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9. ORGANIC GEOCHEMISTRY OF SURFACE SEDIMENTS OF THE SULU TRENCH/PHILIPPINES[1]

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INTRODUCTION

During cruise SO 58 of the FRG research vessel *Sonne* in 1988, surface sediments were collected from the deep waters of the Sulu Trench (Philippines) for organic geochemical investigations. The purpose of geochemical analyses of surface sediments is to obtain information on the nature and origin of gaseous hydrocarbons detected in these sediments and from this information to estimate the hydrocarbon potential of the Sulu Trench.

In this paper molecular composition, gas concentrations, and stable isotope analyses, including both carbon and hydrogen, are used to characterize light hydrocarbons in marine surface sediments of the Sulu Trench. In addition, sulfate concentrations of interstitial waters and the redox potential of the sediment support gas geochemical interpretations.

METHODS

Marine sediments were obtained by piston and gravity coring. Several sediment samples of about 300 g each were collected from the individual cores. The redox potential was measured *in situ* using a calibrated Eh-probe. The samples were subsequently degassed on board in a blender apparatus by an acid/vacuum treatment described by Faber and Stahl (1983). Desorbed hydrocarbon gases were collected in glass bulbs for isotopic analyses at the BGR (Bundesanstalt für Geowissenschaften und Rohstoffe) Laboratory. Gas chromatographic FID (Flame Ionization Detector) analyses were carried out on board using a Shimadzu GC-Mini-3 chromatograph provided with a 30-m capillary column (Megabore type). The gases were injected into the GC using gas-tight syringes of 0.1 to 1 mL volumes. For the calibration of the GC measurements, a standard gas mixture was used that contained alkanes methane to pentane and the alkenes ethene and propene.

Gas samples were analyzed for their carbon and (if possible) hydrogen isotope ratios at the BGR laboratory. The individual gas components were separated chromatographically and combusted to CO_2 and H_2O using a preparation technique described by Dumke et al. (1989). The stable isotope measurements on the combustion product CO_2 was carried out using a Finnigan MAT 250 mass spectrometer. The combustion production H_2O was reduced to H_2 by reaction with zinc in sealed glass tubes at 450°C. For the subsequent deuterium analyses, a Finnigan Delta mass spectrometer was used. Carbon and hydrogen isotope ratios are reported in reference to the PDB (Pee Dee Belmenite) and SMOW (Standard Mean Ocean Water) standard, respectively.

Interstitial waters were squeezed out of the sediments on board using a sediment press of the University of Kiel, FRG, applying pressures of 5 to 8 bars. For the subsequent fixation of dissociated sulfur ions, Zn acetate was added. The analyses of the sulfate content of the pore waters were carried out at the BGR Laboratory using standard titration methods.

RESULTS AND DISCUSSION

Two areas were selected within the Sulu Trench for geochemical investigations. They are located offshore Negros Island (Negros Trench) and off Zamboanga Peninsula (Zamboanga Trench).

Negros Trench

A total of 12 sediment cores were obtained from offshore Negros Island (Fig. 1). Geochemical analyses were carried out on 43 sediment samples from sub-bottom depths varying between 55 and 1380 cm (Table 1). The negative redox-potential values (Table 1) are indicative of a reducing environment. Methane concentrations (Table 2) are controlled by bacterial activity, which is indicated by the stable isotope data (Fig. 2, Table 3) and the reverse trend of sulfate and methane concentrations with increasing depth (Fig. 3, Tables 2 and 4). Within the sulfate zone, methane concentrations are low because methanogens are inactive in the presence of sulfate (Claypool and Kvenvolden, 1983). After the sulfate is almost completely consumed, bacteria start methane production (an example from Core KL 52 is given in Fig. 3).

Methane is generated by CO_2 reduction, as indicated by carbon and hydrogen isotope analyses (Fig. 2). Methane that migrates from the methane production zone into the sulfate zone seems to be altered by bacterial consumption via sulfate reduction (Whiticar and Faber, 1986). This is indicated by the decrease of ^{12}C with decreasing sediment depth and increasing sulfate concentrations (Fig. 3). Methane-consuming bacteria preferentially consume the lighter isotope (Whiticar and Faber, 1986). The association of high methane and sulfate concentrations in KL-71 (Tables 2 and 4) is artificial because samples were collected from sediments disturbed by the coring process. However, this does not affect the stable isotope data of methane, which points to bacterial CO_2-reduction as the source for methane.

Gas components from methane to butanes were found in all sediment cores (Table 2). This indicates a thermogenic origin of the higher homologues in samples where C_{3+} concentrations exceed background (Fig. 4). The low level of organic maturity implies that these components migrated from greater sediment depth where organic matter reached the appropriate maturity for thermal hydrocarbon generation. A general increase of gas concentrations with increasing sediment depth is observed for most cores (examples are Cores KL 49 and KL 52, Table 2) leading to background concentrations in the upper part of the individual cores. This is attributed to a diffusion effect caused by concentration differences between the sediment and the ocean water.

Zamboanga Trench

Thirteen cores were collected offshore Zamboanga Peninsula (Fig. 1). We analyzed 26 gases from sediments of reducing environments (indicated by the negative redox-potential values, Table 5) for their molecular composition (Table 6). Except for Samples KL 86-1, KL 86-3, KL 97-2, KL 98-1, KL 101-1, and Core KL 105, all of which contained higher amounts of methane, only background concentrations were measured for components from methane to butanes (Table 6). The isotope data of methane in samples with high methane concentrations indicate a bacterial generation from CO_2 reduction (Fig. 2, Table 7). Although sulfate data are rare, the correspondence between high sulfate and low methane concentrations in Core KL 96 (Tables 6

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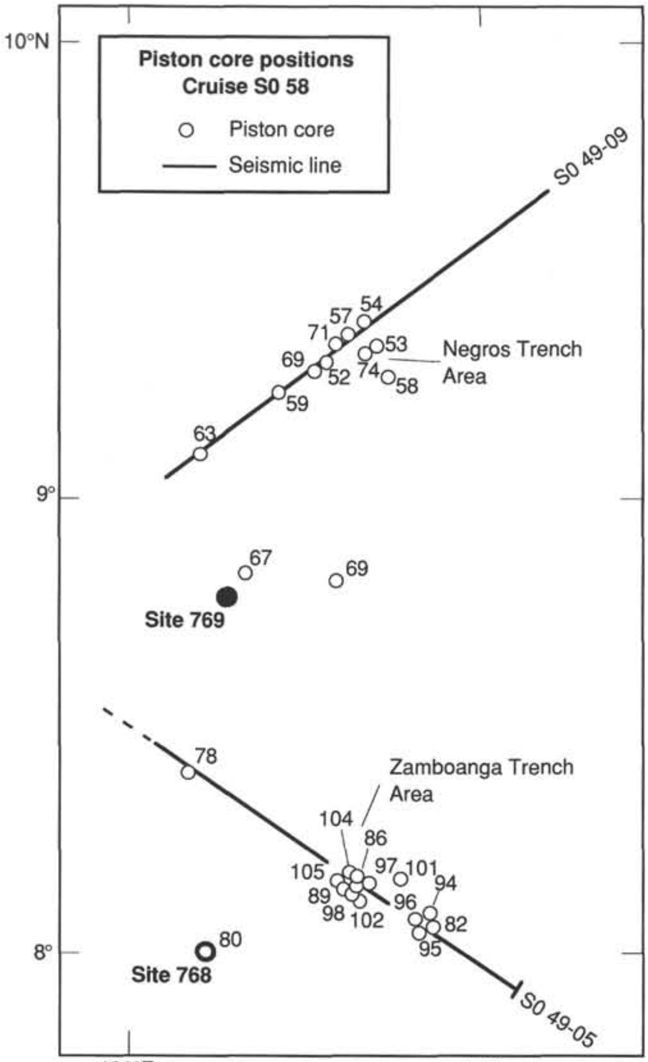

Figure 1. Sampling locations for Cruise SO 58.

Table 1. Sediment depth and type, and redox potential (Eh) of piston core samples from the Negros Trench (Philippines).

Sample	Sediment depth (cm)	Sediment type	Eh (mV)
KL49-1	790	silty clay	−117
KL49-2	590	silty clay	−134
KL49-3	390	silty clay	−108
KL52-1	1340	silty clay	−182
KL52-2	1130	silty clay	−160
KL52-3	935	silty clay	−128
KL52-4	735	silty clay	−171
KL52-7	130	silty clay	−140
KL53-1	235	stiff silty clay	−67
KL54-1	1280	stiff silty clay	−45
KL54-2	1080	stiff silty clay	−178
KL54-3	880	stiff silty clay	−102
KL54-6	280	stiff silty clay	−140
KL57-1	1380	stiff silty clay	−120
KL57-2	1150	silty clay	−129
KL57-4	275	clay	−100
KL58-1	1370	stiff clay	−141
KL57-2	1170	stiff clay	−163
KL57-6	370	soft clay	−127
KL59-1	1360	clay	−77
KL59-2	1150	clay	−73
KL59-3	945	clay	−97
KL59-4	755	clay	−100
KL59-7	155	clay	−43
KL63-1	1360	silty clay	−90
KL63-2	1180	sandy clay	−70
KL63-5	380	sandy clay	−54
KL67-1	1230	sandy clay	−30
KL67-3	825	sandy clay	−110
KL67-6	225	silty clay	−86
KL69-1	1355	clay	−83
KL69-3	955	silty clay	−113
KL69-6	355	silty clay	−107
KL71-1	955	silty clay	−402
KL71-3	755	silty clay	−350
KL71-5	555	silty clay	−218
KL71-8	255	silty clay	−403
KL71-10	55	silty clay	−384
KL74-1	1065	silty clay	−400
KL74-3	890	sandy clay	−420
KL74-5	765	sandy/silty clay	−407
KL74-8	465	sandy clay	−363
KL74-10	265	sandy silty clay	−157

and 8) implies that bacterial methanogenesis is controlled by sulfate concentrations. One exception is KL 101, which contains 622 ppb methane concurrent with high sulfate level (2300 mg/L). This can be attributed to core disturbance during coring.

Regional Distribution of Thermogenic Hydrocarbons

Significant concentrations of homologues propane to butane (C_{3+}) in surface sediments are indicative of thermogenic hydrocarbon generation at greater sediment depth and migration into surface sediments (Stahl et al., 1986). This is the case in the Negros Trench where the average C_{3+} concentrations in the sediments exceed the normal background level and are higher than in the Zamboanga Trench, where no significant C_{3+} concentrations (except for Core KL 105) have been observed (Figs. 4 and 5). The low C_{3+} concentrations offshore Zamboanga are attributed to diagenetic processes at low temperatures in the surface sediments. The source for the thermogenic hydrocarbons offshore Negros can be terrestrial organic matter transported by turbidites into the Sulu Basin in previous geological periods and buried deeply during the formation of the basin. It is assumed that there does not exist a well-defined source rock but rather a number of organic-matter-rich turbidites, similar to the situation that we have observed in Sabah, East Malaysia (unpubl. results). A recent turbidite transport was observed in many surface sediment samples during our study in the Sulu Trench.

Hinz and Block (this volume) report the highest thermal gradients for the Negros Trench and lower gradients for the Zamboanga Trench. It is obvious that the depth of thermogenic hydrocarbon generation changes regionally in the Sulu Trench. Given higher thermal gradients in the Negros Trench, hydrocarbon generation (HCG) occurs at a shallower sub-bottom depth than in the Zamboanga Trench. The migration distance from the presumed generation zone to the surface sediments is therefore shortest in the Negros Trench. A shorter vertical migration distance, higher permeability of the sediments above the HCG zone, and perhaps a different time of the onset of HCG may be responsible for the preferential occurrence of thermogenic gas components in the surface sediments of the Negros Trench.

CONCLUSIONS

The dominant factor of methane generation in the surface sediments of the Sulu Sea is bacterial activity toggled by sulfate concentrations in the pore water.

Isotopic composition of methane indicates a bacterial CO_2 reduction mechanism. Thermogenic C_{3+} components in significant concentrations are observed almost exclusively in the Ne-

Table 2. Gas concentrations in sediment samples from the Negros Trench (Philippines).

Sample	Sediment depth (cm)	CH_4 (ppb)	C_2H_6 (ppb)	C_3H_8 (ppb)	iC_4 (ppb)	nC_4 (ppb)	ΣC_4 (ppb)
KL49-1	790	22.4	4.6	2.3	1.4	1.0	2.4
KL49-2	590	16.2	2.8	1.6	0.7	0.7	1.4
KL49-3	390	11.2	1.9	1.0	0.5	0.5	1.0
KL52-1	1340	2870.9	7.2	3.5	0.0	7.1	7.1
KL52-2	1130	84.2	10.7	5.9	2.5	3.5	6.0
KL52-3	935	39.4	9.1	5.0	1.8	2.4	4.2
KL52-4	735	31.0	7.2	3.9	1.8	1.8	3.6
KL52-7	130	11.2	1.8	1.0	0.0	0.5	0.5
KL53-1	235	20.3	4.5	2.3	1.1	1.1	2.1
KL54-1	1280	3838.7	15.6	9.6	n.d.	n.d.	n.d.
KL54-2	1080	2452.8	8.0	5.2	n.d.	n.d.	n.d.
KL54-3	880	104.8	11.7	5.9	0.4	2.6	3.1
KL54-6	280	17.4	2.4	1.3	0.0	0.0	0.0
KL57-1	1380	22.5	4.3	2.3	1.1	1.1	2.2
KL57-2	1150	15.9	3.3	1.8	1.1	0.8	1.9
KL57-4	275	19.8	3.5	1.9	1.0	1.0	2.0
KL58-1	1370	4274.6	6.7	3.3	1.8	1.5	3.3
KL58-2	1170	39.9	5.6	2.5	1.2	1.6	2.8
KL58-6	370	17.8	2.9	1.6	0.6	1.0	1.6
KL59-1	1360	17.3	3.6	1.9	0.7	0.9	1.6
KL59-2	1150	21.3	4.5	2.4	1.0	1.4	2.3
KL59-3	945	15.8	3.3	1.9	0.0	0.9	0.9
KL59-4	755	12.1	2.6	1.5	0.9	0.7	1.7
KL59-7	155	15.2	3.1	1.6	0.8	0.7	1.5
KL63-1	1360	13.7	2.8	1.5	0.7	0.9	1.5
KL63-2	1180	7.2	1.4	0.8	0.0	0.4	0.4
KL63-5	380	6.2	1.3	0.7	0.0	0.0	0.0
KL67-1	1230	8.6	3.8	2.8	1.9	1.1	3.1
KL67-3	825	6.4	2.4	1.9	1.1	0.7	1.8
KL67-6	225	4.3	0.8	0.7	1.1	0.0	1.1
KL69-1	1355	33.7	7.7	3.7	1.7	1.7	3.3
KL69-3	955	12.9	2.7	1.3	0.0	0.6	0.6
KL69-6	355	11.4	2.0	1.1	0.0	0.5	0.5
KL71-1	955	2908.9	8.7	3.4	1.1	1.5	2.6
KL71-3	755	587.6	8.2	4.6	n.d.	n.d.	n.d.
KL71-5	555	912.6	4.6	2.3	n.d.	n.d.	n.d.
KL71-8	255	1788.7	5.5	2.8	n.d.	n.d.	n.d.
KL71-10	55	88.2	4.1	2.3	1.0	1.0	2.0
KL74-1	1065	10256.8	8.5	0.4	n.d.	n.d.	n.d.
KL74-3	890	6628.9	8.5	0.0	n.d.	n.d.	n.d.
KL74-5	765	75.3	6.1	0.0	0.0	0.0	0.0
KL74-8	465	24.6	3.7	1.6	0.0	0.0	0.0
KL74-10	265	14.4	2.7	1.6	0.0	0.6	0.6

Note: Concentrations are reported as $(g_{gas}/g_{wet\ sediment}) \times 10^9$. n.d. = no data.

Table 3. Stable isotope data of methane (Negros Trench, Philippines).

Sample	Depth (cm)	$\delta^{13}C_1$ (ppt)	δD_1 (ppt)
KL49-1	790	−51.6	
KL52-1	1340	−97.8	−195
KL52-2	1130	−72.3	
KL52-3	935	−43.3	
KL52-4	735	−48.0	
KL53-1	235	−45.5	
KL54-1	1280	−94.0	−191
KL54-2	1080	−97.5	−183
KL57-1	1380	−51.1	
KL58-1	1370	−92.9	−185
KL58-2	1170	−57.9	
KL59-1	1360	−53.3	
KL69-1	1355	−53.3	
KL71-1	955	−62.3	
KL71-3	755	−81.1	−151
KL71-5	555	−83.0	−190
KL71-8	255	−81.1	−191
KL71-10	55	−77.2	
KL74-1	1065	−81.8	−187
KL74-3	890	−88.7	−179
KL74-5	765	−79.0	
KL74-8	465	−60.3	
KL76-1	160	−48.7	

gros Trench, where thermal gradients are higher than in the Zamboanga Trench.

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Table 4. Sulfate concentrations in interstitial waters of the Negros Trench (Philippines).

Sample	Depth (cm)	Sulfate (mg/L)	Sample	Depth (cm)	Sulfate (mg/L)
KL49-1	790	2130	KL58-7	270	1930
KL49-2	590	2240	KL59-1	1360	1650
KL49-3	390	2520	KL59-2	1150	1870
KL49-4	190	2350	KL59-3	945	1990
KL52-1	1340	10	KL59-4	755	2190
KL52-2	1130	210	KL59-5	555	2100
KL52-3	935	570	KL59-6	355	2190
KL52-4	735	870	KL59-7	155	n.d.
KL52-7	130	2180	KL63-1	1360	2430
KL54-1	1280	0	KL63-2	1180	n.d.
KL54-2	1080	70	KL63-5	380	2390
KL54-3	880	420	KL71-1	955	160
KL54-4	680	890	KL71-3	755	1440
KL54-6	280	2600	KL71-5	555	1850
KL57-1	1380	1330	KL71-8	255	1170
KL57-2	1150	n.d.	KL71-10	55	1780
KL57-4	275	n.d.	KL74-1	1065	90
KL58-1	1370	80	KL74-3	890	110
KL58-2	1170	230	KL74-5	765	760
KL58-3	970	620	KL74-7	565	1540
KL58-4	770	1070	KL74-8	465	n.d.
KL58-5	570	1340	KL74-10	265	2030
KL58-6	370	1710	KL76-1	160	2110

Note: n.d. = no data.

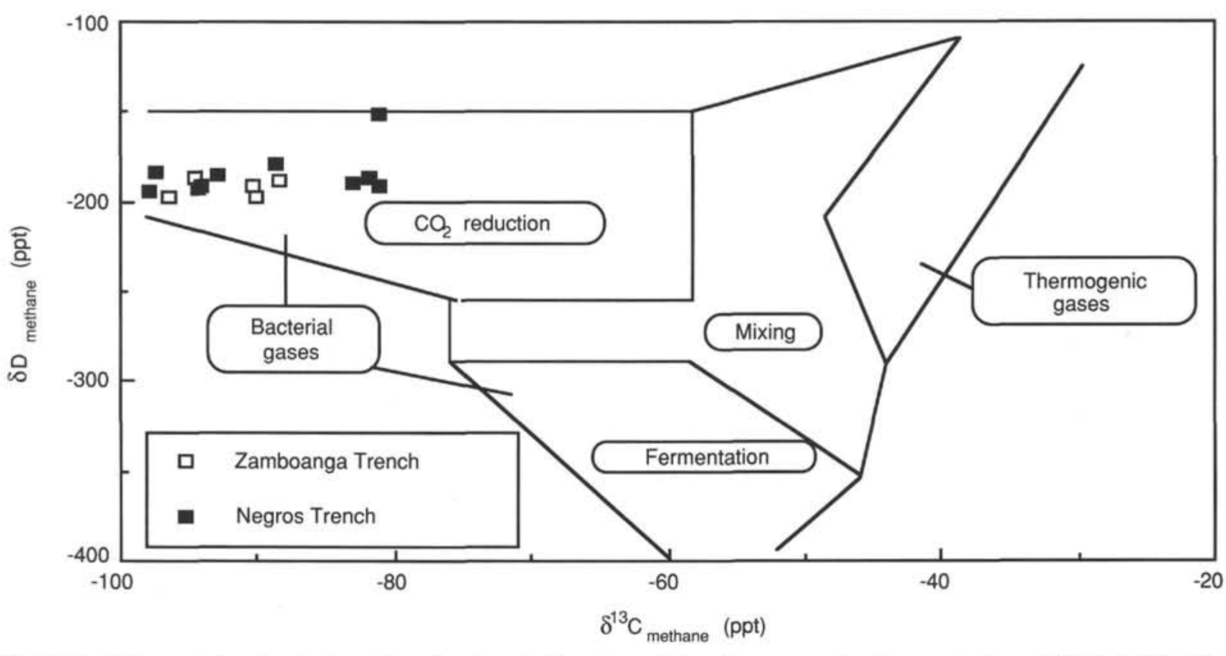

Figure 2. Hydrogen and carbon isotope data of methane indicate bacterial methane generation from reduction of CO_2 in the Negros and Zamboanga trenches (diagram modified after Whiticar and Faber, 1986).

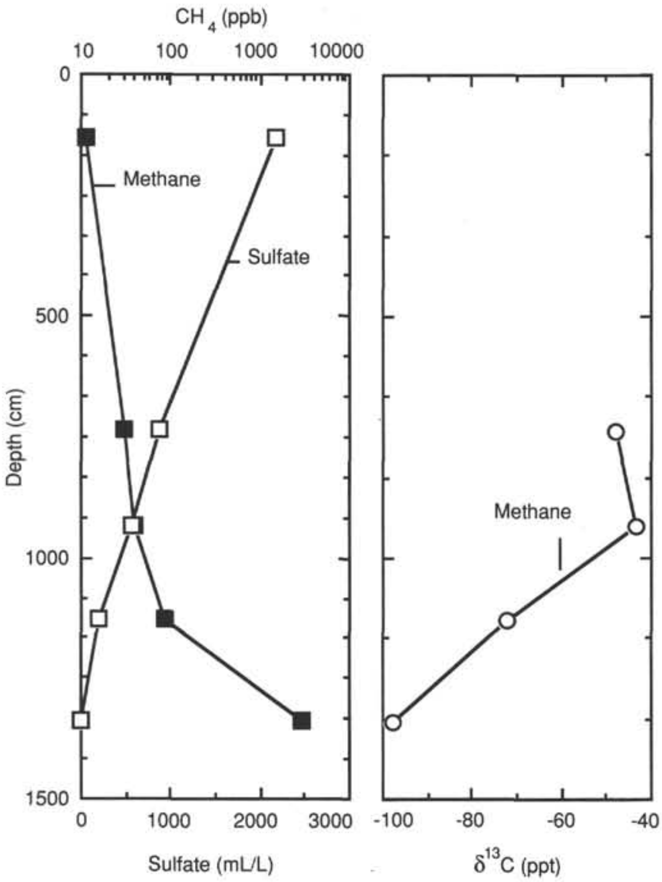

Figure 3. Within the sulfate zone of Core KL 52, methanogens are inactive. Bacterial generation of methane starts when sulfate concentrations are low. The stable isotope data of methane shows an increase of ^{13}C with decreasing sediment depth at the transition from the methane generation zone to the sulfate reduction zone, indicating a preferential consumption of the lighter isotope during bacterial oxidation of migrated methane.

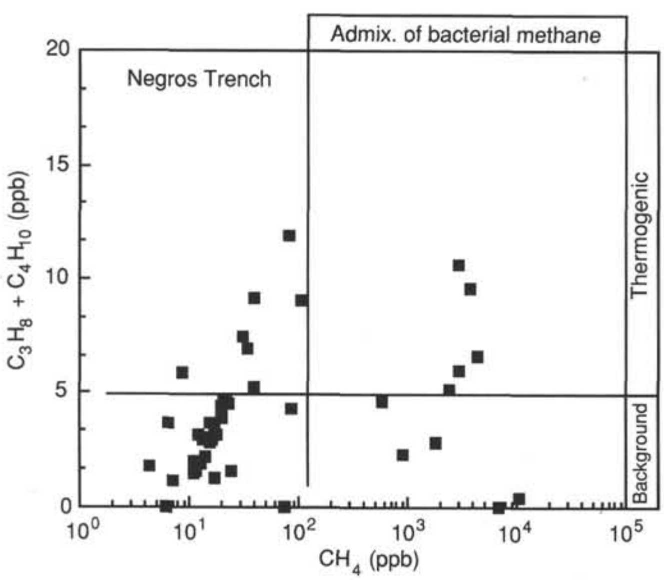

Figure 4. Gas concentrations in sediments from the Negros Trench. Samples with more than 100 ppb methane are influenced by bacterial methane.

Table 5. Sediment depth and type, and redox potential (Eh) of piston core samples from the Zamboanga Trench (Philippines).

Sample	Sediment depth (cm)	Sediment type	Eh (mV)
KL76-1	160	silt	−48
KL78-1	1400	silty clay	−14
KL78-7	100	silty clay	−100
KL80-1	1260	silty sandy clay	−20
KL80-5	260	sandy clay	−77
KL82-1	1345	sandy clay	−113
KL82-5	345	sandy clay	−131
KL86-1	110	sandy clay	−132
KL86-3	132	sandy clay	n.d.
KL86-2	55	sandy clay	−93
KL89-1	220	sandy silty clay	−108
KL94-1	1300	stiff sandy clay	−43
KL94-7	100	calc sandy clay	−97
KL96-1	1130	silty clay	−95
KL96-6	130	sandy clay	−131
KL97-1	90	clay	−135
KL97-2	40	clay	−135
KL98-1	145	clay	−125
KL101-1	635	stiff silty clay	−346
KL101-3	380	silty clay	−324
KL101-6	55	stiff silty clay	−250
KL102-1	850	clay	−82
KL102-4	270	soft clay	−98
KL102-1	850	clay	−82
KL105-1	245	clay	−150
KL105-2	100	clay	−130

Table 6. Gas concentrations in sediment samples from the Zamboanga Trench (Philippines).

Sample	Sediment depth (cm)	CH_4 (ppb)	C_2H_6 (ppb)	C_3H_8 (ppb)	iC_4 (ppb)	nC_4 (ppb)	ΣC_4 (ppb)
KL76-1	160	28.3	6.0	2.9	0.0	1.4	1.44
KL78-1	1400	9.7	1.7	1.0	0.0	0.4	0.42
KL78-7	100	7.3	1.5	0.8	0.0	0.4	0.35
KL80-1	1260	5.0	1.4	1.2	0.6	0.5	1.08
KL80-5	260	6.0	1.6	0.9	0.0	0.5	0.54
KL82-1	1345	3.9	0.6	0.4	0.0	0.0	0.00
KL82-5	345	2.9	0.4	0.0	0.0	0.0	0.00
KL86-1	110	16152.6	3.2	3.5	0.0	0.0	0.00
KL86-3	132	6760.5	5.4	3.1	0.0	0.0	0.00
KL89-1	220	12.9	4.5	2.1	1.5	1.2	2.71
KL94-1	1300	9.7	0.8	0.5	0.0	0.0	0.00
KL94-7	100	1.5	0.0	0.0	0.0	0.0	0.00
KL96-1	1130	6.8	1.1	0.6	0.0	0.0	0.00
KL96-6	130	5.4	0.9	0.5	0.0	0.0	0.00
KL97-1	90	17214.0	2.5	2.8	0.0	0.0	0.00
KL97-2	40	927.9	4.2	2.2	0.0	0.0	0.00
KL98-1	145	12152.6	3.4	2.2	0.0	0.0	0.00
KL101-1	635	622.0	7.8	3.4	0.0	0.0	0.00
KL101-6	55	61.5	8.4	4.2	0.0	0.0	0.00
KL102-1	850	18.4	4.0	1.9	0.0	0.0	0.00
KL102-4	270	14.7	2.2	1.0	0.0	0.0	0.00
KL101-3	380	56.6	9.0	4.8	0.0	0.0	0.00
KL102-1	850	14.2	2.2	1.2	0.0	0.0	0.00
KL105-1	245	29.9	13.5	7.0	3.4	3.2	6.61
KL105-2	100	32.4	8.1	4.1	2.3	1.7	4.02

Note: Concentrations are reported as $(g_{gas}/g_{wet\ sediment}) \times 10^9$.

Table 7. Stable isotope data of methane (Zamboanga Trench, Philippines).

Sample	Depth (cm)	$\delta^{13}C_1$ (ppt)	δD_1 (ppt)
KL86-1	110	−94.3	−193
KL86-3	132	−90.3	−191
KL97-1	90	−90.2	−198
KL97-2	40	−88.5	−188
KL98-1	145	−96.5	−198
KL101-1	635	−94.6	−186
KL101-6	55	−61.9	
KL105-1	245	−46.8	
KL105-2	100	−47.6	

Table 8. Sulfate concentrations in interstitial waters of the Zamboanga Trench (Philippines).

Sample	Depth (cm)	Sulfate (mg/L)
KL78-1	1400	1960
KL78-7	100	n.d.
KL86-1	110	40
KL86-2	55	380
KL86-3	132	n.d.
KL94-1	1300	n.d.
KL94-7	100	2390
KL96-1	1130	1950
KL96-3	730	2150
KL96-6	130	2420
KL97-1	90	20
KL97-2	40	300
KL98-1	145	0
KL101-1	635	2300
KL101-3	380	2530
KL101-6	55	2580
KL102-1	850	570
KL102-4	270	2070
KL104-1	110	900

Note: n.d. = no data.

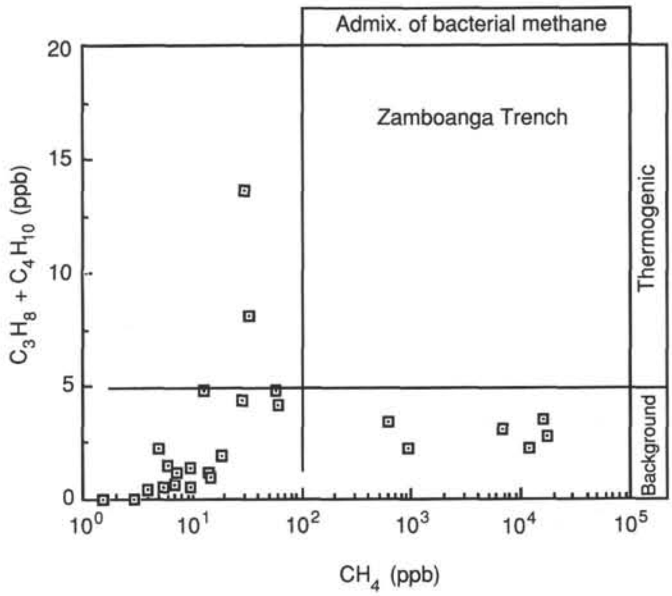

Figure 5. Gas concentrations in sediments from the Zamboanga Trench. Samples with more than 100 ppb methane are influenced by bacterial methane.