

Determination of kinetic parameters for individual compounds on release from kerogen by thermal analysis

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Introduction

In order to obtain the activation energy (E) and pre-exponential factor (A) for an individual compound on release from thermal decomposition of kerogen, we analyzed kerogens (in Neogene sediments of the Shinjo basin, Yamagata, Japan) by a thermogravimetric analyzer with a gas chromatograph-mass spectrometer or a mass spectrometer. And we calculated depth profiles of release extents for individual compounds, using a mathematical model.

Results and Discussion

The obtained E and A for six released compounds are shown in Table 1. The rate constants of each compound at 120°C (the onset of the intense petroleum generation in the Shinjo basin) indicated in order of indene > benzene, toluene > phenol > hexane, heptane, whereas the E were inverse in order. Therefore, it was found that hexane and heptane were more strongly bound with kerogen matrix than benzene, toluene, and indene.

Table 1. E , A and rate constants at 120°C of individual compounds on release from kerogen in the Shinjo sediments.

Compounds	E (kcal/mol)	A (s ⁻¹)	Rate constants at 120°C (s ⁻¹)
Benzene	49.0	2.46x10 ¹²	1.41x10 ⁻¹⁵
Hexane	55.3	2.60x10 ¹⁴	4.69x10 ⁻¹⁷
Toluene	50.5	6.83x10 ¹²	5.75x10 ⁻¹⁶
Phenol	52.8	4.95x10 ¹³	2.19x10 ⁻¹⁶
Heptane	54.6	2.21x10 ¹⁴	9.77x10 ⁻¹⁷
Indene	46.7	4.90x10 ¹¹	5.34x10 ⁻¹⁵

The depth profiles of release extents for six compounds were different in temperature (therefore, depth) each other. Furthermore, the model indicated that hexane and heptane of aliphatic hydrocarbons were released in sediments deeper than benzene, toluene and indene of aromatic ones. These depth profiles were similar in pattern to those reported for solvent extractable aliphatic and aromatic hydrocarbons in the Shinjo sediments.

References

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Sea surface temperatures off the east coast of the Japanese Islands since the last glacial maximum inferred from oxygen isotope of foraminiferal tests

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The Northwest Pacific Ocean is a region where pronounced temperature changes occurred in the surface water between the cold Oyashio Current and the warm Kuroshio Current in the glacial-interglacial cycles. Four piston cores were collected from the Oyashio Current to the Kuroshio Current regions off the east coast of the Japanese Islands. The oxygen isotope differences between benthic and planktonic foraminiferal tests increased from the northernmost core (0.9 per mil) to the southernmost core (3.7 per mil) during the Holocene, due to increasing sea surface temperature (SST) towards the south. In contrast, these differences are much smaller during the last glacial maximum (LGM) than during the Holocene, especially in the case of the southernmost core (2.0 per mil). This suggests that the water mass similar to the present surface water off the east coast of the Japanese Islands shifted southward at the LGM.

The SST off the east coast of the Japanese Islands can be calculated from the relationship between the present temperature differences of the surface and bottom at the four core sites and the oxygen isotope differences of benthic-planktonic foraminiferal species. The results show that the SST at the northernmost core site remains almost the same as present, because the cold Oyashio Current has occupied the site since the LGM. On the other hand, the decreased SST of about 9 degrees centigrade is found at the southernmost core site, where the Kuroshio Current was replaced by the mixed water mass between the Oyashio and Kuroshio Currents at the LGM.

Such a water mass movement is also supported by the carbon isotope shifts of planktonic foraminiferal tests in the four cores. Furthermore, abnormal light carbon isotope values, which must be related to methane hydrate, are observed in the northernmost core during the LGM.