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Organic Compounds from Insoluble Organic Matter Isolated from the Murchison Carbonaceous Chondrite by Heating Experiments

Masatoshi Komiya*,† and Akira Shimoyama*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

†Fuel Resources Department, Geological Survey of Japan, Tsukuba, Ibaraki 305

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Insoluble organic matter isolated by an HF/HCl treatment of the Murchison carbonaceous chondrite was heated from room temperature to 800 °C at a rate of 10 $^\circ\mathrm{C\,min^{-1}}$ under a helium atmosphere. Over 130 organic compounds were identified in its pyrolyzates, which mainly comprised the following two groups: (1) benzene and naphthalene, and their alkyl derivatives; and (2) sulfur-containing heterocycles and their alkyl derivatives. The relative amounts of compounds released with increasing temperature during the heating process were monitored by a mass spectrometer. Those hydrocarbons were observed mainly over a temperature range of 300—600 °C. These results are generally similar to those of Yamato-791198, an Antarctic carbonaceous chondrite which we had previously analyzed. The results indicate that aliphatic and aromatic hydrocarbons, as well as S-containing heterocycles, are the major constituents of the insoluble organic matter of Murchison. Furthermore, the results suggest that the thermal history of Murchison on its parent body was similar to that of Yamato-791198.

Carbonaceous chondrites contain minor amounts, but many kinds, of organic compounds which were formed during the early solar system by abiotic processes. A major portion of organic matter is present as insoluble matter with organic solvents, acids, and water, while a minor portion is present as soluble organic matter. Many experiments have been carried out to examine the insoluble organic matter, while aiming to obtain information concerning its constituents and structures.[1—5] We examined the organic compounds by gradually heating bulk samples of several Antarctic carbonaceous chondrites using a thermal analyzer connected to a gas chromatograph and/or a mass spectrometer.[6] Furthermore, we isolated insoluble organic matter from these chondrites, and examined it by a new method, which was partly modified from a previous one (Ref. 6).[7]

In the present study we applied this new method to examine insoluble organic matter recovered from the Murchison carbonaceous chondrite. Murchison is probably the most well-studied non-Antarctic carbonaceous chondrite by various solvent extractions. These studies were recently reviewed.[8] However, insoluble organic matter in the chondrites has not been sufficiently revealed because of its complex structure and various constituents. Therefore, it has now become important to reveal insoluble organic matter in Murchison. For this purpose, we attempted to identify as many organic compounds as possible from the insoluble organic matter, and to study the thermal behavior of the major compounds from this material. The constituents of the insoluble organic matter of Murchison were suggested from these results. In addition, we compared these results of Murchison with those of the Antarctic samples which were analyzed previously, and considered the degree of thermal history of Murchison on its parent body.

Experimental

The sample used was a piece of Murchison (a CM2 chondrite) weighing 71.1 g, which was kindly provided by Dr. E. Olsen (Field Museum of Natural History, Chicago). The sample preparation, analytical procedures, and instruments used in this study were the same as those which we previously used for the Antarctic samples.[7] Therefore, the procedures are only briefly described here. About 1.5 g of interior pieces of Murchison were first pulverized to fine powder, and then treated with a 1 : 1 (by vol.) mixture of 46% HF and 6 M HCl ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$) repeatedly to demineralize and concentrate the insoluble organic matter. It was then washed with carbon disulfide and methanol successively to remove any inorganic sulfur. Approximately 5 mg of the insoluble organic matter was placed in a thermal analyzer and heated under a helium flow from room temperature to 800 °C at a rate of 10 $^\circ\mathrm{C\,min^{-1}}$. The helium flow transferred the released compounds directly into a mass spectrometer (MS), and the relative amounts of the compounds were continuously observed along with the heating temperature. For identification, compounds appearing from 100 to 800 °C in a separate heating experiment were stored in a cold trap; the stored components were then introduced to a gas chromatograph (GC) combined with the MS (GC/MS). A packed GC column was used to separate any volatile compounds, and a capillary GC column was used for compounds less volatile than benzene. Compounds were primarily identified by comparisons to MS library data of the National Bureau of Standard, U.S.A. In addition, the identifications of some compounds, especially structural isomers, were confirmed by comparisons to the retention times of standard compounds on the gas chromatogram. Elemental analyses of C, H, and N were carried out before and after the heating by a conventional method using a CHN analyzer.

Results

The gas chromatogram of volatile compounds from the insoluble organic matter isolated from Murchison is shown in Fig. 1. The peaks with numbers were identified, and are listed in Table 1. These organic compounds are aliphatic hydrocarbons, aromatic hydrocarbons, and sulfur-containing compounds. Among these, benzene and thiophene are the most abundant. Other compounds are present at a level less than those of benzene and thiophene.

A gas chromatogram of compounds less volatile than benzene is shown in Fig. 2. One hundred and eighteen compounds, ranging from benzene to acenaphthene in size, were identified; their structures are given in Table 2. Among these, over one half are aromatic hydrocarbons and their alkyl derivatives. Sulfur-containing heterocycles, such as thiophene and its alkyl derivatives as well as benzothiophene and its alkyl derivatives are also abundant. Aliphatic hydrocarbons having seven or more carbon atoms were not detected. Because of the limitation to the maximum temperature (200 °C) allowed for the connector part between the GC column and the MS interface, we could not detect molecules larger than two aromatic rings and their alkyl derivatives. However, molecular ions corresponding to mass numbers of tricyclic and tetracyclic aromatics were found in the MS monitoring analysis during the continuous-heating experiments (Fig. 3). Therefore, compounds having three or more aromatic rings were present in the pyrolyzate. Many structural isomers were identified. For example, eighteen structural isomers of C_4-alkylbenzene were found. The relative amount of 2-methylthiophene to 3-methylthiophene was approximately 1.2, and that of 2-methylnaphthalene to 1-methylnaphthalene was 1.7.

Table 1. Volatile Compounds Released from the Insoluble Organic Matter Isolated from Murchison by the Treatment with HF/HCl

No.	Compounds	No.	Compounds
1	Sulfur dioxide	13	C_5-alkene
2	C_3-alkene	14	C_5-alkadiene
3	Methanethiol	15	C_5-alkene
4	C_4-alkene	16	C_6-alkene
5	C_4-alkene	17	Thiophene
6	C_4-alkene	18	Benzene
7	C_4-alkene	19	C_6-alkene
8	C_4-alkane	20	C_6-alkene
9	Ethanethiol	21	Methylthiophene
10	Carbon disulfide	22	Methylthiophene
11	C_5-alkene	23	Toluene
12	C_5-alkadiene		

The intensities of major organic compounds during continuous heating are shown in Fig. 3. Although most of the ions at m/z 58 and 72 were from C_4- and C_5-aliphatic hydrocarbons, respectively, they might contain fragment ions of larger aliphatic hydrocarbons. During the heating, hydrocarbons generally appeared at 300—400 °C, and disappeared at 600 °C with a maximum at 400—500 °C. Higher-molecular hydrocarbons were detected over relatively higher temperature ranges compared with lower ones.

The total weight loss from room temperature to 800 °C of the Murchison insoluble sample was 32.3%. The sample contained 56.9% C, 3.3% H, and 2.6% N before heating, and 72.8% C, 1.6% H, and 2.3% N after heating at 800 °C.

Discussion

Detected Compounds and Constituents of the Insoluble Organic Matter. Organic compounds in pyrolyzates from the Murchison carbonaceous chondrite have been investigated by several other workers. An organic residue re-

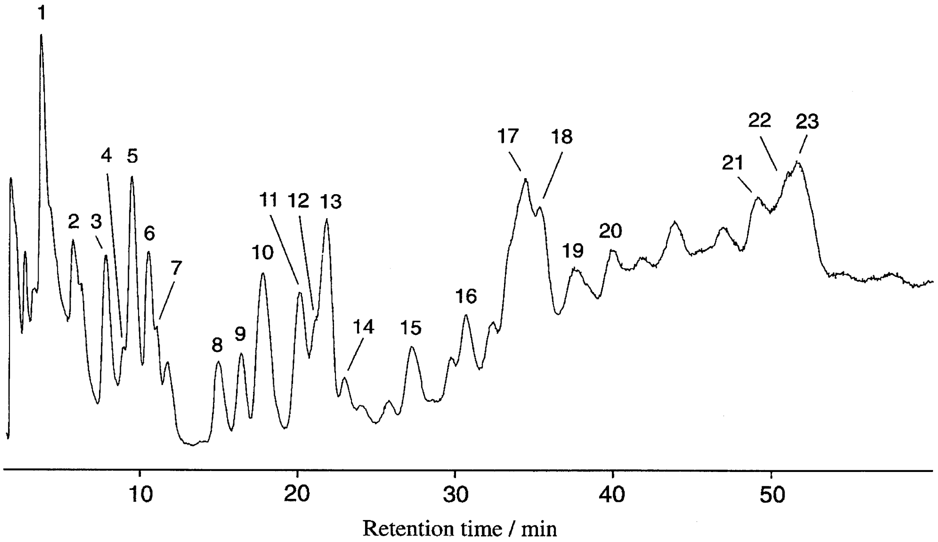

Fig. 1. Gas chromatogram of compounds released from the insoluble organic matter isolated from Murchison by the treatment with HF/HCl GC/MS: Shimadzu GCMS-QP1000A, Column: Gaskuropack-54 80/100 (2 mm×3 m), Col temp: 100—180 °C, 2 °C min^{-1}. Peak numbers correspond to those for the compounds in Table 1.

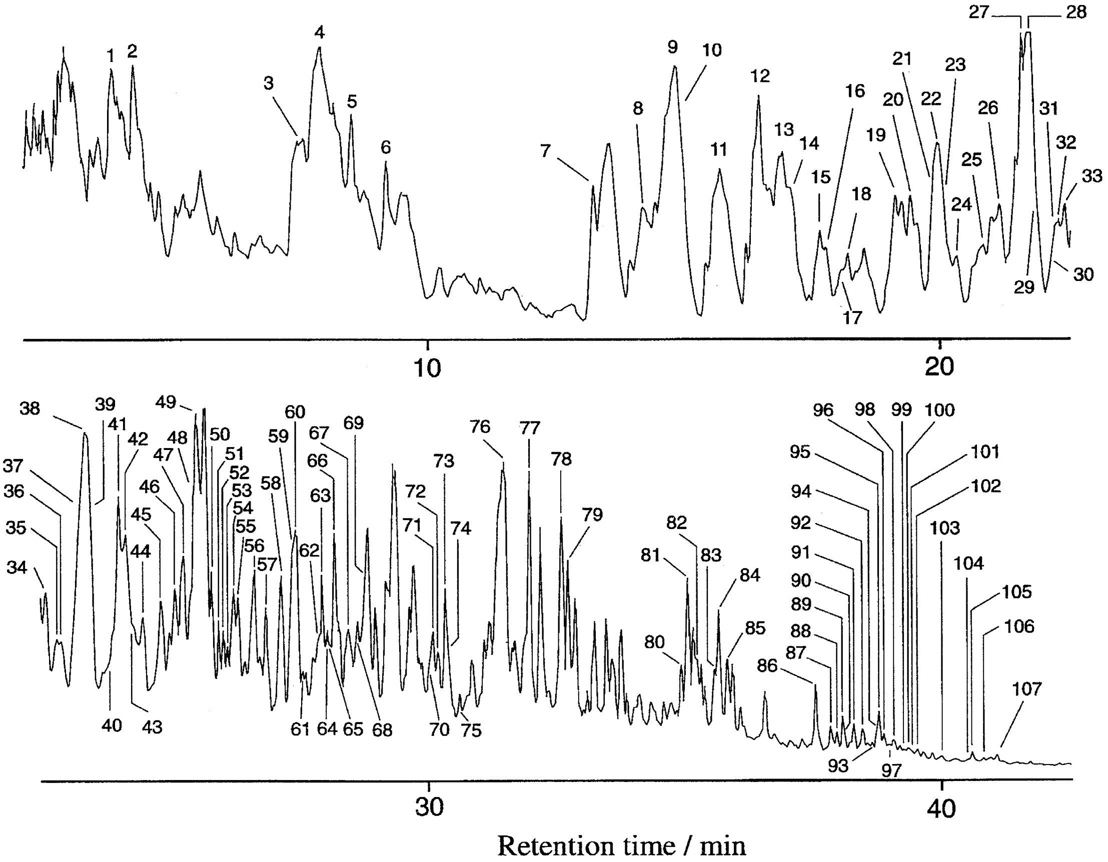

Fig. 2. Gas chromatogram of compounds released from the insoluble organic matter isolated from Murchison by the teratment with HF/HCl. GC/MS: Shimadzu GCMS-QP1000A, Column: TC-1701, FS-WCOT column (0.25 mm i.d. × 60 m), Col temp: 50 °C 10 min hold; 50—200 °C, 5 °C min^{-1}. Peak numbers correspond to those for the compounds in Table 2.

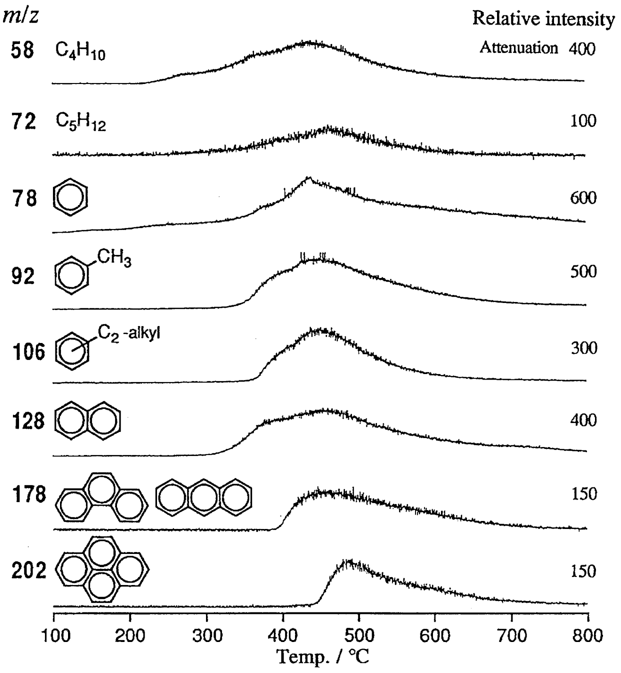

Fig. 3. Thermal release patterns of ions for compounds from the insoluble organic matter isolated from Murchison by the treatment with HF/HCl.

covered after solvent extraction of Murchison was examined by a gradual heating in the source region of an MS.[2,5] These studies found benzene, naphthalene, and their alkyl derivatives, as well as methylindan and aliphatic hydrocarbons as the major components. A bulk sample of Murchison was heated at several different temperatures, in which *n*-alkanes (C_8 to C_{13}), alkenes (C_4 to C_8), aromatic hydrocarbons (benzene and its alkyl derivatives, and naphthalene), and thiophene and its alkyl derivatives were identified.[3] In the present study, rather large amounts of aromatic compounds were detected. The number of aromatic compounds was 96 out of the total 136 compounds identified.

Many of the aromatic hydrocarbons have alkyl side chains. These side chains vary in length (C_1 to C_4) and structure (straight or branched), as well as the substituting position on the rings. These features were clearly observed with C_3- and C_4-alkylbenzenes due to the presence of many isomers (Tables 1 and 2). In addition, aliphatic hydrocarbons (C_3 to C_6), which were found remarkably in the volatile fraction, comprised many alkene isomers (Table 1). All of the possible four structural and geometrical isomers of C_4-alkenes were present. Two of the possible seven structural isomers of C_5-alkenes were identified. The detection of these alkenes suggests that breakages of those alkyl side chains attached to the aromatic rings occurred during the heating.

Table 2. Compounds Released from the Insoluble Organic Matter Isolated from Murchison by the Treatmet with HF/HCl[a)]

No.		Compounds	No.		Compounds	No.		Compounds
1	*	Benzene	36		C_4-Alkylbenzene	70		$C_{5:1}$-Alkylbenzene
2	*	Thiophene	37		C_3-Alkylthiophene	71		C_5-Alkylbenzene
3		Dimethyl disulfide	38	*	1,2,3-Trimethylbenzene	72		C_5-Alkylbenzene
4	*	Toluene	39		Benzofuran and	73		Methylphenol
5	*	2-Methylthiophene		*	Benzaldehyde	74		1-Methylene-1*H*-indene
6	*	3-Methylthiophene	40		C_4-Alkylbenzene	75		C_5-Alkylbenzene
7		Ethyl methyl disulfide	41	*	Indan	76	*	Naphthalene
8	*	Ethylbenzene	42		C_4-Alkylbenzene	77		Benzothiophene
9	*	1,3-Dimethylbenzene and	43		C_4-Alkylbenzene	78		Thienothiophene
	*	1,4-Dimethylbenzene	44		C_4-Alkylbenzene	79		Thienothiophene
10		C_2-Alkylthiophene	45		C_4-Alkylbenzene and	80		Methylbenzothiophene
11		C_2-Alkylthiophene			C_4-Alkylthiophene	81	*	2-Methylnaphthalene
12		C_2-Alkylthiophene and	46		C_4-Alkylbenzene	82		Methylbenzothiophene
	*	1,2-Dimethylbenzene	47	*	Indene	83		Methylbenzothiophene
13		Styrene	48		C_4-Alkylbenzene	84	*	1-Methylnaphthalene
14		Ethenylthiophene	49		C_4-Alkylbenzene and	85		Methylbenzothiophene
15		C_2-Alkylthiophene		*	Benzonitrile	86	*	Biphenyl
16		(1-Ethylmethyl)benzene	50		C_4-Alkylbenzene	87		C_2-Alkylbenzothiophene
17		C_3-Alkylthiophene	51		$C_{4:1}$-Alkylbenzene	88		Ethylnaphthalene
18		Ethenylthiophene	52		$C_{4:1}$-Alkylbenzene	89		Ethylnaphthalene
19		C_3-Alkylthiophene	53		C_5-Alkylbenzene	90		C_2-Alkylbenzothiophene
20	*	Propylbenzene	54		C_4-Alkylbenzene	91		Dimethylnaphthalene
21		C_3-Alkylthiophene	55		$C_{4:1}$-Alkylbenzene	92		C_2-Alkylbenzothiophene
22	*	3-Ethyltoluene and	56		$C_{4:1}$-Alkylbenzene and	93		Phenylthiophene
	*	4-Ethyltoluene			C_5-Alkylbenzene	94		C_2-Alkylbenzothiophene
23		C_3-Alkylthiophene	57		C_4-Alkylbenzene	95		Dimethylnaphthalene
24	*	1,3,5-Trimethylbenzene	58		C_4-Alkylbenzene	96		Dimethylnaphthalene
25		C_3-Alkylthiophene	59		C_4-Alkylbenzene and	97		C_2-Alkylbenzothiophene
26	*	2-Ethyltoluene			Methylbenzofuran	98		Phenylthiophene
27		C_3-Alkylthiophene and	60		Methylbenzofuran	99		C_2-Alkylbenzothiophene
		$C_{3:1}$-Alkylbenzene	61		C_5-Alkylbenzene	100		C_2-Alkylbenzotbiophene
28	*	1,2,4-Trimethylbenzene	62		C_5-Alkylbenzene	101		Dimethylnaphthalene
29		$C_{3:1}$-Alkylbenzene	63		C_5-Alkylbenzene	102		Dimethylnaphthalene
30		C_4-Alkylbenzene	64		Methylbenzofufan	103		Dimethylnaphthalene
31		C_4-Alkylbenzene	65		C_5-Alkylbenzene	104		Methylbiphenyl
32		$C_{3:1}$-Alkylbenzene	66		C_5-Alkylbenzene	105		Acenaphthylene
33		$C_{3:1}$-Alkylbenzene	67		C_5-Alkylbenzene	106		Methylbiphenyl
34		C_3-Alkylthiophene and	68		C_5-Alkylbenzene and	107		Acenaphthene
		$C_{3:1}$-Alkylbenzene			Phenol			
35		C_4-Alkylbenzene	69		C_4-Alkylbenzene			

a) $C_{m:n}$ where m is the sum of carbon atoms in alkyl group(s) which substituted to ring(s) and n is the number of double bonds. All the compounds were identified by comparison to MS library data (see text). Identification of compounds with asterisks (*) were further confirmed by comparison to retention time of standard compounds.

The H/C atomic ratio also indicates aromatic compounds as being major constituents. If insoluble organic matter comprised only aliphatic hydrocarbons, its H/C ratio would be close to 2.0. The H/C atomic ratio in the insoluble organic matter was 0.70, which is close to that of phenanthrene (0.71). In addition, the N content was very small. Only one compound with N (benzonitrile) was found in the pyrolyzate. Likewise, seven O-bearing compounds were detected. Judging from these results, the insoluble organic matter contained small numbers of N and O in its structure.

Some compounds detected in this experiment were directly derived from the insoluble organic matter by the breakage of bonds between components of the insoluble organic matter, while others were derived from reactions among chemical species released from the insoluble organic matter during the heating. Though it is difficult to know which compounds were constituents of the insoluble organic matter, the following speculations can be made. Sulfur-containing heterocycles and their derivatives, which were found as major components, seem to have been formed during the heating experiment, due to the presence of inorganic sulfur, which could not be completely removed in the isolation process of the insoluble organic matter. However, some of these compounds might have existed as constituents of the insoluble organic matter. An analysis of extractable aromatic compounds from Murchison showed the presence of dibenzothiophene and benzonaphthothiophene.[9)]

Thermal Release Patterns of Compounds. The temperature profiles of organic compounds released from the insoluble organic matter from Murchison in this experiment are consistent with a previous study which examined a Murchison sample by stepwise heating.[3,4] Also, the temperature profiles in this experiment resemble those of Yamato-791198 and Yamato-74662, which we previously examined by the same method.[7]

We analyzed kerogen isolated from Shinjo sedimentary rocks by the same method[10] as the present one. The kerogen released organic compounds within a narrow temperature range of 400—500 °C, whereas the insoluble organic matter from Murchison released organic compounds within a rather broad temperature range of 300—600 °C. These results suggest that the constituents and structures of the insoluble organic matter from Murchison differ partly from those of the terrestrial kerogen.

Kerogen comprises insoluble macromolecular organic matter, and is considered to have been formed by condensation-polymerization of monomeric organic compounds, such as amino acids and sugars of biological origin. Biologically common amino acids are twenty-protein types, all of which are in the α-form and the L-enantiomer. The number of amino acids which have been found in carbonaceous chondrites now exceeds 70.[11] They contain protein and non-protein ones, and are racemic. Therefore, the insoluble organic matter in carbonaceous chondrites appears to have more varieties as constituents compared with terrestrial kerogen. These constituents are linked by various chemical bonds, some of which can be easily cleaved at relatively low temperature; others are resistant at relatively high temperature. If so, the insoluble organic matter in carbonaceous chondrites releases organic compounds over a relatively broad temperature range by heating, compared with the case of terrestrial kerogen.

Thermal History of Murchison Carbonaceous Chondrite. Pulverized samples of Murchison were extracted with an organic solvent and analyzed for aromatic compounds.[9,12,13] Among the compounds detected, naphthalene was the smallest in molecular weight and fluoranthene and pyrene were the largest.[12] At least 9 alkylnaphthalenes were identified, whereas 10 alkylnaphthalenes were identified in the pyrolyzate of the present study. The compounds detected from naphthalene to acenaphthene in the solvent extracts were similar to those in the pyrolyzate of insoluble organic matter, except for S-containing compounds. This similarity also suggests a possibility that those solvent-extractable aromatic compounds might have been released from insoluble organic matter by a thermal event on the parent body.

Bunch and Chang estimated a maximum temperature of less than 400 K for a heating event which had taken place on the parent body of Murchison by a petrographic study.[14] In the same study, they also suggested the possibility of a temperature of 300 K for the event, based on the presence of malonic acid, reported by another study,[15] since the acid seems to decompose rapidly on a geological time scale at 300 K. Later, an oxygen isotopic study on Murchison suggested that the heating event occurred at a temperature of 20 °C or less.[16] Similarly, it has been reported that Yamato-791198 experienced a mild thermal history by a petrographic study.[17]

The H/C atomic ratio of insoluble organic matter recovered from Murchison was 0.70, which is close to that of Yamato-791198 (0.67). The insoluble organic matter from Yamato-791198 released a rather large amount of organic compounds by the heating experiment compared to other samples having low H/C ratios (0.11—0.36).[7] Therefore, the insoluble organic matter having a relatively high H/C ratio seems to contain a thermally labile organic fraction, whereas one having a low H/C ratio contains less, or a small amount, of such a fraction. Our previous results indicate that among Antarctic CM2 chondrites, those which experienced a slight, or mild, thermal effect on their parent bodies contain insoluble organic matter with a relatively high H/C ratio. Therefore, it is also indicated from the H/C ratio that the thermal effect was, at most, mild on the Murchison parent body.

The similarities in the organic compounds detected in the pyrolyzates, their temperature profiles and the H/C atomic ratios indicate that the constituents and the structure of insoluble organic matter of Murchison and Yamato-791198 seem to be similar to each other. The similarity in the characteristics between the insoluble organic matter from these two carbonaceous chondrites also supports a mild thermal history of Murchison and Yamato-791198 on their parent bodies, which did not decompose a thermally labile organic fraction of the insoluble organic matter.

References

1) R. Hayatsu, R. E. Winans, R. G. Scott, R. L. McBeth, L. P. Moore, and M. H. Studier, *Science*, **207**, 1202 (1980); G. Holzer and J. Oró, *J. Mol. Evol.*, **13**, 265 (1979); J. R. Cronin, S. Pizzarello, and J. S. Frye, *Geochim. Cosmochim. Acta*, **51**, 299 (1987).

2) M. H. Studier, R. Hayatsu, and E. Anders, *Geochim. Cosmochim. Acta*, **36**, 189 (1972).

3) R. L. Levy, M. A. Grayson, and C. J. Wolf, *Geochim. Cosmochim. Acta*, **37**, 467 (1973).

4) E. L. Bandurski and B. Nagy, *Geochim. Cosmochim. Acta*, **40**, 1397 (1976).

5) R. Hayatsu, S. Matsuoka, R. G. Scott, M. H. Studier, and E. Anders, *Geochim. Cosmochim. Acta*, **41**, 1325 (1977).

6) A. Shimoyama, M. Komiya, and K. Harada, *Proc. Natl. Inst. Polar Res. Symp. Antarct. Meteorites*, **4**, 247 (1991).

7) M. Komiya, A. Shimoyama, and K. Harada, *Geochim. Cosmochim. Acta*, **57**, 907 (1993).

8) J. R. Cronin and S. Chang, "The Chemistry of Life's Origins," Kluwer Acad. Publ., Netherlands (1993), p. 209.

9) B. P. Basile, B. S. Middleditch, and J. Oró, *Org. Geochem.*, **5**, 211 (1984).

10) M. Komiya, A. Shimoyama, and K. Harada, *Res. Org. Geochem.*, **7**, 59 (1990).

11) J. R. Cronin and S. Pizzarello, *Geochim. Cosmochim. Acta*, **50**, 2419 (1986).

12) K. Pering and C. Ponnamperuma, *Science*, **173**, 237 (1971).

13) J. Oró, J. Gilbert, H. Lichtenstein, S. Wikström, and D. A. Flory, *Nature*, **230**, 105 (1971).

14) T. E. Bunch and S. Chang, *Geochim. Cosmochim. Acta*, **44**, 1543 (1980).

15) J. G. Lawless, B. Zeitman, W. E. Pereira, R. E. Summons, and A. M. Duffield, *Nature*, **251**, 40 (1974).

16) R. N. Clayton and T. K. Mayeda, *Earth Planet. Sci. Lett.*, **67**, 151 (1984).

17) H. Kojima, Y. Ikeda, and K. Yanai, *Mem. Natl. Inst. Polar Res. Spec. Issue*, **35**, 184 (1984).