Estimating in situ gas hydrate saturation from core temperature observations, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well

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Abstract: During drilling of the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, core temperatures were measured immediately upon recovery in the core-logging trailer. Gas-hydrate-bearing cores were typically frozen, with temperatures as much as 6°C lower than cores containing no gas hydrate. This temperature depression is attributed to the endothermic dissociation of gas hydrate during uphole tripping, and can be used to estimate minimum in situ gas hydrate saturation.

Numerical modelling of heat exchange between core and circulating mud during tripping demonstrates that cores cool to mud temperature before leaving the methane hydrate P-T stability field. Simple arguments support the hypothesis that the endothermic heat of gas hydrate dissociation is supplied largely by the release of latent heat during coincident freezing of pore waters. Assuming minimal heat exchange with circulating mud, energy-balance calculations yield estimates of the quantity of gas hydrate lost to dissociation during recovery. These estimates are comparable to the in situ gas hydrate concentrations inferred from downhole geophysical logs.

Résumé: Lors du forage du puits de recherche sur les hydrates de gaz JAPEX/JNOC/GSC Mallik 2L-38, la température des carottes a été mesurée dans la remorque de diagraphie, immédiatement après leur extraction. Les carottes renfermant des hydrates de gaz étaient généralement gelés et avaient des températures jusqu'à 6 °C inférieures à celles des carottes sans hydrates de gaz. Cette dépression de la température, attribuable à la dissociation endothermique des hydrates de gaz au cours du retour du train de tiges vers la gueule du puits, peut être utilisée pour évaluer la saturation minimale en place en hydrates de gaz.

La modélisation numérique de l'échange thermique entre la carotte et la boue circulante au cours du retour du train de tiges montre que les carottes se refroidissent et atteignent la température de la boue avant de quitter le champ de stabilité de pression et de température des hydrates de méthane. Des arguments simples corroborent l'hypothèse selon laquelle la chaleur endothermique de dissociation des hydrates de gaz émane en grande partie de la chaleur latente dégagée au cours de la congélation simultanée de l'eau interstitielle. Les calculs du bilan énergétique, qui partent de l'hypothèse selon laquelle l'échange thermique avec la boue circulante est minimal, fournissent des estimations de la quantité d'hydrates de gaz perdue par dissociation au cours de la récupération. Ces estimations sont comparables à celles des concentrations d'hydrates de gaz en place déduites des diagraphies géophysiques en sondage.

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INTRODUCTION

In situ natural gas hydrate occurrences in both marine and terrestrial environments generally exist under pressure and temperature conditions that are close to their natural stability thresholds. Retrieval of gas hydrate samples with conventional or wireline coring systems is often problematic, as the pressure and temperature conditions during retrieval and handling of the core barrel cannot be controlled. While precautions can be taken to reduce these effects by chilling the drilling mud or minimizing the retrieval time, a certain amount of gas hydrate dissociation is unavoidable as the gashydrate-bearing sediments eventually cross the pressuretemperature (P-T) stability threshold during the uphole trip. Upon crossing this threshold, gas hydrate dissociates into liquid water or ice (depending on thermal conditions) and a free-gas component. The dissociation of gas hydrate is endothermic (heat absorbing), and is analogous to the melting of ice in that it primarily involves the breaking of many hydrogen bonds linking individual water molecules. Initially, dissociation heat is supplied by the decomposing gas hydrate itself. As the core barrel is raised above the minimum depth for gas hydrate stability, the pressure experienced by the core is further reduced, such that the temperature of gas hydrate dissociation is also reduced. Progressive dissociation therefore tends to occur at a lower temperature than that of the surrounding sediment matrix (including water-ice components and any gas hydrate not yet dissociated). Thus, a thermal gradient is established between the dissociating gas hydrate and the sediment matrix, and heat for continued dissociation is provided largely by the enclosing sediment, resulting in depressed core temperatures relative to the ambient conditions (Wright et. al, 1998, 1999). Specifically, the largest available source of dissociation heat is the fusion heat released during freezing of the free-water component of recovered cores.

During Leg 164 of the Ocean Drilling Program (ODP) conducted offshore of the east coast of the United States, the temperature of recovered cores considered to have contained in situ gas hydrate were found to be 7 to 10°C lower than cores assumed to have contained no gas hydrate (Shipboard Scientific Party, 1994, p. 183). Through modelling of heat exchange within cores during recovery operations, the magnitudes of the temperature depressions were related to the quantity of gas hydrate dissociated during core retrieval, thus establishing a lower limit for estimates of in situ gas hydrate saturation levels. For the ODP situation, estimates of in situ gas hydrate saturation were generally quite low, typically less than 15%. In the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, gas-hydrate-bearing core samples (from 896 to 952 m depth) (all depths were measured from kelly bushing [8.31 m above sea level]) were retrieved using conventional drillstring coring methods (Ohara et al., 1999). In addition to visible evidence for the presence of gas hydrate (i.e. vigorous and persistent bubbling on core surfaces), temperatures of core when recovered were as much as 6°C lower than mud temperatures and cores for which there was no evidence of gas hydrate. While the temperature depressions at Mallik 2L-38

were less than the range observed in Leg 164 cores, Mallik cores typically were completely bonded upon recovery (by residual gas hydrate and ice), showing no evidence of the presence of liquid water. This paper presents a simple estimation of the concentration of gas hydrates from the coretemperature observations. Our analysis assumes the hypothesis that the endothermic heat of gas hydrate dissociation is supplied largely by the core, but with the important inclusion of the latent heat of freezing of sediment pore water. Dissociation of gas hydrate in excess of that needed to balance the freezing of the core causes an additional reduction of core temperatures below 0°C.

CORE-RECOVERY PROGRAM AT MALLIK 2L-38

Measured temperatures of recovered core, recovery depths, mud temperatures, and other pertinent data from the Mallik 2L-38 well are presented in Table 1. The drill-mud system utilized for the gas hydrate interval consisted of KCl/polymer/lecithin mud chilled to near-freezing temperatures using a plate-type heat exchanger (Ohara et al., 1999). The purpose of the chilled mud and the Drilltreat additive was to enhance the stability of gas hydrate both within the formation sediments intersected by the well bore and within core samples during their trip uphole. During drilling of the main hole from 670 m to the target depth of 1150 m, the mud system performed well, with mud temperatures generally being maintained between 1.5 and 5°C. Data loggers in the mud tanks provided continuous recording of the in-and-out circulation temperatures. Manual measurements with a thermometer were also made at regular intervals.

A number of coring runs were successfully completed within a major gas-hydrate-bearing interval at Mallik 2L-38, located between the depths of 896 and 926 m. Core trip time to the surface averaged about 1.5 to 2.0 hours in most cases; however, trip time above about 260 m depth (i.e. outside of the methane hydrate stability field) was considerably less. averaging about 30 minutes (Dallimore et al., 1999; Dallimore and Nixon, pers. comm., 1998). An additional 20 to 40 minutes were required for rig-floor disassembly, and for transport of the inner core barrel to the logging trailer. Core temperatures were measured immediately upon arrival in the core-logging trailer. Gas-vield measurements conducted on cores between 880 and 1102 m below ground level indicated the presence of trace to moderate amounts of pore-space gas hydrates when recovered to the surface. Equivalent times in the Leg 164 example were 10 minutes for wireline core tripping, and an additional 5 to 10 minutes before core temperatures were taken (Shipboard Scientific Party, 1994).

Core and mud temperature data are summarized in Table 1. Well-log interpretations (Miyari et al., 1999) and core observations (Uchida et al., 1999) confirmed that the highest gas hydrate concentrations occurred within sandy sediments in the interval from 897 m to 922 m. Visible forms of gas hydrate included thin lenses and veins (<2 mm) and

random gas hydrate clasts (2–10 mm), which, in one instance, formed the matrix of a sandy gravel deposit. However, fine-grained pore-space gas hydrate (<2 mm) was predominant, with gas hydrate generally filling the intergranular pores of medium-grained sands. Gas devolved from core in this interval consisted of greater than 99% methane with a C1/(C2+C3) ratio of about 500 (Lorenson et. al., 1999), supporting our assumption that Structure I methane hydrate dominates at Mallik 2L-38. This has been confirmed by researchers at the National Research Council of Canada through powder X-ray diffraction of gas hydrate separated from Mallik cores (Tulk et al., 1999). Most cores arrived at the surface with measured core temperatures generally between -1 and -3°C (cores no. 15–20, 896.4–921.0 m depth).

In virtually all cases, sediments at subzero temperatures were well indurated and described as well bonded by well-site geologists. Given that these sediments are unconsolidated when thawed, we interpreted this character to result from grain cementation caused by the presence of pore ice and/or gas hydrate. Occasional unfrozen zones having core temperatures just above 0°C were observed within this interval. These were generally associated with interbedded silts and silty sands, often with enhanced pore-water salinity (Cranston, 1999).

In contrast, gas hydrate concentrations in a thick sequence of silts below about 926 m (which continued to the bottom of the cored interval) were much lower. Cores recovered from this section were uniformly unfrozen, with temperatures of 4 to 5°C (e.g. core no. 22, 922.7–929.3 m).

Table 1. Comparison of model calculations of gas hydrate dissociated during core recovery with estimated in situ values and measured residual gas hydrate concentrations.

Core	Dept Top	:h (m) Bottom	Texture class	Core temperature (ref. 1) (°C)	Mud temp (avg.) (°C)	Temperature depression (note 1) (°C)	Porosity (ref. 2) (%)	Hydrate dissociated (note 2, 5) (%)	In situ hydrate saturation (ref. 3, note 5) (%)	GH sat. (well-site) (note 3) (%)	GH sat. (NRC) (note 4) (%)
15 ★	896.40 897.65	897.00 900.30	silt (sand lam.) sand	0.7 -2.6	1.85 1.85	1.15 4.45	39 33	insuff. 78	0-15 74-85	19-38	20;41;49
16	901.20	902.00	sand	-1.8	2.5	4.3	42	76	44-77	2	
17	902.00 902.15	902.15 902.30	sand silty sand	-0.9 0.4	2 2	2.9 1.6	37 35	75 insuff.	75 75	trace	
18	902.50 903.44 904.14 904.90 905.50 906.25	903.44 904.14 904.90 905.50 906.25 907.15	sand (silt lam.) silt (sand lam.) sand pebbly sand sand (silt lam.) silt/sand lam.	0.9 1.3 -1.7 n/a -1.5 2.2	2.5 2.5 2.5 3.85 2.5 2.5	1.6 1.2 4.2 n/a 4 0.3	42 40 45 30 39 38	insuff. insuff. 76 not modelled 76 insuff.	52-75 ~40 70-80 80-85 75-80 ~20	trace 15-20 15-20 trace	13 5
19	911.60 912.60 913.05 913.75 914.27 914.60	912.60 913.05 913.75 914.27 914.60 914.90	silty sand sand pebbly sand gravel/sand coarse sand sandy gravel	-1.1 -1.4 n/a -1.8 -2.1 -1.6	3.85 3.85 3.85 3.85 3.85 3.85	4.95 5.25 n/a 5.65 5.95 5.45	33 39 30 30 33 26	78 78 not modelled 80 80 82	50-70 70-80 75-80 79-83 71-79 72-78	10 8-11	12 3
20	919.00 921.00 922.15	921.00 922.15 922.70	fine sand fine sand sand (silt lam.)	-1.8 -1.2 n/a	3.95 3.95 3.95	5.75 5.15 n/a	37 42 37	79 77 not modelled	72-80 60 40-50	3 trace	
22	926.70 926.92 927.10	926.92 927.10 928.10	sandstone clayey silt clayey silt	4.8 4.4 4.8	2.2 2.2 2.2	-2.6 -2.2 -2.6	34 34 31	0 0 0	0-10 0-10 0-10		

NOTES:

- 1. Temperature depression = average mud temperature minus core temperature.
- 2. Calculation of hydrate dissociated during core tripping:
 - ★ denotes core section modelled in finite-element simulation
 - (a) if core temperature < 0°C, the latent heat of freezing of core pore water is considered (330 J/g)

Hydrate -> Ice + Gas

Heat of dissociation =150 J/g (Handa, 1986); gas hydrate density = 0.9 g/cm³

Heat capacity of soil = 0.94 J/cg/K.

Heat capacity of ice/hydrate = 2 J/g/K.

(b) if core temperature > 0°C, only sensible heat of core cooling is considered

Hydrate -> Water + Gas

Heat of dissociation =450 J/g (Sloan, 1990, p.387); gas hydrate density = 0.9 g/cm3

- Based on well-site measurements of the volume of gas devolved from subsamples of cores.
- 4. Based on pressure/volume relations during devolution of gas from GSC samples preserved in liquid nitrogen.

Post-field testing was carried out at the Steacie Institute for Molecular Sciences of the National Research Council in Ottawa by Tulk et al. (1999).

5. See 'Discussion and Conclusions' section of text for explanation of shaded areas.

ADDITIONAL REFERENCES:

- 1. Dallimore et al., 1999.
- 2. Winters et.al., 1999.
- 3. Collett et al., 1999.

THERMAL MODEL OF CORE TRIPPING

A commercial finite-element thermal-modelling program was used to simulate the sensible cooling of a core as the inner core barrel was tripped up the well through the mud column. Starting at the initial in situ temperature estimated for the depth interval from which the core was retrieved, the modelling assumed that drilling-mud circulation rates were sufficient to keep the outer surface of the core at mud temperatures, and that the trip speed was constant. Core no.15 was chosen for the simulation, primarily because of the presence of two adjacent core sections with distinctly different physical properties deemed to be characteristic of gashydrate-bearing and non-gas-hydrate-bearing sediments at Mallik 2L-38. Contrasting core temperatures measured for these adjacent sections (Table 1: core sections 15-1 and 15-2,) were assumed to result from variations of in situ gas hydrate content. For modelling purposes, the physical and thermal properties of individual core sections were determined from well-site core descriptions (Dallimore et al., 1999) and from field and post-field laboratory tests (Winters et al., 1999).

The description of the core is as follows:

<u>Section 15-1</u>: (896.4–897.65 m) Silt; no evidence of gas hydrate when recovered; core temperatures of 0.6 to 0.8°C; estimated in situ gas hydrate saturation 0–15% (Collett et. al., 1999); porosity 33% (Winters et. al., 1999).

<u>Section 15-2</u>: (897.65–900.3 m) Sand; gas hydrate bearing when recovered; core temperatures of -2.3 to -3°C; in situ gas hydrate saturation 74–85% (Collett et. al., 1999); porosity 31% (Winters et. al., 1999).

The core-retrieval history indicates that core no. 15 spent 105 minutes coming up the well while still within the gas hydrate stability field; 42 minutes within the well, but outside the stability field; and about 40 minutes on the surface, before core temperature measurements were taken. In total, the core was outside of the methane hydrate P-T stability field for approximately 82 minutes ('Core Runs'; Dallimore et al., 1999).

The result of the finite-element thermal-modelling indicates that core no. 15 cooled rapidly to the average mud temperature (~1.85°C, Table 1) prior to leaving the methane hydrate stability field. Note that because of the higher specific gravity of the circulating mud (1.15) relative to that of water, the effective pressures experienced by core within the well bore are greater than the normal in situ pressures. This means that during the trip to the surface, gas hydrate within cores remains stable up to about 260 m depth, rather than the 300 m depth suggested by the P-T curve for in situ methane hydrate stability (Fig. 1). At this point, temperatures throughout the core were within a few tenths of a degree of the mud temperature. Note that following initial rapid cooling, core temperature remained at approximately 4–8°C inside the gas hydrate P-T stability field for most of the trip between 900 and 260 m depth. Modelling results suggest that the major effect of the cooling mud during core tripping was to increase the thermal stability of gas hydrate within the core, and to prolong its residence time within the P-T stability field, such that

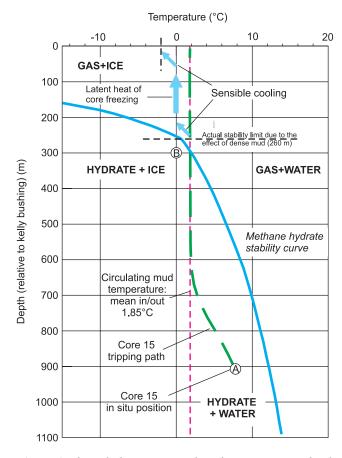


Figure 1. The uphole tripping path in the temperature-depth field, relative to the methane hydrate phase stability curve (Holder and Hand, 1982, reported in Collett, 1993), for core no. 15 from its in situ position (A). The sensible cooling of the core to mud temperatures (average 1.85°C) was calculated using a finite-element numerical heat-flow model. The thermal effects of hydrate dissociation after the core exits the hydrate stability field (at B) were calculated separately (see text).

the core exits the field at the shallowest depth possible. However, P-T stability thresholds for Mallik 2L-38 cores having elevated pore-water salinity and/or substantial fine-grained components will be shifted downward (i.e. to greater pressures/depths) from the stability curve established for freshwater sands (Wright et. al., 1999: Fig. 7). Upon retrieval, these cores will exit the methane hydrate stability field at depths somewhat greater than 260 m.

Heat transfers associated with the dissociation of gas hydrate were not accounted for in this stage of modelling. The modelling suggests that in the absence of gas hydrate dissociation, core temperatures remain well above the freezing point during tripping. Therefore, the predicted coretemperature history reflects the exchange of sensible heat only. This result provides a baseline for consideration of the thermal effect of gas hydrate dissociation and subsequent freezing of core pore waters during the final stage of core tripping (above 260 m depth, after the cores have exited the methane hydrate P-T stability field).

HEAT-BUDGET MODEL FOR HYDRATE DISSOCIATION IN MALLIK CORES

Finite-element modelling predicts that without gas hydrate dissociation, cores would reach the ground surface at the temperature of the circulating mud (Fig. 1). Gas-hydrate-bearing core is considered to begin dissociating as soon as the core barrel passes the minimum depth for methane hydrate stability (about 260 m). Assuming that the gas hydrate is disseminated uniformly throughout the core pore volume, we propose the following simple scenario for heat exchange within a gas-hydrate-bearing core after it leaves the P-T stability field on its uphole trip to the surface:

- a) As pore-space gas hydrate begins to dissociate above 260 m depth, most of the endothermic heat of dissociation is taken from the core itself (rather than the surrounding mud). The core is thus cooled, and quickly reaches the freezing point (lower oblique arrow, Fig. 1).
- b) Continuing gas hydrate dissociation gradually freezes the core isothermally (large vertical arrow, Fig. 1). During this stage, the heat of dissociation is supplied by the latent heat of freezing of the free water in the core (according to the reaction pathway assumed below). Core temperatures are assumed to remain at or near 0°C during this stage.
- c) Once all of the remaining pore water has frozen, further gas hydrate dissociation reduces the temperature of the core below 0°C (upper oblique arrow, Fig. 1).

Whether the core reaches the surface during stage a), b), or c) depends on the in situ gas hydrate saturation and porosity of the cored sediments. We invoke a simple heat budget model to account for heat exchange between the gas hydrate, free water, and matrix components of the core:

- 1) Core temperature depression (the difference between mud temperature and measured core temperature) is due entirely to the exchange of sensible heat, through processes a) and c) above. The contribution of sensible heat to the overall heat budget is easily calculated considering the specific heats of the soil components.
- 2) For gas-hydrate-bearing cores, we assume a reaction pathway for the dissociation of methane hydrate to ice and free gas, such that:

$$CH_4$$
 hydrate + 150 J/g > ICE + CH_4 gas (Handa, 1986)

The endothermic heat of dissociation (150 J/g) is balanced by the latent heat of freezing of sediment pore water (330 J/g). Complete freezing of the liquid pore-water component during core tripping is dependent on the presence of sufficient in situ gas hydrate disseminated throughout the core. This is the dominant heat-exchange process because of the large latent heat component (for pore-water freezing) relative to the average specific heat of the sediment matrix (about 0.94 J/g), and the free-water component (4.1 J/g)

Heat balance calculations for core no. 15-2 (33% porosity) are shown in Figure 2. At approximately 70% in situ pore saturation, just enough gas hydrate is present to freeze all in situ free water. At less than 70% saturation, insufficient gas

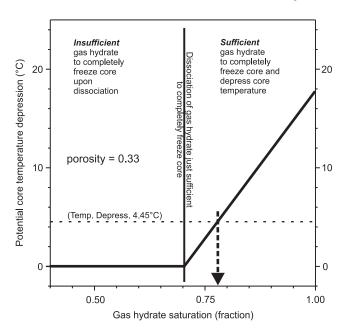


Figure 2. Potential core-temperature depression for mud temperature versus gas hydrate saturation necessary to freeze all core pore water (based on core section 15-2, 33% porosity). An observed core temperature depression of 4.45°C suggests an in situ gas hydrate saturation of at least 78%. Actual in situ gas hydrate saturation may be greater, depending on the amount of residual gas hydrate remaining in the core upon recovery.

hydrate is present to remove the latent heat of freezing, and cores will arrive at the surface at temperatures above 0°C. For saturations greater than 70%, dissociation of gas hydrate in excess of that required to completely freeze the core will depress the core temperature below 0°C. For core no. 15-2, an observed core temperature depression of 4.45°C (from mud temperature) suggests an in situ gas hydrate saturation of at least 78%. Theoretically, adding the measure of the residual gas hydrate remaining in the core would provide an estimate of the actual in situ saturation.

Figure 3 is constructed from results of heat balance calculations for hypothetical cores having a range of porosity and gas hydrate saturation values. The figure indicates that in situ gas hydrate saturations in excess of 70% are required to depress core temperatures at the surface, regardless of porosity (this is because the exchange of dissociation/latent heat primarily involves the pore-space components only [water and gas hydrate]). However, for a given in situ saturation in excess of 70% (e.g. 85%), the magnitude of core-temperature depression increases with increasing porosity, due to the progressively lower volumetric proportion of soil matrix (which provides sensible heat to support continued dissociation of gas hydrate).

Also included in Figure 3 (red circles) are the observed temperature depressions measured for actual gas-hydrate-bearing cores recovered from Mallik 2L-38, plotted against core porosity measurements (data from Table 1). Extending a line from each data point parallel to the x axis

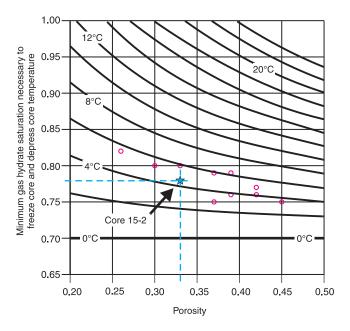


Figure 3. Relations between core-temperature depression, porosity, and the minimum in situ pore saturation by gas hydrate, calculated using a simple heat-balance model. Observations for Core no. 15-2 (0.33 porosity, 4.45°C temperature depression) are indicated by the blue star. Extending a line parallel to the x axis yields the model estimate of the minimum in situ gas hydrate saturation necessary to produce the core temperature depression observed. Data for Mallik 2L-38 cores 16 through 22 (from Table 1) are plotted as red circles. Results are for cores that were frozen upon recovery only.

provides the model estimate of gas hydrate dissociated during the uphole trip (expressed as the minimum in situ pore saturation necessary).

DISCUSSION AND CONCLUSIONS

A two-stage modelling approach has been used to relate surface observations of core temperatures and core thermal state (frozen or unfrozen) to minimum in situ gas hydrate saturation levels. Results of finite-element simulation and simple heat-budget modelling support the conclusion that sediments within the major zones of gas hydrate accumulation at Mallik 2L-38 contain substantial quantities of in situ gas hydrate. Modelling results confirm the general magnitude of estimates of in situ gas hydrate saturation determined through analysis of downhole well-log data (Collett et. al., 1999). For cores that arrived at the surface in a frozen state, well-log estimates of in situ gas hydrate saturation are generally in excess of the 70% threshold the model predicts is necessary to completely freeze the cores, and to produce subzero core temperatures (see shaded areas, Table 1).

Two of the modelled cases (core no. 17-2 and core no. 20-2) do not conform to the general trend observed. Core no. 17-2 did not freeze, even though the estimated in situ gas

hydrate saturation (75%) was in excess of the 70% threshold for complete core freezing. However, the in situ gas hydrate saturation may have been overestimated in this case, given that section no. 17-2 consisted of a very thin (15 cm) silt layer situated between two sections of gas-hydrate-bearing sands. It is likely that, in this situation, a thin layer of gas-hydratepoor sediments would not be adequately resolved by downhole logging techniques. Core no. 20-2 on the other hand, was frozen when recovered, even though well-log estimates suggest an in situ gas hydrate saturation of only 50–60%. In this case, core no. 20-2 was cut from sediments in a zone of transition between low-salinity, gas-hydrate-rich sands and suspected high-salinity, gas-hydrate-poor sands overlying a 2 m section of cemented sandstone of very low porosity. We speculate that well-log responses may have been influenced locally by this low-porosity, high-salinity zone, and thus the estimate of in situ gas hydrate concentration for core no. 20-2 is probably artificially low. It should also be noted that an inherent uncertainty exists with respect to the precision of the in situ depths assigned to recovered core sections. This arises due to the difficulty in accurately fixing the downhole position of core barrel at great depths (~ 1 km), and the potential for slippage of the cut core section within the core barrel

In several cases, well-log estimates of in situ gas hydrate saturation cover a rather broad range, spanning the predicted 70% threshold necessary for core freezing (e.g. cores no. 16, 18-1, 19-1), suggesting a non-uniform distribution of gas hydrate within these core sections. These cases provide ambiguous support for both the presence of sufficient in situ gas hydrate to produce frozen core at the surface (upper limit of range >70%, core no. 16), or the converse situation in which the core was unfrozen due to insufficient in situ gas hydrate (lower limit < 70%, core no. 18-1). Note that field-log descriptions (Dallimore et. al., 1999) indicate the presence of organic-rich laminations within both core no. 16 and core section 19-1. These organic-rich zones probably contain little or no gas hydrate, and in any case, their anomalous physical properties (relative to surrounding sediments) would tend to influence well-log estimates of in situ saturation levels within these core sections.

A limited number of well-site measurements were made of the volume of gas devolved during forced dissociation of gas hydrate in subsamples of the recovered cores. No attempt was made to distinguish between gas released from gas hydrate and that which may have been 'trapped' within pores as ice formed during the final stages of core recovery (the latter is expected to be a proportionally small amount). Gas yields from well-site measurements are presented in Table 1, along with much more precise determinations of gas yields (from much smaller subsamples of core sections preserved by the GSC in liquid nitrogen) at the laboratories of the Steacie Institute, National Research Council, Ottawa (Tulk et. al, 1999). Where in situ concentrations of gas hydrate are substantially in excess of the amount predicted to have dissociated during recovery operations, we should expect this excess gas hydrate to be detectable in well-site tests and post-field sampling of preserved core sections. In general, available gas-yield measurements confirm the presence of substantial quantities of residual gas hydrate in cores for which maximum in situ saturations were greater than 75%, with the largest residuals occurring in cores having gas hydrate saturations of 80% or more (core no. 15-2; 18-3, 4; 19-3, 4). Only trace amounts of devolved gas were recovered from cores having in situ gas hydrate saturations lower than about 70–75%. This supports the conclusion that insufficient in situ gas hydrate was present in these cores to remove the latent heat of freezing of the free water component during uphole tripping.

Implications of the modelling assumptions

Given the general simplicity of our modelling technique, we suggest that only coarse agreement between model predictions and well-log estimates (within about 10%) are sufficient to reconcile surface observations of core thermal conditions with probable in situ concentrations of natural gas hydrate at Mallik 2L-38. In this context, interpretation of the results should be undertaken with reference to the primary assumptions and uncertainties relevant to this work (outlined below).

The assumptions adopted in this exercise tend to promote conservative estimates of pore saturation by gas hydrate. For example, we assumed that there was no exchange of heat between the core and circulating mud during the dissociation of pore-space gas hydrate. Any exchange that might have occurred would have retarded the freezing of free water by providing some of the heat required for gas hydrate dissociation. In this case, the dissociation of additional gas hydrate would have been necessary to offset this input, but would not be accounted for in our modelling. Consequently, we would have underestimated the actual amount of gas hydrate dissociated to produce the core temperatures observed at the surface. We also discounted the contribution of surface ambient conditions (temperatures were generally well below 0°C) to core freezing. This decision was supported by the fact that temperatures of cores containing little or no gas hydrate were uniformly above 0°C, in spite of a limited exposure to subzero ambient air prior to the measurement.

We have assumed a reaction pathway that produces ice rather than liquid water immediately upon dissociation of methane hydrate (absorbing 150 J/g of methane dissociated). This is a reasonable assumption given the near-freezing temperatures of core as it exits the methane hydrate P-T stability field (Fig. 1), and laboratory observations indicating that vigorous gas hydrate dissociation in sediments typically progresses for several hours at temperatures depressed several degrees below ambient (Wright et al., 1998, 1999). Note that a temperature gradient must be established to enable the transfer of reaction heat between dissociating gas hydrate and the surrounding core material (i.e. free water and the soil matrix). In a practical sense, this assumption simplified the model by excluding consideration of the thermal fate of water incorporated into, and/or released from, the gas hydrate crystal lattice, such that only the latent heat of freezing of the free-water component need be considered. The alternative pathway, in which methane hydrate dissociates to liquid water and gas (450 J/g; Sloan, 1990), results in a requirement for a somewhat higher minimum in situ gas hydrate saturation (about 75%) to cause complete freezing of core pore water.

We should also note that the kinetics of gas hydrate dissociation were ignored in this modelling. This is justified both on the basis of the simplicity of the approach adopted, and the fact that we were primarily concerned with whether or not enough gas hydrate was present in situ to produce the observed end-member states of the cores (i.e. frozen or unfrozen upon recovery relative to the initial in situ condition).

Non-homogeneity and self-preservation effects

We consider it likely that gas hydrate was essentially uniformly distributed throughout individual core sections (i.e. within like sedimentary units, as described in core logs) prior to the start of uphole tripping. We have little direct evidence with which to evaluate the homogeneity of the distribution of residual gas hydrate upon recovery of cores to the surface, other than the thermal contrasts between adjacent core sections, and a limited number of gas-yield measurements conducted on relatively small subsamples of cores. In this context, these gas yield measurements are considered only as coarse indicators of the residual gas hydrate distribution in bulk cores.

Our experience with field and laboratory samples leads us to expect that gas hydrate dissociation within cores probably progresses with considerable local variability, particularly in the latter stages when the bulk of gas hydrate has already dissociated. Thermal contrasts between adjacent sections of core (with different in situ gas hydrate concentrations) establish temperature gradients and subsequent flows of heat during the uphole trip that are not accounted for in this modelling exercise. Thus, measured core temperatures may, in some cases, reflect an influence of thermal conditions in adjacent core sections. Furthermore, pockets of residual gas hydrate may become encapsulated by ice during the latter stages of dissociation, thereby retarding further dissociation of a portion of the gas hydrate still present in the core (the so-called self-preservation effect). This effect can persist for many hours (Ershov and Yakushev, 1992).

We should therefore not expect to obtain precise agreement between model predictions and well-log estimates of in situ gas hydrate concentrations. Nor can we assume that the well-log estimates represent the 'correct' in situ values on which to base an evaluation of model performance. Notwith-standing these concerns, this modelling appears to successfully reconcile surface observations of the thermal state of recovered cores with our best estimates of in situ gas hydrate saturation, through analysis of the primary exchanges of heat during gas hydrate dissociation, pore water freezing, and sensible cooling of cores.

SUMMARY

At Mallik 2L-38, core temperatures were measured upon reaching the surface, after an uphole trip time of 1.5–2.5 hours. Temperatures of cores from gas-hydrate-bearing intervals were depressed several degrees Celsius below the temperature of the circulating mud. Two-dimensional finite-element modelling of the thermal behaviour of the core during a trip run from bottomhole to the

surface demonstrated that core temperatures were within a few tenths of a degree of mud temperatures upon exiting the methane hydrate P-T stability field. Since mud temperatures were lower than in situ core temperatures, this cooling tended to bring the core further into the gas hydrate stability field (i.e. to increase the stability of gas hydrate within cores) during the initial stage of the uphole trip. Dissociation of gas hydrate in cores does not begin until the P-T stability threshold is breached (at about 260 m depth).

A simple heat-exchange model predicts the minimum in situ gas hydrate saturation that, upon dissociation, would produce the core temperatures observed at the surface. For gashydrate-bearing cores observed to be frozen when recovered, the model predicts that a minimum in situ gas hydrate saturation of 70–80% is necessary to completely freeze cores and produce the temperature depressions observed. Where in situ gas hydrate saturation was in excess of this amount, we should expect to detect significant amounts of residual gas hydrate in recovered cores. This was confirmed following measurements of gas yields conducted on subsamples at the well site and in post-field laboratory analysis.

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