Origin of shallow gas in Skagerrak and Kattegat - evidence from stable isotopic analyses and radiocarbon dating

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In the Danish coastal waters of northern Kattegat - southern Skagerrak, methane occurs both within sediments and as numerous gas seeps. Stable isotopic analysis of methane collected from 5 gas seeps (δ^{13}C; -64.7 to -69.0‰; δ^2H; -173 to -205‰) and 6 piston cores (δ^{13}C; -71.3 to -91.4‰; δ^2H; -157 to -195‰) shows that the gas is microbial in origin. ^{14}C dating has demonstrated that the seepage gas is generally much older (19,000 to >44,000 yr BP) than the gas in the gas-bearing sediments (540 - 2570 yr BP). The seepage gas is derived from the thick marine Eemian sediments that underlie the low permeable glacial deposits. Methane in the gas-bearing sediments have been formed in-situ and differences in ^{14}C ages of the methane at different are mainly controlled by the age of the organic matter in the sediment. Down slope sediment transport on the southern slope of Skagerrak has led to locally high methane production due to high burial efficiency of organic matter and very narrow zones of sulphate reduction. Methane seeps reported from this area which contain the youngest methane (540 yr BP) analysed so far are therefore not due to migration of deeper old gases.

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Introduction

Methane occurs widely in the northern Kattegat - Skagerrak region (Fig. 1). Seeps of methane from the sea floor are observed in Kattegat (Laier et al. 1992, Dando et al. 1994a) and gas-bearing sediments are found in large areas of the Kattegat and Skagerrak (Fält, 1982, van Weering, 1982, Hovland, 1991). Gas seeps occur characte-

Fig. 1. Location map. Gas-bearing sediments shown as light shaded areas. Piston core sample stations indicated by solid circles. Open circles represent gas seeps and/or methane-derived carbonate cement in coarser sediments. Sampling stations for seepage gas are denoted by A - E. F shows the site of seepage gas studied by Dando et al. (1994a).

ristically where thin (<10m), relatively coarse-grained, Holocene sediments overlie glacial deposits (Laier et al. 1991). In general, gas seeps are not observed in areas with thick, fine-grained, Holocene deposits (Laier et al. 1992). This is probably due to the fact that the buoyancy of the gas is insufficient to overcome the high capillary forces of the narrow pore-throats in fine-grained sediments. Consequently the gas cannot migrate as free gas. Diffusion of gas will occur in these sediments but diffusion rates are much lower than migration rates; thus, methane will not reach the sea floor as it is completely oxidised due to sulphate reduction in the upper layers. The methane seeps are most likely derived from small accumulations of gas in the Eemian below the compacted glacial deposits which seal the reservoirs (Laier et al. 1992). ^{14}C ages of >39,000 years BP of the methane from seeps confirm its pre-Holocene origin (Dando et al. 1994a). Methane-derived carbonate cements are commonly associated with the methane seeps (Jørgensen 1989). Evidence for the presence of most gas seeps (Fig. 1) stems from observations of these cemented sediment 'reefs' rather than direct observation of gas bubbles.

Gas-bearing sediments are observed on acoustic profiles from areas with thick fine-grained deposits. The presence of methane in the sediments from some of these areas has been confirmed by piston coring (e.g. Jørgensen et al. 1990); however, no study has yet been carried out to determine the origin of the gas.

Gas-bearing sediments exist north of the area outlined by van Weering (1982) (Fig. 1). Dando et al. (1994b) recorded gas within the upper 3 m of sediment using deep-towed boomer and sediment coring in an area between PC127 and PC128 (Fig. 1). Within this area, methane seeps
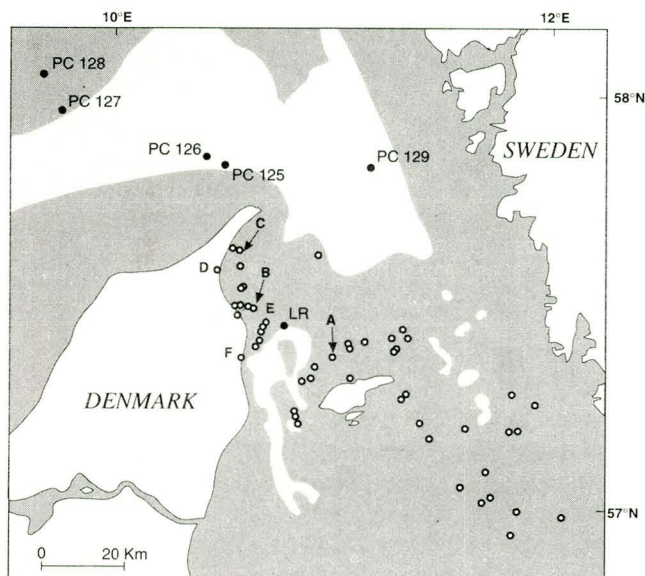
have been reported to occur, particularly near site PC128 (Flügel & Callsen-Cencic 1992, Dando et al. 1994b) This is the only area where gas seeps in fine-grained sediments have been observed in the Skagerrak-Kattegat region. Methane with an isotopic value of $\delta^{13}C = -80.3$ ‰ was obtained from the upper 10 cm of sediment from one seep by Schmaljohan et al. (1990). The stable carbon isotopic value clearly shows this methane to be of microbial origin.

In this paper we present the results of gas analyses, including stable isotopic analyses, and radiocarbon dating of methane from gas seepages and gas-bearing sediments, in order to determine the origin of these gases. Radiocarbon dating has also been carried out on organic matter which is the likely precursor of methane in the fine-grained sediments, in order to elucidate the likely mechanism for the occurrence of gas seepages in the fine-grained sediments at site PC 128..

Sampling and methods

Seepage gas

Gases from submarine seepages were collected in 100 ml steel cylinders equipped with two valves using a sampling device constructed by the Geological Survey of Denmark. The sampling device consist of 4 steel cylinders and a large plastic funnel mounted on a rack with lead weights. The top valves of the cylinders are connected to the funnel which is placed on the sea floor above a gas seepage. Both valves on the sample cylinders are open and gas conducted through the funnel replaces the water in the cylinders. Both valves are closed when gas starts to flow from the bottom valve. The emplacement of the sampling device and the closing of the valves are performed by scuba divers.

Piston cores

Six piston cores, 1.4 - 2 m long and 6 cm in diameter, were taken in the Kattegat and the Skagerrak during a cruise of R/V Svanic (University of Gothenburg) in September 1991 and April 1992 (Table 1). The sediments were recovered

in PVC liners using a Kullenberg piston corer. The liners were sealed with end caps as soon as possible after the cores were retrieved.

For quantitative analysis of the gas content, a subsample (2 ml) was taken from the end of the core (core catcher) immediately (< 5 min.) after it arrived on deck. The sample was transferred to a 15 ml serum flask containing 2 M sodium hydroxide solution (5 ml) and the flask was sealed with a crimp cap. The mixture was allowed to equilibrate and the gas phase was analysed by gas chromatography.

Gases for chemical and isotopic analyses were extracted for each 10 cm of the core by means of 60 ml plastic syringes which penetrated the PVC liner through 4 mm holes drilled just before attaching each syringe. A spring was mounted on the plunger of the syringe in order to overcome friction and to maintain a slight sub-atmospheric pressure inside the syringe. Gas extraction was usually completed within 15 to 60 minutes. In many cases, a small amount of sediment (0-3 cm³) was forced into the syringe due to the overpressure in the core liner. However, the sediment did not block the slow flow of gas into the syringes. The gas was transferred to a serum flask and analysed on board by gas chromatography.

It is worth considering to what extent the gas extracted from the piston cores represents *in situ* gas in the sediment at each level. The following observation made during the gas extraction suggests that the gas does represent *in situ* gas at the level where it was taken. Once the syringe penetrated the core liner, gas steadily flowed into the syringe. Drilling new holes in the liner for more syringes (10 cm apart) did not affect the gas flow rate in the syringes already attached to the liner. Furthermore, with the exception of PC128, no gas flowed into the syringes placed in the upper 90 - 120 cm of the core where methanogenesis does not occur (Jørgensen et al. 1990). Thus, it may be concluded that the sediment completely filled the core liner and that the gas that flowed into the syringe came from a relatively narrow sediment interval.

Organic matter

For sediment analyses a 30 cm³ sub-sample was taken at 10 cm intervals through the core using a 60 ml tipless syringe. The sub-samples were withdrawn through a 30 mm hole in the liner, which was cut just before the removal of each sub-sample. A 30 cm³ wood-plug (30 mm in diameter) was then fitted into the hole and the hole in the liner was sealed with tape. The sub-samples were stored in 100 cm³ cans in a freezer for onshore laboratory analysis.

Chemical analyses

Gas chromatography was performed using a Microlab GC82 gas chromatograph equipped with a thermal conductivity detector (TCD). Separation of the gas compo-

Table 1. Sample stations.

Station	Coordinates north	east	Water depth m	Sample type	length cm
PC125	57° 51.96'	10° 19.97'	95	piston core	137
PC126	57° 53.48'	10° 14.27'	83	-	182
PC127	57° 59.06'	9° 42.8'	170	-	142
PC128	58° 58.22'	9° 39.81'	340	-	212
PC129	57° 49.10'	11° 10.05'	47	-	220
LR	57° 26.69'	10° 43.09'	26	-	180
A	57° 25.19'	11° 00.86	12	seepage gas	
B	57° 30.58'	10° 35.27	10	-	
C	57° 38.99'	10° 31.01	4	-	
D	57° 35.54'	11° 25.46	0	-	
E	57° 28.31'	10° 37.39	12	-	

nents was carried out on 2 columns packed with molecular sieve 5A and Porapac C using helium (60 ml/min) as the carrier gas.

TOC. For determination of total organic carbon (TOC), 200 mg of dry sediment sample was treated with hot hydrochloric acid in order to remove the carbonate. The sample was then heated to 1000-2000 °C in pure oxygen and the weight percent organic matter was calculated using the amount of CO_2 measured by an infra-red detector.

Isotopes and ^{14}C dating

Gases. For stable carbon isotope analysis, methane was separated from the other gas components and combusted over copper oxide at 900 °C. The resulting CO_2 and H_2O was purified cryogenically and isolated in sealed glass and quartz tubes, respectively. H_2O was reduced by Zn at 700 °C to give H_2 and measurement of the stable isotopic ratios, $^{13}C/^{12}C$ and $^2H/^1H$, were carried out on a Finnigan Mat 251 mass spectrometer at the University of Copenhagen. The results are reported in the usual delta notation relative to the PDB and SMOW standards δ(‰) = 1000xR/(R-1), where R = $^{13}C/^{12}C$ or $^2H/^1H$.

A larger quantity of methane (approx. 2 ml STP) was combusted for ^{14}C dating. The CO_2 formed was then reduced to graphite with hydrogen over cobalt at 700 °C and the ^{14}C concentration was determined in an accelerator mass spectrometer at the University of Århus.

Organic matter was isolated for ^{14}C dating by removing most of the inorganic matrix by consecutive treatment of approximately 30 g of sample with hydrochloric acid and hydrofluoric acid. Organic matter isolated from the sediments was combusted at 700 °C in a stream of pure oxygen over a Ni catalyst. The resulting carbon dioxide was reduced to graphite and the ^{14}C concentration measured. The ^{14}C age was calculated using the international convention (Stuiver & Polach 1977).

Results

Sediments

The sediments in most piston cores consist of homogeneous brownish-grey to greenish-grey silty clays with dark iron sulphide below 50 to 70 cm bsf. The hydrogen sul-

Table 2. Methane concentration in pore water.

Station	Methane* mmol/l	Solubility** mmol/l
PC125	13	18
PC127	12	33
PC128	26	65
PC129	14	9

* Measured on subsample from core catcher.
** Calculated from the equation given by Duan et al. (1992).

Table 3. Gas extracted from piston cores.

Core	Depth cm bsf	Gas ml	CH₄ vol%	N₂ vol%	O₂ vol%	CO₂ vol%	Gas ml	CH₄ vol%	N₂ vol%	CO₂ vol%	δ¹³C$_{CH4}$ ‰PDB	δ²H$_{CH4}$ ‰SMOW
PC125	90	3	29.78	56.63	13.50	0.09	1.1	78.6	21.2	0.2	-91.4	-170
	100	15	70.93	23.48	4.56	1.02	11.9	89.8	8.9	1.3	-91.4	-178
	110	15	73.29	21.79	4.24	0.68	12.1	91.1	8.1	0.8	-90.9	-159
	120	3	57.30	33.89	8.62	0.19	1.8	94.9	4.8	0.3		
	130	12	60.75	30.64	7.54	1.07	7.8	93.0	5.4	1.6	-90.9	-159
PC126	100	17	71.52	23.11	4.63	0.74	13.4	90.9	8.2	0.9	-90.1	-172
	110	17	78.49	16.51	3.56	1.43	14.2	93.9	4.4	1.7	-90.5	-182
	120	130	83.27	14.36	1.61	0.76	120.4	89.9	9.2	0.8	-90.2	-179
	130	80	88.27	9.59	1.40	0.74	74.8	94.4	4.9	0.8	-90.9	-178
	140	15	75.68	18.89	4.39	1.04	12.0	94.8	3.9	1.3	-91.3	-176
	150	25	88.85	8.77	1.81	0.56	22.9	96.9	2.5	0.6	-91.3	-177
	160	20	88.46	9.06	2.17	0.31	18.0	98.3	1.4	0.3	-90.7	-179
	170	30	83.78	12.91	2.73	0.59	26.2	95.8	3.5	0.7	-90.0	-173
	180	22	72.22	22.29	5.14	0.36	16.8	94.6	5.0	0.5	-89.7	-180
PC127	110	8	82.04	14.68	1.90	1.37	7.3	89.9	8.6	1.5	-89.2	-181
	120	2	64.35	28.37	5.20	2.09	1.5	84.6	12.7	2.7		
	128	12	48.41	39.81	10.21	1.57	6.4	91.3	5.7	3.0	-88.0	-175
	137	11	71.40	22.61	4.55	1.43	8.7	90.3	7.9	1.8	-87.9	-185
PC128	10	5	60.79	30.67	7.77	0.76	3.2	94.6	4.2	1.2		
	20	30	72.13	22.05	5.31	0.51	22.7	95.4	3.9	0.7	-82.6	-184
	30	25	70.92	22.88	5.75	0.44	18.4	96.4	3.0	0.6	-82.7	-189
	40	5	74.85	20.09	4.45	0.60	4.0	94.1	5.1	0.8		
	50	120	90.00	7.69	0.87	1.44	115.2	93.7	4.8	1.5	-83.0	-190
	60	85	85.74	11.13	1.86	1.28	77.7	93.7	4.9	1.4	-82.7	-184
	70	46	83.64	12.94	2.69	0.73	40.3	95.5	3.7	0.8	-82.8	-191
	80	34	76.69	18.32	4.56	0.43	26.9	97.0	2.4	0.5	-82.8	-193
	90	56	90.35	7.15	1.23	1.26	52.8	95.8	2.9	1.3	-83.3	-190
	100	39	83.56	12.93	3.08	0.43	33.5	97.4	2.1	0.5	-83.6	-195
	110	20	85.80	9.91	1.87	2.43	18.3	93.9	3.5	2.7	-83.3	-194
	120	22	86.04	10.29	1.47	2.20	20.5	92.3	5.4	2.4	-83.2	-183
	130	48	82.39	13.07	3.27	1.27	40.8	97.0	1.5	1.5	-83.1	-164
	140	57	81.77	13.16	3.31	1.76	48.3	96.4	1.5	2.1	-83.1	-
	150	56	90.25	6.21	1.30	2.24	52.6	96.0	1.6	2.4	-82.9	-190
	160	15	84.92	9.46	2.01	3.61	13.6	93.6	2.5	4.0	-82.8	-192
	170	35	85.26	8.75	1.93	4.06	31.9	93.6	2.0	4.5	-82.3	-190
	180	37	84.45	11.03	3.05	1.47	31.8	98.2	0.1	1.7	-82.4	-191
	190	36	87.66	8.16	2.46	1.72	31.9	98.8	-0.8	1.9	-82.1	-190
	200	135	89.93	5.84	1.28	2.95	127.0	95.6	1.3	3.1	-82.2	-186
PC129	120	14	94.01	3.78	1.06	1.15	13.3	98.8	0.0	1.2	-73.8	-189
	130	6	26.80	56.84	15.86	0.50	1.6	99.1	-1.0	1.9		
	140	13	66.74	25.11	7.01	1.14	8.8	98.5	-0.2	1.7	-72.5	-182
	150	13	81.22	13.46	3.52	1.80	10.9	96.9	0.9	2.1	-72.5	-173
	160	15	85.53	10.16	2.81	1.50	13.1	98.2	0.1	1.7	-72.5	-186
	170	20	93.48	3.36	1.00	2.16	19.1	98.0	-0.2	2.3	-72.3	-157
	180	28	94.42	2.59	0.75	2.24	27.0	97.8	-0.1	2.3	-72.0	-185
	190	29	92.93	3.76	0.86	2.45	27.9	96.8	0.7	2.5	-71.3	-183
	200	22	88.16	7.11	1.82	2.92	20.2	96.2	0.6	3.2	-71.8	-183
	207	7	49.16	39.83	10.36	0.64	3.7	93.9	4.8	1.2	-72.2	-181
LR	109	6	47.61	44.11	7.91	0.62	3.8	74.2	24.8	1.0		
	119	11	59.53	35.19	4.52	0.76	8.6	75.0	24.0	1.0		
	129	17	66.42	25.83	6.41	1,34	12.2	93.9	4.2	1,9		
	149	20	74.15	20.28	4,35	1.23	16.0	92.5	5.9	1.5		
	159	28	79.13	15.51	4.06	1.31	23.0	97.1	1.3	1.6		
	169	24	64.88	27.16	6.47	1.50	16.8	92.1	5.8	2.1	-80,1	-193
	175	5	32.52	52.87	14.60	0.67	1.7	95.6	2.5	2.0		

phide smell was detected only in cores PC128 and LR. The smell was particularly strong in core LR, which had a thin black layer in the top 7 cm. Black iron sulphide was also seen in the uppermost 100 cm of PC128, although brownish-grey silty clay with some lamination occurred from 103 to 143 cm bsf. From 143 to 207 cm bsf, black iron sulphide was seen in PC128 with the exception of a single 5-8 mm stringer of silt at 150 cm bsf.

The organic matter content (TOC: 0.6 - 2.1 %) was only determined on the three samples for which ^{14}C dating was carried out (Table 6).

Gases

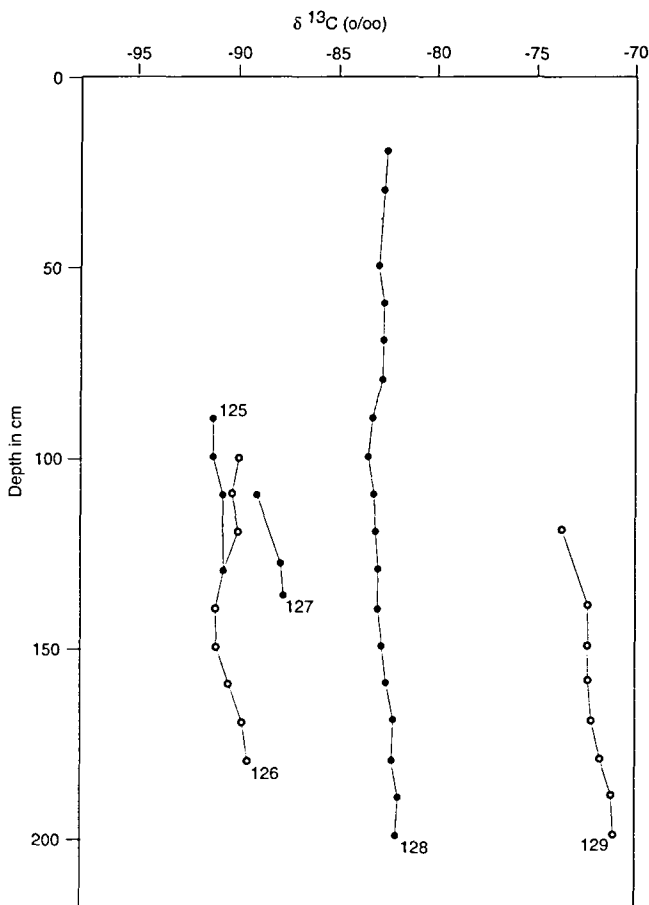*Piston core gases.* The concentration of methane in the

Fig. 2. Stable carbon isotopic ratio of methane vs. depth.

Seepage gases. The seepage gases consist of methane (96.2 - 98.7 vol%) with a little nitrogen (0.5 - 1.7 vol%) and carbon dioxide (0.6 - 2.0 vol%) plus traces of oxygen (Table 4). The oxygen may be due to a small contamination of the seepage gases during sampling.

Stable isotopes

The stable carbon isotopic ratio of methane from the piston cores did not vary significantly with depth (Fig. 2), but fairly large differences in $\delta^{13}C$; -71.3 to 91.4 ‰, were found for the different sample stations (Table 3). Hydrogen isotopic ratios of the methanes (δ^2H; -157 to -195 ‰) did not differ significantly either with depth or location (Table 3). Methane from the gas seepages was generally isotopically heavier with respect to carbon ($\delta^{13}C$; -64.7 to - 73.6 ‰) (Table 4) compared to methane from the piston cores.

^{14}C ages

The ^{14}C age was determined on the deepest methane sample obtained from each of the six different piston cores (Table 5). The ^{14}C ages (940 to 2970 yr BP) have been corrected for a reservoir effect of 400 yr. Marine

Table 4. Seepage gas.

Station	CH_4 vol%	N_2 vol%	CO_2 vol%	O_2 vol%	$\delta^{13}C_{CH4}$ ‰ PDB	δ^2H_{CH4} ‰SMOW
A	96.2	1.7	2.0	0.1	-68.3	-193
B	98.4	0.6	0.8	0.2	-64.7	-191
C	96.5	2.8	0.6	0.1	-69.7	-173
D	96.3	2.9	0.6	0.2	-73.6	-205
E	98.7	0.5	0.8	0.0	-69.0	-176

Table 5. ^{14}C age of methane.

ID No AAR	Station	Depth cm bsf	14C age BP	corr. for reservoir effect
Piston core gas				
787	PC125	130	1430±110	1030
789	PC126	180	1650±100	1250
790	PC127	137	1500±120	1100
791	PC128	200	940±110	540
788	PC129	207	2970±140	2570
945	LR	169	2965±105	2565
Seepage gas				
233	A	sea floor	>44000	-
711	B	-	>39000	-
784	C	-	28000±370	27600
786	D	coast	23000±340	22600

pore water, calculated from the headspace analyses of sealed sub-samples taken from the core catcher, varied from 12 to 26 mmol/l, being highest for the greatest water depth (Table 2). The solubility of methane in pore water at the same water depths ranges from 9 to 65 mmol/l, as calculated from the equation of Duan et al. (1992) assuming normal sea-water salinity and a temperature of 5 °C.

The volume of gas extracted from different levels of the piston cores varied from 2 to 135 ml, but no trend with respect to sediment depth was observed for any of the cores (Table 3). No gas was extracted from the upper 90-120 cm of the piston cores, with the exception of core PC128 which contained gas in excess of atmospheric pressure over its entire length. The main constituents of the gas were methane (26.8 - 94.4 vol%) and nitrogen (2.6 - 56.8 vol%). The presence of oxygen (0.8 - 15.9 vol%) in the gas is most likely due to atmospheric contamination of the samples, and gas compositions corrected for air are also shown in Table 3 to give a better representation of the gases in the sediment. The negative numbers for nitrogen in some of the samples are due to the analytical uncertainty of the gas analyses. The corrected gas composition shows that methane makes up over 90 vol% in most samples, which also contain a few per cent nitrogen and carbon dioxide.

Table 6. Total organic carbon (TOC) and ^{14}C age of organic matter.

ID No AAR	Station	Depth cm bsf	TOC %	14C age BP effect ‰	corr. for reservoir	$\delta^{13}C$
950	PC126	180	1.0	6440±170	6040	-23.0
951	PC128	200	2.1	2980± 90	2580	-22.6
952	PC129	207	0.6	9950±130	9550	-25.0

samples are influenced by the apparent age of CO_2 in seawater, which is affected by both young CO_2 in the atmosphere and older CO_2 from re-mineralisation of organic matter. The balance between these two contributions typically makes the ^{14}C age of marine samples appear 400 yr older than contemporaneous terrestrial matter (Stuiver et al. 1986). Using this correction, it is assumed that all of the methane is formed from carbon derived from marine organic matter. Corrected methane ^{14}C ages varied from 540 to 2570 years (Table 5), the oldest methanes being found in the Kattegat.

The ^{14}C ages of the seepage gases were generally much older (23,000 to >44,000 yr BP) than the piston core gases (Table 5). The ^{14}C contents (relative to modern carbon) of methane from gas seeps A and B were low (<0.42% and <0.78%) compared to the background level of the instrument (0.2 - 0.5%); therefore, no finite ^{14}C ages were assigned to these two gases.

The ^{14}C ages of organic matter, 180 - 207 cm bsf, from piston cores PC126, PC128 and PC129 varied from 2980 to 9950 yr BP (Table 6), the oldest organic matter being found in the Kattegat (PC129).
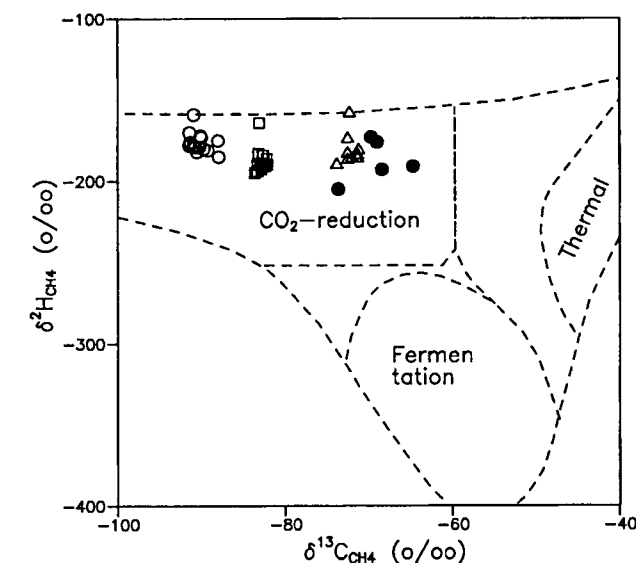

Fig. 3. Stable carbon and hydrogen isotopic ratios plotted on the classification scheme of Whiticar et al. (1986). Circles = PC125, PC126 and PC127; squares = PC128; triangles = PC129; solid circles = seepage gases.

Discussion

Piston core gases

Analyses of gases in the sediments are usually performed by extracting the gas from core subsamples which are placed in sealed containers (e.g. Jørgensen et al. 1990). The cores recovered during the cruise in September 1991 had to be kept in sealed core liners for onshore investigation. The gas was therefore extracted into syringes though tiny holes, 10 cm apart, in the liner. Thus, the gas collected may derive from any part of the core in the liner. However, from the observations made during extraction of the gases described above, and from the fact that gas was only extracted from the sediment depth where methanogenesis is known to occur (Jørgensen et al. 1990, Dando et al. 1994b), we conclude that the gas collected in the syringes derives from a relatively narrow interval of the core.

The methane concentration below the sulphate reduction zone increases rapidly (e.g. Claypool & Kvenvolden 1983) and acoustic profiles from the Kattegat and Skagerrak indicate that free gas exists at shallow depths below the sea floor (Fält 1982, van Weering 1982). The concentration of methane in the pore water (Table 2) shows that free gas is most likely present at 2 m bsf at site PC129 in Kattegat. The pore waters of the cores from greater water depths in the Skagerrak are not saturated with respect to methane at those depths. This, however, does not prove that free gas is not present in these sediments, since some methane is likely to have escaped from the core during retrieval. The concentrations of methane in pore water in the piston cores (Table 2) greatly exceed that of methane solubility at atmospheric pressure, ca 1.5

mmol/l (Duan et al. 1992). The supersaturation with respect to methane ranges from 10.5 (PC127) to 24.5 mmol/l (PC128). Expressed as the volume of gas, this corresponds to 0.20 to 0.47 ml of methane per ml of sediment, assuming a sediment porosity of 80 pct, which is equivalent to 56 to 133 ml of gas per 10 cm of core. Comparing these volumes with the volumes of gas collected in the syringes (Table 3), one sees that only of fraction of the gas assumed to be present in the pore water was actually collected. The methane concentrations within the methanogenic zone may vary, but the large variation in volumes of gases extracted at different levels is most likely due to inhomogeneities in the core. Such inhomogeneities may have been induced by the pressure drop and gas expulsion during retrieval of the core.

The gases collected from piston cores consist mainly of methane (Table 3) when the measured values were corrected for air. However, a few samples contained significant amounts of nitrogen, up to 24.8 vol%. The corrected nitrogen contents are probably not very representative of the gases in the sediment, particularly for those samples which contained a large percentage of air. However, the nitrogen content from all cores except PC129 appears to be higher than one would expect from analytical uncertainty. The nitrogen contents were highest for the cores which had a distinct smell of hydrogen sulphide, particularly core LR. Labile sulphide compounds may have reacted with oxygen and as a result the amount of air calculated from the oxygen content will be underestimated. The highest nitrogen contents may therefore be due to the fact that we have underestimated the contents of the air in those samples.

Origin of gases

The stable isotopic values of carbon and hydrogen in the methane (Fig. 3) clearly point to a microbial gas formed via carbon dioxide reduction (Whiticar et al. 1986). The fairly large variation in the stable carbon isotopic ratio of methane obtained from the different piston cores, $\delta^{13}C$; -71.3 to - 91.4‰ (Fig. 2), may be due to different $\delta^{13}C$ values of the carbon dioxide reduced to methane by the bacteria, and does not provide a clue as to how much of the gas has been generated in the sediment and how much may have migrated into the sediment. Radiocarbon dating of methane offers a much better possibility to discriminate between gases formed in situ and migrated gases. Indeed, the difference in the ^{14}C ages of the two types of gases is very significant, the seepage gases being much older (22,600 to >44,000 yr BP) compared to the piston core gases (540 to 2570 yr BP) (Table 5).

The high ^{14}C ages of the seepage gases reported here are in line with the ^{14}C ages, >39,000 to >44,000 yr BP, of the seepage gases from the shallow subtidal site (Fig. 1) investigated by Dando et al. (1994a). Thus, the results of radiocarbon dating of the seepage gases are in accordance with the assumption that the gases derive from Pleistocene sediments (Laier et al. 1992).

Sediment accumulation rates at the different piston-core sampling stations were calculated by Kunzendorf et al. (1994) using the ^{210}Pb and ^{137}Cs methods. Using their accumulation rates we find that the sediments are significatly younger, 170 - 340 yr, than the methane contained in the sediments. The reason for this difference may by either that older methane has migrated into the sediment or that the carbon dioxide reduced by the bacteria forming the methane may be older than the sediment itself. Most carbon dioxide in the pore waters of sediments derives from degradation of organic matter. The age of the organic matter in the sediments was therefore also determined by radiocarbon dating. It turned out that the organic matter is considerably older (2580 - 9550 yr BP) (Table 6) than the sediment as well as the methane contained in the sediments.

The older ages of the organic matter are probably the result of there beeing significant amounts of older terrigenous organic matter present in the sediments (Anton et al. 1993, Kuijpers et al. 1993). The stable carbon isotopic values for the organic matter (Table 6) also indicate the presence of considerable amounts of terrigenous organic matter. Sedimentary organic carbon with $\delta^{13}C$ values of -24 to -32 ‰ is generally considered to have a continental origin, whereas organic matter of marine origin has $\delta^{13}C$ values between -10 and -22 ‰, most often between -19 and -21 ‰ (Sackett 1964, Stein 1991). Both ^{14}C age data and $\delta^{13}C$ data point to an increase in the terrigenous fraction of the organic matter in moving from the Skagerrak to the Kattegat; PC128-PC126-PC129. Detailed analysis by pyrolysis gas chromatography also shows a more terrigenous type of organic matter in the Kattegat than in the Skagerrak (J.B. Koefoed, pers. comm.

1995). The old ^{14}C ages of the methane may be explained by a contribution from the terrigenous organic matter to the methane. This may appear a little surprising, considering the old age of the terrestrial organic matter and the fact that it has probably been subjected to aerobic degradation for a long time. However, as pointed out by Henrichs & Reeburgh (1987), anaerobes are capable of degrading certain compounds that are stable under aerobic conditions, and this may explain why old terrigenous organic matter is still reactive when buried in marine sediments.

In situ vs migrated gas

Læsø Rende, LR (Fig. 1), represents a local depression containing gas-bearing fine-grained sediments in an area where numerous gas seepages are known to occur. This area was therefore considered to be the most suitable site for examining the possible effects of gas migration in fine-grained sediments. The ^{14}C age of the methane from LR, 2565 yr BP, is similar to that of the methane from the other site in the Kattegat (PC129) which is far away from any known gas seepages; therefore, the age of the methane at LR does not indicate any significant contribution of older gases from the underlying Pleistocene sediments.

The reason for performing the investigations at LR was that one might hope to obtain a clue as to how methane seepages could form in fine-grained sediments, such as those reported for the area around PC128 (Flügel & Callsen-Cencic 1992, Dando et al. 1994b). However, the investigation at LR failed to provide any information on why such seepages may form. Furthermore, the age of the methane collected at PC128 was significantly younger than the gases from any of the other sites. The ^{210}Pb data for the PC128 suggested that the accumulation rates varied with time (Kunzendorf et al. 1994) and that this might be the reason for the occurrence of gas seeps. Because of this it is worthwhile to consider how accumulation rates may affect methane generation in marine sediment.

The effect of sediment accumulation rates on methane generation

Methane formation in marine sediments essentially starts when sulphate has been exhausted, because sulphate-reducing bacteria compete more efficiently for the common substrate, H_2, than the CO_2-reducing bacteria. Henrichs & Reeburgh (1987) estimated that methane generation accounts for approximately 12% of the anaerobic decomposition of organic matter in marine sediments. This figure represents a mean of a very wide range of values. In deep-sea sediments, sulphate has been detected down to 700 m bsf (Claypool & Kvenvolden 1983) and the fraction of organic matter that ends up as

methane is virtually zero in such an enviroment. This is due to the very low rates of accumulation in the deep sea. The higher accumulation rates on the continental shelf empirically lead to higher burial efficiency of the organic matter and thus to an increase in the relative amount of methane formed. Methane formation becomes relatively more important with increasing sedimentation rate, because less sulphate will be available for sulphate reduction due to the shorter time for exchange of constituents between pore water and sea water. Assuming no exchange between pore water and sea water, we estimate that sulphate reduction using the sulphate initially present in the pore water will account for only 50% of the anaerobic decomposition of organic matter in a sediment containing 80% porewater and 1% TOC. Thus, 50% of the potentially degradable organic matter may end up as methane at very high sedimentation rates. In our calculation we assume that only a half of the organic matter in the upper sediment will decompose under anaerobic conditions. The data of Kuijpers et al. (1993) and Henrichs & Reeburgh (1987) show that approximately a half of the organic matter in the upper sediments will decompose during burial.

Methane seepage at PC128

Methane was found thorugout the entire length of piston core PC128, suggesting that the zone of sulphate reduction must be very thin at this site. Very high sulphate reduction rates were measured in this area (Dando et al. 1994b) where black sulphide layers occur in places on the sea floor together with a certain pognophore containing methane-oxidising bacteria. Jørgensen et al. (1990) demonstrated that the thickness of the sulphate reduction zone generally varies with sedimentation rate in the Kattegat - Skagerrak region with the thinner zones being associated with the lowest sedimentation rates. Thus, there seems to be a paradox at site PC128 - the large quantities of methane point to a high rate of sedimentation whereas the thin zone of sulphate reduction indicates a low sedimentation rate. This paradox may be resolved if one assumes that the sedimentation rate has varied considerably with time due to downslope sediment transport on the fairly steep slope in this area. Large amounts of fresh organic material may be buried in the zone of methanogenesis during the formation of turbidites, and this may explain the rather large quantities of methane that are occasionally found in these areas. The very high sulphate reduction rates reported by Dando et al. (1994b) may lead to a faster depletion of sulphate in the pore waters compared to the replenishment of sulphate from sea water, e.g. by benthic activity, which may lead to methane formation at shallow sediment depths. The occurrence of the discrete seepages of methane reported may be due to re-exposure of the methanogenic zone due to down-slope sediment transport, as pointed out by Dando et al. (1994b).

Conclusions

Methane from gas seepages and from gas-bearing sediments in the Kattegat -Skagerrak region is microbial in origin. The seepage gas is much older than the gas in the gas-bearing sediments, and the ^{14}C ages point to a pre-Holocene source for the seepage gas. Methane in gas-bearing sediments is older than the sediment that contains the gas. This is due to a certain contribution from older organic matter present in the sediment in the formation of methane. The methane seeps reported from the southern slope of Skagerrak are due to very high formation rates of methane, which are in turn due to very high rates of sedimentation as a result of down-slope sediment transport.

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