

## PYROLYTIC STUDIES OF CARBONACEOUS MATTER IN ANTARCTIC CARBONACEOUS CHONDRITES

Tatsushi MURAE, Akimasa MASUDA  
and Takeyoshi TAKAHASHI

*Department of Chemistry, Faculty of Science, The University of Tokyo,  
Hongo 7-chome, Bunkyo-ku, Tokyo 113*

**Abstract:** Pyrolysis products of the major carbonaceous matter in six Antarctic carbonaceous chondrites, Y-74662 (C2), Y-791198 (C2), Y-793321 (C2), B-7904 (C2), Y-791717 (C3), and ALH-77307 (C3), have been examined by GC-FID and GC-MS. There is apparently a similarity in the structure of all samples. Many sulfur-containing compounds have been detected as major products in pyrolysis of the residues which were obtained by partial mineral dissolution of Y-791717 and ALH-77307 with concentrated hydrochloric acid.

### 1. Introduction

The major carbonaceous matter in carbonaceous chondrite is not extractable in any solvent (MUELLER, 1953). Various methods have been applied to the characterization of solvent-unextractable carbonaceous matter (SCHULZ and ELOFSON, 1965; HAYES and BIEMANN, 1968; SIMMONDS *et al.*, 1969; GREEN II *et al.*, 1971; BREGER *et al.*, 1972; LEVY *et al.*, 1973; BANDURSKI and NAGY, 1976; HAYATSU *et al.*, 1977, 1980; HOLZER and ORÓ, 1979; WHITTAKER *et al.*, 1980; SMITH and BUSECK, 1981). A polyaromatic structure has been proposed for this material in Murchison and other several carbonaceous chondrites (HAYATSU *et al.*, 1977). Although carbines have been claimed to be the material in Murchison (WHITTAKER *et al.*, 1980) and Allende (WHITTAKER *et al.*, 1980; HAYATSU *et al.*, 1980), it has been suggested that the major carbonaceous matter in Allende occurs possibly as a noncrystalline graphite like compound (SMITH and BUSECK, 1981). Although analysis of the pyrolysis products is one of the most useful methods for the investigation of organic polymer in meteorites (HAYES and BIEMANN, 1968; SIMMONDS *et al.*, 1969; LEVY *et al.*, 1973; BANDURSKI and NAGY, 1976; HOLZER and ORÓ, 1979; MURAE *et al.*, 1984a), the effect of coexisting minerals (whose contents are much higher than that of carbon) on pyrolysis is not clear. Analysis of acid-resistant residues obtained by mineral dissolution (treatment with hydrochloric and hydrofluoric acids) gives direct information on residual carbonaceous matter (SMITH and BUSECK, 1981), but the possibility of alteration of the polymeric structure during acid treatment remains.

The authors have investigated the major carbonaceous matter in six Antarctic carbonaceous chondrites by examination of pyrolysis products with gas chromatography equipped with a flame ionization detector (GC-FID) or a mass spectrometer (GC-MS). These chondrites are Y-74662 (C2), Y-791198 (C2), Y-793321 (C2), B-7904 (C2), ALH-

77307 (C3), and Y-791717 (C3) (Y for Yamato, B for Belgica, and ALH for Allan Hills). Carbonaceous matter in the HCl-resistant residues from Y-791717 and ALH-77307 was also examined by the same method. The results are reported in this paper.

## 2. Sample Preparation and Experimental Apparatus

Samples used in the present work were taken from small chips delivered from the meteorite curator of National Institute of Polar Research. After washing with *n*-hexane, the chips were powdered (grain size: 10–20  $\mu\text{m}$ ) and the powder was used for pyrolytic studies. A part of the powdered sample of Y-74662 was extracted with benzene-methanol (2: 1) for 12 hrs using a Soxhlet extractor. Partial mineral dissolution of ALH-77307 (144 mg) and Y-791717 (152 mg) was carried out by treatment with conc. hydrochloric acid (12N: 2.5 ml) at room temperature for 3 days, followed by washing with distilled water, treatment again with conc. hydrochloric acid (12N: 2.5 ml) at room temperature for one day, filtration using a glass filter, washing the residue with distilled water, and then drying under air stream. In the acid treatments 52 and 58% weight losses were observed for ALH-77307 and Y-791717, respectively.

The same instruments and conditions as those described previously (MURAE *et al.*, 1984a) were used for the present work (pyrolysis followed by analysis by GC-FID or GC-MS), although the GC column and oven temperature were different. An open tubular fused silica capillary column (25 m  $\times$  0.25 mm i.d.) coated with silicon OV-101 as stationary phase (film thickness: 0.40  $\mu\text{m}$ ) was used for GC-FID analysis. The rate of temperature increase was programmed to be 4°C/min from 60 to 260°C after keeping the initial temperature for 16 min. An open tubular fused silica capillary column (25 m  $\times$  0.25 mm i.d.) chemically bonded with silicon OV-1 as stationary phase (film thickness: 1.5  $\mu\text{m}$ ) was used for GC-MS analysis, because it was confirmed that this column had the applicability to the same type of compounds with much better resolution (sharp peaks with high intensity) compared with that of the wall coated OV-101 column used for GC-FID analysis. Incremental increase in oven temperature at a rate of 4°C/min from 60 to 230°C was started immediately after pyrolysis. The operation of an exhaust valve after pyrolysis, required in the previous study (MURAE *et al.*, 1984a) was not necessary when these capillary columns were used.

## 3. Results and Discussion

Extraction with organic solvents has been carried out for several carbonaceous chondrites to show the presence of organic monomers (reviewed by ANDERS *et al.*, 1973). No change in the components produced in pyrolysis of Y-74662 before and after solvent extraction showed that those components were yielded by thermal degradation of unextractable major carbonaceous matter. It was difficult to detect extractable organic monomers from the sample amount used for pyrolysis, because concentration of each monomer is known to be very low (PERING and PONNAMPERUMA, 1971).

Chromatograms of the components yielded in pyrolysis at 740°C of Y-791198, Y-74662, Y-793321, Y-791717, B-7904, and ALH-77307 are shown in Fig. 1. The major products shown in Fig. 1 were identified by the comparison of the mass spectrum

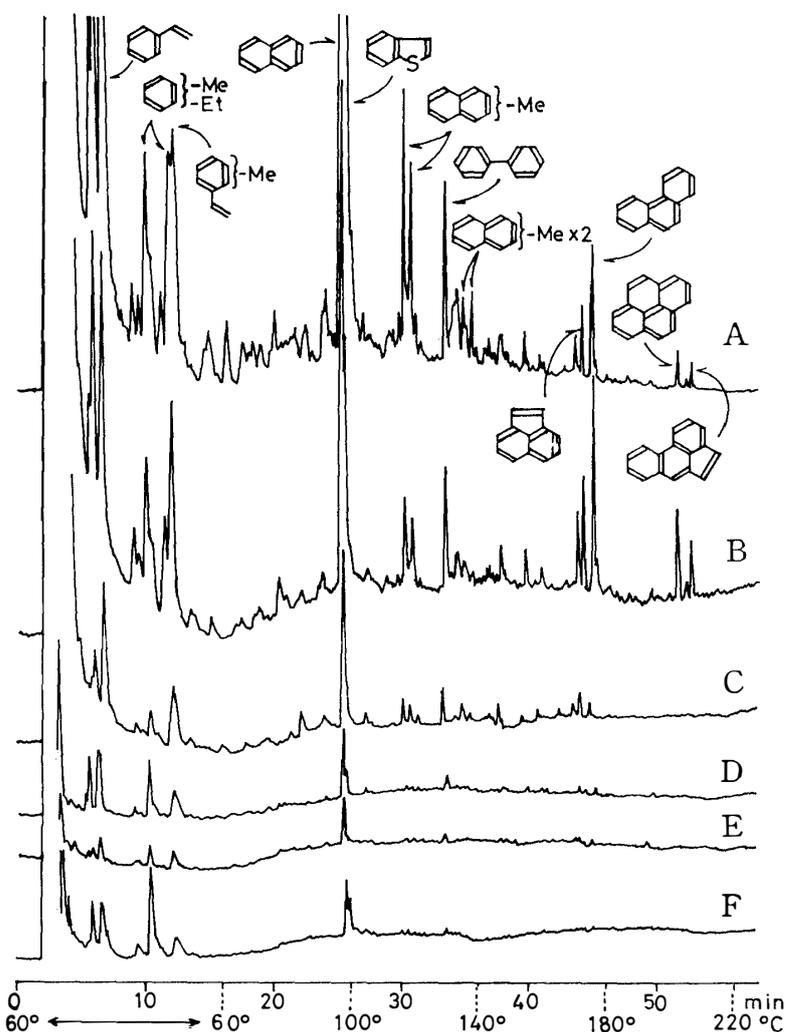


Fig. 1. Gas chromatograms of the products yielded in pyrolysis at 740°C for 3 s using Curie point pyrolyser for A: Y-791198 (5 mg), B: Y-74662 (3 mg), C: ALH-77307 (15 mg), D: B-7904 (15 mg), E: Y-791717 (16 mg), and F: Y-793321 (15 mg). Column: OV-101, 25 m × 0.25 mm i.d. Detector: FID, Attenuation: 1 for all chromatograms. Range: 16 for A, B, D, and F, and 8 for C and E.

and the retention time in gas chromatography with those of the authentic samples (tentative identification for acephenanthylene). A number of types of compounds are analyzable (ex. hydrocarbons, organic halides, organic sulfides, ethers, esters, ketones, alcohols, phenols, nitriles, amines) under the gas chromatographic conditions. Nevertheless, all of the major pyrolyzates are aromatic hydrocarbons (except benzothiophene). The intensities of the peaks of the pyrolyzates are low in the chromatograms of ALH-77307, B-7904, Y-791717, and Y-793321 (C, D, E, and F in Fig. 1), but the same compounds are detected as the major products in the chromatograms of all samples. It has been shown by many examples that chromatographic patterns of pyrolysis products clearly reflect the structure of the organic polymer originally present (OKUMOTO and TAKEUCHI, 1972; TAKEUCHI and TSUGE, 1977; GLAJCH *et al.*, 1979). The similarity in the chromatographic patterns (components and their relative in-

tensities) of the pyrolysis products suggests the presence of the similar partial structure in the carbonaceous matter of these chondrites. The components indicate that the partial structure does not contain hetero atoms (oxygen, nitrogen, etc.) except sulfur. Although highly nonvolatile compounds such as free carboxylic acids or amino acids cannot be detected under the analysis condition, the functional groups which yield such compounds are probably not present in the partial structure, because the oxygen- or nitrogen-containing compounds were not found in the pyrolysis products. The carbon contents of these chondrites (Table 1: determined by combustion method using a CHN analyzer) did not agree with the amounts of pyrolysis products. Those differences are attributed to the differences of the number of the partial structures in the carbonaceous matter in the meteorites.

Table 1. The carbon content and the ratio of the amount of naphthalene observed in pyrolysis to the amount of carbon contained in the sample used for the pyrolysis.

Chondrite	Class	Carbon (%)	Ratio (%)
Y-74662	C2	1.89	0.11
Y-791198	C2	2.17	0.1**
Y-793321	C2	1.77	0.003
B-7904	C2	0.96	0.014
ALH-77307	C3	0.74	0.014
ALH-77307	*	1.17	
Y-791717	C3	0.12	0.02**
Y-791717	*	0.22	

\* Treated with hydrochloric acid.

\*\* Roughly estimated and not calibrated.

The similarity of the partial structure and the different number of the partial structures are explained by the whole structure which has been proposed by the authors for major carbonaceous matter in carbonaceous chondrites (MURAE *et al.*, 1984b). The proposed structure is characterized by a large network of polyaromatic compounds similar to that of graphite layer. This structure bears edge defects as shown by UBBELOHDE (1957) and then ZIMMER and WHITE (1976) (Fig. 2). The pyrolysis products are considered to be produced mainly by degradation of the edge defects which are constructed with thermally weaker bonds compared with those in the condensed aromatic network (OTANI and SANADA, 1980). Similarity among the chromatographic patterns of the pyrolysis products suggests that the structure of edge defects is the same for all carbonaceous chondrites investigated in this work. Difference of the chromatographic intensity of the pyrolysis products among the chondrites shows that the number of edge defects is different for the carbonaceous matter in each chondrites.

As shown in Fig. 1 naphthalene gives the most intense peak except very volatile components. The ratios of naphthalene yielded in pyrolysis to the amounts of carbon contained in the chondrites are shown in Table 1. The ratios are considered to reflect the number of edge defects in the carbonaceous matter. The ratio did not accord with the chemical and petrographical classification. This fact suggests that the process of the formation of the carbonaceous matter may be independent of that of the parent body.

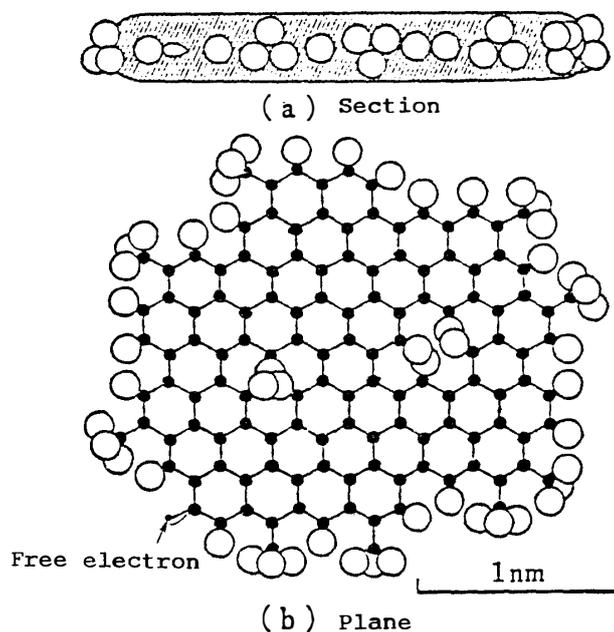


Fig. 2. Molecular model shown by ZIMMER and WHITE (1976) for the molecule constructing carbonaceous mesophase.

Mineral dissolution by treatments with hydrochloric and hydrofluoric acids has been carried out to recover solvent-unextractable carbonaceous matter in carbonaceous chondrites (ex. BAUMAN *et al.*, 1973; WHITTAKER *et al.*, 1980; HAYATSU *et al.*, 1980; SMITH and BUSECK, 1981). Some changes in the structure of the carbonaceous matter may have been caused by the acid treatment. Since the edge defects in the proposed structure are reactive positions, in the treatment with hydrochloric acid halogenation and/or oxidation reactions may occur at such positions. When the minerals in the meteorites were dissolved with hydrochloric acid, the reactions may be accelerated after the formation of  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , etc. as catalysts.

Pyrolytic studies are considered to give useful information on alteration of the structure of carbonaceous matter by mineral dissolution of carbonaceous chondrite. Figure 3 shows pyrograms at  $740^\circ\text{C}$  for the samples of Y-791717 and ALH-77307 before and after treatment with hydrochloric acid. The carbon content of the residues after the hydrochloric acid treatments was approximately twice that of untreated samples (Table 1). The chromatographic intensities of the components yielded in pyrolysis of the residues after the hydrochloric acid treatment are higher than those of the untreated samples on the basis of carbon contents. Two explanations are possible for the increase in chromatographic intensities of the pyrolysis products from acid-resistant residue. One is that there is an increase in the number of edge defects in the carbonaceous matter by the treatment with the acid. A second possibility is an increase of chemical species by the mineral dissolution. These chemical species might aid the formation of pyrolysis products in reactions with the radicals produced on thermal fragmentation of the carbonaceous matter.

The pyrolysis products of the acid-treated samples were examined by mass chromatography using all ions from  $m/z$  50 to  $m/z$  250 (ex. Fig. 4). A number of organic

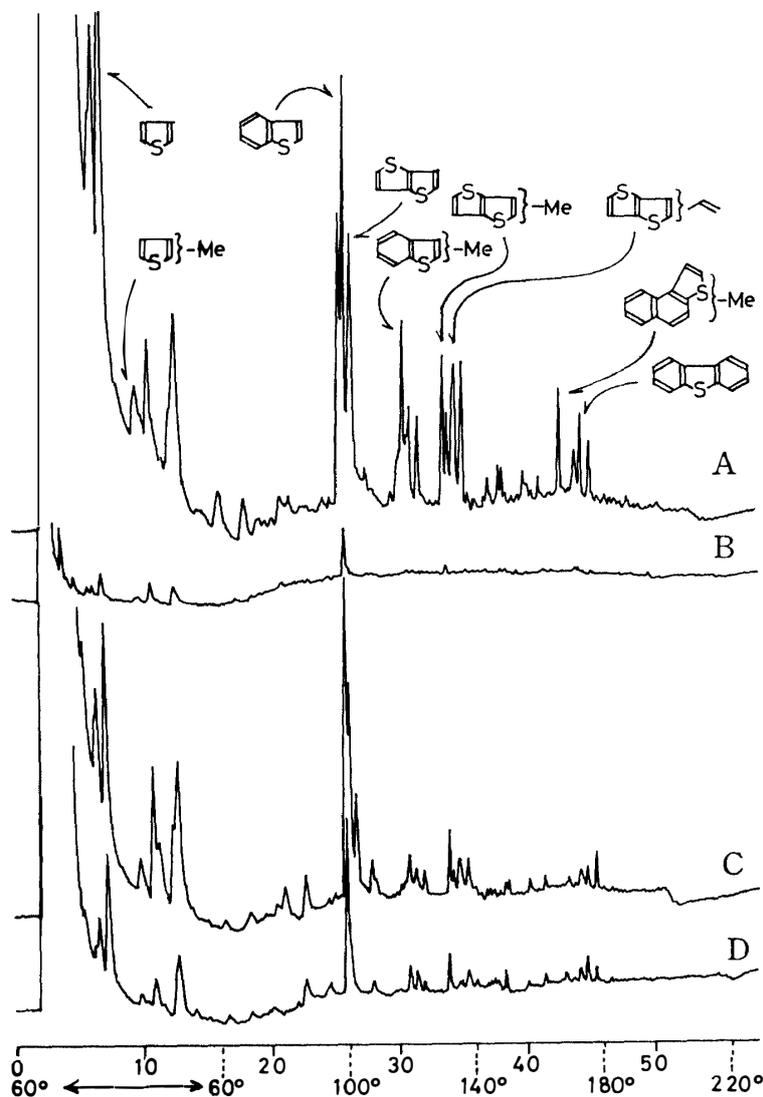


Fig. 3. Gas chromatograms of the products in pyrolysis for A: Y-791717 (9 mg) (after the acid treatment), B: Y-791717 (16 mg) (before the treatment), C: ALH-77307 (7 mg) (after the acid treatment), and D: ALH-77307 (15 mg) (before the treatment). Range: 8 for all chromatograms. Other conditions are the same as those in Fig. 1.

sulfur compounds were observed with significant intensities in the pyrolysis products (Fig. 3). These sulfides (except thiophen and benzothiophen) did not give intense peaks in the pyrograms of acid-untreated samples. This fact indicates two possibilities which may have occurred during treatment of the carbonaceous chondrite with hydrochloric acid: sulfenylation of the carbonaceous matter and an increase in the amount of reagents (or catalysts) concerned with the formation of sulfur-containing compounds during pyrolysis. There was no indication of the occurrence of chlorinated compounds. Removal of free sulfur to obtain more exact information by pyrolysis is under way.

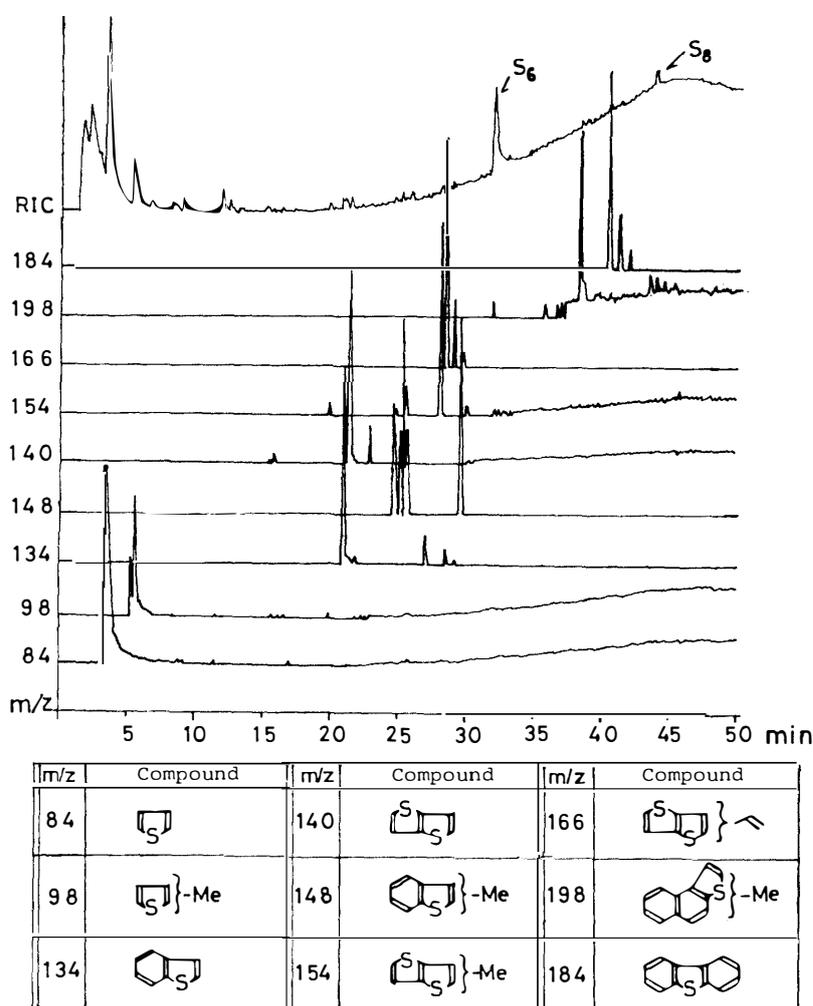


Fig. 4. Mass chromatograms of the products in pyrolysis at 740°C for the partially mineral dissolved Y-791717 (20 mg) and tentative identification of the components. Scan interval: 6 s. Ionization voltage: 70 V. Column: silicon OV-1 chemically bonded fused silica capillary (25 m × 0.25 mm i.d.). Oven temp.: 60–230°C at 4°C/min.

#### 4. Summary

Similarity of the pyrolysis products from all of the carbonaceous chondrites shows the presence of the common partial structures in the carbonaceous matter. This suggests that the carbonaceous matter in all of the chondrites was probably synthesized by similar processes. Difference of the amount of the pyrolysis products indicates the difference of the number of the partial structures (edge defects). Three explanations are possible for the difference: i) the numbers of the edge defects in the same molecule are different among the chondrites, ii) degrees of incorporation of the same structure molecules are different among the chondrites, or iii) different molecules having similar partial structures are incorporated in the same chondrite. A number of sulfur-containing compounds were found in the pyrolysis products of the acid-resistant residues. They were probably formed by trapping of the radicals yielded in the

thermal degradation of the carbonaceous matter with free sulfur which was given in the acid treatment. The pyrolytic nature of the carbonaceous matter did not accord with the chemical and petrographical classification of the chondrites. This probably suggests that the carbonaceous matter has been synthesized before the incorporation into the parent body.

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