METHANE DISTRIBUTION IN PERMAFROST: EVIDENCE FOR AN ENTERPORE PRESSURE METHANE HYDRATE

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We report on studies of intergranular methane found in near-surface permafrost in northeastern Siberia, located outside oil and gas producing regions. This methane occurs in discrete layers at various depths, with negligible lithostatic pressure. Discontinuities in the methane distribution indicate that the methane is in a bound form and not able to diffuse. Upon thawing, the methane is released abruptly, in a phase change with associated enthalpy. These two facts suggests that the methane is held in a clathrate form within the sediments. Samples from cores containing deep methane hydrate which were degassed at low pressure while still frozen also exhibited this release of bound methane upon thawing. We conclude that, when temperatures are below freezing, methane hydrate can form at atmospheric pressure independently of high pressure forms of hydrate. The presence of discrete horizons containing methane in the permafrost provides a record of changing temperature and water conditions at the surface and their effect on anaerobic microbial activity. Unlike the deep high-pressure methane hydrates, this reservoir of bound methane could be released by warming in the polar regions.

Deep below the surface methane is found in the form of a clathrate [1,2] and it is believed that low temperatures and high pressures are required for its formation [3]. It is relevant to note, however, that hydrate formed at high pressure remains stable as the pressure is reduced lower than theoretical limits [4,5].

Investigations were conducted at 6 field sites of the Kolyma-Indigirka lowland (152-162°E, 68-72°N), northeast Eurasian Arctic tundra (Fig. 1). Permafrost occurs throughout the area to depths of ca. 600-800m. In this study, we consider the upper 100 m of the late Cenozoic permafrost. These layers have average temperatures about -10°C and are mostly syngenetically frozen (sedimentation occurred concurrently with freezing in which case the age of the permafrost was taken to be equal to the age of the sediments).

To correlate our results we also analyzed samples from Alaska (Fairbanks area) and CH_4-hydrate bearing fields in the Canadian (Mackenzie Delta).

Methane was determined in specimens extracted from 37 drill holes (DH) and kept frozen. The temperatures of the sample did not exceed -7°C; they were degassed by warming. The methane concentration was measured in the field (about 1200 samples) and laboratory by the "head space" method [6], using a KhPM-4 gas chromatograph (Russia) with a flame ionization detector. The sensitivity limit of the methane detection was 10 ppm and the results were reproducible to within 15%. CO_2 concentration was

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Figure J. Map and geological cross-section of late Cenozoic frozen sediments of study area.

also determined in 300 samples using a nondispersive infrared detector "Infralit" (Germany) with the same level of sensitivity.

Figure 2 shows the resulting data and Table 1 summarizes the methane distribution in the general late Cenozoic cross-section for the different sites within the area [7]. Methane is found primarily on a present-day floodplain bog (site II), in the "covered" layer (sites III-V), the Alas horizons (sites I, IV - VI), marine deposits (site VI), late Pliocene-early Pleistocene (sites I-V) and Pliocene (sites I, V, VI) suites. The lowest concentrations of methane (< 0.01 ml/kg) are present in modern alluvial plains in virtually all the river valleys of the area (site I), in Holocene eolian and late Pleistocene river-bed sands (site II) and in Icy Complexes of both ages in different locations in the region (sites I, III-VI).

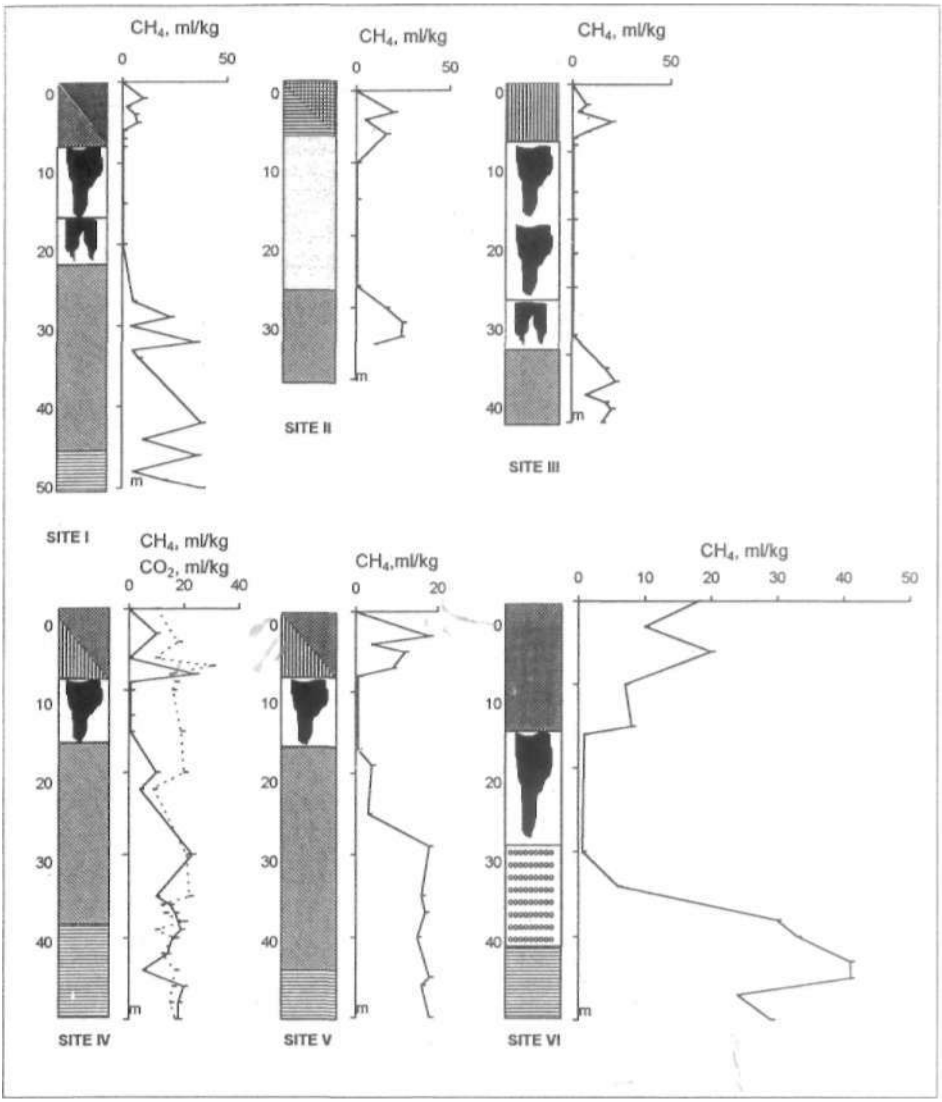


Figure 2. Methane distribution in drill holes penetrating late Cenozoic permanently frozen sediments of Kolyma-Indigirka lowland

Sediments from the late Pleistocene Icy Complex are located under the epigenetically frozen (melted during the Holocene thermal maximum , and refrozen 5 to 7 thousand years ago) "covered" layer or Alas horizon. At these holes methane was found only in Holocene samples; trace amounts were found at any depth in underlying late Pleistocene deposits. In all pure ice samples, CH_4 either was absent or occurred at a trace concentration. In contrast to methane, carbon dioxide was present in both - Holocene and late Pleistocene deposits (site IV), as well as in all older deposits that

*Table 1. Methane concentration (ml/kg) * in the main late Cenozoic suites of Kolyma-Indigirka lowlan*

suites		suites of study (see map on Fig.1)					
		I	II	III	IV	V	VI
elQ$_{IV}$, modern aeolian sands	▨		0.0 (27)				
lhQ$_{IV}$, modern swamp sediments	▤		0.3-7.0 3.6 (15)				0.3-1.9 1.4 (5)
alQ$_{IV}$, modern alluvial sediments	■	0.0 (5)			0.0-0.3 0.15 (6)		
tdQ$_{IV}$, "covered" layer	▥			0.6-7.5 5.4 (4)	0.4-5.3 2.4 (8)	0.2-3.8 2.5 (8)	
lhQ$_{IV}$, Alas horizons	▩	1.4-9.9 4.6 (8)			1.0-6.1 2.8 (15)	0.1-5.7 2.0 (15)	0.2-10.5 3.9 (16)
lal Q$_{III}^{2-4}$, late Pleistocene Icy Complex	▼	0.0 (55)		0.0 (42)	0.0 (45)	0.0 (7)	0.0-0.2 0.0 (94)
Q$_{III}$, late Pleistocene sands	░		0.0 (54)				
lal Q$_{II}$, middle Pleistocene Icy Complex	▼	0.0-0.5 0.2 (27)		0.0-0.6 0.3 (37)			
mQ$_{II}$, middle Pleistocene marine sands and loams	○						1.3-12.4 6.7 (42)
N$_2^3$-Q$_I$, late Pliocene-early Pleistocene sandy-loams	▩	1.4-40.0 7.8 (62)	0.5-15.3 7.2 (14)	0.6-2.2 1.6 (7)	0.2-7.5 2.7 (165)	0.9-10.9 5.6 (32)	
N$_2$, Pliocene sands	▤	1.5-22.8 12.1 (13)			1.5-3.8 2.6 (14)	2.5-9.7 5.1 (14)	0.5-11.3 6.0 (17)

* In numerator: the minimal and maximal values; in denominator: the average value and (in brackets) the number of investigated probes

were analyzed. At the transition from the middle (sites I, III) or late Pleistocene (sites I, IV, V) Icy Complexes to the underlying late Pliocene-early Pleistocene suite, the methane concentration increased sharply. In over more than 50 m of this methane rich layer, the methane concentration varied from 0.3 to 7.5 ml/kg (site IV) and 0.4 to 40.0 ml/kg (site I). The higher concentrations were typical of peaty and organic rich sequences.

The methane concentration also increased sharply from trace levels to 11.0 ml/kg at the transition from the late Pleistocene sands to the late Pliocene-early Pleistocene suite (site II) and from the Icy Complex to the marine sediments (site VI). At the same time, where the Alas horizons overlay marine deposits there is no change in methane, both layers contain similar levels of methane.

Continuity in methane also occurs when going from the late Pliocene-early Pleistocene or marine sediments to the underlying late Pliocene sands (sites I, IV-VI). When the Holocene alluvial sediments overlay the late Pleistocene Icy Complex or when the latter is over the middle Pleistocene one (site I, III), the CH_4, concentration is again continuous, and equal to trace level.

The methane concentration does not appear to be correlated to any textural or chemical characteristics of the sediments, age, or the depth of burial. The methane content does not exhibit any systematic trend with depth that would suggest a deep subsurface source or penetration downward from the surface. Unlike CO_2, which is found in all layers, CH_4 shows a distinct and alternating pattern with depth (site IV). In a generalized geological cross-section, in which all the geological layers exist in chronological order, methane-containing layers would be sandwiched between layers free of methane (mostly the Icy Complexes).

The fact that for at least several hundreds of thousands years methane has not diffused from the methane-rich layers into adjacent layers which are devoid of methane implies that there is negligible diffusion of methane in the permafrost under both present and past conditions. We can estimate an upper limit on the diffusion of methane by using the profile shown in Fig. 2 (site I). The methane profile in sediments that are from 0.6 to 3 million years old retain structure over length scales of about 3 m. The relationship between time (T), and distance diffused (x), is given by $T = x^2/D$, where D is the diffusion coefficient. From this relationship we calculate that D must be less than 10^{-13} m^2/s, i.e. the upper limit on the diffusion of methane through permafrost is surprisingly low. The calculation, as well as sandwiched methane distribution, conflict with the data of Starobinets and Murogova [8].

Evidence from the Bovanenkovskoe natural gas fields (West Siberia) further supports our conclusion that methane does not diffuse through the permafrost. Firstly, the methane fluxes determined from the tundra surface over natural gas reservoirs [9] are similar to reviewed [10,11] fluxes from the tundra surface in non gas-bearing regions. Secondly, the methane concentration in near-surface permafrost here [9] exhibits the same discontinuous pattern with concentrations similar to those observed in Table 1.

We tested one explanation for the absence of methane diffusion by searching for a phase change, as indicated by a enthalpy deficit, when a CH_4-containing sample was heated and compared to an otherwise identical methane-free control. Two permafrost samples (one was degassed for use as a control) from the same depth, ice content (20%) and weight (20 g) were placed in hermetically sealed ml tubes. To characterize any phase changes we employed differential thermal analysis utilizing a cryostat MK-70 (Germany). This instrument can maintain temperature scanning rates as low as 0.5°C /h and as a result the temperature gradient within the samples is negligible. In the experiments we increased the temperature from -12 to +4°C. As the temperature increased, gas analysis for methane was conducted at temperature increments of 0.5°C. If methane were merely adsorbed onto the grain surfaces it would be gradually released and no discrete phase change would be expected. If instead the methane is bound, presumably in a hydrate, then its release will be accompanied by heat absorption. The results of our experiments (Fig. 3) are consistent with methane released from a hydrate.

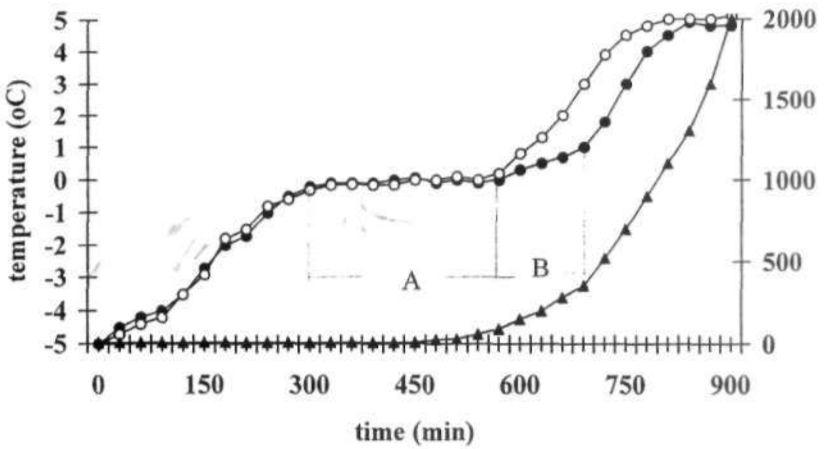


Figure 3. Temperature history and CH_4 release from laboratory experiments to determine methane form

From the initial temperature of -12°C until approximately 0°C (the melting point of the samples) the methane content in the head space did not increase. During and after melting we observed that the temperature of the control sample (previously degassed) increased faster than the temperature of the methane-containing sample. The temperature profile of the sample exhibited a period of constant temperature as would be expected during a phase change occurring near 0°C. We discount the melting of water as the source of the phase change observed only in the sample because both the control and the sample had identical ice fractions. Furthermore, there was an abrupt release of methane associated with this phase change. As the sample was heated to higher temperatures the methane released increased smoothly and no further temperature plateaus were recorded.

Results indicate that there exists a low pressure form of methane hydrate in permafrost. One implication of this is that samples of high pressure methane hydrate should contain this low pressure form of hydrate even after degassing at atmospheric pressure. To test this conclusion we obtained cores from gas-hydrate bearing fields in Mackenzie Delta. The presence of methane-hydrate was reported [12] in these samples, and methane, released when the pressure was reduced varied from hundreds to thousands of ppm. We obtained samples form these cores that had been stored frozen for several years with no further release of CH4 We analyzed a number of these samples identically to our permafrost samples. The results (Table 2) show the presence of additional methane, in concentrations up to 5 ml-CH_4/kg, was released abruptly when the samples melted.

Table 2. Methane released from Mackenzie Delta deep core samples after melting. (High pressure methane hydrate had been previously removed).

DH "Taglu"		DH "Unipkat"	
depth, m	CH_4, ppm	depth, m	CH_4, ppm
17.90-18.05	21000	9.46-9.54	0
38.72-38.80	0	20.50-20.55	28735
44.82-44.87	6143	29.25-29.32	21549
49.93-50.01	7183	41.18-41.25	49512
114.88-114.94	154525		
124.27-124.31	117 225		
128.98-129.03	58187		
143.93-144.02	15200		
155.81-155.87	144856		
175.85-175.90	79162		
182.73-182.79	151544		
203.02-203.09	102176		
206.85-206.93	19720		
215.10-216.02	42539		
220.81-220.90	21812		
250.28-250.36	13633		
253.30-253.38	92067		
323.00-323.05	61329		
326.48-326.55	221150		
344.50-344.58	41484		
357.60-357.65	0		

One possible way to reconcile our observations of methane hydrate formation at low pressures with the theoretical requirement for stability only at high pressures is to assume that, within the pore spaces of the permafrost, high pressures are created by the freezing process and that it is within these zones of high pressure that the methane hydrate is located. The matrix formed by the sediment grains in permafrost may be crucial to the formation of these intrapore high-pressure zones. In the pore spaces methane concentration possible much higher than it was measured in the sample. This provides methane/water ratio sufficient for methane hydrate formation.

Field investigations show a discontinuous CH_4 distribution in permafrost sediments. Even though the detailed nature and phase status of methane in permafrost is not fully understood, its layered distribution can be utilised for palaeo-reconstructions. Methane in sediments is produced only by a specific group of strictly-anaerobic methanogenic bacteria[13]. The trace level of methane in the syngenetically frozen deposits in both Icy Complexes implies that the surface soil conditions were unfavourable either for methane production or accumulation. Such conditions would have been characteristic of dry grasslands of the tundra-steppe landscape[14], which have long vanished from the Arctic north.

The modern analogue of these sediments is the present day alluvial deposits. In these sediments, below the active layer (0.5 m), methane concentrations are at trace levels, while in the active layer methane is produced each year and lost to the atmosphere. The efficiency with which methane present in the active zone is incorporated into the permafrost depends on several factors. At the start of each winter a small layer of the active zone becomes permanently frozen. In steady state this layer corresponds to the sediments accreted during the summer. By early winter methane production has ceased due to low temperatures. If the active layer is thin, the flux of methane from the sediments is large enough to reduce the methane concentration to trace levels. These data corespondent with alluvial origin of late Pleistocene Icy Complex [15].

The methane profile suggests that during the second half of Pliocene and the beginning of the Pleistocene conditions were not as cold and dry as during the formation of the Icy Complexes. Under these conditions the active layer would be expected to be much deeper and hence able to trap methane at the permafrost boundary with greater efficiency. In addition, the increased variability of climate at this time could be expected to produce localised melting and lake basins. In these basins methane concentrations would be high.

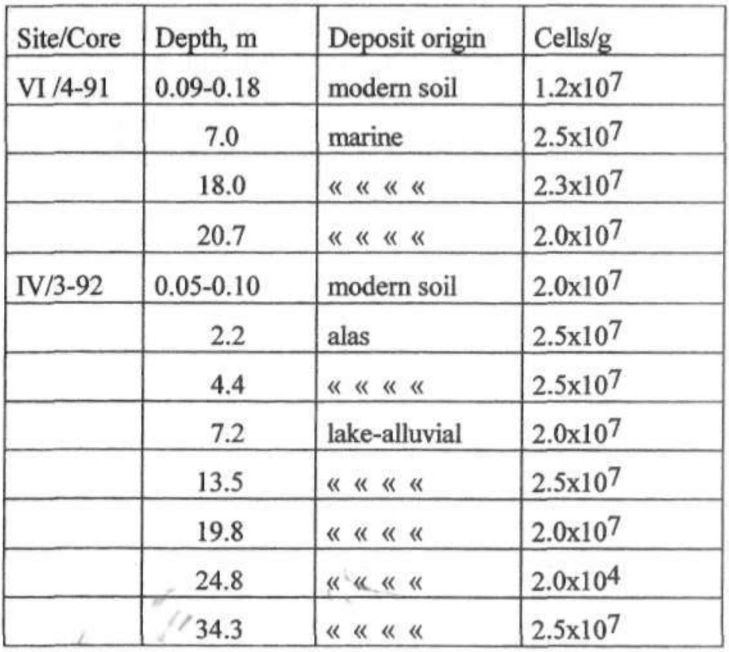
The traces of methane in river bed deposits and eolian sands can be explained because, under these conditions, no methane appears to have been generated, owing to the absence of reducing conditions - as seen in modern analogues. The presence of methane in marine sediments can be explained by anoxic conditions on the bottom of lagoons (Table 3).

As a marker biogenic methane survey even in Antarctic permafrost: it could be found in frozen lake sediments and never found in deposits of fluvial or eolian origin (Table 4).

During the Holocene optimum, when thawing extended to a depth of several meters in the upper late Pleistocene sediments, conditions were favourable for reducing processes, and methane was produced. This is why the Alas formation and "covered" layer may provide a model that can be used to estimate the increase of methane production within an expanded active layer. If our analyses are correct we would expect that methane production would increase significantly if climatic conditions returned to level of the Holocene thermal maximum.

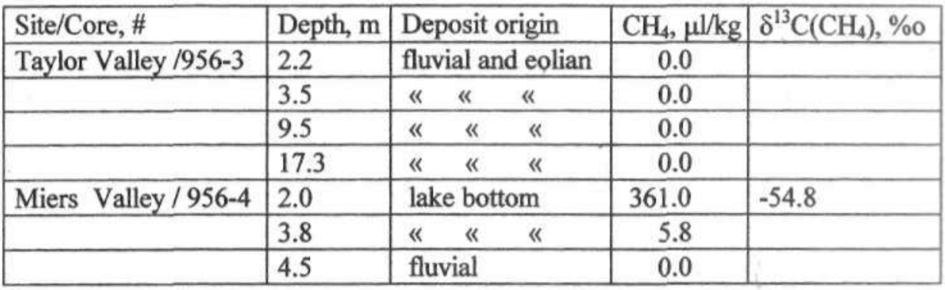
We note that melting of the permafrost will result in the release of this ancient methane hydrate, as well as in retain activity of viable methanogens, preserved in permafrost [16] in addition to any increased production of methane in the active zone [17]. This is in fact observed on northeasten Eurasia exposures under present

Table 3. The number of methanogens in Kolyma lowland permafrost



Site/Core	Depth, m	Deposit origin	Cells/g
VI /4-91	0.09-0.18	modern soil	$1.2\text{x}10^7$
	7.0	marine	$2.5\text{x}10^7$
	18.0	« « « «	$2.3\text{x}10^7$
	20.7	« « « «	$2.0\text{x}10^7$
IV/3-92	0.05-0.10	modern soil	$2.0\text{x}10^7$
	2.2	alas	$2.5\text{x}10^7$
	4.4	« « « «	$2.5\text{x}10^7$
	7.2	lake-alluvial	$2.0\text{x}10^7$
	13.5	« « « «	$2.5\text{x}10^7$
	19.8	« « « «	$2.0\text{x}10^7$
	24.8	« « « «	$2.0\text{x}10^4$
	34.3	« « « «	$2.5\text{x}10^7$

Table 4. Methane in Antarctic Dry Valleys permafrost



Site/Core, #	Depth, m	Deposit origin	CH_4, µl/kg	$\delta^{13}C(CH_4)$, ‰
Taylor Valley /956-3	2.2	fluvial and eolian	0.0	
	3.5	« « «	0.0	
	9.5	« « «	0.0	
	17.3	« « «	0.0	
Miers Valley / 956-4	2.0	lake bottom	361.0	-54.8
	3.8	« « «	5.8	
	4.5	fluvial	0.0	

conditions with an associated release of about 40 mg-CH_4/day [18], which is of similar magnitude to the direct production in present Arctic tundra [10,11]. In discontinuous permafrost in Alaska, where frozen and thawed sections are found in the same exposures, methane is present only in the frozen part. It has also been suggested that in this area methane escapes during the melting of frozen ground[19].

We note in closing that the formation of methane clathrate in frozen sediments at low pressures has implications beyond Arctic studies. Similar processes may represent important reservoirs of methane on other icy bodies in the solar system, in particular in the surface materials of comets [5,20].

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