TRACKING THE DECOMPOSITION OF SUBMARINE PERMAFROST AND GAS HYDRATE UNDER THE SHELF AND SLOPE OF THE BEAUFORT SEA

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ABSTRACT

A cruise was conducted in 2010 to provide ground truth observations of the seafloor along the outer shelf edge and slope of the Beaufort Sea where multibeam mapping in 2009 identified water column acoustic anomalies which were inferred to be gas plumes. Here we report on seafloor observations, gas sampling, pore water chemistry, and preliminary sediment dating from ROV dives and sediment coring conducted during this cruise. These observations confirm that methane is venting from the seafloor at these sites. The location and style of the vents may be attributed to the on-going impact of thermal warming on relict permafrost and gas hydrate on the margin of the Arctic Ocean. We also provide documentation for the existence of gas hydrate occurrences on the Arctic continental slope overlying large fluid expulsion features.

Keywords: gas hydrate, permafrost, gas venting, thermal warming

NOMENCLATURE

ROV - Remotely Operated Vehicle
PLF - Pingo-Like Features
WCAA - Water Column Acoustic Anomaly
SESZ - Shelf Edge Seep Zone
mM - milimolar
$\delta^{13}C$ - Carbon isotope (H_2O or CH_4)
$\delta^{18}O$ - Oxygen isotope (H_2O)
δD - Deuterium isotope (H_2O or CH_4)
PDB - PeeDee Belemnite standard
SMOW - Standard Mean Ocean Water standard
pMC – Percent Modern Carbon

INTRODUCTION

Sediments beneath the continental shelf of the Arctic Ocean are arguably undergoing some of the most dramatic warming on earth. This warming is associated with the transgression of sea level at the end of the last ice age, when relatively warm ocean water (mean bottom temperatures >-1.8° C) flooded over a much colder terrestrial periglacial landscape (mean annual surface temperatures <-12° C). The thermal wave generated by this transgression is still propagating down into subsurface sediments causing warming and initiating the slow decomposition of both permafrost and gas-hydrate-bearing sediments

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(Fig. 1). While these phenomena can be thermally modeled [1-2], there has been little consideration of the geologic processes (sediment strain, gas and fluid flux) that can result as the subsurface gas hydrate and permafrost-bearing zones diminish. This paper provides an overview of multidisciplinary studies of geologic processes and methane release observed in the outer shelf area of the Beaufort Sea.

Permafrost/gas hydrate setting

The regional stratigraphy of the upper kilometer of Beaufort Shelf is primarily composed of unconsolidated, horizontally bedded, transgressive/ regressive sands and silts with varied physical properties [3, 4]. The occurrence of up to 700 m of ice bonded permafrost and up to 1200 m of gas hydrate stability has been documented in numerous industry exploration wells [5, 6]. Detailed investigations have also been conducted on land quantifying gas hydrate occurrence before transgression [6]. Similar to many other Arctic continental shelves, the existence of this relict permafrost and gas hydrate in subsurface sediments can be expected to substantially affect the ground water regime by reducing the sediment permeability. The thick and laterally extensive permafrost/hydrate bearing zones may be partial seals for vertical fluid migration over much of the shelf.

Modeling of the thermal effects of the transgression of the Beaufort Shelf suggests that decomposition of gas hydrate is likely occurring at the top and the bottom of the gas hydrate stability zone [1, 2]. The methane and bound water released by the decomposition of gas hydrate will initially increase the subsurface pressure within a closed system. Increases in pore pressure subsequently may dissipate through fluid and/or material flow along the preferred permeability pathways. The large topographic features on the central Beaufort Shelf, known as pingo-like-features (PLF [7, 8]), may have been generated by these processes [9] and develop where vertical conduits in the overlying permafrost cap occur.

More recently a remarkable coalescence of geologic features and water column acoustic anomalies (WCAA) suggesting seabed gas release have been mapped along the edge of the shelf and upper slope [10, 11]. Thermal reconstruction of the transgression history of this part of the Beaufort Shelf (Taylor, Pers. Comm.) suggest that relict permafrost and permafrost gas hydrates pinch out laterally at approximately 90 to 110 m water depth (Fig. 1). Given the present sea bottom temperature regime on the slope and the pressure-temperature conditions required for stable marine gas hydrates, we anticipate that there is an interval between about 110 and 270 m water depth where neither gas hydrate nor permafrost are present. In this paper we extend our hypothesis for the formation of PLFs through vertical conduits, to consider if unimpeded lateral pathways for fluid and gaseous gas escape may occur along the edge of the continental shelf towards the slope.

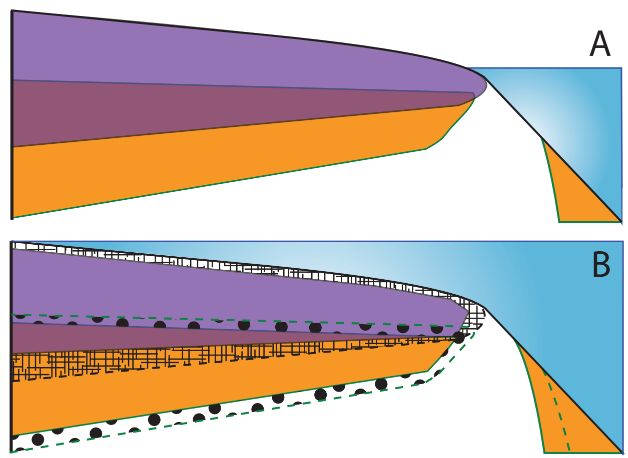

Figure 1 Schematic cross section of the Arctic Continental Shelf and Slope outlining subsurface zones where permafrost (purple), permafrost with gas hydrate (pink), and gas hydrate (orange) occur in the late Pleistocene (A) and at present after transgression (B). Note that the areas of permafrost and gas hydrate are less in B. Areas where permafrost (cross hatch) and gas hydrate (dots) have decomposed are indicated.

EXPEDITION OVERVIEW

Investigations of the seafloor associated with features from four different geological environments in the outer shelf and upper slope of the Beaufort Sea were conducted from the Canadian Coast Guard icebreaker *Sir Wilfrid Laurier* in the fall of 2010 (Fig. 2). These sites were chosen to provide ground truth data to characterize areas where indications of

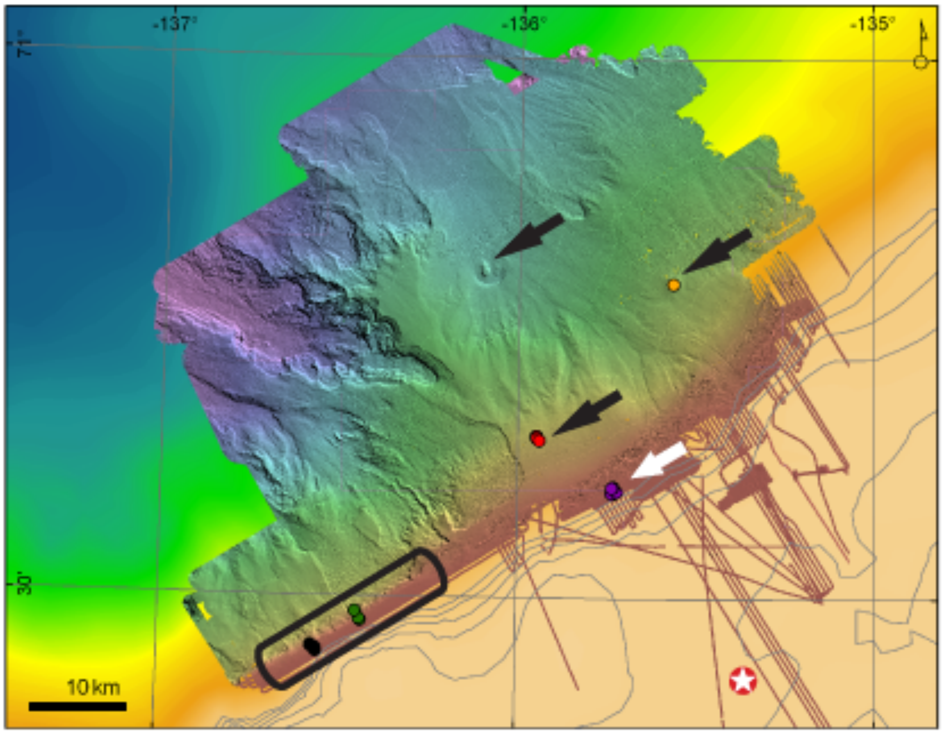

Figure 2 Map showing multibeam data collected by ArcticNet through 2009 [10, 11] as well as the locations of ROV dives and gravity cores (filled circles) within the Beaufort Sea in 2010. More detail is show in Fig. 4. Black box outlines shelf edge seep zone (SESZ). White arrow points small shelf edge topographic high. Black arrows point to circular features on the slope. Star shows Kopanoar PLF.

seafloor gas venting had been observed [9-11].

In total eight ROV dives and 26 gravity cores were conducted (Figs. 2 and 4). The first two ROV diving and coring sites (dives 1-5; cores 1-11; at sites previously identified as 0634H and 0634D [11]) are near the shelf edge in 80-120 m water depth (Figs. 2, and 4A & B). This area is called the shelf edge seep zone (SESZ) because numerous (>50) WCAA were identified in 30 kHz multibeam sonar surveys conducted in 2009 [10, 11] within a 20 km by 3 km wide area (Figs. 2 and 3). These WCAA are inferred to be associated with plumes of gas bubbles rising from the seafloor. The multibeam data from the SESZ indicates a relatively featureless seafloor in this area (Fig. 4 A & B).

Another shelf edge site was investigated that is about 30 km to the east of the SESZ in an area where the sea floor is studded with small topographic highs (Figs. 2 and 4C; previously identified as site 0466A [11]). Here an isolated WCAA was identified in 2009 over a topographic high that is ~50 m across and ~3 m higher than the surrounding seafloor. ROV dives 6-7 and cores 12-17 were conducted to help document the nature of this WCAA.

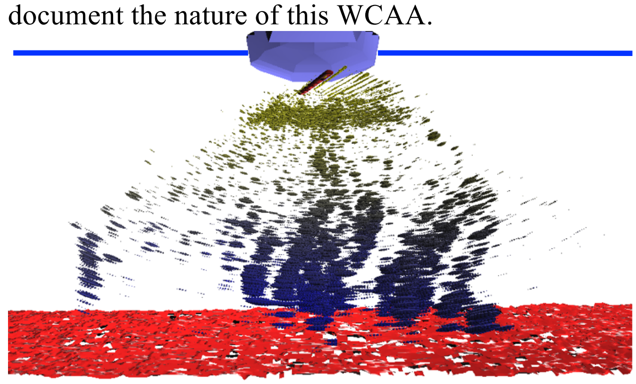

Figure 3 Image showing a WCAA detected using multibeam data collected within the SESZ in 2009 [10, 11]. The bottom of the ships hull is shown in light blue and the ocean surface with a blue line. Echos from seafloor are shown in red. Echos in blue and green are from the water column. Shapes of WCAA shapes suggest gas plumes.

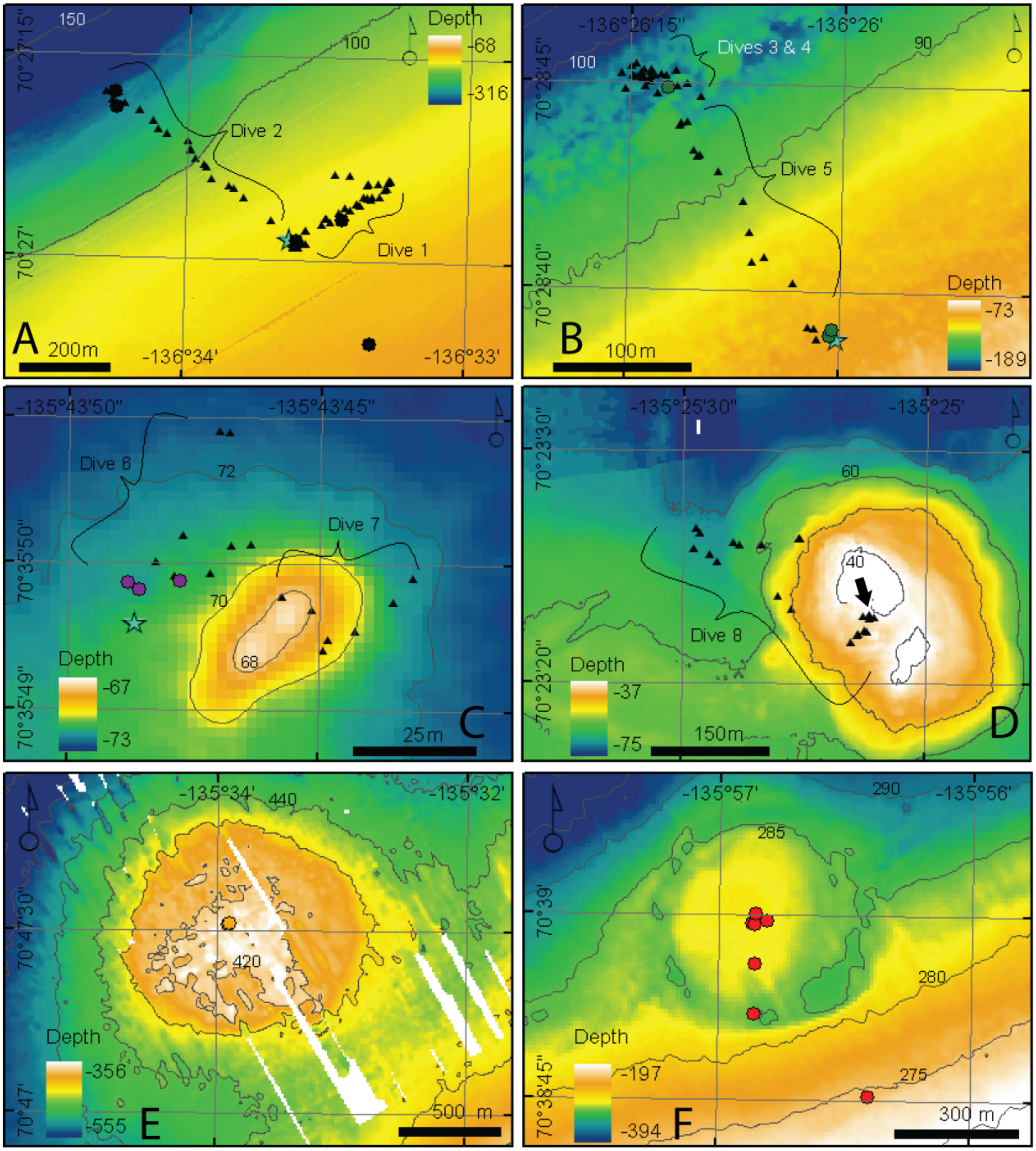

***Figure 4** Maps showing the detailed bathymetry of areas suspected of gas venting investigated in 2010. Part A shows coverage of ROV dives (triangles) 1 and 2; part B shows ROV dives 3 to 5; and part C shows ROV dives 6 and 7. Positions of WCAA (0634H, 0634D, and 0466A) are indicated in parts A, B, and C respectively with a star. Part D shows location of ROV dive 8 at the Kopanoar PLF [11]. Location of vigorous gas venting is indicated with arrow. Part E and F show bathymetry over circular morphologic structures on the slope. Part E shows cores 25 and 26. Part F shows cores 18-24. Contour labels are in m. Triangles indicate waypoints along ROV dive transects. Circles indicate core sites.*

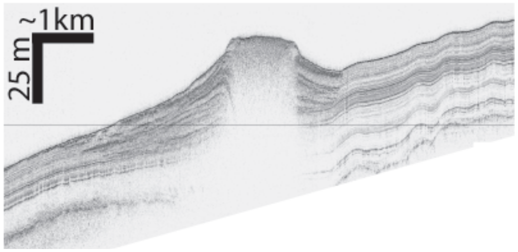

Figure 5 High-resolution seismic reflection profile collected up-dip over the circular morphologic structure in 420 m water depth (Figs. 2 and 4E).

The last dive (dive 8) was at Kopanoar, the best known of the PLFs, which is on the mid-shelf in water depths of 40-60 m (Figs. 2 and 4D). Core and ROV observations made in 2003 had shown that Kopanoar was venting gas [9]. The survey in 2010 was partly to establish whether gas venting from this feature was continuing.

Multibeam data revealed the existence of three circular morphologic features in water depths of 290 to 746 m on the continental slope (Figs. 2, 4, and 5). These features are ~750 m in diameter and stand more than 10 m higher than the surrounding seafloor (Figs. 2, 4E & F). WCAA were identified over each of these features. Gravity cores were collected from two of these structures.

ROV operations

A Phantom S2 ROV was used to image the seafloor and collect gas samples. The ROV carried a Sony HD Video Cam Recorder, Insite Nova Camera, Falmouth Scientific Instruments (FSI) Micro CTD, and gas sampling equipment. In total 33.3 hours of digital high definition video data were collected. Gas sampling equipment was developed by William Ussler and Larry Bird at MBARI specifically for this cruise. The objective was to obtain enough gas to make ^{14}C measurements on the methane carbon enabling a distinction from gas generated locally through on-going biochemical processes and fossil methane. The gas sampler consists of a coil of clear (3/8" inside diameter) plastic tubing wrapped around a spool with valves on both ends. One side is plumbed to a funnel, which could be rotated by the ROV to be vertical or overturned. The other side was connected to a Gulper [12]. The Gulper is a spring driven syringe that pulls 1.7-L of water. For some applications the Gulper is used as a water sampler. However, in this application the Gulper was used as a pump. The assembly allows fluid to be sucked from the funnel into the coils when the gulper springs are released. The coils were made so that their interior volume was replaced by an individual throw of the Gulper. Thus, rising gas trapped under the funnel is pulled into the coils. While gas trapped within the coils can expand as the ROV surfaces, air locks within the coils prevents the trapped gas from escaping. Gas samples were collected during ROV dives 4, 5, and 8 (Table 1).

The gas samples collected with the ROV and from the gravity core headspace were transferred into 250 ml bottles underwater and sealed with Belco Stoppers and crimp seals. The bottled gas samples were left in the cooler on the ship to be offloaded in Victoria, BC. From Victoria the gas samples were shipped to Isotech Laboratories, Champaign, Illinois for analysis. The gases were analyzed for hydrocarbon gases from C_1 to C_5, methane $\delta^{13}C$ and δD. The ^{14}C content of methane samples collected with the ROV were also analyzed.

Table 1: Locations and water depth where ROV collected gas samples were taken.

ROV dive #	Latitude dd° mm.m	Longitude ddd° mm.m	Depth (m)
4	70 28.7555	136 28.7531	97
5	70 28.7531	136 26.2428	97
8	70 23.3709	135 25.1176	42

Gravity Core Sampling

Gravity cores were collected using a ~160 kg weight stand. Coring sites were selected based on multibeam bathymetry and backscatter (Figs. 2 and 4). Recovery in 26 cores ranged up to 166 cm. Upon recovery, all the cores from the crests of the circular structures (i.e., 18, 19, 20, 21, 22, 25, and 26) were observed to be bubbling profusely. Gas bubbles continued to come out of the sediment for ~1 hour. The core caps were observed to bulge out when the cores were left standing upright. Samples of the headspace gas at the tops of these cores were taken by inserting syringe needles through the core cap and withdrawing gas into gas tight syringes.

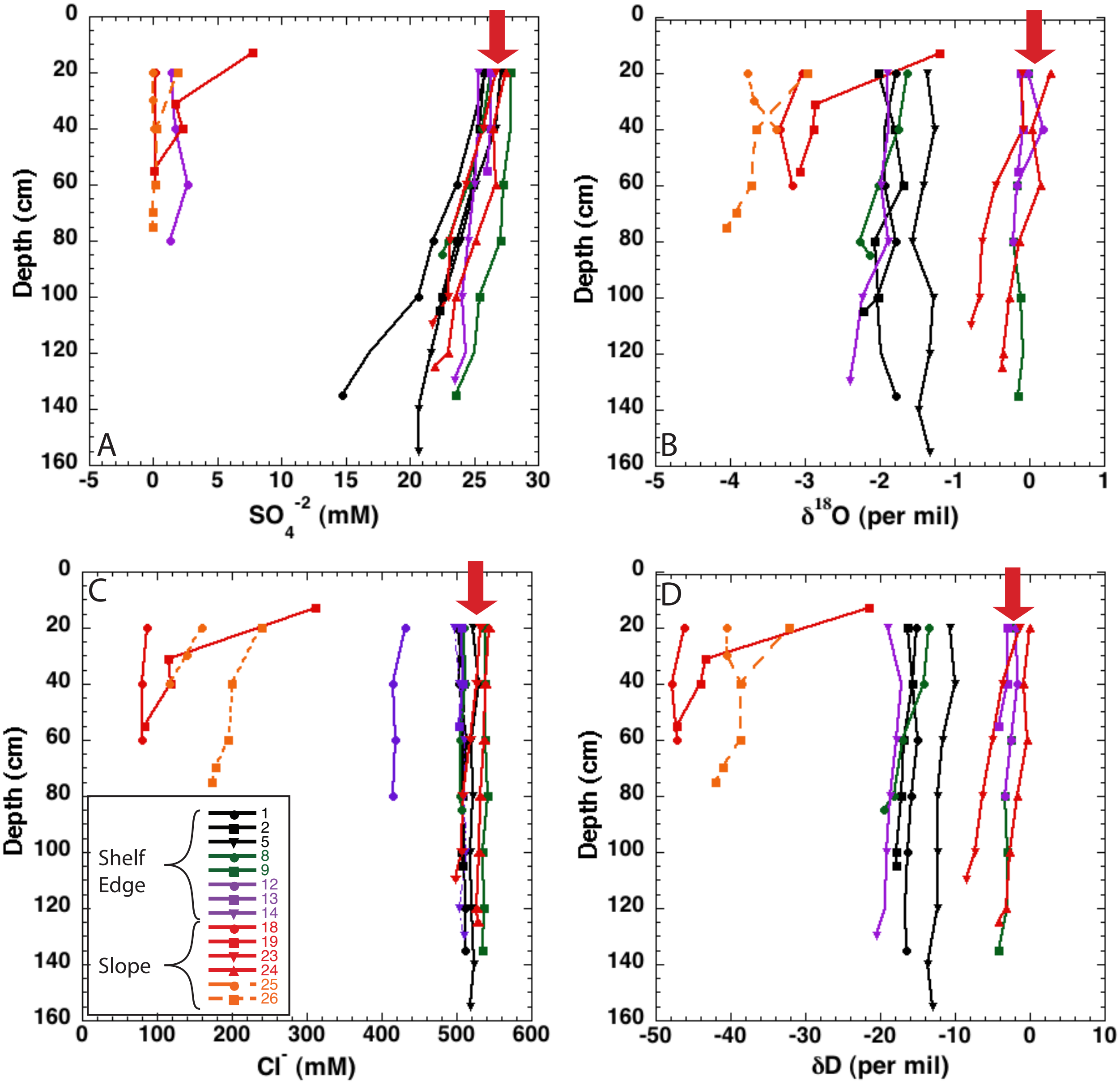

Figure 6 Plot of the concentrations of sulfate (A), concentration of chloride (B), oxygen isotope composition (C), and deuterium isotope composition (D) of pore water from gravity cores versus depth in core. Red arrow indicates typical seawater values. Cores are color-coded by area with black, green, and purple being ROV dive areas on the shelf edge (Figs. 2 and 4A, B & C) and red and orange being from the tops of circular topographic structures on the slope (Figs. 2 and 4E & F).

Twelve of the longer cores were selected for pore water analysis to assess variations in the local environments. Immediately after the selected cores were capped and labeled, they were laid horizontal within a lab. Pore water was extracted using rhizon samplers [13]. Holes were drilled at ~10 cm spacing down the core liner's side and the rhizons were inserted through the liner, plumbed to a Fisher Scientific, 10mL luer tip syringe. A vacuum was created by securing the syringe plungers back allowing water to be slowly withdrawn for ~4 hours.

Pore water samples were sealed with tight luer caps and refrigerated. Samples were analyzed for their sulfate and chloride concentrations by ion chromatography at MBARI (Fig. 6; Table 2). The remaining water was sent to Isotech Laboratories, Champaign, Illinois for δD and $\delta^{18}O$ analysis.

Table 2: Locations, depth, and length of gravity cores from which pore water or gas samples were taken.

Core #	Latitude dd mm.m	Longitude ddd mm.m	Depth (m)	Length (cm)
1	70 27.0231	136 33.6041	89	144
2	70 27.0506	136 33.4440	90	121
5	70 27.2026	136 34.2571	133	166
8	70 28.7482	136 26.2024	96	92
9	70 29.1553	136 26.8883	231	146
12	70 35.8311	135 43.8117	72	90
13	70 35.8417	135 44.1607	77	65
14	70 35.9284	135 43.2772	76	140
18	70 38.9918	135 56.8106	293	69
19	70 38.8990	135 56.8671	287	66
20	70 38.9338	135 56.8578	293	50
21	70 38.9878	135 56.8609	287	62
22	70 39.0008	135 56.8563	286	79
23	70 38.8659	135 56.8563	292	120
24	70 38.7548	135 56.4057	282	135
25	70 47.5152	135 33.9157	428	51
26	70 47.5175	135 33.9082	422	76

The cores were sealed on shipboard and returned to the Geological Survey Canada in Sidney BC where they were split, described, and sampled. The ^{14}C content of the disseminated organic matter in 17 selected sediment samples and 10 articulated bivalue shells were analyzed at the University of California Irvine Accelerator Mass Spectrometry Laboratory.

RESULTS AND DISCUSSION

Seafloor observations

In addition to collecting gas samples, ROV dives were designed to observe seafloor morphology, assess any unique biological habitat, and quantify the nature of gas release that had been detected on previous marine sounder surveys. The ROV video images show that white patches, identified as being microbial mat (Fig. 7A-C & G), are common on the seafloor at all dive sites. Occasional slow releases of gas bubbles were observed to emanate from small orifices penetrating many of these mats.

The gas releases from the seafloor within the SESZ was observed to occur as diffuse venting over a widespread area, rather than being concentrated at a few discrete point sources. In comparison a unique observation was made on dive 8 on Kopanoar PLF (Fig. 7H). Here, vigorous and continuous gas venting was observed. Apparently the venting was energetic enough to carry sediment up into the water as clouds of suspended sediment surrounded the venting area. The position of the venting gas bubbles was also observed to propagate along a linear trend at a rate of several meters per minute. To our knowledge this is a phenomena that has never been observed previously.

Although the multibeam data within the SESZ shows a relatively smooth seafloor (Fig. 4A & B), the texture of the seafloor observed during the ROV dives reveals a distinct rough texture (Fig. 8). This texture is associated with small mounds and ridges that are 20 to 50 cm high and 1 to 5 m across (Fig. 7A-D) and occasional beds of bivalve shells crop out on the sides of these mounds (Fig. 7D). One explanation for the existence of this texture is that these mounds are composed of slightly more erosionally resistant material within areas of widespread seafloor erosion.

The sediments that underlay much of the seafloor, especially near sites where gas bubbles were observed, are black (Fig. 7E & F), suggesting highly reduced sediments are also widespread within the SESZ (Figs. 2 and 4A & B) and around the small shelf edge topographic highs (Fig. 4C). The combinations of the distinctive seafloor textures, occurrence of bacterial mats, diffuse seafloor venting of gas bubbles and widespread occurrence of reducing sediment in the immediate subsurface is atypical of the shelf edge environments. These observations suggest methane permeates the shelf edge sediments in this region.

Core and pore water sampling

The dominant lithology encountered in the shelf edge consists of silty-clay and silt. The cores contained occasional shell rich horizons. Shell specimens were identified by Linda Kuhnz (MBARI) as being of the Family Arcidae Genus *Bathyarca* and Family Nuculanidae Genus *Nuculana*, both modern marine species common on the Arctic shelf.

The major element and isotopic composition of the pore waters from these cores reveals multiple distinctions between the cores (Fig. 6; Table 3). Of the eight cores taken near the shelf edge (cores 1-14), seven show chloride concentrations similar to the with depth and overlying seawater, but distinct sulfate gradients starting from seawater at the seafloor and reducing at depth. While δD and δ^{18}O values of the pore waters in these cores characteristically showed little variations with depth, variability of these parameters from site to site was substantial considering they are from similar water depths and lithologies. These variations suggest a variable shallow ground water regime with different local sources and possibly different ongoing processes at each site.

Table 3: Sulfate and chloride concentrations and oxygen and deuterium isotope composition of pore water samples.

Core #	Depth cm	ml	CL^-	$S0_4^{-2}$	δD	$\delta^{18}0$
1	20	10	505	25.9	-15.2	-1.8
1	40	10.5	503	24.9	-15.6	-1.9
1	60	10.2	513	23.7	-15.0	-1.9
1	80	7.1	508	21.8	-15.8	-1.8
1	100	9.3	510	20.7	-16.3	-2.0
1	120	8.3	512	16.9	-16.6	-2.0
1	135	7.1	512	14.7	-16.5	-1.8
2	20	9.8	502	25.8	-16.3	-2.0
2	40	10.1	510	25.4	-15.7	-1.8
2	60	10.2	509	25.0	-16.8	-1.7
2	80	10.1	509	23.7	-17.2	-2.1
2	100	7.8	507	22.5	-17.9	-2.0
2	105	7.9	509	22.3	-17.9	-2.2
5	20	9.9	523	27.1	-10.7	-1.4
5	40	10.1	530	26.7	-10.0	-1.3
5	60	9.9	520	25.1	-11.7	-1.4
5	80	10	522	24.0	-12.3	-1.6
5	100	10.1	519	22.7	-12.3	-1.3
5	120	10.1	521	21.7	-12.4	-1.3
5	140	10	523	20.7	-13.6	-1.5
5	155	10.1	518	20.7	-13.0	-1.3
8	20	9.9	510	26.3	-13.5	-1.6
8	40	7.3	511	25.7	-14.2	-1.8
8	60	10	506	24.6	-17.0	-2.0
8	80	7.9	504	23.0	-18.2	-2.3
8	85	7	506	22.5	-19.5	-2.1
9	20	10.5	538	27.9	-1.8	0.0
9	40	10	539	27.9	-1.7	0.2
9	60	10.2	538	27.3	-2.5	-0.2
9	80	9.9	542	27.1	-3.4	-0.2
9	100	9.9	535	25.4	-3.0	-0.1
9	120	9.9	536	25.0	-3.0	-0.1
9	135	10	535	23.6	-4.2	-0.2
12	20	9.6	432	1.5	-1.8	0.0
12	40	9.6	416	1.7	-1.7	0.2
12	60	10.1	418	2.7	-2.5	-0.2
12	80	9.8	415	1.3	-3.4	-0.2
13	20	9.6	507	26.3	-3.0	-0.1
13	40	10.2	509	26.3	-3.0	-0.1
13	55	10	504	26.0	-4.2	-0.2
14	20	9.9	497	25.4	-19.0	-1.9
14	40	4.1	504	25.3	-17.2	-1.9
14	60	6.1	510	25.0	-17.8	-2.0
14	80	10.5	510	24.6	-18.6	-1.9
14	100	10	511	24.1	-19.1	-2.2
14	120	10	503	24.3	-19.3	-2.3
14	130	9.9	510	23.5	-20.5	-2.4
18	20	3.5	86	0.1	-46.1	-3.0
18	40	3.2	81	0.1	-47.8	-3.3
18	60	3.1	81	0.1	-47.1	-3.2
19	13	6	312	7.7	-21.5	-1.2
19	31	4.1	116	1.7	-43.3	-2.9
19	40	2.3	118	2.3	-44.0	-2.9
19	55	2.3	83	0.1	-47.2	-3.1
23	20	6	532	26.7	-1.4	-0.1
23	40	6	527	25.7	-3.6	-0.1
23	60	6	519	24.4	-5.0	-0.5
23	80	5	508	23.1	-6.4	-0.6
23	100	9	506	23.0	-7.3	-0.7
23	110	7	499	21.8	-8.5	-0.8
24	20	6	543	27.5	0.0	0.3
24	40	6	539	26.5	-0.8	0.0
24	60	10	537	26.7	-0.4	0.2
24	80	10.5	532	25.2	-1.6	-0.1
24	100	9	530	23.6	-2.6	-0.3
24	120	9	527	23.0	-3.2	-0.4
24	125	6	528	21.9	-4.1	-0.4
25	20	6	161	0.0	-40.5	-3.8
25	30	8	140	0.0	-40.5	-3.7
25	40	10	118	0.1	-38.5	-3.4
26	20	9.4	240	1.9	-32.2	-3.0
26	40	8	200	0.3	-38.6	-3.7
26	60	7	194	0.2	-38.7	-3.7
26	70	6	178	0.0	-41.0	-3.9
26	75	8	173	0.0	-42.0	-4.1

δD and δ^{18}O values are with respect to SMOW

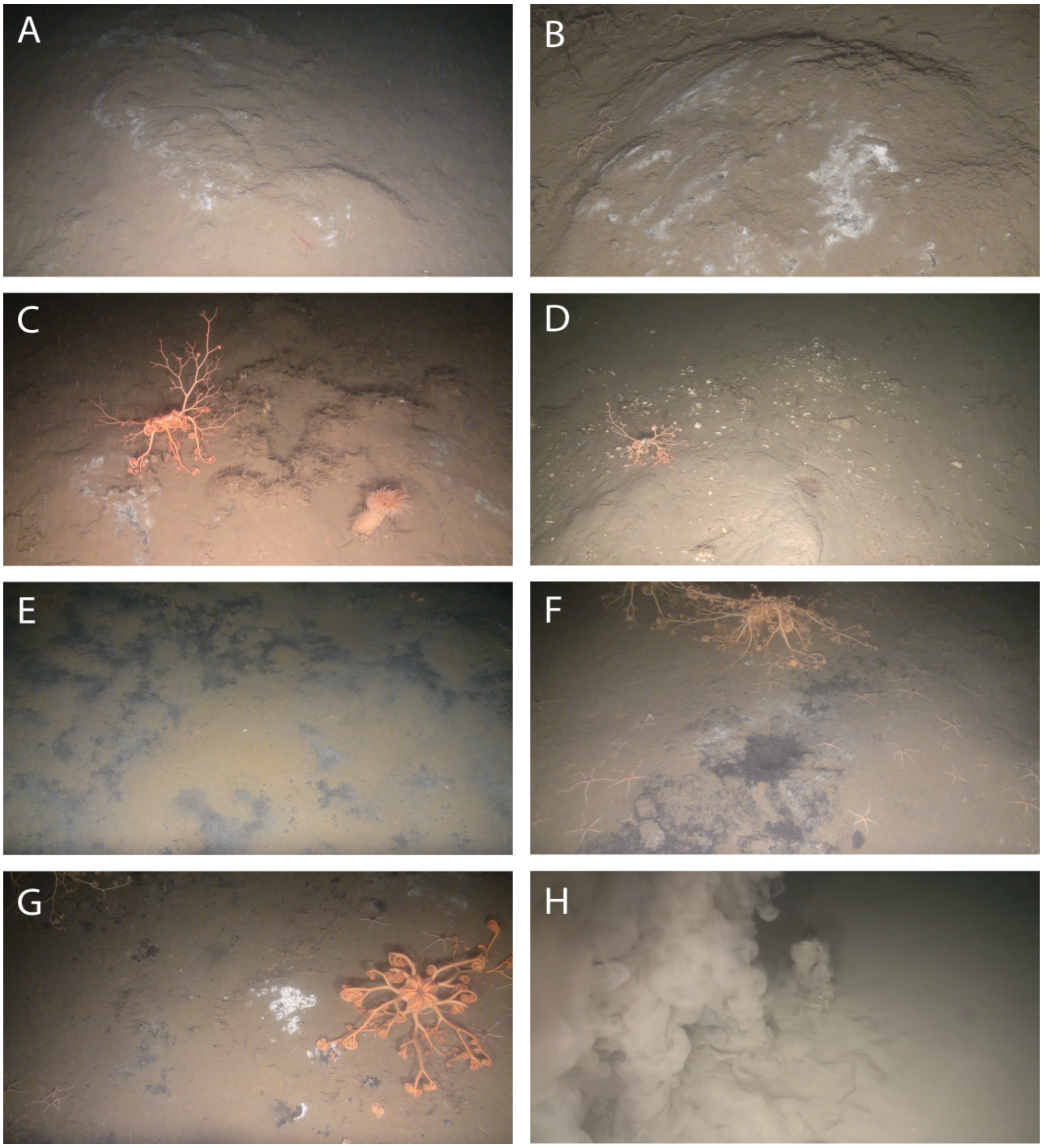

Figure 7 Video images of Arctic Shelf. The field of view is estimated to be ~3 m along the lower edges of these images. Parts A-G show seafloor near the shelf edge within area mapped to have multiple water column plumes. These positive relief features are commonly associated with patches of white that are interpreted as being bacterial mats (A, B, C, and G). Basket stars (Gorgonocephalus **sp.*) are common (C, D, F, and G). The existence of an anemone (*Actinostolid*) indicates a firm substrate underlying the mounds (C). Parts E, F, and G show black sediment exposed at the seafloor. When the seafloor in this area is disturbed, similar black sediment is seen to underlay broad areas surrounding the mounds. Part D shows bivalve shells. Periodic gas bubbling was observed coming from near A-G. Part F shows hole surrounded by a patch of black sediment. Apparently the hole shown in F was made by gravity core 12 that was collected a few hours earlier that day. Part H shows an area where vigorous gas venting occurs near the crest of Kopanoar PLF. The escaping gas is entraining sediment and producing the water column sediment clouds.***

The pore water from core 12, which was taken from the crest of a small mound near the shelf edge (Figs. 2 and 4C), was very distinct. This core contained sulfate concentrations that were largely depleted near the seafloor and chlorinities significantly fresher than that overlying seawater (Fig. 6A & B). ROV observations subsequently identified the core hole (Fig. 7F) and showed that methane bubbles were intermittently emanating from the seafloor near this feature. The cored sediments were too shallow to have hosted gas hydrate and we interpret the low chlorinties, low sulfate, and observed gas bubbles emanating from the seafloor near the core site to be indicative of advection of fluid to the seafloor from depth. The source of this advecting fluid could be from either the decomposition of permafrost or gas hydrate.

The pore waters extracted from cores collected on crests of the circular structures on the slope (cores 18, 19, 25, & 26; Fig. 6 A & B) show unusually fresh pore water chlorinities (down to 83 mM), and substantially depleted sulfate (0.1 mM). These cores were observed to actively bubble for ~ 1 hour after recovery. When split, the cores from the crest of the circular topographic structures on the slope (Figs. 2, 4D & E and 5) all exhibited a 'moussey texture' characteristic of gas charged and previously gas hydrate bearing cores (Fig. 8). These circular features appear to be the crests of active fluid expulsion features. Because the Beaufort Sea water temperatures [14] are unusually cold at these water depths (<0.5° C), these cores come from areas within the stability zone for methane hydrate [15]. Thus, we infer that gas hydrate is present within the surface sediments overlying these circular structures.

Gas and ^{14}C measurements

The elemental composition and methane isotopes of the gases sampled from the shelf edge (Fig. 8 and Table 4) indicate that the methane in these samples was produced by microbial CO_2 reduction [16]. The gas from the crests of the circular structures show a shift on a co-isotope plot ($\delta^{13}C$ versus δD) toward values commonly ascribed as being gases from mixed sources. However, C3 and higher hydrocarbons were not detected.

Figure 8 Photograph illustrating 'moussey texture' characteristic of gas charged and previously gas hydrate bearing cores. Image covers upper 20 cm (top to left) of gravity core 18 from the crest of the circular structure at 290 m water depths (Fig. 4F).

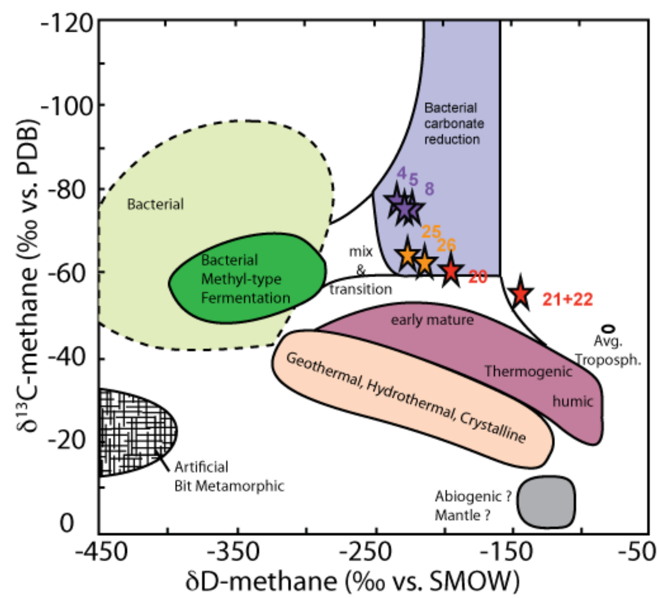

Figure 9 Crossplot of the δD versus $\delta^{13}C$ values of methane samples collected on the shelf edge of the Beaufort (purple) and over the circular structures (orange and red). Superimposed on the figure are the boundaries for the known ranges for methane produced via microbial fermentation, microbial carbon dioxide reduction, and thermogenic processes [16].

In order to further ascertain the origin of the gases using conventional a ^{14}C dating approach we also assessed the age of the host sediment, the disseminated organic material in the host sediment

Table 4 Percent contribution of major gases, stable isotopic composition of methane, and ^{14}C content of methane samples collected from Beaufort Sea seeps in 2010.

Sample Name	O_2 %	CO_2 %	N_2 %	C_1 %	C_2 %	$\delta^{13}C_1$ ‰	δDC_1 ‰	$^{14}C_1$ pMC
ROV Dive 4	0.3	0.03	1.7	97.9	0.004	-77.9	-226	< 0.2
ROV Dive 5	1.4	0.04	5.9	92.6	0.004	-78.0	-226	< 0.2
ROV Dive 8	1.0	0.04	4.3	94.6	0.008	-81.8	-240	< 0.3
Gravity Core 20	5.3	0.97	30.8	62.5	0.042	-60.6	-199	
Gravity Core 21+22	12.1	1.27	67.3	18.5	0.009	-53.8	-146	
Gravity Core 25 #1	1.3	0.37	4.8	93.5	0.121	-65.6	-226	
Gravity Core 25 #2	0.1	0.78	5.5	93.4	0.119	-65.7	-228	
Gravity Core 26	0.2	1.28	19.7	78.5	0.058	-63.6	-221	

and the gases themselves. Ten shells from sub-bottom depths of 31 to 135 cm in cores from the SESZ and the small mound area yielded ages ranging from 4,960±20 to 8,140±20 uncorrected ^{14}C years before present. This implies that sediments along the shelf edge accumulated in the Holocene. Eight ^{14}C measurements of the disseminated organic matter from samples taken from 38 to 130 cm sub-bottom depths from within the SESZ contained between 4.00±0.05 and 16.88±0.08 percent modern carbon with a mean value of 8.49±0.05 percent modern carbon. When expressed in ^{14}C years indicate finite ages between 25,950 and 14,290 years before present. These older dates are consistent with previous studies [9] and can be accounted for by the presence of older re-worked organic material within the fine-grained fraction of the host sediment.

In contrast to the dating of the sediment samples, the ^{14}C content of the gas samples collected from the SESZ (Table 4) contained 0.3 percent or less modern carbon. Such values are virtually at the detection limit of ^{14}C dating technique and suggest a date of ~50,000 years or much older. The large discrepancy between the organic matter in the host sediments and the escaping methane shows that the gas emanating from the seafloor is not produced locally by microbial activity within the present day seafloor sediment. We suggest that this indicates that the methane migrated from older deposits, possibly in association with decomposing permafrost and/or gas hydrate deposits beneath the shelf.

CONCLUSIONS

ROV diving and sediment coring document that methane is venting from the seafloor in four distinct environments on the margin of the Beaufort Sea. These include the crests of a mid-shelf PLF, a widespread area along the shelf edge, from one small mound near the shelf edge, and from the crests of circular topographic features on the slope.

The ROV observations suggest that the gas that is venting near the shelf edge is coming out in small amounts, but over a widespread area. Conversely, vigorous gas venting from a focused vent was observed at the Kopanoar PLF. Moreover the ^{14}C depletion in the venting gas indicates fossil methane is the source. The location of the venting sites on both the mid-shelf and near the edge of the slope are consistent with fluid and gas sources provided by decomposing relict permafrost and gas hydrate.

The vigorous release of methane upon core recovery, low sulfate concentrations, and mousey textures in the cores from the crests of the circular topographic features on the slope indicates that these are fluid expulsion features. Moreover, extremely low pore water chlorities, the prolonged gas venting, and mousey textures in these cores strongly suggest that gas hydrate occurs on the surface of these fluid expulsion features. This is among the first documentations of gas hydrate within the Arctic Ocean basin.

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