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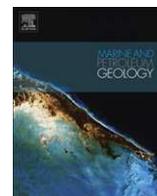
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The characteristics of gas hydrates recovered from the Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope

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ABSTRACT

Systematic analyses have been carried out on two gas hydrate-bearing sediment core samples, HYPV4, which was preserved by CH₄ gas pressurization, and HYLN7, which was preserved in liquid-nitrogen, recovered from the BPXA-DOE-USGS Mount Elbert Stratigraphic Test Well. Gas hydrate in the studied core samples was found by observation to have developed in sediment pores, and the distribution of hydrate saturation in the cores imply that gas hydrate had experienced stepwise dissociation before it was stabilized by either liquid nitrogen or pressurizing gas. The gas hydrates were determined to be structure Type I hydrate with hydration numbers of approximately 6.1 by instrumentation methods such as powder X-ray diffraction, Raman spectroscopy and solid state ¹³C NMR. The hydrate gas composition was predominantly methane, and isotopic analysis showed that the methane was of thermogenic origin (mean $\delta^{13}\text{C} = -48.6\text{‰}$ and $\delta\text{D} = -248\text{‰}$ for sample HYLN7). Isotopic analysis of methane from sample HYPV4 revealed secondary hydrate formation from the pressurizing methane gas during storage.

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1. Introduction

Natural gas hydrate is believed to be a potential unconventional gas resource due to the large volume of gas hosted in gas hydrate accumulations throughout the world, containing about twice the volume of organic carbon that occurs in all other conventional oil and gas resources (Collett, 2002). A key to exploiting natural gas hydrate as an energy resource is the establishment of the method for producing gas from a hydrate reservoir effectively. For this purpose extensive field tests (Dallimore et al., 2005; Yamamoto and Dallimore, 2008; etc) and modeling studies (Moridis et al., 2004; Pooladi-Darvish, 2004; etc) have been carried out, and such endeavors are still ongoing. As the bases of these studies, detailed information on hydrate reservoirs is indispensable. Among the information needed to understand gas production from natural gas hydrate is knowing how much gas is stored in a hydrate accumulation and assessing their relative stability. The volume of gas within a hydrate

accumulation is determined by the distribution of hydrate and its saturation in the reservoir, while the stability is related to the structural and compositional characteristics of gas hydrate. The distribution and saturation of gas hydrate can be determined by seismic interpretations (Inks et al., 2009), and the detailed hydrate-bearing sediment properties are available through well logging or from experimental analyses of hydrate samples. The structural and compositional characteristics of gas hydrate can be obtained only from the recovered hydrate-bearing sample.

The North Slope of Alaska has been well known for gas hydrate occurrences since the existence of gas hydrate was recognized from the data acquired in the Northwest Eileen State-02 well (Collett et al., 1988; Collett, 1993). A gas hydrate project organized by the U.S. Department of Energy (DOE) and BP Exploration (Alaska), Inc. (BPXA) was started in association with the U.S. Geological Survey in 2002, aiming at the assessment of the methods for recovering gas from natural gas hydrates through production tests. In preparation for a production test, BPXA-DOE-USGS Mount Elbert Gas Hydrate Stratigraphic Test Well (Mount Elbert Well) was drilled at Mount Elbert prospect in the Eileen gas hydrate trend in February of 2007 (Hunter et al., 2011). To know the characteristics of the gas hydrates

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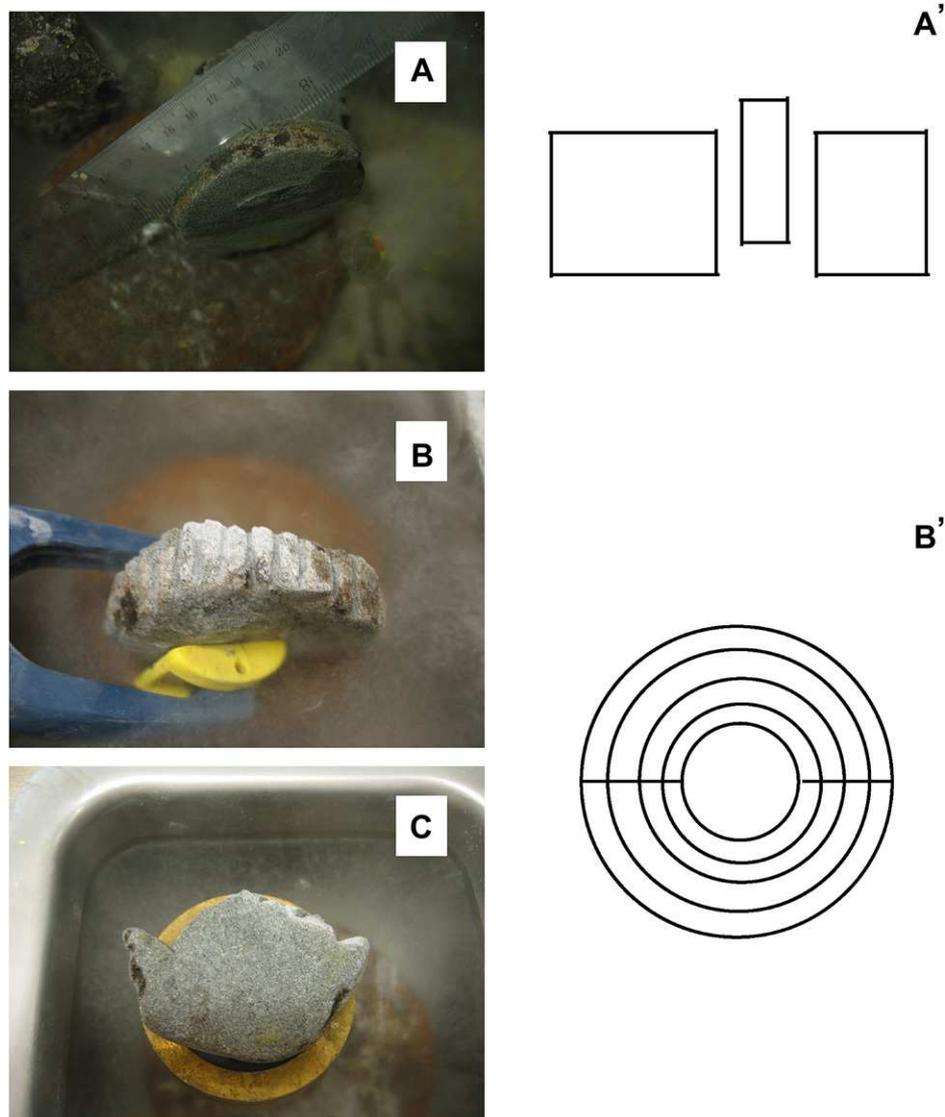


Fig. 1. Subsampling for detailed determination of hydrate distribution in the sediment cores A and A': to cut a 1 cm thick disc from the sediment cores B, C and B': to do subsampling of the disc from the core surface to the center.

in the Mount Elbert reservoir sands was an important task of this investigation. As part of this investigation, 131 m of high quality core were recovered, and 204 samples were collected for post-field analysis. Among the 204 samples, eleven were hydrate-bearing, and we obtained two of these for studying the characteristics of gas hydrates. It was the first time a gas hydrate reservoir was cored for systematic analyses in this region, so the results obtained are critical for further research in this area. Here we report the results obtained on these samples.

2. Methods

The two samples examined in this study, HYPV4 (BBParr 16) and HYLN7 (Hydrate 10) were obtained from the hydrate-bearing C unit in the Mount Elbert well using the Corion (Reed Hycalog) wireline-retrievable coring system with chilled mineral oil-based drilling fluids (Hunter et al., 2011). The recovered cores were handled in the field lab at temperatures of 4 to -15°F (-15 to -26°C). The total time the hydrate samples were outside of the stability regime of methane hydrate was less than 20 min. Gas hydrate samples were collected and then preserved onsite either

in liquid nitrogen (HYLN7) or by pressurizing with methane gas. Sample HYPV4 was initially preserved onsite under pressurized CH_4 gas at a pressure of 5.17–6.34 MPa (750–920 psi) and temperatures down to -40°C . The pressure cell with this sample was shipped in a refrigerated trailer. In the lab it was stored in a refrigerated unit at -6.6 to -1°C . HYPV4 was under the pressure of CH_4 gas for 80 days before being placed in liquid nitrogen. The sample was moved into liquid nitrogen from the pressure cell after the pressurizing CH_4 gas was released, and while the temperature was 2.8°C (37°F). In such a condition, hydrate dissociation was observed because the P – T condition was outside the stable regime of methane hydrate.

Characterization of the gas hydrate samples examined in this study include: (1) description of hydrate occurrence, (2) estimate of hydrate saturation in the recovered sediments, (3) observation of the hydrate dissociation process, (4) determination of hydrate crystal structure, and (5) analyses of chemical and isotopic compositions of enclathrated gas.

The observation of hydrate occurrence in the core was conducted upon recovery in the field and in the laboratory. Generally the conditions of the core, the appearance of gas hydrate, the sediment structure,

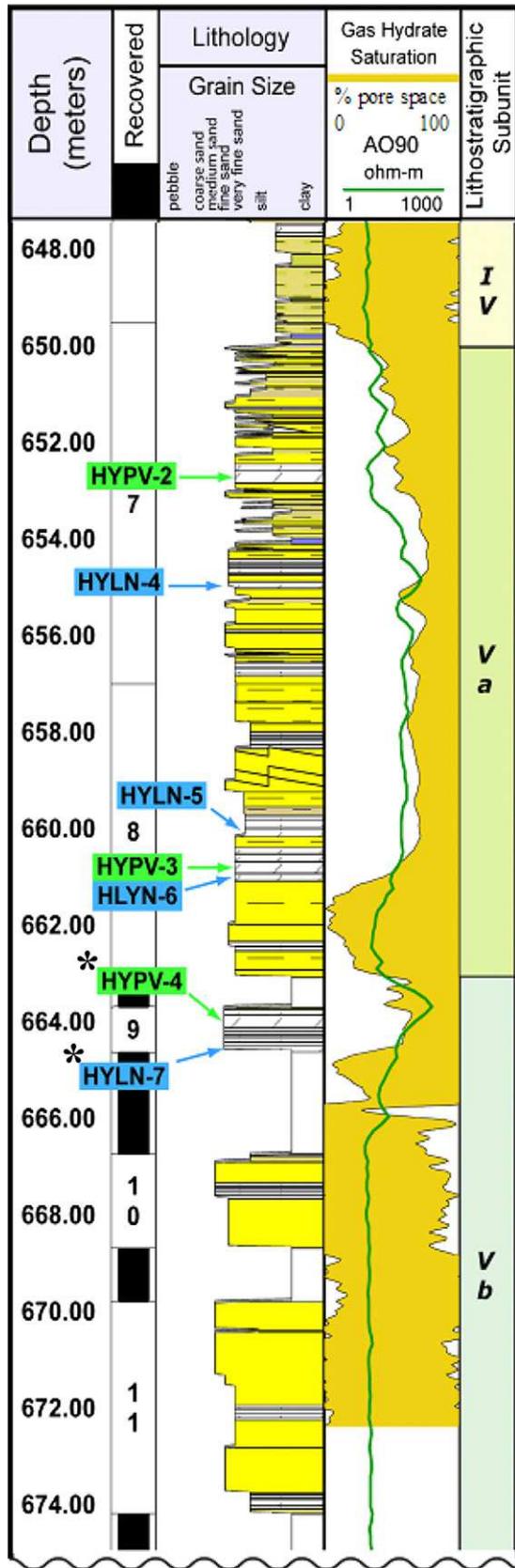


Fig. 2. The locations of the two cores (HYPV4 and HLYN7) in the sediment section (adapted from Rose, 2011).

etc, were observed and noted. To characterize the inner sample portions (less disturbed by core recovery operations), the sample was cleaved.

The amount of gas hydrate in the core was estimated for a limited number of samples by measuring the amount of gas released from a known amount of core material following the method described by Lu et al. (2005a,b). The gas hydrate saturation level can be obtained by comparing the volume of recovered gas hydrate and the volume of available pore space in the sediment sample. The volume of gas hydrate is calculated from the volume of gas evolved from the sample upon hydrate dissociation, the hydration number, which is estimated from integrated peak intensities of Raman or NMR spectra, and the gas composition. The pore volume is estimated from the measured pore water volume. The error associated with this analysis is generally <3%. For detailed distribution of hydrate saturation in a core, the core was subsampled from surface to center as illustrated in Fig. 1. Because the core was stored in liquid nitrogen and all of the operations were carried out in liquid nitrogen, it became extremely hard. As a result, subsampling from an exact interval was not possible, and subsamples generally contained some materials from the neighboring target intervals. Two subsamples were obtained from each core interval shown in Fig. 1B: one was used for determining gas hydrate saturation, and the other for isotopic composition analyses of the included hydrate gas.

The gas hydrate crystal structure was studied using X-Ray powder diffraction, Raman spectroscopy and solid state ¹³C NMR spectroscopy, and the hydration number of gas hydrate was estimated from the Raman peak intensities according to the method described by Ripmeester et al. (2005). Powder X-ray diffraction data were taken at 153 K on a Bruker D8 Advance Powder X-ray diffractometer (Cu K_α, λ = 1.5406 Å). Raman spectra were recorded in the stretching vibration regions of CH, CO, and CC at 77 K on an Acton SpectroPro 2500i spectrometer equipped with a Witec confocal microscope and a laser operating at 514.531 nm. ¹³C NMR measurements were carried out on a Bruker DSSX-400 NMR spectrometer (magnetic field of 9.4 T and ¹³C Larmor frequency of 100.63 MHz) at 173 K using a Bruker BL7 MAS probe with stretched spinners. Samples were cold-loaded at 77 K in liquid nitrogen.

For isotope analyses, several pieces of each subsample from a specific core interval were put into a bottle and sealed with a septum cap. A vacuum was drawn on each sample at liquid nitrogen temperature. The bottle was then warmed to ambient conditions to allow hydrate dissociation. The gas released was used for isotope analyses. The methane carbon isotopic composition was determined by Isotech Laboratories in Champaign Illinois, using a GC-C-IRMS system, consisting of an Agilent 6890 GC combustion unit and Finnegan GCCIII interfaced with a mass spectrometer (Delta V Plus or Delta Plus Advantage). The methane was separated by the GC column in the HP6890, then combusted in a combustion furnace. The resultant CO₂ was introduced directly into the mass spectrometer. Hydrogen isotopic values for methane were completed using the same system, but the methane was channeled through a high-temperature pyrolysis furnace instead of through the combustion furnace. The pyrolysis furnace converted methane into H₂ and carbon, and the H₂ gas was introduced directly into the mass spectrometer. Reference gases were analyzed at the start of each analysis sequence, and then at least 10% of all analyses during a sequence were check samples. 10% of the samples were analyzed in duplicate. The measured stable carbon isotope ratios are expressed in the delta notation, defined as parts per thousand (‰), relative to the standard of Vienna Pee Dee Belemnite (VPDB). The precision of the carbon isotope analysis was ±0.5‰ based on 1σ standard deviation of measurements on the standard.

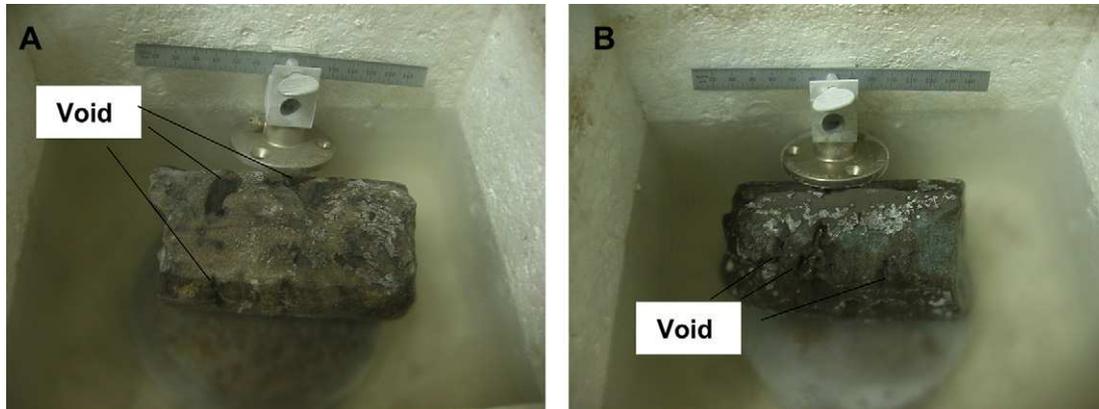


Fig. 3. Photographs of gas hydrate cores recovered from Mount Elbert, North Slope, Alaska. (A) HYPV4, (B) HYLN7.

3. Results and discussion

3.1. The occurrence of gas hydrates

Both HYPV4 (BB Parr 16) and HYLN7 (Hydrate 10) were taken from Section #1 of Core #9, and the former was from the depth interval of 663.89–664.13 m (2178.13–2178.92 feet), and the latter from the depth interval of 664.50–664.63 m (2180.13–2180.54 feet) (Fig. 2). The two samples used in this study are shown in Fig. 3, and are light to dark gray uniform massive sandstone. According to the physical property studies (Winters et al., 2011), the sediments of Section #1 of Core #9 are fine grained (medium grain size: 210 μm), moderately sorted sands with a porosity around 30% in a well-interconnected intergranular pore system. The mineral compositions as determined from powder X-ray diffraction and observed with a microscope are predominantly quartz (90%) with minor amounts of feldspar (4%) and clays (5%, chlorite: 2%, kaolinite: 1%, and illite: 2%) (Winters et al., 2011).

The voids developed in recovered core samples were several millimeter to 2–3 cm in size (Fig. 3), indicating that some hydrate dissociation had taken place before preservation. As shown in Fig. 4, several oil spots can be identified inside the sediment core, probably due to the contamination by oil-based drilling fluid which penetrated the core through original or secondary fractures.

Gas hydrate was not visible in either sample. However, when a small piece of core sediment was placed in water, vigorous gas bubbling was observed. This implies that gas hydrates existed in the sediment pores.



Fig. 4. The oil spots inside the sediment core (HYLN7).

3.2. Hydrate saturation and distribution in the sediment cores

The distributions and saturation of gas hydrate for both cores as determined in the lab are shown in Fig. 5. In HYPV4, hydrate saturation is about 40% of the pore space within 5 mm of the core

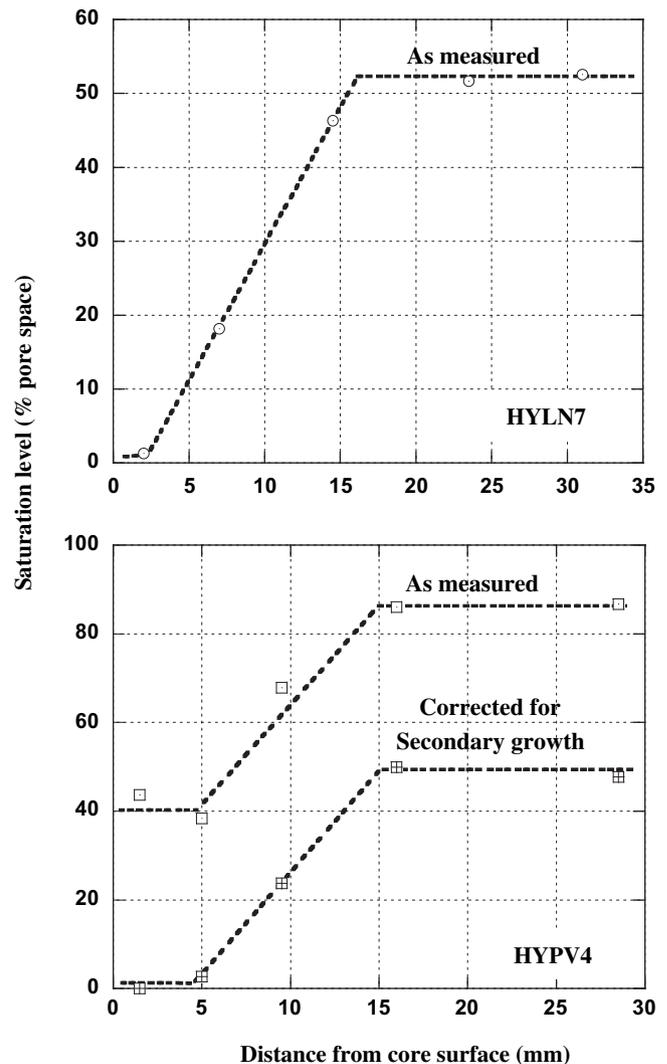


Fig. 5. The distribution of hydrate saturation in HYPV4 and HYLN7. HYLN7: results as measured showed; HYPV4: both results as measured and after correction for secondary hydrate formation presented.

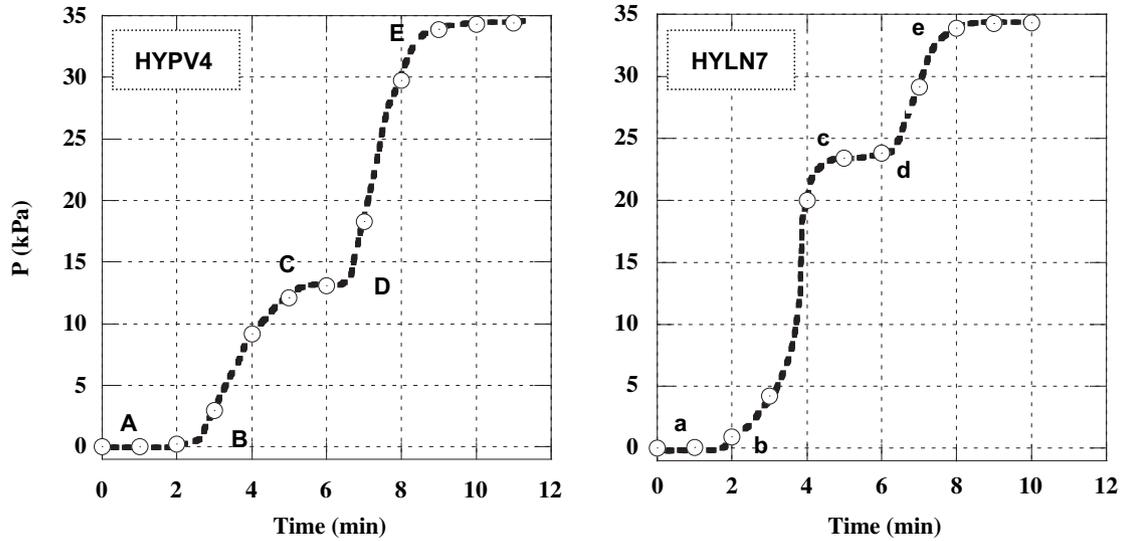


Fig. 6. The pressure buildup in the course of gas hydrate dissociation. A–B (a–b): slow hydrate dissociation, B–C (b–c): intensive hydrate dissociation, C–D (c–d): slow hydrate dissociation, D–E (d–e): intensive hydrate dissociation.

surface, gradually increasing to 86% in 5–17 mm interval and then almost stable at 86% from 17 mm to the core center. In contrast, in HYLN7 there is almost no hydrate within 4 mm of the core surface, and then similar to HYPV4 the hydrate saturation increases gradually to 52% in the interval of 2–29 mm and is almost constant at 52% from 29 mm to the core center.

Both samples studied were recovered under similar conditions and should have had similar hydrate distribution characteristics up to the point when they were stored. However, a much higher hydrate saturation was observed in the surface layer in Core HYPV4 than that in Core HYLN7, even hydrate dissociation happened when transferring HYPV4 from pressure cell into liquid nitrogen. Because Core HYPV4 was initially preserved under pressurizing methane gas, we assume the higher hydrate saturation in its surface layer was the result of secondary hydrate formation from the pressurizing gas during preservation. This is confirmed by the isotopic studies of the gas enclathrated in hydrates of HYPV4, which is discussed in detail by Kneafsey et al. (2011) and in the following section of this paper. After the contribution from secondary hydrate is excluded, the hydrate saturation distribution in sample HYPV4 is very similar to that in sample HYLN7 (Fig. 5).

Although measures were taken to minimize hydrate dissociation, such as the use of chilled oil-based drilling mud, some hydrate

dissociation is inevitable in the course of core recovery (Dallimore et al., 2005). The sediment core subsample, cut from the same portion of the core for the estimation of hydrate saturation, was selected from sections with uniform lithologies, so hydrate distribution within the subsamples should be similar. The heterogeneous distribution of hydrate saturation indicates that different portions of the subsamples experienced dissociation to different extents before the core was preserved. The gradual increase in hydrate saturation from the core surface to the center implies that hydrate dissociation was most prevalent near the outer surface of the core. Although it is difficult to have an accurate log of the core pressure–temperature history because of the long and complicated sample preservation history from field to lab, it is clear that gas hydrates had been maintained under stable conditions. For HYPV4 hydrate dissociation happened when transferring it from pressure cell into liquid nitrogen. As a result the heterogeneous distribution of hydrate saturation in the core was caused in the process of core recovery, during sampling and upon changing preservation method.

The base of permafrost at the Mount Elbert Well is 594 m below ground, and the pressure–temperature condition below that depth is in the stability regime of methane hydrate. As a result, the dissociation of gas hydrate in the recovered cores happened in the upper permafrost section during core recovery and while being handled at the surface, meaning that hydrate dissociated at temperatures below the freezing point of water. Because hydrate dissociation is an endothermic process and the heat needed for hydrate dissociation is transferred from the core surface into the core, at a certain depth into the core the heat supplied might be less than that needed to support

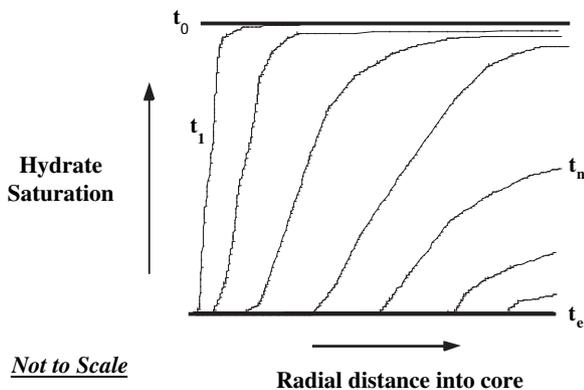


Fig. 7. A simple model to show the change in hydrate saturation through hydrate dissociation process in a sediment core, t_0 : before hydrate dissociation, t_n : at time n , t_e : after complete hydrate dissociation.

Table 1
The $\delta^{13}\text{C}$ and δD compositions of gas hydrates from Mount Elbert, Alaska.

Sample	Interval (mm)	$\delta^{13}\text{C}$ (‰)	δD (‰)	Method for sample preservation
HYLN7	4–11	–48.6	–253	In LN ₂
	9–20	–48.5	–252	
	27–35	–48.7	–239	
HYPV4	0–4	–41.2	–170	Pressurized by CH ₄
	2–8	–41.7	–178	
	6–13	–43.8	–205	
	10–22	–45.5	–220	
	22–32	–45.3	–225	
	Pressurizing CH ₄	–	–41.3	

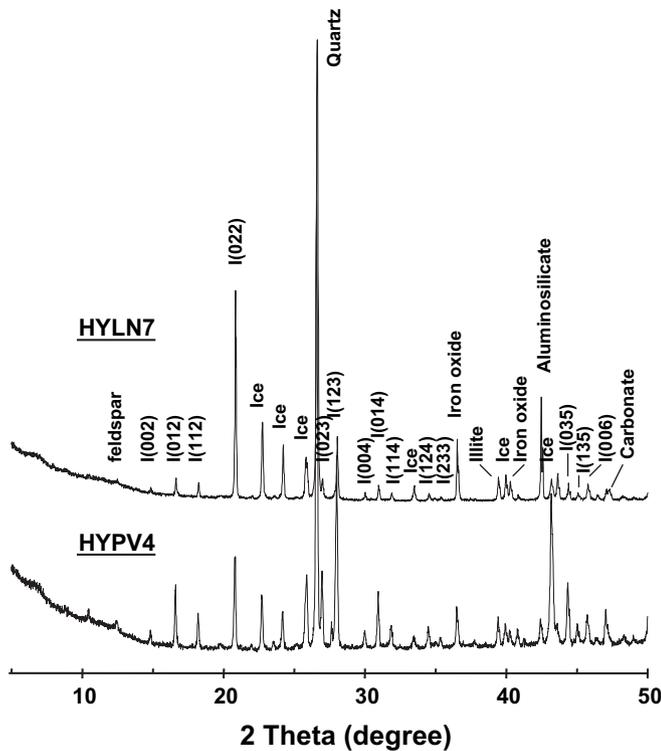


Fig. 8. XRD diffraction patterns of gas hydrates in HYPV4 and HYLN7 recovered from Mount Elbert Well, Milne Point, North Slope, Alaska. The number in the bracket indicates a crystal plane of structure I hydrate.

hydrate dissociation. When this happens, ice will form and become the barrier for further hydrate dissociation until the ice is melted by further heat, similar to the mechanism of heterogeneous hydrate dissociation within a sample as discussed by Circone et al. (2004). As a result, hydrate dissociation in sediments can proceed in a stepwise fashion towards the center of the core.

The stepwise hydrate dissociation has been confirmed by the pressure change during gas hydrate dissociation as observed in the subsamples taken for core analysis (Fig. 6). Because the sediment pieces were initially removed from liquid nitrogen, hydrate was

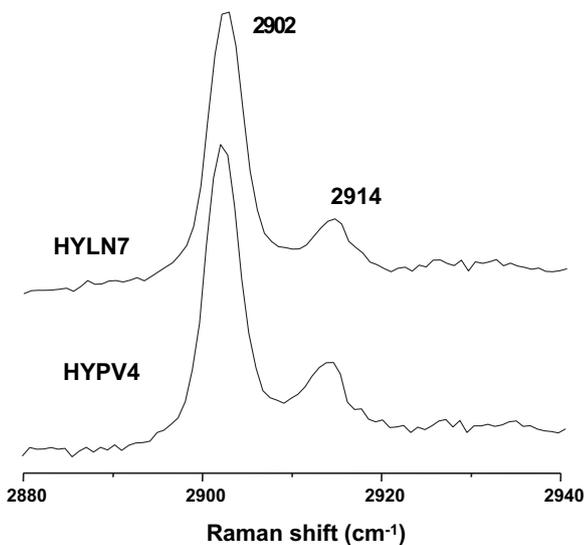


Fig. 9. Raman spectra of gas hydrates in HYPV4 and HYLN7 recovered from the Mount Elbert Well, Milne Point, North Slope, Alaska. 2902 cm and 2914 cm: representing the Raman shifts for CH₄ in small and large cage of structure I hydrate, respectively.

Table 2

The cage occupancies and hydration number of gas hydrates recovered from Mount Elbert Well, Milne Point, Alaska.

Sample #	Depth Interval (m)	Cage occupancy		Hydration number	
		θ_s	θ_L	Specific point	Average
HYPV4	663.59–663.71	0.98(8)	0.91(7)	6.15	6.14 ± 0.06
		0.95(7)	0.94(6)	6.06	
		0.99(2)	0.90(6)	6.20	
HYLN7	664.50–664.63	0.96(7)	0.94(0)	6.07	6.10 ± 0.03
		0.91(2)	0.95(7)	6.08	
		0.89(9)	0.95(9)	6.09	
		0.85(5)	0.96(4)	6.14	

stable at the beginning period of A-B and a-b although the initial pressure was 0 MPa. With temperature increase the gas hydrate became unstable and started to dissociate in the period of B-C and b-c. Because the temperature ramp of the test specimen started from liquid nitrogen temperature and hydrate dissociation is an endothermic process, in addition to the original ice formed from pore water some new ice would be produced from hydrate dissociation when the temperature of the system was below the freezing point of water. After a certain time at a certain depth in the sediment the heat supplied might be less than that needed to support hydrate dissociation, the ice would be the barrier for further hydrate dissociation as discussed by Circone et al. (2004). As a result, hydrate dissociation almost stopped until D and d, at which point the ice had melted sufficiently, trapped gas could be released, and any remaining hydrate could resume dissociating. The final pressure established in the dissociation tube was less than 0.05 MPa for both samples studied. This stepwise dissociation is depicted in Fig. 7. When a core is taken from the reservoir, gas hydrate will dissociate at the pressure-temperature conditions outside of the stability regime of the hydrate. With the endothermic nature of hydrate dissociation and heat transfer direction from core surface to center, gas hydrate dissociation will have a recognizable stepwise response.

The saturation of gas hydrate in sediments can be estimated with logging methods as well. According to the CMR (Combinable Magnetic Resonance) logging results (Collett et al., 2006), hydrate saturation around the 663.89 m and 664.13 m interval for HYPV4, is about 60 to 65% of the pore space, and about 40–48% around the 664.50–664.63 m interval for HYLN7. However the EPT (Electromagnetic Propagation Travel-time) logging gave slightly higher hydrate saturations around the same intervals: 68–77% in the 663.89–664.13 m interval for HYPV4 and 70 to 87% in the 664.50–664.63 m interval for HYLN7, respectively (Sun et al., 2011). Because the CMR result is an average hydrate saturation over a vertical interval of about 15 cm in which sediments of various types may be interbedded, the hydrate saturation in a complex interbedded sedimentary section of coarse-grained sand and fine-grained silt will be underestimated when averaged together. As shown in Fig. 2, HYLN7 is just above a clay layer which might have been the reason for the comparatively low hydrate saturation reported by CMR. EPT can yield results with high vertical resolution on a centimeter scale, and so can reflect the in situ condition more precisely. We therefore compare our results with those obtained with EPT.

Because gas hydrate around the core center was better preserved, our following discussion about hydrate saturation will be mainly based on the results obtained from the center portion of sediments. It can be seen that the hydrate saturations in the center portions of both samples, 50% for HYPV4 after correction and 52% for HYLN7, respectively, are lower than those estimated from logging results, implying that some hydrate even dissociated in center portion before the sample was stabilized by the pressurizing gas.

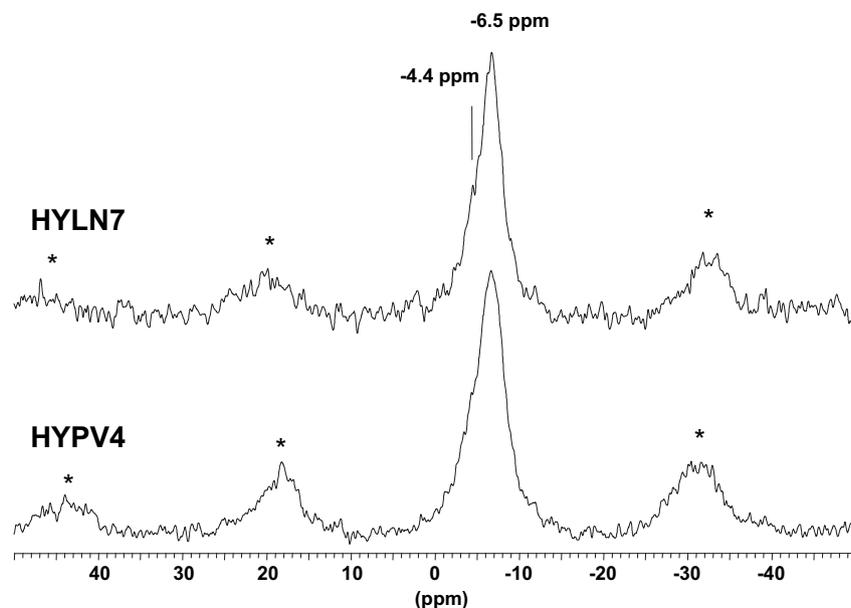


Fig. 10. Solid ^{13}C NMR spectra of gas hydrates in HYPV4 and HYN7 recovered from the Mount Elbert Well, Milne Point, North Slope, Alaska. *: side band; -4.4 ppm and -6.5 ppm: the chemical shifts for CH_4 in small and large cage of structure I hydrate, respectively.

The hydrate saturation of 86% of the pore space, including both original and secondary hydrates, around the center of Core HYPV4 is slightly higher than the result estimated from EPT logging. Because the EPT result was based on in situ logging, the hydrate saturation estimated with this method represents that in the hydrate reservoir. The higher hydrate saturation may imply that some secondary hydrate was formed around the core center as well.

3.3. Methane isotopic composition of gas in hydrates

It was proposed that gas hydrate in the Mount Elbert reservoirs was formed from pre-existing conventional natural gas accumulations with a uniform gas chemistry at the onset of cold arctic conditions about 1.8 Ma (Collett et al., 2011), thus the isotopic composition of methane within the gas hydrates should be generally homogeneous in the Mount Elbert Well. This has been verified for the Mount Elbert Well, where the isotopic $\delta^{13}\text{C}$ and δD values of methane are approximately -49‰ and -244‰ , respectively (Lorenson et al., 2011). The isotopic compositions of sample HYN7 are -48.6‰ for $\delta^{13}\text{C}$ and -239 to 253‰ for δD , respectively (Table 1), consistent with the results from other sections of the Mount Elbert Well and indicative of a thermogenic origin. The results from sample HYPV4 are very different, with the $\delta^{13}\text{C}$ and δD values in the surface layer almost the same as those of the pressurizing methane gas, implying secondary hydrate formation from this pressurizing methane gas. As shown in Table 1, both $\delta^{13}\text{C}$ and δD values become progressively lighter on approaching the center of Core HYPV4, indicating less formation of secondary hydrate.

Secondary hydrate formation occurs during hydrate preservation from introduced pressurized methane and water ice remaining from the original pore water and from the dissociation of in-situ gas hydrate during core recovery and handling as discussed by Kneafsey et al. (2011) and Waite et al. (2008). This process proceeds toward the center of the core as a function of methane diffusion and the amount of water ice available for hydrate formation. Less of the original gas hydrate remains intact near the surface of the core, while progressively more remains near the center of the core. The isotopic composition of the methane becomes lighter towards the core interior supporting this supposition.

3.4. The structural characteristics of gas hydrates

The powder X-ray diffraction patterns for the two subsamples from sample HYPV4 and HYN7 are plotted in Fig. 8. It can be seen that, in addition to the peaks for ice, quartz, and several other minerals, the remaining peaks can be best indexed as gas hydrate with structure Type I (sl).

The Raman spectra of C–H stretching for the two subsamples from sample HYPV4 and HYN7 are shown in Fig. 9. The double peak positions for both samples are the same, around 2902 cm^{-1} and 2914 cm^{-1} , characteristic of CH_4 . Although scans were also taken in the Raman shift interval for C–C and C–O stretching, no resolvable signals were obtained, indicating that the hydrated gas is predominantly CH_4 . Hydration numbers for the gas hydrates in the two cores were calculated from the areas of the peaks for small and large cages and are listed in Table 2. The two subsamples have similar hydration numbers of around 6.1. However, the occupancies of methane in the small cages of hydrates in HYPV4 are comparatively larger than those in HYN7. Although it might be the effect of methane repressurization, it needs further work for verification.

The magic angle spinning (MAS) solid state ^{13}C NMR spectra obtained on the two subsamples are shown in Fig. 10. The two peaks characteristic of CH_4 at -4.4 ppm and -6.5 ppm are significantly broader than in synthetic methane hydrate and in gas hydrate from a seafloor cold vent field on the Cascadia margin offshore Vancouver Island, and are overlapped due to this broadening. There are also relatively strong spinning sidebands. Both peak broadening and spinning sidebands arise due to the high contents of sediment particles in the samples which probably have trace amounts of paramagnetic materials.

It seems that the separation of gas hydrate from sediment particles was not perfect, because PXRD identified the existence of quartz, plagioclase, etc and side bands were observed by NMR. This is due to the fine particle sizes of sediments studied, which made the purification of gas hydrate difficult.

In summary, the spectroscopic studies revealed that the hydrates in the sediment cores studied are sl with the main composition of CH_4 and hydration number of ~ 6.1 , and composed predominantly of methane. Although sample HYPV4 had a significant contribution from secondary hydrate, the hydrate structure was also sl, because

the pressurizing gas was methane. Although minor components of carbon dioxide and ethane were identified by GC from the gases associated with the dissociated gas hydrate (Lorenson et al., 2011), Raman and NMR spectra did not resolve C_{2+} hydrocarbons and CO_2 , probably because their concentrations were below the detection limit. The spectroscopic results are very similar to those obtained on gas hydrates from Mallik 5L-38, Mackenzie Delta, N.W.T., Canada (Ripmeester et al., 2005), with variable methane occupancy in the small cages and hydration number of ~ 6.1 . Interestingly, the hydration numbers of gas hydrates in sediments from Mount Elbert, Alaska and Mallik, Mackenzie Delta are also very similar to those of bulk hydrate from offshore Vancouver Island, ~ 6.1 (Lu et al., 2005a,b). This may imply that the hydrates formed in porous media are not much different from the bulk hydrate, as recognized on synthesized methane hydrate in silica sands and in the bulk state (Liu et al., 2008). Circone et al. (2005) synthesized methane hydrate by reacting H_2O ice with methane gas under various P – T conditions, and the hydration numbers they obtained were all around 6.0. Although further effort is needed, it seems the hydration number of methane hydrate is around 6.0, no matter how it is formed.

4. Conclusions

Based on the studies above, the following conclusions can be drawn.

1. Gas hydrate developed in the pore of the fine-grained sand sediments at the site of the Mount Elbert Well.
2. The hydrates are structure Type I with hydration numbers of ~ 6.1 and predominantly composed of methane as determined by PXRD, Raman and solid-state ^{13}C NMR.
3. The carbon isotopic composition of the methane in the hydrates recovered from the Mount Elbert Well indicates a thermogenic origin of gas.
4. The presence of secondary hydrate has been confirmed in sample HYPV4, resulting from the formation of gas hydrate from the methane used to stabilize the natural gas hydrates and the original pore water or that released by gas hydrate dissociation during core recovery.
5. Gas hydrates experienced stepwise dissociation when they were outside of their stability regime due to the ice barrier which was formed either from original pore water or from hydrate dissociation.

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References

Circone, S., Stern, L.A., Kirby, S.H., 2004. The role of water in gas hydrate dissociation. *Journal of Physical Chemistry B* 108, 5747–5755.
 Circone, S., Kirby, S.H., Stern, L.A., 2005. Direct measurement of methane hydrate composition along the hydrate equilibrium boundary. *Journal of Physical Chemistry B* 109, 9468–9475.

Collett, T., Bird, K., Kvenvolden, K., Magoon, L., 1988. Geologic interrelations relative to gas hydrates within the North Slope of Alaska. USGS Open File Report, pp. 88–389.
 Collett, T., 1993. Natural gas hydrates of the Prudhoe Bay and Kuparuk River area, North Slope, Alaska. *American Association of Petroleum Geologists Bulletin* 77, 793–812.
 Collett, S.T., 2002. Energy resource potential of natural gas hydrates. *AAPG Bulletin* 86, 1971–1992.
 Collett, T., Lee, M., Goldberg, D., Rack, F., Williams, T., 2006. Ocean drilling program leg 204 nuclear magnetic resonance logging while-drilling. In: Trehu, A.M., Bohrmann, G., Torres, M.E., Colwell, F.S. (Eds.), *Proceedings of the Ocean Drilling Program Scientific Results*, v 204, 25 p. http://www-odp.tamu.edu/publications/204_SR/103/103.htm.
 Collett, T.S., Lee, M.W., Agena, W.F., Miller, J.J., Lewis, K.A., Zyrianova, M.V., Boswell, R.M., Inks, T.L., 2011. Permafrost-associated natural gas hydrate occurrences on the Alaska North Slope. *Journal of Marine and Petroleum Geology* 28 (2), 279–294.
 Dallimore, S.R., Taylor, A.E., Wright, J.F., Nixon, F.M., Collett, T.S., Uchida, T., 2005. Overview of the coring program for the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well. *Geological Survey of Canada Bulletin* 585, 82.
 Hunter, R.B., Collett, T.S., Boswell, R.M., Anderson, B.J., Digert, S.A., Pospisil, G., Baker, R.C., Weeks, L.M., 2011. Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope: Overview of scientific and technical program. *Journal of Marine and Petroleum Geology* 28 (2), 295–310.
 Inks, T.L., Lee, M.W., Agena, W.F., Taylor, D.J., Collett, T.S., Hunter, R.B., Zyrianova, M.V., 2009. Seismic prospecting for gas hydrate and associated free-gas prospects in the Milne Point area of Northern Alaska. *AAPG Memoir*, 89.
 Kneafsey, T.J., Lu, H., Winters, W., Boswell, R., Hunter, R., Collett, T.S., 2011. Examination of core samples from the Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope: Effects of retrieval and preservation. *Journal of Marine and Petroleum Geology* 28 (2), 381–393.
 Liu, C., Lu, H., Ye, Y., Ripmeester, J.A., Zhang, X., 2008. Raman spectroscopic observations on the structural characteristics and dissociation behavior of methane hydrate synthesized in silica sands with various sizes. *Energy and Fuels* 22, 3986–3988. doi:10.1021/ef800440s.
 Lorenson, T.D., Collett, T.S., Hunter, R.B., 2011. Gas geochemistry of the Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope: Implications for gas hydrate exploration in the Arctic. *Journal of Marine and Petroleum Geology* 28 (2), 343–360.
 Lu, H., Dutrisac, R., Ripmeester, J., Wright, F., Uchida, T., 2005a. Measurements of gas hydrate saturation in sediment cores recovered from the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well. *Geological Survey of Canada Bulletin* 585, 89.
 Lu, H., Moudrakovski, I., Riedel, M., Spence, G., Ripmeester, J.A., Wright, F., Dallimore, S., 2005b. The occurrence and structural characteristics of the gas hydrates associated with a cold vent field, Offshore Vancouver Island. *Journal of Geophysical Research* 110 (B10), B10204.
 Moridis, G.J., Collett, T.S., Dallimore, S.R., Satoh, T., Hancock, S., Weatherill, B., 2004. Numerical studies of gas production from several CH_4 hydrate zones at the Mallik site, Mackenzie Delta, Canada. *Journal of Petroleum Science and Engineering* 43, 219–238.
 Pooladi-Darvish, M., 2004. Gas production from hydrate reservoirs and its modeling. *Journal of Petroleum Technology* 56, 65–71.
 Ripmeester, J.A., Lu, H., Moudrakovski, I., Dutrisac, R., Wright, R., Dallimore, S., 2005. Structure and composition of gas hydrate in sediment recovered from the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well, determined by X-ray diffraction and Raman and solid state nuclear magnetic resonance spectroscopy. *Geological Survey of Canada Bulletin* 585, 106.
 Rose, K., Boswell, R., Collett, T., 2011. Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope: Coring operations, core sedimentology, and lithostratigraphy. *Journal of Marine and Petroleum Geology* 28 (2), 311–331.
 Sun, Y., Goldberg, D., Collett, T., Hunter, R., 2011. High-resolution well-log derived dielectric properties of gas-hydrate-bearing sediments, BPXA-DOE-USGS Mount Elbert Gas Hydrate Stratigraphic Test Well, North Slope, Alaska. *Journal of Marine and Petroleum Geology* 28 (2), 450–459.
 Waite, W.F., Kneafsey, T.J., Winters, W.J., Mason, D.H., 2008. Physical property changes in hydrate-bearing sediment due to depressurization and subsequent repressurization. *Journal of Geophysical Research* 113, B07102. doi:10.1029/2007JB005351.
 Winters, W., Walker, M., Hunter, R., Collett, T., Boswell, R., Waite, W., Torres, M., Patil, S., Dandekar, A., 2011. Physical properties of sediment from the BPXA-DOE-USGS Mount Elbert gas-hydrate stratigraphic test well. *Marine and Petroleum Geology* 28 (2), 361–380.
 Yamamoto, K., Dallimore, S.R., 2008. Overview of the 2006–2008 JOGMEC/NRCAN/Aurora Mallik gas hydrate production test program. *American Geophysical Union, Fall Meeting 2008, San Francisco. Abstract #OS43F-06*.