

## RELEASE OF ORGANIC COMPOUNDS FROM SOME ANTARCTIC CI AND CM CHONDRITES BY LABORATORY HEATING

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**Abstract:** Thermal release of organic compounds from three CI chondrites (Belgica(B)-7904, Yamato(Y)-82162, and Y-86720) and three CM chondrites (Y-74662, Y-791198, and Y-793321) was examined by DTA/TG-MS analysis. For identification of the compounds released, Y-791198 was also examined by DTA/TG-GC/MS analysis. The relative amounts of organic compounds released from these chondrites are,

$Y-74662 \approx Y-791198 > Y-82162 > Y-793321 \approx B-7094 > Y-86720$

The compounds released are aliphatic and aromatic hydrocarbons and N-, S-, and O-containing compounds. Of these, benzene and thiophene are the most abundant. Release patterns of some representative compounds were obtained along a programmed temperature profile from room temperature to 800°C. These patterns fall under one of two kinds; in one the release starts around 250°C and continues to 700°C, and in the other release starts at 100°C or 150°C and ends at 300°C. The kinds and amounts of the organic compounds released are roughly related to the extent of the alteration and/or metamorphism of the chondrites as determined by mineralogical and petrographic studies.

### 1. Introduction

Carbon contents of 2 to 3 percent are common for CI and CM chondrites and in some CI chondrites the amount may exceed 4 percent (KERRIDGE, 1985). Most of the carbon in these chondrites exists as organic compounds which are known to be abiotic in origin and provide useful information on primordial organic chemistry in the early solar system. Recent studies have revealed that most of the Antarctic CI and CM chondrites experienced either or both aqueous alteration and thermal metamorphism (TOMEOKA *et al.*, 1989a, b). These events more or less affected the kinds and amounts of organic compounds in the chondrites and, therefore, the interpretation of their origin and subsequent history has become complicated.

According to their chemical properties, organic compounds in the chondrites are of two types: (1) compounds extractable with various organic solvents, water, and acid solutions, and (2) insoluble organic matter or macromolecular compounds which cannot be extracted with any solvents or solutions. Studies on these extractable and insoluble organic compounds in carbonaceous chondrites were reviewed and the origins of these compounds were discussed recently (SHIMOYAMA, 1987; CRONIN *et al.*, 1988).

Analyses of the organic compounds extracted or isolated from the chondrites

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reveal their identities and abundances fairly precisely, but these analyses require relatively large amounts of the chondrites as well as rather long and difficult analytical processes, even for a single class of compounds.

The analysis by pyrolysis of a bulk chondrite requires only a rather small amount of the sample and simple processes, especially when a pyrolyzer is combined with a gas chromatograph and a mass spectrometer (GC/MS). The information obtained by this method is of a rather different kind, *i. e.*, the compounds detected are volatile and not necessarily the same ones that preexisted in the chondrite, but rather may be products converted or degraded from organic matter, particularly the insoluble organic matter, originally present in the chondrites.

For the above reasons, we developed a modification of the ordinary pyrolysis experiment by connecting a combined differential thermal analyzer and thermogravimetric analyzer (DTA/TG) to a MS or a GC/MS. This analytical system (DTA/TG-MS or DTA/TG-GC/MS) makes it possible, in a continuous manner, to release compounds from a sample during temperature-programmed heating in a DTA/TG and almost simultaneously to transfer them into a MS or a GC/MS where detection of the compounds is performed.

The results thus obtained reveal the kinds and relative amounts of organic compounds released thermally, and their release patterns with temperature could provide useful information in characterizing the organic compounds in relation to the alteration and/or metamorphism experienced by the chondrites. Thus, we used this method in the present study, and examined six Antarctic carbonaceous chondrites of the two groups, CI and CM, in order to see whether the organic compounds of either the individual chondrites or the two chondrite classes show characteristic features.

## 2. Samples

The chondrite samples we examined are Belgica-7904,2 (4.7 g), Yamato-82162,90 (269 mg), and Yamato-86720,87 (207 mg) of the CI group and Yamato-74662,52 (1.7 g), Yamato-791198,60 (1.8 g), and Yamato-793321,4 (3.5 g) of the CM group (hence, Y stands for Yamato and B for Belgica). The B-7904 chondrite is classified as CM (YANAI and KOJIMA, 1987) and Y-86720 also as CM (TOMEOKA *et al.*, 1989b). On the other hand, the oxygen isotopic studies (MAYEDA *et al.*, 1987; MAYEDA and CLAYTON, 1990) classify B-7904, Y-82162, and Y-86720 as CI chondrites. In this study, we regard these three chondrites as CI, according to the consortium study on Antarctic Carbonaceous Chondrites with CI Affinities with which this study is involved.

The chondrite samples were supplied to us in individual Teflon bags by the National Institute of Polar Research. The samples were taken out of the Teflon bags in our clean room, where they were pulverized individually. Portions of each powdered chondrite sample have been used already for our previous analyses of organic compounds (SHIMOYAMA and HARADA, 1984; NARAOKA *et al.*, 1988; SHIMOYAMA *et al.*, 1989), and carbon and nitrogen contents (SHIMOYAMA *et al.*, 1987).

### 3. Experimental

We used the analytical systems of DTA/TG-MS and -GC/MS as described in our previous study of sedimentary kerogen samples (KOMIYA *et al.*, 1990). Therefore, we describe the system and analyses only briefly. A known amount of each powder sample (*ca.* 40 to 50 mg) was placed in a platinum cell in the DTA/TG. The system was evacuated and then He gas was allowed to flow to the MS or the GC/MS through the sample cell at the rate of 50 ml/min. The sample heating in the DTA/TG was carried out from room temperature to 800°C at the rate of 10°C/min. The He flow transferred compounds released thermally from the sample to a cold trap and then to the MS.

For DTA/TG-MS experiments, the cold trap was cooled to the temperature of liquid nitrogen for 3 min (corresponding to the temperature increase of 30°C) and then heated at 280°C for the subsequent 2 min to release compounds. The cooling and heating of the trap was cycled continuously during the heating experiment from 50°C to 800°C. For DTA/TG-GC/MS experiments, the cold trap was cooled to collect compounds released thermally from the sample over the range of 100°C to 800°C. As soon as the trapping process was over, the trap was heated at 280°C to transfer the compounds into the GC/MS.

The cold trap was a stainless tube (18 cm×3 mm) packed with diatomaceous earth (C-22 SK DMCS) which had been preheated to remove contaminants before the analyses. The GC was equipped with a Gaskuropack 54 column (2 m×3 mm) and the MS was scanned every 1.5 s over *m/z* 45 to 300 in the EI mode.

### 4. Results and Discussion

#### 4.1. DTA/TG analyses

The DTA and TG curves of the six chondrites are shown in Fig. 1. All of the DTA curves show the baseline drift to the endothermic side, which is known to be an inevitable consequence of the gas flow at the sample cell. Therefore, the curves are generally not good enough to show clear endothermic and/or exothermic peaks, and any comparison of the curves is not valid except for two peaks.

The curves of Y-74662, Y-791198, and Y-82162 show very broad exothermic peaks over the temperature range of about 200°C to 400°C, which are due partly to the degradation of insoluble organic matter. Y-86720 also shows this peak in spite of its low carbon content. On the other hand, the two curves of Y-793321 and B-7904 do not show this broad peak, suggesting less abundance of the insoluble organic matter. It should be mentioned here that a graphite sample did not degrade in our heating experiment to 800°C under a He atmosphere. Therefore, the broad peak is not due to graphite, nor does the absence of the peak eliminate the presence of graphite in Y-793321 and B-7904.

A clear exothermic peak appears around 700°C in the three CM chondrites, while this peak is absent from the three CI chondrites. Assignment of the peak cannot be made except that it is likely due to a change in inorganic rather than organic matter. It is known that magnetite had an exothermic peak around 600°C to 700°C, while

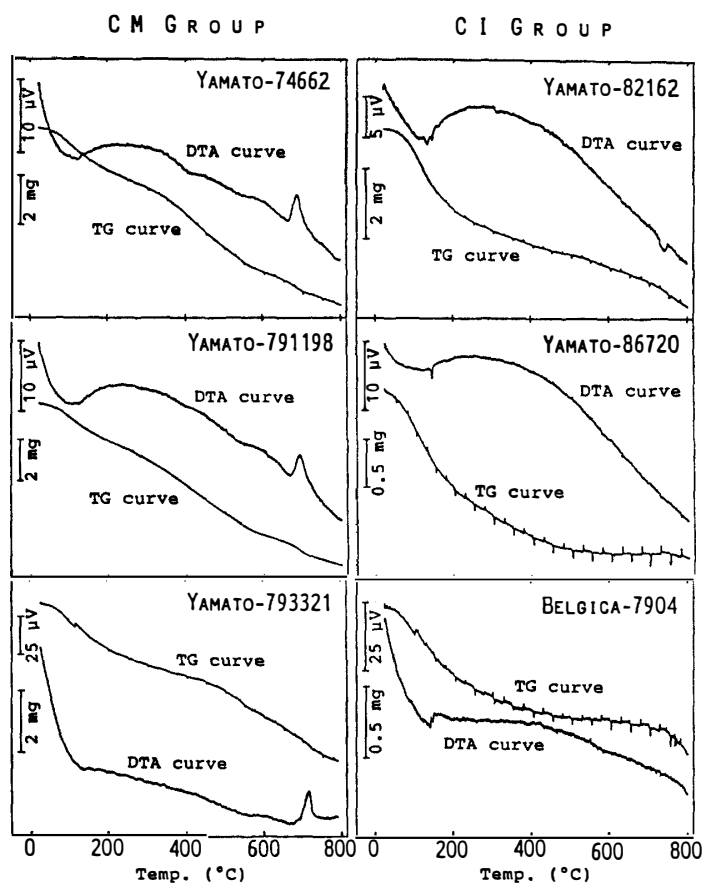


Fig. 1. DTA and TG curves of the Antarctic CM and CI chondrites.

Table 1. Carbonaceous chondrites examined in the heating experiment to 800°C.

Chondrite	Sample wt		Carbon (%) in heating		
	used (mg)	reduced (%) (r)	before (b)	after (a)	remained a/b (100-r)
Y-74662,52	51.6	13.8	1.94*	0.70	31
Y-791198,60	43.5	15.7	2.30*	1.04	38
Y-793321,4	42.4	12.1	1.66*	F	—
B-7904,2	39.7	3.8**	1.13*	0.33**	28**
Y-82162,90	50.9	9.8	2.36	1.37	52
Y-86720,87	47.9	3.7	0.67	0.46	66

\* Data from SHIMOYAMA *et al.* (1987).

\*\* Data obtained by heating to 1000°C.

F: failed to measure.

calcite and dolomite do not show an endothermic or exothermic peak below 800°C. Terrestrial phyllosilicates have an exothermic peak above 900°C. We do not know the thermal behavior of PCP (Partly Characterized Phases by TOMEOKA *et al.*, 1989c) found in CM Chondrites.

The weight losses of the samples obtained by the TG analyses are listed in Table

1. There is no clear indication in weight loss to differentiate the CI chondrites from the CM, although the weight losses of the two CI chondrites, B-7904 and Y-86720 are much smaller than the other four chondrites. The carbon contents of these two chondrites are smaller than those of the four, supporting the results of the TG analyses that the amounts of volatiles are also smaller in these two chondrites.

Table 1 also lists the carbon contents of the samples before and after the heating experiment. The contents after the heating indicate that one-third (*i. e.*, Y-86720) to two-thirds (*i. e.*, Y-74662 and Y-791198) of the initial carbon was lost during the heating to 800°C under the He atmosphere. The carbon lost is largely of organic matter, and the carbon remaining is probably graphite (or graphitic carbon) and a small amount of inorganic compounds.

The TG curves of the three CM chondrites are different from those of the three CI chondrites. The former curves show a rather gradual decrease of the sample weight from room temperature to 800°C, while the latter curves show a relatively rapid decrease up to a temperature of about 400°C. This rapid decrease reflects largely the loss of inorganic matter based on the amount lost, although a portion of the decrease may be due to organic loss.

#### 4.2. DTA/TG-GC/MS analyses

We examined the Y-791198 sample by DTA/TG-GC/MS because we knew that this chondrite contains meteoritic organic compounds, such as amino acids (SHIMO-

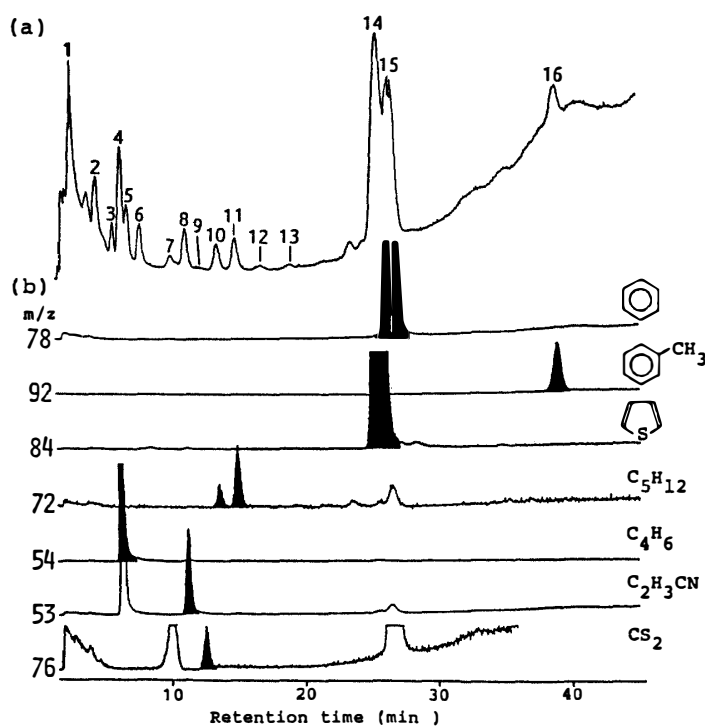


Fig. 2. Total ion chromatogram (a) and mass chromatograms (b) of compounds released from Y-791198 by DTA/TG-GC/MS analysis. Peaks with shadow correspond to the compounds shown at the end of the mass chromatograms. Peak numbers and their compounds names are the same ones listed in Table 2.

Table 2. Organic compounds from Y-791198 during the heating experiment by DTA/TG-GC/MS.

No.	Compounds	No.	Compounds
1	Sulfur dioxide	9	Carbon disulfide
2	Sulfur (S <sub>2</sub> )	10	i-Pentane
3	i-Butane	11	n-Pentane
4	Butadiene	12	Pentene
5	n-Butane	13	Butenenitrile
6	Acetonitrile	14	Thiophene
7	Furan	15	Benzene
8	Propenenitrile	16	Toluene

Nos. correspond to those peak nos. in Fig. 2.

YAMA *et al.*, 1985), carboxylic acids (SHIMOYAMA *et al.*, 1986), and hydrocarbons (NARAOKA *et al.*, 1988).

Figure 2 shows the total ion chromatogram of the compounds released from Y-791198. Because of the instrumental connections, we had to use a packed column in the GC which did not separate several compounds as single peaks. Nevertheless, the use of the mass chromatograms made it possible to recognize individual compounds within overlapping peaks.

Compounds identified are listed in Table 2. Half of these compounds are aliphatic and aromatic hydrocarbons. The others include nitrogen compounds (nitriles), an oxygen compound (furan), and sulfur compounds (carbon disulfide and thiophene). Benzene and thiophene are predominant among the compounds detected. The largest molecule detected is toluene in this analysis because of the limitation imposed by the GC column and its maximum temperature. Larger, or less volatile, compounds such as naphthalene were not eluted from the column, although the release of such compounds was found as described in the later dealing with the DTA/TG-MS analyses.

Although the results of this study cannot be compared directly to those of pyrolytic studies, the compounds found in this study are similar to those found by the pyrolytic study of an Antarctic C2 chondrite, ALH-77306, in which the major compounds were butene, benzene, thiophene, toluene, and naphthalene (HOLZER and ORO, 1979). Pyrolytic studies were also reported with several Antarctic C2 and C3 chondrites in which mainly aromatic hydrocarbons, but not benzene, and benzothiophene (MURAE *et al.*, 1984, 1987) were found. However, these studies did not detect nitrogen containing compounds, while an earlier pyrolytic study of Orgueil (CI) found nitriles in addition to aliphatic and aromatic hydrocarbons (BANDURSKI and NAGY, 1976).

Most of the compounds found are probably not present in free form in the chondrite, but appear rather as degradation products of organic matter during the heating. Those compounds with aliphatic structure may be primary degradation products and they, in turn, might be converted further to the compounds with aromatic structure during heating. For example, thiophene could be formed from H<sub>2</sub>S and butadiene which may have been released from inorganic sulfur compounds and organic matter

with alkyl structure, respectively, in the chondrite during the heating.

#### 4.3. DTA/TG-MS analyses

Figures 3 to 6 show the relative peak intensities of organic compounds released from the six chondrite samples during the heating as detected by the MS. A peak intensity of a compound at a given temperature corresponds to a relative amount of the released compound accumulated within the 30°C period starting at the indicated temperature. Some intensities in the scale 4095 are over-saturated and are shown only full scale. Although these intensities are shown at 50°C intervals and, therefore,

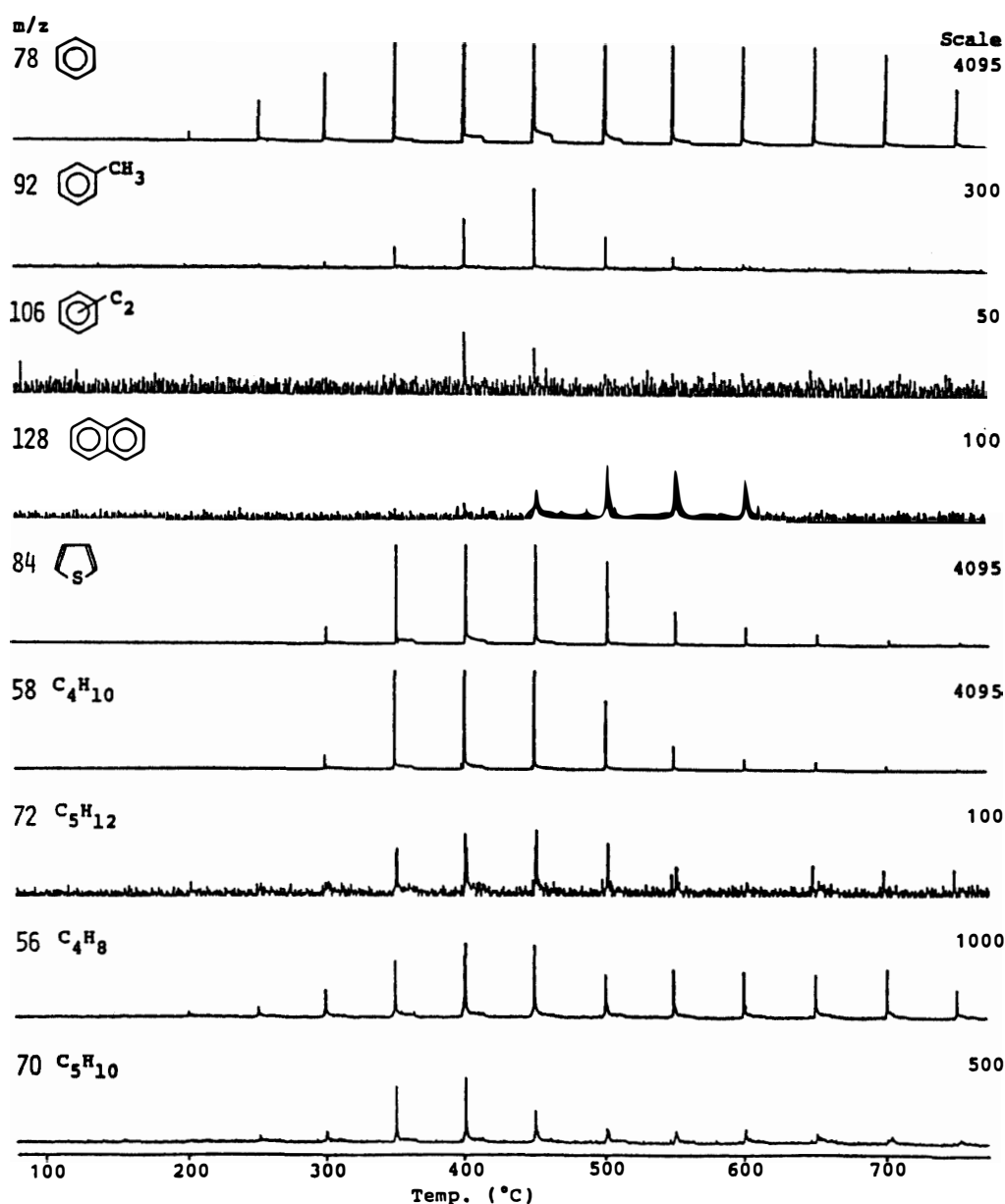


Fig. 3. Thermal release patterns of ions for compounds from Y-74662 determined by DTA/TG-MS analysis.

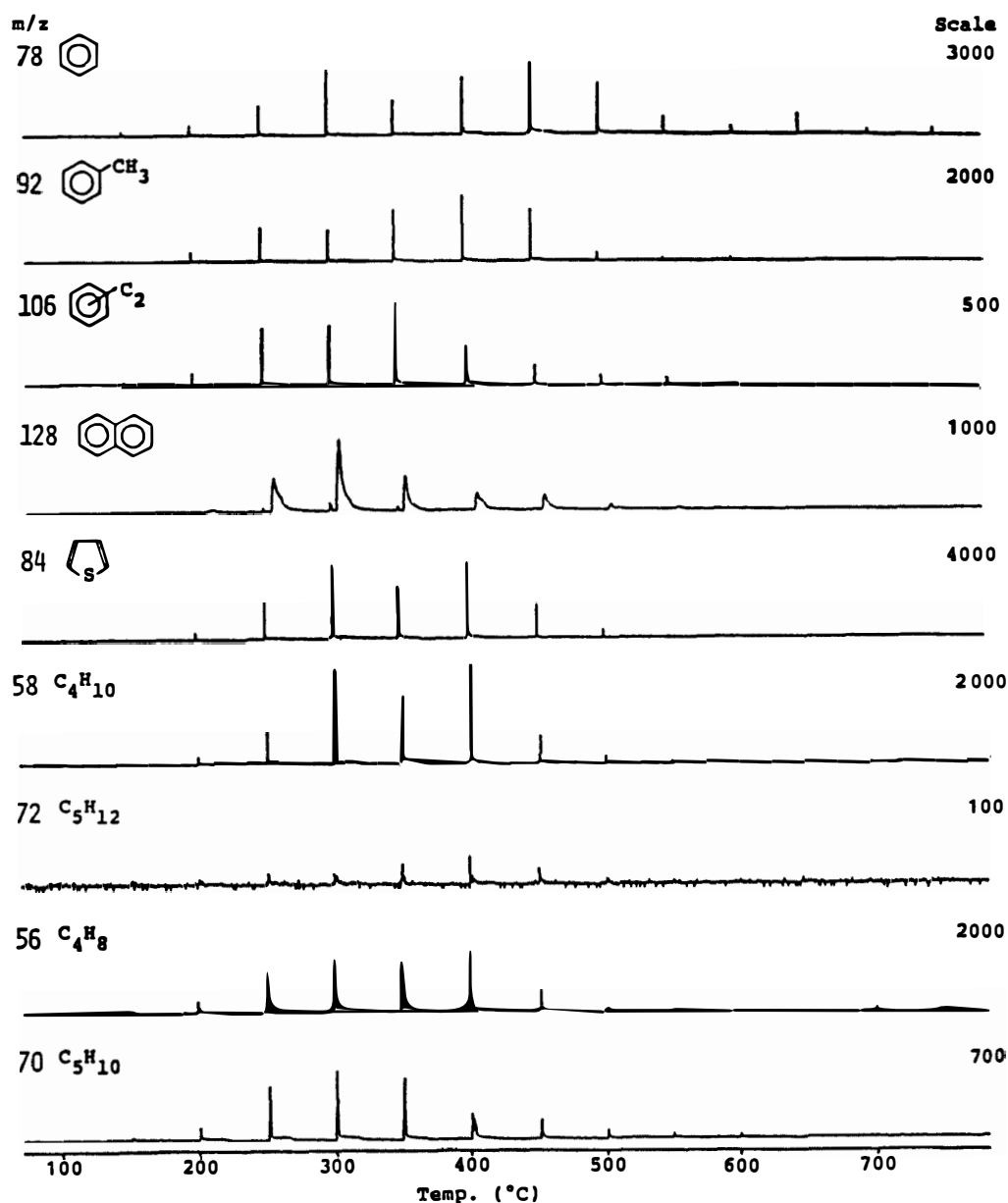


Fig. 4. Thermal release patterns of ions for compounds from Y-791198 determined by DTA/TG-MS analysis.

are shown discontinuously along the temperature scale, the compounds were continuously released and the intensities approximately represent continuous release patterns of the compounds with temperature. It should be mentioned that a comparison of the relative abundances of those compounds from a single chondrite sample is possible but any comparison among the samples is not, because of the different amounts of the samples used and the different sensitivities of the MS detection.

Those ions shown by m/z in Figs. 3 to 6 were assigned to the corresponding organic compounds shown in those figures. The m/z 78 ion was assigned to benzene because of the presence of its fragment ions at m/z 50, 51, and 52 at the same peak



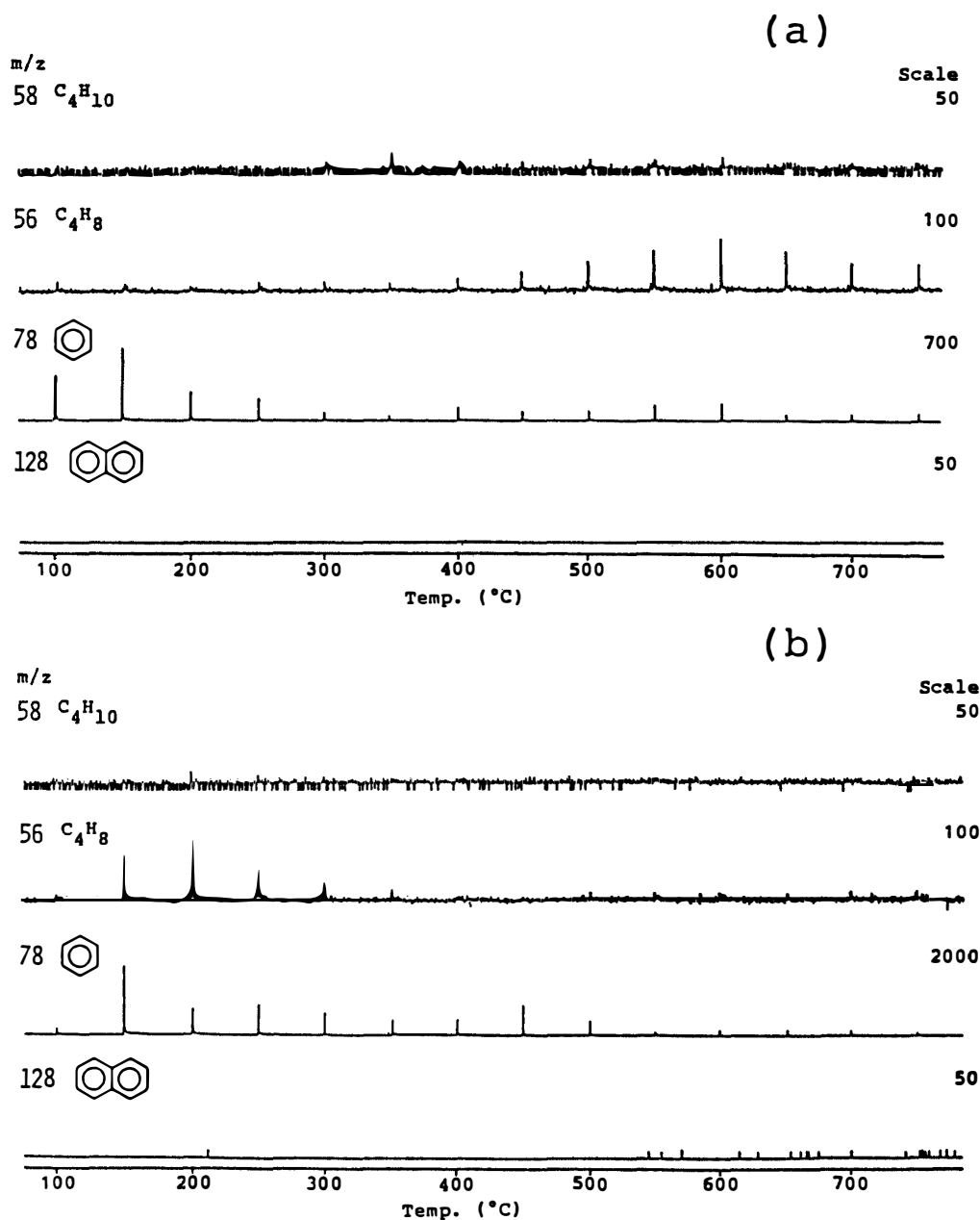


Fig. 5. Thermal release patterns of ions for compounds from Y-793321 (a) and B-7904 (b) determined by DTA/TG-MS analysis.

position. The ion at  $m/z$  78 might have also come from  $C^{82}S^{34}S$ . However, the abundance of  $CS_2$  was very small as revealed by the DTA/TG-GC/MS analyses (Fig. 2). Therefore, the contribution of  $CS_2$  to the ion at  $m/z$  78 was very small. The ion at  $m/z$  128 was assigned to naphthalene. The compound  $S_4$  also shows an ion at  $m/z$  128 in addition to 130 and 132 from the presence of the isotope  $^{34}S$ . However, the abundances of ions at  $m/z$  130 and 132 were almost nil, which eliminates the contribution of  $S_4$  to the ion at  $m/z$  128. The four ions at  $m/z$  56, 58, 70, and 72, can be attributed largely to the  $C_4$  and  $C_5$  aliphatic hydrocarbons shown in the figures, although some portion of these peaks also contains the fragment ions of larger ali-

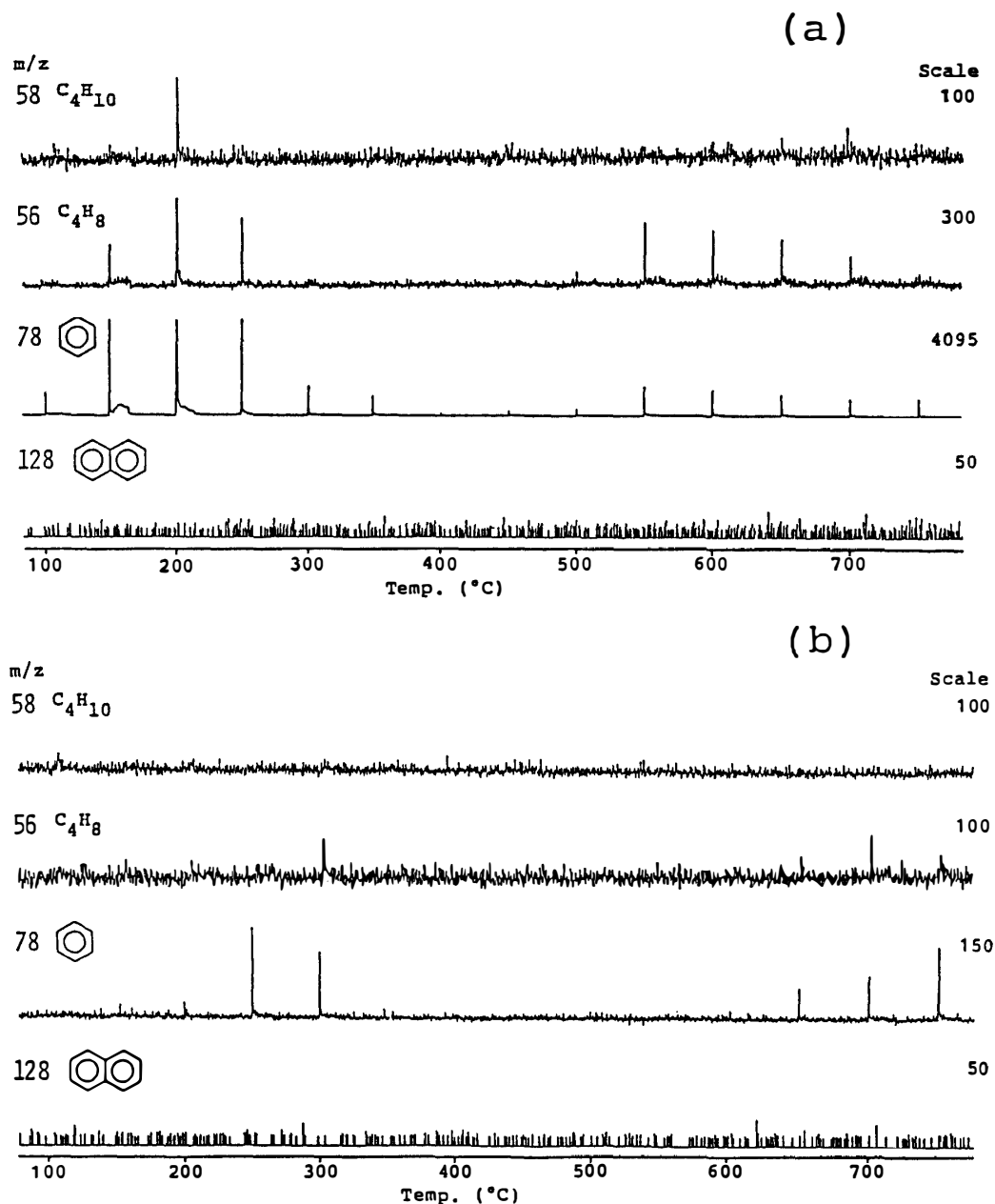


Fig. 6. Thermal release patterns of ions for compounds from Y-82162 (a) and Y-86720 (b) determined by DTA/TG-MS analysis.

phatic hydrocarbons. The ion at  $m/z$  58 also contains a fragment of thiophene.

Among the six chondrites, Y-74662 and Y-791198 released organic compounds rather abundantly as seen in Figs. 3 and 4, respectively, followed by Y-82162 (Fig. 6). These releases are roughly reflected in the carbon contents of the three chondrites before and after the heating as seen in Table 1. Y-793321 and B-7904 released much smaller amounts (Fig. 5). Y-86720 released the smallest amount (Fig. 6) which is insignificant in comparison with those of the other five chondrites.

Benzene is the most abundant organic compound released by all six chondrites. In general, its release patterns are of two kinds: in one, the release starts around  $250^{\circ}\text{C}$

and continues to over 700°C as seen in Y-74662 and Y-791198; in the other the release starts at 100°C or 150°C, soon reaches its maximum, and decreases rapidly around 300°C as in Y-793321, B-7094, and Y-82162. Other aromatic hydrocarbons found from the two CM chondrites, Y-74662 and Y-791198, were toluene, xylene and/or ethylbenzene, and naphthalene. These compounds were not found from the other four chondrites. The release patterns of these aromatics were essentially the same as that of benzene, *i. e.*, they are within its release temperature range, although the pattern of naphthalene in Y-74662 seems to be shifted by about 100°C to higher temperatures.

The C<sub>4</sub> aliphatic hydrocarbons released are more abundant than are the C<sub>5</sub> in all cases. The release patterns of the C<sub>4</sub> and C<sub>5</sub> aliphatics are in general similar to each other and to that of benzene from the same chondrite except for Y-793321.

As to the abundance of saturated vs unsaturated structures, only the C<sub>4</sub> aliphatics from Y-74662 show the saturated structures to be more abundant than the unsaturated ones, and Y-791198 shows them to be similar in amount. The C<sub>5</sub> aliphatics from these two chondrites and the C<sub>4</sub> aliphatics of the other four chondrites all show a predominance of the unsaturated structures over the saturated ones. This predominance of the unsaturated structures indicates that the compounds released are largely the products of thermal degradation of organic matter, particularly the insoluble organic matter, in these chondrites.

#### 4.4. Relation to alteration and metamorphism

The amounts of organic compounds released could reflect the thermal history of the chondrites. Y-74662 and Y-791198 received rather mild alteration (IKEDA, 1983; KOJIMA *et al.*, 1984) which many organic compounds could have survived. The findings of such organic compounds as amino acids (SHIMOYAMA *et al.*, 1979), carboxylic acids and hydrocarbons (SHIMOYAMA *et al.*, 1989) from Y-74662, and from Y-791198 (SHIMOYAMA *et al.*, 1985, 1986; NARAOKA *et al.*, 1988) have been reported. Therefore, it is reasonable that these two chondrites, among the six studied, contain insoluble organic matter abundantly and release organic compounds rather abundantly.

The degree of alteration of Y-793321 was reported to be as mild as that of Y-791198 (KOJIMA *et al.*, 1984). However, a recent study suggested the possibility that thermal metamorphism took place on Y-793321 and B-7904 with heating as high as 500°C or above (AKAI, 1988), a temperature at which many organic compounds would be degraded as shown in this work. Y-793321 and B-7904 contain only small amounts of extractable organic compounds (SHIMOYAMA and HARADA, 1984; SHIMOYAMA *et al.*, 1989). The results of these previous organic analyses support the finding that the kinds and amounts of organic compounds released from Y-793321 and B-7904 are much smaller than from Y-74662 and Y-791198. It is likely that the abundances of organic compounds in these chondrites are related to their thermal histories. No evidence was found to relate that organic compounds in Y-793321 and B-7904 were lost by Antarctic weathering or leaching, although the possibility cannot be excluded completely.

Y-82162 has a carbon content as high as Y-791198, but released only a moderate

amount of organic compounds, much less than that expected for an ordinary CI chondrite. Although the chondrite has received only mild thermal metamorphism, it may have been derived from a source different from non-Antarctic CI chondrites (TOMEOKA *et al.*, 1989a). If so, the different source may explain the low release of organic compounds in kind and amount.

Y-86720 was affected by both thermal metamorphism (heated above 500°C) and extensive aqueous alteration (TOMEOKA *et al.*, 1989b). These metamorphic events are probably sufficient to release most of the organic compounds in the chondrite parent body, resulting in the negligible release of those compounds observed during the heating experiment.

Y-82162 and Y-86720 have not been analyzed for any extractable organic compounds, such as amino acids, hydrocarbons, etc. However, it would be expected that Y-82162 might yield a moderate amount of those organic compounds, while Y-86720 might not, judging from the results of this heating experiment.

## 5. Conclusion

Organic compounds released during a heating experiment reflect thermal history of each carbonaceous chondrite examined. Y-74662 and Y-791198, both of which are relatively rich in extractable organic compounds such as amino acids, etc., thermally released organic compounds abundantly among the six chondrites. These two chondrites are reported to have been affected by a mild aqueous, low temperature alteration but not thermal metamorphism.

The low release of organic compounds from Y-793321 and B-7904 coincides with a low abundance of extractable organic compounds. These two chondrites and Y-86720 have experienced thermal metamorphism probably extensively enough to degrade a large portion of organic compounds in their parent bodies.

Y-82162 released a lower amount of those compounds than Y-74662 and Y-791198 but more than the other three, suggesting that the intensity of its thermal event was intermediate among the six chondrites.

The results of this study of organic compounds correlate with mineralogical and petrographic studies of carbonaceous chondrites which reveal their thermal histories. A study of insoluble organic matter isolated from these chondrites is under way, particularly the effects of inorganic materials, especially those volatile ones and those able to act as catalysts for the thermal release of organic compounds. These studies will contribute to a better understanding of the origin and subsequent history of these chondrites.

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