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Chemical Analysis of the Dolgorae-1 well Petroleum Source Rock

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돌고래-1 공 석유근원암의 화학분석

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Abstract : The chemical composition and characteristics of the source rock collected from Dolgorae-1 well in Korea continental shelf block VI(35° 18′ N.L., 130° 28′ E) have been investigated. An oil show analyzer(OSA) has been used to determine the contents of gas, oil and total organic carbon(TOC). The average TOC value for the sample is found to be 0.59%. The OSA has also provided hydrogen index and T_{max}, the maximum temperature which generate maximum hydrocarbons from kerogen. From a T_{max}-hydrogen index diagram the type of organic matter in the source rock was estimated to be type III kerogen. The content of bitumen and its molecular weight have been determined by means of extraction method and gel permeation chromatograph, respectively. The physicochemical properties has been studied using X-ray diffraction spectrometer, IR spectrometer and thermogravimetric method. On the basis of the results obtained in the present work, the samples collected from Dolgorae-1 well are evaluated to be poor source rocks.

Key Words : Petroleum source rock, Pyrolysis, Kerogen

요 약

한국 대륙붕 블럭 VI의 돌고래-1공에서 채취한 근원암의 화학성분 및 특성에 관해 조사하였다. 유징분석기를 사용하여 가스, 기름 및 총추출유기물의 양을 구했으며 총추출 유기물의 양은 0.59%이었다. 비투멘의 양과 분자량은 용매추출법과 겔투과 크로마토그라피에 의해 구했으며, X-선회절법, 적외선분광법 및 열무게 측정법으로 물리화학적 성질을 고찰하였다. 분석 결과로부터 돌고래-1공의 시료는 미미한 석유근원암으로 평가되었다.

1. INTRODUCTION

In recent years the efforts to search for petroleum is extremely emphasized in Korea, where the consumption of energy is rapidly increasing and no single economical oil deposit is found so far[1,2]. A syste-

matic geochemical studies can help to decrease the uncertainty in predicting a petroleum-filled structure. This is important especially in offshore areas and remote exploration regions where drilling cost is comparatively high. The key in the basin study is to identify petroleum source rock, which is called for the rock that is, or may become, or has been able to generate petroleum. The nature of the source rock is a powerful guide to the present condition of any accumulated oil in areas where the wells have not penetrated the relevant rocks at a position where a potential trap for hydrocarbons exists, with an appropriate geological histroy. The requirement for a potential source rock is the presence of insoluble organic matter (kerogen) and it is generally accepted that any rock containing about 0.5 % of organic carbon may produce oil or gas. A facet of major attention in recognition of a source rock has been the determination of its content of organic matter, the type of kerogen, and the evolutionary stages of kerogen which is commonly referred to as maturity. Therefore, the prerequisite for a valuable application of the source rock is the improved analytical technique employed to identify the composition in detail. Analytical methods used widely for source rock evaluation have been total organic carbon determination[3,4], pyrolysis[5,6], organic petrography[7,8], optical analysis[9], and various organic and inorganic geochemical analyses[10~12]. The quality and maturation of organic matter are the basis of the characterization of the source rock. It is well known that pyrolysis is the best routine tool since this technique allows the determination of type and maturation simultaneously[3~5].

In the present study, source rock samples from Dolgorae-1 well in Korea continental shelf were evaluated using an oil show analyzer(OSA). The OSA technique is based on the quick analysis of cuttings by pyrolysis cycle followed by the oxidation in air of the organic matter remaining after pyrolysis. We have carried out X-ray diffraction measurements and thermogravimetric analysis to investigate the composition of the samples. To further characterize the source rock, total extractable organic matter(TOM) was determined by extraction method. A gel permeation chromatograph was used for the determination of molecular weight of TOM.

2. EXPERIMENTAL

2. 1. Sample Preparation

Sixteen ditch cutting samples in approximately 100 m intervals in depth were obtained from Dolgorae-1 well (Location : 35° 18′ N.L., 130° 28′ E) in Korea continental shelf block VI (Figure 1). These samples covered a depth range of 2700−4300 m from sea level. Samples were not collected from 222 m(drilling start position) down to 2700 m because this region does not contain materials for our analytical purpose. To prepare samples for oil show analyzer each cutting was separated from mud and other contaminants using 3 mm sieve, washed with water, and then air dried on a filter paper. One hundred milligrams of the clear sample was weighed in a small Ni crucible for each oil show analyzer measurement. In order to determine the composition of the source rock, clean

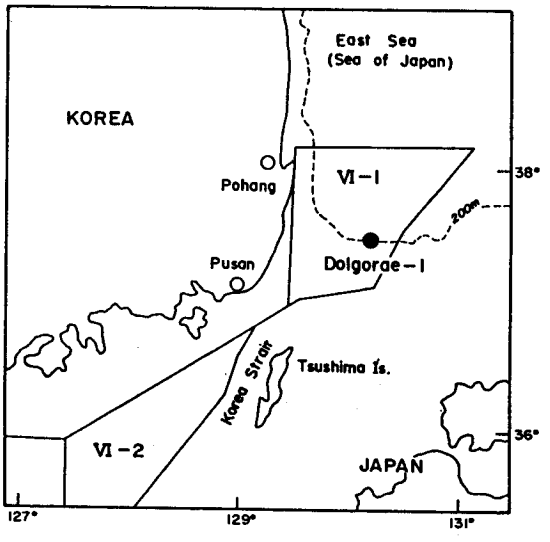

Fig. 1. Location of the Dolgorae-1 well (35° 18′ N. L., 130° 28′ E). The 200 meter depth line is indicated by dotted line.

samples were used after crushing using a Jaw crusher, followed by grinding in about 80 to 100 meshes.

2. 2. Measurements

X-ray diffraction measurements were carried out with a Philips Model 1730 using Cu target and K_α radiation. The instrument operation conditions used are as follows : slit 1°, 0.1°, 1° ; accelerating voltage, 40 KV/20 mA ; scanning, 2°/min ; chart speed, 2 cm /min ; range, 3°−55°. IR spectra were obtained on a Bio-rad FTS-40 FT-IR spectrometer. Thermogravimetric analysis (TGA) studies was done using Chino Mode PN system. The TGA range was +50 mg (full scale) and the rate of temperature increase was 9°C/min. A Waters Model 244 Gel permeation chromatograph (GPC) was used in conjunction with refractive index detector for the determination of molecular weight distribution of TOM. For GPC studies, μ-strangel columns of 100, 500 and 100 Å were used and the mobile phase was tetrahydrofuran. An IFP-FINA type oil show analyzer was employed in this study. The helium and hydrogen flow rates for pyrolysis were adjusted to 50± 1 and 28± 1 ml/min, respectively. To purge the system helium with flow rate of 40± 1 ml/min was used. The total extractable organic matter (TOM) was determined using Soxhlet apparatus with benzene/acetone/methanol (2 : 1 : 1 V/V) mixture as extraction solvent[13].

3. Results and Discussion

3. 1. Physical Properties and Inorganic Composition

Inorganic chemical composition determined by wet silicate analysis is found to be very similar for all the rock samples. The major components found for the sample collected from the 3102−3125 m region are SiO_2, Al_2O_3, Fe_2O_3 and CaO, and their weight percentages are 56.30, 3.95, 6.51 and 2.05 %, respectively. The loss of ignition for the sample is 26.50 %, and MgO, Na_2O and K_2O are found to be trace components. Fig. 2 represents the X-ray diffraction pattern of source rock sample collected from 4006−4026 m region. Similar results are obtained for the other samples. The results of X-ray diffraction studies indicate that the samples are mainly composed of clay minerals. Quartz, feldspar and kaolinite are major components and illite and siderite exist as minor ones.

Fig. 3 shows a typical differential thermal analysis (DTA) curve obtained using α-Al_2O_3 as standard together with TGA curve for the sample collected from

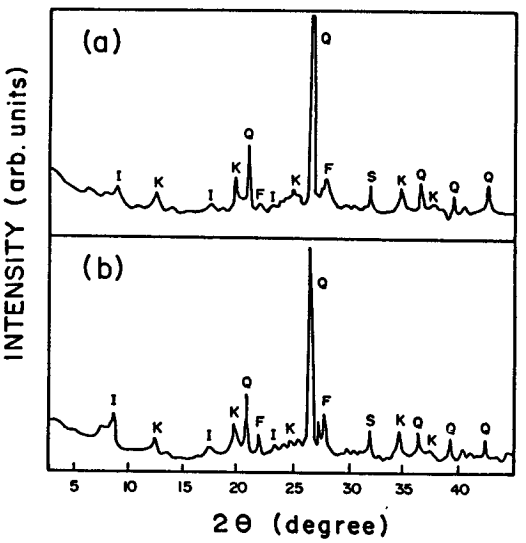

Fig. 2. X-ray diffraction pattern of source rock sample collected from Dolgorae-1 well : (a) 3102−3126 m ; (b) 4006−4026 m ; Q, quartz ; F, feldspar ; K, kaolinite ; I, illite ; S, siderite.

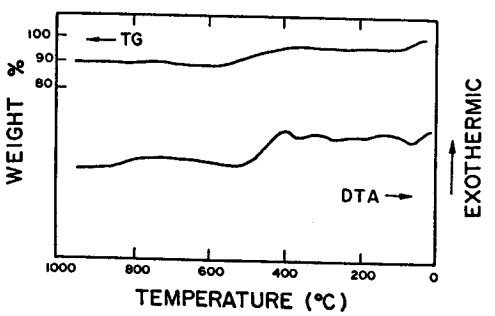

Fig. 3. Thermal curves of source rock sample collected from 4006−4026 m region of Dolgorae-1 well.

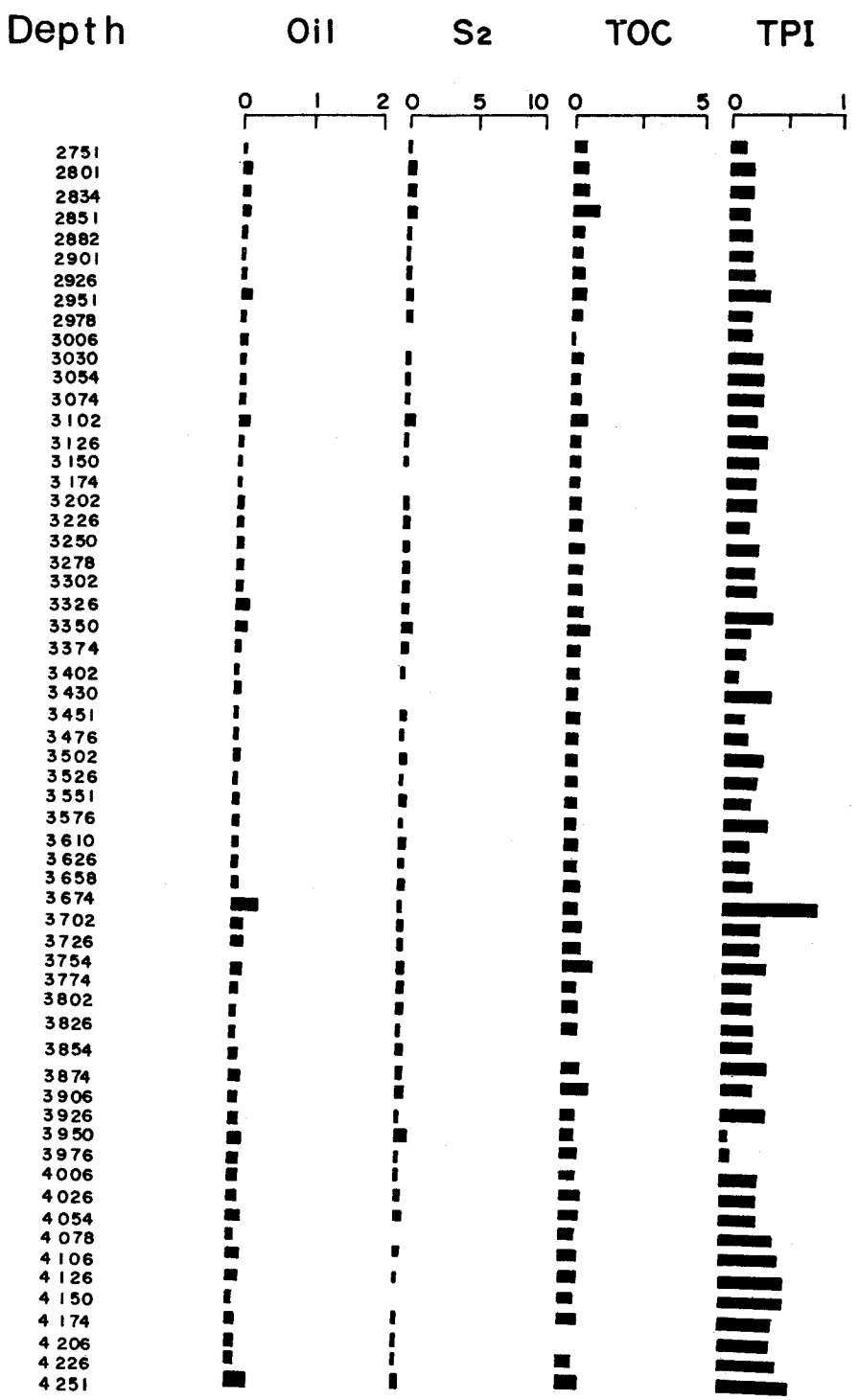

Fig. 5. Geochemical log of Dolgorae-1 well source rock obtained by OSA.

4006−4026 m zone. An endothermic peak appeared at 66 °C is due to the release of adsorbed water in the sample. Several exothermic peaks occurred in the range 250−530 °C indicate that organic matter in the sample oxidize. The observed weight loss is found to be about 4%. The peak shown at 572 °C is thought to be the result of phase change of quartz.

3. 2. Organic Composion

A typical IR spectra of the samples are shown in Fig. 4. Of note here are the C-H out of plane deformation peak around 870 cm^{-1} and the C-H stretching band around 2900 cm^{-1}. The broad band appeared in the range 930−1800 cm^{-1} represents the combination of various stretching, bending and skeletal vibrations which indicate the multiplicity of various functional groups. Table 1 provides a summary of the results for all the samples studied and Fig. 5 represents the geochemical log printed on the OSA plotter. The T_{max} is the temperature in °C when maximum generation of hydrocarbons from kerogen occurs. Therefore, the T_{max} values indicate the organic matter maturation degree : $T_{max} \leq 430-435$ °C, immature zone ; 430−435 °C$\leq T_{max} \leq$ 465 °C, oil zone ; $T_{max} \geq$ 465 °C, gas zone[3]. According to this classification Dalgoral-1 well source rock falls under the oil zone category. The GPI, OPI and TPI is gas, oil and total production index, respectively ; GPI=$S_0/(S_0+S_1+S_2)$, OPI=$S_1/(S_0+S_1+S_2)$ and TPI=$(S_0+S_1)/(S_0+S_1+S_2)$ where S_0 and S_1 are the quantity of gas and oil, respectively, in mg/g rock sample and S_2 is the quantity of hydrocarbons produced by thermal conversion of kerogen contained in the rock sample in mg hydrocarbons produced by thermal conversion of kerogen contained in the rock sample in mg hydrocarbons/g rock. The S_2 value is a good indicative of sou-

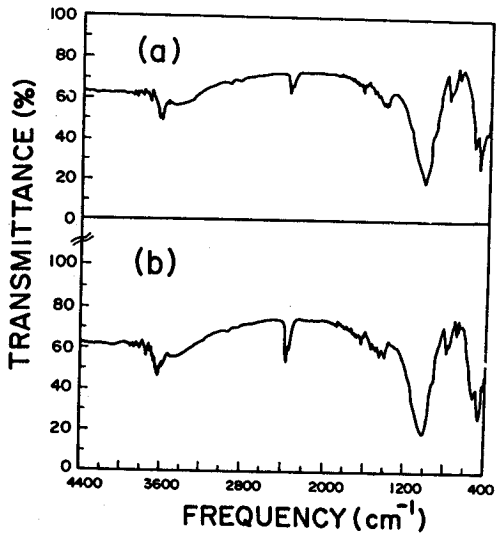

Fig. 4. FT-IR spectra of source rock collected from Dolgorae-1 well : (a) 3610−3620 m ; (b) 4006−4026 m.

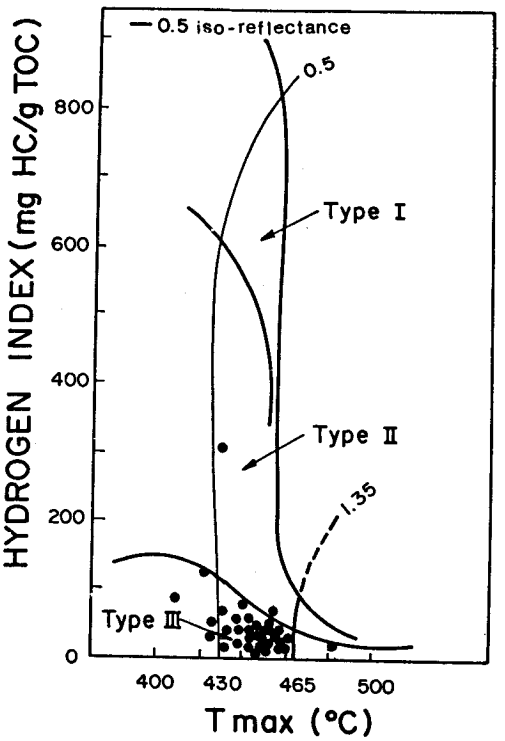

Fig. 6. Estimation of the organic matter type and of maturation for rock samples : (●) plots of hydrogen index vs. temperature for Dolgorae-1 well source rock samples. The vitrinite reflectance value of 0.5 is the criteria to distinguish the diagenesis and categenesis stages [3].

Table 1. Pyrolysis Results for the Dolgorae-1 Well Source Rock

Depth, m	Oil	S_2[a]	T_{max}[a]	OPI[a]	TOC[a]	HI[a]
2751	0.03	0.24	435	0.12	0.50	48
2801	0.13	0.62	411	0.18	0.57	186
2834	0.12	0.56	437	0.18	0.64	87
2851	0.18	0.64	439	0.14	0.01	63
2882	0.07	0.33	441	0.17	0.55	60
2901	0.04	0.20	441	0.17	0.45	44
2926	0.08	0.37	441	0.18	0.53	69
2951	0.15	0.38	435	0.19	0.58	69
2978	0.09	0.44	441	0.17	0.48	91
3006	0.08	0.40	440	0.20	0.50	70
3030	0.09	0.29	442	0.24	0.45	64
3054	0.09	0.26	441	0.26	0.41	63
3074	0.08	0.25	441	0.25	0.43	58
3102	0.17	0.07	429	0.20	0.64	104
3126	0.06	0.17	432	0.22	0.38	44
3150	0.04	0.15	444	0.22	0.38	38
3174	0.03	0.12	446	0.21	0.42	28
3202	0.08	0.32	427	0.20	0.46	66
3226	0.05	0.28	441	0.16	0.47	59
3250	0.08	0.28	445	0.22	0.52	57
3278	0.06	0.29	426	0.18	0.49	59
3302	0.08	0.32	441	0.20	0.43	74
3326	0.03	0.37	444	0.33	0.52	71
3350	0.14	0.63	444	0.18	0.87	72
3374	0.05	0.37	444	0.14	0.51	62
3402	0.06	0.22	444	0.11	0.44	59
3430	0.05	0.12	450	0.31	0.39	30
3451	0.04	0.26	444	0.13	0.46	56
3476	0.03	0.18	449	0.15	0.38	47
3502	0.08	0.25	448	0.25	0.43	58
3526	0.04	0.14	448	0.22	0.39	35
3551	0.06	0.28	449	0.18	0.42	66
3576	0.05	0.15	453	0.30	0.37	40
3610	0.07	0.36	435	0.17	0.49	67
3626	0.07	0.35	448	0.17	0.43	81
3658	0.00	0.34	452	0.19	0.55	61
3674	0.35	0.20	456	0.35	0.56	35
3702	0.11	0.37	448	0.23	0.52	71
3726	0.08	0.28	456	0.22	0.54	51
3754	0.13	0.30	458	0.31	0.97	30
3774	0.08	0.31	454	0.21	0.48	64
3802	0.07	0.25	464	0.22	0.51	49
3826	0.07	0.22	466	0.23	0.54	42
3854	0.03	0.33	460	0.19	0.60	58
3874	0.14	0.35	458	0.32	0.62	48
3906	0.12	0.43	463	0.22	0.90	47
3926	0.10	0.23	467	0.31	0.49	46
3950	0.17	0.28	432	0.32	0.52	50
3976	0.14	0.19	469	0.37	0.56	33
4006	0.04	0.24	459	0.25	0.56	42
4026	0.21	0.71	420	0.26	0.69	44
4054	0.16	0.43	445	0.26	0.67	68
4078	0.06	0.11	476	0.37	0.51	21
4106	0.14	0.22	451	0.39	0.59	37
4126	0.15	0.20	477	0.44	0.63	31
4150	0.07	0.09	472	0.44	0.52	17
4174	0.12	0.01	444	0.37	0.63	33
4206	0.00	0.18	475	0.35	0.60	30
4226	0.14	0.24	455	0.41	0.62	33
4251	0.32	0.33	454	0.48	0.76	46

[a]See text.

rce rock quality. The content of total organic carbon (TOC) is calculated from the sum of residual organic carbon (CO_2) and pyrolysed organic carbon (82 % of the quantity $S_0+S_1+S_2$). The CO_2 resulting from the cracking of kerogen during pyrolysis is not taken into consideration to evaluate TOC. The HI (hydrogen index) is defined as $HI=100S_2/TOC$ with S_2 expressed is mg hydrocarbons/g rock and TOC in % by weight. It is generally accepted that a rock with more than 2 % of TOC is a very good source rock[3~5]. The TOC values of Dolgorae-1 samples range from 0.38 to 1.88% and the average value is 0.59 %. This value is close to the 0.5 % which is considered to be the low limit for source rock[4].

Types of organic matter can be estimated and differentiated by means of a T_{max}-HI diagram as shown in Fig. 6. Such rocks containing abundant organic mat-

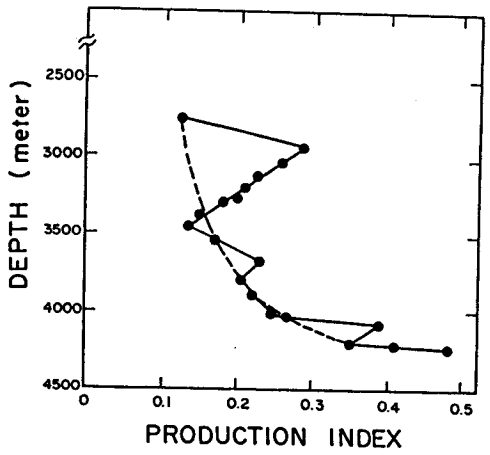

Fig. 7. Plots of depth vs. production index for Dolgorae-1 well source rock samples.

ter of type I or II are excellent source rocks. The plot of HI vs. T_{max} for Dolgorae-1 well sample indicate that the source rock in this region contains type III kerogen.

To obtain the information on migration, depth vs. production index were plotted for Dolgoral-1 well samples (Fig. 7). The production index (PI) is defined as $PI=S_1/(S_1+S_2)$. This plot suggests that migration is expected at about 3000, 3700 and 4100 m regions[3, 4, 10].

The total extractable organic matter (TOM), which is commonly called bitumen was determined by solvent extraction of the finely ground sample followed by hydrocarbon separation and weighing. The TOM content of the rock sample in Dolgorae-1 well is found to be 0.010, 0.025 and 0.026 % for 3000−3300, 3500−3800 and 4000−4200 m region, respectively. The TOM content has a trend to slightly increase in deep samples but the values are generally low comparing with those of good source rock[3]. Molecular weight of TOM determined by gel permeation chromatograph is 348.9 and 589.3 for 3000−3300 and 4000−4200 m zone, respectively. The detailed analysis of bitumen and its structural identification is still under investigation in our laboratory.

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