

Chapter 5

Summary and Conclusions

Organic compounds in the Murchison carbonaceous chondrite have been studied by many investigators (see review by Cronin and Chang, 1992). These studies provide the information about pristine prebiotic organic compounds and their alternation processes occurred in the early solar nebula and/or parent bodies. Previously, thiophene, benzothiophene (BT) and up to C₄-alkylthiophenes were detected 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. However, little is known about the presence of polynuclear aromatic thiophenes in an organic solvent extract. Therefore, the author analyzed for polynuclear aromatic thiophenes in the Murchison carbonaceous chondrite in order to clear the presence of those thiophenes not in bound form but in free one. On the other hand, many studies have been carried out on organic compounds in terrestrial sedimentary rocks (Tissot and Welte, 1984). These studies offered the information about the past biological organic compounds and their alternation processes during diagenesis of sediments. Although thiophenes have been studied by many investigators, their formation pathways in sediments have not been clear yet. Therefore, the author performed analysis of thiophenes in sedimentary rocks in this study.

Eighteen Neogene sediments from the Shinjo basin were analyzed for alkyl and polynuclear aromatic thiophenes, and the following conclusions were drawn to characterize the thiophenes in the sediments.

Three kinds for each of C₂₀ isoprenoid and C₂₅ highly branched isoprenoid (HBI) thiophenes, and eight kinds of polynuclear aromatic thiophenes were detected. The concentrations of dibenzothiophene (DBT) and benzo[b]naphto[1,2-d]thiophene (BNT) ranged from 10 to 730 and 14 to 210 pmol g⁻¹, respectively. The C₂₅ HBI thiophenes showed a unique depth profile, *i.e.*, they existed from the Nakawatari to the upper part of the Kusanagi Formations. However, they were absent at the middle and lower Kusanagi Formation. It was postulated that the number and position of the double bonds in C₂₅ HBI

alkadienes were primary important for the formation of the C₂₅ HBI thiophenes during early diagenesis. The variation in composition of the C₂₅ HBI thiophene isomers was observed in the sediments indicating that they were derived from different kinds of C₂₅ HBI alkadienes. The depth profiles of polynuclear aromatic thiophenes were different from those of the C₂₅ HBI thiophenes and similar to that of the reported total *n*-alkanes (Ishiwatari and Shioya, 1986). The concentrations of all polynuclear aromatic thiophenes increased in the range from the upper to middle Kusanagi Formation and decreased at deeper depth. This result possibly indicates that the polynuclear aromatic thiophene formation followed a similar process to *n*-alkane generation and caused by different processes from those of the C₂₅ HBI thiophenes. In this connection, a possibility was postulated that the polynuclear aromatic thiophenes were formed from sulfur-containing aromatic moieties of macromolecules and were released during later stage of diagenesis.

The Cretaceous/Tertiary (K/T) boundary claystone and the sediments above and below it at Kawaruppu were analyzed for thiophenes. Examination of the result led the following conclusions.

Only one kind each for the C₂₅ HBI thiophenes and the C₂₅ HBI alkanes, and five kinds of polynuclear aromatic thiophenes were detected in the sediments. Concentrations of DBT and BNT were at a level of ten to hundred-pmol g⁻¹ (mean value was 50 pmol g⁻¹ for each). The C₂₅ HBI thiophene was found in the sediments below the boundary claystone, and was absent in the claystone and sediments above it. The compound was likely derived from specific diatoms through four kinds of C₂₅ HBI alkadienes. If so, the population of the specific diatoms extremely decreased at the end of Cretaceous. The C₂₅ HBI alkane was present in all sediments being less concentrated in the boundary claystone than sediments above and below it. The compound was likely derived from non-specific diatoms. If so, they decreased intensely at the lowest horizon of the boundary claystone. However, those non-specific diatoms started recovering their population

around the upper one third horizon of the claystone. The concentrations of the DBT and the BNT were roughly constant over the sediments below the boundary claystone to the lower two third of it. Increase of their concentrations began at the upper one third horizon of the boundary claystone (10.6 cm). The increase ceased at the 40 cm horizon and then changed to decrease in the sediments above the horizon. The depth profiles of the polynuclear aromatic thiophenes were different from that of the C₂₅ HBI thiophene, indicating that the polynuclear aromatic thiophenes had not been related to the biomass extinction event. The ratio of 4- to 1-methylDBT (MDBT) is roughly constant over the sediments above, within and below the boundary claystone, indicating that the 65 million year diagenesis had taken place evenly over the K/T sediment horizons. The depth profiles of the polynuclear aromatic thiophene concentrations showed a similar pattern to that of the sulfide one (Kajiwara and Kaiho, 1992). Therefore, the concentrations of these thiophenes were likely related to that of the sulfide. The DBT at 60 pmol g⁻¹ corresponds a boundary level of reducing (higher) and oxidizing (lower) conditions for the Kawaruppu K/T sediments.

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

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. The abundance pattern of the polynuclear aromatic thiophenes in the chondrite was marked different from those in the two 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. 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. 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 alteration process on the parent bodies.

This study provided useful information not only about the presence of thiophenes in a carbonaceous chondrite and sedimentary rocks but also about formation and alteration processes of thiophenes in the parent bodies of carbonaceous chondrite in extraterrestrial environments and in the sedimentary rocks on the Earth.

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