BEAUFORT SEA DEEP-WATER GAS HYDRATE RECOVERY FROM A SEAFLOOR MOUND IN A REGION OF WIDESPREAD BSR OCCURRENCE

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ABSTRACT

Gas hydrate was recovered from the Alaskan Beaufort Sea slope north of Camden Bay in August 2010 during a U.S. Coast Guard Cutter Healy expedition (USCG cruise ID HLY1002) under the direction of the U.S. Geological Survey (USGS). Interpretation of multichannel seismic (MCS) reflection data collected in 1977 by the USGS across the Beaufort Sea continental margin identified a regional bottom simulating reflection (BSR), indicating that a large segment of the Beaufort Sea slope is underlain by gas hydrate. During HLY1002, gas hydrate was sampled by serendipity with a piston core targeting a steep-sided bathymetric high originally thought to be an outcrop of older, exposed strata. The feature cored is an approximately 1100 m diameter, 130 m high conical mound, referred to here as the Canning Seafloor Mound (CSM), which overlies the crest of a buried anticline in a region of sub-parallel compressional folds beneath the eastern Beaufort outer slope. An MCS profile shows a prominent BSR upslope and downslope from the mound. The absence of a BSR beneath the CSM and occurrence of gas hydrate near the summit indicates that free gas has migrated via deep-rooted thrust faults or by structural focusing up the flanks of the anticline to the seafloor. Gas hydrate recovered from near the CSM summit at a subbottom depth of about 5.7 meters in a water depth of 2538 m was of nodular and vein-filling morphology. Although the hydrate was not preserved, residual gas from the core liner contained >95% methane by volume when corrected for atmospheric contamination. The presence of trace C4+ hydrocarbons (<0.1% by volume) confirms at least a minor thermogenic component. Authigenic carbonates and mollusk shells found throughout the core indicate sustained methane-rich fluid advection and possible sediment extrusion contributing to the development of the mound. Blister-like inflation of the seafloor caused by formation and accumulation of shallow hydrate lenses is also a likely factor in CSM growth. Pore water analysis shows the sulfate-methane transition to be very shallow (0-1 mbsf), also supporting an active high-flux interpretation. Pore water with chloride concentrations as low as 160 mM suggest fluid migration pathways may extend to the mound from buried non-marine sediments containing low-salinity fluids.

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NOMENCLATURE
AOM = anaerobic oxidation of methane
APM = Alaska passive margin
BSR = bottom simulating reflection
CDZ = Canning displacement zone
CMDM = Canning-Mackenzie Deformed Margin
MCS = multichannel seismic
SMT = sulfate-methane transition
USGS = U. S. Geological Survey

INTRODUCTION
Naturally occurring submarine gas hydrates are common in outer continental margin deep-sea sediments and within permafrost beneath polar continental shelves [1]. Gas hydrate composed of low-molecular weight gases, primarily methane, within a lattice of water molecules contains a tremendous volume of natural gas [2]. In addition to the potential of gas hydrates as a significant source of energy, hydrate occurrences are being studied for possible effects on global climate and for their role as a marine geohazard. Within the United States Exclusive Economic Zone (EEZ), seismic reflection mapping of bottom simulating reflections (BSRs) combined with geologic sampling confirm several well-known gas hydrate accumulations including those offshore of Oregon at Hydrate Ridge [3] and offshore of South Carolina at Blake Ridge [4,5]. BSRs indicate deep-marine hydrate (> than approximately 300 m water depth) beneath the Bering Sea [6] and the Beaufort Sea [7,8]. Drilling and geophysical data have identified extensive zones of permafrost-related hydrate across the onshore northern Alaska and beneath the shallow waters of the inner Beaufort Shelf [9]. Coring programs in 1989 [10] and 2009 [11] acquired piston cores from the Beaufort slope but did not recover hydrate. In the summer of

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Figure 1. Shaded area shows the BSR across the Beaufort Sea slope north of Alaska [7]. Black contours are water depth in meters; red contours are subbottom depth of BSR in meters. The USGS 1977 MCS tracklines are displayed as thin black lines with Line 725 (Figure 3) highlighted in green. The location of the Canning Seafloor Mound (CSM) and the multibeam and backscatter coverage on figure 4 is shown by the red square along Line 725. The area shown in this map and in the Figure 2 map is indicated by the red box on the regional Arctic map on the upper right.
2010, the first deep-marine Alaskan hydrate sample was recovered during HLY1002.

The distribution of hydrate across the Alaskan Beaufort Sea slope inferred from mapping the BSR is shown in Figure 1. This map also shows the tracklines for a multichannel seismic reflection (MCS) survey conducted by the U.S. Geological Survey (USGS) in 1977 (a summer of relatively ice-free conditions in the Beaufort) aboard the Research Vessel S.P. Lee [12]. These data are the only publicly available MCS profiles imaging the Alaskan Beaufort outer continental margin and can be downloaded from the USGS website: http://walrus.wr.usgs.gov/NAMSS/.

The Beaufort shelf immediately north of Alaska has been extensively mapped with geophysical surveys conducted by the hydrocarbon exploration industry, but normally heavy sea-ice further north has restricted additional deep-water Beaufort exploration until the U.S.-Canadian icebreaker expeditions of 2007-2010 [13]. In addition to providing the basis for gas hydrate mapping and analysis [7,14], the 1977 USGS MCS data have been used for regional geologic interpretations [15], petroleum potential evaluations [16], and a slope stability study [17]. These data also provided guidance to the 1989 and 2009 coring programs already mentioned and the 2010 U.S. Coast Guard Cutter Healy (HLY1002) program detailed below that did sample deep-marine hydrate. Remarkably, the 1977 survey was conducted without the support of an icebreaker.

Beginning early August 2010, the USGS and the Canadian Geological Survey conducted a collaborative Arctic Ocean exploration program collecting data to be used for Extended Continental Shelf (ECS) evaluation as defined by Article 76 of the United Nations Convention on the Law of the Sea (UNCLOS). This two-icebreaker program included the U.S. Coast Guard cutter Healy (USCG Cruise ID HLY1002; USGS Field Activity ID H-3-10-AR) and the Canadian Coast Guard Ship Louis S. St. Laurent (LSSL) and followed successful joint operations completed in the summers of 2008 and 2009 [13]. The principal objectives of these programs were to acquire MCS data and wide-angle seismic refraction data to determine sediment thickness and to acquire multibeam bathymetric data to map critical ECS requirements such as the 2500 m isobath and the foot of the slope. The MCS data acquisition was run from LSSL and multibeam bathymetry data were acquired from Healy. While operating in ice-covered waters, one ship would break ice and lead the second to enable continuous high-quality data acquisition, with the ship order determined by which data type was more critical in a particular area.

Geologic Setting of the Canning-Mackenzie Deformed Margin

The Alaskan Beaufort Sea continental margin forms the southern limit of the Arctic Ocean Canada Basin and extends over 1000 km from the Mackenzie Delta off northwest Canada to the Northwind Ridge northeast of Alaska (Figure 2). This margin formed when the Canada Basin opened in the Jurassic-Early Cretaceous, by rifting between Arctic Alaska and Arctic Canada [16]. One model for this rifting is counter-clockwise rotation of the Alaskan margin away from the Canadian Arctic margin about a pole in the Mackenzie Delta [18]. The Alaskan margin is buried with thick progradational sedimentary prisms characterized by listric growth faults and gravity-driven slope failures. The margin is bordered on the south by the high-standing Alaskan rift shoulder and the Alaskan Arctic platform. [16]. It is divided into two main sectors, the Alaska passive margin (APM) in the west and the Canning-Mackenzie deformed margin (CMDM) in the east. [16]. The CMDM, also referred to as the Mackenzie-Beaufort fold belt [19], is a broad region of compressional folds trending roughly shore-parallel from the Mackenzie Delta to the Canning Displacement Zone, a north-south strike-slip fault that separates the CMDM from the APM [18] The CMDM folding extends from the Beaufort shelf seaward to the outer slope in response to on-going Brooks Range tectonism in northern Alaska and Canada with generally more than 10 km and in places greater than 14 km of post-rift strata [16]. The folds are comprised of Tertiary sediments and are shown on seismic profiles to have displacement amplitudes as great as 4 km. Thrust faults extend from the cores of the fold anticlines and sole into a 10-15 km deep flat-lying decollement [19]. Houseknecht and Bird [16] report that the CMDM contains an active petroleum system and has the highest potential for undiscovered petroleum reserves of any of the Canada Basin margin sectors.
Beaufort Sea BSR
Anomalous high amplitude reflections, interpreted to be hydrate-related BSRs, were first identified on the Beaufort Sea slope north of Alaska in the mid 1970s. Grantz et al. [20] used single-channel analog seismic reflection data collected from an icebreaker during the summers of 1972 and 1973 to conclude that at least 7500 km² of the Beaufort slope in water depths greater than 400 to 600 m is underlain by an interval of sediments containing gas hydrate with a subjacent layer of free gas. During the 1970s, similar BSRs were reported from other continental margins including the western North Atlantic [21], the Blake-Bahama Outer Ridge off the eastern coast of the United States, the western Gulf of Mexico, the Pacific Ocean off Central America, and the Caribbean north of Panama and Columbia [5]. In 1977 the USGS collected over 5400 km of MCS data in the Beaufort Sea using a 24-channel, 2400 m hydrophone streamer and a 1326 in³ 5-tuned air gun source array [12] which provided much more definitive imaging of the BSR. The BSR is present in 80% of 2800 km of MCS profiles between 400 and 2800 m water depth, extending the lateral extent of the Beaufort slope BSR to over 30,000 km² [8] (Figure 1). The Beaufort slope BSR has the characteristics used to interpret the solid hydrate/free gas phase boundary: high negative polarity reflection amplitude, and crosscutting lithologic reflections while trending sub-parallel to the seafloor (bottom simulating) (Figures 3a and 3b). In the three decades following the interpretation of the 1977 MCS data, numerous examples worldwide of BSRs, combined with gas hydrate drilling programs have confirmed that naturally occurring submarine gas hydrates are a common component of continental slope sediments. However, during this period of increasing knowledge of submarine gas hydrates, until HLY1002, no new geophysical or geological data have been acquired to improve the understanding of deep-marine Beaufort Sea gas hydrates.

Figure 2. Regional geologic provinces of northern Alaska and the Beaufort Sea from Houseknecht and Bird (2010) [16]. APM is the Alaska passive margin; CMDM, the Canning-Mackenzie deformed margin; CDZ, the Canning displacement zone. The Canning seafloor mound (CSM) is located within the area highlighted by the red square in the CMDM.
HLY1002 CORING
In addition to the seismic and multibeam bathymetric data acquisition, a limited coring program was conducted from USCGC Healy during HLY1002 in which six piston cores and four gravity cores (three as trigger cores for the piston cores) were recovered at six sites. The first two coring sites are discussed here. Figures 3a, and 3b show USGS MCS line 725 that crosses a steep-sided seafloor high. This site was targeted for coring because it lies above the crest of an anticline bringing older sediments closer to the seafloor. Though the BSR is easily identifiable on this profile,

Figures 3a and 3b. Line 725, reprocessed in March 2011 at the University of Texas seismic data processing center. Detailed velocity analysis improved the imaging of the steeply dipping folds when compared to the original processing. Fig 3a shows a post-stack migrated section and Fig 3b shows a depth conversion of the portion of 3a indicated by the red box.
sampling gas hydrate was not the objective of these cores. Multibeam data collected from *Healy* using a hull-mounted Kongsberg-Simrad EM122 multibeam echosounder system delineated the seafloor feature as a 130 m high conical feature approximately 1100 m wide at the base, referred to here as the Canning Seafloor Mound (CSM) (Figures 4a and 5). Previously, based on the single 2D USGS line 725, the lateral shape of the seafloor high was indistinguishable. Backscatter intensity data recorded with the EM122 system show the CSM has generally lower backscatter than the surrounding seafloor (Figure 4b).

Sediment coring was accomplished using two sampling devices – (1) a 3-m-long gravity core with a 1090 kg (2400 lb) weight stand and (2) a 6-m-long piston core with the same 1090 kg weight stand that was triggered by an associated 75-kg (175 lb) 1-m-long gravity core. Both the gravity and piston core systems used steel-walled barrels with 8.7-cm o.d. polybutyrate liners. During the cruise, *USCGC Healy* recovered five cores from two sites in the CMDM (Figure 6; Table 1). Three cores were recovered at the CSM Site 1 on August 12, 2010: 1) A gravity core (1-GB1) from near the summit in approximately 2500 m water depth with 1.33 m of sediment; 2) A piston core (1-P1) within ~50 m of Core 1-GB1 that recovered 5.71 m of sediments including an eight cm section of nodular gas hydrate in the core catcher (Figure 7); and 3) the trigger core (1TC) for 1-P1 that recovered 0.83 m of sediment. The gas hydrate from Core 1-P1 was not preserved or sampled. Following the CSM coring, a 3.02 m reference piston core (2-P1) and a 0.79 m trigger core (2-TC1) were recovered at Site 2, located 40 km to the south in a water depth of 1157 m. All cores were sealed and shipped to the USGS core laboratory in Menlo Park for sampling and analysis of gas voids, sediments and pore waters. Results from these analyses are discussed below. The cores were maintained at 4°C during storage aboard the *USCGC Healy*, transport to Menlo Park CA USA and subsequent storage at the USGS sediment laboratories in Menlo Park.

The cores were logged with the USGS’s Geotek MultiSensor Core Logger (MSCL; http://www.geotek.co.uk/products/mscl-s) in early November and split, photographed, described, and subsampled in December, 2010. Although recovered at locations separated only by 50 m, visual description of cores 1GB-1 and 1P-1/1TC-1 document somewhat similar lithologies but with distinctly different characteristics. The upper parts of cores from both locations are fine grained, with 1GB-1 being somewhat coarser grained (silty clay) than 1P-1 which is a clay with some silt (Figure 6). Core 1GB-1 (1.3 m long) had evidence of iron sulfides in all parts of the core with numerous authigenic carbonate nodules scattered throughout. The core split smoothly and exhibited open voids and fractures indicative of gas voids. In contrast, the sediment recovered in core 1P-1 and its associated trigger core (1TC-1), were more clay-rich, were highly plastic, and split with difficulty (resealed immediately upon cutting with a tensioned wire). Evidence of iron sulfides and authigenic carbonate were lacking in core 1P-1 until deep in the core (>3 m) where facies became significantly coarser grained (clayey sands to sand-silt-clays). Indicators of gas charging (e.g., small open voids, fractures, and large continuous gaps) were evident throughout cores 1P-1 and 1TC-1. Additionally, small (~ 1 cm) mollusk valves and a gastropod shell were recovered in core 1P-1. Although equivocal, the differences in silt content and particularly the plasticity and depth within the cores of iron sulfides and authigenic carbonate between cores 1GB-1 and 1P-1, as well as the thin sand and sandy silt layers in the upper 50 cm of 1P-1 and 1TC-1 but absent from 1GB-1 suggest the facies are significantly different and that the processes emplacing the sediments vary at these two closely-spaced locations. More detailed analyses (e.g., quantitative textural analysis; Atterberg limits; faunal identification of the recovered mollusks and gastropods) are planned to better document the sedimentological variability within the study area. In contrast, piston core 2P-1 and its associated trigger core (2TC-1) recovered from the upslope reference site were primarily silty clay with some sand-rich layers and did not exhibit the plasticity evident in cores 1P-1 and 1TC-1. The site 2 cores split smoothly, showed no evidence of gas charging (i.e., no voids, cracks, or gaps), and contained only broken shell fragments.

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**Table 1. Core location information**

<table>
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<tr>
<th>Site</th>
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<th>Recovery (cm)</th>
<th>Latitude</th>
<th>Longitude</th>
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</tr>
<tr>
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<td>1P-1 &amp; 1TC-1</td>
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<td>571 cm &amp; 83 cm</td>
<td>71.3174°</td>
<td>-143.9997°</td>
</tr>
<tr>
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<td>2P-1 &amp; 2TC-1</td>
<td>1157 m</td>
<td>302 cm &amp; 59 cm</td>
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<td>-144.0524°</td>
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</tbody>
</table>
Figure 4a. Shaded relief multibeam bathymetry of the seafloor near the CSM. Contour interval is 200 m.

Figure 4b. Backscatter intensity map. The core locations near the CSM summit are marked by the red dot. The CSM shows lower backscatter intensity (darker shades) than the surrounding seafloor, though low backscatter intensity is also observed on the ridge extending to the southeast.
Figure 5. 3D perspective display of the CSM looking south. Scale decreases from front to back of this image as shown by the two 1 km scale bars. White lines are 20 m interval water depth contours. Red dots show the locations of core 1GB-1 and 1P-1/1TC-1. The 1GB-1 location is approximately 50 m north of the 1P-1/1TC-1 location.

Figure 6. Photographs of the upper parts (to 58 cm) of the split cores. Dashed lines show correlation of units in the paired trigger and piston cores. Note the disturbance evident in cores 1P-1 and 1TC-1 due to the plasticity of the sediment. See text for additional description.
PORE WATER CHEMISTRY

Methods
Sixty-four pore water samples were extracted from the five sediment cores (1GB-1, 1P-1, 1TC-1, 2P-1, and 2TC-1) using rhizion water samplers (Rhizosphere Research Products), transferred into 2-ml plastic vials and maintained at 4 °C until analysis. Sulfate and chloride concentrations were determined using a Metrohm 881 Compact Ion Chromatograph (IC) pro equipped with a Metrosep A Supp 5 250 column. The peak areas from samples diluted by a factor of 100 were quantified against equivalently diluted International Association of Physical Sciences of the Oceans (IAPSO) standard seawater analyzed at the beginning of the run and after every fifth sample. The analytical precision for dissolved sulfate and chloride was < 2% of the IAPSO standard values, which are 28.9 mM for sulfate and 559 mM for chloride.

Results and Discussion
Sulfate profiles as indicators of gas flux. Simultaneous consumption of methane and sulfate during the anaerobic oxidation of methane (AOM) by microbes,
\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}, \]  
(Eq. 1)
generates sulfate concentration profiles that have been used as a proxy for the upward flux of methane [22]. The interface where AOM occurs is termed the sulfate-methane transition, or SMT. Assuming AOM is the only sink for sulfate, under similar fluid flux regimes, the change in sulfate concentration with depth \( \frac{\partial \text{SO}_4^{2-}}{\partial z} \) is proportional to the methane flux. Thus, a shallow SMT, which has a steep sulfate concentration with depth, indicates a greater methane flux than a deeper SMT with a less steep sulfate concentration gradient. Furthermore, if the background chloride values can be established, chloride profiles may be used to calculate gas hydrate saturation in the pore space [23]. Alternatively, when deep fluid sources have chloride concentrations distinct from the overlying seawater, the chloride profiles may be used to calculate rates of upward fluid advection [24]. We applied these concepts to describe the methane and fluid flux regimes at the CSM.

Reference Core 2P-1. Reference Core 2P-1 collected 40 km to the south of the mound in 1157 m water depth had uniform sulfate (28.2 ± 0.4 mM) and chloride (563 ± 5.2 mM) profiles (Figure 8a) that are similar to standard seawater and indicate negligible methane and fluid fluxes. By contrast, all of the cores from the CSM discussed below had profiles indicative of active methane and/or fluid fluxes.

Piston Core 1P-1. With the exception of the extremely high sulfate concentration of 68.4 mM from the gas hydrate-bearing core catcher at 575 cm below the seafloor (cmbsf), Core 1P-1 contained low and relatively uniform sulfate concentrations (6.3 ± 1.4 mM) throughout the core (8b), which is consistent with an exceptionally high methane flux [25]. The presence of deep-penetrating sulfate through the core may be related to gas ebullition [26], but might also be an artifact of reoxidation of sulfides (see Eq. 1) during the 3 month core storage. As the sulfate concentration in the core catcher exceeds the seawater sulfate concentration (~29 mM), this value most certainly reflects sulfide reoxidation.

Chloride concentrations in Core 1P-1 (Figure 8b) vary from 459 mM at the core top to 238 mM at the base (238 cmbsf). The concave down chloride concentration profile indicates deep fluid advection of an exceptionally low salinity fluid. The samples near the base of the core may have been affected by fresh-water released during dissociation of gas hydrate visually identified in the core catcher. It is highly improbable that the low-salinity fluids through the rest of the core were altered by gas hydrate dissociation as gas hydrate was not identified in that portion of the
We saw no evidence of fluidized sediment commonly observed from the addition of dissociated gas hydrate water into the cored sediments. Furthermore, gas hydrate dissociation typically generates jagged concentration profiles [27]. Lower than seawater chloride concentrations present at the surface (see Reference Core 2P-1 for a typical chloride profile) suggests material from the core top may have been lost during the coring process or that advective fluid flux limited penetration of chloride into the sediment, as observed in the sulfate profile. Potential origins for the low salinity fluids are discussed below.

**Trigger Core 1TC-1.** The sulfate profile from Core 1TC-1 (Figure 8c), the trigger core for the piston core 1P-1, is distinct from the core 1P-1 collected 1 m away. Lower than seawater sulfate concentrations of 16.0 mM from 1-3 cmbsf decrease to 0.8 mM at 72 cmbsf. Chloride profiles decrease linearly from 540 mM at the top of the core to 446 mM at the base of the core. The different sulfate and chloride concentration ranges and profile shapes for the proximal piston (1P-1) and trigger (1TC-1) suggest extreme spatial methane and fluid flux variability on the apex of the CSM.

**Gravity Core 1GB-1.** Core 1GB-1 contained a large number of mollusk shells and authigenic carbonates, which suggests the core was recovered from an area that was once and may still be a active chemosynthetic biological community [28]. Based on the sulfate profile, which is 28.6 mM at 2 cmbsf and reaches a relatively constant sulfate concentration of ~1 mM at 93 cmbsf, the sulfate profile inferred methane flux (based on the sediment depth where sulfate reaches a minimal value) at this location is not as great as the location where cores 1P-1 and 1TC-1 were collected and has a depth of sulfate depletion similar to CBCs at the Haakon Mosby mud volcano [25]. The shape of the chloride concentration profile is similar to the sulfate profile, which suggests the

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![Figures 8a-8d. Plots of sulfate and chloride concentrations vs sediment depth for the CSM cores and reference piston core.](image-url)
profile shape of the sulfate profile is controlled by physical processes above the zone of AOM occurring at the base of the sulfate-bearing sediments (Figure 8d). Chloride concentrations decrease from a near seawater value of 550 mM at 2 cmbsf to a remarkably and study-wide low 160 mM at the base of the core. Seawater dilution with freshwater to produce a solution with 160 mM chloride would be composed of ~80% freshwater. Explaining how such a low value is possible at the CSM in ocean water depths of ~2500 m approximately 150 km offshore is difficult. The presence of sulfate concentrations in excess of ~1 mM generally indicates an absence of methane and, thus, gas hydrate. Therefore, gas hydrate dissociation is not a practical explanation for the low chloride concentrations observed in this core. Alternative explanations include clay mineral dehydration, meteoric water influx and clay membrane ion filtration. Clay dehydration and ion filtration processes for pore fluid freshening have been demonstrated in deep sedimentary systems, but, to our knowledge, none have yielded fluids as freshened as measured in these near-seafloor sediments. The structural folds of the CMDM where the CSM occurs extend toward the shelf and contain deep-rooted thrust faults that could provide fluid migration conduits to sediments as deep as 10-15 km below the seafloor [19]. It is conceivable that low-salinity pore water from buried non-marine sediments migrated along these thrust faults to the seafloor at the CSM. Delineating the fluid origins and mechanisms for this dramatic fluid freshening at the seafloor of an offshore seep is an area of active investigation.

**GAS SOURCES**

Gas voids in the gas hydrate bearing Core 1P-1 were sampled with a core penetration tool and transferred into evacuated glass vials. The gases were analyzed for their molecular and isotopic composition by Isotech Laboratories Inc. Despite being stored at 4 °C for four months prior to sampling, the gas voids contained 10 to 26% methane by volume. To estimate the original composition of the gas voids, the gaseous hydrocarbon and CO₂ concentrations were corrected for the introduction of the atmospheric gases nitrogen, oxygen and argon. The hydrocarbon and CO₂ normalized concentrations, as well as the isotopic composition of the methane (δ¹³C and δ¹³ D) and carbon dioxide (δ¹³C), are presented in Table 2. Trace quantities of the strictly thermogenic gases n-butane (n-C₄), n-pentane (n-C₅) and C₆+, gases are definitive evidence for at least a partial thermogenic origin [29]. A detailed analysis of the molecular and isotopic composition of the gases suggest the predominant gas source is either a mixed source of degraded thermogenic gas with overprinting by secondary microbial methane or a primary microbial source that was partially oxidized in the core liner.

The average nitrogen to oxygen ratio in the gas voids (N₂/O₂ = 27) was elevated relative to the atmosphere (N₂/O₂ = 3.7) this is also true for the Ar/O₂ ratios suggesting oxygen introduced during core processing on the Healy may have been consumed by oxidative processes during storage. For example, persistent sulfate in the core (Figure 8b) is consistent with oxidation of dissolved and mineral sulfides. Aerobic oxidation of methane is also of concern due to long storage times, and

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<th>C₃</th>
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Table 2. Isotopic and atmospheric carbon dioxide and hydrocarbon gases Core 1P-1
results in methane depletion and CO₂ production. Thus, the normalized methane concentrations (95.2 to 98.3%, Table 1) most likely underestimate the in-situ methane concentration. Nevertheless, the gas from Core 1P-1 is still enriched with methane relative to conventional thermogenic gas. The C₁/(C₂+CH₄) ratios range from ~1000 to 4000; classified as a primary microbial gas according to the conventional Bernard parameter (Figure 9; modified from [30]). However, the δ¹³C values of methane from this core range from -50 to -59‰, becoming more ¹³C-enriched with depth in contrast to pure primary (~-60 to -70‰) microbial methane typically observed in marine sediments (Figure 9). Mixing of primary microbial methane with a δ¹³C of ~-69‰ or less and a conventional thermogenic gas cannot explain the dry and ¹³C-depleted methane carbon isotopic composition measured from Core 1P1-1 (Figure 9). Alternate microbial sources are: 1) ¹³C-enriched methane from primary microbial methanogenesis using ¹³C-enriched CO₂ [31]. However, in Core 1P-1, the δ¹³C of the CO₂ ranged from -9 to -21‰, which would yield a primary microbial methane product with a δ¹³C of ~-69 to -81‰ using a typical fractionation factor of 1.060 for carbonate reduction [29]. 2) microbial methane generated during acetate fermentation, which has δ¹³C values for the range observed in Core 1P-1 [29]. However, the δD-CH₄ values from Core 1PC-1 (-188 to -200‰) are inconsistent with such a source [29].

If the molecular and isotopic compositions of hydrocarbon gases from Core 1P-1 were not altered during storage, the data are most consistent with a degraded thermogenic gas containing secondary microbial methane. Biodegradation of oil within hydrocarbon reservoirs converts the wet (C₂+₁) hydrocarbon fraction into CO₂, leaving a gas residue of primarily thermogenic methane (δ¹³C > 50‰) and CO₂. The subsequent reduction of the oil-derived CO₂ by microbial methanogenesis (a process known as secondary microbial methanogenesis), produces ¹³C-depleted relative to CO₂ with a methane-rich gas composition similar to that from Core 1P-1. Reduction of the oil-derived CO₂ by secondary microbial methanogenesis drives the residual CO₂ pool toward ¹³C-enriched values. The δ¹³C-CO₂ values from Core 1P-1 are consistent with values observed in the west Siberian Vanyegeanskoie oil field, where ~20% of the oil-derived CO₂ was converted to methane by secondary microbial methanogenesis [32]. Alternatively, if oxidation of primary microbial methane with an initial δ¹³C value of ~-60 to -80‰ occurred during core storage, the residual methane in the core liner could have the measured δ¹³C values of -50 to -59‰. At the present time, we are unable to distinguish between these two potential sources.

**DISCUSSION**

**Fluid flux at the Canning Seafloor Mound**

Although the CSM overlies the crest of a linear buried anticline, its conical shape indicates that it is not a direct result of structural uplift associated with the CMDM folding with the uppermost
folded sediments pushed above the surrounding seafloor as a ridge. Rather, we conclude that thrust faulting associated with the compressional folding provides pathways for deep-seated pore water, natural gas and sediments to migrate to shallow subbottom depths where high-angle fractures along the sharply folded anticline crest could allow venting at the seafloor. An alternate fluid migration process could be structural focusing upwards along the sedimentary layers flanking the anticline [33,34]. Several lines of evidence from the CSM cores support high seafloor flux at this site; the shallow SMT determined from the sulfate profiles result from active flux; the presence of authigenic carbonates, mollusk valves and a gastropod shell within the cores demonstrate a once and possibly still active cold seep site with a chemosynthetic community [35]; the thermogenic component of the residual gas samples has likely migrated from thermogenic depths sediment depths in excess of 2000 m [36]; and the low chloride values may have emanated from deep pore water migration to the surface. Additional support for interpreting gas flux through the hydrate stability zone at the CSM comes from MCS profile 725 (Figures 3a and 3b). The BSR is high-amplitude and continuous beneath the bathymetric high just 10 km to the northeast of the CSM. This is an expected and common characteristic of BSRs as the base of hydrate stability mimics the seafloor relief and if sufficient hydrate is present, forms a trap for free gas. However, the BSR is absent or weak beneath the CSM, possibly the result of gas migrating to the surface with relatively warm pore water, thinning the gas hydrate stability zone and locally perturbing the hydrate phase boundary upwards to the seafloor.

**Origin of the Canning Seafloor Mound**

Two processes of seafloor mound development, each dependant on high fluid flux, are likely factors in the origin of the CSM. Hovland and Svensen [35] interpret small seafloor mounds in the Norwegian Sea to be pingos created by shallow lenses of hydrate that deform the sediment surface. These mounds occur in greater than 700 m water depth within pockmark features containing authigenic carbonates and seep-associated organisms indicating active fluid flow. Paull et al. [37] and Hein [38] describe dome-shaped features greater than 10 m high and 100 m across protruding from the crests of broad compressional folds in approximately 800 m water depth in the Santa Monica Basin offshore southern California. Authigenic carbonates, chemosynthetic communities and continuous streams of methane bubbles were observed at the site. The authors propose that blister-like inflation of the seafloor caused by the formation and accumulation of hydrate lenses has created these mounds in a manner analogous to terrestrial ice-formed pingoes. Similar “hydrate pingo” mounds have been observed in the Barkeley Canyon offshore British Columbia, Canada [39,40]. The CSM, though much larger, has much in common with these hydrate pingos: the presence of hydrate, authigenic carbonates, and chemosynthetic organisms; high fluid flux; and steep-sided conical morphology. However, we conclude that sediment extrusion is also a factor in the growth of the CSM. Inflation alone, bowing the seafloor sediments into a mound, should result in uniform shallow sediments across the mound. However, the cores 1GB-1 and 1P-1, taken only 50 meters apart, show enough lithologic variation to indicate that they were taken from localized zones of sediment extrusion from CSM vents. The backscatter intensity variation from the CSM compared to the surrounding seafloor is also evidence for at least some sediment extrusion. It cannot be determined without additional sampling how much each process, hydrate pingo inflation and mud volcano extrusion, has contributed to building the CSM; we conclude that each has been a factor. We anticipate that future exploration in the CMDM will find additional features similar in origin to the CSM aligned atop the anticlinal fold crests.

**CONCLUSIONS**

1. The hydrate sample recovered in the HLY1002 piston core 1P-1 confirms the long-standing geophysical interpretation that gas hydrate exists beneath the Beaufort Sea continental slope.
2. The thermogenic component of the residual gas samples from 1-P1 extends the CMDM petroleum system much further offshore than previously known.
3. The CSM is a site of active natural gas flux.
4. The CSM is a result of both pingo-like inflation of the seafloor due to the formation of shallowly buried gas hydrate and the accumulation of extruded sediments such as found at a mud volcano.
5. Additional seafloor mounds similar to the CSM are likely to exist along the fold crests of the CMDM.
6. Further analysis of the HLY1002 CSM cores and future sampling and geophysical data acquisition will be necessary to better understand the natural gas system within the CMDM.

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