A New Maturity Indicator of Sedimentary Organic Matter Based on Thermal Fission of Allylic Bond in Porphyrins

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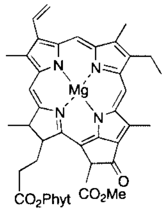
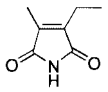
A 3-ethyl-4-methylpyrrole unit in etioporphyrin was shown to be converted to a 3,4-dimethylpyrrole unit by the action of heat, which was proved to be catalyzed by Na-montmorillonite. Time courses of the reaction could be followed by analyzing 2-ethyl-3-methyl- and 2,3-dimethylmaleimide after chromic acid oxidation of the porphyrin. The ratio of these maleimides was proposed as a new maturity indicator for sedimentary organic matter.

Investigations which had related the chemical properties or features of compounds found in sediments to their thermal histories have gathered general interest. The ages of fossils or ancient sediments were estimated by a molecular clock based on their contents of D-amino acids.[1] The carbon preference index that describes the odd-over-even carbon number preference of *n*-alkanes found in crude oils or sediments can provide information on the levels of maturity, which represents their time-temperature histories.[2] It is therefore important to know organic transformation of natural products incorporated into sedimentary organic matter.

Since Treibs discovered porphyrins in sediments in 1934,[3] much attention has been denoted to these biomarker compounds that can be linked to chlorophylls.[4–11] The sedimentary porphyrins are usually complicated mixtures with various substituents on their pyrrole rings as a result of diagenetic modification of precursor chlorophylls. The substitution patterns can be conveniently determined after decomposition to maleimides by chromic acid oxidation.[8] In the oxidation products of crude oils and sediments previously reported, the predominant maleimide was always 2-ethyl-3-methylmaleimide (**1**), which can be attributed to the common presence of a 3-ethyl-4-methylpyrrole ring in many chlorophylls.[7,10,11] 2,3-Dimethylmaleimide (**2**) was usually found as the second most abundant and is considered to be a diagenetic product because of the lack of the corresponding chlorophyll.[7,8,10,11] In the present study, we confirmed, for the first time, thermal transformation from an ethylmethyl- into a dimethylpyrrole moiety of porphyrins by heating experiments of etioporphyrin. The **1** to **2** ratio can therefore be used as a new maturity indicator of sedimentary organics.



Chlorophyll-a
(Phyt: phytyl)



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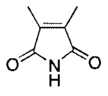

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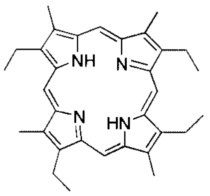

Etioporphyrin

Etioporphyrin (0.19 mg) was heated at 250 to 350 °C, and in the presence of Na-montmorillonite (20 mg) at 150 to 350 °C up to 72 h in a degassed sealed tube. Heating with the clay was performed, since clay minerals are well known to have played important roles on maturation of organic matter in sediments.[12] The products were oxidized, according to the method of Furlong and Carpenter,[6] with 10% CrO_3 in 25% H_2SO_4 (1 mL) at 0 °C for 2 h and then at room temperature for 2 h to afford a mixture of maleimides, which was extracted with benzene and analyzed by GC–MS. Identification and quantification of maleimides were performed by comparison of GC–MS data with those of authentic samples.

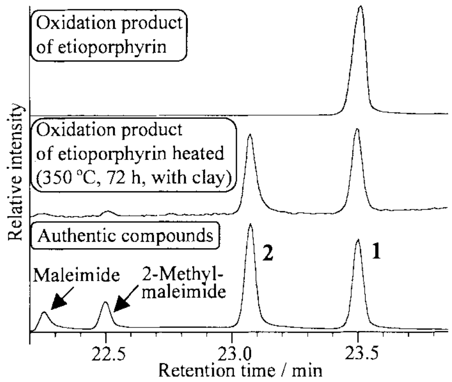

Figure 1. Gas chromatograms of maleimides obtained by oxidation of etioporphyrin. **1**: 2-Ethyl-3-methylmaleimide, **2**: 2,3-dimethylmaleimide.

Figure 1 shows typical gas chromatograms obtained by the heating experiment. The unheated substrate yielded only **1** after oxidation in 10 runs, corresponding 10 to 20% of the initial etioporphyrin. After heating, etioporphyrin, which is soluble in methanol, afforded products that were insoluble in methanol. Although heating seemed to cause serious degradation or polymerization of etioporphyrin, both of maleimides **1** and **2** were successfully detected after oxidation of the products, indicating that the alkylpyrrole moieties survived to some extent after heating. The total yields of **1** and **2** on the basis of etioporphyrin were 10 to 20% in the reactions at 150 and 200 °C, and 0.3 to 10% in those at 250 to 350 °C. 2-Methylmaleimide was formed only in a trace amount, and 2-ethylmaleimide and maleimide were not found in all the reactions performed. These facts indicate that the selective thermal cleavage of an allylic C–C bond in the ethylmethylpyrrole moiety of etioporphyrin was the predominant reaction that can be observed after oxidation of the heating products.

This result may explain the fact that maleimide and 2-methyl- and 2-ethylmaleimide had been found in crude oils or sediments in considerably smaller amounts than those of **1** and

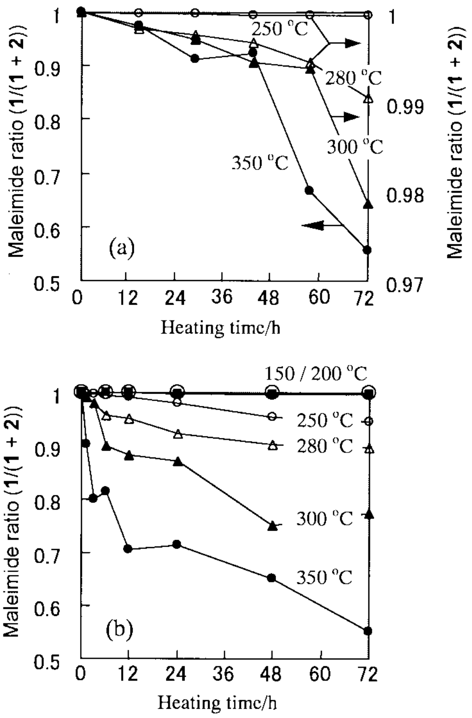

Figure 2. Time-course plots of heating experiments of etioporphyrin without (a) and with Na-montmorillonite (b).

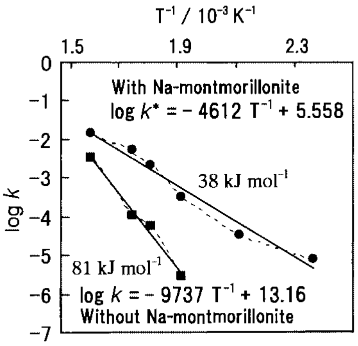

Figure 3. Arrhenius plots of heating experiments of etioporphyrin. k^* : initial rate constant.[15]

2. This phenomenon can be chemically understood in terms of the lower bond energy of the allylic C–C bond, compared to those of the other bonds that exist in etioporphyrin.

The ratio of **1** to **2**, expressed as **1**/(**1** + **2**), obtained in heating of etioporphyrin without and with the clay is plotted against the reaction time in Figures 2a and 2b, respectively. The decreasing trends of the ratio with time were observed, although the data were somewhat scattered. The clay mineral accelerated the transformation as seen in Figure 2, and the accelerating effect was obvious at the early stage of the reaction. This result is in agreement with our previous studies indicating the deactivation of Na-montmorillonite within 48h in reactions above 250 °C.[13,14] In order to evaluate kinetically the role of the clay, we calculated activation energies in the presence and absence of the clay by using the Arrhenius plots,[15] shown in Figure 3. The activation energy (81 kJ mol^{-1}) was lowered by the presence of the clay to 38 kJ mol^{-1}, suggesting that the clay acts as a catalyst in the C–C bond fission. Clay minerals are known to be an acidic catalyst,[12] and often used for catalytic thermal cracking of hydrocarbons.[16,17] The detailed mechanism of C–C bond fission on the clay is still not clear.

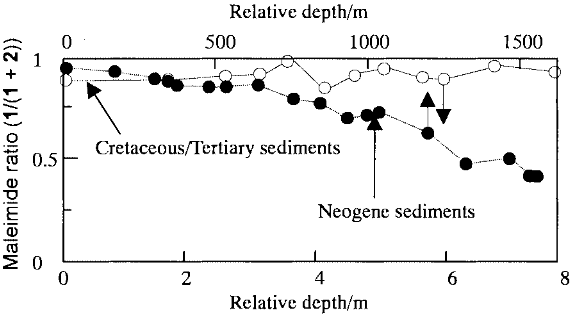

Figure 4. Depth profiles of maleimide ratio (**1**/(**1** + **2**)) in the natural sediments.

The present study demonstrated that transformation from an ethylmethyl- into a dimethylpyrrole moiety in porphyrins proceeds by the action of heat, and that the progress of the reaction can be observed as a ratio of **1** to **2**. Therefore, it was expected that the ratio (**1**/(**1** + **2**)) can be used as a new maturity indicator of sedimentary organic matter, since the maleimides could have been oxidatively extracted from sediments. The ratio of **1** to **2** in oxidation products of two different series of natural sediments (Neogene and Cretaceous/Tertiary sediments) has been found to be in agreement with the thermal maturity of the sediments (Figure 4), which was evidenced by other maturity indicators.[14,18] The ratio of **1** to **2** provides a new type of maturity indicator, which can be obtained from insoluble stable organic geopolymers in sediments.

References and Notes

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