Chapter 4

Polynuclear Aromatic Thiophenes in the Murchison Carbonaceous Chondrite

ABSTRACT – The Murchison carbonaceous chondrite was analyzed for polynuclear aromatic thiophenes in organic solvent extract. Benzothiophene, dibenzothiophene and their methyl derivatives, and benzonaphtothiophenes were detected in concentration at levels of ten and hundred-pmol g^{-1}. The abundance pattern of these thiophenes in the chondrite was markedly different from those in the two kinds of terrestrial sediments, indicating abiotic origin of these thiophenes. It is reasonable to conclude that the polynuclear aromatic thiophenes found in our study had been released from the insoluble organic matter during a low temperature aqueous alteration process that had occurred on the parent body of Murchison. The relative abundance of 4-methyldibenzothiophene was 2.8 times more than that of 1-methyl one. The ratio 2.8 suggests that they had experienced probably a weak thermal event on the parent body of Murchison. The ratio of 4- to 1-methyldibenzothiophene may be a good indicator for comparison of the order of the aqueous alternation process on the parent bodies.

INTRODUCTION

Carbonaceous chondrites contain various kinds of extraterrestrial organic compounds (Cronin and Chang, 1992). These organic compounds were formed in the early solar nebular process as most of the inorganic constituents of the chondrites and were abiotic origin. Therefore, the analyses of the organic compounds provide useful information to the primordial organic chemistry in the early solar system and chemical evolution on the primitive earth. Less than 25% of the organic matter in carbonaceous chondrites is present as free compounds which can be extracted with common organic solvents (Hayatsu and Anders, 1981). These compounds include aliphatic hydrocarbons, aromatic hydrocarbons, carboxylic acids, alcohols, aldehydes, ketones, amino acids, nitrogen heterocycles, amides, amines and phosphonic acids (Cronin and Chang, 1992). Previously, the analyses of organic compounds in Yamato-791198 and 74662 have revealed the presence of several classes of them, such as amino acids (Shimoyama *et al.*, 1979, 1985), carboxylic acids (Shimoyama *et al.*, 1986 and 1989), dicarboxylic acids (Shimoyama and Shigematsu, 1994), nucleic acid bases (Shimoyama *et al.*, 1990), and hydrocarbons (Naraoka *et al.*, 1988; Shimoyama *et al.*, 1989).

Among those organic compounds sulfur-containing ones were incidentally found; dibenzothiophene (DBT) in an organic solvent extract of the Yamato-791198 (Naroka *et al.*, 1988) and 74662 (Shimoyama *et al.*, 1989) chondrites for the analysis of polynuclear aromatic hydrocarbons (PAHs), and thiophene, benzothiophene (BT) and up to C_4-alkylthiophenes in a pyrolyzed fraction of Yamato-791198 (Komiya *et al.*, 1993) and Murchison (Komiya and Shimoyama, 1996) for the analysis of insoluble macromolecular organic matter. Meantime, up to C_4-alkyl sulfonic acids were detected in a water extract of Murchison (Cooper *et al.*, 1992).

Therefore, the author analyzed for polynuclear aromatic thiophenes in an organic solvent extract of Murchison in order to clear the presence of thiophenes not in bound form but in free one. In this chapter, the author describes the result of the analysis and discusses characteristics of those thiophenes in comparison to those found in terrestrial sediments (Katsumata and Shimoyama, 2000a and b).

EXPERIMENTAL

Sample

The Murchison sample analyzed was a piece provided by Dr. Olsen (Field Museum of Natural History, Chicago). A portion of the piece was pulverized in a clean room and a part of it was previously used for dicarboxylic acid analysis (Shimoyama and Shigematsu, 1994) and pyrolysis of insoluble macromolecular organic matter (Komiya and Shimoyama, 1996).

Analyses

Analytical procedure for polynuclear aromatic thiophenes is schematically shown in Fig. 4-1. The procedure is basically same as that of sedimentary rock samples.

Another portion of the powdered sample (1 g) was extracted six times with 5 ml of a mixture of dichloromethane and methanol (4:1 by vol.) by sonication for 30 min. The extracted solutions were combined, carefully concentrated under reduced pressure, and applied to a silica gel column (130 mm × 10 mm i.d.; Kieselgel-60, Merck). The column was washed with 10 ml of hexane and then 10 ml of dichloromethane. Polynuclear aromatic thiophenes were recovered in the dichloromethane solution. The solution was carefully concentrated to 50 μl under a nitrogen flow, and analyzed by a gas chromatography-mass spectrometry (GC-MS). The GC-MS was performed using a Hewlett-Packard 6890 instrument coupled with a Hewlett-Packard 5973 mass spectrometer. The GC was equipped with a splitless injection system and a fused silica capillary column (30 m × 0.25 mm i.d.) coated with DB-5ht (J&W Scientific), and its oven temperature was programmed to hold 60 °C for initial 3 min, increase from 60 to

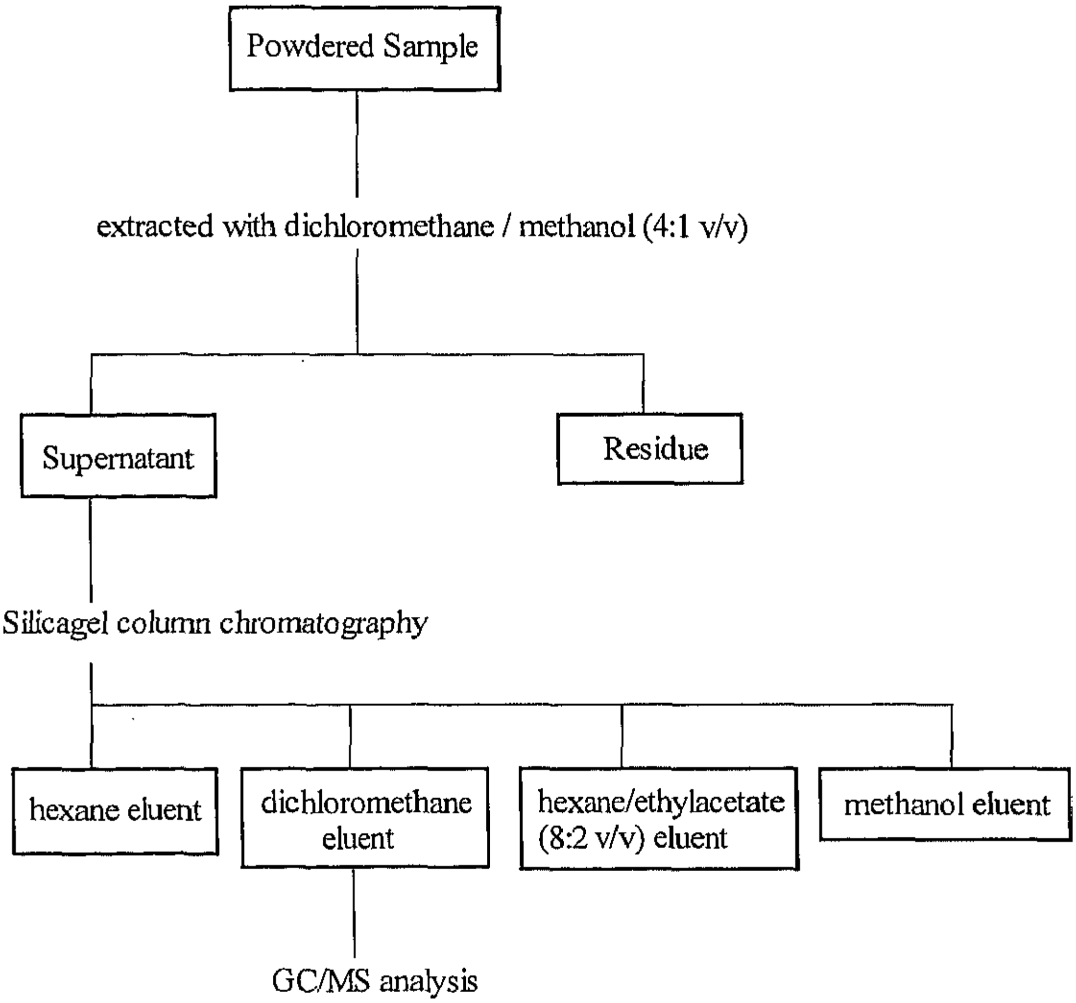


Fig. 4-1. Analytical procedure for polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite.

90 °C at a rate of 10 °C min^{-1}, from 90 to 280 °C at a rate of 3 °C min^{-1} and to hold at 280 °C for 10 min. Helium was used as a carrier gas with a flow rate of 1 ml min^{-1}. Mass spectra were obtained by scanning *m/z* 50 to 600 every 1.4 s in the electron impact mode at 70 eV. Polynuclear aromatic thiophenes were identified and quantified by comparison of peak retention times and areas, respectively, on mass fragmentograms of selected ions with those of standard compounds.

All glassware was heated at 500 °C for 3 h prior to use to remove organic contaminants. Organic solvents were doubly distilled and used. All analytical and preparative processes were carried out in the clean room, or when necessary, on a clean bench in the room. A procedural blank was performed with 1 g of pre-ignited sand powder and it was found that there was no significant contamination during the analysis.

RESULTS AND DISCUSSION

Figure 4-2 shows mass fragmentograms for molecular ions of polynuclear aromatic thiophenes in Murchison. Specific mass numbers of *m/z* 134, 148, 184, 198 and 234 for the polynuclear aromatic thiophenes gave at least 10 compounds numbered from 1 to 10. Identifications of these compounds were made by their mass spectra shown in Fig. 4-3 and are listed in Fig. 4-4. The position of a methyl group in methylDBTs (MDBTs) was determined based on the previous studies (Chackhmakhchev and Suzuki, 1995; Santamaría *et al.*, 1998). However, the peak number 6 (Fig. 4-2) corresponds 2- and/or 3-MDBTs because of their nearly same retention times. In addition, C_2- and C_3-alkylBTs were detected at trace levels on their mass fragmentograms (not shown in Fig. 4-2) and their mass spectra, but longer alkyl derivatives of BT, DBT and benzonaphtothiophene (BNT) were not detected. Concentrations or relative ones of these 10 compounds are at 10 to 100 pmol g^{-1} level and shown in Table 4-1.

An abundance pattern of the polynuclear aromatic thiophenes in Murchison is shown in Fig. 4-5, together with those of the Neogene (Katsumata and Shimoyama, 2000a) and Cretaceous/Tertiary (K/T) boundary sediments (Katsumata and Shimoyama, 2000b). BT and its methyl derivatives were present in Murchison but not in the two terrestrial sediments. The difference is partly due to relatively high volatility of these compounds. Carbonaceous chondrites generally stayed at a low temperature (ca. 100 K) region in space, while the sediments received geothermal heat (ca. 50-150 °C) during diagenesis. In addition, Murchison shows DBT most abundant, and MDBTs and BNT markedly low. On the contrary, DBT is less abundant than MDBTs in the sediments. It was reported that alkylation of DBT in sediments took place by an uncertain biological process during

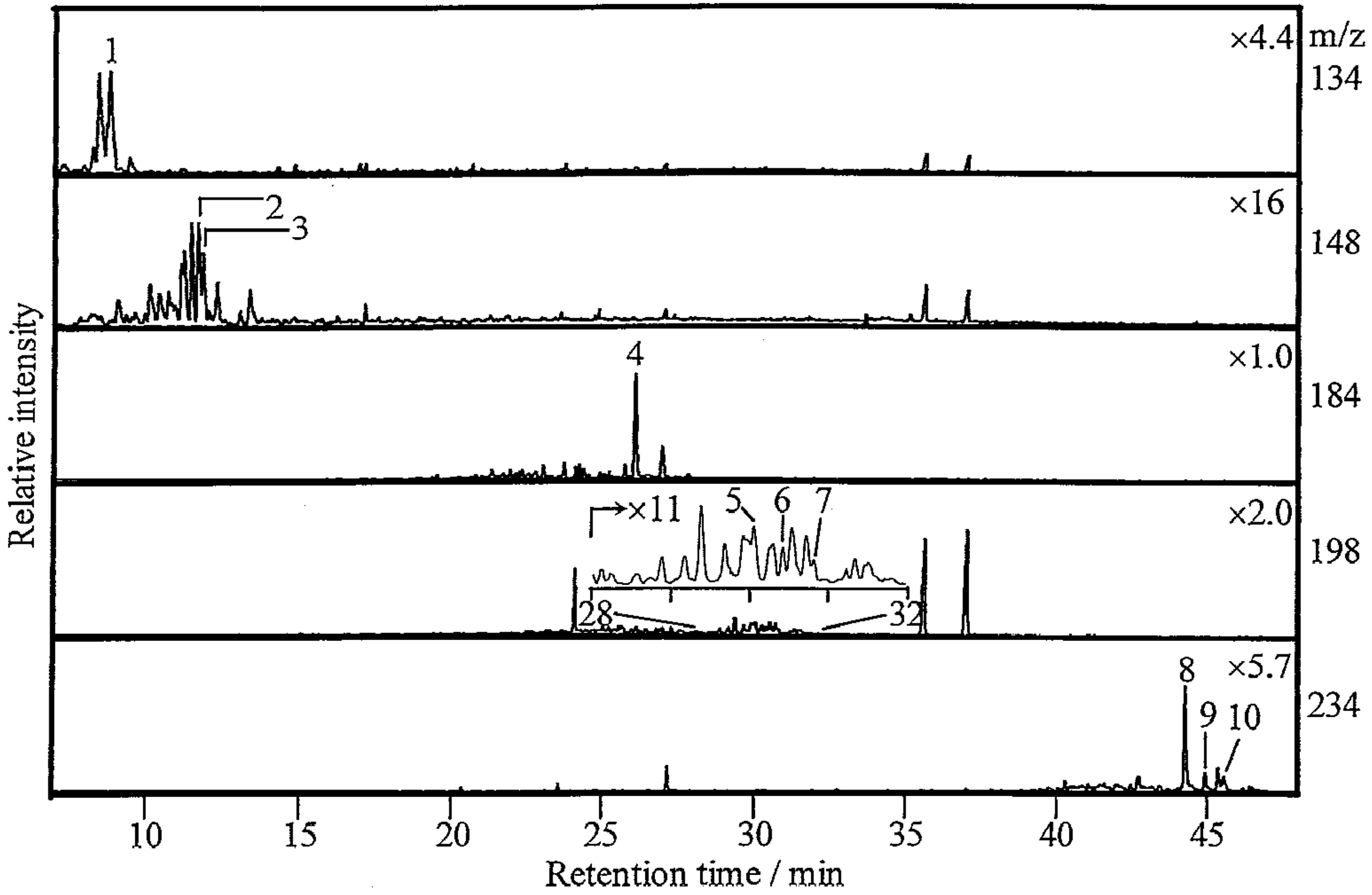


Fig. 4-2. Mass fragmentograms of polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite. Peak numbers correspond those in Table 4-1.

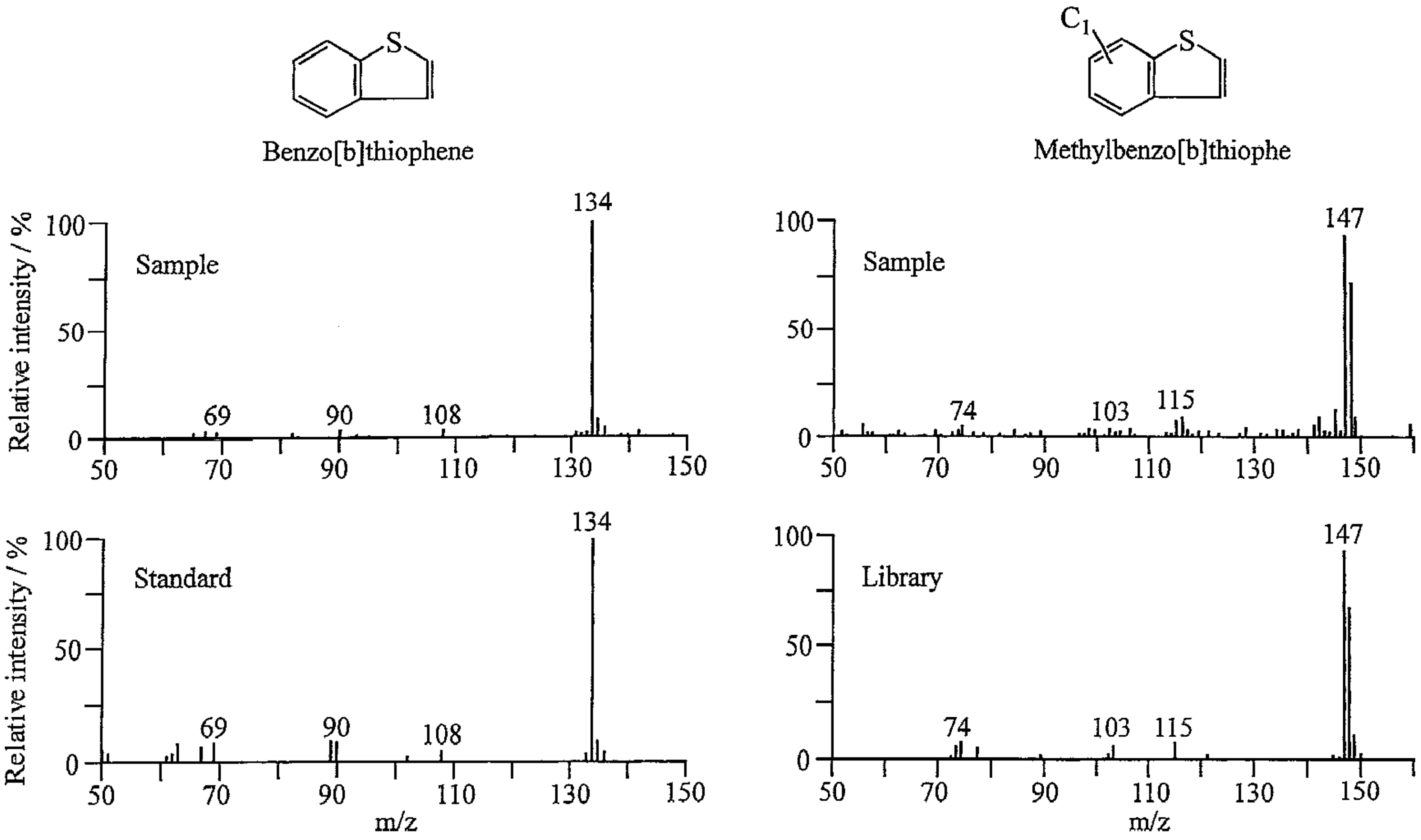


Fig. 4-3. Mass spectra of polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite.

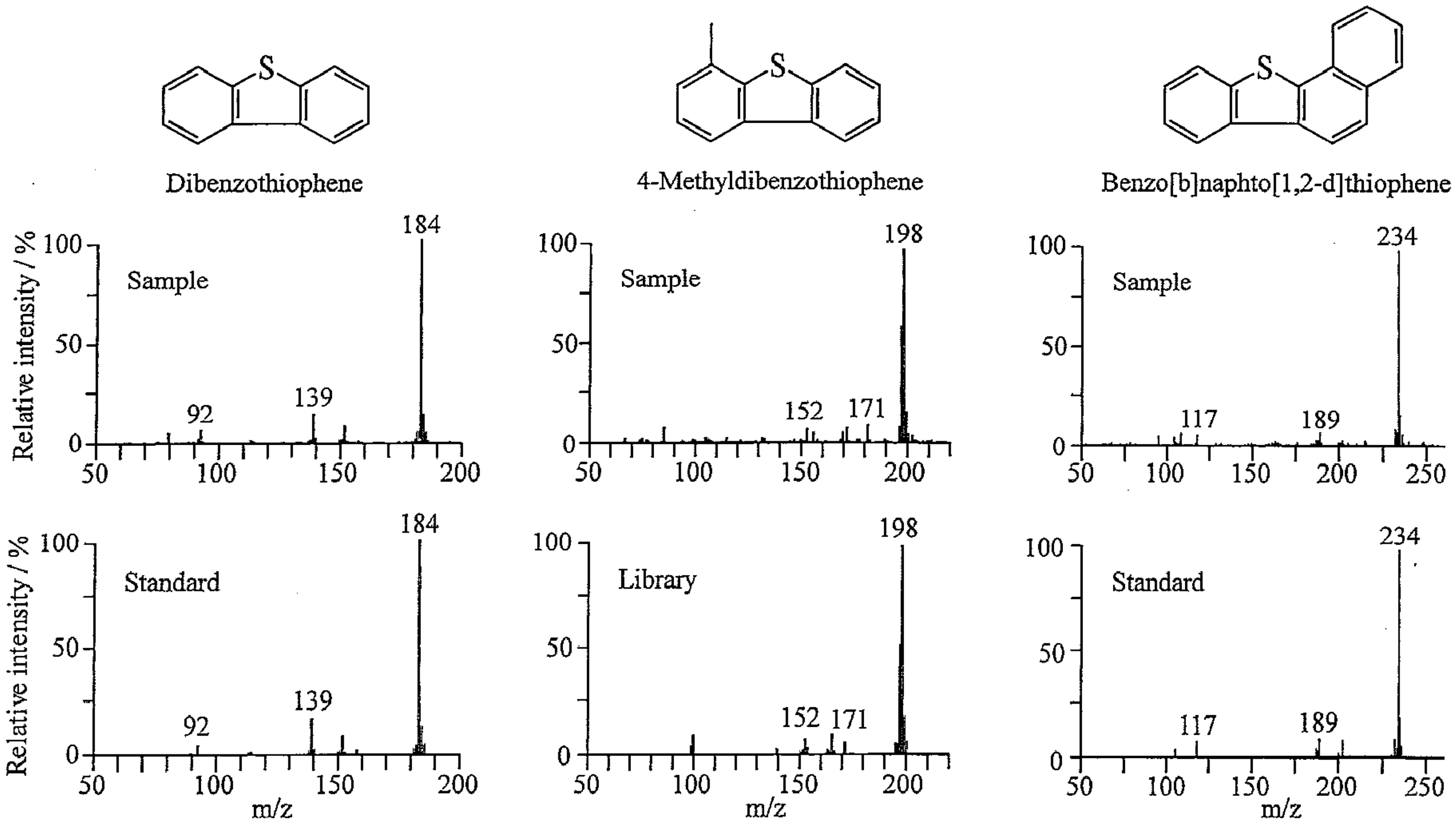


Fig. 4-3. *(continued)*

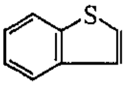
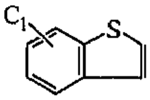
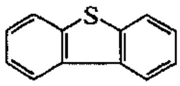
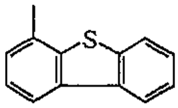
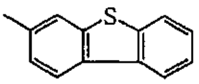
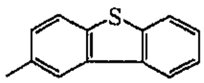
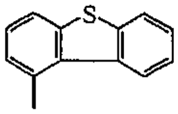
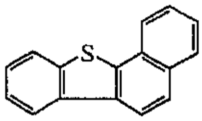
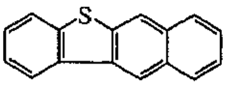
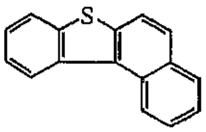
No.	m/z	Structure
1	134	
2 · 3	148	
4	184	
5	198	
6	198	 & 
7	198	
8	234	
9 · 10	234	 or 

Fig 4-4. Structures of polynuclear aromatic thiophenes found in the Murchison carbonaceous chondrite. Numbers correspond those peak numbers in Fig. 4-2.

Table 4-1. Concentrations of polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite

No.[a]	Compound	pmol g^{-1}
1	Benzo[b]thiophene	430
2[b]	Methylbenzothiophene isomer	73[c]
3[b]	Methylbenzothiophene isomer	50[c]
4	Dibenzothiophene	800
5[b]	4-Methyldibenzothiophene	39[c]
6[b]	2- & 3-Methyldibenzothiophene	29[c]
7[b]	1-Methyldibenzothiophene	14[c]
8	Benzo[b]naphto[1,2-d]thiophene	130
9[b]	Benzonaphtothiophene isomer	18[c]
10[b]	Benzonaphtothiophene isomer	18[c]

[a] Numbers correspond those shown at the peaks in Fig. 4-2. [b] Compounds were identified by the mass spectra database of NIST. [c] Relative concentrations.

diagenesis (Radke *et al.*, 1982). These unique features in compound abundance of Murchison in comparison with those in the sediments indicates that the compounds in Murchison are abiotic in origin.

A study of stable carbon isotopic compositions indicated that organic solvent extractable PAHs were degradation products from insoluble macromolecular organic matter in Murchison (Sephton *et al.*, 1998, 2000). In addition, the study showed that BT pyrolyzed from the insoluble organic matter had a similar carbon isotopic composition to PAHs with the same carbon number. As to the insoluble organic matter, there remain many unknown aspects. It is insoluble and macromolecular, and mainly comprised of condensed aromatic, heteroatomic and hydroaromatic ring systems. A typical elemental composition reported for Murchison insoluble organic matter is C 76.5%, H 4.5%, N 2.4%, S 4.3% and O 12.4% (Hayatsu *et al.*, 1980). It is generally accepted that the insoluble organic matter was formed from the primitive solar nebular gases such as CO, N_2, and H_2O (Cronin and Chang, 1992). Therefore, it is reasonable to conclude that the polynuclear aromatic thiophenes found in our study had been released from the insoluble organic matter during a low temperature aqueous alteration process that had occurred on the parent body of Murchison (Bunch and Chang, 1980; Tomeoka and Buseck, 1985).

The relative abundance of 4-MDBT was 2.8 times more than that of 1-MDBT. It has been reported that 4-MDBT is thermally more stable than 1-MDBT, increasing the ratio of 4- to 1-MDBT with increasing temperature during diagenesis of sediments (Radke *et al.*, 1986; Chakhmakhchev and Suzuki, 1995). The ratio 2.8 suggests that they had experienced probably a weak thermal event on the parent body of Murchison. This event was probably the same or a part of the low temperature aqueous alteration. A similar type of results was observed in Murchison where the ratio of 2- to 1-methylnaphthalene was 1.6 (Pering and Ponnamperuma), showing a predominance of thermally more stable isomer. It was proposed, using also data of Yamato-74662 and Yamato-791198, that the

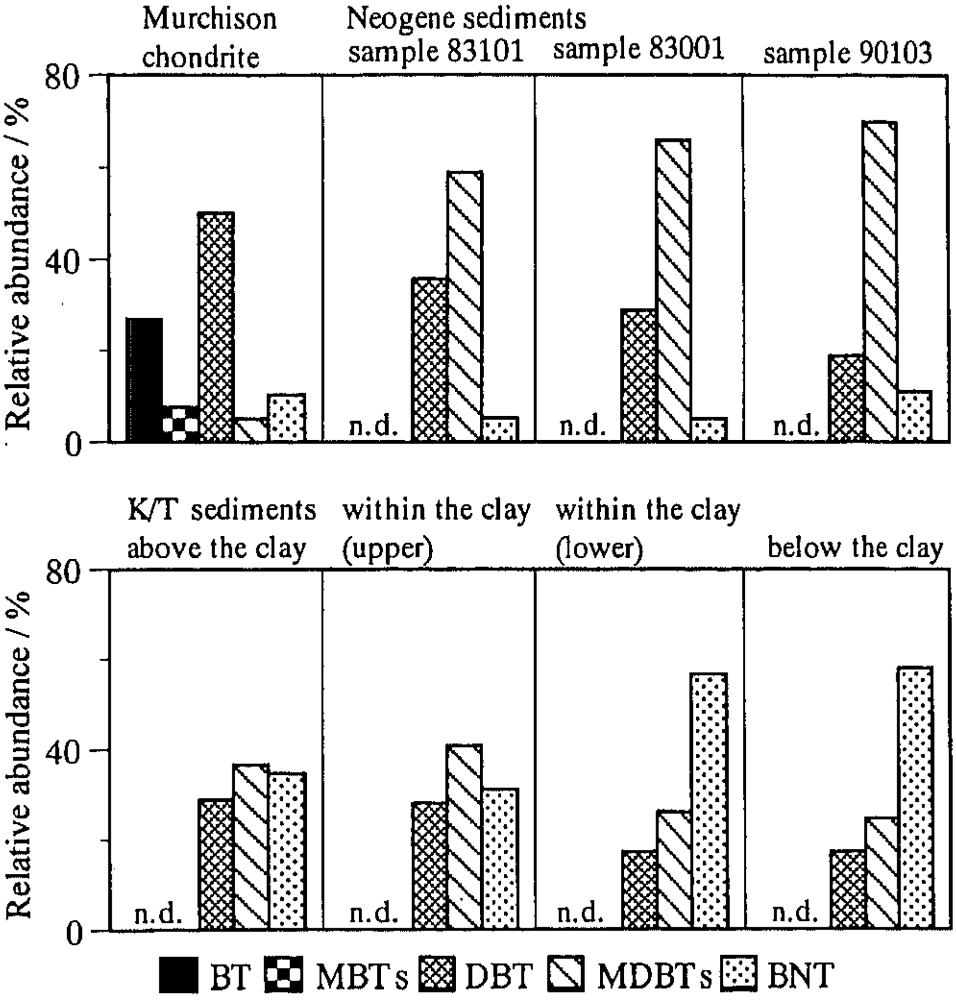


Fig. 4-5. Abundance patterns of polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite, Neogene and K/T boundary sediments.

methylnaphthalene ratio was a useful parameter on comparison of the order of the aqueous alternation process on the parent bodies (Shimoyama *et al.*, 1988). Similarly, the ratio of 4- to 1-MDBT may be a good indicator for the comparison. However, further study is necessary as to the usefulness of the ratio by the examination of other carbonaceous chondrites.

CONCLUSIONS

The Murchison chondrite was analyzed for polynuclear aromatic thiophenes in organic solvent extract. Examination of their characteristics led the following conclusions.

1. Ten kinds of polynuclear aromatic thiophenes were detected in the chondrite. Among these thiophenes BT, DBT and BNT were rather predominantly present and their concentrations were 430, 800 and 130 pmol g^{-1}, respectively.
2. The abundance pattern of the polynuclear aromatic thiophenes in the chondrite was markedly different from those in the two kinds of terrestrial sediments. In the chondrite, the relative concentration of the MDBTs was remarkably lower than that of the DBT. Therefore, this result on characteristic abundance of the polynuclear aromatic thiophenes from the chondrite clearly indicates that these compounds are not related to biological ones.
3. The soluble PAHs in the chondrite are considered to be degradation products of insoluble organic matter based on the analysis of the stable carbon isotopic compositions (Sephton *et al.*, 1998). Therefore, the polynuclear aromatic thiophenes were possibly derived from sulfur-containing aromatic moieties of the insoluble organic matter and were formed by the degradation of the organic matter.
4. The relative abundance of 4-MDBT was 2.8 times more than that of 1-MDBT. The ratio 2.8 suggests that they had experienced probably a weak thermal event on the parent body of Murchison. The ratio of 4- to 1-MDBT may be a good indicator for comparison of the order of the aqueous alternation process on the parent bodies.

REFERENCES

Bunch, T. E. and Chang, S. (1980) Carbonaceous chondrites: II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.

Chakhmakhchev, A. and Suzuki, N. (1995) Aromatic sulfur compounds as maturity indicators for petroleums from the Buzuluk depression, Russia. *Org. Geochem.* **23**, 617–625.

Cooper, G. W., Onwo, W. M. and Cronin, J. R. (1992) Alkyl phosphonic acids and sulfonic acids in the Murchison meteorite. *Geochim. Cosmochim. Acta* **56**, 4109–4115.

Cronin, J. R. and Chang, S. (1992) "*Chemistry of Life's Origins*" (eds. J. M. Greenburg and V. Pirronello), pp. 1–49, Kluwer.

Hayatsu, R. and Anders, E. (1981) Organic compounds in meteorites and their origins. *Top. Curr. Chem.* **99**, 1–37.

Hayatsu, R., Winans, R. E., Scott, R. G., McBeth, R. L., Moore, L. P. and Studier, M. H. (1980) Phenolic ethers in the organic polymer of the Murchison meteorite. *Science* **207**, 1202–1204.

Katsumata, H. and Shimoyama, A. (2000a) Alkyl and polynuclear aromatic thiophenes in Neogene sediments of the Shinjo basin, Japan. *Geochem. J.*, in press.

Katsumata, H. and Shimoyama, A. (2000b) Thiophenes in the Cretaceous/Tertiary sediments at Kawaruppu, Hokkaido, Japan. *Geochem. J.*, submitted.

Komiya, M. and Shimoyama, A. (1996) Organic compounds from insoluble organic matter isolated from the Murchison carbonaceous chondrites by heating experiments. *Bull. Chem. Soc. Jpn.* **69**, 53–58.

Komiya, M., Shimoyama, A. and Harada, K. (1993) Examination of organic compounds from insoluble organic matter isolated from some Antarctic carbonaceous chondrites by heating experiments. *Geochim. Cosmochim. Acta* **57**, 907–914.

Naraoka, H., Shimoyama, A., Komiya, M., Yamamoto, H. and Harada, K. (1988) Hydrocarbons in the Yamato-791198 carbonaceous chondrite from Antarctica. *Chem. Lett.* **1988**, 831–834.

Pering, K. and Ponnamperuma, C. (1971) Aromatic hydrocarbons in the Murchison meteorite. *Science* **173**, 237–239.

Radke, M., Willsch, H., Leythaeuser, D. and Teichmüller, M. (1982) Aromatic components of coal: relation of distribution pattern to rank. *Geochim. Cosmochim. Acta* **46**, 1831–1848.

Radke, M., Welte, D. H. and Willsch, H. (1986) Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. *Org. Geochem.* **10**, 51–63.

Santamaría, O. D., Horsfield, B., Primo, R. D. and Welte, D. H. (1998) Influence of maturity on distributions of benzo- and dibenzothiophenes in Tithonian source rocks and crude oils, Sonda de Campeche, Mexico. *Org. Geochem.* **28**, 423–439.

Sephton, M. A., Pillinger, C. T. and Gilmour, I. (1998) $\delta^{13}C$ of free and macromolecular aromatic structures in the Murchison meteorite. *Geochim. Cosmochim. Acta* **62**, 1821–1828.

Sephton, M. A., Pillinger, C. T. and Gilmour, I. (2000) Aromatic moieties in meteoritic macromolecular materials: Analyses by hydrous pyrolysis and $\delta^{13}C$ of individual compounds. *Geochim. Cosmochim. Acta* **64**, 321–328.

Shimoyama, A. and Shigematsu, R. (1994) Dicarboxylic acids in the Murchison and Yamato-791198 carbonaceous chondrites. *Chem. Lett.* **1994**, 523–526.

Shimoyama, A., Ponnamperuma, C. and Yanai, K. (1979) Amino acids in the Yamato carbonaceous chondrite from Antarctica. *Nature* **282**, 394–396.

Shimoyama, A., Harada, K. and Yanai, K. (1985) Amino acids from the Yamato-791198 carbonaceous chondrite from Antarctica. *Chem. Lett.* **1985**, 1183–1186.

Shimoyama, A., Naraoka, H., Yamamoto, H. and Harada, K. (1986) Carboxylic acids in the Yamato-791198 carbonaceous chondrite from Antarctica. *Chem. Lett.* **1986**, 1561–1564.

Shimoyama, A., Naraoka, H., Komiya, M. and Harada, K. (1989) Analyses of carboxylic acids and hydrocarbons in Antarctica carbonaceous chondrites, Yamato-74662 and Yamato-793321. *Geochem. J.* **23**, 181–193.

Shimoyama, A., Hagishita, S. and Harada, K. (1990) Search for nucleic acid bases in carbonaceous chondrites from Antarctica. *Geochem. J.* **24**, 343–348.

Tomeoka, K. and Buseck, P. P. (1985) Indicators of aqueous alternation in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O and Ni. *Geochim. Cosmochim. Acta* **49**, 2149–2163.