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Isoprenoid Thiophenes in Miocene Onnagawa Siliceous Sediments, Japan

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The isoprenoid thiophenes with 20 carbons (3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene and 3-(4,8,12-trimethyltridecyl)-thiophene) are significantly detected in Miocene Onnagawa siliceous sediments (sample 82408) from Oomagari, Akita Prefecture, Japan. Associated kerogen is also rich in organosulphur ($S=7.7\%$ and atomic $S/C=0.063$) and can be classified as Type II-S kerogen. The isoprenoid thiophenes are possibly formed abiogenically by reactions of H_2S with several phytadiene isomers derived from dehydration and reduction of phytol in the very early stage of diagenesis. The isoprenoid thiophenes are not always detected in contemporaneous siliceous and non-siliceous sediments. The unique presence of isoprenoid thiophenes in Onnagawa siliceous sediments from Oomagari is due to the followings: (1) the sample is anomalously poor in clay minerals having active iron which removes H_2S, (2) the marked contribution of diatom-derived organic matter rich in chlorophyll-derived phytol as a precursory compound of isoprenoid thiohenes, and (3) the anoxic condition favorable for the formation of abundant H_2S as source of organosulphur.

Introduction

The abundance of organically-bound sulphur in living biomass is very low relative to that present in oils, source rocks and sediments. Therefore, it is now generally accepted that reduced sulphur species, hydrogen sulphide, elemental sulphur and/or polysulphides are major donors of sulphur in reactions with organic molecules (Orr, 1986; Sinninghe Damste and De Leeuw, 1990). The origin of some organosulphur compounds in geological samples is probably closely related to the environmental conditions at the time of deposition. For instance, enrichment of organosulphur compounds appears to correlate with a marine carbonate type of depositional environment (Gransh and Posthuma, 1974). Other examples include hypersaline depositional environments such as those responsible for the formation of Rozel Point Oil (Sinninghe Damste *et al.*, 1987), and various oils from China (Philp *et al.*, 1989). In a closed environment, the oxygen supply will be rapidly utilized and sulphate-reducing bacteria will extract the sulphate from saline water and reduce it to H_2S, which in turn acts as an alternative source of sulphur for incorporation into residual organic matter during diagenesis. Some possible incorporation mechanisms of inorganic sulphur into organic matter in recent and ancient sediuments are introduced by Shinninghe Damste and De

Leeuw (1990). The addition of H_2S (or possible polysulphides) to double bonds or reaction with other functionalities initiates the formation of OSC (organosulphur compounds) during early diagenesis (Sinninghe Damste *et al.*, 1990; Fukushima *et al.*, 1992). The reaction of H_2S with activated carbonyl groups to form thiols is also proposed as one of major reaction processes for the sulphur incorporation into sediumentary organic matter (Suzuki and Philp, 1990).

Among those OSC, acyclic isoprenoid thiophene found in both recent and ancient sediments are of interest. Isoprenoid thiophenes (3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene and 3-(4,8,12-trimethyltridecyl)-thiophene) are firstly found in DSDP (Deep Sea Drilling Project) sediments by Brassell *et al.* (1986). Most isoprenoid thiophenes are generally found in sediments deposited in the saline environments (Sinninghe Damste *et al.*, 1990). However, Fukushima *et al.* (1992) recently showed a significant presence of C_{20} isoprenoid thiophenes in a freshwater lake of low pH (Lake Usori-ko, Japan). The possible formation of isoprenoid thiophene by the incorporation of sulphur into chlorophyll-derived phytol or phytadiene in the very early stage of diagenesis is proposed by Brassell *et al.* (1986). However, the geochemical significance of their presence is not necessarily clear because of limited reports of their occurrences in geological samples. We recently found significant amount of C_{20} isoprenoid thiophenes in Japanese siliceous marine sediments of Miocene Onnagawa Formation. The result of identification of isoprenoid thiophenes and geological background of the sample are described in the present paper. The abundant presence of isoprenoid thiophenes in ancient siliceous sediments can provide several clues to understand the origin of isoprenoid thiophenes and their geological significance.

Experimental

Samples

Diatomaceous siliceous sediments were widely deposited in northeast Japan in Middle to Late Miocene time shortly after the Japan Sea opening due to anticlockwise tectonic rotations of Hokkaido-Sakhaline-Northeast Japan domains (Tamaki, 1988; Iijima and Tata, 1990). The primary production in northeast Japan Sea was markedly increased due to the invasion of nutrient rich cold sea water from the north accompanied by the Japan Sea opening. Those organic rich Miocene siliceous sediments are widely distributed along the Japan Sea side of northeastern Japan. Similar Miocene siliceous sediments are widely observed in and around the north Circum-Pacific region. Onnagawa siliceous sediments are often correlated to Monterey siliceous sediments in California, U.S.A.. The characteristic Onnagawa siliceous sediments (Sample No. 82408) discussed in the present paper are obtained in Oomagari in Akita Prefecture, Japan. The sampling location is shown in Fig. 1.

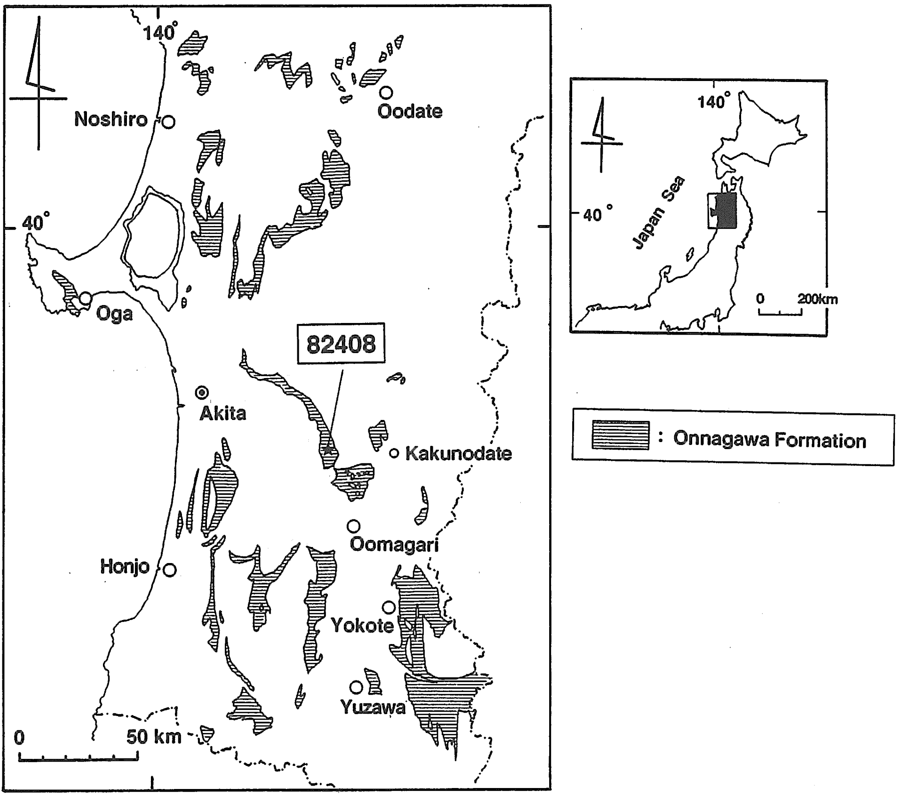

Fig. 1. Sampling location of Miocene Onnagawa siliceous sediments (82048) which was obtained near Oomagari city. The distribution of cropped out Onnagawa siliceous sediments is also shown in figure.

Instrumental

The samples from the fields were dried at room temperature, carefully cleaned by grinder, and then pulverized by jaw crusher and ball-mill to less than 200 mesh. The powdered samples were extracted in a soxhlet extraction apparatus with benzene/methanol (9 : 1) for 48 hrs. The extracts were evaporated and subjected to preparative thin layer chromatography on silicic acid (KISELGEL 60 PF_{254}, MERK) with elution by n-hexane to isolated saturated hydrocarbons.

All analyses were performed using a Shimadzu GC-14A or Shimadzu QP2000A Gas Chromatograph-Mass Spectrometer equipped with a 30 m×0.25 mm i.d. fused silica capillary column coated with DB-5 (J & W). The oven was programmed from 40 to 300°C at 4°C/min. Samples were injected using splitless injection system. The mass spectrometer was operated at an electron energy of 70 eV, an ion source temperature of 250°C and a separator temperature of 250°C.

The CHN elemental analyses are performed by using YANACO CHN-corder MT-3. The organic sulphur concentration in kerogen is determined according to Orr (1986) and Sampei *et al.* (1991). The X ray powder diffraction analysis is performed using Rigaku Denki Co. X ray diffractometer with a library search system RAD-B ver. 3.00.

Results

Many organic geochemical analyses for Japanese Miocene sedimentary rocks, especially mudstones, have been carried out up to now to reveal their characteristics as petroleum source rocks. Onnagawa siliceous sediments are typical of Japanese Miocene petroleum source rocks. Alkylthiophenes are generally present in saturated hydrocarbon fraction of thin layer or column chromatography. However, the alkylthiophenes have never been identified and described in those papers on petroleum geochemistry of Japanese possible source rocks. Alkylthiophenes are found generally in small amount comparing to abundant normal alkanes in saturated hydrocarbon fraction. It is, therefore, not necessarily easy to distinguish alkalythiophenes from abundant alkanes without paying much attention. The analyses by GC with FPD (flame photometric detector) is generally used for the detection of small amount of

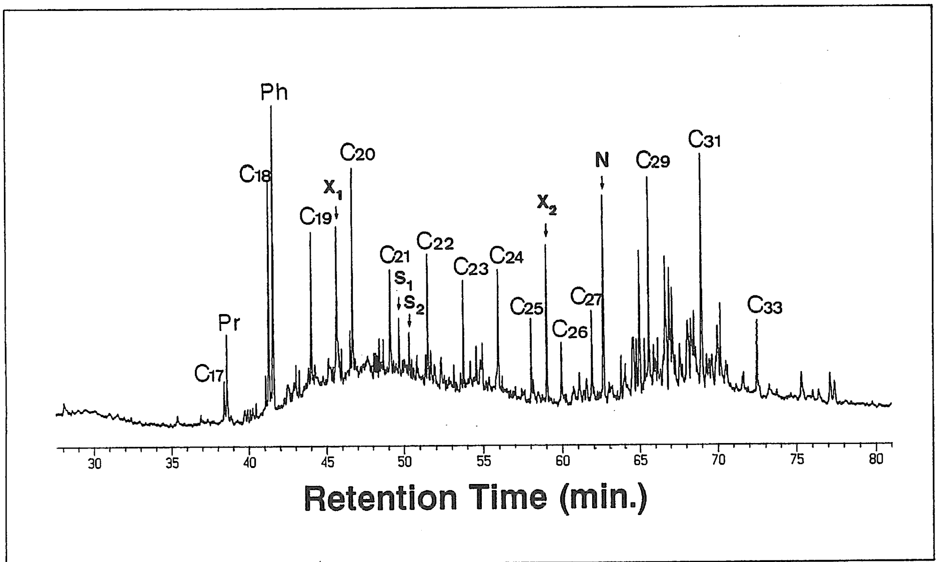

Fig. 2. Gas chromatogram of saturated hydrocarbon fraction from Onnagawa siliceous sediments (Oomagari-82408). S_1 and S_2 are identified as C_{20} alkyl-thiophenes. C_{17} to C_{33} are n-alkanes with corresponding carbon numbers. Pr and Ph are pristane and phytane, respectively. N is norcholestane, and peaks around C_{29} and C_{31} are steroidal and terpenoidal hydrocarbons. X_1 and X_2 have not been identified yet.

organic sulphur compounds. However, the alkylthiophenes we found in Onnagawa siliceous sediments are abundant enough to be distinguished from saturated hydrocarbons.

The gas chromatogram of saturated hydrocarbon fraction from Onnagawa siliceous sediments (Sample No. 82408) is shown in Fig. 2. The compounds of S_1 and S_2 are identified as alkylthiophenes. Normal alkanes show a bimodal distribution with a minimum valley at n-C_{26}. The strong odd-carbon-number predominance is observed in the higher molecular weight n-alkanes ranging from C_{25} to C_{34}. The n-alkanes ranging from C_{17} to C_{24} show the even-carbon-number predominance. Phytane is more abundant than pristane to give a pristane/phytane ratio of 0.28 indicating anoxic depositional environment. Various compounds in the retention time ranging from 65 to 70 min. are

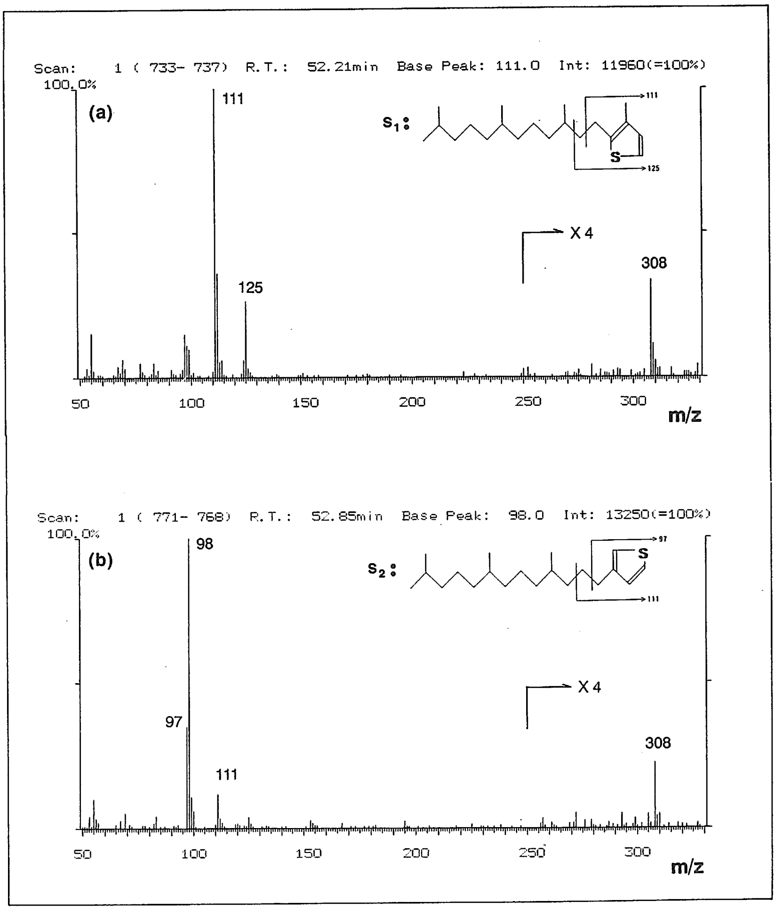

Fig. 3. Mass spectra of peaks S_1 and S_2 in gas chromatogram shown in Fig. 2. They are identified as 3-methyl-2-(3,7,11 trimethyldodecyl)-thiophene (S_1) and 3-(4,8,12-trimethyltridecyl)-thiophene (S_2), respectively.

steroidal and triterpenoidal hydrocarbons. Compound N is identified as 24-norhcolestane. The unique presence of 24-norcholestane in Onnagawa siliceous sediments will be reported with a discussion on its possible origin of diatom membranes (Suzuki *et al.,* 1993). The lack of 20S isomer of 5α (H), 14α (H), 17α (H)-ethylcholestane shows immaturity of the sample (Suzuki *et al.,* 1993).

Mass spectra of S_1 and S_2 are shown in Figs. 3-(a) and 3-(b), respectively. Molecular fragments of m/z 111 and 125 and molecular ions of m/z 308 in the mass spectra of compound S_1 show that this compound is 3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene. Mass spectra of compound S_2 are characterized by a fragment of m/z 98 with molecular ions of m/z 308 showing S_2 is 3-(4,8,12-trimethyltridecyl)-thiophene. Both S_1 and S_2 are identified as isoprenoid thiophenes with 20 carbons considering their relative retention times reported by Brassell *et al.* (1986) and Fukushima *et al.* (1992). The major compounds of X_1 and X_2 have not been identified yet.

Organic carbon and nitrogen concentration of the sample (82408) are measured to be 1.42% and 0.081%, respectively. Elemental composition of kerogen from the same sample is shown in Table 1. The kerogen sulphur concentration of 7.7% is markedly high, since kerogen sulphur concentrations of normal marine kerogens are generally less than 6% (Orr, 1986). Considering atomic ratios of S/C=0.063 and O/C=0.60, kerogen from the sample (82408) can be classifed as Type II-S kerogen proposed by Orr (1986).

Table 1. Elemental composition of kerogen from Onnagawa siliceous sediments (82408) obtained from Oomagari area, Akita Prefecture

% Concentration					Atomic Ratio			
H	C	N	S	O	H/C	O/C	N/C	S/C
5.4	46.1	3.8	7.7	36.9	1.41	0.60	0.071	0.063

(dry ash free)

The X-ray diffraction analysis for the Onnagawa siliceous sediments (82408) showed that the silica minerals (SiO_2) such as opal-CT (cristobalitic silica with tridimite reflection) and quartz are identified as major constituents (Fig. 4). Clay minerals, which are generally abundant in fine clastic sediments, are very poor in the isoprenoid thiophene rich Onnagawa siliceous sediments. Open pores of the same sample were observed with SEM (scanning electron microscope). Siliceous micro fossils are not observed, but spherulitic aggregates or lepispheres of typical morphology of Opal-CT are observed.

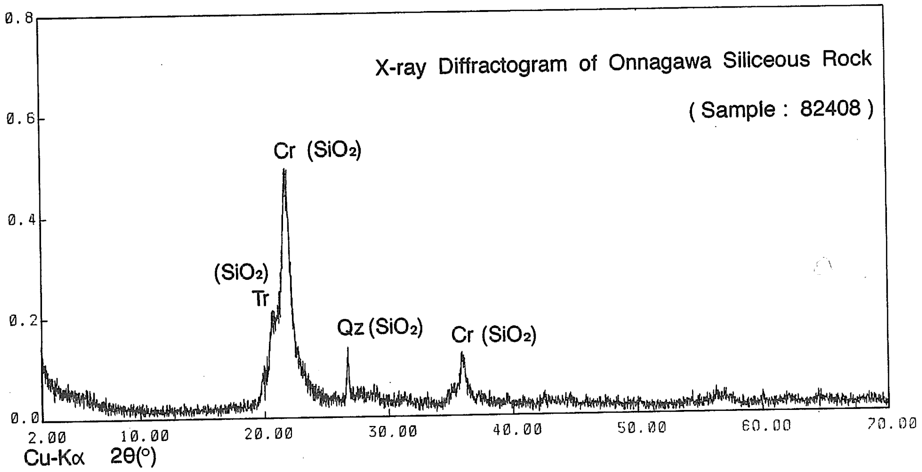

Fig. 4. X-ray powder diffractogram of Onnagawa siliceous sediments (82408) showing the abundance of diatom derived silica minerals (Opal-CT).

Discussion

Diatomaceous earth (diatomite) is well distributed in the same stratigraphic horizons with Onnagawa siliceous sediments. Siliceous skeletons of diatom fossils can be major source of those siliceous components in Onnagawa siliceous sediments, although sponge spicules could be another candidate. Radiolarians are not common in Onnagawa sediments. The accumulation rate of biogenic silica during Onnagawa Formation deposition is estimated to have been about 6 to 7 g/cm^2/kyr, which is in the similar order as that of Monterey Formation (Tada *et al.*, 1986).

The Onnagawa siliceous sediments are characteristically formed in the major stage of Japan Sea opening due to anticlockwise tectonic rotations of northeast Japanese islands. The invasion of nutrient rich cold sea water from the north to expanding Japan Sea is considered as one of major reasons for the marked increase of primary production which formed abundant siliceous sediments. This stage is corresponding to the global climatic deterioration in Middle Miocene time, when Monterey siliceous sediments are deposited (Vail *et al.*, 1977). Phytoplanktons such as diatoms are major sources of chlorophylls. If the isoprenoid thiophenes are formed by reactions of chlorophyll-derived phytols or phytadiene with H_2S (Brassell *et al.*, 1986, Fukushima *et al.*, 1992), much contribution of phytoplankton derived organic matter is favorable for the formation of isoprenoid thiophenes. The relatively high organic carbon concentration (1.42%) and the abundant cholestane (Suzuki *et al.*, 1993) of the sample supports the much contribution of primarily produced phytoplankton derived organic matter. In addition, the abundant H_2S can be expected because of anoxic depositional environment suggested by low pristane/phytane ratio. Moreover, the kerogen from the Onnagawa siliceous sediments (82408) is markedly rich in organosulphur (Table 1), suggesting that the incorporation of H_2S sulphur into sedimentary organic matter has taken place significantly in the early stage of diagenesis.

The MTT (3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene) tends to be present more abundant than the TTT (3-(4,8,12-trimethyltridecyl)-thiophene) considering limited reports on isoprenoid thiophenes (Brassell *et al.,* 1986; Fukushima *et al.,* 1992). The MTT/TTT ratio in those papers are generally more than 2. The MTT/TTT ratio of Onnagawa siliceous sediments (82408) is calculated as *ca.* 1.3 showing that TTT is relatively abundnat in case of the Onnagawa siliceous sediments (82408). According to Fukushima *et al.* (1992), the formation of TTT is dependent on the formation of phytadiene isomers from phytol. The formation of phytadiene isomers in the very early stage of diagenesis can be closely related to the geochemical condition of deposition such as pH, oxic/anoxic condition, and supplies of H_2S and chlorophyll-derived phytol. The value of MTT/TTT could reflect the geochemical environment of sediment/water interface at the time of deposition.

Fukushima *et al.* (1992) suggest that the low pH condition can facilitate the formation of isoprenoid thiophenes because of its favorable condition for dehydration of phytol. However, various kinds of isoprenoid thiophenes are generally detected in marine and hypersaline sediments formed under alkaline condition with the higher pH (Brassell *et al.,* 1986; Sinninghe Damste and De Leeuw, 1990). Many siliceous and non-siliceous sediments were analyzed in a similar manner by GC and GC-MS methods. We, however, could not detect any isoprenoid thiophenes significantly in FID chromatograms except for the sample (82408), suggesting that marine siliceous mudstones are not always composed of isoprenoid thiophenes. Further investigation by GC-FPD may be useful to detect small amount of sulphur compounds in saturated hydrocarbon fraction.

Conclusion

The isoprenoid thiophenes with 20 carbons (MTT; 3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene and TTT; 3-(4,8,12-trimethyltridcyl)-thiophene) are significantly detected in Miocene Onnagawa siliceous sediments (82408) from Oomagari, Akita Prefecture. The MTT/TTT ratio is measured to be 1.3, which is less than those previously reported for marine and non-marine mudstones. The sample (82408) is characterized by relatively high TOC (1.42%) and high organic sulphur concentration (7.7% of sulphur and $S/C=0.063$) of kerogen. Analytical results of many siliceous and non-siliceous sediments showed that isoprenoid thiophenes are not always present in normal marine mudstones. The significant formation of isoprenoid thiophenes in Onnagawa siliceous sediments (82408) is possibly due to the following: (1) the sample is anomalously poor in clay minerals having active iron which removes H_2S, (2) the marked contribution of diatom derived organic matter rich in chlorophyll-derived phytol as source of isoprenoid thiophenes, and (3) the anoxic conditions favorable for the formation of abundant H_2S as source of organosulphur.

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