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PYROLYTIC NATURE OF CARBONACEOUS MATTER IN CARBONACEOUS CHONDRITES AND SECONDARY METAMORPHISM

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Abstract: Major carbonaceous matter in five C2 carbonaceous chondrites (Y-791198, Y-74662, Murchison, B-7904, and Y-793321) and six C3 carbonaceous chondrites (Allende, Y-790992, Y-791717, Y-81020, ALH-77003, and ALH-77307) was investigated by pyrolysis-gas chromatography. The amount of naphthalene produced on the pyrolysis varied largely from chondrite to chondrite, and the carbonaceous matter in these chondrites could be divided into five groups by the efficiency of formation of pyrolysis products. The groups did not accord with any conventional subdivisions of carbonaceous chondrites. The grouping based on the pyrolytic nature of the major carbonaceous matter may give additional information about secondary metamorphism in carbonaceous chondrites.

1. Introduction

The carbonaceous chondrites are subdivided into CI, CM, CV and CO chondrites, primarily on the basis of bulk composition (VAN SCHMUS and HAYES, 1974; KALLEMEYN and WASSON, 1981). In VAN SCHMUS and WOOD's (1967) classification, CI are all type 1, CM are all type 2 and CV and CO are primarily type 3. It has been suggested that types 1 and 2 have been heavily altered by aqueous processes (DUFRESNE and ANDERS, 1962; BUNCH and KERRIDGE, 1979; MCSWEEN, 1979) and type 3 chondrites most closely resemble the solid material that agglomerated in primordial solar nebula. MCSWEEN (1977) subdivided C3 (O) chondrites into types I, II and III on the basis of metamorphism experienced (I being least metamorphosed). Correlation of thermoluminescence (TL) sensitivity with various metamorphism-related phenomena in the C3 (O) chondrites has been shown (KECK and SEARS, 1987), and the thermal histories of the C3 (O) chondrites have been discussed on the basis of TL data (SEARS *et al.*, 1990).

The presence of carbon in primitive extraterrestrial materials has long been considered a useful indicator of prevailing geochemical conditions early in the formation of the Solar System. Major carbonaceous matters in carbonaceous chondrites are present as solvent-unextractable high-molecular organic compounds. Analytical electron microscope studies of acid residues of the Allende C3 (V) meteorite show that carbon phases form as tangled, fibrous (graphitic) crystallites, or aggregates of crystallite, in a featureless (possibly amorphous) matrix (SMITH and BUSECK, 1981). The mean apparent interlayer spacing (d_{002}) can be related to the degree of order (degree of graphitization), or the fraction of sp^2 carbon layers in poorly graphitized carbon

(PGC). RIETMEIJER and MACKINNON (1985) have shown that the graphitization temperature, or the degree of ordering in PGC could be a useful cosmothermometer reflecting metamorphic temperature for primitive extraterrestrial materials.

Pyrolytic nature of PGC is correlated with its degree of ordering (d_{002} spacing, size and morphology). Pyrolytic study is a useful method which gives information about the average of gross ordering degree of organic or poorly graphitized carbon contained as a minor component in metamorphosed rocks without special sample treatments. A similar to PGC but more detailed molecular model which has a highly condensed polycyclic aromatic sheet bearing edge defects has been proposed for the major carbonaceous matter in carbonaceous chondrites by the present authors based on pyrolytic and spectroscopic data (MURAE *et al.*, 1987, 1990). The mean molecular (sheet) size and the number of the edge defects are different among chondrites and may reflect the formation processes of the high molecular organic matter and the history (mainly thermal history) of the meteorite. Gas chromatogram of the pyrolysis products of the organic matter suggested the presence of the edge defects (MURAE *et al.*, 1987). The organic matter containing more edge defects, which gives a larger amount of pyrolysis products, corresponds to less graphitized and less ordered carbon. In this paper we discuss possibility of classification of carbonaceous matter based on pyrolysis experiments of carbonaceous matter in the chondrites.

2. Sample Preparation and Experimental Apparatus

Sample preparation and conditions for analyses of Allende, Y-791717, and ALH-77307 were mentioned already (MURAE *et al.*, 1987). Samples of ALH-77003, Y-81020, and Y-790992 were taken from small chips delivered from the meteorite curator of the National Institute of Polar Research. After washed with hexane, the chips were powdered (grain size: 10–20 μm) and the powder was used for pyrolytic studies. Pyrolyses were carried out using a Curie point pyrolyser (Japan Analytical Industry Co., LTD: Model JHP-2) at 740°C for 3 s. The powdered sample of the meteorite was wrapped with a pyrofoil and preheated at 160°C for 40 min in the stream of carrier gas (nitrogen). During preheating the carrier gas was exhausted through a valve situated at the connector between the carrier line and the gas chromatograph capillary column.

The analyses of pyrolysis products by gas chromatography (GC) were carried out using an open tubular OV-101 wall coated fused silica capillary (25 m $\times$ 0.25 mm i. d., film thickness: 0.4 μm) for Allende, ALH-77307, and Y-791717, and 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 μm) for ALH-77003, Y-790992 and Y-81020. The rate of temperature increase was programed to be 4°C from 60 to 260°C after keeping the initial temperature for 16 min. Identification of naphthalene peak in the pyrograms was carried out by monitoring the ion at m/z 128 using a JEOL D-300 GC-MS spectrometer equipped with JMA-2000 data analyzer. The quantity of naphthalene yielded on pyrolysis was determined using a Shimadzu 7A-PF GC instrument equipped with a flame ionization detector (FID) and a System Instruments Labchart 80 integrator.

3. Results and Discussion

We analyzed five C2 and six C3 carbonaceous chondrites by pyrolysis-GC (Table 1). Except B-7904 (C2, C: 0.96%), Y-81020 (C3, C: 0.96%) and ALH-77307 (C3, C: 0.74%), the carbon content in the C2 chondrites (more than 1.5%) is much higher than that in the C3 chondrites (less than 0.3%) as usually observed for carbonaceous chondrites. Carbon concentration exhibits a negative correlation with metamorphic grade in ordinary chondrites (MOORE and LEWIS, 1967). The carbon contents in the C3 (O) chondrites which we analyzed do not accord with the subdivision based on the metamorphic grade determined by TL sensitivity (Table 1). MCSWEEN (1977) has shown the systematic decrease of carbon contents in C3 (O) chondrites following increasing metamorphic grade.

The amount of naphthalene yielded on pyrolysis was used as an indicator of productivity of the pyrolytic components, because accumulation of the total amount of pyrolysis products was difficult by our system, and because the peak of naphthalene is the most distinguishable among the products. And the ratio of the amount of naphthalene produced on pyrolysis to the total carbon contained in the sample before the pyrolysis was used as the efficiency of formation of pyrolysis products (EFP: Table 1). The EFP is related with the number of edge defects in the molecule as well as the number of the molecules in the meteorite sample. The meteorite showing the higher EFP contains more molecules with more edge defects. Therefore, when the EFP is low even if the carbon concentration is high, the meteorite contains molecules with few edge defects. Although the polycyclic aromatic structure is very stable, the edge defects are unstable and affected by various environmental conditions. If

Table 1. Subdivision, carbon content, and ratio of naphthalene produced on pyrolysis to total carbon contained in the sample before pyrolysis.

Meteorites	Class[a]	Carbon content (%)	Total carbon (μg)	Produced naphthalene (ng)	Naphthalene /carbon (w/w %)	TL type[b]	EFP class[c]
Y-791198[d]	CM2	2.17	106	380	0.36		I
ALH-77003	C3 (O)	0.28	35	105	0.30	3.3	I
Y-74662[d]	CM2	1.89	95	100	0.11		II
Murchison	CM2	1.98	40	52	0.13		II
Allende	C3 (V)	0.23	35	50	0.14		II
Y-790992	C3 (O)	0.25	31	20	0.065		III
B-7904[d]	CM2	0.96	144	20	0.014		IV
ALH-77307[d]	C3 (O)	0.74	148	20	0.014	3.0	IV
Y-791717[d]	C3 (O)	0.12	17	3	0.018	3.4	IV
Y-793321[d]	CM2	1.77	266	9	0.003		V
Y-81020	C3 (O)	0.96	120	3	0.003	3.4	V

[a] Classification according to the criterion by VAN SCHUMUS and WOOD (1967).
[b] Subdivision based on thermoluminescence (TL) sensitivity (the type number increases with increasing metamorphism: SEARS *et al.*, 1990).
[c] Subdivision based on efficiency of formation of pyrolysis products (EFP: the type number increases with decreasing degree of EFP).
[d] Cited from MURAE *et al.* (1987).

the meteorite has experienced high temperature, the thermally unstable edge defects would have been cleaved off and the meteorite would show a low EFP value.

Although no correlation between the amount of the naphthalene yielded on pyrolysis and the total carbon in the sample was observed, the carbonaceous matter studied in this work could be clearly divided into five classes based on EFP values. This subdivision does not accord with the conventional chemical and petrographical classification of the chondrites (Table 1). However, a rough correlation was observed between the division and the degree of thermal metamorphism (PAUL and LIPSCHUTZ, 1989; AKAI, 1990). Although the carbon concentration of Y-793321 (CM2) is adequate for usual C2 chondrites and B-7904 (CM2) contains a considerable amount of carbon while its concentration is lower than that of usual C2 chondrites, the EFP values are much lower than those of other CM2 chondrites (Y-791198, Y-74662, and Murchison). This fact is compatible with that the two chondrites (B-7904 and Y-793321) are metamorphosed at high temperature (PAUL and LIPSCHUTZ, 1989; AKAI, 1990). The edge defects of the carbonaceous molecule are probably cleaved off at the temperature to give more thermally-stable well-ordered graphitic molecule.

Although the carbon concentration of ALH-77003 (C3 (O)) is one order of magnitude lower than that of Y-791198 (CM2) which produced pyrolysis products most efficiently in the chondrites under investigation, both chondrites showed almost the same EFP value. On the other hand, Y-81020 (C3 (O)) whose carbon content is close to that of C2 chondrites and much higher than that of ALH-77003 gave a very small amount of pyrolysis products. The EFP value of Y-81020 (C3 (O)) is two order less than that of ALH-77003 and the same as that of Y-793321 (CM2) which showed the lowest EFP value. The EFP values of ALH-77307 (C3 (O)) and Y-791717 (C3 (O)) are similar to that of B-7904 and between those of ALH-77003 and Y-81020. Allende (C3V) showed almost the same EFP value as those of Y-74662 (CM2) and Murchison (CM2), and the value is one order lower than that of ALH-77003 but one order higher than that of Y-81020. The value of EFP for Y-790992 (C3 (O)) is intermediate of those of Allende and ALH-77307.

If the organic matter in carbonaceous chondrites was formed before the incorporation into the parent body, the structure of the carbonaceous matter could have been modified before and/or after the incorporation. Based on the results of the above pyrolytic studies, we may presume the following:

1) According to the EFP values, the carbonaceous matter examined in this investigation is divided into five groups (Table 1) which probably reflect the difference of the secondary thermal metamorphism of the meteorites.

2) The CM2 chondrites, B-7904 and Y-793321, show very low EFP values. This fact indicates that these meteorites experienced high temperature. Although the maximum temperature of metamorphism estimated by T-T-T diagram for B-7904 is much higher than that for Y-793321 (AKAI, 1990), the EFP values indicate that Y-793321 may have experienced much higher temperature than that B-7904 experienced. The reason of this disagreement is unclear.

3) Although Y-81020 (C3 (O)) contains carbon (0.96%) as much as do C2 chondrites, specific pyrolysis product (such as naphthalene) was little observed. This fact suggests that Y-81020 was probably thermally altered seriously to lose most of

the edge defects of the organic matter, and the remaining organic matter in this meteorite may have been converted into nearly complete graphite.

4) Although the carbonaceous matter in ALH-77307 and Y-791717 is assigned to the same group based on EFP value, the type of these meteorites based on TL sensitivity is very different (Table 1). This is probably due to the fact that the TL sensitivity is affected not only by thermal metamorphism but aslo other alteration processes such as aqueous alteration (KECK and SEARS, 1987).

5) The carbon content of ALH-77003 is of the same level as that of usual C3 carbonaceous chondrites, and the pyrogram of ALH-77003 and that of Allende resemble each other. But the amount of the pyrolysis products from ALH-77003 is much larger than that from any other C3 chondrites and its EFP value is almost the same as that of Y-791198 whose EFP value is the highest among those of CM2 chondrites examined by the authors. This fact suggests that this meteorite did not experience the temperature higher than that Y-791198 did after the incorporation of the organic polymer. And the temperature was probably lower than those which Y-74662 (CM2), Murchison (CM2), and Allende (CV3) have experienced. The type of ALH-77003 based on TL sensitivity indicates that the degree of metamorphism of this meteorite is considerably higher than that of ALH-77307, but the EFP value of ALH-77003 is much higher than that of ALH-77307. These facts may suggest that TL sensitivity observed is affected seriously by alteration processes other than heating.

4. Summary

Carbonaceous matter in five C2 and six C3 carbonaceous chondrites was examined by pyrolysis GC and divided into five groups by the efficiency of formation of pyrolysis products (EFP). On the assumption that the organic polymer in the chondrites was formed prior to the formation of the meteorites and the initial structure of the polymer was similar in all meteorites, it is suggested that the division based on the EFP reflects the thermal history of the organic polymer in the meteorites. The division based on the EFP did not accord with the conventional subclassifications of carbonaceous chondrites based on the degree of the metamorphism observed with several methods including thermoluminescence sensitivity. We consider that the classification by EFP values is especially effective for investigations of secondary thermal metamorphism of carbonaceous chondrites.

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