Chapter 1

General Introduction

Meteorites are extraterrestrial materials formed in the early solar nebula about 4.6 billion years ago. Carbonaceous chondrites which belong one of meteorite groups contain various kinds of extraterrestrial organic compounds formed by abiotic process. Therefore, characteristic features of organic compounds in carbonaceous chondrite provide useful information to the primordial organic chemistry in the early solar system and chemical evolution on the primitive earth. On the other hand, sedimentary rocks were formed on the earth and contain terrestrial organic compounds derived from organisms lived on the past earth. Therefore, analyses of organic compounds in sedimentary rocks provide good information to biological activity on the past earth and their alternation process occurred during their burial periods.

Thiophenes in carbonaceous chondrites

Meteorites are usually classified into three major groups: iron, stony-iron and stony meteorites. Furthermore, each group is divided into several subgroups. Stony meteorites are divided into two groups: chondrite and achondrite, according to the presence or absence of chondrules which are spherical aggregates of olivine and/or pyroxene.

Carbonaceous chondrites, which belong to one of the subgroups of chondrites, contain volatile matter such as water, organic compounds in some extent and are regarded as the most primitive meteorites because of their quite similar elemental compositions to the solar one except volatile elements (Fig. 1-1) (Ringwood, 1979). This fact suggests that carbonaceous chondrites have not been experienced any high temperature and intense alternation process since their formation. Therefore, organic compounds in carbonaceous chondrite are likely primitive materials in the solar system.

Carbonaceous chondrites have been divided into three types (C1, C2 and C3) on the basis of the chemical compositions (Wiik, 1956). Among the three types of the chondrites volatile constituents such as carbon, water and sulfur are most abundant in C1 chondrites

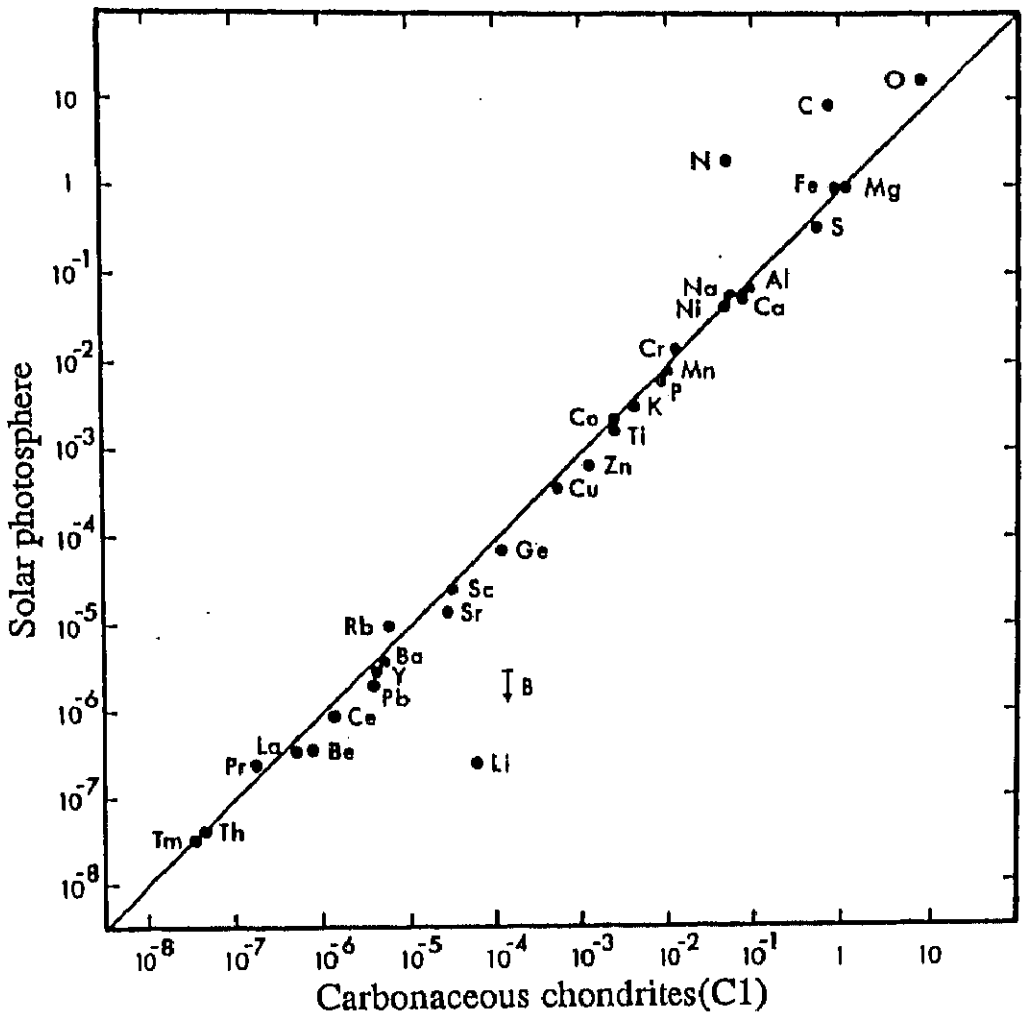

Fig. 1-1. Elemental abundances of carbonaceous chondrites (C1) and the solar photosphere (Ringwood, 1979).
All abundances are normalized to Si = 10^6.

and the least in C3 chondrites. In addition to this classification, carbonaceous chondrites were divided into four subtypes (CI, CM, CO and CV) on the basis of a variety of petrographic and chemical properties (van Schmus and Hayes, 1974). In general, CI and CM chondrites correspond to C1 and C2 ones, respectively.

In 1969, the Murchison carbonaceous chondrite (CM2 type) fell near Murchison, Australia. Soon after the fall, the chondrite was recovered and analyzed carefully. As a result, relatively large amounts of amino acids were found containing 12 non-proteineous and 6 proteineous ones some of which were racemic (Kvenvolden *et al.*, 1970, 1971). These results were the first unambiguous evidence of the presence of indigenous organic compounds in carbonaceous chondrites. Since this finding, various kinds of organic compounds have been found in carbonaceous chondrites. Amino acids in Murchison were examined (Oró *et al.*, 1971; Cronin and Moore, 1971), and in other carbonaceous chondrites by many researchers (Cronin and Moore, 1976; Cronin *et al.*, 1979; Holzer and Oró, 1979; Kotra *et al.*, 1979; Shimoyama *et al.*, 1979, 1985). The other organic compounds found in carbonaceous chondrites were monocarboxylic acids (Yuen and Kvenvolden, 1973; Lawless and Yuen, 1979; Shimoyama *et al.*, 1986, 1989), dicarboxylic acids (Lawless *et al.*, 1974; Shimoyama and Shigematsu, 1994), aliphatic and aromatic hydrocarbons (Kvenvolden *et al.*, 1970; Pering and Ponnamperuma, 1971; Studier *et al.*, 1972; Naraoka *et al.*, 1988; Shimoyama *et al.*, 1989), nitrogen heterocycles (Folsome *et al.*, 1971; Hayatsu *et al.*, 1975; Shimoyama *et al.*, 1990) and insoluble organic matter (Bandurski and Nagy, 1976; Hayatsu *et al.*, 1977, 1980; Komiya *et al.*, 1993; Komiya and Shimoyama, 1996).

Among those organic compounds sulfur-containing ones were incidentally found; dibenzothiophene 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 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).

Thiophenes in sedimentary rocks

Organic compounds in sedimentary rocks have been studied to obtain information about their distribution and alternation processes through the burial periods. These compounds are derived from organisms and accumulated after their decease, and received alternations due to decomposition and polymerization in the early stage of sediment burial. These processes are caused by bacterial activities and chemical reactions of organic compounds. Furthermore, the compounds are gradually varied by geothermal heat and pressure in sediments with burial time. Most of the organic compounds become insoluble organic matter (kerogen) which is polymer-like materials containing various constituents, while minor portions remain as initial form. Furthermore, relatively low molecular weight compounds are partially released and formed from kerogen in sediments. These processes are generally considered to be the major process for most petroleum and natural gas generation. These series of processes are called "diagenesis" of organic compounds (Eglinton and Murphy, 1969; Tissot and Welte, 1978; Hunt, 1979).

Many studies of organic compounds in sedimentary rocks have been performed especially to investigate the origin of petroleum. The earlier work on this subject had stared by the detection of porphyrin derivatives in petroleum and sediments (Treibs, 1936). In the 1950s, analysis of hydrocarbons in sediments was carried out (Smith, 1952; Stevens *et al.*, 1956). It was found that odd/even ratio of *n*-alkanes (concentration ratio of odd carbon numbered molecules to even ones) decreased from recent to ancient sediments (Evans *et al.*, 1957; Bray and Evans, 1961; Cooper and Bray, 1963). This result indicates

that the *n*-alkanes of biological origin were altered by diagenesis because the *n*-alkanes formed by the decarboxylation of fatty acids of plants and animals were odd carbon numbers. The extent of this phenomenon is expressed quantitatively as carbon preference index (CPI).

Isoprenoid hydrocarbons, especially pristane and phytane, derived from phytol chain in chlorophyll, were found in petroleum (Dean and Whitehead, 1961; Bendoraitis *et al.*, 1962), and discussed as indicator of redox condition during deposition (Brooks *et al.*, 1969). These compounds as indicator of the palaeoenvironment are called as "biomarker". Biomarkers have been widely studied to investigate alternation processes of organic compounds, ancient environments and ages of sediments. For these purposes, the types of porphyrin derivatives (Orr *et al.*, 1958), epimerization of steranes (Mackenzie *et al.*, 1980) and racemization of amino acids (Hare and Abelson, 1968; Bada *et al.*, 1970) have been studied. Fatty acids (Abelson and Parker, 1962; Cooper, 1962), alcohols (Sever and Parker, 1969) and kerogen (Forsman and Hunt, 1958; Forsman, 1963) have been also examined to investigate their alternation processes. The presence of sugars (Palacas *et al.*, 1960) and bases of nucleic acids (van der Velden and Schwartz, 1974) were reported.

Among these compounds a variety of thiophenes have been found in immature sediments and petroleum (Sinninghe Damsté and de Leeuw, 1990). The early diagenetic sulfurization of organic matter was first evidenced at the molecular level by the identification of a C_{35} hopanoid thiophene in immature sediments (Valisolalao *et al.*, 1984). The available evidence indicates that inorganic sulfur species such as hydrogen sulfide or hydrogen polysulfide react with functional groups of lipids during early diagenesis to yield thiophenes and sulfur-bound moieties in macromolecules (Brassell *et al.*, 1986; Sinninghe Damsté *et al.*, 1988, 1989; Kohnen *et al.*, 1990, 1991; Schouten *et al.*, 1995). Therefore, thiophenes are excellent indicators for palaeoenvironments, especially for biological activity and redox condition at deposition (Sinninghe Damsté *et al.*, 1990;

Kohnen *et al.*, 1993). It has been reported that natural sulfurization can be simulated in laboratory, and the results show that alkenes, aldehydes, and ketones can incorporate inorganic sulfur (Fukushima *et al.*, 1992; de Graaf *et al.*, 1992; Rowland *et al.*, 1993; Schouten *et al.*, 1993). Although the mechanisms involved in incorporation of inorganic sulfur into lipids in nature are not completely understood yet, studies of thiophenes have revealed that early diagenetic sulfurization is highly dependent on the structural features of precursors (Kohnen *et al.*, 1991; de las Heras *et al.*, 1997). Polynuclear aromatic thiophenes are a useful indicator for the evaluation of source rocks and diagenetic maturation (Chakhmakhchev and Suzuki, 1995a and b). However, little is known about the precursors and formation pathways of polynuclear aromatic thiophenes, although some studies suggested that these thiophenes were formed by cyclization and aromatization of alkyl thiophenes (Sinninghe Damsté *et al.*, 1987, 1989).

The purpose of this study

In the present study, the author performed organic cosmo- and geochemical studies on thiophenes examining carbonaceous chondrite and two kinds of sediment samples, and attempted to elucidate formation processes of the thiophenes in the samples. A three-step approach was followed to achieve the objectives.

The present thesis consists of five chapters.

In Chapter 2, the distribution of thiophenes in sediments from a stratigraphic sequence from Miocene to Pliocene in the Shinjo basin in Yamagata Prefecture, northern Japan was uncovered. Furthermore, the author discussed the formation pathways of thiophenes in the sediments based on their depth profiles.

In Chapter 3, the author detected thiophenes in the Cretaceous/Tertiary (K/T) boundary sediments at Kawaruppu, Hokkaido, Japan. The depth distribution of alkyl thiophenes was discussed in relation to the massive extinction of organisms, and

polynuclear aromatic ones to the redox conditions during the deposition and the diagenesis of the K/T boundary sediments at Kawaruppu.

In Chapter 4, the author analyzed for polynuclear aromatic thiophenes in an organic solvent extract of Murchison carbonaceous chondrite in order to clear the presence of thiophenes not in bound form but in free one. Furthermore, the author described the result of the analysis and discussed characteristics of those thiophenes in comparison to those found in the above terrestrial sediments.

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