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## THERMAL ALTERATION OF KEROGEN BY BASALT DYKES INTRUDED IN THE OLIGOCENE PORONAI FORMATION, HOKKAIDO, JAPAN

by

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(with 5 text-figures and 2 tables)

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### *Abstract*

Thirteen kerogens separated from the siltstone of the Oligocene Poronai Formation were analysed to examine the thermal alteration effect by the basalt intrusion. This intrusion gave a drastic decrease of kerogen content in the siltstone within a meter from the contact. At the proximity of the basalt the increase of H/C and of n-alkanes generated from the kerogen by laboratory pyrolysis suggests hydrogenation to the kerogen by superheated steam provided from the igneous intrusion.

### Introduction

Recent sediments and sedimentary rocks contain a complex mixture of a great variety of organic matter which is insoluble in organic solvents. This organic matter is defined as kerogen (Abelson, 1963, 1967). Recently, it has become a leading hypothesis that kerogen is the source material of petroleum generated in the subsurface during diagenesis (Abelson, 1963; Tissot et al., 1971, 1974). The diagenetic change of kerogen in the petroleum generation seems to have been controlled by temperature and duration of heating time. It is, therefore, very important to determine the thermal alteration of kerogen in the subsurface.

The purpose of this study is to examine the thermal alteration of kerogen in argillaceous rocks at various distances from the basalt dykes intruded in the Oligocene Poronai Formation. We have conducted the laboratory pyrolysis experiment with kerogen to evaluate factors for petroleum-like hydrocarbon generation. In comparison, this study concerns the natural pyrolysis of kerogen in the argillaceous rocks.

The studies of thermal alteration of organic matter by the contact metamorphism of igneous rocks were performed from elemental analysis (McIver, 1967), vitrinite reflectance (Bostick, 1971, 1974 and Dow, 1977), and X-ray diffraction and chemical analyses (Grew, 1974). Our study was performed by chemical and infrared spectroscopy analyses of kerogen, and gas chromatographic analysis of the generated hydrocarbons by laboratory pyrolysis. Recently, Simoneit et al. (1978) reported such a study on kerogens of the Cretaceous black shale of the DSDP site 41-368 in the eastern Atlantic.

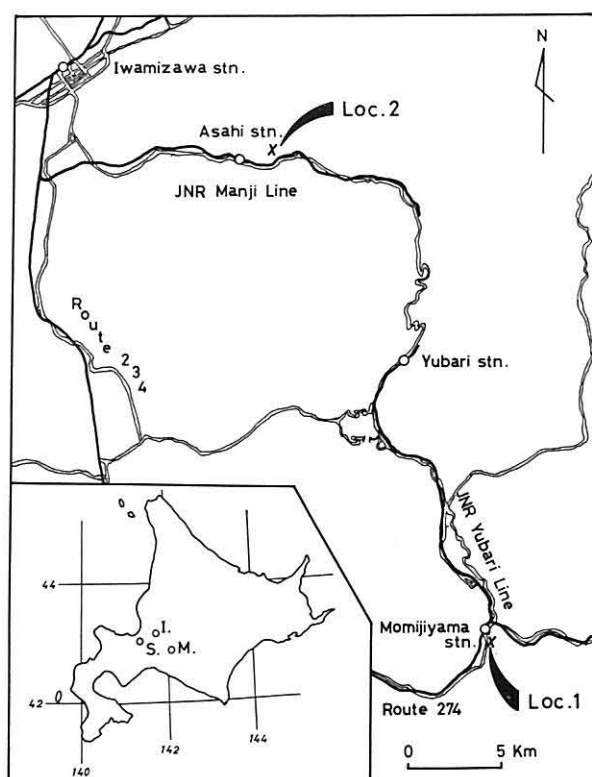
Prof. M. Minato reported the migration of metallic elements between the basalt dyke and the surrounding argillaceous rocks at one of our sampling locations (Minato and Kayama, 1949), and suggested the significance of studying the thermal alteration effect to the sedimentary rocks to one of us (M.A.) several years ago. We wish to express our thanks for his suggestion and to dedicate this paper to him on the occasion of his retirement from

the Hokkaido University.

### Samples and experiments

#### Geological setting

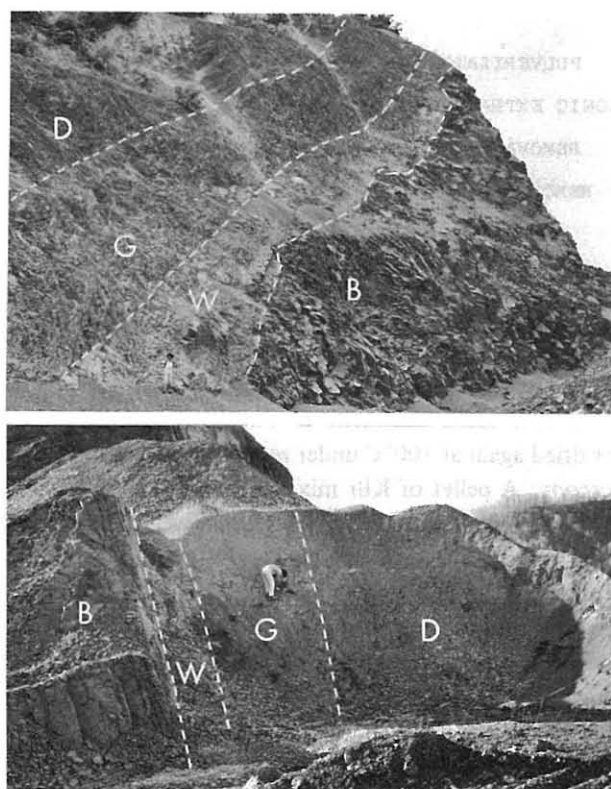
Thirteen siltstone samples were collected at various distances from the basalt dykes intruded in the Oligocene Poronai Formation at the two locations, Momijiyama and Asahi (Fig. 1). The Poronai Formation is distributed in the western skirts of the Yubari



**Fig. 1** Sample locations

S: Sapporo, I: Iwamizawa, M: Momijiyama Loc. 1: Momijiyama location, Loc. 2: Asahi location.

mountainlands in central Hokkaido. This formation consists predominantly of the massive siltstone of marine origin and is more than 1200 m thick in the Yubari district (Geol. Surv. Japan, 1973). Seven of the thirteen samples were collected for analysis in Momijiyama, Yubari City. The upper part of the Poronai Formation near the Momijiyama Station of JNR Yubari Line is intruded by the basalt dyke. The sample location is the quarry at the southern edge of the intrusive body, 750 m long and 175 m wide. The color of siltstone at the outcrop changes from white (nos. M-01, -02 and -04) at the contact with basalt to gray (nos. M-07 and -08) in the intermediate distances and to dark-gray (nos. M-09 and -10) at the



**Fig. 2** Siltstone of the Poronai Formation intruded by the basalt dykes at Momijiyama (upper) and Asahi (lower) locations.

B: basalt dyke, W: white siltstone, G: gray siltstone, D: dark-gray siltstone

distance away from the contact (Table 1; Fig. 2)

Six siltstone samples were collected from the quarry, east of Asahi-machi, Iwamizawa City, where the upper part of the Poronai Formation is intruded by the intrusive body, and 29 km NNW from the former location. The contact metamorphism decolored the siltstone from dark-gray (nos. A-06 and -07) to white (nos. A-01 and -02) through gray (nos. A-03 and -05) in the intermediate distances by the same manner as in the Momijiyama location (Table 2; Fig. 2).

#### Kerogen separation

Kerogen was separated from the argillaceous rocks by the method (McIver, 1967) with some modifications (Fig. 3). X-ray diffraction analysis was carried out to check the presence of any residual of the inorganic minerals in kerogen samples. The concentrated kerogens were kept in a vacuum desiccator after drying at room temperatures under reduced pressure (Ujiié and Akiyama, 1978).

#### Analytical methods for kerogen

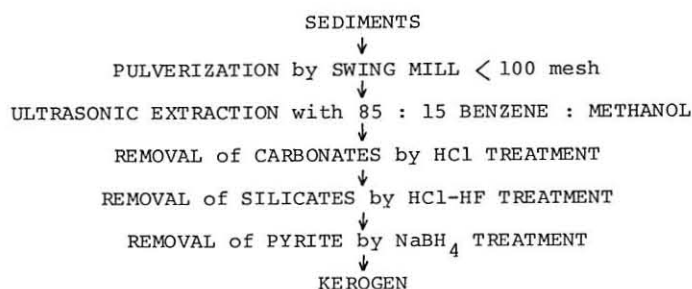


Fig. 3 Separation procedure for kerogen from argillaceous rocks

*Elemental analysis:* Carbon and hydrogen analyses of kerogen were carried out at the Elemental Analysis Laboratory, Department of Pharmacy, Hokkaido University. Before analyses, kerogen was dried again at 100°C under reduced pressure overnight.

*Infrared spectroscopy:* A pellet of KBr mixed homogeneously with 1 or 2% of kerogen was prepared for i.r. spectroscopy. I.r. absorption spectra were measured by a Nihon Bunko IRA-1 spectrometer equipped with a beam condenser at the Earth Science Laboratory, Tokyo College of Economics.

*Pyrolysis and gas chromatography:* n-Alkanes ( $C_1$ – $C_{20}$ ) generated from dried kerogens under  $N_2$  atmosphere by pyrolysis at 400°C for 30 sec. were identified by a Hitachi 063 gas chromatography equipped with a Yanagimoto pyrolysis pipetter (GP-1008). Two stainless steel columns (2 m × 3 mm) were packed with 2% squalane on 60–80 mesh activated alumina for  $C_1$ – $C_6$  alkanes and with apiezon grease L on 60–80 mesh Chromosorb PAW for  $C_7$ – $C_{20}$  alkanes, respectively.

### Results and discussion

Microscopic observation reveals that a considerable amount of opaque material is included in the siltstone of the Poronai Formation. This material decreases from 7 vol. % in the dark-gray siltstone far from the basalt dykes to less than 1 vol. % in the white siltstone at the contact. A large part of this material is supposed to be organic matter because of its low reflectance under a reflective microscope. Since all samples contain illite, kaolinite and chlorite except no. A-10 having only illite from X-ray diffraction analysis, the effect of thermal metamorphism to clay minerals is hardly recognized at these two locations.

Kerogen concentrations in the siltstone samples and their elemental analyses are shown in Tables 1 and 2. The kerogen content decreases significantly towards the basalt dykes in the both localities. The intrusion of the basalt into the Poronai Formation gave a distinct pyrolysis effect to the kerogen within about 1 m from the contact and some thermal effect even to the kerogen of several meters apart. The white or gray color of the siltstone reflects the pyrolysis by the intrusion intensely or weakly, respectively (Tables 1 and 2; Fig. 2). Relative contents of the total n-alkanes ( $C_1$ – $C_{20}$ ) generated from kerogens by the laboratory pyrolysis at 400°C for 30 sec. decrease in the samples towards the contact. This result coincides with that by the elemental analyses as well as from the microscopic observation.

**Table 1** Analytical data of kerogens separated from the siltstones of the Poronai Formation at Momijiyama, Yubari City

| Sample nos. | Distances from the dyke (cm) | Color at the outcrop | Kerogen content mg/g of rocks | Elemental analysis |      |       |            | n-Alkane*   |                | Wt loss (%) |
|-------------|------------------------------|----------------------|-------------------------------|--------------------|------|-------|------------|-------------|----------------|-------------|
|             |                              |                      |                               | C                  | H    | ash   | atomic H/C | /g of rocks | /mg of kerogen |             |
| M-01        | 0 - 5                        | whitish              | 0.027                         | 7.79               | 0.60 | 86.96 | 0.92       | 1.1         | 42             | 24.59       |
| -02         | 34                           | whitish              | 0.044                         | 1.07               | —    | 98.27 | —          | 6.8         | 152            | 30.16       |
| -04         | 70                           | whitish              | 0.092                         | 2.57               | 0.19 | 96.37 | 0.89       | 7.3         | 79             | 51.15       |
| -07         | 190                          | gray                 | 3.128                         | 54.73              | 1.64 | 38.80 | 0.36       | 88          | 28             | 9.62        |
| -08         | 310                          | gray                 | 5.364                         | 70.78              | 2.29 | 15.81 | 0.39       | 102         | 19             | 9.45        |
| -09         | 400                          | dark-gray            | 6.872                         | 70.38              | 2.29 | 11.53 | 0.39       | 45          | 6.5            | 10.62       |
| -10         | 710                          | dark-gray            | 5.607                         | 70.87              | 2.98 | 25.75 | 0.50       | 100         | 18             | 10.92       |

\* Relative amount of total n-alkanes ( $\text{CH}_4\text{-C}_{20}\text{H}_{42}$ ) of each sample calculated from the gas chromatogram on the basis of the contents in a gram of siltstone of the sample no. M-10 as 100

**Table 2** Analytical data of kerogens separated from the siltstones of the Poronai Formation near Asahi-machi, Iwamizawa City

| Sample nos. | Distances from the dyke (cm) | Color at the outcrop | Kerogen content mg/g of rocks | Elemental analysis |      |       |            | n-Alkane*   |                | Wt loss (%) |
|-------------|------------------------------|----------------------|-------------------------------|--------------------|------|-------|------------|-------------|----------------|-------------|
|             |                              |                      |                               | C                  | H    | ash   | atomic H/C | /g of rocks | /mg of kerogen |             |
| A-01        | 0 - 5                        | whitish              | 0.039                         | 14.40              | 0.91 | 79.45 | 0.76       | 3.1         | 80             | 35.72       |
| -02         | 65                           | whitish              | 0.066                         | 15.12              | 0.46 | 81.13 | 0.37       | 4.8         | 72             | 34.33       |
| -03         | 145                          | gray                 | 0.613                         | 13.73              | 0.26 | 55.09 | 0.23       | 8.0         | 13             | 15.73       |
| -05         | 465                          | gray                 | 1.658                         | 30.83              | 1.46 | 62.14 | 0.57       | 33          | 20             | 13.88       |
| -06         | 760                          | gray                 | 2.726                         | 52.71              | 1.72 | 28.60 | 0.39       | 17          | 6.2            | 15.95       |
| -07         | 1100                         | dark-gray            | 5.407                         | 43.80              | 1.90 | 36.08 | 0.52       | 43          | 7.9            | 10.20       |

\* Relative amount of total n-alkanes ( $\text{CH}_4\text{-C}_{20}\text{H}_{42}$ ) of each sample calculated from the gas chromatogram on the basis of the contents in a gram of siltstone of the sample no. M-10 as 100

A similar trend of the amino acid concentration was found in the Upper Cretaceous Pierre shale intruded by a basic dyke with 1 m width. Total amount of amino acids decreases distinctly from  $3.27 \mu\text{M/g}$  of shale at 250 cm from the dyke to  $0.75 \mu\text{M/g}$  of shale at 60 cm (Degens, 1967). Contact metamorphism gives a similar effect to the hydrocarbons, sugars and phenols in the sedimentary rocks. Degens (1967) stated "The ultimate goal of this type of research is to find a number of organic compounds that can be used as a geological thermometer". Kerogen in argillaceous rocks should be added to these organic compounds.

Infrared spectra of kerogen show a progressive decrease in the ratio of absorption intensity of  $\text{C}=\text{O}$  at  $1700 \text{ cm}^{-1}$  to aromatic  $\text{C}=\text{C}$  at  $1600 \text{ cm}^{-1}$  with an increase of burial depth (Durand and Espitalié, 1976; Tissot et al., 1971, 1974; Ujiié and Akiyama, 1978). In the present study, kerogens of the gray siltstones show smaller ratios of  $\text{C}=\text{O}$  to aromatic  $\text{C}=\text{C}$  than those of the dark-gray siltstones. However, in the white siltstone infrared absorption peaks are too faint to be examined. In the white siltstones at the both locations

the atomic H/C increases significantly, while a rather decreasing trend is found from the dark-gray to the gray siltstone (Fig. 4). n-Alkane generation and weight loss/mg of kerogen

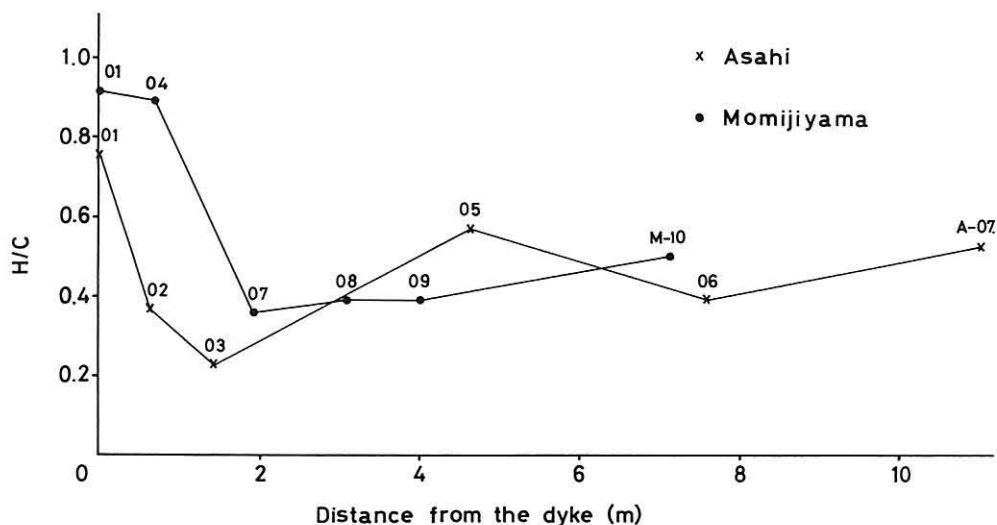


Fig. 4 Atomic H/C of kerogen versus distances from the dykes

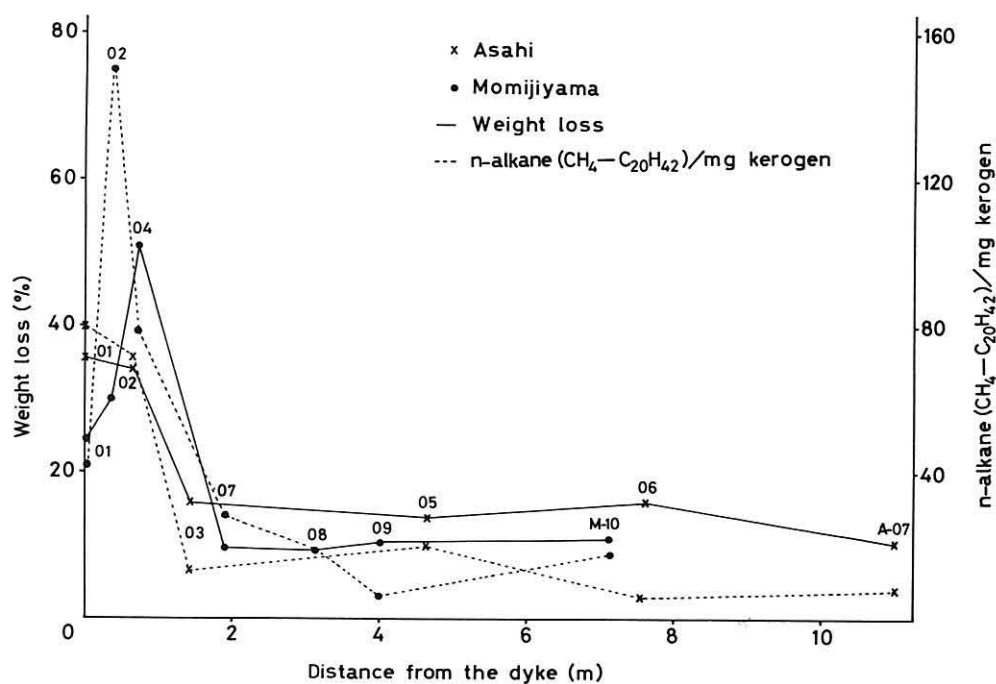


Fig. 5 Generation of n-alkanes and weight loss of kerogens by laboratory pyrolysis

by the laboratory pyrolysis experiment also increase in the white siltstones at the contact of the both locations, though no significant change appears between the gray and dark-gray siltstone (Fig. 5).

McIver (1967) showed the compositional change of kerogen in the Upper Cretaceous Pierre shale taken at various distances (30 – 900 cm) from an igneous dyke. The composition near the dyke indicates a large loss of methane on his normalized C – H – O content diagram. This compositional change of kerogen is parallel to the compositional change of coal in diagenesis. However, he did not show any data at the very contact with the basic dyke. Since the dyke is smaller in his case than in our basalt dykes, the contact metamorphosed zone within 30 cm from the dyke might have shown a similar characteristic of kerogen which we found in the white siltstone of the Poronai Formation within 1 m distance. Thermal alteration effects of the Cretaceous black shale by basalt intrusions in the eastern Atlantic indicate a drastic decrease of H/C in the sill proximity, though no measurement of H/C to the closest sample, no. 9 (Simoneit et al., 1978).

It is very unusual that H/C values and n-alkanes generated from mg of kerogen by the laboratory pyrolysis increase at the proximity of the basalts. This unusual behaviour of kerogen nature could be explained by the hydrogenation of superheated steam provided from the basalt intrusion.

In conclusion, the kerogen remaining in the siltstone after the thermal metamorphism by the basalt dykes showed unexpectedly a rather high content of hydrogen. This type of kerogen yields a large amount of n-alkanes by laboratory pyrolysis, though the kerogen does not generate a large quantity of n-alkanes because of its low concentration in the siltstone near the contact of the basalt dykes.

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