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# 포항 D공 근원암의 화학조성 및 특성

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# Chemical Composition and Characteristics of the Pohang D Well Source Rock

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## INTRODUCTION

The efforts to search for petroleum is greatly demanded in Korea recently[1,2], where the consumption of energy is rapidly increasing and no single economical oil deposit is found so far. In the early history of exploration for petroleum, wells were usually drilled in the immediate neighbourhood of oil or gas seepages which indicate the presence of petroleum. Recently, the decision to drill a well was taken on the basis of the systematic study utilizing all the possible information on geology, geophysics and geochemistry[3~12]. Since the cost of drilling is high, it is important to extract maximum amount of information from the well before further drilling. The nature of petroleum source rock, which is called for the rocks that are, or may become, or have been able to generate petroleum, is a powerful guide in petroleum exploration. The requirement for a potential source rock is the presence of insoluble organic matter (kerogen) and it is generally accepted that any source rock containing about 0.5% of organic carbon may produce oil or gas[12]. The quality of source rock is defined in terms of amount and type of kerogen and bitumen, and the evolutionary stages of kerogen which is commonly referred to as maturity. Therefore, the prerequisite of source rock evaluation is the improved analytical technique employed to identify the composition in detail.

Frequently used analytical methods have been pyrolysis[13~16], total organic carbon determination[12,17], organic petrography[4,18], optical analysis[19], and various organic geochemical analyses[20,21]. The pyrolysis method is the most widely used screening technique for rapid analyses. This technique also provides geochemical logs which can be interpreted in terms of level of maturity and hydrocarbon migration. The immediate benefit of geochemical logging by pyrolysis obtained directly at the well site is to prevent waste of money by discontinuation of drilling when the pyrolysis results indicate that no oil is to be expected.

In the present study, the core samples were collected from the Pohang D well and they were investigated using an oil show analyzer (OSA). The OSA technique is based on the quick analysis of samples by pyrolysis cycle followed by the oxidation in air of the organic matter remaining after pyrolysis. We have also carried out X-ray diffraction and thermogravimetric analysis to investigate the chemical composition of the sample. In order to further characterize the source rock, the total extractable organic matter (TOM) was determined by extraction method[22], and a gel permeation chromatograph was used for the determination of molecular weight of TOM. The main facet of this report concerns the application of our various experimental results to the evaluation of the samples

collected.

## EXPERIMENTAL

Seventeen core samples were collected in approximately 25 m intervals from the Pohang D well which is located in the southeastern part of Korea. The samples studied here covered a depth range of 104-500 m. For the measurements of X-ray diffraction pattern, thermogravimetry and total extractable organic matter, samples were used after crushing using a Jaw crusher, followed by grinding in about 80 to 100 meshes. For the OSA studies, each core sample was crushed and passed through a 3 mm sieve and was used immediately to prevent from drying. One hundred milligrams of the sample weighed in a Ni crucible was used for each OSA measurement.

An IFP-FINA type oil show analyzer was used in this study. The helium and hydrogen flow rates for pyrolysis were adjusted to $50\pm 1$ and $28\pm 1$ m$l$/min, respectively. The system was purged with helium with flow rate of $40\pm 1$ m$l$/min. The total extractable organic matter (TOM) was determined by means of Soxhlet apparatus, and benzene/acetone/methanol (2:1:1 v/v) mixture was used as extractable solvent[22]. A Philips Model 1730 using Cu target and K$_\alpha$ radiation was employed for X-ray diffraction measurements. The instrument operating 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°; X-ray dosage, 400 cps. Thermogravimetric analysis
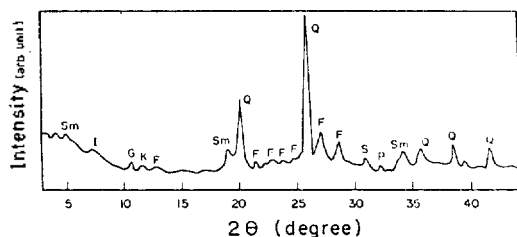


Fig. 1. X-ray diffraction pattern of the Pohang D well sample collected at the depth of 104 m: Cu target and K$_\alpha$ radiation; Q, quartz; F, feldspar; K, kaolinite; I, illite; S, siderite; P, pyrite; G, gypsium; Sm, smectite.

(TGA) was done using a Chino Mode PN system. The TGA range was 50 mg (full scale) and the temperature increase rate was 9℃/min. In order to determine the molecular weight distribution of TOM a Waters Model 244 gel permeation chromatograph (GPC) was used in conjunction with refractive index detector. For the GPC studies, μ-styragel columns of 100, 500 and 1000 Å were used, and tetrahydrofuran was used for mobile phase. For microscopic examination, a Philips Model 505 scanning electron microscope (SEM) was used with accelerating voltage of 30 kV and 20~100 nm beam.

## RESULTS AND DISCUSSION

*Fig.* 1 exemplifies the X-ray diffraction pattern of core sample collected at the depth of 104 m of the Pohang D well. The X-ray diffraction patterns of seventeen samples which cover a depth range of 104~500 m are found to be very similar. The results indicate that the major constituents are quartz, feldspar and smectite, and the minor ones are gypsium, siderite, pyrite, illite and kaolinite. Inorganic chemical compositions determined by wet silicate analysis are also similar for all the samples. Our findings for the sample collected at the depth of 104 m are 59.56, 15.11, 4.69, 1.85, 1.92, 2.41 and 1.66% for SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, CaO, Na$_2$O and K$_2$O, respectively. *Fig.* 2 represents TG and DTA curves for the sample. Several exothermic peaks shown in the range of 200~500℃ indicate that organic matter in the sample oxidize. The observed weight loss is found to be about 4~6% due to the oxidation of organic matters. Since the sample contains a small amount of clay minerals, an endothermic peak appeared at 73℃ mainly due to the release of water molecules. The release of the adsorbed water gave about 5% of weight loss. For the sample collected at the depth of 302 m, a scanning electron micrograph was also taken. The micrograph showed the framboidal pyrite and calcite crystal.

The total extractable organic matter (TOM), which is commonly called bitumen was determined by solvent extraction of the finely ground sa-
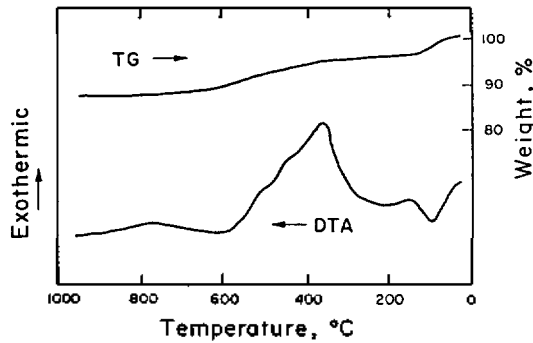
*Fig.* 2. Thermal curves of source rock sample collected at the depth of 302 m of the Pohang D well.

*Table* 1. Summary of Pyrolysis Results for the Pohang D Well Samples

| Depth, m | Oil | $S_2{}^a$ | $T_{max}{}^a$ | $OPI^a$ | $TPI^a$ | $TOC^a$ | $HI^a$ |
|---|---|---|---|---|---|---|---|
| 104 | 0.39 | 4.71 | 427 | 0.08 | 0.08 | 1.77 | 266 |
| 125 | 0.27 | 3.07 | 422 | 0.08 | 0.08 | 1.65 | 186 |
| 150 | 0.22 | 2.91 | 424 | 0.07 | 0.07 | 1.63 | 178 |
| 175 | 0.27 | 4.75 | 426 | 0.05 | 0.05 | 2.10 | 226 |
| 200 | 0.21 | 3.52 | 425 | 0.06 | 0.06 | 1.84 | 191 |
| 225 | 0.40 | 4.12 | 423 | 0.09 | 0.09 | 1.88 | 219 |
| 250 | 0.32 | 6.47 | 427 | 0.05 | 0.05 | 2.12 | 305 |
| 275 | 0.15 | 2.61 | 420 | 0.05 | 0.05 | 1.95 | 133 |
| 302 | 0.56 | 9.55 | 424 | 0.06 | 0.06 | 2.62 | 364 |
| 325 | 0.36 | 6.20 | 428 | 0.05 | 0.05 | 1.96 | 316 |
| 350 | 0.35 | 5.46 | 427 | 0.06 | 0.06 | 1.77 | 308 |
| 375 | 0.33 | 4.93 | 425 | 0.06 | 0.06 | 1.53 | 322 |
| 400 | 0.70 | 10.02 | 426 | 0.07 | 0.07 | 2.80 | 357 |
| 425 | 0.10 | 3.19 | 434 | 0.03 | 0.03 | 1.15 | 277 |
| 450 | 0.24 | 2.74 | 434 | 0.08 | 0.08 | 1.48 | 185 |

$^a$See text.

mple followed by hydrocarbon separation and weighing. The TOM content of the rock sample in the Pohang D well is found to be 0.320, 0.315, and 0.219% for the 104, 302 and 475 m region, repectively. The TOM content tends to slightly decrease in the deep samples but the values are generally low comparing with those of good source rocks[12]. Molecular weight of TOM determined by gel permeation chromatograph is 408.1 and 801.1 for 104 and 302 m region, respectively.

The summary of the results for all the samples studied are provided in *Table* 1. The GPI, OPI, and TPI is gas, oil and total production index,
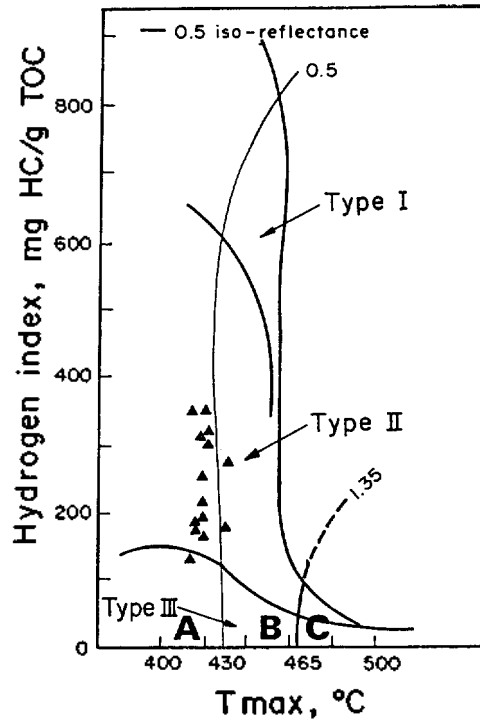


*Fig.* 3. Estimation of the organic matter type and of maturation for the rock samples: A, immature zone; B, oil zone; C, gas zone; ▲, plots of hydrogen index *vs.* temperature for the Pohang D well source rock samples.

respectively. These indices are defined as $GPI = S_0/(S_0 + S_1 + S_2)$, $OPI = S_1/(S_0 + S_1 + S_2)$ 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/g rock. Therefore, the $S_2$ value is a good indicative of source 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 $S_0 + S_1 + S_2$)[23]. The $CO_2$ gas resulting from the cracking of kerogen during pyrolysis is not taken into consideration to evaluate $TOC$[14,23]. The HI (hydrogen index) is defined as $HI = 100S_2/TOC$ with $S_2$ expressed in mg hydrocarbons/g rock and TOC in % by weight[12,23]. It is generally accepted that a rock with more than 2% of TOC is a good source rock[3-5]. The
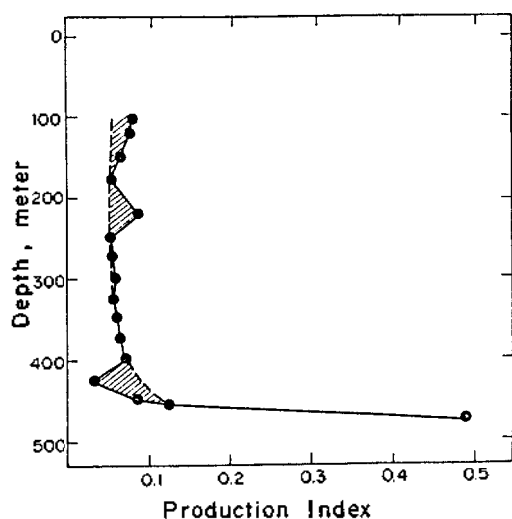
*Fig.* 4. Plots of depth *vs.* production index for the Pohang D well source rock samples.

TOC values of the Pohang D well samples range from 0.04 to 2.02% and half of the samples contain 1.4~2.0%. The total TOC average is 1.42%. This value is a little higher than the 0.5% which is considered to be the low limit for source rock[12]. 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: $T_{max} \leq 430 \sim 435$°C, immature zone; $430 \sim 435$°C$\leq T_{max} \leq 465$°C, oil zone; $T_{max} \geq 465$°C, gas zone[12]. According to this classification the Pohang D well source rock falls under the immature zone category.

Types of organic matter can be estimated and differentiated by means of $T_{max}$-HI diagram as exemplified in *Fig.* 3[23]. The values of vitrinite reflectance can be used to estimate the evolution stage of organic matter. The value of 0.5 is the criteria to distinguish the diagenesis and categenesis stages[12,14]. According to the plot of HI *vs.* $T_{max}$ for the Pohang D well samples, the type of kerogen is close to type II.

*Fig.* 4 represents the plot of depth *vs.* production index (PI) for the Pohang D well samples. The production index is defined as PI=$S_1/(S_1 + S_2)$. This type of plot can provide information on migration. The results suggest that migration is expected at about 230 and 420 m regions.

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