

Gaseous Composition in Thermal Decomposition of Organic Matter in Sediments and Sedimentary Rocks

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Abstract

The thermal decomposition gases generated by heating at various temperatures (80, 150, 200, 300, 600°C for 1 hr. and 400°C for 10 min.) from the organic matter in sediments and sedimentary rocks are analysed by gas chromatography, and the results are summarized as follows:

1) With the exception of natural gas in Recent sediments, the contents of H₂ and olefins are very low in CH₄-type natural gas in sedimentary rocks. On the other hand, the contents of H₂ and olefins in the gases generated from sediments and sedimentary rocks by heating at temperatures above 80°C are very high. This phenomenon indicates that the organic matters in sediments and sedimentary rocks are decomposed thermally at temperature as low as 80°C.

2) The volume ratios of total amount of hydrocarbons** (carbon number ranging C₁ to C₅) generated by heating from the organic matters in sediments and sedimentary rocks are relatively high at 300°C or 600°C.

3) Kerogen is pyrolyzed at above 300°C and it is assumed that the kerogen is more stable thermally than the soluble organic matter in sedimentary rocks.

4) Based on the experimental data, the authors deduced that there is positive correlation between the composition of pyrolyzed gases and geologic age or buried depth of sedimentary rocks, however the clear conclusion cannot be drawn from these data due to the insufficient number of examined samples.

I. Introduction

EVANS (1964), DUGLAS (1966) and ROBINSON (1969) have reported that the gaseous hydrocarbons could be detected in the pyrolysis gases generated from sedimentary rocks by heating above 200°C. In this paper following subjects are investigated.

a) The relationship between thermal change of organic compounds in sedimentary rocks and genesis of petroleum, b) The chemical structure of kerogen.

The authors' experiments were performed in order to infer the pyrolysis temperature of organic matter in sediments and sedimentary rocks and to elucidate the relation between pyrolyzed gas composition and geologic age or depth of sedimentary rocks.

II. Sample and experiment

II. 1 Sample

a) Bottom sediment 6 (Recent; Naka-umi, Shimane Prefecture), Peat 7 (Recent; Ozegahara, Gunma Prefecture), b) Nittantakamatu-drilling core 8-11 (Tertiary; 9, 245, 415, 1050 m, Orio,

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**The ratio display, (total amount of hydrocarbons by heating at 150°C/total amount of hydrocarbons by heating at 80°C), (total amount of hydrocarbons by heating at 200°C/total amount of hydrocarbons by heating at 150°C), (total amount of hydrocarbons by heating at 300°C/total amount of hydrocarbons by heating at 200°C) and (total amount of hydrocarbons by heating at 600°C/total amount of hydrocarbons by heating at 300°C).

Fukuoka Prefecture),c) Shimanto group 12 (Cretaceous; Uwajima),d) Kerogen (Miocene; Ikume, Miyazaki Prefecture), e) Coal 13 (Tertiary; Nittantakamatu, Fukuoka Prefecture), f) Ryoke-metamorphic rock 14, 15 (Kiso),g) Coral 16 (Recent; Kikaijima), Limestone 17-22 (Quaternary-Silurian; Kikaijima, Sagara, Garo, Akasaka, Ofunabara),h) Kasukabe-drilling core (Pliocene; 506, 800, 1028 m, Miocene; 1050, 1456, 1900, 2000, 2600, 2900 m).

II. 2 Experimental condition

The total amount and chemical composition of pyrolyzed gases from sediments and sedimentary rocks are variable with heating temperature and time.

The experiment is operated under the following condition.

At first, 0.06 g of a powdered sample (sieve between 100 and 150 mesh) is placed in platinum boat, then the boat is inserted in to the combustion tube of the SIMAZU PYR-A type pyrolyzer combined with a gas chromatograph. Second, air in the combustion tube is purged by passing argon through the tube, and then the tube is heated progressively at 80, 150, 200, 300 and 600°C each for 1 hr. or at 400°C for 10 min.

The pyrolyzed gases are analysed by a gas chromatograph. Gaseous components such as H₂, N₂, CO₂, CH₄, C₂H₆, C₃H₈, C₃H₆, i-C₄H₁₀, n-C₄H₁₀, 1-Butene, i-Butylene, i-C₅H₁₂ and n-C₅H₁₂, are analysed in this study.

III. Results

The chemical components of pyrolyzed gases are listed in Tables 1 and 2. The components

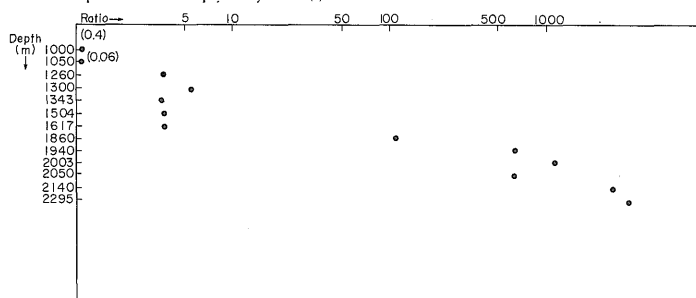


Fig. 1 Relation between the depth and the (C₂H₆/C₂H₄) ratios in extracted gases of Kasukabe-drilling cores.

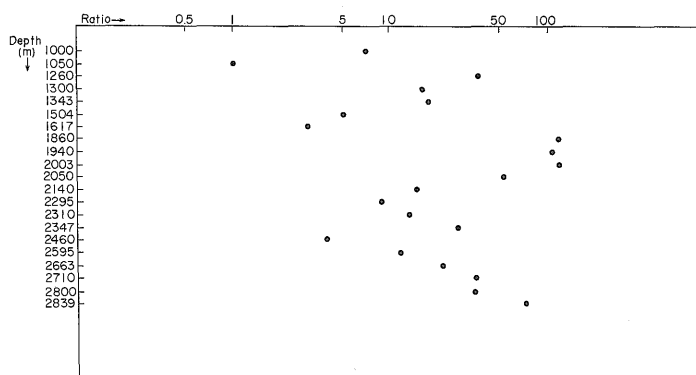


Fig. 2 Relation between the depth and the (C₃H₈/C₃H₆) ratios in extracted gases of Kasukabe-drilling cores.

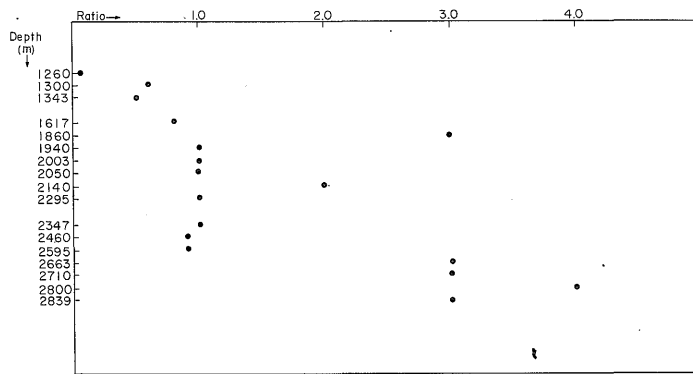


Fig. 3 Relation between the depth and the $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratios in extracted gases of Kasukabe-drilling cores.

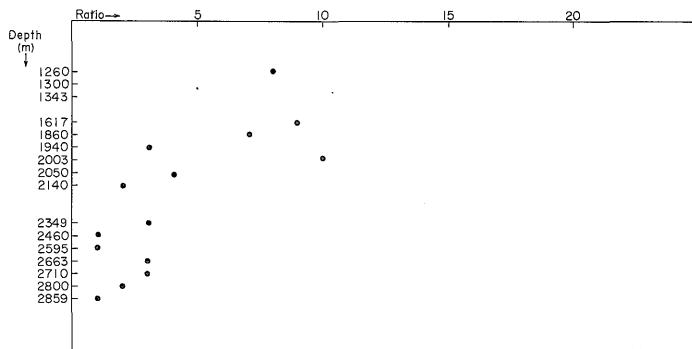


Fig. 4 Relation between the depth and the $i\text{-C}_5\text{H}_{12}/n\text{-C}_5\text{H}_{12}$ ratios in extracted gases of Kasukabe-drilling cores.

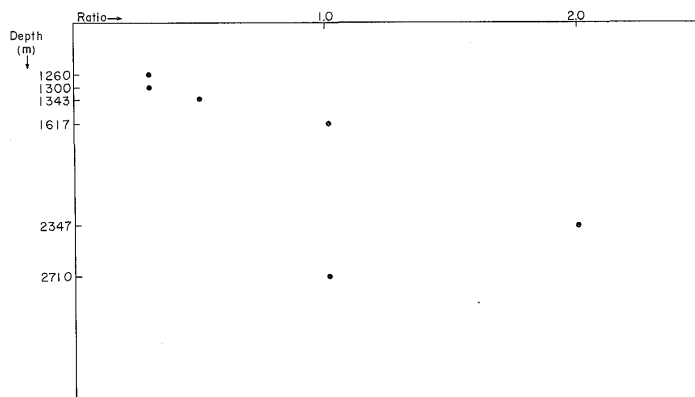


Fig. 5 Relation between the depth and the 1-Butene/*i*-Butylene ratios in extracted gases of Kasukabe-drilling cores.

of pyrolyzed gases are compared with those of the extracted gas from Kasukabe-drilling cores (YONETANI and HIRUKAWA, 1971) (Figs. 1-5).

III. 1 The relation between the total amount of pyrolyzed gases and the temperature of heating

Table 1 Chemical components in pyrolysis gases generated at different temperature from various sediments and sedimentary rocks. ($\mu\text{l}/0.06\text{g}$.)

Sample number	Sample name	Geologic age Depth (m) Lithofacies	Temp. (°C)	H ₂	N ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-Butene	i-Butylene	i-C ₅ H ₁₂	n-C ₅ H ₁₂
6	Nakaumi bottom sediment	Recent	80	0.6	830	0.00	4	0.06	0.030	0.014	0.008	0.056	0.000	0.000	0.001	0.096	0.000	0.000
			150	1.2	540	0.00	30	0.4	0.012	0.108	0.012	0.279	0.012	0.006	0.016	0.149	0.037	0.000
			200	3.1	720	1.30	405	2.6	0.018	0.180	0.046	0.461	0.020	0.020	0.028	0.252	0.030	0.006
			300	15.6	540	1.00	860	16	0.944	3.271	0.620	1.806	0.082	0.205	0.248	0.743	0.240	0.024
			600	190.8	620	1.80	4803	48	0.122	0.600	0.014	0.088	0.002	0.0004	0.014	0.014	0.002	0.002
7	Ozegahara moor peat	Recent	80	7.8	490	0.00	2000	1.3	1.329	0.609	0.409	2.137	0.209	0.310	0.300	0.300	0.251	0.108
			150	14.0	540	4.40	2300	8.8	0.569	1.138	0.619	2.440	0.200	0.200	0.567	0.669	0.390	0.001
			200	93.7	800	37.00	4000	51	1.725	8.609	0.819	8.265	0.341	6.420	2.503	2.503	2.110	0.522
			300	943.7	610	108.0	7750	1900	24.310	24.310	94.650	94.650	5.460	21.607	21.300	42.601	10.605	7.015
			600	26000	670	275.8	8020	440.200	11051	5513	221.01	884	88.40	88.40	41.221	81.553	20.751	10.374
8	Nittan Takamatu drilling core	Tertiary 9 sand stone	80	0.3	520	0.00	15	1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			150	1.4	590	0.00	15	32	0.603	6.000	0.435	6.590	0.339	0.011	0.000	0.000	0.000	0.000
			200	3.1	700	0.00	24	75	0.375	2.200	0.370	1.000	0.340	0.012	0.000	0.000	0.000	0.000
			300	29.4	620	0.00	63	180	36.097	36.207	18.215	36.255	0.700	4.390	3.020	4.319	5.745	1.980
			600	676	660	0.30	445	1020	21.250	170.000	22.439	—	0.001	0.001	0.000	0.000	0.000	0.000
9	Nittan Takamatu drilling core	Tertiary 245 silt	80	0.04	500	0.00	20	0.01	0.001	0.005	0.000	0.000	0.005	0.001	0.005	0.002	0.002	0.003
			150	0.07	550	0.00	30	0.05	0.001	0.010	0.001	0.006	0.000	0.000	0.003	0.003	0.001	0.001
			200	0.1	740	0.00	20	0.7	0.020	0.120	0.002	0.007	0.001	0.001	0.000	0.000	0.000	0.000
			300	10.5	520	0.30	60	5.0	0.127	0.624	0.074	0.335	0.005	0.030	0.020	0.020	0.036	0.012
			600	63.4	610	0.20	230	30	0.115	10.000	0.089	4.961	0.803	0.128	0.133	0.154	0.960	0.010
10	Nittan Takamatu drilling core	Tertiary 415 silt	80	0.1	580	0.00	15	0.02	—	—	—	—	0.008	0.001	0.003	0.001	0.000	0.000
			150	0.1	500	0.0	12	0.20	0.007	0.015	0.021	0.125	0.010	0.001	0.040	0.080	0.000	0.000
			200	0.2	760	0.0	30	1.0	0.019	0.118	0.029	0.174	0.020	0.001	0.035	0.046	0.023	0.011
			300	162.5	640	0.3	520	12.0	1.241	1.110	0.576	1.987	0.074	0.192	0.178	0.500	0.277	0.097
			600	480	640	1.3	1520	106	0.850	6.191	0.100	1.030	0.001	0.020	0.055	0.111	0.220	0.001
11	Nittan Takamatu drilling core	Tertiary 1050 silt	80	0.1	760	0.0	15	0.005	0.003	0.003	0.001	0.003	0.000	0.000	0.000	0.000	0.000	0.000
			150	0.3	530	0.0	20	0.05	0.002	0.020	0.004	0.025	0.003	0.006	0.000	0.000	0.000	0.000
			200	0.1	740	0.0	40	3.0	0.033	0.312	0.040	0.322	0.054	0.027	0.002	0.003	0.012	0.001
			300	7.8	560	0.3	150	12.0	1.362	1.559	0.602	1.207	0.080	0.030	0.123	0.133	0.260	0.080
			600	236.8	550	0.5	480	120	1.321	13.210	0.044	2.250	0.120	0.041	0.061	0.071	0.000	0.000
12	Sedimentary rock of Shimanto group	Cretaceous sand stone	80	0.0	980	0.0	8	0.2	0.011	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			150	0.1	720	0.0	10	1.0	0.002	0.020	0.007	0.071	0.012	0.001	0.011	0.031	0.010	0.001
			200	1.5	780	0.0	20	16.1	0.107	0.530	0.239	1.218	0.184	0.061	0.129	0.278	0.278	0.001
			300	10.1	600	0.0	60	49.2	1.598	3.182	1.025	5.000	0.206	0.308	0.647	0.743	0.499	0.069
			600	165.6	720	0.3	180	36.5	0.598	4.189	0.151	9.090	0.104	0.052	0.100	0.100	0.051	0.001
13	Coal (Nittan Takamatu)	Tertiary	80	3.2	760	0.0	750	3.0	0.608	0.365	0.302	0.904	0.000	0.000	0.000	0.000	0.000	0.000
			150	3.7	530	2.0	1260	18.1	1.980	2.593	1.205	3.031	0.000	0.000	0.000	0.000	0.000	0.000
			200	3.9	740	2.0	2040	60.5	7.515	12.096	7.574	7.574	0.418	1.405	1.321	1.982	0.000	0.000
			300	191	560	26	5940	2226	741.20	369.00	184.51	922.53	18.50	22.23	8.854	18.532	13.205	8.043
			600	60600	550	2230	10800	34750	1935	967	80.600	115.55	58.127	58.127	3.428	21.050	4.525	9.036
14	Ryōke metamorphic rock	Slate	80	—	—	—	—	0.390	0.001	0.197	0.066	0.131	0.099	0.920	0.000	0.000	0.000	0.000
			150	—	—	—	—	0.470	0.001	0.190	0.061	0.061	0.049	0.252	0.000	0.000	0.000	
			200	—	—	—	—	11.50	—	—	—	—	—	—	—	—	—	
			300	—	—	—	—	32.50	1.545	0.534	0.706	0.162	0.027	0.191	0.000	0.000	0.000	
			600	—	—	—	—	397	14.200	69.982	0.530	6.965	0.021	0.108	1.350	1.350	0.000	0.000

(Table 1 Continued)

Sample number	Sample name	Geologic age Depth (m) Lithofacies	Temp. (°C)	H ₂	N ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	1-Butene	i-Butylene	i-C ₅ H ₁₂	n-C ₅ H ₁₂	
15	Ryōke metamorphic rock	Mica-schist	80	—	—	—	—	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			150	—	—	—	—	3.7	0.001	0.311	0.061	0.033	0.001	0.000	0.000	0.000	0.000	0.000	0.000
			200	—	—	—	—	29.3	0.326	0.865	0.226	1.125	0.133	0.133	0.711	2.660	0.000	0.000	0.000
			300	—	—	—	—	47.5	1.825	3.161	0.881	2.370	0.207	0.412	0.517	1.321	0.412	0.000	0.000
			600	—	—	—	—	225.0	11.805	62.550	0.000	5.360	0.000	0.000	21.400	26.805	0.000	0.000	0.000
16	Coral	Recent	80	0.0	790	0.0	—	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			150	0.0	790	0.0	—	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			200	0.0	630	0.0	—	0.01	0.001	0.002	0.001	0.011	0.000	0.000	0.001	0.007	0.001	0.001	0.007
			300	3.9	480	0.0	—	0.80	0.040	0.050	0.020	0.030	0.003	0.006	0.003	0.003	0.003	0.001	0.001
			600	69.6	447	8.0	—	10.0	0.241	1.445	0.007	0.072	0.004	0.005	0.004	0.005	0.005	0.002	0.001
17	Limestone (Kikaijima)	Quaternary	80	0.0	1330	0.0	0.0	0.01	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			150	0.0 _s	450	0.0	0.0	0.10	0.001	0.010	0.001	0.010	0.000	0.000	0.007	0.021	0.000	0.000	
			200	0.0 _s	520	0.0	40.0	0.90	0.011	0.033	0.011	0.097	0.000	0.000	0.002	0.004	0.002	0.002	
			300	9.8	450	0.0	70.0	26.0	0.242	0.402	0.121	0.242	0.050	0.400	0.087	0.054	0.037	0.024	
			600	53.1	550	14.0	2500	20.5	0.232	1.159	0.022	0.300	0.000	0.000	0.017	0.010	0.00	0.00	
18	Limestone (Sagara)	Tertiary	80	0.0	470	0.0	0.0	0.16	0.001	0.008	0.001	0.100	0.000	0.000	0.001	0.001	0.220	0.000	0.000
			150	0.0 _s	490	0.0	12	0.8	0.081	0.162	0.004	0.040	0.020	0.001	0.083	0.415	0.209	0.001	
			200	0.0 _s	670	0.0	25	3.0	0.119	0.481	0.106	0.136	0.209	0.292	0.159	0.319	0.257	0.001	
			300	0.4	950	0.0	35	50.3	3.641	7.267	1.573	0.629	0.342	0.907	2.233	2.546	5.930	2.277	
			600	40.6	550	1.5	160	190	0.032	0.605	0.005	0.093	0.021	0.021	0.002	0.001	0.005	0.001	
19	Limestone (Garo)	Triassic (presumptive age)	80	0.0	770	0.0	—	0.000 _s	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
			150	0.0 _s	540	0.0	—	0.001	0.000 _s	0.002	0.000	0.000 _s	0.000	0.000	0.000 _s	0.000 _s	0.000	0.000	
			200	0.0 _s	550	0.0	—	0.00 _s	0.000 _s	0.000 _s	0.000 _s	0.000 _s	0.000	0.001	0.000 _s	0.000 _s	0.000		
			300	2.8	460	0.0	—	1.0	0.169	0.337	0.090	0.270	0.004	0.032	0.066	0.033	0.040		
			600	118.7	660	1.7	—	45.2	0.389	10.950	0.104	1.249	0.000	0.000	0.105	0.053	0.000		
20	Limestone (Akasaka)	Permian	80	0.0	480	0.0	—	0.1	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
			150	0.0	440	0.0	—	0.5	0.007	0.007	0.006	0.018	0.000	0.000	0.003	0.009	0.003		
			200	0.0	460	0.0	—	0.4	0.008	0.015	0.007	0.050	0.000	0.000	0.009	0.012	0.006		
			300	0.0 ₁	490	0.0	—	0.9	0.020	0.040	0.010	0.031	0.001	0.005	0.007	0.003	0.002		
			600	24.2	450	0.0	—	5.0	0.025	0.590	0.007	0.075	0.005	0.002	0.010	0.010	0.010		
21	Limestone (Ō funato-4)	Carboniferous	80	0.0 ₁	3560	0.0	—	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
			150	0.0 ₁	490	0.0	—	0.16	0.001	0.003	0.001	0.030	0.000	0.000	0.051	0.153	0.000		
			200	0.0 ₁	660	0.0	—	0.5	0.005	0.100	0.032	0.069	0.032	0.030	0.045	0.090	0.000		
			300	7.9	520	0.0	—	5.0	0.403	1.005	0.203	0.792	0.062	0.124	0.251	0.181	0.040		
			600	93.7	410	1.3	—	25.8	0.102	1.461	0.004	0.012	0.029	0.020	0.078	0.048	0.000		
22	Limestone (Ō funato-8)	Silurian	80	0.0	—	0.0	0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
			150	0.1	480	0.0	20	0.023	0.000 ₁	0.001	0.000	0.000	0.000	0.000	0.001	0.010	0.000		
			200	0.1	1350	0.0	20	0.070	0.001	0.004	0.001	0.006	0.001	0.007	0.002	0.007	0.002		
			300	4.6	480	0.0	—	1.0	0.041	0.102	0.011	0.032	0.003	0.010	0.025	0.015	0.007		
			600	121.8	610	0.3	460	8.0	0.062	0.810	0.006	0.061	0.003	0.006	0.016	0.016	0.000		
23	Kerogen (Ikume, Miyazaki prefecture)	Miocene	80	0.0	—	0.0	0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
			150	0.0	—	0.0	0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
			200	0.0	—	0.0	—	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
			300	0.0	—	—	—	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
			600	850	—	14.0	1194	50.0	7.025	35.459	2.030	2.030	0.000	0.000	4.610	0.001	0.000		

Table 2 Chemical components of Low-Molecular-Weight hydrocarbons in pyrolyzed gases from the Kasukabe-drilling cores, by heating at 400°C for 10 minutes ($\mu\text{l}/0.06\text{g}$).

Components	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁₀	1-Butene	i-Butylene	i-C ₅ H ₁₂	n-C ₅ H ₁₂
Depth (m)											
506	62	3.260	10.333	1.161	4.427	0.100	0.203	0.207	0.240	0.286	0.010
800	16	0.122	3.209	0.073	0.506	0.000	0.000	0.000	0.000	0.000	0.000
1028	48	0.640	9.605	0.298	8.000	0.018	0.015	0.257	0.149	0.251	0.014
1050	32	0.345	1.774	0.232	4.002	0.051	0.015	0.182	0.244	0.205	0.014
1456	55	4.236	5.505	0.981	3.053	0.080	0.154	0.257	0.451	0.197	0.018
1900	10	0.830	2.501	0.153	1.110	0.046	0.050	1.116	0.838	1.422	0.017
2000	40	10.000	13.336	2.000	8.000	0.011	0.378	0.631	1.216	0.749	0.142
2200	20	0.839	6.660	0.544	6.665	0.015	0.082	0.323	0.554	0.463	0.010
2600	30	4.281	3.755	1.150	2.505	0.013	0.229	0.139	0.181	0.215	0.050
2900	50	8.331	5.004	2.087	5.000	0.056	0.431	0.425	0.763	0.693	0.277

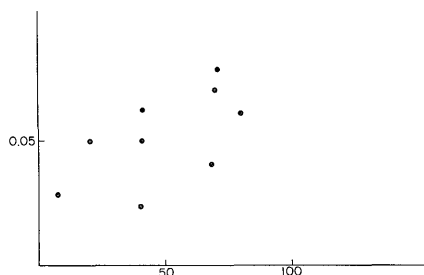


Fig. 6 Relation between the extracted organic matter and the sum of hydrocarbons in pyrolyzed gases Kasukabe-drilling cores.

Except for the total amount of pyrolyzed gases generated from coal, peat and petroleum reservoir rocks, the quantity of thermally decomposed gases, in general, is less than 1000 $\mu\text{l}/0.06\text{g}$.

There is positive correlation between the temperature of pyrolysis and quantity of gases generated by heating sediments.

The same tendency is shown in Fig. 6 as regards the relation between the amount of pyrolyzed gases and the content of soluble organic matter in sediments.

Fig. 7 shows the volume ratios of total amount of hydrocarbons at different temperatures. Generally, the volume ratios of pyrolysis gases are relatively high at 300°C to 600°C. On the other hand, the volume ratios of most limestones is relatively high at about 300°C.

EISMA and JURG (1964) reported that gaseous paraffins and olefins were generated remarkably by heating the behenic acid in the presence of clay minerals at temperatures ranging from 275 to 300°C.

Considering the results of EISMA and JURG (1964) and the authors' experiment, it is estimated that the thermal change of organic matter in sediments and sedimentary rocks takes place extensively at temperatures above 300°C.

The thermal decomposition of kerogen takes place at higher temperature than 300°C. From this fact, it is assumed that the kerogen exists as a thermally stable form in sedimentary rocks.

III. 2 H₂, N₂, CO₂ and CO

a) H₂

The quantity of H₂ in pyrolyzed gases from coal and peat by heating at 600°C is 60,600 $\mu\text{l}/0.06\text{g}$ and 26,000 $\mu\text{l}/0.06\text{g}$ respectively (Table 1), and this amount is very large compared with those of normal sediments and limestones.

Except for volcanic gas, H₂ content is generally low in natural gases (YONETANI, 1967b) and

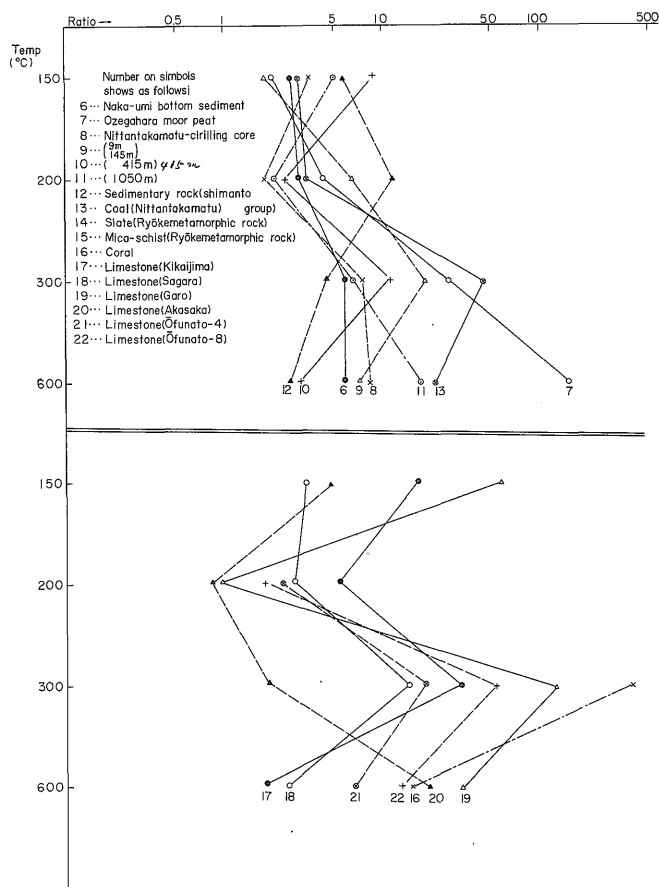


Fig. 7 The volume ratios of total amount of hydrocarbons generated at different temperatures.

the CH_4/H_2 ratio is more than 10,000. On the other hand, the values of thermally decomposed gases are mostly lower than 100.

On the basis of the fact that a larger amount of H_2 exists in pyrolyzed gases than the content of H_2 in natural gas in Japan (YONETANI, 1963, 1967, 1967b, 1971, 1972), it is presumed that the pyrolysis temperature of organic matter in sediments and sedimentary rocks is as low as 80°C.

b) N_2

Avery small amount of O_2 is detected in all pyrolyzed gases. This is probably due to insufficient substitution of air in combustion tube by argon. Accordingly N_2 in pyrolyzed gas is not under consideration.

c) CO_2 , CO

When the air remains in the combustion tube there is a possibility that O_2 in remaining air combines with organic matter in sediments and sedimentary rocks forming CO_2 and CO . CO_2 is detected by heating the sample above 80°C

The quantity of CO_2 generated from coal and peat by heating is very large, reaching the maximum values of 10,800 $\mu\text{l}/0.06 \text{ g}$ and 8,020 $\mu\text{l}/0.06 \text{ g}$ (Table 1), although most of the values

are less than $1,000 \mu\text{l}/0.06 \text{ g}$.

Judging from the amount of N_2 in pyrolyzed gases, all of measured CO_2 do not originate from the reaction with remaining O_2 in the tube, however as proposed by ROBINSON (1969), it is considered that a part of total CO_2 may be produced from the thermal decomposition of $-\text{COOH}$ groups.

CO is detected in pyrolyzed gases from coal and peat by heating above 150°C . On the other hand, CO is detected at above 300°C from sediments and sedimentary rocks.

The maximum amount of CO in pyrolyzed gases obtained from coal and peat is $2,330 \mu\text{l}/0.06 \text{ g}$ and $275 \mu\text{l}/0.06 \text{ g}$ respectively (Table 1), however the amount of CO from sediments and sedimentary rocks does not exceed the value of $10 \mu\text{l}/0.06 \text{ g}$.

A part of total CO in pyrolyzed gas may be produced by the thermal decomposition of $-\text{CO}$ groups in organic compounds.

III. 3 Low-molecular-weight aliphatic hydrocarbons (carbon number C_1-C_5)

The mechanism of thermal decomposition of organic matter, which exists as various types of organic compounds in sediments and sedimentary rocks, is complicated. It is impossible to estimate the original organic compounds in the composition of pyrolyzed gas from sediments and sedimentary

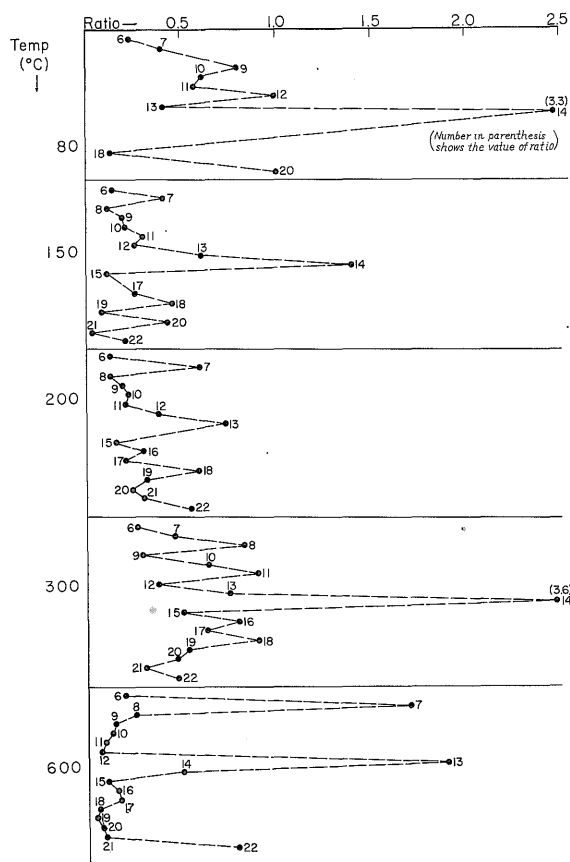


Fig. 8 Total paraffine/Total olefine ratios in pyrolyzed gases of varioustypes of sediments and sedimentary rocks at different heating temperatures.

rocks.

It is an interesting problem whether the degree of maturation and diagenesis of organic compounds in sediments and sedimentary rocks is reflected or not on pyrolyzed gas composition.

a) paraffin and olefin

The correlation between the values of total paraffin (C_2-C_5)/total olefin (C_2-C_5) ratios and pyrolysis temperature is listed in Fig. 8.

The values of total paraffin/total olefin ratio are generally more than 1.0 and these values (YONETANI, 1967) are similar to those of the natural gas in Recent sediments. The values of total paraffin/total olefin ratio in the natural gas (Quaternary-Cretaceous) produced from the gas fields in Japan are more than 10,000 (YONETANI, 1967b), and these values are remarkably high as compared with those of Recent gases. But a small amount of olefin is detected in natural gas involved in limestone (FUJINUKI, 1971) and CO_2 -type natural gas. Consequently, the values of the above gas are less than 1.0 in some cases (YONETANI, 1967b, FUJINUKI, 1971).

The values of total paraffin/total olefin ratio in pyrolyzed gases from coal, peat and slate are extremely high at some temperatures.

In general, total paraffin/total olefin ratios are somewhat increased at 300°C.

Although it is obscure to some extent, the total paraffin/total olefin ratios of gases from Nittantakamatu-drilling cores increase with the depth of cores at the pyrolysis temperatures of 150, 200, and 300°C.

The same tendency is seen on Kasukabe-drilling cores (Fig. 9) by pyrolyzing at temperature

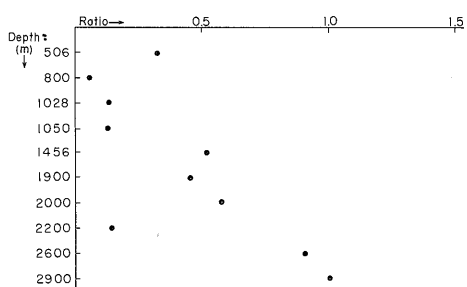


Fig. 9 Relation between the depth and the Total paraffin ($C_2 \sim C_5$)/Total olefin ($C_2 \sim C_5$) ratios in pyrolyzed gases of Kasukabe-drilling cores.

FUJINUKI, 1971) especially, a large amount of C_2H_4 (YONETANI, 1967) is found in the natural gas in Recent sediments.

The values of C_2H_6/C_2H_4 ratio in the pyrolyzed gases ordinarily fall below 1.0 (Fig. 10), but sometimes coal, peat and slate show the values of more than 1.0. Generally the values of C_2H_6/C_2H_4 ratio in pyrolyzed gases in various temperatures are comparatively high at 300°C.

GUGGENHEIM (1941) calculated the thermodynamic equilibrium constant between C_2H_6 and C_2H_4 at 400°C and 600°C, and obtained the values of equilibrium constant 12,000 and 32 respectively. Compared with the equilibrium constant calculated by GUGGENHEIM, the C_2H_6/C_2H_4 ratio in pyrolyzed gases of authors' data (Fig. 5) are higher at 300°C than 600°C, and the equilibrium does not exist between mutual components in pyrolyzed gases generated under 300°C. From the

400°C for 10 minutes. It may be interesting to suggest that the degree of diagenesis of organic matter in sedimentary rocks is indirectly reflected on the pyrolyzed gas compositions.

b) C_2H_4 and C_2H_6

In general, C_2H_4 may exist in trace amount of CH_4 -type natural gas (YONETANI, 1967b), if C_2H_4 is present in it.

On the contrary, C_2H_4 is detected very often in natural gas extracted from limestone and CO_2 -type natural gas (YONETANI, 1967b;

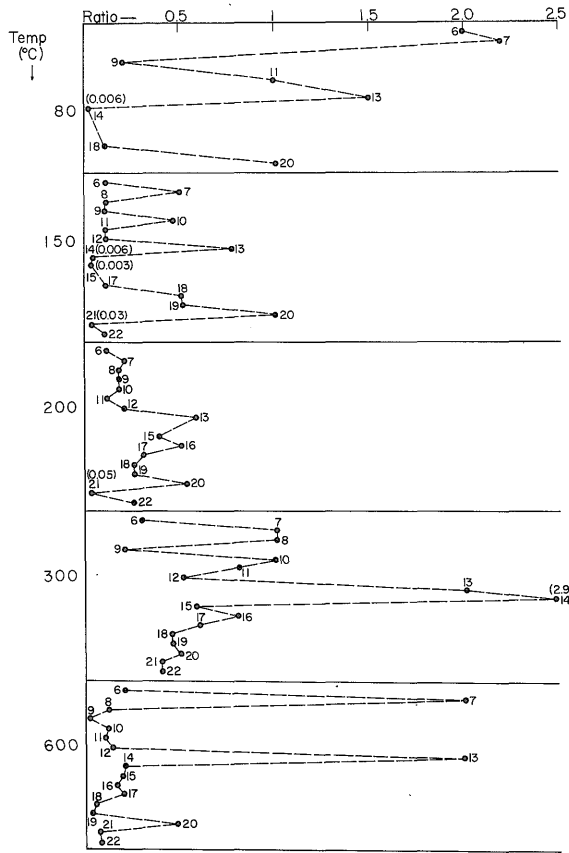


Fig. 10 C_2H_6/C_2H_4 ratios in pyrolyzed gases of various types of sediments and sedimentary rocks at heating temperatures.

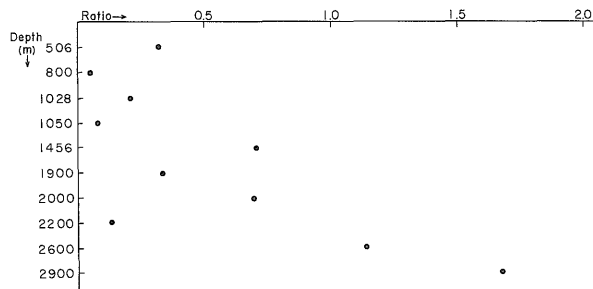


Fig. 11 Relation between the depth and the C_2H_6/C_2H_4 ratios in pyrolyzed gases of Kasukabe-drilling cores.

above phenomena, it is assumed, that the gas composition decomposed up to 300°C reflects indirectly the character of organic matter in sediments and sedimentary rocks.

It is presumed that C_2H_6/C_2H_4 ratios of pyrolyzed gases from limestones (geological age ranging from Recent to Silurian) at 200 and 300°C increase with the geological age, and on the contrary, as seen in Fig. 11, the C_2H_6/C_2H_4 ratios in pyrolyzed gases from Kasukabe-drilling cores increase with the depth.

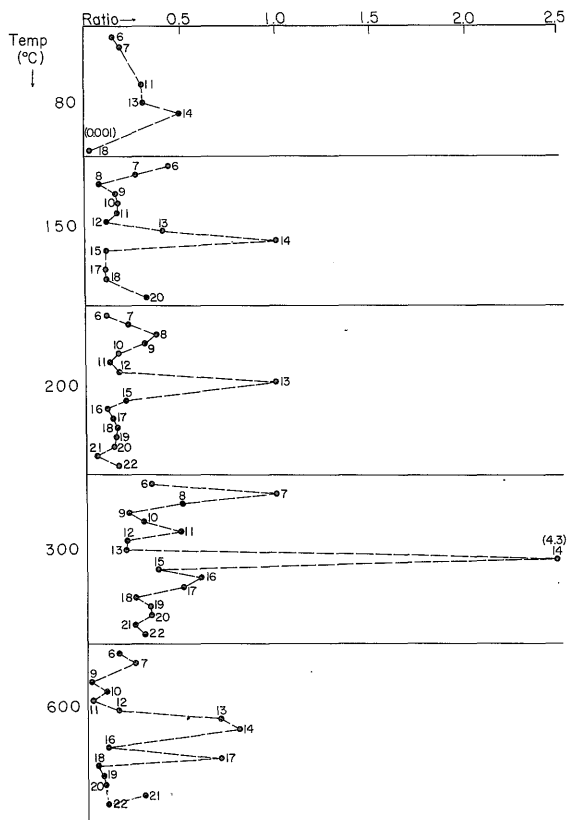


Fig. 12 C_3H_8/C_3H_6 ratios in pyrolyzed gases of various types of sediments and sedimentary rocks at different heating temperatures.

c) C_3H_8 and C_3H_6

C_3H_6 component generally exists in Recent natural gas, and the values of C_3H_8/C_3H_6 ratio in the gases are more than 1.0 (YONETANI, 1967, 1972). While C_3H_6 is in trace amount of CH_4 -type natural gas (YONETANI, 1967b). The values of C_3H_8/C_3H_6 ratio in most pyrolyzed gases are less than 1.0 (Fig. 12) and the relatively high values are found at 300°C.

As in the case of C_2H_6/C_2H_4 ratio, the pyrolyzed gases of coal, peat and slate have the higher values of C_3H_8/C_3H_6 ratio than others.

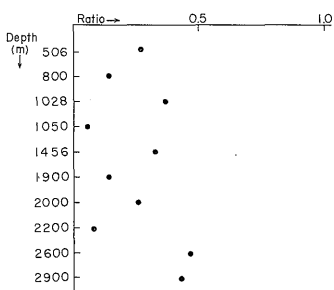


Fig. 13 Relation between the depth and the C_3H_8/C_3H_6 ratios in pyrolyzed gases of Kasukabe-drilling cores.

The C_3H_8/C_3H_6 ratio is influenced by temperature and this value, as similar to C_2H_6/C_2H_4 ratio, appears to be the maximum at 300°C. On the other hand, as seen in Fig. 13, it is obscure there is the correlation between depth and the C_3H_8/C_3H_6 ratio in pyrolyzed gas of Kasukabe-drilling cores heated at 400°C for 10 minutes. A similar relation between depth and C_3H_8/C_3H_6 ratio in pyrolyzed gas is seen also in extracted gas

from Kasukabe-drilling core.

d) $i\text{-C}_4\text{H}_{10}$ and $n\text{-C}_4\text{H}_{10}$

The oil field gas contains large amounts of $i\text{-C}_4\text{H}_{10}$ and $n\text{-C}_4\text{H}_{10}$ components. 50% of casinghead gases produced from gas fields, oil field and coal field regions in Japan are more than 1.0 (YONETANI, 1972) for $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratios. The values of natural gas in Recent marine deposit are more than 1.0 (YONETANI, 1967). On the contrary, the values of peat are less than 1.0.

The values of $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratio of thermal decomposition gases are predominantly in the range from 0.1 to 10 (Fig. 14) and the minimum values are indicated at 300°C. Compared with the notably high values of total paraffin/total olefin, $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$

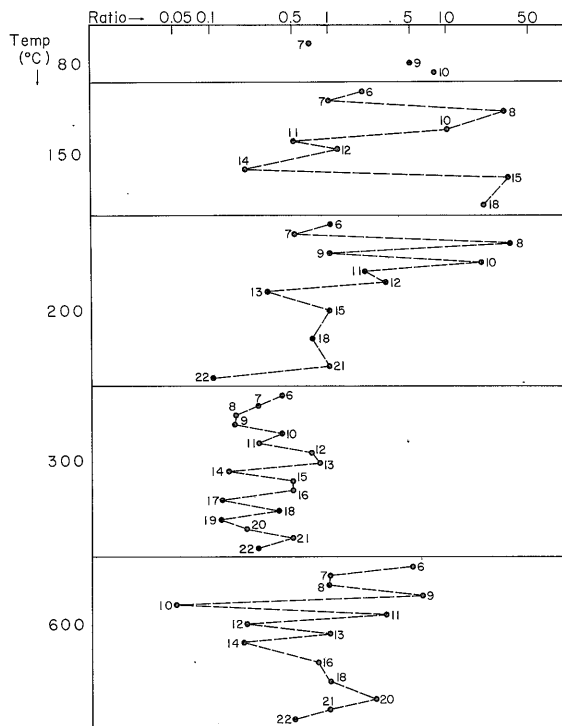


Fig. 14 $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratios in pyrolyzed gases of various types of sediments and sedimentary rocks at different temperatures.

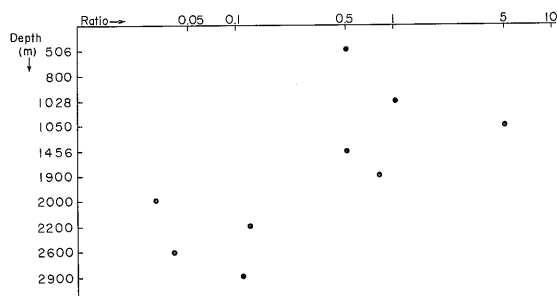


Fig. 15 Relation between the depth and the $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratios in pyrolyzed gases of Kasukabe-drilling cores.

ratios in pyrolyzed gases from coal, peat and slate, in the case of $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratio, there have not been seen such peculiar values in these samples. As seen in Figs. 14, 15, the values of $i\text{-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$ ratio in pyrolyzed gases of Nittantakamatu-drilling cores heated at 150 and 200°C for 1 hr. and Kasukabe-drilling cores at 400°C for 10 minutes indicate a tendency to decrease with depth.

e) $i\text{-C}_5\text{H}_{12}$ and $n\text{-C}_5\text{H}_{12}$

The values of $i\text{-C}_5\text{H}_{12}/n\text{-C}_5\text{H}_{12}$ ratio in the natural gas in Japan are more than 1.0 (YONETANI, 1967b), while the pyrolyzed gases of sediments and sedimentary rocks give the values in a wide range of 1.0 to 50. However these values do not change notably by temperature (Fig. 16).

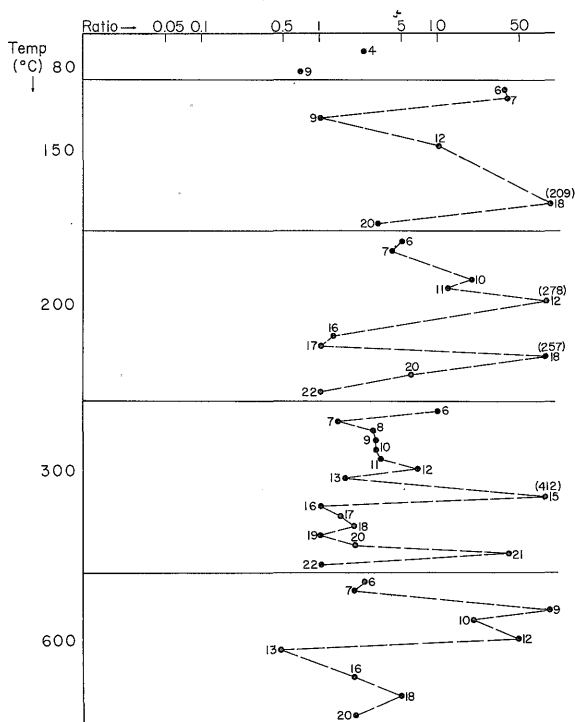


Fig. 16 $i\text{-C}_5\text{H}_{12}/n\text{-C}_5\text{H}_{12}$ ratios in pyrolyzed gases of various types of sediment and sedimentary rocks at different heating temperatures.

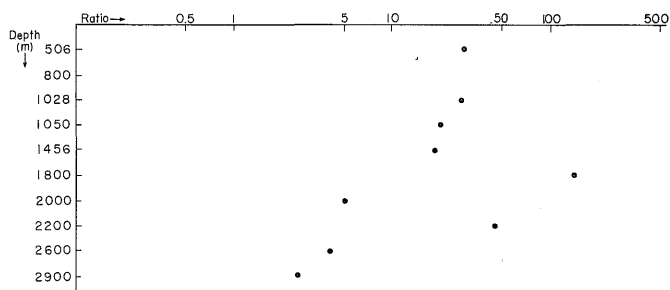


Fig. 17 Relation between the depth and the $i\text{-C}_5\text{H}_{12}/n\text{-C}_5\text{H}_{12}$ ratios in pyrolyzed gases of Kasukabe-drilling cores.

The values of $i\text{-C}_5\text{H}_{12}/n\text{-C}_5\text{H}_{12}$ ratio in pyrolyzed gases of Kasukabe-drilling cores indicate a tendency to decrease with depth (Fig. 17) and the same tendency for the values is seen in extracted gases of Kasukabe-drilling cores (Fig. 4).

f) 1-Butene and i-Butylene

1-butene and i-butylene must be contained in trace amounts of casinghead gases from oil, coal and gas field regions (YONETANI, 1967b), if these gas components exist in them, although 1-butene

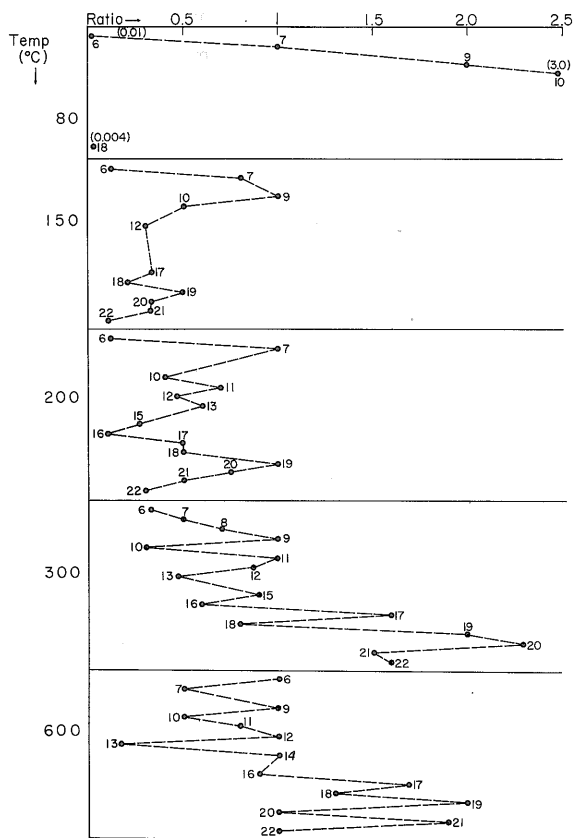


Fig. 18 1-Butene/i-Butylene ratios in pyrolyzed gases of various types of sediments and sedimentary rocks at different heating temperatures.

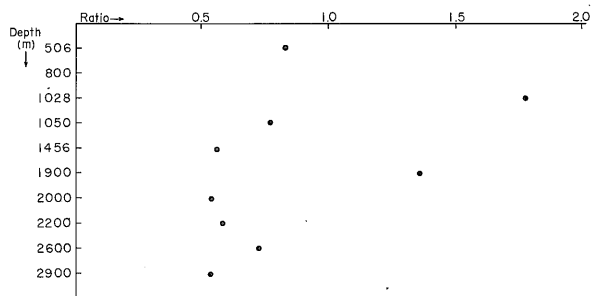


Fig. 19 Relation between the depth and the 1-Butene/i-Butylene ratios in pyrolyzed gases of Kasukabe-drilling cores.

and *i*-butylene are detected usually in the gases originated from Recent deposits and limestones (YONETANI, 1967, FUJINUKI, 1971).

Fig. 18 shows the values of 1-butene/*i*-butylene ratio in pyrolyzed gases at various temperatures. Generally, the values of 1-butene/*i*-butylene ratio in pyrolyzed gases do not exceed 1.0 and the value shows a tendency to increase with pyrolysis temperature. As seen in Figs. 18 and 19, the values of 1-butene/*i*-butylene ratio in pyrolyzed gases of Nittantakamatu-drilling cores by heating at 150 and 200°C and Kasukabe-drilling cores at 400°C for 10 minutes indicate a tendency to decrease with depth of cores. It is noteworthy that the pyrolyzed gases of limestones have high 1-butene/*i*-butylene ratio at 300 and 600°C.

g) CH₄ and total amount of hydrocarbons (C₂-C₅)

It is elucidated that the relations between geologic age and the values of CH₄/total hydrocarbons (C₂-C₅) ratio in natural gas in Japan are in the following order (YONETANI, 1967b):

(Recent and Quaternary natural gas) > (Tertiary natural gas dissolved in water and coal field gas) > (oil field gas) < (Cretaceous natural gas and other older gas)

Fig. 20 shows the values of CH₄/total hydrocarbons (C₂-C₅) ratio in pyrolyzed gases. Commonly, the values of CH₄/total hydrocarbons (C₂-C₅) ratio in pyrolyzed gases increase with depth of sediments and most of the values range from 1 to 20 at temperature above 200°C.

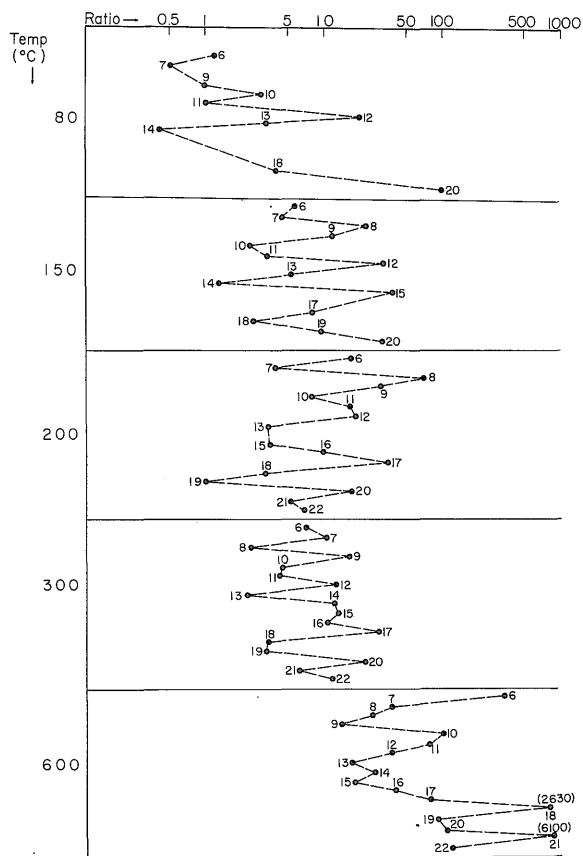


Fig. 20 CH₄/total hydrocarbons (C₂~C₅) ratios in pyrolyzed gases of various types of sediments and sedimentary rocks at different heating temperatures.

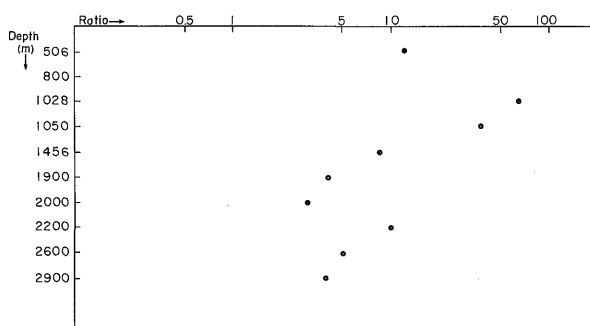


Fig. 21 Relation between the depth and the $\text{CH}_4/\text{total paraffine (C}_2\sim\text{C}_5)$ ratios in pyrolyzed gases of Kasukabe-drilling cores.

The clear relationship is not seen between geologic age, depth and $\text{CH}_4/\text{total hydrocarbons (C}_2\sim\text{C}_5)$ ratio in pyrolyzed gases of Nittantakamatu-drilling cores (Fig. 20), but the values in pyrolyzed and abstracted gases of Kasukabe-drilling cores (Fig. 21) have a tendency to increase with depth.

IV. Summary

In this study, it is an important problem whether the thermodynamic equilibrium relation exists or not among gas constituents in the pyrolyzed gas. According to the authors' experimental data, the degree of maturation and diagenesis of organic matter in sediments and sedimentary rocks is reflected to some extent on the gas composition generated from the sediments and sedimentary rocks by heating at temperature below 400°C . The above-mentioned phenomenon leaves some doubt because the authors' result is obtained from the insufficient number of experimental samples. Further study is needed to confirm this phenomenon.

In this experiment, authors demonstrate that the organic matter in sediments and sedimentary rocks is pyrolyzed even at 80°C . But, the CH_4 -type natural gas originated from deeper zone (depth 2,000–3,000 m, estimated formation temperature exceeds 80°C) and natural gas accompanying with hot-spring water do not contain olefine at the limiting sensitivity level of 0.0001 in vol. %. This fact brings forward the interesting problem with regard to the metamorphic factor of organic matter in sedimentary rocks.

It is assumed that kerogen is pyrolyzed between 300 and 600°C . Namely, the kerogen exists in thermally more stable form than the soluble organic matter with benzene-methanol-acetone solvent. The kerogen is also the most stable form of organic matter to survive in sedimentary rocks.

Acknowledgment

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たい積物・たい積岩中の有機物の熱分解ガス組成

米谷 宏・大場 信雄

要 旨

たい積物・たい積岩を Ar 気相中で80~600°Cに加熱し、そのさい発生したガスを分析して以下に述べる考察をまとめた。

1) たい積物・たい積岩を加熱したさい発生したガス中の H_2 およびオレフィン系炭化水素は、 CH_4 系天然ガスのそれと比較して、いちじるしく多い。このことは、たい積物・たい積岩中の有機物が80°Cでも熱分解することを暗示する。

2) 加熱によって発生した炭化水素ガスの量は、300°Cあるいは600°Cで比較的多い。

3) Kerogen の熱分解は、300°Cからみとめられた。このことは、Kerogenがたい積物・たい積岩中の抽出性有機物より熱的に安定であることを示す。

4) たい積岩の熱分解ガス組成と地質時代および深度との関係については、今後の検討に待つところが多い。