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Evaluating the thermal metamorphism of CM chondrites by using the pyrolytic behavior of carbonaceous macromolecular matter

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Abstract—The degrees of thermal metamorphism of 10 CM chondrites and of the Allende CV3 chondrite were evaluated from the viewpoint of "graphitization" of the carbonaceous macromolecular matter by means of flash pyrolysis–gas chromatography (GC). The unheated chondrites, Yamato- (Y-) 791198, Murray and Cold Bokkeveld, yielded larger amounts and wider varieties of pyrolyzates than the chondrites strongly heated in the parent asteroids, Y-82054, Y-86695, and Belgica- (B-) 7904, and Asuka- (A-) 881334 (more strongly heated than Y-793321, which has been weakly heated, but lesser than the other strongly heated meteorites). The weakly heated chondrites, Y-793321 and A-881458, showed intermediate features. The data indicate that graphitization of the carbonaceous matter is most extreme in the strongly heated chondrites and that during graphitization, the matter has lost its labile portion, which can generate pyrolyzates such as naphthalene. In order to establish a new method for the evaluation of the degree of graphitization of chondritic carbonaceous matter, a diagram was developed to show the relationship between the total amounts of pyrolyzates with retention times later than 5 min (=$S_{RT>5}$) and the ratio of the amount of naphthalene, a pyrolysis product, to $S_{RT>5}$ (=$S_N/S_{RT>5}$). The diagram indicates a possible evolutionary pathway of graphitization of the carbonaceous matter in carbonaceous chondrites. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The Mighei-group (CM) carbonaceous chondrites—for meteorite classification, e.g. Van Schmus and Wood (1967), Van Schmus and Hayes (1974), Wasson (1974), for more recently defined CR-, CK-, CH-groups, e.g. Bischoff (2001)—are primitive meteorites that are thought to have been a part of water-bearing hydrated asteroids, and some of their matrix phases were formed in outer and low-temperature regions (<400 K) in the early solar system (Clayton and Mayeda, 1984), where presolar grains such as SiC can survive (Huss, 1990). However, the dehydration of phyllosilicates in CM chondrites was observed in some Antarctic meteorites (e.g., Akai, 1988, 1990; Tomeoka et al., 1989; Ikeda et al., 1992), suggesting that thermal metamorphism had occurred after aqueous alteration (e.g., McSween, 1979a) in their parent asteroids.

The CM chondrites contain ~2 wt% of carbon mainly as solvent unextractable macromolecular matter, an analog to terrestrial kerogen or poorly crystalline graphite (e.g., Simmonds et al., 1969; Hayatsu et al., 1977; Cronin et al., 1987; Alexander et al., 1998; Sephton et al., 2000). Aside from the carbon-containing presolar grains such as interstellar graphite (Amari et al., 1990; Huss and Lewis, 1995), the carbon and deuterium isotopic heterogeneities indicate that the carbonaceous macromolecular materials have multiple origins (e.g., Kerridge, 1993; Sephton et al., 1998), such as dense interstellar clouds (Kolodny et al., 1980), the solar nebula (Hayatsu and Anders, 1981), and the surfaces and atmospheres of parent asteroids (Peltzer et al., 1984). Low-temperature stepwise combustion up to 450°C exhibited two organic components: a labile portion released between 250 and 350°C, which is carbon isotopically heavier than −12.4‰, and more stable portion released up to 450°C, which is carbon isotopically lighter at −18.7‰ (Kerridge et al., 1987). The labile portion can act as a parent for the free aromatic hydrocarbons in meteorites (Sephton et al., 1998). And the portion corresponds to a D-enrichment component identified by Kerridge et al. (1987), suggesting that the labile portion and the free aromatics produced by degradation of the macromolecular matter are at least partly interstellar in origin (Penzias, 1980; Sephton et al., 1998).

The carbonaceous macromolecular matter was modified by secondary processes on meteorite parent asteroids. The liquid water on the parent asteroids exerts a strong control on the architecture of the carbonaceous macromolecular matter. During extensive aqueous alteration, water-derived hydrogen thereby preserves an open organic structure by terminating organic free radical sites. For lower levels of the alteration, the free radical termination would have proceeded within the carbonaceous matter itself, leading to greater cross-linking and aromatization (Sephton et al., 1998, 1999, 2000). And the alteration gave rise to the free aromatic hydrocarbons from the decomposition of the labile portion of the macromolecular matter (Sephton et al., 1998).

Several CM chondrites experienced thermal metamorphism after the aqueous alteration. When the chondritic carbonaceous matter was heated in the parent asteroids, it became graphitic due to carbonization and "graphitization" reactions. During thermal metamorphism, the (002) interlayer spacing of the graphitic matter decreases to a constant value of 3.35 Å with an increasing degree of ordering of the carbonaceous matter (Rietmeijer and Mackinnon, 1985).

Pyrolysis–gas chromatography (GC) can also provide information on the degree of graphitization. The open structure is relatively susceptible to both thermal degradation and oxida-

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tion, whereas more condensed organic material, which would be relatively resistant to both thermal and oxidative degradation, would not produce degradation products during a relatively mild condition (Sephton et al., 1998). Therefore, poorly graphitized carbon can generate larger amounts and more diverse pyrolysis products than highly graphitized carbon. And chondrites that experienced serious thermal metamorphism contain such highly graphitic matter that they yield little pyrolyzate on analytical pyrolysis. Murae et al. (1991) have analyzed five CM, five CO3, and a CV3 chondrites by pyrolysis-GC and found that the chondrite samples analyzed can be classified into five classes, I to V. The classification did not correlate to the conventional CM, CO3, and CV3 classification. The classes I to V are categorized on the basis of their efficiency of the formation of naphthalene as a pyrolysis product normalized to total carbon content, which is named EFP (efficiency of formation of pyrolysis products) class. The class number increases with decreasing of the degree of EFP. Shimoyama et al. (1991) also evaluated the degree of thermal metamorphism of three CIs (they classified Belgica- (B-) 7904 as a CI chondrite in that article) and three CM chondrites with a mass spectrometer (MS) equipped with a combined differential thermal analyzer and thermogravimetric analyzer (DTA/TG-MS).

In this study, we analyzed carbonaceous macromolecular matter of 10 CMs and one CV3 chondrites by pyrolysis-GC, determined their degree of graphitization, and developed a diagram that represents the evolutionary path of graphitization of the carbonaceous matter, to establish a new method of evaluating the degree of thermal metamorphism of meteorites.

2. SAMPLES

Ten samples of CMs and the Allende CV3 chondrite were analyzed. Yamato- (Y-) 791198, Murray, and Cold Bokkeveld have undergone aqueous alteration but escaped subsequent heating. Y-791198 has suffered the least degree of aqueous alteration (Metzler et al., 1992), Murray is moderately altered and Cold Bokkeveld is heavily altered (McSween, 1979b; Browning et al., 1996). Asuka- (A-) 881458 (<250°C?) and Y-793321 (300 to 500°C) were moderately heated after aqueous alteration (Akai, 1990, 1992; Akai and Tari, 1997). Y-86789 (Matsuoka et al., 1996), B-7904, Y-86695, and Y-82054 (Akai, 1990, 1992; Akai and Tari, 1997) were strongly heated. Y-86789 is paired meteorite with Y-86720 (Matsuoka et al., 1996). A-881334 is included in the strongly heated group by Akai and Tari (1997), and Nakamura et al. (2000a) claimed that it has experienced a lesser degree of heating—more strongly heated than Y-793321 but lesser than the other strongly heated meteorites. Allende (CV), which belongs to the petrographic subtype 3.2 to 3.3 (Symes et al., 1993; Weinbruch et al., 1994), was also analyzed for comparison.

3. EXPERIMENTAL METHODS

Each powdered sample was wrapped with pyrohoil and pyrolyzed at 740°C for 3 s with a Curie-point pyrolyzer (JHP-3; Japan Analytical Industry). At a temperature of 740°C, the carbonaceous matter yielded the most variable pyrolyzates (e.g., Murae et al., 1987). The GC was a Hitachi G-5000 gas chromatograph, and the column was a Neutrabond-5 (30 m × 0.25 mm inner diameter). The rate of GC oven temperature increase was programmed to be 4°C/min from 60°C to 260°C after keeping the initial temperature for 10 min. Pyrolyzates were detected by a flame ionization detector, and their amounts were calculated by a Labchart 80 integrator (System Instruments). Naphthalene was identified by comparison with the results of the previous GC-MS studies (e.g., Kitajima and Masuda, 1991, 1992), and comparison with the retention time and mass spectrum of a standard. Mass spectra were obtained with a JEOL D-300 mass spectrometer. Several samples were also analyzed by stepwise pyrolysis performed at 333, 445, and 740°C for 3 s, respectively. For Y-791198, a stepwise pyrolysis at 333, 500, and 740°C was also performed. Table 1 summarizes the samples and the treatments in this investigation.

4. RESULTS AND DISCUSSION

4.1. Features of Pyrograms

Figures 1 a–d show the pyrograms of the CM chondrites. The observed pyrolyzates from strongly heated chondrites Y-82054 and Y-86695, and A-881334 (but less strongly than Y-82054 and Y-86695) were simple (Fig. 1b) compared with those of the unheated chondrites, Y-791198, Murray, and Cold Bokkeveld (Fig. 1a). The two weakly heated chondrites, A-881458 and Y-793321, yielded intermediate amounts of pyrolyzates (Fig. 1c). Naphthalene was the main product among the pyrolyzates whose retention times were later than 5 min, in accordance with previous reports (e.g., Murae et al., 1987; Kitajima and Masuda, 1991).

Proposed structures of the carbonaceous macromolecular matter in carbonaceous chondrites are characterized by a condensed aromatic core and more labile portion with thermally weaker bonds such as -C-C-, -C-O-C- compared with the condensed aromatic network (e.g., Hayatsu and Anders, 1981; Hayatsu et al., 1983; Hayatsu, 1984; Murae et al., 1987, 1990; Sephton et al., 2000). The size of condensed aromatic rings varies among the investigators; one or two rings (Sephton et al. 2000) and up to four rings, but the one-ring size is dominant (Hayatsu and Anders, 1981; Hayatsu et al., 1983; Hayatsu, 1984); there is a large polyaromatic condensed network (8 to 12 nm) similar to that of graphite (Murae et al., 1987, 1990). A model structure depicted in Figure 2 shows the labile portion as edge defects. Pyrolyzates are considered to be derived from the labile portion, or the edge defects (e.g., Murae et al., 1987). Actually, it is still unclear whether these labile and more stable portions of macromolecular material are present as two distinct phases or as different fractions of a single material. The results of Sephton et al. (1998) support that idea of labile portion origin of pyrolyzates. They showed that the macromolecular matter in Murchison (CM2) is present as a network of labile and more stable portions that are different in carbon isotopic composition. The carbon isotopic data allow that free aromatics in meteorites, which resulted from the degradation of the macromolecular matter, and hydrous pyrolyzates found during laboratory experiments correspond to the labile portion of the matter.

Unheated carbonaceous macromolecular matter generates a large amount and a wide variety of pyrolyzates. On the other hand, highly graphitized carbonaceous matter yields much less pyrolyzates (Fig. 2). At high degrees of graphitization, the variety of pyrolyzates is lost and naphthalene becomes the dominant pyrolysis product whose retention time is later than 5 min, as in Y-82054 (Fig. 1b). When graphitization is complete, even the naphthalene peak disappears. This pyrolytic behavior

Table 1. Samples and their treatments.[a]

Meteorite	Thermal metamorphism	Estimated metamorphic temperature (°C)	Aqueous alteration	Single pyrolysis[b]	Stepwise pyrolysis[b]
Y-791198	Unheated		Weak[15]	X	X
Murray	Unheated		Moderate[16]	X	X
Cold Bokkeveld	Unheated		Extensive[16]	X	X
A-881458	Very weakly heated	<250?[4]		X	X
Y-793321	Weakly heated	300–500[5] 400–470[6] >500[7]		X	X
A-881334	Strongly heated[2] but less than the other strongly heated meteorites[3]	300–500, but higher than Y-793321[8]		X	
Y-86695	Strongly heated				
Y-82054	Strongly heated				
B-7904	Strongly heated	750–900[9]		X	X
Y-86789	Strongly heated	700[10] 700–850[11]		X	X
Allende (CV 3.2–3.3)[1]	Weakly heated	330, upper limit 530[12] 335[13] 430–530[14]		X	

[a] Superior numbers refer to the following references. (1) Symes et al.(1993); Weinbruch et al. (1994). (2) Akai and Tari, (1997). (3) Nakamura et al., (2000a). (4) Akai and Tari, (1997). (5) Akai, (1992); Akai and Tari, (1997). (6) Nakamura et al., (2000b). (7) Shimoyama et al., (1989; 1991). (8) Nakamura et al., (2000a). (9) Akai, (1990, 1992); Akai and Tari, (1997). (10) Matsuoka et al. (1996). (11) Akai, (1990, 1992); Aai and Tari, (1997). Value for Y-86720, which is paired meteorite with Y-86789 (Matsuoka et al., 1996). (12) Weinbruch et al., (1994). (13) Rietmeijer and Mackinnon, (1985). (14) McSween, (1977). (15) Metzler et al., (1992). (16) McSween, (1979b); Browning et al., (1996).

[b] X represents "performed."

is typical for carbonaceous macromolecular matter in meteorites, but terrestrial or artificial graphitic matter does not always exhibit the same behavior.

Although B-7904 and Y-86789 are classified as strongly heated chondrites on the basis of mineralogical and bulk chemical studies (Akai, 1990, 1992; Matsuoka et al., 1996; Akai and Tari, 1997; Wang and Lipschutz, 1998), unexpectedly large amounts of pyrolyzates were observed (Fig. 1d). This will be discussed later.

4.2. Graphitization Diagram

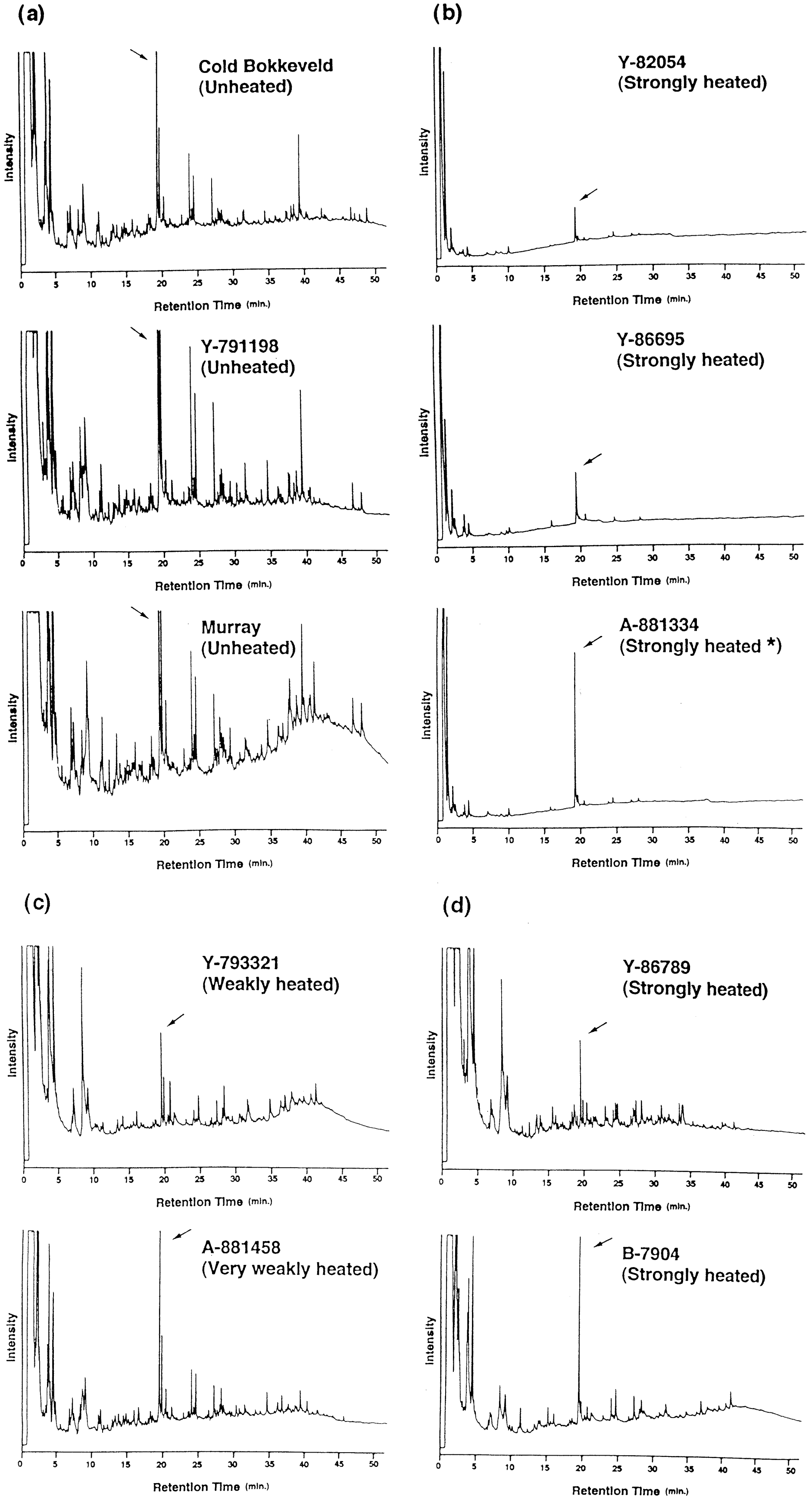
4.2.1. System of Graphitization Diagram

A pyrogram usually contains much information on the detailed structure of macromolecular matter. However, in many cases, pyrograms are too complicated to be interpreted—in particular in the case of naturally occurring macromolecular matter that has no obvious "monomers." In this study, we focused on the information on the degree of graphitization of the chondritic macromolecular matter in the pyrograms and developed a graphitization diagram to establish a new method for evaluating the extent of graphitization of the matter.

The total peak area of pyrolyzates with a retention time later than 5 min ($=S_{RT>5}$) is plotted against the ratio of peak areas of naphthalene to $S_{RT>5}$ ($=S_N/S_{RT>5}$) for each chondrite (Fig. 3a). In this "Y graphitization" diagram, strongly heated, and thus highly graphitized, samples will be plotted at the lower left-hand corner. On the other hand, unheated, primitive samples will be distributed in the upper right area. The results of stepwise pyrolysis at 740°C were also plotted in the same manner (Fig. 3b). Because the samples of stepwise pyrolysis at 740°C have been heated at 445 or 500°C in the pyrolyzer, these results can be taken as the single-step data of the samples that experienced heating at 445 or 500°C. We recognize, however, that the heating conditions of analytical pyrolysis are quite different from those in the meteorite parent asteroids. Pyrolyzates whose retention times are less than 5 min (their molecular weights are lighter than approximately 110 amu) are excluded because this fraction can be easily influenced by terrestrial adsorbates on the sample surfaces.

As expected, highly graphitized samples Y-82054 and Y-86695 plot at the lower left-hand corner of the diagram, and the primitive samples—Y-791198, Murray, and Cold Bokkeveld—plot in the upper right area (in particular, the single-step results for these meteorites). A-881334, which was more strongly heated than Y-793321 but less than Y-82054 and Y-86695, plots between the more strongly heated group and Y-793321. Most samples are plotted on the curve from upper right-hand to lower left-hand area, suggesting an evolutionary graphitization pathway. The locations of the data of Y-791198—single step (i.e., unheated), stepwise data of 445 and 500°C (i.e., experienced 445 or 500°C)—move on the curve from the upper right-hand to the lower left-hand area (Fig. 3b), supporting the idea that graphitization proceeds along that curve. The degree of heating of most samples estimated from the locations in the diagram (Figs. 3a,b) are basically consistent with that estimated from mineralogical and noble gas evidence (Nakamura et al., 2000a,b).

This diagram is useful to evaluate to what extent metamorphism has proceeded, and this diagram shows the pathway and degree of graphitization. However, graphitization depends on many factors—not only temperature, duration, and heating


(a)
Cold Bokkeveld (Unheated)
Y-791198 (Unheated)
Murray (Unheated)
(b)
Y-82054 (Strongly heated)
Y-86695 (Strongly heated)
A-881334 (Strongly heated *)
(c)
Y-793321 (Weakly heated)
A-881458 (Very weakly heated)
(d)
Y-86789 (Strongly heated)
B-7904 (Strongly heated)
Intensity
Retention Time (min.)
0 5 10 15 20 25 30 35 40 45 50

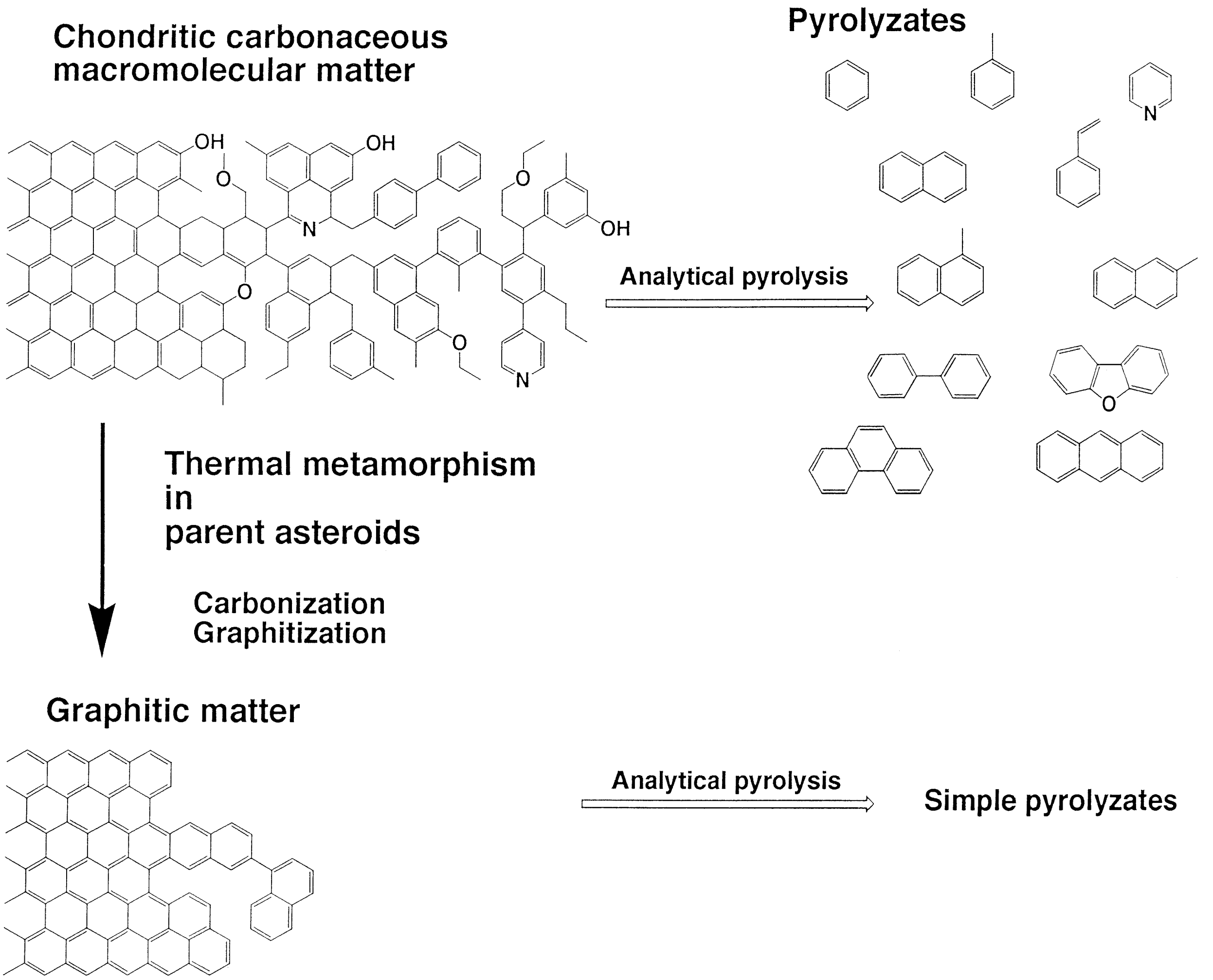


Fig. 2. A model structure of the carbonaceous macromolecular matter and graphitization process. Unheated carbonaceous matter has large amounts of labile portion and yields diverse pyrolyzates on flash pyrolysis; on the other hand, strongly heated matter becomes more graphitic and generates only simple pyrolyzates.

mechanisms, but also the structures of the precursors of the graphitic matter, or the structure of the macromolecular matter after aqueous alteration (e.g., Franklin, 1951; Bonijoly et al., 1982). Some investigators emphasize the effect of pressure (Bonijoly et al., 1982); however, the effect still remains unclear (Weinbruch et al., 1994). Therefore, in the present stage, it is still difficult to directly determine absolute values, such as metamorphic temperature from this diagram. In addition, this diagram does not always assure the development of crystallite of graphite because this diagram is mainly based on the loss of the labile portion of the carbonaceous matter.

We discuss next the data of some individual chondrites.

4.2.2. Allende (CV)

Studies of the thermal history of the Allende CV chondrite are reviewed in Krot et al. (1995). Thermoluminescence measurements indicate only minimal metamorphism (Symes et al., 1993; Weinbruch et al., 1994). Estimated maximum temperature for the presolar diamond in Allende was ~600°C (Huss and Lewis, 1994). However, Weinbruch et al. (1994) concluded that the upper limit for peak metamorphic temperatures on the Allende parent asteroid was approximately 800 K (~530°C), and that 600 K (~330°C) is more realistic. Several other constraints are consistent with peak metamorphic temperatures of 700 to 800 K (~430 to 530°C; McSween, 1977). Krot et al. (1995, 1997) suggested that the virtual absence of phyllosilicates in Allende is indicative of more extensive heating than the metamorphosed CM/CI chondrites, of which metamorphic temperatures during partial dehydration were poorly constrained and vary from 400 to 700°C (Paul and Lipschutz, 1989; Johnson and Prinz, 1991). According to the above discussions, Allende is rather moderately heated chondrite (as a whole, Allende cannot have been heated to the Curie temper-

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Fig. 1. Single-step pyrograms of the CM chondrites analyzed in this investigation. (a) Unheated chondrites. (b) Strongly heated chondrites. (c) Weakly heated chondrites. (d) Chondrites with irregular pyrograms. * A-881334 was less strongly heated than the other strongly heated chondrites. Pyrolysis: 740°C for 3 s (Curie point). Column: Neutrabond-5 (30 m × 0.25 mm inner diameter). GC oven temperature: 60 to 260°C after holding at 60°C for 10 min. The arrow indicates the peak of naphthalene.

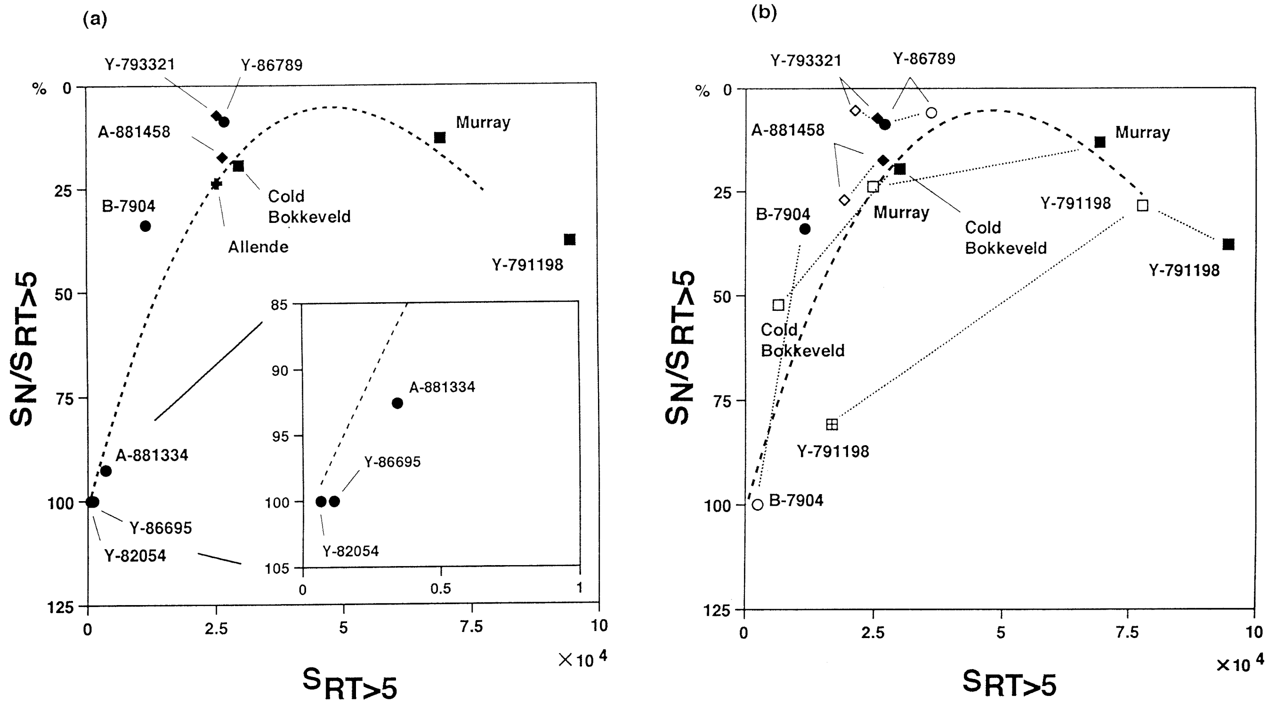

Fig. 3. Graphitization diagram of the chondritic carbonaceous macromolecular matter in the carbonaceous chondrites. (a) Single-step pyrolysis data at 740°C. (b) Stepwise pyrolysis data at 740°C. Stepwise pyrolysis was performed at 333, 445, and 740°C. For Y-791198 (an unheated chondrite), stepwise pyrolysis at 333, 500, and 740°C was also performed. S_N represents the peak area of naphthalene; $S_{RT>5}$ represents the total peak area of pyrolyzates with a retention time later than 5 min. Solid square = single-step pyrolysis data of unheated chondrites; solid diamond = single-step pyrolysis data of weakly heated chondrites; solid circle = single-step pyrolysis data of strongly heated chondrites; solid cross = single-step pyrolysis data of CV3; open square = stepwise pyrolysis data of unheated chondrites (after pyrolysis at 333 and 445°C), open diamond = stepwise pyrolysis data of weakly heated chondrites; open circle = stepwise pyrolysis data of strongly heated chondrites; open box with cross = stepwise pyrolysis data of unheated chondrites (after pyrolysis at 333 and 500°C).The dashed line is a possible evolutionary pathway of graphitization, estimated by the least-squares method ($Y = -0.25X^3 + 6.5X^2 - 46X + 1.0 \times 10^2$). The data that were, or may be, influenced by terrestrial contaminants or unknown secondary process (single-step datum of B-7904, single-step and stepwise data of Y-86789, single-step and stepwise data of Y-793321) were excluded from calculation. The $S_{RT>5}$ values are normalized by sample weights (mg), and the value of Allende is also normalized as Allende has 2% of carbon.

ature of magnetite, i.e., 858 K [~585°C]); therefore, the location of Allende in the moderately heated region in the graphitization diagram is consistent with the data. The relation of Cold Bokkeveld and Allende in the diagram do not conflict with the results of Rietmeijer and Mackinnon (1985), although the spacing of the poorly ordered graphite (002) reflection indicates rather low maximum metamorphic temperature of 600 K (~335°C; Rietmeijer and Mackinnon, 1985), and the accuracy of this technique has been questioned because the effect of pressure has been unclear (Weinbruch et al., 1994).

4.2.3. A-881334

Akai and Tari (1997) categorized A-881334 as a strongly heated chondrite. The analysis of mineralogy and trapped noble gases indicated the lesser degree of metamorphic temperature at 300 to 500°C than the other strongly heated meteorites, but this meteorite was heated more extensively than Y-793321 (Nakamura et al., 2000a). In the graphitization diagram, the location of A-881334 between Y-793321 and the other strongly heated meteorites is in accord with the results of Nakamura et al. (2000a), but it is plotted seemingly rather close to the more strongly heated group (Fig. 3a). However, whether the distance between each plot is proportional to the degree of heating is unclear in the present stage. The close distance between A-881334 and the more strongly heated group may partly result from the pyrolysis temperature of 740°C. Because this temperature may result in a lower resolution of the higher graphitized region in the diagram—that is, the sample once heated near the pyrolysis temperature on the parent asteroids may have already lost major parts of its labile portion that would decompose at the temperature—it may be difficult to find small difference of the degree of metamorphism from simple pyrolyzates in the pyrograms. It would result in a large distance in the lower graphitized region, but in a short distance in the higher graphitized region for the same degree of difference of heating.

Samples that do not fall on the graphitization pathways in the diagram are discussed next.

4.3. Remarks on Some Individual Chondrites

4.3.1. B-7904

Figure 4a shows the pyrograms of the stepwise pyrolysis of B-7904. By use of the data from the single-step pyrolysis,

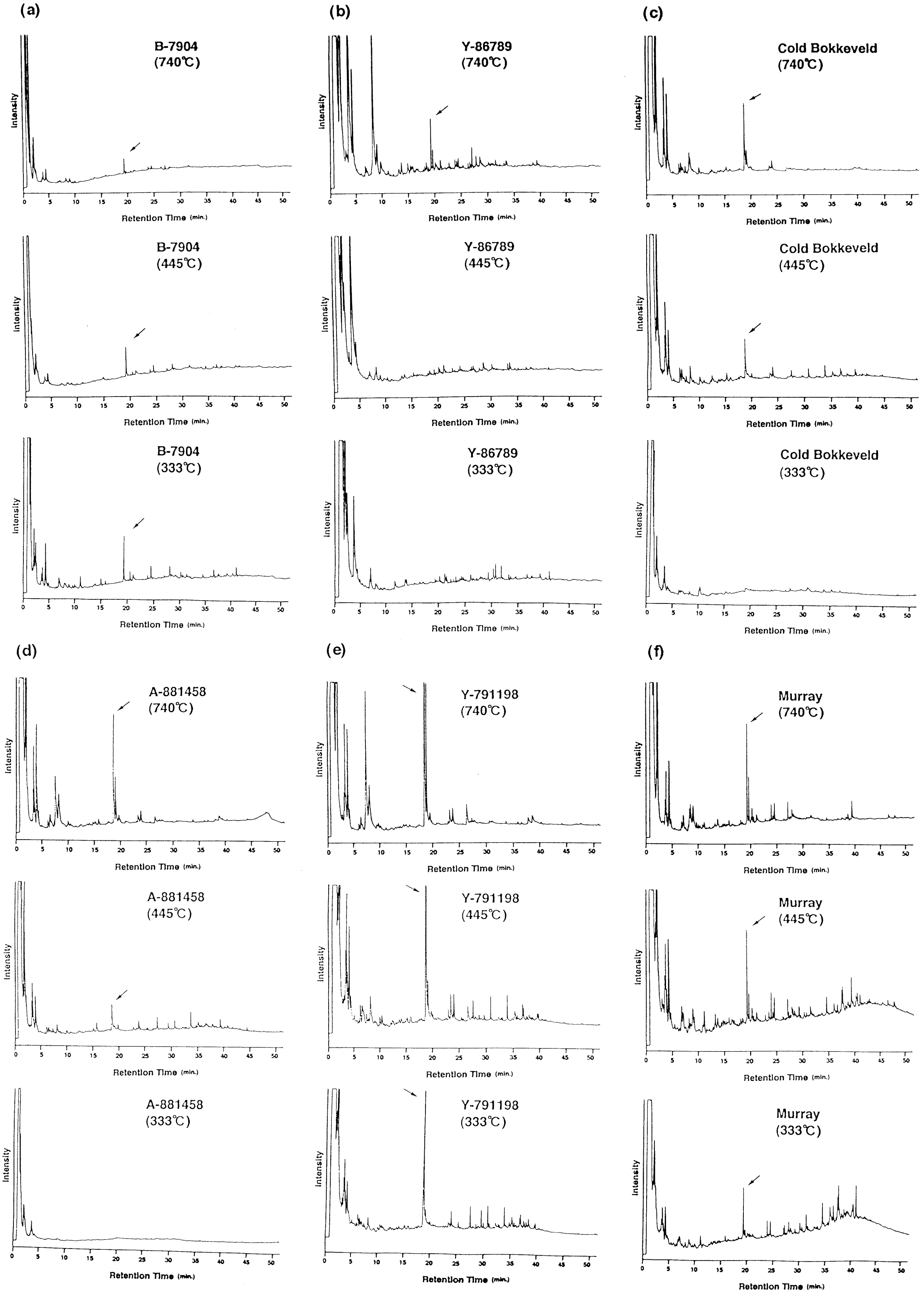

Fig. 4. Stepwise pyrograms of several CM chondrites. (a) B-7904. (b) Y-86789. (c) Cold Bokkeveld. (d) A-881458. (e) Y-791198. (f) Murray. Pyrolysis: 333, 445, and 740°C for 3 s (Curie point), respectively. Column: Neutrabond-5 (30 m × 0.25 mm inner diameter). GC oven temperature: 60 to 260°C after holding at 60°C for 10 min. The arrow indicates the peak of naphthalene.

B-7904 is plotted in the region of weakly heated samples (Fig. 3a), although this chondrite was proposed to have been strongly heated to 750 to 900°C on the basis of the degree of decomposition of pyllosilicates (Akai, 1990, 1992; Akai and Tari, 1997). However, when the datum of stepwise pyrolysis at 740°C is used, it is plotted at the consistent location with mineralogical and noble gas observation on the evolutionary pathway (Fig. 3b). The major fraction of the detected compounds at 333°C is evaporated material from sample surfaces rather than pyrolyzates because C-C single bonds tend to cleave at temperatures higher than 500°C (Sugiura and Tsuge, 1978) and the evaporated fraction can be easily influenced by terrestrial contaminants (e.g., Naraoka et al., 1997; Alexander et al., 1998). In contrast, compounds detected only at high temperature, "true" pyrolyzates from macromolecular matter are less strongly influenced by terrestrial contaminants than those detected at lower temperatures because the macromolecular materials are generally assumed to be completely indigenous due to their high molecular weight and immobility (Sephton et al., 2000). The results of B-7904 show a large quantity of pyrolyzates at lower temperature, suggesting considerable terrestrial contamination (Fig. 4a). This is confirmed by the following consideration. If the low-temperature fraction is indigenous, the carbonaceous matter in B-7904 would have large amounts of labile portion, and the portion should be retained after the pyrolysis at 445°C that means moderate heating. And the high-temperature fraction would yield much more pyrolyzates, and the value for stepwise pyrolysis at 740°C should remain in the region of moderately heated samples.

4.3.2. *Y-86789*

Y-86789 is an exception. Its estimated metamorphic temperature is approximately 700°C (Matsuoka et al., 1996). It is a paired meteorite, with Y-86720 (Matsuoka et al., 1996), and the estimated metamorphic temperature for Y-86720 is 700 to 850°C (Akai, 1990, 1992; Akai and Tari, 1997). Figure 4b shows the pyrograms of stepwise pyrolysis of Y-86789. This sample does not lie on the evolutionary path, even if the value for stepwise pyrolysis at 740°C is used (Fig. 3b). The single-step pyrogram of Y-86789 differs from all other samples for peaks other than naphthalene (Fig. 1d). However, Y-86789 yields a considerable quantity of pyrolyzates at higher temperatures than lower temperatures (Fig. 4b), suggesting that the pyrolyzates are indigenous and reflect little influence from terrestrial contaminants. Therefore, the carbonaceous matter must have been partially decomposed after graphitization to form a disordered structure. This chondrite must have experienced an event in which a degradative process occurred—for instance, shock events or terrestrial weathering. However, shock metamorphism would be expected to promote graphitization during postshock heating after pressure release. Iron hydroxide observed in the thin section of our specimen is suggestive of the terrestrial weathering; therefore, the unique pyrogram of Y-86789 may be the result of the weathering.

4.3.3. *Cold Bokkeveld*

Figure 4c shows the pyrograms of the stepwise pyrolysis of Cold Bokkeveld. The notable feature of the pyrograms of this chondrite is the lack of pyrolyzates in the 333°C fraction, which is similar to those of the weakly heated chondrite A-881458 (Fig. 4d) but different than the other primitive chondrites, Y-791198 (Fig. 4e) and Murray (Fig. 4f). The single-step data of Cold Bokkeveld and A-881458 lie close together in the graphitization diagram due to the lack of the 333°C fraction (Fig. 3a). A-881458 is considered to have lost its 333°C fraction during thermal metamorphism; however, Cold Bokkeveld has not because it is an unheated meteorite. The most likely mechanism that could be responsible for the loss of parts of the organic materials of Cold Bokkeveld is intensive aqueous alteration on the parent asteroid (McSween, 1979b; Browning et al., 1996). The possible removal or destruction of solvent extractable organic matter during aqueous alteration was suggested on the basis of carbon isotopic studies (Naraoka et al., 1997). Also, Sephton et al. (1999, 2000) observed that the yield of phenols resulted from the cleavage of ether linkage as the hydrous pyrolyzates had inverse correlation with preterrestrial aqueous alteration, indicating that such labile portion of the carbonaceous matter has already been lost on the parent asteroids. That idea is also supported by the fact that Cold Bokkeveld shows a similar single-step pyrogram to that of the Boriskino CM chondrite (Kitajima and Masuda, 1992), which belongs to the same "altered" group of aqueous alteration as Cold Bokkeveld (McSween, 1979b).

4.3.4. *Y-793321*

The pyrolytic results of this chondrite in this study seem to be consistent with its mineralogy in suggesting moderate heating. However, Shimoyama and Harada (1984) and Shimoyama et al. (1989, 1991) showed that Y-793321 contained only small amounts of extractable organic compounds. According to the suggestion of Akai (1988) that Y-793321 and B-7904 experienced thermal metamorphism as high as 500°C or above, they concluded that a large portion of the organic compounds in this chondrite have degraded in its parent asteroid by thermal metamorphism, like B-7904, and thus proposed that Y-793321 experienced thermal metamorphism at a temperature higher than 500°C, similar to B-7904. Murae et al. (1991) reported that Y-793321 showed a highly graphitized pyrolytic feature and classified it as EFP class V, indicating that it experienced a higher temperature than B-7904, which is class IV. Komiya et al. (1993) also reported that the insoluble organics in Y-793321 do not possess a thermally labile organic fraction. But later, this meteorite was grouped into a less altered group on the basis of $\delta^{18}O$-$\delta^{13}C$ data (Naraoka et al., 1997). The N/C-H/C diagram also shows the less altered nature of Y-793321 relative to B-7904 (Naraoka et al., 2000). And Akai (1990, 1992) estimated the peak metamorphic degree in the order of B-7904 $\geqq$ Y-86720 $>$ Y-82162 $>$ Y-793321. Akai (1992) showed that the maximum temperature for B-7904 (750 to 900°C) is much higher than that for Y-793321 (300 to 500°C); his data are based on a time–temperature–transformation (T-T-T) diagram, which describes the progress of a transformation on a graph of temperature T against the logarithm of the time t. Nakamura et al. (2000b) estimated that the metamorphic temperature of Y-793321 is close to 470°C because of the presence of trace amounts of cronstedtite. The loss of solar gases in this meteorite also indicates heating at ~400°C (Nakamura et al., 2000b).

In this study, the value for single-step pyrolysis of Y-793321 plots in the moderate metamorphic region, with a lower temperature than that of B-7904 (Fig. 3a). The stepwise pyrolysis value for 740°C also lies in the moderate region (Fig. 3b), although the 500°C fraction of this sample showed some terrestrial contaminants. It indicates a lesser degree of thermal metamorphism (~500°C) than B-7904, or partial decomposition and disordering of the carbonaceous matter after graphitization. The former process is consistent with mineralogical and noble gas studies, although the latter can not be excluded entirely by the fact that the data of this sample are plotted outside the graphitization curve (Figs. 3a,b). The disagreement between the organic features and the mineralogical–noble gas profiles may also partly be due to heterogeneity within the Y-793321 chondrite because Y-793321 is a regolith breccia that shows solar–noble gas enrichment and impact features (Nakamura et al., 2000b). Y-793321 has experienced postshock heating whose effects must have been heterogeneous between places, resulting in the disagreement of the degree of heating estimated from the analysis of different portions of the meteorite.

5. CONCLUSIONS

A correlation between the intensity of thermal metamorphism and the degree of graphitization of carbonaceous macromolecular matter in CM chondrites was established on the basis of the efficiency of pyrolyzate generation in analytical pyrolysis. The unheated chondrites generate larger amounts of pyrolyzates than the strongly heated chondrites. The newly developed graphitization diagram represents an evolutionary path for graphitization. The diagram is basically consistent with the reported graphite (002) spacing cosmothermometer, as well as mineralogical and noble gas signatures.

Graphitization is associated with aqueous alteration and thermal metamorphism.

5.1. Aqueous Alteration

Aqueous alteration leads to cleavage of ether bonds and loss of labile portions (Sephton et al., 1999, 2000). If liquid water was not available in sufficient quantity, the termination of free radicals within the carbonaceous matter itself furthers graphitization, whereas an open structure is generated if enough liquid water was available (Sephton et al., 1998, 1999, 2000).

5.2. Thermal Metamorphism

The degree of graphitization depends on temperature, duration, heating mechanism, and the type of the precursor, or the structure of the carbonaceous matter after aqueous alteration (Franklin, 1951; Bonijoly et al., 1982). The effect of pressure remains unclear (Weinbruch et al., 1994). Possible heat sources are solar radiation, shock metamorphism, and decay of short-lived radionuclides such as ^{26}Al.

Terrestrial contamination indicates a lower graphite content; however, these data plot in the graphitization diagram outside the graphitization pathway. Unknown secondary degradative processes after graphitization (including terrestrial weathering?) yield the same features.

5.3. Remarks on Some Individual Chondrites

Y-86789 has unique pyrogram and plots in an exceptional region in the diagram; this may be caused by terrestrial weathering. A-881458 and Cold Bokkeveld both lack pyrolyzates in the 333°C fraction. We suggest that this is due to moderate thermal metamorphism for A-881458 and to intensive aqueous alteration for Cold Bokkeveld. The results of Y-793321 suggest a lesser degree of metamorphism for this chondrite relative to B-7904. The graphitization diagram can also be useful for evaluating secondary changes to the carbonaceous matter, which occur after graphitization on the meteorite parent asteroids, such as terrestrial contamination or weathering.

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