Polynuclear Aromatic Thiophenes in the Murchison Carbonaceous Chondrite

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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.

Carbonaceous chondrites contain various kinds of extraterrestrial organic compounds,[1] whose characteristic features provide useful information to the primordial organic chemistry in the early solar system and chemical evolution on the primitive earth. Among those organic compounds, sulfur-containing ones were incidentally found; dibenzothiophene (DBT) in an organic solvent extract of the Yamato-791198[2] and 74662[3] 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[4] and Murchison[5] for the analysis of insoluble macromolecular organic matter. Although sulfur is the 10th most abundant element in solar and meteorite,[6] sulfur-containing organic compounds in meteorites (chondrites) have been studied little. Only one study reported that up to C_4-alkyl sulfonic acids were detected in a water extract of Murchison.[7] Therefore, we analyzed for polynuclear aromatic thiophenes in Murchison in order to clear the presence of thiophenes not in bound form but in free one. Here we report the result of the analysis and discuss characteristics of those thiophenes in comparison to those found in terrestrial sediments.[8,9]

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[10] and pyrolysis of insoluble macromolecular organic matter.[5] Another portion of the powdered sample (1 g) was extracted six times with 5 mL of a mixture of dichloromethane and methanol by sonication for 30 min. The extracted solutions were combined and applied to a silica gel column (130 mm × 10 mm i.d.). 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 was equipped with a DB-5ht capillary column, and its oven temperature was programmed to hold 60 °C for initial 3 min, increase from 60 to 90 °C at a rate of 10 °C min^{-1} and from 90 to 280 °C at a rate of 3 °C min^{-1}, and to hold at 280 °C for 10 min. 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.

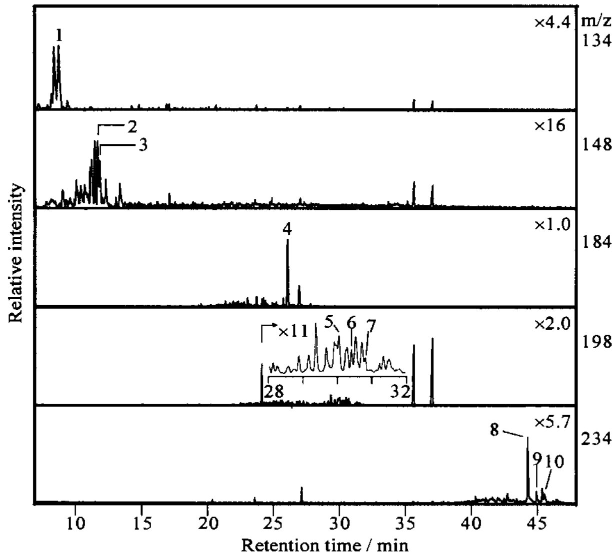

Figure 1. Mass fragmentograms for polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite. Peak numbers correspond to those in Table 1.

Figure 1 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 and are listed in Table 1. The position of a methyl group in methylDBTs (MDBTs) was determined based on the previous studies.[11] However, the peak number 6 (Figure 1) corresponds to 2- and/or 3-MDBTs because of their nearly same retention times. In addition, C_2- and C_3-alkylBTs were detected on their mass fragmentograms (not shown in Figure 1) and their mass spectra at trace levels, 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 1.

An abundance pattern of the polynuclear aromatic thiophenes in Murchison is shown in Figure 2, together with those of the Neogene[8] and Cretaceous/Tertiary (K/T) boundary sediments.[9] The characteristic features of the two sediment samples were described elsewhere.[8,9] BT and its methyl derivatives

Table 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-Methyldibenzothiophenes	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 to those shown at the peaks in Figure 1. [b] Compounds were identified by the mass spectra database of NIST. [c] Relative concentrations for methylbenzothiophene isomers were determined by benzo[*b*]thiophene standard, for methyldibenzothiophene isomers by dibenzothiophene standard and for benzonaphtothiophene isomers by benzo[*b*]naphto[1,2-*d*]thiophene standard.

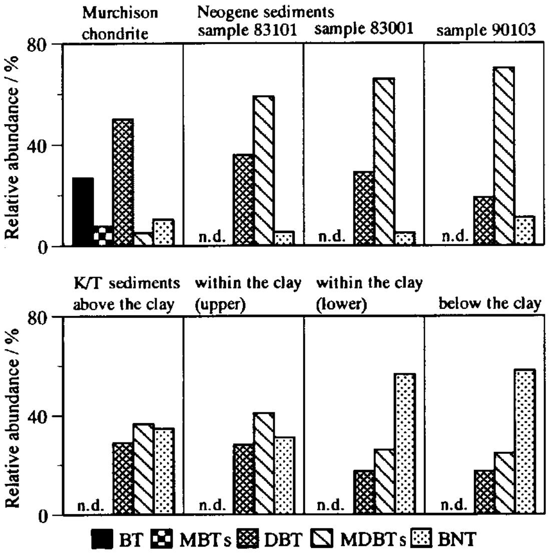

Figure 2. Abundance patterns of polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite, Neogene and K/T boundary sediments.

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 diagenesis.[12] 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.[13] 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. This indicates that the BT and PAHs were formed from the same precursors by similar processes. 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%.[14] 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.[1] 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.[15]

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.[9] 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 that the ratio of 2- to 1-methylnaphthalene was 1.6,[16] showing a predominance of thermally more stable isomer. It was proposed, using also data of Yamato-74662 and 791198, that the methylnaphthalene ratio was a useful parameter on comparison of the order of the aqueous alteration process on the parent bodies.[3] Similarly, the ratio of 4- to 1-MDBT may be a good indicator for the comparison.

Further studies are necessary on the thiophenes by analyses of other carbonaceous chondrites as well as alkyl thiophenes whose characteristic feature is still known.

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