

NRC Publications Archive Archives des publications du CNRC

Formation of methane clathrate hydrates in coal moisture: Implications for coalbed methane resources and reservoir pressures

Bustin, A. M. M.; Bustin, R. M.; Moudrakovskim, I. L.; Takeya, S.; Ripmeester, J. A.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

https://doi.org/10.1021/acs.energyfuels.5b01922 Energy and Fuels, 30, 1, pp. 88-97, 2015-12-04

NRC Publications Record / Notice d'Archives des publications de CNRC:

https://nrc-publications.canada.ca/eng/view/object/?id=d7c82d87-4444-4ade-8d7f-c730740165e8 https://publications-cnrc.canada.ca/fra/voir/objet/?id=d7c82d87-4444-4ade-8d7f-c730740165e8

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at <u>https://nrc-publications.canada.ca/eng/copyright</u> READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site https://publications-cnrc.canada.ca/fra/droits LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





energy&fuels-

Formation of Methane Clathrate Hydrates in Coal Moisture: Implications for Coalbed Methane Resources and Reservoir Pressures

A. M. M. Bustin,[†] R. M. Bustin,^{*,†} Igor L. Moudrakovskim,[‡] Satoshi Takeya,[§] and John A. Ripmeester^{||}

[†]Department of Earth, Ocean, & Atmospheric Sciences, The University of British Columbia, Vancouver, BCV6T 1Z4, Canada [‡]Max-Planck-Gesellschaft, München, Hofgartenstrasse 8, 80539 München, Germany

[§]National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, Japan

^{II}Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, ONK1A 0R6, Canada

ABSTRACT: Adsorption, X-ray diffraction, and nuclear magnetic resonance analysis of subbituminous to high-volatile bituminous coal at in situ moisture content, low temperatures, and moderate pressures demonstrate that a significant proportion of the inherent moisture (nonmobile water) is available to form methane clathrate hydrates. These results have implications for coal gas resources and reservoir pressures in current areas of permafrost and the much larger regions that were glaciated during the Pleistocene. Methane adsorption tests indicate the clathrates form comparatively rapidly in coal micro- and mesopores from an immobile water phase, at lower pressures than those formed in macroporous materials. At successively higher experimental pressures, hydrates nucleate and grow rapidly on the scale of minutes to hours, until an "apparent" equilibrium pressure is reached. The onset of hydrate formation at 0 °C is at about 3.25 MPa for a Tarn coal with 33% moisture and at slightly higher pressures for the other coals with lower inherent moisture. The amount of gas consumed in hydrate formation, in excess of that attributed to sorption, is 11.6 cm³/g coal for the Tarn coal (Alaska) with 33% moisture, 8.15 cm³/g coal for a Dietz coal (Wyoming) with 22% moisture, and 1.85 cm³/g coal for a Texas coal with about 8% moisture. On a volume of gas (STP) per volume of water basis at 8 MPa, the Tarn and Dietz coal have similar values (35 and 37 cm³/cm³), whereas the Texas coal is measureably less (24 cm³/cm³). At 8 MPa and 0 °C, about 20% of the inherent moisture has participated in hydrate formation for the Tarn and Deitz coals and 13% for the Texas coal. If hydrate formation strips methane from the sorbed state, the proportion of water contributing to hydrate calculates was over 100% for the Texas coal, which suggests that methane is mainly forming from free gas. The methane hydrates analyzed by X-ray diffraction and nuclear magnetic resonance (NMR) spectroscopy are cubic (Pm3n space group) and have small and large cage sI structures. NMR and PXRD spectra indicates that the small cages are about 90% occupied, while the large cages are completely full, yielding a stoichiometry of ca. CH4 ·6H2O, which is consistent with other natural hydrates. There is some evidence that some methane gas remains trapped in the smallest pores, whereas the hydrates occupy large pores, which may be due to the suppression of hydrate formation by high capillary pressures. The formation of methane hydrates, particularly in low-rank coals, markedly increases the capacity of the coal to store gas. Depending on the coal moisture content and coal rank, methane storage capacity in gas hydrates is up to 2 orders of magnitude greater than the gas storage capacity of the coal by sorption alone. Since low-rank coals invariably have high moisture content, if the strata lie with the hydrate stability zone, significant gas storage in hydrates is anticipated, if gas is available. At the low temperature required for hydrate formation, however, self-sourced methane from methanogenesis or thermal alteration is not anticipated. Successive formation and dissociation of methane hydrates during glacial and interglacial times in the Pleistocene can be anticipated to have impacted shallow gas reservoirs, including coals, to depth up to about 800 m, depending on the surface temperature and geothermal gradient. It is speculated that during the Pleistocene free and sorbed coal gas was scavenged during the formation of hydrates, and this process may explain the low gas content of some high-latitude coals. Similarly, lower than anticipated pore pressure and lack of free water in the Horseshoe Canyon coals in western Canada may be the result of dissociation of hydrates forming overpressures, which potentially could hydraulically fracture the coal and flush the coal of free water. Subsequent dissipation of the gas pressure would lead to the current low reservoir pressure.

INTRODUCTION

Gas clathrate hydrates are crystalline solids formed by the entrapment of guest molecules, such as CH_4 and CO_2 , by water cages at low temperature and pressure.^{1,2} The cage is formed by water molecules that are hydrogen bonded, and the structure is stabilized by the repulsive interactions between the water and the guest molecule.³ In nature, hydrates form when guest molecules, mainly light hydrocarbons and carbon dioxide, interface with water at low temperature and high pressure to become enclatherated. Methane hydrates are widely distributed

in nature, wherever gas and water are present under the appropriate temperature and pressure conditions (i.e., within in the hydate sability field). Today these conditions exist in permafrost areas and the continental margins in water depths greater than about 350 m. During the Pleistocene glacials, the area of methane hydrate stability was much more expansive,

Received:August 23, 2015Revised:December 3, 2015Published:December 4, 2015

Energy & Fuels

containing many important shallow coal deposits and petroleum reservoirs.

The presence of naturally occurring methane hydrates in the relatively shallow subsurface has received enormous interest. They are potentially a major methane resource and a sink for sequestering carbon dioxide as well as a geohazard. The methane resource in hydrates has been variably estimated; Boswell and Collett⁴ conservatively estimate 1.8×10^3 GtC in hydrates, corresponding to a gas resource of about 3×10^{15} m³. Other estimates are up to 1.5×10^{16} m³ of gas.⁵ Such numbers are equivalent to about twice all the nonhydrate methane deposits in the world.^{6,7} Large-scale melting of hydrates and associated liberation of methane, a potent greenhouse gas, has led to much speculation of their impact on global warming (e.g., see refs 8, 9). If the methane from all hydrates was instantaneously released to the atmosphere, the methane content is estimated to rise from 1774 to 2900 ppb.9 There are numerous studies linking dissociation of hydrates and release of gas to the creation of overpressure, leading to sea floor instability, including submarine slides,¹⁰ which potentially trigger tsunamis.

Natural gas clathrate hydrates have been experimentally shown to exist in several structures depending on pressure, temperature, availability and type of guest molecules, and method of preparation.^{11,12} Methane clathrate hydrates that form in nature at low temperature and relatively low pressures have a cubic structure (sI with space group $Pm3\overline{n}$). The cubic structure can be in two forms of polyhedral cages, each of which entrap a single methane molecule. The structure, referred to as a small S cage, is comprised of 12 pentagonal 5-member rings of water (5^{12}) with a cage dimension of 7.9 A, and the large cage has 12 pentagonal 5-member rings of water and 2 hexagonal 6-member rings $(5^{12}6^2)$ with a cage dimension of 0.86 nm. The stoichiometry is CH₄·5.75H₂O, which, if the cages are fully occupied, yields about 180 volumes of CH4 at standard temperature and pressure per volume of hydrate.¹³ At extreme pressures (i.e., >0.8 GPa) the cubic methane hydrate structure gives way to a hexagonal one and subsequently to an orthorhombic phase.^{3,12} The methane gas density in hydrates compares to that of compressed gas reservoirs at pressures of about 18 MPa at 0 °C.¹⁴

Much modern hydrate research is directed toward exploiting the vast methane resources, the potential for carbon dioxide sequestration in hydrates, and mitigating hydrate formation in pipelines. Such studies focus on the rate of hydrate formation (growth), dissociation, and thermodynamic stability. Since hydrate nucleation is a heterogeneous process in the geosphere, hydrate formation occurs at interfaces, be it at the liquid water vapor or at the liquid water—suspended particulate matter interfaces,² and is impacted by pressure, temperature, composition of the water/brine, and type of guest molecules.

Hydrate dissociation has been investigated in field and laboratory studies; dissociation occurs in response to depressurization to less than hydration pressure, to raising the temperature beyond the hydrate stability field, or to the presence of inhibitors, which shift the pressure–temperature stability field. Of interest to this paper are the recent studies of how hydrates form and dissociate in porous media, particularly the studies of Babu et al.¹³ and Casco et al.,¹⁴ who have demonstrated the importance of pore size and wetting in activated carbons upon hydrate formation.

The present study was initiated as a result of a preliminary study of gas in subbituminous coals from the permafrost zone in the Tarn field in Alaska.^{15,16} The tested coal yielded essentially no gas on desorption of a wire-line-retrieved core nor was there evidence of gas in the mud log (Bustin and Barker in ref 17). Subsequent methane adsorption isotherm tests of the coal at reservoir temperature (0 °C) and equilibrium moisture showed dramatic spikes "in apparent adsorption" at pressures exceeding about 2.5 MPa that we here attribute to methane hydrate formation. In the current study, we document the formation of methane hydrates in the immobile water [inherent moisture; i.e., water that is present in the adsorbed state and tightly held in small capillaries and hence is not mobile (see ref 18)] in coal pores, characterize the structure of the clathrates, and discuss the broader implications of their formation.

METHODS

Samples. The samples utilized in this study are three Tertiary coals: the subbituminous Tarn coal from the Tarn field in Alaska and Dietz coal from the Powder River Basin in Wyoming and a high-volatile bituminous coal from the Texas Gulf coast. Apart from the Tarn coal, which motivated the study, the other coals were selected on the basis of their equilibrium moisture content and coal rank.

Adsorption Analysis. Laboratory methane adsorption isotherm experiments were performed using a Boyle's law apparatus at the adsorption laboratory at The University of British Columbia. The custom-built adsorption apparatus was designed for operation at high pressures and low and stable temperatures. The analyzed samples were either preserved in the field at in situ moisture conditions or brought back to equilibrium moisture following the Australian Standard.¹⁹ The isotherms were tested at a variety of temperatures and pressures up to 10 MPa, and the relationship between adsorption and pressure was fitted with the Langmuir equation,²⁰ which is the usual practice with coal.

Proximate analysis was performed following American Society of Testing Materials (ASTM) procedures.²¹

Low-pressure gas sorptions was measured on a Quantachrome Autosorb-1 using carbon dioxide at 273 K and nitrogen at 77 K. Adsorption and desorption isotherms were run at 78 pressure steps over the a P/P_o range from 0.01 to 0.99. Pore size distributions were determined by the BJH method²² and using the density function theory (DFT).²³

Nuclear Magnetic Resonance (NMR) Spectroscopy. For NMR analysis, the coal samples were ground into a powder in liquid nitrogen and transferred into thick-walled glass tubes with calibrated volumes. The tubes were connected to a vacuum line and briefly (1-2 min) evacuated at 77 K to remove the air. Known amounts of ¹³C-enriched methane (99% enrichment) were condensed into the tubes, which were then flame-sealed. The amount of ¹³CH₄ introduced into the tubes was calculated to produce a pressure of about 3 MPa at 0 °C. After sealing, the temperature of the tubes was slowly raised from that of liquid nitrogen to ca. -5 °C (\sim 5 h). The samples were kept at this temperature for 2 days and then opened under liquid nitrogen.

All NMR measurements were performed on a Bruker DSX-400 instrument at ¹³C and ¹H resonance frequencies of 100.6 and 400.3 MHz, respectively (magnetic field 9.4 T). The samples were packed into 7 mm MAS spinners in liquid nitrogen and transferred into a cold $(-100 \,^{\circ}\text{C})$ Bruker BL7MAS probe. The spinning speed was between 2000 and 3500 Hz. Cross-polarized spectra were recorded with a mixing time of 4 ms and relaxation delay of 3 s. Also, Bloch decay (HPDEC) spectra were recorded with relaxation ad quantitative analysis of spectral intensities. Composite pulse proton decoupling was used in both experiments. Between 128 and 256 accumulations were sufficient for good signal-to-noise levels. Deconvolution and integration of the signals were accomplished with the DMFIT simulation program.²⁴

Powder X-ray Diffraction Analysis (PXRD). The Deitz coal sample (D1) was ground under a N_2 gas atmosphere at a temperature below 100 K and then introduced into a high-pressure vessel at a

temperature around 243 K. The vessel was made of brass with inner dimensions of 35 mm in diameter and 50 mm in height. The cell was first degassed and then charged with CH_4 gas up to 8.0 MPa. The cell was kept at 243 K for 38 h, and then the temperature was ramped up to 274 K for 24 h and it was cooled down to 253 K for 24 h. The temperature cycle (253 \leftrightarrow 274 K) was repeated twice. Then the vessel was opened under a N₂ gas atmosphere at a temperature below 100 K.

For powder X-ray diffraction (PXRD) measurements, the coal samples pressurized with CH₄ were top-loaded on a specimen holder made of Cu in a N₂ gas atmosphere at a temperature below 100 K. The PXRD measurements were performed by a $\theta/2\theta$ step scan mode with a step width of 0.041° in the 2θ range of 5°-50° (40 kV, 40 mA; BRUKER AXS model D8 Advance) using Cu K α radiation (λ = 1.5406 Å), and the measurements were performed at 173 K under a dry N₂ gas atmosphere to prevent vapor condensation on the sample surface. Temperature deviations of the sample during measurements were within 1.0 K. Determination of the unit cell parameter was done by the Rietveldt method using the RIETAN-2000 program.²⁵

Temperature-dependent PXRD measurements were also made with the same method and a step width of 0.041° in the 2θ range of $21.5^{\circ}-29.0^{\circ}$. Each PXRD measurement took 5.0 min and was carried out at 10 K intervals from 163 K up to 273 K. During each PXRD scan, the temperature was kept at a constant value (within 0.1 K temperature deviation). After each PXRD measurement, the temperature of the sample was ramped up 10 K and the next measurement was started.

RESULTS

Methane Adsorption Analyses. High-pressure methane adsorption analyses of the Tarn coal were run at 0 and 10 $^{\circ}$ C, the Dietz coal at 0, 10, and 20 $^{\circ}$ C, and the Texas coal at 0 $^{\circ}$ C (Figure 1, Table 1). For all three coals at 0 $^{\circ}$ C, there is a marked "apparent adsorption" jump that is a departure from the type I Langmuir isotherm characteristic of microporous solids, which fits methane adsorption on coal at pressures that exist in nature. This departure is a manifestation of an abrupt decline in free gas pressure greater than predicted by sorption. As we will confirm below, this anomalous behavior marks the onset of methane clathrate hydrate formation. The pressure decline occurs due to the greater gas density in the hydrate than in the free state and the greater volume of free gas consumed by the hydrates than predicted by the sorption isotherm.

The adsorption isotherms were derived under computer control in a series of discrete pressure steps. The final pressure of each step is not known prior to the test, since the final pressure of each step is dependent on the amount of adsorption and, in our study, hydrate formation. Hence, the pressure of the onset of hydrate formation is only known from the range of pressures of the bracketing pressure steps. At 0 °C, the initiation of hydrate formation occurs between 3.25 and 3.69 MPa in the Tarn coal, which has the highest moisture content (33%); at about 4.2 MPa for the Dietz coal, with 22% moisture; and between 3.75 and 5 MPa for the Texas coal, with 8% moisture (Figure 1, Table 1). The amount of gas consumed in hydrate formation at a particular pressure in excess of that anticipated to be stored by adsorption is proportional to the initial moisture content of the samples (Table 1). Higher pressures in nature correspond to greater depths of burial and hence higher temperatures; thus, we have chosen a pressure of 8 MPa to compare samples. If fluid pressures are hydrostatic, 8 MPa corresponds to a depth of about 1000-1100 m and thus would be near the maximum pore pressure that can be anticipated in the hydrate stability field for typical surface temperatures and heat flows during glacial periods.²⁶ At 8 MPa pressure, hydrate gas in excess of the anticipated adsorbed gas comprises about 11.6 cm³/g of rock for the Tarn coal, 8.15



Figure 1. High-pressure methane adsorption isotherms at indicated temperatures showing the jump in "apparent" adsorption at the onset of hydrate formation. The regression statistics shown are for the 0 $^{\circ}$ C adsorption isotherms at pressures lower than the onset hydrate formation.

 cm^3/g for the Dietz coal and, 1.85 cm^3/g for the Texas coal. On a volume of gas per volume of water basis at 8 MPa, the Tarn and Dietz coals have similar values (35 and 37 cm^3/cm^3), whereas the Texas coal is measurably less (24 cm^3/cm^3).

The rate and volume of uptake of methane during hydrate formation at successive pressure steps are shown for the Tarn coal at 0 $^{\circ}$ C in Figure 2, as an example. At 2.65 MPa, there is a minor drop in pressure that corresponds to that anticipated by adsorption. The pressure point lies on the Langmuir isotherm (Figure 1), and there is no evidence of hydrate formation. At the successively higher pressure steps of 3.69, 4.96, 6.21, and

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	с	oal	density, g/cm ³	wt % ash	wt % moisture 33.10	hydrate gas at 8 MPa, cm ³ /g coal 11.6 1.9	total gas adsorbed + hydrate, cm³/g coal 13.0		hydrate gas, cm ³ /cm ³ water (in execess of sorbed gas)				% of total water in hydrate at 8 MPa		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Т	arn	1.56	33.80					35				19		
Detz 1.29 3.70 2.195 8.2 1.22 37 20	Т	exas	1.29	5.30	7.83		15.0		24				13		
$\begin{array}{c} 2.65 \\ 0.003 \\ 0.001 \\ 0.000 \\ 0.001 \\ 0.000 \\ 0.001 \\ 0.000 \\ $	D	eitz	1.29 3.		.70 21.95	8.2	12.2	37		37			20		
$\begin{array}{c} 0.002\\ 0.002\\ 0.002\\ 0.000\\ 0.000\\ 0.000\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$					2.65					6.21					
$\begin{array}{c} 0.0025\\ 0.002\\ 0.0005\\ 0.001\\ 0.0005\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$		0.003					0.18								
	(0.0025					0.16								
$\frac{1}{9}$ 0.0015 0.000 0 0.0005 0 0 1000 2000 3000 4000 5000 $\frac{1}{1000}$ 2000 3000 4000 5000 $\frac{1}{1000}$ 2000 3000 4000 5000 $\frac{1}{1000}$ 2000 1000 1200 1400 1600 1800 2000 $\frac{1}{1000}$ 2000 4000 5000 $\frac{1}{1000}$ 2000 $\frac{1}{1000}$ 1		0.002					0.12								
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	Pa	0 0015	1				e 0.1								
$\begin{array}{c} 0.00 \\ 0.000 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	Σ		100				≥ 0.08								
$\begin{array}{c} 0.0005 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$		0.001					0.06								
$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	(0.0005		A ada	2000		0.02				_				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0				0. 0. 0 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.	o								
3.69 7.63 7.64 7. 7. 7. 7. 7. 7. 7. 7. 7. 7.			0 1	1000	2000 Times Sec	3000 4000 5 onds	5000 0	2000	4000 6000	8000 1 Times	0000 120 Seconds	00 1400	0 16000	18000	20000
1.15 0.14 0.12 0.08 0.04 0.02 0 0.00 0.00 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0					3 60					7 62					
0.12 0.08 0.06 0.04 0.02 0 0 0 0 0 0 0 0 0 0 0 0 0	(0.14			5.05		0.12			7.05					
$ \begin{array}{c} 0.1 \\ 0.06 \\ 0.04 \\ 0.02 \\ 0.06 \\ 0.04 \\ 0.02 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	(0.12					0.1								
g 0.08 0.08 0.08 0.08 0.08 0.08 0.09 <t< td=""><td></td><td>0.1</td><td></td><td></td><td></td><td></td><td>0.1</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>		0.1					0.1								
B 0.06 0.04 0.02 0.04 0.02 0.04 0.02 0 2000 4000 50000 0 0 2000 4000 10000 12000 14000 16000 18000 20000 0.05 0 0.06 0.02 0 2000 4000 6000 8000 10000 12000 14000 16000 18000 20000 0.05 0.02 0 0.06 0.06 0.00 10000 12000 14000 16000 18000 20000 0.05 0.02 0 0.00 0.00 0.00 0.00 0.00 10000 16000 18000 20000 0.05 0.04 0 0.05 0.04 0	т (0.08					0.08								
0.04 0.02 0 0 0 0 0 0 0 0 0 0 0 0 0	Wb.	0.06					₩ ^{0.06}				-				
0.02 0 1000 2000 3000 4000 50000 Times Seconds 0.02 0 2000 4000 6000 8000 10000 12000 14000 16000 18000 20000 Times Seconds 8.79 8.79 0.05 0.04 0.05 0.	(0.04					0.04				_				
0 0 0 0 0 0 0 0 0 0 0 0 0 0	(0.02					0.02				_				
0 1000 2000 3000 4000 5000 0 2000 4000 5000 Times Seconds 0 2000 4000 6000 8000 1000 1200 1400 16000 1800 2000 Times Seconds 8.79		0													
Times SecondsTimes Seconds 4.96 8.79 0.35 0.25 		0	100	00 2	20000 3	80000 40000 50	0000 0	2000	4000 6000	8000 1	0000 120	00 1400	0 16000	18000	20000
4.96 8.79					Times Secor	nds				Times	Seconds				
0.35 0.3 0.25 0.25 0.25 0.25 0.15 0.1 0.05 0.1 0.05 0.1 0.05 0.04 $\frac{m}{2}$ 0.3 0.02 0.15 0.1 0.05 0.04 $\frac{m}{2}$ 0.3 0.02 0.01 0.02 0.02 0.03 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.02 0.03 0.02 0.03 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05					4.96					8.79)				
0.3 0.25 0.25 0.2 0.2 0.1 0.05 0.04 0.03 0.02 0.1 0.05 0.04 0.03 0.02 0.03 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05 0.05 0.04 0.05	(0.35					0.06								
0.25 0.2 0.2 0.15 0.1 0.05 0 0 0 0 0 0 0 0 0 0 0 0 0		0.3					0.05				_				
mg 0.2 0.3 0.3 0.1 0.05 0.01 0.05 0 0	(0.25					0.04								
\$\begin{aligned} \$\begin{aligned} \$\begin{aligned} & \$\ \$\ \$\ \$\ \$\ \$ \ \$\ \$\ \$ \ \$ \	a	0.2													
0.1 0.05 0 0	Ĕ,	0.15					₩ 0.03								
		0.1					0.02								
	(0.05					0.01								
		0					o 🗠								
0 5000 10000 15000 20000 25000 30000 0 2000 4000 6000 8000 10000 12000		0	5000	10000	0 15000	20000 25000 30	0000	200	400	0 6	6000	8000	100	00	12000

Table 1. Coal Moisture and Ash and Amount of Adsorbed and Hydrate Gas

Figure 2. Change in cell pressure at successive "adsorption" pressure steps for Tarn sample at 0 °C showing the onset of clathrate formation at 3.69 MPa and a marked decrease in pressure through steps 3.69, 4.96, 6.21, and 8.70 MPa and reduced rates at 8.70 MPa.

7.63 MPa, there are significant drops in pressure that exceed that predicted for adsorption by about an order of magnitude. At each successive pressure step, there is a rapid consumption of methane followed by a slowing of the rate of pressure change to, at the scale of measurements, "apparent" equilibrium. The last pressure step ending at 8.79 MPa shows a similar pattern to lower pressures but a marked slowing in the rate of free gas methane consumption and a decrease in volume of methane consumed for a given change in pressure.

The Tarn and Deitz samples were further tested at 10 $^{\circ}$ C (Figure 1). Both samples showed a demarcation in the adsorption curves indicative of hydrate formation. The onset of hydrate formation in the Tarn samples occurred between about 2.7 and 3.7 MPa and in the Dietz sample between about 4 and 5.2 MPa. Based on the hydrate stability field it is most probable that hydrate formation would have required pressures at the high end of the pressure range for Tarn sample and the

lower end for Dietz samples as discussed later. For comparative purposes an isotherm for the Dietz coal is shown at 20 °C (Figure 1). With declining temperature, gas is favored in the free over the sorbed state since sorption is exothermic, thus there is an overall increase in sorption capacity (independent of hydrate formation) at lower temperatures.²⁷ As anticipated at 20 °C, there is no evidence of hydrate formation.

Nuclear Magnetic Resonance. In order to characterize the structure of the clathrates formed in the nonmobile coal water, the NMR spectra of two Dietz coal samples were investigated from two wells, D1 and D2. The ¹³C NMR spectrum of sample D1 was a broad, featureless line at -4.8 ppm (Figure 3). The features are not characteristic of methane in gas hydrate, so we interpret the line as arising from methane dissolved in the coal matrix. The spectrum of sample D2 is more complex (Figure 4). In addition to the broad line seen for sample D1, there are a number of superimposed sharper



Figure 3. ¹³C HPDEC MAS spectrum of sample D1.



Figure 4. 13 C HPDEC MAS spectrum of sample D2 and its deconvolution. The position and width of the component at -4.8 ppm were constrained to the signal observed in the spectrum of sample D1.

resonances. The spectrum can be analyzed by fitting four components to the spectrum, as shown in Figure 3. The broad line is assigned to methane dissolved in the coal matrix. The two sharp components at -4.2 and -6.7 ppm are typical of methane in the small and large cages of sI hydrate, and the weak line at -10.8 ppm is attributed to some methane gas trapped in the coal pores. The peak intensity ratio for the large and small cages is 0.29, which implies that the small cages are 90% occupied by methane if the large cages are completely full, which is the usual situation with synthetic and natural methane hydrates. This gives a hydrate composition of ca. $CH_4 \cdot 6H_2O$, which is consistent with previously determined values.

Powder X-ray Diffraction. The X-ray diffraction profile at 173 K shows formation of type I CH₄ hydrate in the coal sample (Figure 5). Some reflections in the plots are from hexagonal ice that may have formed from adsorbed water in the coal sample. The ratio of CH₄ hydrate was estimated to be 87 wt % and that of ice was 13 wt %. The lattice constant of the hydrate was 1.1920(1) nm at 173 K. This value is slightly larger than reported values for CH₄ hydrate that was synthesized from

water and CH₄ gas [1.1903(3) nm at 173 K].²⁸ However, the results of the pattern fitting using the Rietveldt method ($R_{wp} \sim 1.8\%$ assuming full cage occupancy of CH₄) suggest that the hydrate crystal formed in the coal sample is the same as in the bulk hydrate. The X-ray diffraction profile does not show any peak broadening of the hydrate due to the small crystallite size (<1 μ m).

Figure 6 shows the X-ray diffraction profiles from CH_4 hydrate as the hydrate transformed into hexagonal ice during an increase in temperature from 163 to 273 K. Reflections from ice are evident at 163 K, and these peaks increase with temperature while the CH_4 hydrate diffraction peak heights decrease with temperature. This indicates that the amount of hydrate decreased and the amount of ice increased; the dissociated CH_4 hydrate likely transforms into ice as it releases CH_4 gas. The integrated intensities of the (321) reflection of CH_4 hydrate and the (100) reflection of the hexagonal ice are plotted as a function of temperature in Figure 7. The integrated intensity of X-ray diffraction is proportional to the crystal volume; hence, the relative change of intensity is a measure of



Figure 5. X-ray diffraction profile at 173 K.



Figure 6. X-ray diffraction profiles from CH_4 hydrate as the hydrate transformed into hexagonal ice during the increase in temperature from 163 to 273 K.



Figure 7. Integrated intensities of the (321) reflection of CH₄ hydrate and the (100) reflection of the hexagonal ice as a function of temperature.

the relative volume of CH_4 hydrate. The hydrate samples dissociated as they were heated and disappeared completely below 250 K (at ambient pressure). The ice reflections similarly disappeared below 260 K. This result may indicate the freezing point depression of ice in the micropores due to capillary effects or the presence of salt that lowers the activity of the water. On the other hand, the X-ray diffraction profile does not show peak broadening of the hydrate due to the small crystallite size.

DISCUSSION AND CONCLUSIONS

Hydrate Formation. The results of this study show that nonmobile water in coal, referred to as inherent moisture, is available for formation of methane clathrate hydrates, under the appropriate thermodynamic conditions. The hydrate structure is cubic and cages of both small (5^{12}) and large ($5^{12}6^2$) type occur and yield a stoichiometry of about CH₄·6H₂O. The amount of hydrate that forms in coal is directly correlated with total moisture. At pressures of about 8 MPa and 0 °C, the amount of hydrate that forms in excess of that in the adsorbed state is 1.85 cm³/g coal for the Texas coal, 8.15 cm³/g coal for

93

Article



Pore Size Distribution of Dietz Coal using N₂ and CO₂ Adsorption

Figure 8. Pore size distribution of Dietz coal by a combination of low-partial-pressure nitrogen and carbon dioxide adsorption.

the Deitz coal, and 11.56 \mbox{cm}^3/g coal for the Tarn coal. These calculations assume that gas adsorbed at lower pressures than the hydrate stability field remain in the adsorbed state and that hydrates form from methane in the free state. If all the gas at 8 MPa is attributed to hydrates, the percentage of gas in hydrates that is theoretically possible is 21% for the Tarn coal, 30% for the Deitz coal, and 103% of the Texas coal (Table 1). There is no evidence whether the previously adsorbed methane participates in the formation of hydrates. Since the system is supersaturated with methane, there is no motivation for the methane to diffuse from the adsorbed state to the hydrate. For the Texas coal, it is reasonable to assume that all the adsorbed gas is not participating in hydrate formation, since the amount of sorbed gas prior to hydrate formation is large and more gas is taken up by the coal than the theoretical limit based on the stoichiometry of the hydrate.

The NMR results for the Deitz coal from two locations yielded different results. Since the coals have similar moisture content, the fact that hydrate was observed in one sample, but not in the other probably relates to difference in ease of hydrate nucleation of the individual coal samples. For the NMR experiments, the driving force for hydrate formation was lower than for the X-ray experiments (13C-enriched methane was used). In order to evaluate the exact driving force, knowledge of the P-T phase equilibrium curve of methane hydrate in the coal is required. The thermodynamics of the pure methanewater system may not directly apply to the coals, due to the pore size effects. The importance of pore size on hydrate nucleation is complex. For example, Casco et al.¹⁴ argue that the hydrates in activated carbons nucleate at lower pressure and "faster kinetics", due to the enhanced interaction potential of molecules in small spaces. Sun and Duan,²⁹ on the other hand, based on theoretical considerations, argue that capillary pressure inhibits formation of hydrates in narrow pores. Torres et al.³⁰ also found that the hydrates grow preferentially in coarse-grained sediments. Capillary forces in smaller pore

spaces will prevent exsolution of methane gas, and because methane solubility is low, the presence of guest molecules for the formation of gas hydrate is much lower than in coarsergrained sediment.

Coal is variably hydrophobic and micro- and mesoporous with a high surface area, which varies with coal rank (e.g., see ref 31). The pore size distribution of the Deitz coal, as an example shown in Figure 8, is typical of low ranks showing substantial porosity in the meso- and micropore range. The observed growth of hydrate is rapid (measured in minutes to hours), which undoubtedly is due in part to the high surface area afforded by coal. However, the presence of free gas in our tests indicates the likely impact of capillaries on hydrate formation. Experimental and modeling³² studies have suggested that capillary effects inhibit hydrate growth in narrow pores by depressing water activity, which increases the CH₄ solubility in pore water required to form hydrate in pores. Consequently, the capillary effect on hydrate stability is equivalent to that of a thermodynamic inhibitor (e.g., methanol). As pointed out by Liu and Fleming,³² there are also capillary effects on the gas phase when dealing with hydrophilic pores. The organic matter in coal is partially hydrophobic at the rank studied here, and therefore, those regions should not display capillary effects toward the gas phase. This uncertainty in classifying the hydrophobic vs hydrophilic region in the coal pores does not allow the development of a more quantitative analysis.

The pressure change in the Tarn coal during hydrate formation (Figure 3) shows a rapid growth of the hydrate at a given pressure step followed by a slowing in rate and eventually an "apparent" equilibrium, perhaps better described as a steady state. The impact of pressure and surface area, as well as other factors, on kinetics of methane hydrate formation are wellestablished (e.g., see ref 33). The steady-state pressure we observe (Figure 2) is attributed to kinetics, and on a geological time scale, the hydrate formation would eventually proceed to an equilibrium not realized in the laboratory experiments. As in sediments with a broad pore size distribution, in coal, hydrate or gas will fill the largest pores first and then will grow into progressively smaller pores. How much of the pore water can be converted to hydrate and how quickly this can be done remain open questions. Experiment and modeling have shown that in sediment pores there are large regions where a waterhydrate-gas three-phase equilibrium may persists under conditions where bulk material would be converted completely to hydrate and gas, or hydrate and water. The kinetics observed in this study are probably a function of higher pressures enabling access of gas successively to smaller pores and potentially to different portions of the inherent moisture,³⁴ for example, the progression from bulk water, capillary water, multilayer, to monolayer sorbed water on the coal surface. However, we can conclude that at the current stage of knowledge it is premature to try and develop detailed models that describe the thermodynamics and kinetics of methane hydrate formation in coal pores.

The volume of gas stored in hydrates, in excess of that which is (or could be) stored in the sorbed state, is directly proportional to their moisture content, given excess gas. In the Dietz and Tarn coals, which have low adsorbed gas contents and high moisture contents, the gas capacity of the coal is primarily in the methane hydrates. In higher-rank coals, such as the Texas coal, which has progressively lower inherent moisture and higher associated sorption capacity, hydrates are progressively less important. Coals in northern climates, in the zone of permafrost, hence within the hydrate stability field, can be anticipated to have comparatively higher sorption capacity, due to the low temperature and methane hydrate formation. Higher gas pore pressures result in higher adsorption capacity of the coal up to a maximum value (Langmuir volume), which increases with coal rank and decreasing moisture content. Higher gas pressure impacts the kinetics of hydrate formation and also results in greater hydrate formation, assuming no other limiting factors, since higher gas pressures correspond to greater gas volumes available for the formation of hydrates.

Coals below the water table invariably are saturated with water (at equilibrium moisture) unless unusual circumstances exist, such as dehydration by migrating and expanding gas or leaching by migration of ground waters.³⁵ Hence if gas is available, and in the adsorbed state, and if conditions are suitable, hydrates should exist. Most of the gas in coals (coalbed methane) is self-sourced at low temperatures by methanogensis and high temperatures by thermal alteration. Hence coals, which invariably retain significant inherent moisture and selfsource methane, should provide an ideal host for methane hydrate development under appropriate pressures and temperatures. The absence of significant gas found during canister desorption in the Tarn coals through the hydrate zone reported by Bustin and Barker¹⁷ are unusual. The coals are low-rank, and self-sourced gas would be biogenic in origin. The absence of biogenic gas suggests that either the conditions were not appropriate for biogenic gas formation (i.e., lack of nutrients, low temperature) or the generated gas leaked or was stripped by migrating water. Similar arguments have been made for the lack of gas in the gas-barren Fort Union coals in the Powder River Basin.³⁴

Broader Implications. During the Pleistocene, temperatures were periodically low enough that the shallow subsurface was in the hydrate stability zones over an area of up to 30% of the earth.³⁶ The temperature and pressure profiles below ice sheets and during interglacial periods are the subject of many studies. The temperature profile is dependent on the surface temperature and the thermal conductivity of the frozen and unfrozen rock and on the heat flow. The weight of the ice sheets impacts both the lithostatic and hydrostatic pressure. The importance of the ice sheet on pore pressure depends on whether the ice sheet is wet-based, with liquid water at the base that is in contact with underlying pore water or has a frozen base.³⁷ Majorowicz²⁶ has calculated the range of depths at which permafrost may exist and the hydrate stability assuming various Pleistocene surface temperatures. Depending on assumptions of surface temperature, thermal conductivity, and heat flow, it is reasonable to assume that hydrate stability extended to depths in the range of 1000 m. In the Mittelplat oil field of north Germany, for example, Grassmann et al.³⁸ suggested that there were some 20 periods of permafrost and at least 5 phases of hydrate formation to depths of about 750 m in the last 750 000 years.

Shallow hydrocarbon reservoirs, including coal seams, were undoubtedly impacted by the repeated formation of hydrate during glacial periods and dissociation of hydrate during interglacial periods. The reservoirs would have been subjected to varying lithostatic stress, pore pressures, and variable temperatures due to low surface temperatures and thick ice sheets. There are few studies, however, on the impact of Pleistocene hydrate formation on reservoirs.³⁸ The creation of overpressures by hydrate dissociation is well-established and to it has been attributed soft sediment deformation, well bore damage, and, it has been speculated or theorized, submarine landslides (e.g., see refs 39–42).

Initial formation of hydrates, with onset of cooling, in a gasrich reservoir/system would result in a decrease in gas pressure, promotion of diffusion, and advective transport of gas to the pressure sink resulting from hydrate formation. In a coal seam, free gas in equilibrium with the adsorbed gas would decrease, causing progressive desorption until an equilibrium is reached. Since at low pressure the hydrate capacity to gas is much greater than the adsorption capacity, additional gas may diffuse or advect into the coal seam. Generation of self-sourced gas would be unlikely, since neither biogenic nor thermogenic processes operate at low temperatures. During hydrate dissociation, the gas, depending on pressure, will displace pore and fracture water, either flushing or creating overpressures and potentially hydraulically fracturing the reservoir. Speculatively, the dissociation of hydrates may give rise to overpressures, if the reservoir is sealed, or underpressures, if the gas pressure dissipates after flushing of the fluids. A possible example is the shallow (<500 m) gas-producing Horseshoe Canyon coal in the Western Canadian Sedimentary Basin that currently lacks free/mobile water, and the coals are markedly underpressured.⁴² These coals would have been at depths of hydrate stability and growth of hydrates and dissociation would have occurred repeatedly with temperature fluctuations during the Pleistocene.

The repeated formation and dissociation of hydrates during glacial and interglacial periods would have impacted the mechanical properties of the reservoir. Formation of hydrates results in an expansion of 26% over that of water.⁴³ Hence, like freeze—thaw cycles on the earth surface, the cyclic formation of hydrates would be reasonably anticipated to impact the rock fabric under undrained conditions. Evidence of the impact on the fabric of coal or other reservoirs of hydrate formation is, however, not known. If hydrate-induced fabric elements occur, they are currently interpreted as due to other factors.

AUTHOR INFORMATION

Corresponding Author

*E-mail:bustin@mail.ubc.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Associate Editor John Shaw, reviewer Jack Pashin, and an anonymous reviewer for their constructive review of the paper. Funding for this study was received from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

(1) Kvenvolden, K. A. Methane hydrate- a major reservoir of carbon in the shallow geosphere? *Chem. Geol.* **1988**, *71*, 41–51.

(2) Sloan Jr., E. D.; Koh, C. Clathrate Hydrates of Natural Gases, 3rd ed.; CRC Press: Boca Raton, FL, 2008.

(3) Loveday, J. S.; Nelmes, R. J.; Klug, D. D.; Tse, J. S.; Desgreniers, S. Structural systematics in the clathrate hydrates under pressure. *Can. J. Phys.* **2003**, *81*, 539–544.

(4) Boswell, R.; Collett, T. S. Current perspectives on gas hydrate resources. *Energy Environ. Sci.* **2011**, *4*, 1206–1215.

(5) Makogon, Y. F.; Holditch, S. A.; Makogon, T. Y. Natural gashydrates- A potential energy source for the 21st century. *J. Pet. Sci. Eng.* **2007**, *56* (1–3), 14–31.

(6) Kvenvolden, K. A. Gas hydrate and humans. Ann. N. Y. Acad. Sci. 2000, 912, 17–22.

(7) Boswell, R. Is gas hydrate energy within reach? *Science* **2009**, 325 (5943), 957–958.

(8) Archer, D.; Buffett, B.; Brovkin, V. Ocean methane hydrates as a slow tipping point in the global carbon cycle. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106* (49), 20596–20601.

(9) Ruppel, C. D. Methane Hydrates and Contemporary Climate Change. *Nature Education Knowledge* **2011**, 3 (10), 29.

(10) Summerhayes, C. P.; Bornhold, B. D.; Embley, R. W. Surficial slides and slumps on the continental slope and rise of South West Africa: a reconnaissance study. *Mar. Geol.* **1979**, *31* (3), 265–277.

(11) Sloan, E. D., Jr. Clathrate Hydrates of Natural Gases, 2nd ed.; Marcel Dekker, Inc.: Monticello, NY, 1997.

(12) Tulk, C. A.; Klug, D. D.; dos Santos, A. M.; Karotis, G.; Guthrie, M.; Molaison, J. J.; Pradhan, N. Cage occupancies in the high pressure structure H methane hydrate: A neutron diffraction study. *J. Chem. Phys.* **2012**, *136* (5), 054502.

(13) Babu, P.; Yee, D.; Linga, P.; Palmer, A.; Khoo, B.; Tan, T.; Rangsunvigit, P. Morphology of Methane Hydrate Formation in Porous Media. *Energy Fuels* **2013**, *27* (6), 3364–3372.

(14) Casco, M.; Silvestre-Albero, J.; Ramírez-Cuesta, A.; Rey, F.;
Jordá, J.; Bansode, A.; Urakawa, A.; Peral, I.; Martínez-Escandell, M.;
Kaneko, K.; Rodríguez-Reinoso, F. Methane hydrate formation in confined nanospace can surpass nature. *Nat. Commun.* 2015, *6*, 6432.
(15) Barker, C. E. Methane hydrate production from Alaskan

permafrost—Coalbed Methane Studies at Hot Ice #1 Gas Hydrate Well; First Report; US Geological Survey: Denver, CO, 2003.

(16) Collett, T. S.; Lee, M. W.; Agena, W. F.; Miller, J. J.; Lewis, K. A.; Zyrianova, M. V.; Boswell, R.; Inks, T. L. Permafrost-associated natural gas hydrate occurrences on the Alaska North Slope. *Mar. Pet. Geol.* **2011**, *28*, 279–294.

(17) Bustin, R. M.; Barker, C. Methane Clathrates in Coal. *Abstracts and Program of The Society of Organic Petrology Annual Meeting*; USGS: Denver, CO, 2002.

(18) Allardice, D. J.; Clemow, L. M.; Favas, G.; Jackson, W. R.; Marshall, M.; Sakurovs, R. The characterization of different forms of water in low rank coals and some hydrothermally dried products \Rightarrow . *Fuel* **2003**, *82* (6), 661–667.

(19) Australian Standard. *Higher rank coal—Moisture-holding capacity* (*equilibrium moisture*) AS 1038.17-2000 (R2013); Standards Australia International: Sydney, Australia, 2000. (20) Langmuir, I. The constitution of and fundamental properties of solids and liquids. Part 1 - Solids. J. Am. Chem. Soc. **1916**, 38, 2221–2295.

(21) American Society of Testing Materials (ASTM). D3172-07a: Standard Practice for Proximate Analysis of Coal and Coke; ASTM: West Conshohocken, PA, 2007.

(22) Barrett, E. P.; Joyner, G. L.; Halenda, P. P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.

(23) Do, D. D.; Do, H. D. Pore characterisation of carbonaceous materials by DFT and GCMC simulations: A review. *Adsorpt. Sci. Technol.* 2003, 21, 389–423.

(24) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling oneand two-dimensional solid-state NMR spectra. *Magn. Reson. Chem.* **2002**, 40, 70–76.

(25) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* 2000, 321–324, 198–203.
(26) Majorowicz, J. Permafrost at the ice base of recent Pleiostocene glaciations- inferences from borehole temperature profiles. *Bull. Geogr. Phys. Geogr.* 2012, *5*, 7–28.

(27) Bustin, A. M. M.; Bustin, R. M. Coal reservoir saturation: Impact of temperature and Pressure. *AAPG Bull.* **2008**, *92*, 77–86.

(28) Takeya, S.; Kida, M.; Minami, H.; Sakagami, H.; Hachikubo, A.; Takahashi, N.; Shoji, H.; Soloviev, V.; Wallmann, K.; Biebow, N.; Obzhirov, A.; Salomatin, A.; Poort, J. *Chem. Eng. Sci.* **2006**, *61*, 2670–2674.

(29) Sun, R.; Duan, Z. An accurate model to predict the thermodynamic stability of methane hydrate and methane solubility in marine environments. *Chem. Geol.* **2007**, *244* (1), *248–262*.

(30) Torres, M. E.; Trehu, A. M.; Cespedes, N.; Kastner, M.; Wortmann, U. G.; Kim, J. H.; Long, P.; Malinverno, A.; Pohlman, J. W.; Riedel, M.; Collett, T. Methane hydrate formation in turbidite sediments of northern Cascadia, IODP Expedition 311. *Earth Planet. Sci. Lett.* **2008**, 271 (1), 170–180.

(31) Clarkson, C. R.; Bustin, R. M. Variation in micropore capacity and size distribution with composition in bituminous coal of the Western Canadian Sedimentary Basin: Implications for coalbed methane potential. *Fuel* **1996**, *75* (13), 1483–1498.

(32) Liu, X.; Flemings, P. B. Capillary effects on hydrate stability in marine sediments. J. Geophys. Res. 2011, 116, B07102.

(33) Vysniauskas, A.; Bishnoi, P. R. A kinetic study of methane hydrate formation. *Chem. Eng. Sci.* **1983**, 38 (7), 1061–1072.

(34) Unsworth, J. F.; Fowler, C. S.; Heard, N. A.; Weldon, V. L.; McBrierty, V. J. Moisture in coal: 1. Differentiation between forms of moisture by NMR and microwave attenuation techniques. *Fuel* **1988**, *67*, 1111–1119.

(35) Cui, X.; Dipple, G.; Bustin, R. M. Differential transport of CO2 and CH4 in coalbed aquifers: Implications for coalbed gas distribution and composition. *AAPG Bull.* **2004**, *88*, 1149–1161.

(36) Tarbuck, E. J.; Lutgens, F. K.; Tsujita, C. J. *Earth*; Prentice Hall: Upper Saddle River, NJ, 2005; p 53.

(37) Thorson, R. M. Glacial tectonics: a deeper perspective. *Quat. Sci. Rev.* **2000**, *19*, 1391–1398.

(38) Grassmann, S.; Cramer, B.; Delisle, G.; Hantschel, T.; Messner, J.; Winsemann, J. pT-effects of Pleistocene glacial periods on permafrost, gas hydrate stability zones and reservoir of the Mittelplate oil field, northern Germany. *Mar. Pet. Geol.* **2010**, *27* (1), 298–306.

(39) Waite, W. F.; Santamarina, J. C.; Cortes, D. D.; Dugan, B.; Espinoza, D. N.; Germaine, J.; Jang, J.; Jung, J. W.; Kneafsey, T. J.; Shin, H.; Soga, K.; Winters, W. J.; Yun, T. S. Physical properties of hydrate-bearing sediments. *Rev. Geophys.* **2009**, *47* (4), RG4003.

(40) Lee, H. J. Timing of occurrence of large submarine landslides on the Atlantic Ocean margin. *Mar. Geol.* **2009**, 264 (1-2), 53–64.

(41) Hustoft, S.; Dugan, B.; Mienert, J. Effects of rapid sedimentation on developing the Nyegga pockmark field: constraints from hydrological modeling and 3-D seismic data, offshore mid-Norway. *Geochem., Geophys., Geosyst.* **2009**, *10* (6), Q06012. (42) Bustin, R. M.; Bustin, A. M. M.; Russel-Houston, J. Horseshoe Canyon and Belly River coal measures, south central Alberta: Part 1 — Total original gas-in-place. *Bull. Can. Pet. Geol.* **2011**, *59* (3), 207–234.

(43) Lee, J. Y.; Santamarina, J. C.; Ruppel, C. Volume change associated with formation and dissociation of hydrate in sediment. *Geochem., Geophys., Geosyst.* **2010**, *11* (3), Q03007.