Results and Discussion

We repeatedly subjected granular ice to both CH₄- and CO₂hydrate forming conditions and observed the superheating effect in both environments. Hydrate-coated ice grains were observed to persist to 290 K at 30 MPa in CH₄ and to 282 K at 6 MPa in CO_2 .¹²

At temperatures well below the H_2O liquidus, visible surface reaction on the ice grains first occurred after relatively brief exposure (<2 min) to either of these hydrate-forming species (Figure 2, A and D). We verified that the mottled surface appearance of the grains in the ice subsolidus region was caused largely by hydrate formation, rather than ice sublimation, by quickly dropping the methane gas pressure of a methane hydrate sample during this initial stage of reaction (see path shown in Figure 1A from points C_1 to C_2) and observing dissociation of this early-forming hydrate film.

This initial surface appearance of the ice grains did not change until the grains were subsequently warmed to the H₂O liquidus (271.5 K at $P_{CH4} = 27.3$ MPa; Figure 1A, point D). Upon further warming, no expulsion of water was observed nor any cracking or collapsing of the hydrate encasement that should attend bulk melting of the ice cores, particularly within the first 30 min above the H₂O liquidus when the hydrate mantles are thin⁶ and presumably weak (Figure 1, point E; Figure 2, B and E). Similarly, a partially reacted sample that was quickly cooled from 276 to 268 K while maintained under elevated methane pressure showed no evidence of tensile cracking or expansion that should accompany sudden refreezing of a melted core.



Figure 3. Melting of the unreacted ice cores of partially reacted grains by reducing methane pressure from 27.6 to 4 MPa, at 275 K (Figure 1, points E to E_1) (see text). (A) Prior to the pressure drop, the grain had been above the H₂O liquidus to 275 K and 27.6 MPa for 0.75 h (comparable to Figures 2B and 2E). (B) After reducing methane pressure to 4 MPa, the grains became increasingly misshapen as liquid pooled within them, causing distortion and partial collapse of the outer hydrate mantle within 10 min. Liquid water radially expelled along small fissures and crystallized as finely crystalline hydrate surrounding the original grains. (C) The sample continued to recrystallize over the following 20 h at 275 \pm 1 K and 4 MPa, indicating that it had remained within the methane hydrate field of stability throughout the test. Hydrate growth along the tube wall sublimated and regrew on the surfaces of existing grains (see grain at right) or as single crystals or coarse-grained aggregates (shown center and left). (D) Slowly warming the sample to 277.5 K (Figure 1, point E_2) produced the expected dissociation of all grains in the tube, confirming that all material was methane hydrate. When slightly cooled to 277 K, the liquid drops slowly crystallized to form methane hydrate polycrystals (center grain). The larger drops of liquid water which have not yet crystallized (those shown at left and right) appear to be pinned to the tube surface by hydrate crystallizes or small gas bubbles in a manner such that they retain the general faceted shape of the original domains (compare D with C).

Instead, individual grains maintained identifiable shapes and approximate sizes throughout reaction (Figure 2, C and F),¹³ and changed only by becoming increasingly mottled and dark in appearance as they approached full conversion to hydrate (Figure 1A, point G; Figure 2C, inset).

The observed progress of reaction throughout the H₂O subsolidus and supersolidus regions, coupled with our previous measurements of hydrate reaction as summarized in Figure 1B, suggest testable hypotheses regarding hydrate nucleation and growth processes. We note that in our earlier experiments in our large-volume apparatus, we detected no evidence of hydrate formation in the ice subsolidus region either by X-ray diffraction or by pressure-temperature anomalies, but speculated that a microlayer of hydrate had possibly coated the ice surfaces but remained below our detection levels [see endnote 21 in Stern et al.⁴]. This hypothesis is now verified optically (Figure 2, A and D) and supports theories of melting that depend on a free external surface for melt formation,14 and also is consistent with the existence of thin surface melt layers even at temperatures below the freezing point.¹⁵ Surface melting may be a necessary condition for appreciable hydrate nucleation, and the very limited growth of hydrate under ice subsolidus conditions suggests that such growth requires continued nucleation of melt at the hydrate-mantle/ice-core interface. At supersolidus conditions, by corollary, a high driving potential for hydrate formation may be required to maintain a stable site for both continuous melt nucleation and hydrate formation at the hydrate/ice interface, to suppress macroscopic melting.

To test the hypothesis that a critical rate of hydrate growth is required for appreciable ice superheating, we conducted an optical-cell experiment designed specifically to induce melting of the interior ice within partially reacted grains at temperatures above the H₂O liquidus, with no attendant hydrate dissociation. This experiment was also conducted to test definitively for the presence of ice within the hydrate-encased grains at elevated temperatures and to observe the development of melt textures. Our premise was that by reducing the rate of reaction of CH₄ with incipient melt at the hydrate-ice core interface, bulk melting could proceed at detectable rates. Our earlier work^{4,8} and that of others¹⁶⁻¹⁸ indicated that reducing the driving potential for hydrate formation, by reducing the pressure overstep of the equilibrium line, should lower the rate of hydrate formation at the hydrate growth front and could thus possibly serve as a method to induce melting of unreacted ice cores. In this experiment, ice grains were first mixed with CH₄ at 23 MPa (Figure 1A, point B) and then slowly warmed from 255 to 275 K (Figure 1A, point E; Figure 3A). After 0.75 h above the metastable H₂O liquidus, P_{CH4} was reduced to 4 MPa, just above dissociation pressure (Figure 1A, point E₁; Figure 3B).

Bulk melting of ice in the grain interiors was readily apparent within 10 min of reducing P_{CH4} . Interior melting produced grossly misshapen and bulbous grain shapes that eventually cracked or collapsed (compare Figure 3B with 3A) and eventually regrew with coarsely crystalline textures (Figure 3C). We confirmed that this sample was maintained within the methane hydrate stability field and that no hydrate dissociation

occurred, by observing (a) rapid hydrate crystallization accompanying liquid expulsion from the grain interiors (Figure 3B), (b) the continual presence of hydrate along the sample tube wall (Figure 3B), and (c) additional growth of methane hydrate crystals during the following 20 h at 275 \pm 1 K (Figure 3C). That all the crystalline material in the optical cell after 20 h was methane hydrate was confirmed by warming the sample to 277.5 K and observing its predicted decomposition to water plus gas when warmed through the dissociation curve (Figure 1A, point E₂; Figure 3D). This full experimental sequence verified that hydrate-mantled ice cores had persisted at elevated pressures to temperatures well above their ordinary melting point and that their bulk melting is easily detectable and produces distinct melt textures when hydrate formation is slowed at lower methane pressures. The dynamic behavior of the surfaces of melting grains and their evolving morphologies were in marked contrast to the stable shapes and relatively smooth surfaces maintained by grains during the standard high-pressure synthesis runs (compare Figures 2 and 3).

It remains unclear, however, how the ΔV of ice \rightarrow hydrate conversion is fully accommodated during reaction.⁵ The large, 16% expansion should produce a pressure gradient within composite ice/hydrate grains at the hydrate growth front, yet we observed no clear evidence for external cracking of the hydrate encasement nor a substantial increase in the dimensions of fully reacted grains (Figure 2). The increasingly slow ice → hydrate conversion rate (Figure 1B inset) also suggests that fracture of the hydrate encasement is not occurring to the extent that it aids transport of the hydrate-forming species to the ice core. We speculate that the volumetric differences may be accommodated by a diffusive flux of H₂O within the hydrate mantle, by removal of some hydrate material through sublimation,¹³ or by brittle/ductile behavior of the hydrate mantle, the effects of which are below our ability to detect by optical observation.

Conclusions

During our standard synthesis procedure, hydrate formation initially occurs in the ice subsolidus region, producing a very thin coating of hydrate on the ice grain surfaces (Figure 2, A and D). Subsequent hydrate growth at temperatures above the metastable ice solidus most likely occurs primarily by solidstate diffusion of the hydrate-forming species through the hydrate mantle and subsequent reaction at the ice/hydrate interface.^{4,8,19} Although these processes are enhanced by the high temperature and pressure conditions of our synthesis methods,^{4,16} hydrate formation in the grain interior evidently is rate-limited by the increasing diffusion distance between reactants as the hydrate mantle grows and thickens, resulting in the long times needed for complete reaction. We hypothesize that reaction of a hydrate-forming species with incipient H₂O melt at the hydrate - ice core interface may effectively inhibit the formation of an equilibrium solid-liquid water interface necessary for bulk melting,¹⁴ and can thus permit superheating. These interpretations are consistent with the optical observations of grains persisting to supersolidus temperatures at elevated pressures, with no appearance of free liquid, and with grain shapes and sizes remaining uniform with only minor outward growth (Figure 2). Furthermore, the success of the inducedmelting test demonstrates by corollary that excess methane pressure is necessary for maintaining a stable hydrate migration front by suppressing bulk melting within the grain interiors at warm temperatures.²⁰ Parallel tests using both gaseous and liquid CO₂ as the hydrate-forming species confirmed that the

superheating effect can be reproduced in other gas-hydrateforming systems under elevated conditions of pressure and temperature.

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(5) The volume of an empt structure I hydrate lattice is 16% greater than the equivalent mass of ice I, regardless of hydrate stoichiometry (the empty structure I lattice has a density of 0.78, and stoichiometric methane hydrate has a density near ice; 0.90 vs 0.92 for ice). There is a large $-\Delta V$ associated with hydrate formation, however, due to the volume reduction of the gas phase into the hydrate structure. In our constant-volume temperature-ramping experiments, the volume change that accompanies reaction is reflected as a reduction in the rate of pressure increase due to thermal expansion alone (Figure 1B).

(6) Control experiments discussed in ref 4, in which Ne (a nonhydrateforming gas) was used in place of CH₄ under otherwise identical test conditions, showed both textural and run record [pressure-temperature (P-T)] evidence that all the ice grains in the sample chamber fully melted within approximately 40 minutes of warming through the H2O liquidus [see Figure 3B in ref 4]. The T measured by the Ne sample thermocouple measurably lagged the rising T in the surrounding alcohol bath during the 40 min interval over which the P dropped [see Figure 3B inset in ref 4], reflecting the absorption of heat due to the endothermic melting of ice. In contrast, the CH₄ + H₂O samples produced only about 20% hydrate reaction over the same 40 min duration after crossing the H2O liquidus [verified by partial reaction experiments discussed in 4] yet showed no P drop associated with bulk melting of the remaining unreacted ice (Figure 1B). Moreover, the T records of standard CH₄ + H₂O runs displayed no thermal disparities between sample and bath thermocouples, indicating that rapid, wholesale melting did not occur [Figure 3B inset in ref 4]. While the reaction CH4 (g) + $6H_2O$ (ice) $\rightarrow CH_4 \cdot 6H_2O$ liberates a small amount of latent heat $\approx 20 \pm 0.3$ kJ/mol at 273 K and 28 MPa methane pressure, calculated as described in endnote 16 in ref 4], this heat is not reflected as a T anomaly that occurs near the ice liquidus because the reaction occurs over a period of ~ 8 h and such heat would be small compared with the exchange of heat of the sample with its surroundings by thermal conduction. In comparison, the standard enthalpy for melting of ice is -6.01 kJ/mol, or -36 kJ/6 mol H₂O in terms of the hydrate-forming reaction.

(7) Tests in which a coarser sized fraction of granular ice was used as starting material $(1-2 \text{ mm}, \text{ vs } 200 \,\mu\text{m})$ in standard runs) showed evidence for significant melt accumulation in the sample chamber during the heating cycle and were unsuccessful in producing bulk, granular aggregates of pure methane hydrate [Figure 6 in ref 8].

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(10) Recent optical investigations of gas hydrate growth have been reported by (a) Smelik and King (Smelik, E.; King, H., Jr. Am. Mineral. **1996**, *82*, 88), in which methane hydrate and methane-propane hydrate crystals were grown along a static, liquid water-gas interface in a high-pressure, flat-plate optical cell, and (b) Brewer et al. (Brewer, P.; Orr, L.; Friederich, G.; Kvenvolden, L.; Orange, D.; McFarlane, J.; Kirkwood, W. *Geology* **1997**, *25*, 5, 407), who documented hydrate formation along gas bubble surfaces during controlled release of CH4, CO₂, and a mixed-gas (methane-ethane-propane) phase through columns of natural seawater in

a deep-ocean environment. We note that while both these investigations elegantly document the initial hydrate crystallization and formation rates along water/gas interfaces, they show incomplete conversion of H_2O to hydrate due to very reduced hydrate growth rates after initial crystallization along the respective growth surfaces. Our method of hydrate growth from delayed melting of ice circumvents this problem and permits observation of full conversion of all H_2O in the sample tube to hydrate, as well as the testing of hypotheses regarding continued growth of hydrate after the initial nucleation phase.

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(12) During CO₂ hydrate formation, persistence of partially reacted ice grains to temperatures above the H₂O liquidus was observed when using either liquid or gaseous CO₂ as the hydrate-forming species. Most tests were conducted using liquid CO₂ in order to trace the superheating effect to higher temperature before dissociation conditions were reached. The equilibrium formation of CO₂ hydrate occurs at considerably lower P-T conditions than CH₄ hydrate, and its dissociation curve becomes strongly *T* dependent at P > 4.5 MPa where it intersects the CO₂ vapor curve at a corresponding dissociation *T* of 283 K (see Figure 9 in the following: Ross, R.; Kargel, J. In *Solar System Ices*; Schmitt, B.; de Bergh, C.; Festou, M., Eds.; Kluwer Academic Publishers: Dordrecht; in press; also Takenouchi, S.; Kennedy, G. J. Geology **1965**, *73*, 383.)

(13) Hydrate formation along the inner wall of the tube at temperatures above the H_2O liquidus (Figure 2, B and C, central region) indicates that H_2O vapor exists in the pore volume of the tube, most likely due to partial sublimation of the hydrate mantle encasing each ice grain. This sublimation process also explains why a significant grain size increase during ice conversion to hydrate is not observed [see ref 5].

(14) Results from measurable superheating in gold-plated silver single crystals (Daeges, J.; Gleiter, H.; Perepezko, J. Phys. Lett. **1986**, 119A, 79),

suggest that either a free external surface or internal defects such as dislocations are critical for bulk melting to take place at the normal melting point (Phillpot, S.; Lutsko, J.; Wolf, D.; Yip, S. *Phys. Rev. B* **1989**,*40*, 2831. See also Phillpot, S.; Yip, S.; Wolf, D. *Comput. Phys.* **1989**, *3*, 20.)

(15) "Premelting" of the ice grains (see reviews by Dash, J.; Fu, H.; Wettlaufer, J. *Rep. Prog. Phys.* **1995**, *58*, 115, and Wettlaufer, J.; Worster, M.; Wilen, L. J. Phys. Chem. B. **1997**, *101*, 6137, and references therein] may enhance reactivity and hydrate formation at the hydrate-ice core interface along a disordered, liquidlike, surface film. See also discussion of interface phase transitions in Sutton A.; Balluffi, R. *Interfaces in Crystalline Materials*; Clarendon Press: Oxford, 1995; Chapter 6.

(16) Makogan¹⁷ first suggested that because hydrate formation is an interfacial process, high concentrations of hydrate-forming species are required at the interface. Hwang et al.¹⁸ confirmed that a high-pressure driving force is required for measurable hydrate formation rates and that, for hydrate formation from melting ice, higher gas pressure yields higher formation rates.

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(19) Conceptual models of hydrate growth by diffusion have been discussed previously by Makogan¹⁷ and by Hwang et al.¹⁸

(20) The melt accumulation that accompanied hydrate conversion in the coarse-grained samples [see ref 7] suggests that a prolonged superheating effect is also partially dependent on other factors that influence diffusion rates, such as the surface area-to-volume ratio of the reacting grains and the thickness of the developing hydrate barrier to the ice core.