GEOCHEMISTRY OF INTERSTITIAL GASES IN QUATERNARY SEDIMENTS OF THE GULF OF CALIFORNIA

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ABSTRACT

Simoneit, B.R.T. and Galimov, E.M., 1984. Geochemistry of interstitial gases in Quaternary sediments of the Gulf of California. Chem. Geol., 43: 151—166.

Interstitial gases from the Deep-Sea Drilling Project (DSDP—IPOD) Leg-*64* Sites *474, 477—479* and *481* in the Gulf of California have been analyzed by gas chromatography and stable-isotope mass spectrometry in order to evaluate their compositions in terms of biogenic and thermogenic sources.

The hydrocarbon gas (C_1—C_5) concentrations were comparable to the shipboard data and no olefins could be detected. The $\delta^{13}C$ data for the CH_4 confirmed the effects of the thermal stress on the sedimentary organic matter, in that the values were typically biogenic near the surface and become more depleted in ^{12}C vs. depth at Sites *474, 478* and *481*. The CH_4 at Site *477* was the heaviest in ^{13}C and at Site *479* it did not show a predominant high-termperature component. The CO_2 at depth from most sites was of a primarily thermogenic origin from carbonate decomposition.

INTRODUCTION

The activity of recent tectonic processes in the Gulf of California area generated extremely diverse thermal conditions within the corresponding sedimentary sequences (Curray et al., 1979, 1982; Einsele et al., 1980). Some of these sediments have such high thermal gradients, that at a depth of several hundred meters subbottom, the in situ temperatures correspond to those of a platform sedimentary sequence which has subsided to a depth of several thousands of meters. Elsewhere within the same sedimentary basin there are areas where the heat flow values do not significantly exceed normal levels. Thus, the geologic conditions of this sedimentary sequence permit the evaluation of thermal effects on the transformation of recent organic matter. The resulting composition of the products from this transformation can be compared with other, more or less constant parameters (e.g., lithology—facies compositions, age of deposits, type and source of organic matter).

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Here we present data for interstitial gases collected during Deep-Sea Drilling Project Leg *64* at the mouth and in the central Gulf of California (Fig. 1).
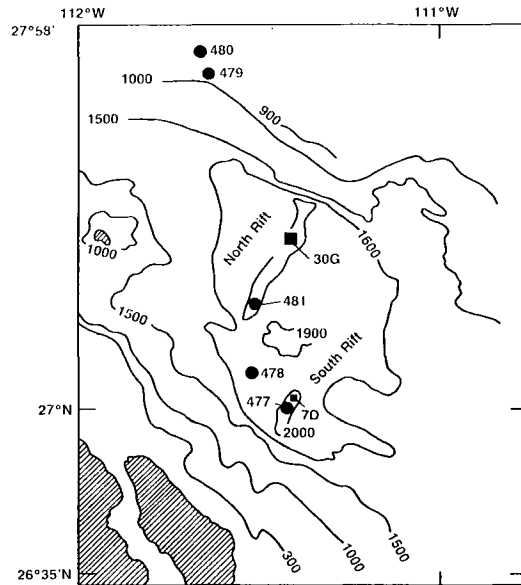

Fig. 1. Location map for the drill sites in the Gulf of California (contours in meters).

EXPERIMENTAL

The interstitial gas samples had been collected onboard the D.V. "Glomar Challenger" in vacutainers (commercial evacuated test tubes) and had also been analyzed there. The samples described in this work were reanalyzed by gas chromatography (GC) for C_1—C_8 hydrocarbons under higher gas chromatographic resolution. The gases had been stored in the same vacutainers from collection to their delivery to the laboratory for analysis.

Quantitative hydrocarbon gas data were obtained using a Hewlett-Packard® model *5830*A reporting gas chromatograph connected to a model *18850*A control terminal. Locking gas-tight syringes (Precision Series A —5.0, 1.0 and 0.25 ml) were used for sample injections. The model *5830*A is a dual column gas chromatograph equipped with a flame ionization detector (FID) for the analysis of C_1—C_8 hydrocarbons (100 pg detection limit) and a thermal conductivity detector (TCD) for H_2, CO, CO_2, CH_4, N_2 and O_2 determinations (100 ng detection limit).

For this work, the FID was operated only, using the following GC conditions: injection temperature 180°C; helium carrier gas (3.6 ml min.$^{-1}$

flow rate, 20 ml min.$^{-1}$ air); column oven programmed from $-50°C$ (2 min. isothermal) to $+10°C$ at $10°C$ min.$^{-1}$, and from $+10°C$ to $100°C$ (45 min. isothermal) at $4°C$ min.$^{-1}$; Durapak® stainless-steel column (n-octane/Porosil C®, 5 m × 0.76 mm I.D.).

The compounds were identified by comparison of their retention times with those of the components of natural gas. The individual compounds of natural gas had been identified by gas chromatography—mass spectrometry (Rohrback, 1979).

The results of these GC analyses are found in Table I. They confirm the shipboard data (cf. Curray et al., 1982), except the methane concentrations are generally lower for the re-analyses due to some loss by diffusion from the vacutainers.

Carbon isotope compositions of CH_4 and CO_2 were measured in the Laboratory of Carbon Geochemistry of the Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences. Barium hydroxide was injected into the vacutainers in order to react with the carbon dioxide. The 5 cm^3 of the remaining gas, sampled by syringe, was introduced into the vacuum system to be incinerated to CO_2 in a furnace consisting of copper oxide heated to $800°C$. The system was equipped with appropriate traps for removal of N_2O, SO_2 and other impurities. The precipitated barium carbonate ($BaCO_3$) was dried and then treated with ortho-phosphoric acid in the standard line and the CO_2 released was used for analysis of the carbon isotope composition. The carbon isotope measurements were performed on a Varian-MAT® model 230 mass spectrometer with an accuracy of $\pm$ 0.1‰ (Galimov et al., 1980). The results are compiled in Table I and are given in the δ notation vs. the PDB standard.

RESULTS AND DISCUSSION

The results of the interstitial gas analyses are found in Table I. The concentrations of CH_4, C_2H_6, C_3H_8 and total C_4H_{10} and C_5H_{12} are comparable to the shipboard data (cf. Curray et al., 1982). No olefinic hydrocarbons were detectable after about three months storage in the vacutainers and the methane concentrations are generally lower due to diffusive loss.

Mouth of the Gulf of California

Sites 474—476 are located at the mouth of the Gulf within the boundary of the continental slope in water depths of 2500—3000 m. Interstitial gas was only present in Site 474 (Simoneit, 1982). The sedimentary sequence at Site 474 is comprised predominantly of hemipelagic diatomaceous oozes with thick interlayers of turbidites, and age ranges from the early Pliocene to Recent. Below 521 m the lithology changed to interlayered dolerites and basalt to a depth of 562.5 m.

The methane concentration exhibits no trend with depth (Fig. 2), how-

TABLE I

Hydrocarbon (C_1–C_5) and carbon dioxide content of interstitial gas samples, with the carbon isotope compositions of methane and carbon dioxide, from the holes drilled in the Gulf of California (DSDP Leg 64)

Site	Core	Section	Subbottom depth (m)	Methane (mg l⁻¹)*¹	δ¹³C (‰)*²	Ethane (μg l⁻¹)	C_2/C_1 (×10⁻⁴)	Propane (μg l⁻¹)	Total C_4H_{10} (μg l⁻¹)	Total C_5H_{12} (μg l⁻¹)	Neopentane (μg l⁻¹)	Carbon dioxide (%)*³	δ¹³C (‰)*²	Δ (Δ = δ¹³C_CO₂ − δ¹³C_CH₄) (‰)
474	3	3	14.5	375	−75.34	75	2.3	10	2.5	8	0.1	4	—	—
474A	9	4	245	355	−49.65	240	8.1	49	15	1.5	—	4	—	—
	12	4	272	83	−40.35	42	6.0	12	5	3.5	—	4	—	—
	24	3	375	361	−59.00	299	10.0	50	17	7	—	2	—	—
	26	2	393	221	−59.96	149	8.1	20	8	—	—	1	—	—
	28	2	413	267	−53.61	175	7.8	25	13	—	—	1	—	—
	40	3	529	0.1	—	—	—	0.5	—	—	—	—	—	—
477	5	1	29.5	400	−67.11	18	0.3	7	2	—	—	7	−10.26	56.9
	5	2	31	516	−65.47	22	0.7	—	—	—	—	17	−6.52	59.0
	7	1	50	0.8	—	5	81	0.3	0.05	1.5	—	0.2	—	—
	16	2	117	5.2	—	39	90	30	21	2	—	8	−10.87	—
	16	3	118	6.6	—	100	34	—	—	—	—	5	−12.19	—
	16	5	120	46	—	207	32	39	8	—	—	15	−11.16	—
	17	1	124.5	36	−44.27	405	44	—	—	—	—	8	−10.44	33.8
	17	2	126	196	−44.39	1,510	55	105	13	2	—	28	−8.22	36.2
	19	2	145.5	145	−28.65*⁴	2,140	56	145	11	1	—	44	−4.00*⁴	24.7
	19	3	147	218	−39.99	1,865	190	161	16	0.5	0.1	32	−11.05	28.9
	20	1	154	194	−44.01	570	21	13	—	—	—	13	−11.81	32.2
	20	2	155	137	−44.40	462	75	14	—	0.5	—	16	−16.43	28.0
	20	CC	163	30	−45.55	600	28	8	—	—	—	3	−13.40	32.2
	22	1	172	369	−45.00	832	16	8	—	—	—	7	−15.44	29.6
	22	2	174	250	−45.08	700	18	—	—	—	—	8	−15.97	29.1
	23	1	182	62	−42.94	159	31	3.5	0.3	0.9	—	1.2	—	—
478	11	3	92	55	−79.17	5	1.0	4	—	—	—	2	—	—
	12	2	100	460	−77.92	—	—	27	0.3	—	—	9	−12.59	65.3
	14	3	121	455	−72.01	35	0.9	7	7	9	—	12	−9.38	62.6

479	*16*	3	140	525	—69.08	—	—
	17	3	149	378	—68.66	34	1.1
	20	4	170	348	—62.46	42	1.4
	21	4	179	566	—64.34	50	1.6
	22	1	184	204	—64.36	35	2.0
	28	2	243	491	—65.66	—	—
	28	3	244	285	—61.93	200	8.4
	31	1	260	122	—65.38	62	6.1
	31	3	263	454	—64.96	180	4
	33	3	282	68	—	35	6.1
	34	5	297	480	—65.02	120	2.8
	35	5	307	335	—63.93	60	2.2
	36	2	309	99	—59.75	39	4.7
	14	6	125	237	—55.62	90	4.5
	18	2	161	252	—58.41	119	5.7
	20	5	180	281	—61.78	110	4.7
	22	5	198	109	—55.48	121	13
	24	5	217	260	—52.04	107	5
	25	2	225	224	—61.78	106	5.7
	27	5	246	246	—61.56	146	7
	29	5	266	240	—57.45	185	9.3
	31	5	285	265	—51.63	323	14
	34	5	314	213	—60.76	285	15
	36	2	329	85	—58.95	159	22
	40	4	370	155	—54.87	610	47
	43	2	394	173	—60.76	309	21
	47	3	435	173	—60.38	482	21
480	*21*	2	101	3.6	—	1	2.8
	25	1	119	278	—66.96	125	5.4
481	*4*	1	15	402	—	20	0.9
481A	*4*	1	70.5	233	—77.64	214	11
	5	3	83	601	—69.90	468	14
	6	3	93	600	—68.39	520	7
	7	6	106	689	—69.75	391	12
	8	2	111	670	—66.90	370	11
	9	5	125	609	—	336	37

61.3	−7.80	9	—	—	—	—
60.6	−8.09	12	—	9	8	26
56.2	−6.31	20	—	—	1	32
59.7	−4.62	18	—	—	2	35
54.6	−9.73	6	0.05	—	3	22
50.2	−15.42	3	—	0.05	—	—
—	—	2	—	—	5	22
—	—	1	—	1	1	5
48.7	−16.28	2	—	0.6	5	20
—	—	2	—	0.3	0.9	5
48.0	−17.00	2	—	—	3	14
51.0	−12.94	2	—	1.0	2	7
—	—	2	—	1.5	0.6	6
58.9	+3.29	30	—	2	0.4	10
—	—	38	—	1.3	0.3	19
60.9	−0.85	32	—	1.5	0.3	16
56.3	+0.80	33	—	1.5	0.4	19
52.1	+0.06	29	—	1.5	0.2	12
59.3	−2.47	33	—	0.5	0.3	9
58.9	−2.71	27	—	0.7	0.7	9
55.7	−1.78	25	—	1.8	1.0	8
47.9	−3.77	24	—	0.3	1.0	10
54.2	−6.57	41	—	0.9	1.0	9
55.3	−3.67	44	—	3.5	0.9	6
50.2	−4.63	33	—	2.5	16.5	39
52.2	−8.53	15	—	5.5	25	19
50.7	−9.67	25	—	0.5	47	38
		1.5	0.2			0.2
62.6	−4.38	6	—	3	3	22
—	−8.43	5	—	—	—	1
—	—	2	—	6	2	6
63.0	−6.85	5	0.2	6	6	11
64.1	−4.27	6	0.1	2	5	8
57.8	−11.95	6	0.05	43	195	44
60.8	−6.25	6	—	35	120	38
—	—	5	—	4	0.1	6

TABLE I (continued)

Site	Core	Section	Subbottom depth (m)	Methane (mg l⁻¹)*1	δ¹³C (‰)*2	Ethane (µg l⁻¹)	C₂/C₁ (× 10⁻⁴)	Propane (µg l⁻¹)	Total C₄H₁₀ (µg l⁻¹)	Total C₅H₁₂ (µg l⁻¹)	Neopentane (µg l⁻¹)	Carbon dioxide (%)*3	δ¹³C (‰)*2	Δ (Δ = δ¹³C_CO₂ − δ¹³C_CH₄) (‰)
481A	10	3	132	700	−63.00	808	30	10	30	10	0.1	7	−6.10	56.9
	10	5	135	672	−59.20	1,097	35	139	177	34	0.2	7	—	—
	12	5	152	673	−54.66	4,388	112	215	164	38	0.3	1	—	—
	13	2	159	585	−55.22	2,347	58	102	248	144	3.1	2	—	—
	13	4	162	642	—	354	66	17	56	119	2.5	1	—	—
	14	3	169	600	−44.18	284	21	37	55	16	0.3	8	—	—
	22	4	246	523	−59.84	103	3	29	26	7	—	8	—	—
	22	6	248	563	−61.13	77	3.5	22	20	6	—	8	−4.28	56.9
	24	6	269	491	−59.68	115	2.8	34	25	6	—	6	−12.87	46.8
	25	6	278	495	−60.61	124	3	34	25	7	—	6	−9.06	51.6
	26	6	287	434	−56.29	111	3.1	29	18	10	—	6	−9.49	46.8
	27	6	297	459	−58.73	107	2.8	26	9	4	—	4	−11.42	47.3
	28	6	306	366	−60.77	118	3.9	29	10	5	—	2	−13.86	46.9
	30	7	326	125	−53.66	339	33	50	89	11	0.01	4	—	—

— = not detectable.
*1 Methane concentrations are slightly lower than shipboard data due to diffusive loss.
*2 Data are in parts per mil vs. PDB standard (underscored values are the average of duplicate analyses).
*3 Volume percent determined by TCD—GC onboard.
*4 Values used to calculate equilibrium temperature of formation.
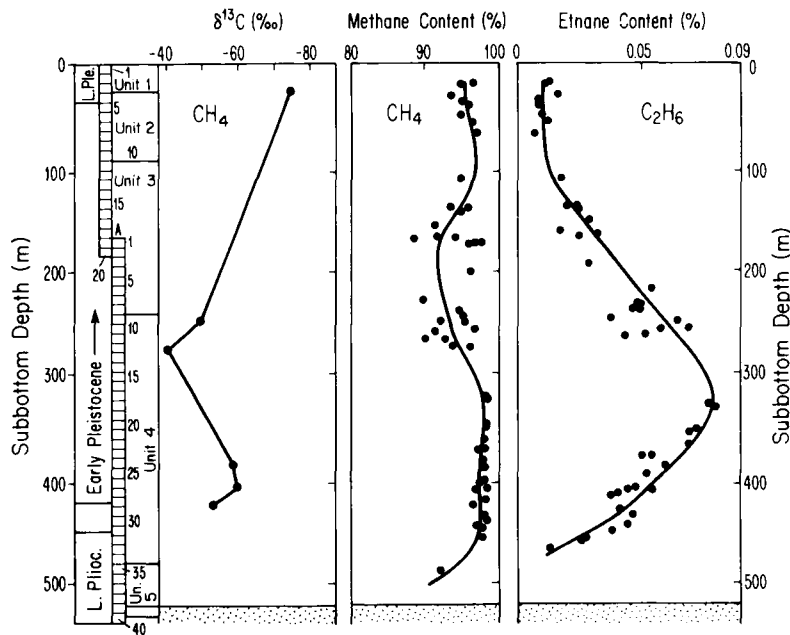
Fig. 2. Plots of the $\delta^{13}C$ and concentration of methane and the concentration of ethane vs. depth for Site 474.

ever, ethane increases in concentration down to ~300 m and then drops to a minimum value above the basalt. This decrease may be due to the high density and cementation of the sediments below 300 m, which slowed the liberation of ethane from the core. Some data supported this explanation. In fact, the density of the sediments increases from 1.6 g cm^{-3} in the upper part of the sequence to 1.8 g cm^{-3} in the lower part (Curray et al., 1982). The upper part also contains a considerable amount of dissolved silicic acid, which is depleted at depth.

The carbon isotope composition of the methane (CH_4 is not dependent on emanation conditions) reveals a similar trend to that of the ethane concentration (Fig. 2). In the upper part of the sequence, the methane has a $\delta^{13}C$-value which is typical for gases of a microbiological origin ($\delta^{13}C$ = —75‰) (Galimov, 1975; Simoneit et al., 1979). But in the zone with the high concentration of ethane, the methane is enriched in ^{13}C and downwards in the sequence it again becomes isotopically lighter. The methane with an isotopic composition of ~ —40‰ does not fit with the depth depletion trend (Galimov, 1975) and should therefore be regarded as allogenic. It is well known that methane with a similar isotopic composition is derived from mature organic matter by thermal transformation (Reitsema et al., 1981). The interstitial gas has a relatively high content of heavy hydrocarbons at this depth (272 m) (Simoneit, 1982). In this context, the higher content of ethane in this section could be accounted for by a lateral migra-

tion of hydrocarbon gas. It should be noted that coarse sandy layers were encountered at a depth of ~260—280 m in Hole 474A, which could serve as permeable horizons, allowing lateral migration of hydrocarbons. The samples recovered from that interval had the highest δ^{13}C-values for CH_4 and the largest C_2—C_5 concentrations.

Guaymas Basin

Sites 477, 478 and 481 are located in the Guaymas Basin in water depths of ~2000 m. The structural geology of the region is determined by the presence of two short axes of bottom expansion, separated by a short transform fault system and confined by two long transform faults. The basin occupies an active rift zone with a typical oceanic crustal structure (Curray et al., 1982). Its heat flow is uneven, maximizing at ~30 μcal. cm^{-2} s^{-1} (1.2 W m^{-2}). The basin has a rather high rate of sediment accumulation (2.7 m/10^3 yr.), with considerable biological productivity and as a consequence, the rapid burial of organic matter which prevents its extensive oxidation. The region is of unique interest as it offers an opportunity to investigate the effect of increased temperatures on diagenetically unaltered organic matter (Einsele et al., 1980).

Hole 477 was drilled in the southern rift zone where heat flow is extremely high. For example at a depth of 260 m, the temperature exceeded 135°C. The lithologic sequence consists of an upper, unaltered member of diatom turbidites (0—58 m), a dolerite intrusion (58—105.5 m) and a lower, altered member of diatom turbidites. The last had undergone extensive hydrothermal reworking, resulting in an unusual (for oceanic sediments) hydrothermal mineralization (Curray et al., 1982).

The methane concentration in the upper section decreases with depth towards the dolerite intrusion, while in the lower sequence, it increases with depth, away from the doleritic intrusion (Fig. 3). The carbon dioxide concentration in the sediments changes in the diametrically opposite fashion. The interstitial gas contains a peculiarly high concentration of CO_2, amountting to 90% adjacent to the intrusion. Ethane was not detected in the upper section; below the sill its concentration first increases and then drops (Fig. 3).

The carbon isotope analyses show that the methane in the lower part of the sequence is depleted in the light isotope and has δ^{13}C-values corresponding to gases generated from organic matter at a high stage of metamorphism (Fig. 3). Methane of similar isotopic composition frequently accompanies crude oils (Galimov, 1975; Reitsema et al., 1981). The gas from core 477-19 reveals the highest value of δ^{13}C and the maximum content of ethane. Thus, the lower sequences of Holes 477 and 477A contain hydrocarbon gases generated by the destruction of organic matter under extreme hydrothermal conditions.

The carbon isotope composition of the carbon dioxide decreases with
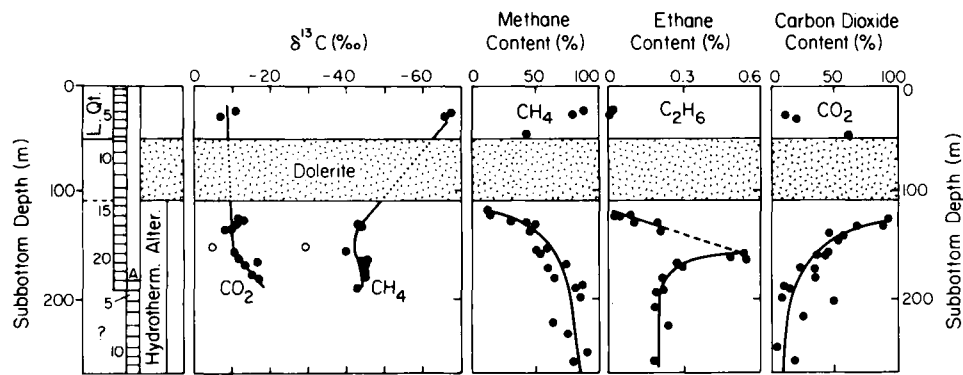
Fig. 3. Plots of the $\delta^{13}C$ of methane and carbon dioxide and the concentrations of methane, ethane and carbon dioxide vs. depth for Site *477* (*open circles* = anomalous data).

depth away from the sill, following the decrease in concentration (Fig. 3). This heavier CO_2 may be due to the relatively higher concentration, derived from a partial decomposition of carbonates by the hydrothermal reworking of the sediments (Galimov and Simoneit, 1982a). This is further confirmed by comparison of the differences between the $\delta^{13}C$ of carbon dioxide and of methane (Fig. 3). In the upper sequence that difference, Δ (Δ = $\delta^{13}C_{CO_2}-\delta^{13}C_{CH_4}$) is $\sim60\%$, typical for an origin from biogenic sources (e.g., Claypool and Kaplan, 1974). In the lower sequences, Δ decreases to $\sim25\%$, the lowest value of the three Guaymas sites and indicates major effects of thermal stress on the isotopic composition of CH_4 and CO_2.

It is of interest to note that the geothermal equilibration temperature for the carbon isotope compositions of CH_4 and CO_2 ($\Delta_{min} = 25\%$; Fig. 3) is $\sim300°C$ at 146-m subbottom, based on the kinetic evaluations of Giggenbach (1982). A temperature of 225°C (at the same subbottom depth) has been estimated (Simoneit, 1982) from the gas composition using the empirical methods of D'Amore and Panichi (1980) and is within reasonable agreement.

Hole *478* was drilled in the transform fault region between the rifts of the Guaymas Basin. In contrast to Hole *477*, it has a moderate heat flow. The sediments do not show any major effects of hydrothermal reworking. They consist of a 300-m-thick deposit of turbidites, overlying basalts. The upper section is composed of diatomaceous oozes with interlayers of turbidite sand (0—188 m), which are underlain by various dolomite sandstones, including two minor dolerite sills (188—260 m). The lower portion of the sediments is composed of homogeneous diatom claystones with interlayered dolomite (260—342.5 m). The density of the sediments does not exceed that of the Hole-*474* sequence and is typical for oceanic deposits. Temperature effects of the intrusions are limited to the zone of immediate contact (several cm).

The gas composition varies only slightly throughout the sequence (Fig. 4). Methane is more or less constant below ~100-m subbottom and ethane increases slightly with depth, while below the dolerite intrusions it goes through a minimum. The carbon dioxide concentration increases to 20% at 170-m subbottom and then drops to 1—2% at depth.
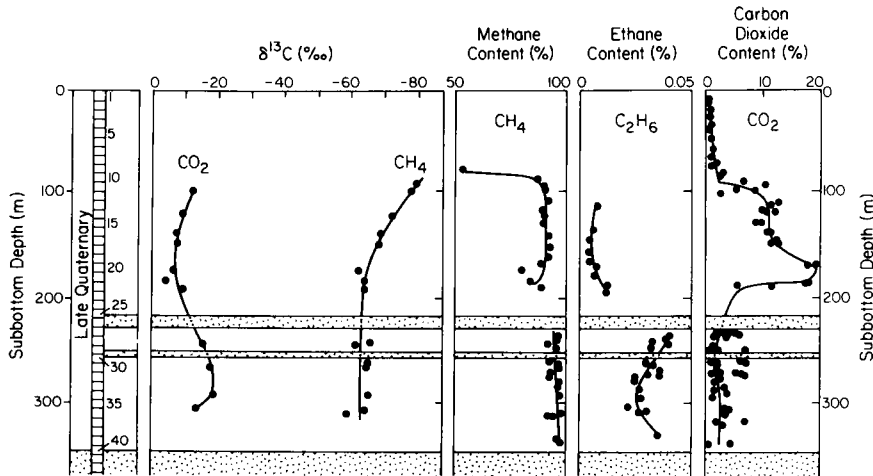

Fig. 4. Plots of the $\delta^{13}C$ of methane and carbon dioxide and the concentrations of methane, ethane and carbon dioxide vs. depth for Site 478.

The isotopic compositions of the CH_4 have relatively low $\delta^{13}C$-values, typical for methane generated from immature organic matter of microbiota. The upper part of the sequence reveals a rather rapid change in the isotopic composition of CH_4 from -79.2 to $-62.5\%_{00}$ with depth (Fig. 4). These values are comparable with the mean $\delta^{13}C = -71\%_{00}$ for CH_4 in surface sediments at station 30G in the northern rift (Simoneit et al., 1979). Further down in the sequence, the isotopic composition of the CH_4 varies around $\sim -62\%_{00}$, which is indicative of an autochthonous origin for the methane under conditions of a moderate thermal gradient.

The $\delta^{13}C$-values for the CO_2 range from -4.6 to $-17.0\%_{00}$ with the trends indicated in Fig. 4. The difference, Δ, in the $\delta^{13}C$-values of CO_2 and CH_4 above the sills is $\sim 60\%_{00}$, typical for biogenic gases (Claypool and Kaplan, 1974), and below the sills Δ drops to $\sim 45\%_{00}$, indicating some contribution from thermogenic components.

Holes 481 and 481A were drilled in the northern rift of Guaymas Basin and the sediments consist of diatomaceous oozes and turbidites, intruded by a major dolerite sill complex. Above the upper sill, the ethane increases in concentration with depth to a maximum at ~150-m subbottom and below it the C_2H_6 concentration goes through a minimum (Fig. 5). The methane concentration is approximately constant from 50—130 m, increases
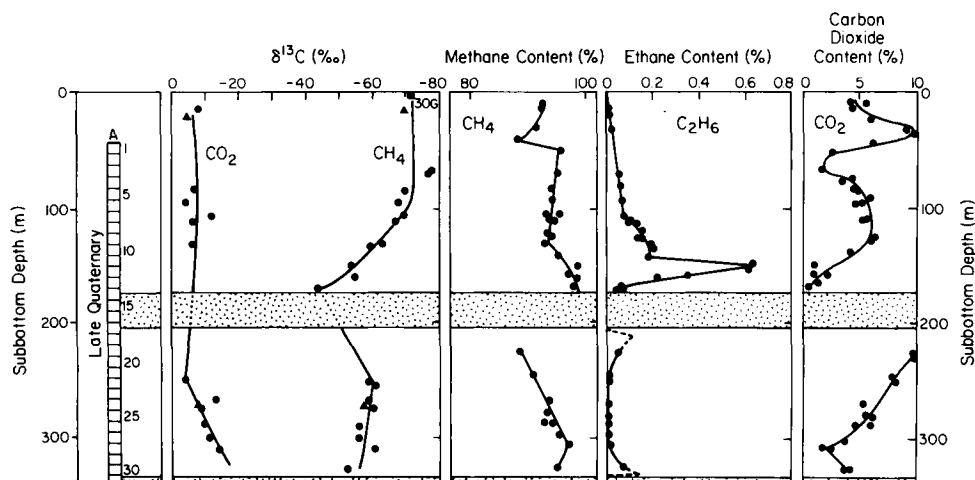
Fig. 5. Plots of the $\delta^{13}C$ of methane and carbon dioxide and the concentrations of methane, ethane and carbon dioxide vs. depth for Site *481* [*triangular data points* = canned samples (Galimov and Simoneit, 1982b); *square data point* = samples from station *30G* (Simoneit et al., 1979)].

slightly toward the upper sill and below it, increases through a maximum. It should be pointed out that neopentane (*2,2*-dimethylpropane, cf. Table I) was detected mainly in this hole. Since *gem*-dimethyl hydrocarbons are relatively unstable to thermal stress, the presence of neopentane may indicate a lower genesis temperature for this interstitial C_2—C_5 hydrocarbon suite. Carbon dioxide reaches a maximum of 7% above the upper sill, decreasing to 1% at the sill, and decreases from 8% through a minimum below it (Fig. 5).

The isotopic composition of CH_4 is typical of biogenic methane to ~110-m subbottom (Claypool and Kaplan, 1974), and is comparable to the $\delta^{13}C$ = —71‰ for the CH_4 in the surface sediment at station *30G*, ~8 km to the northeast (Simoneit et al., 1979). Below 110 m it changes rapidly towards the upper sill, decreasing in the light isotope of carbon (Fig. 5). This trend is more distinct here than in Hole *478*. The CH_4 near the top of the upper dolerite sill approaches a $\delta^{13}C$ of ~ —44‰, typical for CH_4 from thermogenesis of mature organic matter, corresponding to the initial phase of oil generation (Galimov, 1975). The isotopic composition of CH_4 in the lower part of the sequence averages ~ —57‰, a value characteristic for the early stages of thermal transformation of organic matter. The $\delta^{13}C$ of the CO_2 above the upper sill exhibits an average of —6‰ and a range from —4 to —12‰. The differences (Δ) between the $\delta^{13}C$ for CO_2 and CH_4 were ~60‰ in the top of the sequence [typical for biogenic gas, e.g. Claypool and Kaplan (1974)] and drop to ~50‰ above the upper sill, clearly demonstrating the thermal stress due to that sill. The isotopic composition of the CO_2 in the lower sequence between the sills shows a decrease from —4

to —14‰. The Δ drops to 45‰ in this region due to the increased effects of thermal stress.

Continental slope

Holes *479* and *480* were drilled on the continental slope of the north-eastern flank of the Guaymas Basin in water depths of 560—750 m. The sediments of Hole *479* consist of hemipelagic diatom oozes and claystones. The sequence is subdivided into three similar lithologic complexes, which differ only in the concentration of carbonate material. Carbonate is less abundant in the upper part (0—250 m), while the middle (250—355 m) consists of interlayered carbonate claystones, and the lower part (355—440 m) shows a further increase in the abundance of carbonates, present mainly as interlayered claystone.

The methane concentration decreases to ∼60% with depth and then fluctuates between 45 and 70% to hole bottom (Fig. 6). The ethane content remains low and essentially constant, not exceeding 0.02% to a depth of ∼260 m (Fig. 6). At greater depth, however, the C_2H_6 concentration increases to >0.1% accompanying a simultaneous increase in the C_3—C_5 hydrocarbons (Simoneit, 1982). Drilling of Hole *479* was stopped at a depth of 400 m, due to the continuing increase in the concentrations of heavy hydrocarbons with depth.

The isotope composition of CH_4 varies within the range of —50 to —70‰ (Fig. 6). It is noteworthy that the isotopic composition of the CH_4 remains practically uniform and does not reflect a ^{13}C enrichment which could be related to the increase in the C_2—C_5 hydrocarbon concentration. The scatter throughout the sequence does not exceed 10‰ and the range is within
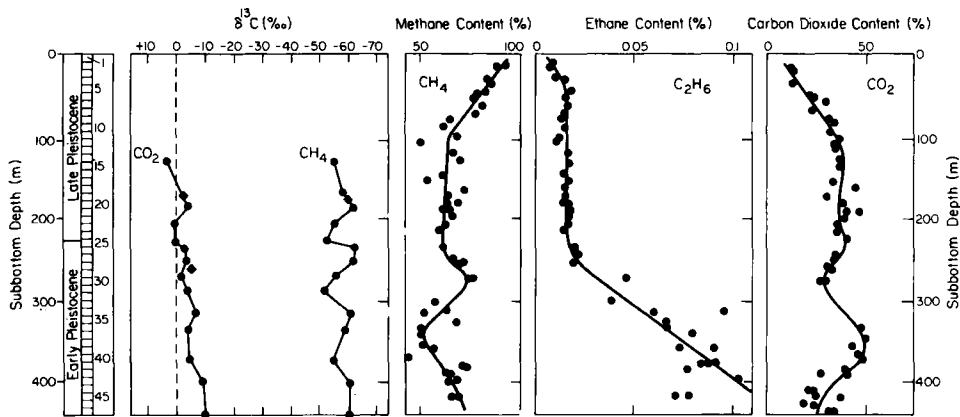

Fig. 6. Plots of the $\delta^{13}C$ of methane and carbon dioxide and the concentrations of methane, ethane and carbon dioxide vs. depth for Site *479* [*diamond data points* = canned samples (Galimov and Simoneit, 1982b)].

values typical for CH_4 derived from immature organic matter. Such a striking difference in the chemical composition of the gas and the isotopic composition of the methane can be attributed, in principle, to diffusion of thermogenic hydrocarbons from underlying deposits. The influx of gas from such an origin to the total gas content of the sediments could be minor (not exceeding several percent). Therefore, any change in the carbon isotope composition of the CH_4 would be imperceptible.

The concentration of carbon dioxide in Hole *479* varies from 10 to 50% and has the highest values of $\delta^{13}C$ observed in the Gulf (Fig. 6; Table I). The isotopic composition of CO_2 shows a tendency of the heavy carbon isotope depletion lower in the sequence. Calculations of average values for all three lithological complexes gave the following results: $\delta^{13}C = +0.31\%_0$ for the upper; $-3.9\%_0$ for the middle; and $-7.6\%_0$ for the lower complex.

The difference (Δ) between the $\delta^{13}C$ of CO_2 and CH_4 is $\sim60\%_0$ in the upper sequence, typical for a biogenic origin (Claypool and Kaplan, 1974) and drops to $\sim50\%_0$ lower in the sequence, lending support to the concept of some contribution of thermogenic components at depth. Additionally, isotopically heavy CO_2 may result from the decomposition of oxygen-bearing organic compounds (e.g., decarboxylation) in reducing environments (Galimov, 1974), as well as from the microbiological reduction of carbon dioxide to methane (Claypool and Kaplan, 1974). The high biological productivity and high rates of organic matter burial imply, that sedimentation at Site *479* took place in oxygen-deficient environments. This is confirmed by the relatively high values of $\delta^{13}C$ for CO_2, particularly in the upper part of the sequence. Due to the high carbonate concentration at greater depths, the carbon isotope composition of CO_2 may possibly become a function of fractionation in the isotope-exchange system $CO_2 \rightleftharpoons CO_3^{2-}$. The evaluation of this possibility requires more comprehensive data on the content of carbonate in the sediments and its isotopic composition.

Site *480* was drilled in the same region of the marginal plateau as Site *479*. A single analysis of the interstitial gas from 119-m subbottom gave the value of $\delta^{13}C = -66.96\%_0$ for CH_4 and $-4.38\%_0$ for CO_2. These values are slightly lower than those for Site *479* at the corresponding depth (~120 m).

CONCLUSIONS

The presence and concentrations of interstitial carbon dioxide and hydrocarbon gases (C_1—C_5) for Leg *64* determined onboard ship (Simoneit, 1982) have been confirmed and, in addition, olefinic hydrocarbons could not be detected.

The carbon isotope composition of methane shows a trend toward depletion of the light isotope with depth in these sedimentary sequences (Galimov and Simoneit, 1982a; Schoell, 1982), a tendency well established elsewhere

(e.g., Galimov, 1975; Galimov et al., 1980; Reitsema et al., 1981; Schoell, 1980). This feature most likely results from the fact that methane generated at different stages of transformation of the organic matter differs in its carbon isotopic composition. The following ranges of isotopic compositions of CH_4 generated (corresponding to the successive stages of organic matter transformation) can be distinguished (Rice and Claypool, 1981; Galimov, 1974, 1975).

(1) Initial (biogenic, consisting only of methane), $\delta^{13}C \leqslant -60\%_0$.

(2) Early (diagenesis, onset of generation of C_2—C_5 hydrocarbons), $\delta^{13}C$ from -40 to $-60\%_0$.

(3) Mature (catagenesis, main phase of oil formation), $\delta^{13}C$ from -30 to $-40\%_0$.

(4) Late (incipient metamorphism, termination of liquid hydrocarbon generation, amorphous stage of organic matter metamorphism), $\delta^{13}C \geqslant -30\%_0$.

For the majority of the holes studied during DSDP Leg 64, the isotopic composition of methane in the upper sections, which are composed of sediments unaffected by thermal events, corresponds to a microbiological origin (i.e. the initial stage of organic matter transformation). The CH_4 in the surface sediments from station 30G in the northern rift of the Guaymas Basin is of a similar origin (Simoneit et al., 1979). Near intrusions, however, the methane is generally depleted in the light carbon isotope, and in such sections this change in the methane isotopic composition increases with depth. The highest values of $\delta^{13}C$ for CH_4 are observed in Hole 477, drilled in the area with the highest heat flow values. Thus, the isotopic composition of methane is, as a rule, in compliance with the thermal history of the surrounding sediments.

Furthermore, some sediments revealed examples of gas migration, two of which are typical. The CH_4 in Hole 474, at a depth of 250—280 m, is depleted in the light carbon isotope ($\delta^{13}C$ ranged from -40 to $-50\%_0$) with respect to both the overlying and the underlying gases. This possibly results from horizontal migration of methane derived from the transformation of mature organic matter. Hole 479 may be another example, where the sequence does not reveal any marked change in the isotope composition of the methane with depth. However, a considerable increase in the concentration of C_2—C_5 hydrocarbons at depths below 300 m implies a vertical gas diffusion from a source with a higher content of heavy hydrocarbons (Simoneit, 1982).

Considerable concentrations of CO_2 were encountered in some of the interstitial gases. In most of the cases, the isotopic composition of the CO_2 carbon varies downhole without any obvious trend. Values of $\delta^{13}C$ ranging from -7 and $-12\%_0$ are predominant, and are close to $-9\%_0$ which corresponds to the average value of CO_2 from marine organic and inorganic origins. In sections with considerable carbonate concentrations, the isotopic composition of CO_2 should be controlled by an exchange in the system

$CO_2 \rightleftharpoons CO_3^{2-}$. The enrichment of CO_2 with the heavy carbon isotope (e.g., in Hole 479), is possibly due to a generation of CO_2 from anaerobic decomposition of organic matter in a sedimentary environment of acute oxygen deficiency. The CO_2 of such an origin can be enriched in ^{13}C in two ways: (1) the carbon combined with oxygen (e.g., carboxyl) in the biogenic organic compounds, is enriched in the ^{13}C isotope, due to a specific intramolecular distribution of carbon isotopes (Galimov, 1974, 1975); and (2) the process of microbiological reduction of CO_2 presumably generates a kinetic isotope effect, leading to the concentration of the ^{13}C isotope in the residual carbon dioxide (Claypool and Kaplan, 1974). The CO_2 enriched in the light carbon isotope (-16 to $-20‰$) is probably a product of organic matter oxidation and thermal alteration, and it inherits the isotopic composition of the total organic carbon.

The difference in the $\delta^{13}C$-values of CO_2 and CH_4 (Δ) is $\sim 60‰$ for the gases in the biogenic zones (Claypool and Kaplan, 1974), and decreases to as low as $25‰$ in the case of Hole 477 due to the thermogenic components present. An equilibration temperature of $300°C$ can be estimated for the gases at 146-m subbottom in Hole 477, based on the kinetic data evaluations by Giggenbach (1982). The high concentration of CO_2 in some holes may aid in the migration of the C_1—C_5 hydrocarbon components away from the thermally affected regions, as was observed for the thermogenic gases in Norton Sound, Alaska (Kvenvolden and Claypool, 1980).

ACKNOWLEDGEMENTS

REFERENCES

Claypool, G.E. and Kaplan, I.R., 1974. Origin and distribution of methane in marine sediments. In: I.R. Kaplan (Editor), Natural Gas in Marine Sediments. Plenum, New York, N.Y., pp. 99—139.

Curray, J.R., Moore, D.G., Aguayo, J.E., Aubry, M.P., Einsele, G., Fornari, D.J., Gieskes, J., Guerrero, J.C., Kastner, M., Kelts, K., Lyle, M., Matoba, Y., Molina-Cruz, A., Niemitz, J., Rueda, J., Saunders, A.D., Schrader, H., Simoneit, B.R.T. and Vacquier, V., 1979. Deep-Sea Drilling Project in the Gulf of California Leg 64, Geotimes, 24(7): 18—20.

Curray, J.R., Moore, D.G., Aguayo, J.E., Aubry, M.P., Einsele, G., Fornari, D.J., Gieskes, J., Guerrero, J.C., Kastner, M., Kelts, K., Matoba, Y., Molina-Cruz, A., Niemitz, J., Rueda, J., Saunders, A.D., Schrader, H., Simoneit, B.R.T. and Vacquier, V., 1982. Initial Reports of the Deep-Sea Drilling Project, Vol. 64, Part I and II, U.S. Government Printing Office, Washington, D.C., 1314 pp.

D'Amore, F. and Panichi, C., 1980. Evaluation of deep temperatures of hydrothermal systems by a new gas thermometer. Geochim. Cosmochim. Acta, 44: 549—556.

Einsele, G., Gieskes, J.M., Curray, J. et al., 1980. Intrusion of basaltic sills into highly porous sediments, and resulting hydrothermal activity. Nature(London), 283: 441—445.

Galimov, E.M., 1974. Organic geochemistry of carbon isotopes. In: B. Tissot and F. Bienner (Editors), Advances in Organic Geochemistry 1973. Technip, Paris, pp. 439—452.

Galimov, E.M., 1975. Carbon isotopes in oil and gas geology. Nedra, Moscow, 1973 (English translation by NASA, F-682, Washington, D.C., 1975).

Galimov, E.M. and Simoneit, B.R.T., 1982a. Geochemistry of interstitial gases in sedimentary deposits of the Gulf of California, Deep-Sea Drilling Project Leg 64. In: J.R. Curray, D.G. Moore et al. (Editors), Initial Reports of the Deep Sea Drilling Project, Vol 64, Part II, U.S. Government Printing Office, Washington, D.C., pp. 781—788.

Galimov, E.M. and Simoneit, B.R.T., 1982b. Variations in the carbon isotope compositions of CH_4 and CO_2 in the sedimentary sections of Guaymas Basin (Gulf of California). Geokhimiya, 7: 1027—1034.

Galimov, E.M., Chinjenov, V.A. and Ivanov, G.N., 1980. Isotopic composition of methane carbon and relative content of gaseous hydrocarbons in the deposits of the Moroccan Basin in the Atlantic Ocean (DSDP Sites 415 and 416). In: Y. Lancelot, E. Winterer et al. (Editors), Initial Reports of the Deep-Sea Drilling Project, Vol. 50, U.S. Government Printing Office, Washington, D.C., pp. 615—622.

Giggenbach, W.F., 1982. Carbon-13 exchange between CO_2 and CH_4 under geothermal conditions. Geochim. Cosmochim. Acta, 46: 159—165.

Kvenvolden, K.A. and Claypool, G.E., 1980. Origin of gasoline-range hydrocarbons and their migration by solution in carbon dioxide in Norton Basin, Alaska. Am. Assoc. Pet. Geol. Bull., 64: 1078—1086.

Reitsema, R.H., Kaltenback, A.J. and Lindberg, F.A., 1981. Source and migration of light hydrocarbons indicated by carbon isotopic ratios. Am. Assoc. Pet. Geol. Bull., 65: 1536—1542.

Rice, D.D. and Claypool, G.E., 1981. Generation, accumulation, and resource potential of biogenic gas. Am. Assoc. Pet. Geol. Bull., 65: 5—25.

Rohrback, B.G., 1979. Analysis of low molecular weight products generated by thermal decomposition of organic matter in Recent sedimentary environments. Ph.D. Thesis, University of California, Los Angeles, Calif., 195 pp.

Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochim. Cosmochim. Acta, 44: 649—661.

Schoell, M., 1982. Stable isotopic analyses of interstitial gases in Quaternary sediments from the Gulf of California. In: J.R. Curray, D.G. Moore et al. (Editors), Initial Reports of the Deep-Sea Drilling Project, Vol. 64, Part II. U.S. Government Printing Office, Washington, D.C., pp. 815—818.

Simoneit, B.R.T., 1982. Shipboard organic geochemistry and safety monitoring, Leg 64, Gulf of California. In: J.R. Curray, D.G. Moore et al. (Editors), Initial Reports of the Deep Sea Drilling Project, Vol. 64, Part II. U.S. Government Printing Office, Washington, D.C., pp. 723—728.

Simoneit, B.R.T., Mazurek, M.A., Brenner, S., Crisp, P.T. and Kaplan, I.R., 1979. Organic geochemistry of recent sediments from Guaymas Basin, Gulf of California. Deep-Sea Res., 26A: 879—891.