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Article

Compositions of *n*-alkanes and *n*-alkanoic acids released by thermochemolysis with tetramethylammonium and trimethylsulfonium hydroxides of a type II kerogen

Shuji Ogata[1]*, Yuma Miyata[1] and Ken Sawada[1]

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Abstract

The type II kerogen from the Miocene Onnagawa Formation Shale was analyzed by pyrolysis and thermochemolysis with tetramethylammonium hydroxide (TMAH) and trimethylsulfonium hydroxide (TMSH) under various thermal conditions. The results were compared with that by alkali hydrolysis. The *n*-alkanes and *n*-alkenes in products by pyrolysis and thermochemolysis might be generated from alkyl moieties in geomacromolecule by thermal cracking of C-C bonds. The *n*-alkanoic acids (as fatty acid methyl esters; FAMEs) were mainly detected in the compounds released from the kerogen by thermochemolysis, indicating that they have been preserved through polymerization of marine plankton-derived compounds. Noticeably, the short chain ($<C_{11}$) FAMEs were abundant in products by thermochemolysis, while those were hardly detected in hydrolysates. These short chain *n*-alkanoic acids might be mainly occluded in intra-aggregates within the geomacromolecule. In addition, the C_7 and C_9 FAMEs predominated in products by TMSH-using thermochemolysis, although the C_7 FAME was minor in TMAH method. It was suggested that the trapped and occluded compounds like C_7 and C_9 acids were more efficiently released from kerogen by TMSH thermochemolysis. On the other hand, total FAME / *n*-alkane ratios in the products by TMAH thermochemolysis were significantly higher than those by TMSH method. These results suggest that total recovery of the FAME released from kerogen by thermochemolysis can be lower in the presences of TMSH than TMAH.

1. Introduction

Knowledge of chemical structure of geomacromolecule such as humic substance and kerogen may help to provide a better understanding of biological source(s), depositional environment and diagenetic processes of sedimentary organic matter. Since the early 1990s, thermochemolysis- gas chromatography (GC)/mass spectrometry (MS), especially thermochemolysis with tetramethylammonium hydroxide [TMAH; $(CH_3)_4$ NOH], has been used in the structural investigation of geomacromolecule such as kerogen (Kralert et al., 1995; del Río et al., 1995; del Río and Hatcher, 1998; Bruan et al., 2001; González-Vila et al., 2001). The TMAH thermochemolysis, also known as "thermally assisted hydrolysis and methylation (THM; Challinor, 2001)", can provide more definitive structural information for original composition of precursor than the pyrolysis. Conventional pyrolysis-GC/MS was known to result in decomposition (e.g. decarboxylation) of functionalized group in geomacromolecule, but heating in the thermochemolysis is primarily driven the reaction between the methylation reagent and the acidic functional groups despite of simultaneously assisting in base-catalyzed

[1]*Department of Natural History Sciences, Faculty of Science, Hokkaido University, N10W8, Kita-ku, Sapporo 060-0810, Japan

*corresponding author; TEL: +81-11-706-2733 FAX: +81-11-746-0394 E-mail: ogatas@mail.sci.hokudai.ac.jp

hydrolysis of ester and ether bonds, and to a lesser extent thermal fragmentation. Similar to TMAH, trimethylsulfonium hydroxide [TMSH; $(CH_3)_3SOH$] has been used as an alternative methylation reagent. This reagent has been shown to be suitable for samples that are alkaline- or heat- sensitive wherein it needs lower thermochemolysis temperatures and decreases the base isomerization of polyunsaturated fatty acids (Estèvez and Helleur, 2005; Ishida et al., 2009). There has been no report for thermochemolysis with TMSH of geomacromolecule such as kerogen. Lower thermochemolysis temperature are required as the most efficient reaction temperature for TMSH, and compositions of the compounds generated/released from kerogen by thermochemolysis can vary depending on thermal condition. On the contrary, it is possible that more information for structure of geomacromolecule can be obtained by the TMAH and TMSH-using thermochemolysis under various thermal conditions.

In the present study, we applied pyrolysis and thermochemolysis with TMAH and TMSH under various thermal conditions to a type II kerogen, in order to examine variability of composition of compounds, especially *n*-alkanoic acids (fatty acids), generated by these thermochemolysis caused by changing their thermal conditions. In addition, we compared compositions of *n*-alkanoic acids generated by the thermochemolysis with those released by alkali hydrolysis to confirm the applicability of the thermochemolysis to exploring carboxylic acid moieties in geomacromolecule.

2. Material and methods

2.1. Kerogen sample

We used a kerogen sample separated from the Miocene Onnagawa Formation Shale On-7, which was collected at 1794 m depth in the Yabase R-1 well, Akita, Japan (Sawada and Akiyama, 1994). Kerogen separation was carried out by the classical method (Durand and Nicaise, 1980; Sawada and Akiyama, 1994). Briefly, rock samples crushed to a 'rice'-sized (diameter 2–5 mm) grain (10 g) were extracted in a Soxhlet apparatus with 100 ml dichloromethane (DCM)/methanol (MeOH) (3/1 v/v) for 24 h. Thereafter, residues were treated sequentially in a water bath shaker as follows: HCl 6 M (100 ml, 60ºC, 12 h), HCl 12 M/HF 46% (1/1 v/v) (100 ml, 60ºC, 24 h), HCl 6 M (100 ml, 60ºC, 4 h). After each treatment, the supernatant was removed after centrifugation (3000 rpm, 10 min). The residue, kerogen, was sequentially washed with HCl 6 M (x 2) and distilled water (x 5), and was recovered and freeze-dried under vacuum. From elemental analysis of carbon (C), hydrogen (H) and oxygen (O) ratios (H/C = 1.22, O/C = 0.11), the Onnagawa Formation Shale On-7 kerogen was confirmed to be a type II kerogen (Sawada and Akiyama, 1994).

2.2. Pyrolysis and thermochemolysis-GC/MS of kerogen

Pyrolysis-GC/MS was performed on-line using a Curie point pyrolyzer JCI-22 (Japan Analytical Industry Co.) with Hewlett Packard 6890N a capillary GC (30 m x 0.25 mm i.d. DB-5HT fused silica column, J&W Scientific) directly coupled to a Hewlett Packard inert XL MSD (quadrupole mass spectrometer, electron voltage 70 eV, emission current 350 μA, mass range m/z 50–600 in 1.3 s) at the Faculty of Science, Hokkaido University. The heat source for the Curie point pyrolyzer is ferromagnetic properties called pyrofoil. Kerogen sample was weighted (ca. 500 μg) and placed on 9 mm-width pyrofoils, which are the F423, F590 and F670 at heating temperatures of 423ºC, 590ºC and 670ºC, respectively. The samples was heated at 423ºC, 590ºC and 670ºC for 5 s in the pyrolyzer, and generated compounds were transferred to the GC splitless injection system at 310ºC with a helium (He) gas. The GC was programmed as follows: 50ºC for 4 min, 50–310ºC at 5ºC /min and 320ºC for 17 min. Compounds were identified on the basis of mass spectra and relative retention times in comparison with library data (NIST05) and the literature.

The methanol solutions of TMAH (2.2 M) and TMSH (0.2 M) were purchased from Wako Pure Chemical Industries (Osaka, Japan) and Tokyo Kasei Kogyo (Tokyo, Japan), respectively. We used 30

μL methanol solutions of 0.4 M TMAH and 0.2 M TMSH. The methanol was dried under the ambient temperature overnight. Thermochemolysis of kerogen was performed by using the same GC-MS equipped a Curie-point pyrolyzer with the same as analytical conditions.

When we performed pyrolysis and thermochemolysis-GC/MS, nonadecanoic acid (n-C_{19} fatty acid) was added in the pyrofoil as an internal standard for quantifying the FAMEs. However, reproducibility of the analysis was confirmed to be poor, so that we did not quantify the compounds generated by pyrolysis and thermochemolysis.

2.3. KOH/methanol hydrolysis of kerogen

Hydrolysis of kerogen was performed as described by Sawada et al. (2008). Briefly, the kerogen was hydrolyzed with 1 M KOH in methanol at 110ºC for 3 hours in a sealed glass tube. The neutral lipids were extracted by partitioning with hexane-diethyl ether (9:1 v/v), and the fatty acids were extracted in the same way after acidification to pH 2 with HCl. The fatty acids were esterified by using 14% BF_3 in methanol at 80ºC for 30 min. After addition of pure water, the fatty acid methyl esters (FAMEs) were extracted with hexane. The d_{50}-tetracosane (n-$C_{24}D_{50}$; Aldrich) was added prior to extraction as internal standards for quantifying the FAMEs. These FAME fractions were analyzed by the same GC/MS. The GC temperature was programmed as follows: 50ºC for 4 min, 50–310ºC at 4ºC/min and 310ºC for 20 min.

3. Results and discussion

3.1. *n*-Alkanes and *n*-alkenes generated from kerogen by pyrolysis and thermochemolysis

The pyrolysates from the Onnagawa Formation Shale On-7 kerogen were principally aliphatic hydrocarbons including *n*-alkanes (Fig. 1). The C_9-C_{30} *n*-alkane/*n*-alkene doublets were mainly identified in pyrolysates from the kerogen, although the *n*-alkenes in the pyrolysates were restricted to be C_{10}-C_{15} homologues as minor compounds at lower pyrolysis temperature condition (423ºC; Fig. 1b). A unimodal distribution maximizing C_{16}-C_{18} *n*-alkanes was observed in the pyrolysate at 423ºC, but the relative abundances of shorter chain (C_9-C_{13}) *n*-alkanes increased in the pyrolysate at higher pyrolysis temperature conditions (590ºC and 670ºC). In general, the *n*-alkanes and *n*-alkenes in pyrolysates are thought to be generated from C-C bonded polymethylene structure in the kerogen via thermal cracking (Larter and Horsfield, 1993). In particular, *n*-alkene is typical compound generated by pyrolysis, and in our data for *n*-alkenes, their relative abundances tended to be lower in pyrolysate at 423ºC. These results indicate that such low temperature condition is not enough to thermally cleave the C-C bonds in the polymethylene structure. Indeed, the C_{10}-C_{15} *n*-alkenes predominated in pyrolysate at 423ºC might be generated from (free) C_{16} alkanoic acid via decarboxylation by pyrolysis as reported by Hartgers et al. (1995). On the other hand, the predominance of short chain *n*-alkenes in pyrolysates at 670ºC indicated that secondary cleavages of C-C bonds in alkyl chains of compounds released from kerogen might occur under high temperature condition.

The *n*-alkanes and *n*-alkenes generated from the On-7 kerogen by thermochemolysis with TMAH (Fig. 2) and TMSH (Fig. 3) were also detected as major components under higher thermochemolysis temperature conditions (590ºC and 670ºC). However, no *n*-alkenes and small amounts of *n*-alkanes were detected at 423ºC. Carbon number distributions of *n*-alkanes generated from kerogen by thermochemolysis with TMAH and TMSH were almost similar to those by pyrolysis at 423ºC, although the distribution maximizing C_{16}-C_{20} homologues were slightly different (Fig. 4). As the result of pyrolysis, the relative abundances of shorter chain (C_9-C_{13}) compounds in the thermochemolysis tended to increase at 590ºC and 670ºC. No preferences of odd carbon numbers of *n*-alkanes and *n*-alkenes were observed in products by both pyrolysis and thermochemolysis. These facts indicate that the *n*-alkanes and *n*-alkenes might not be directly originated from biological precursor such as plant wax but might be generated from polymethylene structure

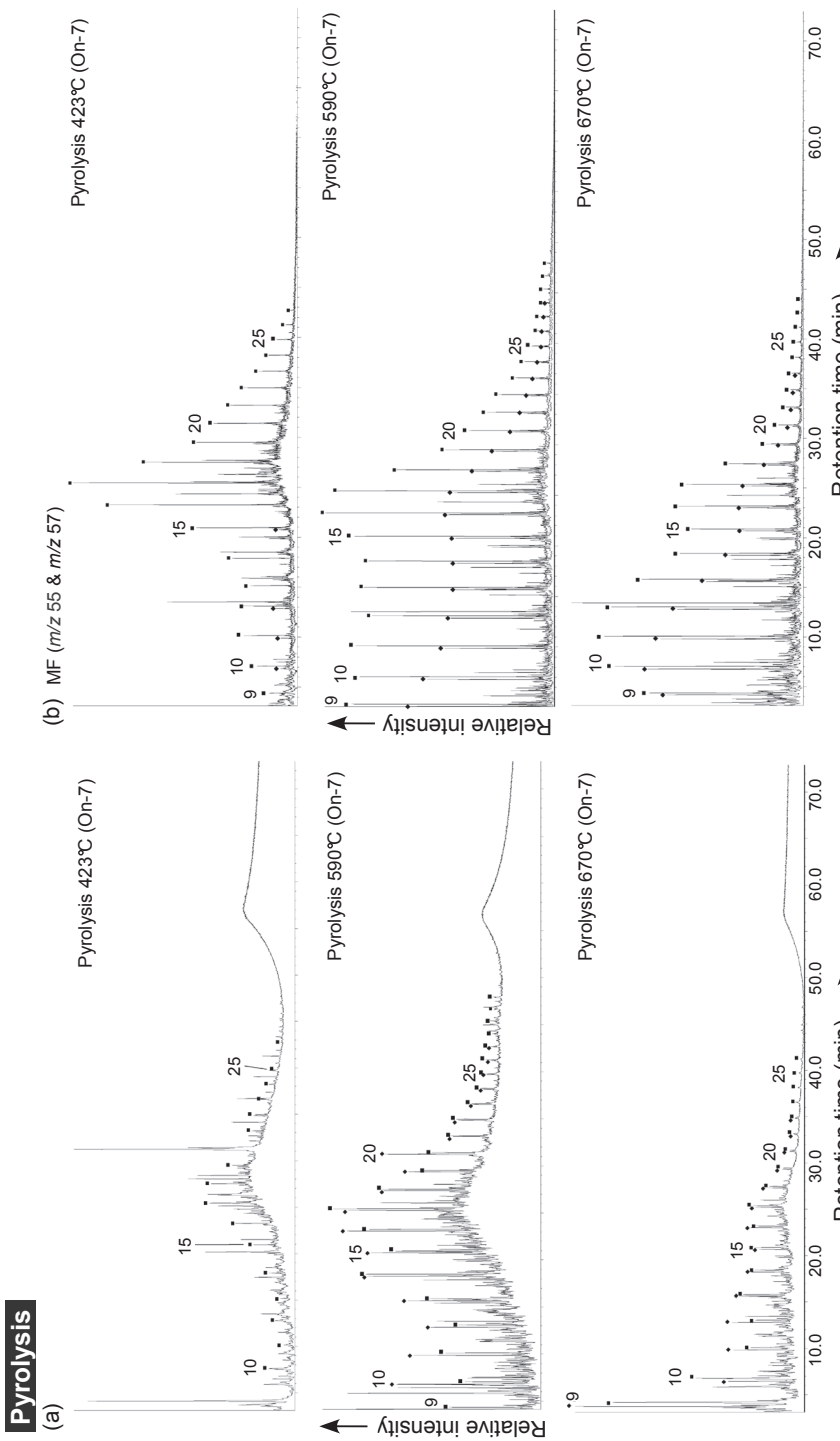

Fig. 1. (a) Total ion chromatograms (TICs) and (b) mass fragmentograms (MFs) of *m/z* 55 and 57 of the products generated for pyrolysis at 423°C, 590°C and 670°C from kerogen in the Omagawa Formation Shale On-7. Solid squares and diamonds are *n*-alkanes and *n*-alkenes, respectively. Numerals are their carbon numbers.

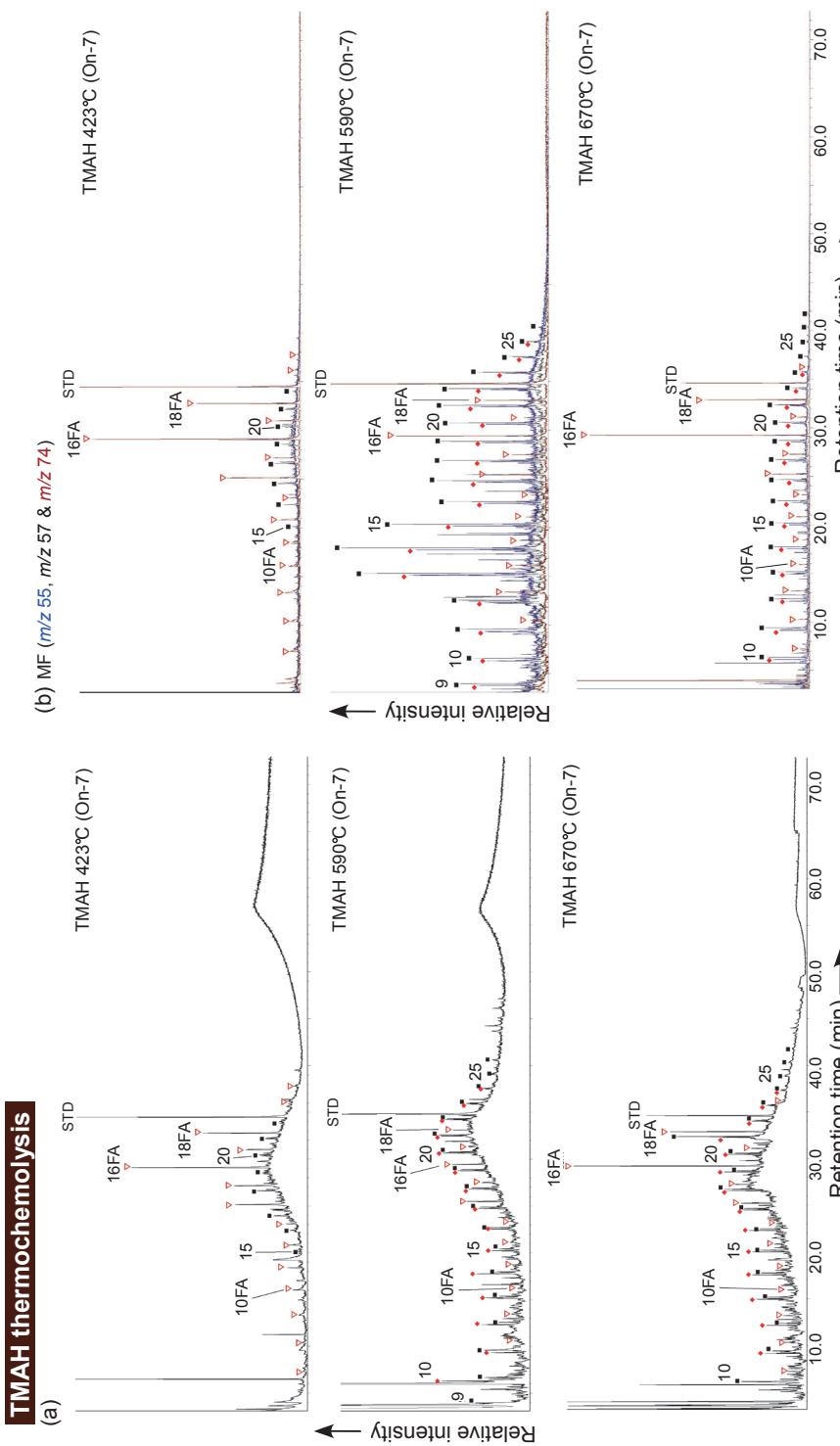

Fig. 2. (a) TICs and (b) MFs of *m/z* 55, 57 and 74 of the products generated for thermochemolysis with the TMAH at 423℃, 590℃ and 670℃ from the On-7 kerogen. Solid squares, diamonds and inverted triangles are *n*-alkanes, *n*-alkenes and *n*-alkanoates (fatty acid methyl esters; FAMEs), respectively. Numerals and nFA (n is numeral) are carbon numbers of *n*-alkanes and *n*-alkanoates, respectively. STD is an internal standard (*n*-C_{19} alkanoic acid).

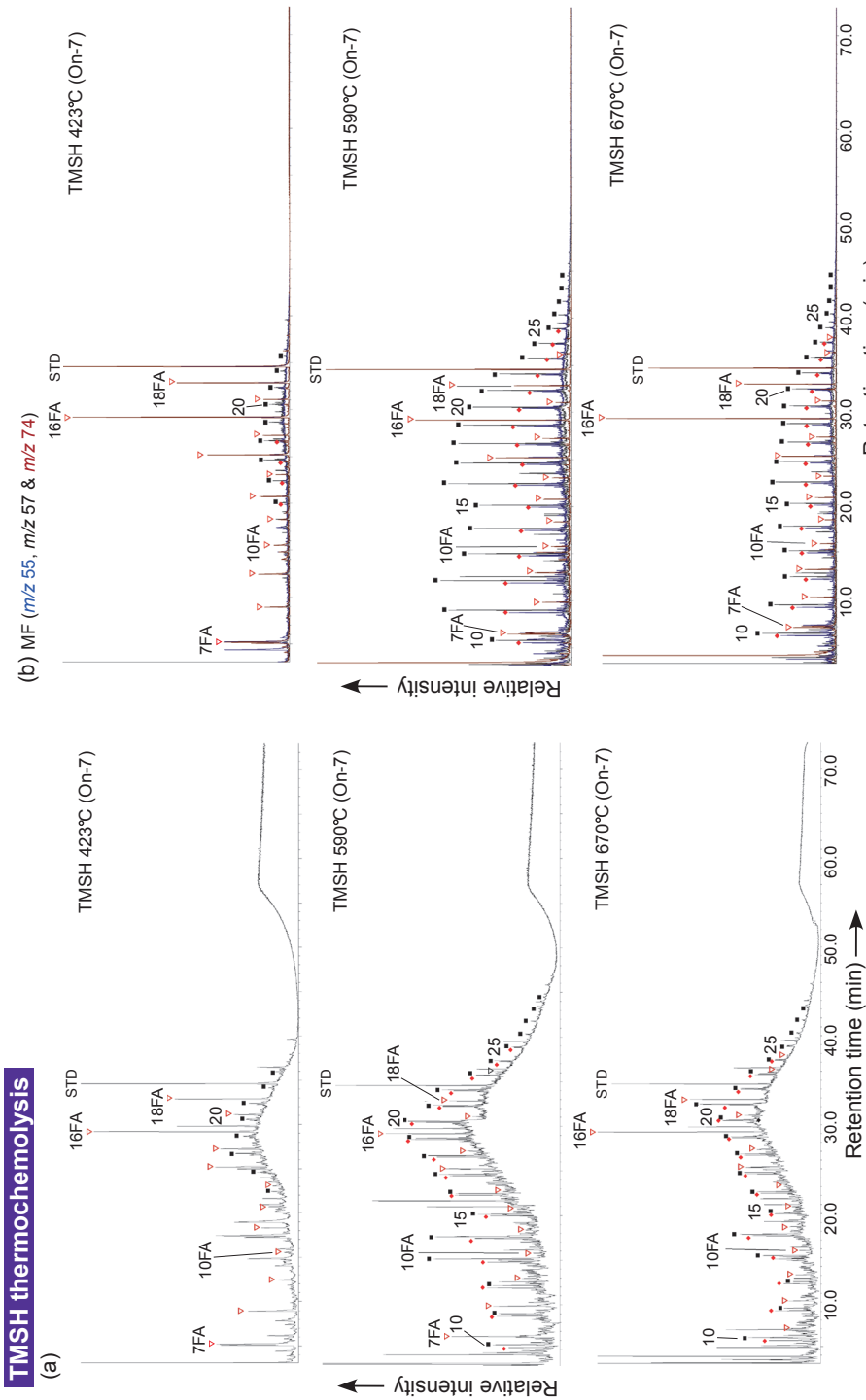

Fig. 3. (a) TICs and (b) MFs of *m/z* 55, 57 and 74 of the products generated for thermochemolysis with the TMSH at 423°C, 590°C and 670°C from the On-7 kerogen. Solid squares, diamonds and inverted triangles are *n*-alkanes, *n*-alkenes and *n*-alkanoates (FAMEs), respectively. Numerals and nFA (n is numeral) are carbon numbers of *n*-alkanes and *n*-alkanoates, respectively. STD is an internal standard (n-C_{19} alkanoic acid).

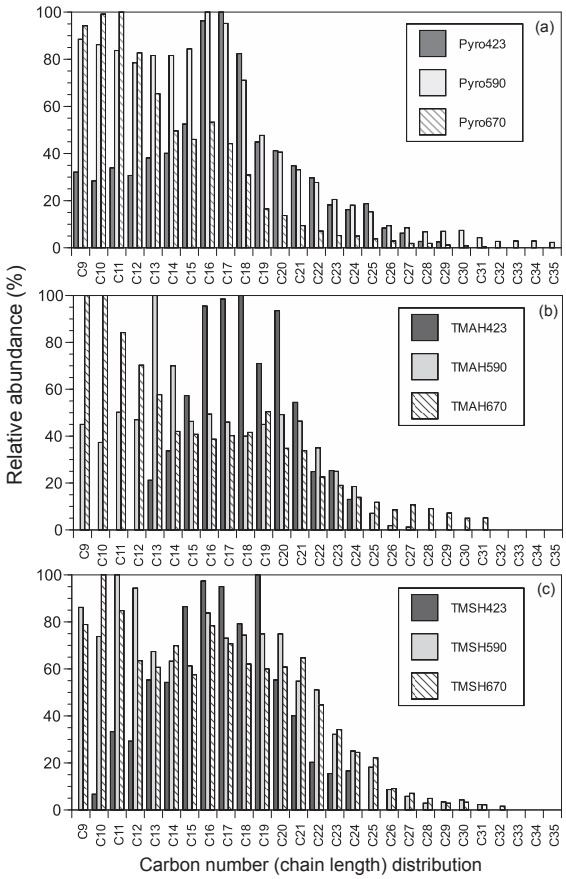

Fig. 4. Carbon number (chain length) distributions of *n*-alkanes released by pyrolysis (a), and thermochemolysis with TMAH (b) and TMSH (c) from the On-7 kerogen.

in geomacromolecule by thermal cracking of C-C bonds as mentioned above. Such formation pathway is supported to the evidence that the abundances of these doublets were lower in products from kerogen by not only pyrolysis but also thermochemolysis at lower temperature.

Aromatic hydrocarbon was hardly identified in the compounds generated from the On-7 kerogen by pyrolysis and thermochemolysis. Such predominance of aliphatic compounds is a common characteristic of type II kerogen (Kralert et al., 1995; del Río et al., 1995; González-Vila et al., 2001). Moreover, the kerogen in the Onnagawa Formation Shale was likely to be mainly originated from marine diatoms (Suzuki et al., 1993), and microscopic observation reported that the On-7 kerogen was found to be overwhelmingly composed of weakly-fluorescent amorphous organic matter (WFA), which was known to be derived from marine plankton (Sawada and Akiyama, 1994). The characteristics of aliphatic compounds such as *n*-alkanes and *n*-alkenes generated from the On-7 kerogen by pyrolysis and thermochemolysis were concordant with those of marine plankton-originated type II kerogen (Kralert et al., 1995; González-Vila et al., 2001).

3.2. *n*-Alkanoic acids released from kerogen by thermochemolysis and hydrolysis

Total ion chromatogram (TIC) and *m/z* 74 chromatograms of compounds released from the On-7 kerogen by thermochemolysis with TMAH and TMSH are shown in Figs. 2 and 3, respectively. FAMEs were mainly detected in the compounds released from kerogen by the thermochemolysis. Therefore, this fact indicates that *n*-alkanoic acid moieties were well preserved in geomacromolecule for the On-7 kerogen. A unimodal distribution maximizing C_{16} FAME was observed in the compounds by thermochemolysis with TMAH and TMSH under all thermal conditions. However, in the FAMEs by TMSH thermochemolysis at 590ºC, a bimodal distribution was observed, with shorter chain (C_7-C_{10}) FAMEs dominated by odd components maximizing at C_7 homologue, and C_{14}-C_{16} homologues dominated by even components maximizing at C_{16}. Also, the relative abundances of shorter chain FAMEs increased in the compounds released by TMAH thermochemolysis at 590ºC.

TIC and *m/z* 74 chromatograms of compounds released from the On-7 kerogen by KOH/methanol hydrolysis are shown in Fig. 5. As the results in the hydrolysis, a unimodal distribution maximizing C_{16} FAME with preference of even carbon number compounds is observed. It was confirmed that the FAMEs were main carboxylic products obtained by hydrolysis and much less cyclic carboxylic acid such as hopanoic acids were detected. These FAMEs, that is, fatty acyl units in geomacromolecule, were likely originated from biological precursors. The C_{14}, C_{16} and C_{18} FAMEs (fatty acyl units) might be formed through

several possible pathways; selective preservation of resistant biomacromolecules such as polyester, random polymerization of diagenetically degraded biomolecules, or *in situ* polymerization of labile fatty acids such as triglyceride and phospholipid (Gupta et al., 2007). The On-7 kerogen was thought to be marine plankton origin, so that the preservation of these FAMEs was presumably attributed to polymerization of marine plankton-derived fatty acids rather than selective preservation of resistant biomacromolecules such as terrestrial plant-synthesized polyesters (Kralert et al., 1995; McKinney et al., 1995). As Figs. 5 and 6, the short chain ($<C_{11}$) FAMEs were abundant in compounds released from the kerogen by thermochemolysis, while those, especially C_7-C_8, were hardly detected in the hydrolysates. We speculate that these short chain FAMEs (fatty acyl units) are occluded in intra-aggregates within the geomacromolecule, so that these moieties were inaccessible to hydrolysis. Such compounds have been reported to be uncombined *n*-alkanoic acids that were tightly trapped in the humin and freed during the alteration of organic matrix (Grasset et al., 2002; 2009). Thus, the C_7-C_{11} FAMEs could be also present as free or uncovalently bound compounds in geomacromolecules by occlusion mechanism. From these insights, we suggest that the thermochemolysis with TMAH and TMSH can be preferable for analyzing alkanoic acid moieties in geomacromolecule such as kerogen, although these are less quantitative.

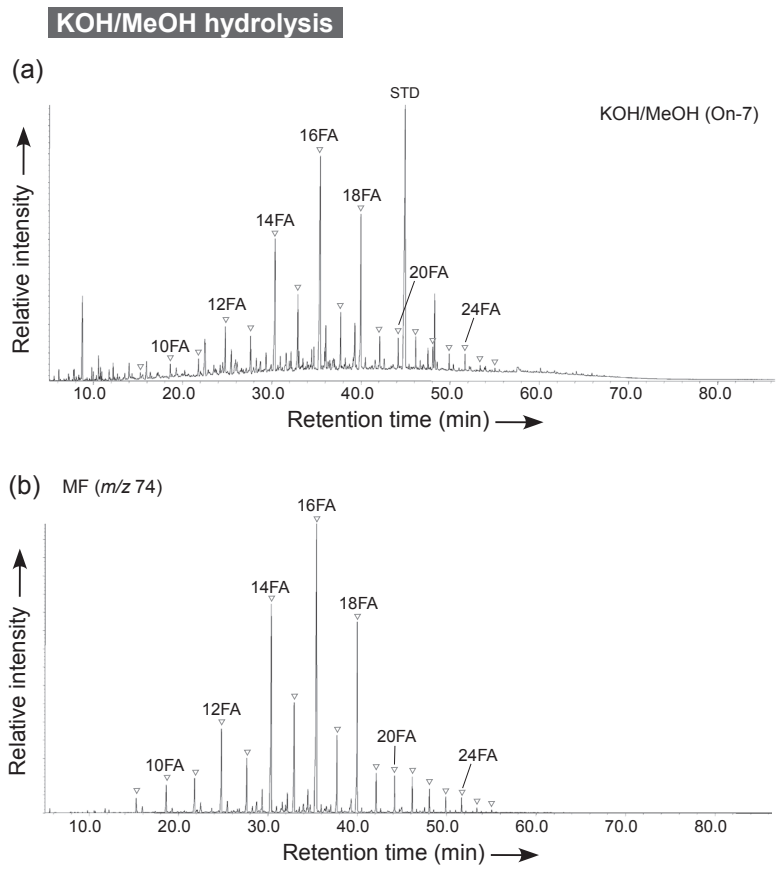

Fig. 5. (a) TIC and (b) MF of *m/z* 74 of the products obtained after hydrolysis with KOH/methanol (MeOH) from the On-7 kerogen. Inverted triangles are *n*-alkanoates (FAMEs). The nFA (n is numeral) are carbon numbers of *n*-alkanoates. STD is an internal standard (n-$C_{24}D_{50}$).

Compared the compounds by TMAH thermochemolysis with TMSH method, the FAME distributions were different in the following points; 1) predominance of the C_7 FAME in the compounds released by TMSH thermochemolysis (at 423ºC and 590ºC), 2) slightly higher abundances of C_{14} and C_{18} FAMEs in the compounds released at 590ºC and 423ºC TMSH thermochemolysis, respectively, than those in TMAH thermochemolysis, 3) slightly higher abundances of long chain ($>C_{20}$) homologues in TMSH than in TMAH (Fig. 6a, b). Noticeably, the C_7 and C_9 FAMEs predominated in the TMSH method , while the C_7 FAME was minor in TMAH method. As mentioned above, the short chain compounds as C_7 might be trapped and occluded in geomacromolecule. It therefore, can be suggested that the trapped and occluded compounds like these were more efficiently released by TMSH thermochemolysis. On the other hand, the ratios of total FAMEs to *n*-alkanes released/generated from the kerogen by TMAH thermochemolysis were significantly higher than those by TMSH method (Fig. 7). From these results, it is suggested that total recovery of the FAME released by thermochemolysis can be higher in the presences of TMAH than TMSH.

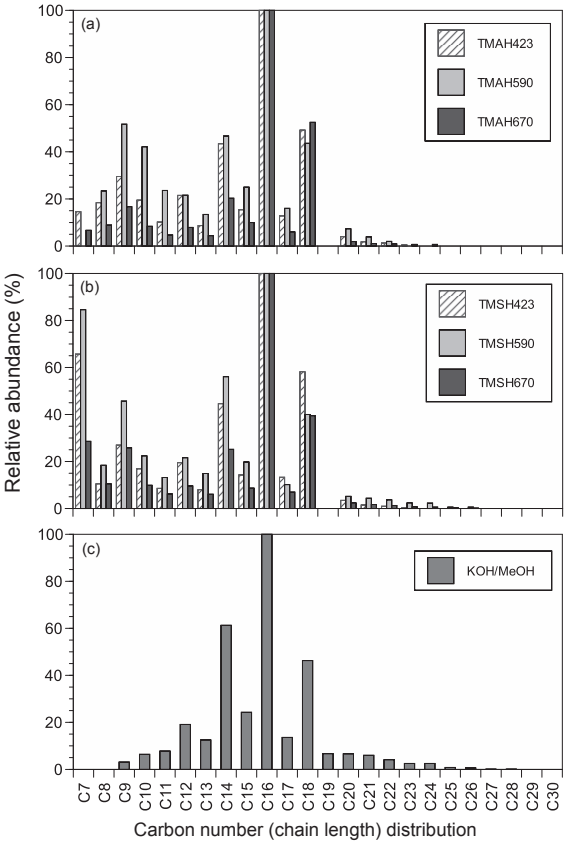

Fig. 6. Carbon number (chain length) distributions of *n*-alkanoic acids released by thermochemolysis with TMAH (a) and TMSH (b), and hydrolysis with KOH/methanol (c) from the On-7 kerogen.

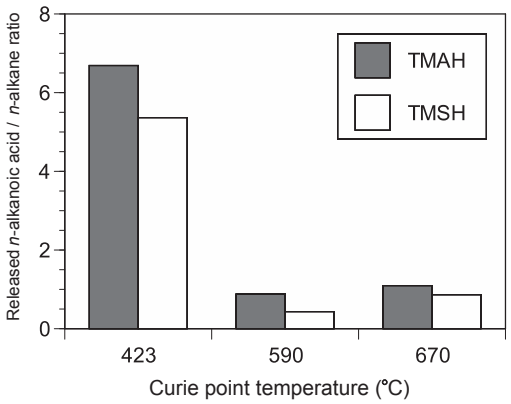

Fig. 7. Ratios of *n*-alkanoic acids to *n*-alkanes released by thermochemolysis with TMAH and TMSH from the On-7 kerogen.

4. Conclusions

In this study, we applied pyrolysis and thermochemolysis with TMAH and TMSH under various thermal conditions (423ºC, 590ºC and 670ºC) as well as alkali hydrolysis to the Miocene Onnagawa Formation Shale On -7 kerogen (type II kerogen). The *n*-alkane/*n*-alkene doublets were observed as major compounds in products by pyrolysis and thermochemolysis, and these might be generated from alkyl moieties in geomacromolecule by thermal cracking of C-C bonds. The *n*-alkanoic acids (as FAMEs) were mainly detected in the compounds released from the kerogen by thermochemolysis. A unimodal distribution maximizing C_{16} FAME is observed in the compounds under all thermochemolysis conditions, although shorter chain ($<C_{11}$) FAMEs were dominated by odd components maximizing at C_7 homologue by TMSH thermochemolysis at 590ºC. The *n*-alkanoic acids were presumably preserved through the polymerization

of marine plankton-derived compounds. Noticeably, the short chain FAMEs were abundant in compounds released by thermochemolysis, while those were hardly detected in hydrolysates. We speculate that these short chain FAMEs (*n*-alkanoic acids) are mainly occluded in intra-aggregates within the geomacromolecule. Also, the C_7 and C_9 FAMEs predominated in the compounds released by TMSH-using thermochemolysis, although the C_7 FAME was minor in TMAH method. We suggested that the trapped and occluded compounds like C_7 and C_9 acids were more efficiently released by TMSH thermochemolysis. On the other hand, the ratios of total FAMEs to *n*-alkanes released/generated from the kerogen by TMAH thermochemolysis were significantly higher than those by TMSH method. Thus, it is suggested that total recovery of the FAME released from kerogen by thermochemolysis can be higher in the presences of TMAH than TMSH. From these results, we conclude that high applicability of the TMAH- and TMSH-using thermochemolysis to exploring *n*-alkanoic (fatty) acid moieties in geomacromolecule.

Acknowledgements

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