

## A chemical sequence of macromolecular organic matter in the CM chondrites

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**Abstract**—A new organic parameter is proposed to show a chemical sequence of organic matter in carbonaceous chondrites, using carbon, hydrogen, and nitrogen concentrations of solvent-insoluble and high-molecular weight organic matter (macromolecules) and the molecular abundance of solvent-extractable organic compounds. The H/C atomic ratio of the macromolecule purified from nine CM chondrites including the Murchison, Sayama, and seven Antarctic meteorites varies widely from 0.11 to 0.72. During the H/C change of  $\sim 0.7$  to  $\sim 0.3$ , the N/C atomic ratio remains at  $\sim 0.04$ , followed by a sharp decline from  $\sim 0.040$  to  $\sim 0.017$  between H/C ratios from  $\sim 0.3$  to  $\sim 0.1$ . The H/C–N/C sequence shows different degrees of organic matter thermal alteration among these chondrites in which the smaller H/C–N/C value implies higher alteration levels on the meteorite parent body. In addition, solvent-extractable organic compounds such as amino acids, carboxylic acids, and polycyclic aromatic hydrocarbons are abundant only in chondrites with macromolecular H/C values  $> \sim 0.5$ . These organic compounds were extremely depleted in the chondrites with a macromolecular H/C value of  $< \sim 0.5$ . Possibly, most solvent-extractable organic compounds could have been lost during the thermal alteration event that caused the H/C ratio of the macromolecule to fall below 0.4.

### INTRODUCTION

Various solvent-extractable organic molecules such as amino acid, carboxylic acid, and sugar-related compounds have been reported from carbonaceous chondrites, particularly the CM2 chondrites including Murchison and some Antarctic meteorites (Cronin et al. 1988; Cooper et al. 2001; Shimoyama et al. 1979; Naraoka et al. 1999). These solvent-extractable organic compounds may have played an important role in chemical evolution and the origins of life on the primitive Earth. Besides the solvent-extractable organic compounds, a solvent-insoluble and high-molecular weight macromolecule is the main component of the total organic matter in chondrites. The macromolecule is sometimes called kerogen-like matter (e.g., Kerridge et al. 1987) because the chemical and structural signature is loosely compatible to terrestrial kerogen in sediments. The macromolecule is composed mainly of carbon with minor amounts of hydrogen, nitrogen, oxygen, and sulfur. Nuclear magnetic resonance

(NMR) spectroscopy has been applied to study the chemical structure of the macromolecule, revealing various proportions of aliphatic and aromatic carbon in addition to heteroelement-linked carboxyl and carbonyl carbon (Cronin et al. 1987; Gardinier et al. 2000). The abundance ratio of aliphatic carbons to aromatic/olefinic carbons in the macromolecule of the Murchison CM chondrite is much higher than that of the Allende CV chondrite but lower than that of the Orgueil CI chondrite (Cronin et al. 1987), which suggests various degrees of aromatization in meteorite macromolecules.

In the CM group, mineralogical and chemical studies have revealed that some CM chondrites are subjected to various types of thermal alteration and metamorphism on their meteorite parent body. For example, Kojima et al. (1984) and Akai (1988, 1990) reported peculiar CM chondrite specimens subjected to different degrees of metamorphism within the Antarctic meteorite population. Oxygen isotope studies also suggest a subclass of CM chondrite associated with the CI group (Clayton 1993). Attempts have been made

to clarify the relative extent of thermal alteration using mineral and chemical compositions (Browning et al. 1996; Lipschutz et al. 1999) and heating experiments (Akai 1992; Hiroi et al. 1993). Pyrolysis experiments of CM2 chondrites also show various release patterns of aliphatic and aromatic hydrocarbons, suggesting different degrees of thermal alteration (Shimoyama et al. 1991; Komiya et al. 1993; Kitajima et al. 2002). However, the chemical signatures of the solvent-insoluble macromolecule have not been fully understood. The elemental composition of the macromolecule has the potential to clarify the thermal alteration history of carbonaceous chondrites.

In this study, carbon (C), hydrogen (H), and nitrogen (N) concentrations of the macromolecule purified from several carbonaceous chondrites are determined to study the alteration of organic matter and its relationship to the thermal history of the chondrites. Organic molecular distribution is also discussed with relevance to aqueous or thermal alteration of the chondrites because solvent-extractable organic compounds such as amino acids are likely to be associated with hydrous activity in meteorite parent bodies (Bunch and Chang 1980; Cronin and Chang 1993). In addition, alteration indices of meteoritic organic matter are proposed using the H/N/C ratio and molecular distributions.

## SAMPLES AND ANALYTICAL PROCEDURES

Nine CM chondrites including Murchison, Sayama, and seven Antarctic meteorites were used in this study (Table 1). The Antarctic meteorites were collected by the Japanese Antarctic Research Expeditions and were classified mineralogically and chemically by Yanai and Kojima (1995).

The Sayama meteorite fell at Sayama city, Japan in 1986 and was identified as a CM chondrite (Yoneda et al. 2001). The bulk carbon concentrations range from 0.67 to 2.5 wt% with an average value of ~1.7 wt% (Kerridge 1985; Naraoka et al. 1997; Yoneda et al. 2001). Powdered samples (0.5–1 g) were extracted with water and organic solvents to analyze solvent-extractable organic compounds such as amino acids, carboxylic acids, and polycyclic aromatic hydrocarbons (PAHs). The detailed analytical procedures and molecular distributions have been reported elsewhere (Cronin et al. 1988; Shimoyama et al. 1985; Naraoka et al. 1988, 1999, 2000).

After solvent extraction, the residue was treated with 6M HCl and subsequently was demineralized with a mixture of concentrated HF and HCl (1/1 by volume) in a Teflon™ bottle by shaking at ~70 °C. The acidified residue was washed with H<sub>2</sub>O several times until the pH was neutral. The residue was successively washed with methanol, benzene, hexane, and CS<sub>2</sub> to remove solvent-extractable organic matter and elemental sulfur. Demineralization and solvent extraction were repeated two or three times. The isolated macromolecule was dried and subjected to CHN elemental analysis (Perkin Elmer 240 or Carlo Erba EA-1180) in duplicate to determine the C-H-N concentrations. The carbon isotopic composition of the isolated macromolecule was determined as in Naraoka et al. (1997). The five purified macromolecules were subjected to a differential thermal analysis-thermogravimetry (DTA-TG, Shimadzu DTG-40) from room temperature to 800 °C at 10 °C/min in a He gas flow (Komiya et al. 1993). After cooling down to room temperature in the He gas flow, the heated residue was also analyzed for the C-H-N concentrations as described above.

Table 1. Carbon, hydrogen, and nitrogen concentrations of purified macromolecular organic matter from the CM2 chondrites with some bulk chemical characteristics.

Meteorites	Y-74662 <sup>a</sup>	Y-791198 <sup>a</sup>	Y-793321 <sup>a</sup>	B-7904 <sup>a</sup>	Y-86720 <sup>a</sup>	A-881280	A-881458	Sayama	Murchison <sup>a</sup>
C (wt%)	57.2	57.6	64.2	64.3	67.3	63.7	57.1	68.3	56.9
H (wt%)	2.70	3.20	1.90	0.79	0.64	1.53	3.44	3.91	3.30
N (wt%)	2.70	3.20	1.90	0.79	1.30	2.75	2.52	2.76	2.60
H/C (atomic)	0.57	0.67	0.36	0.15	0.11	0.29	0.72	0.68	0.70
N/C (atomic)	0.040	0.037	0.039	0.029	0.017	0.037	0.038	0.035	0.039
H/C (atomic) after heating	0.13	0.17	0.13	0.10	0.05	n.d. <sup>b</sup>	n.d.	n.d.	n.d.
N/C (atomic) after heating	0.029	0.026	0.033	0.027	0.016	n.d.	n.d.	n.d.	n.d.
Bulk C (wt%) <sup>c</sup>	1.94	2.29	1.68	1.13	0.67	2.46	1.77	1.99	1.6–2.5
Bulk $\delta^{13}\text{C}$ (per mil versus PDB) <sup>d</sup>	–15.2	–14.9	–7.6	–13.9	n.d.	–15.1	–13.2	–15.3	–17.5
H <sub>2</sub> O(+) (wt%) <sup>e</sup>	13.3	12.8	6.5	2.1	4.8	17.6	15.6	n.d.	n.d.
Solvent-extractable organic compounds <sup>f</sup>	abundant	abundant	depleted	depleted	depleted	depleted	abundant	abundant	abundant

<sup>a</sup>Komiya et al. (1993).

<sup>b</sup>n.d. = not determined.

<sup>c</sup>Naraoka et al. (1997); Kerridge (1985); Yoneda et al. (2001).

<sup>d</sup>Kerridge et al. (1987); Naraoka et al. (1997).

<sup>e</sup>Yanai and Kojima (1995).

<sup>f</sup>Shimoyama and Harada (1984); Shimoyama et al. (1979, 1985, 1986, 1989); Naraoka et al. (1988, 1999, 2000).

## RESULTS AND DISCUSSION

### H/C and N/C Ratios of Macromolecules

The purified macromolecules have carbon concentrations ranging from 57 to 68 wt% (Table 1). These well-purified macromolecules consist mainly of carbon with minor amounts of hydrogen and nitrogen, which collectively account for between 63 and 75 wt% of the sample in addition to some sulfur and oxygen. The H/C atomic ratio of the Murchison macromolecules of this study (0.70) is the same as that of the insoluble organic fraction of Murchison reported by other studies (Hayatsu et al. 1977; Gardinier et al. 2000). The H/C atomic ratios of all meteorite macromolecules in Table 1 vary widely (0.11–0.72), while the N/C atomic ratios are less variable (0.017–0.040). Yamato (Y-86720) has the smallest value of both H/C and N/C ratios.

After heating the macromolecules up to 800 °C, both H/C and N/C ratios of all samples decrease. In Fig. 1, the H/C-N/C change during heating is projected as a dashed arrow. The change of the H/C ratio is much larger than that of the N/C ratio for all samples examined. For example, while the H/C ratio of the pre-heated Y-74662 macromolecule (0.57) is reduced by more than 4 times to 0.13 after heating, the N/C ratio (0.040) changes relatively little to 0.029 (Table 1). On the other hand, the Y-86720 macromolecule does not change its H/C and N/C ratios much after heating.

### H/C-N/C Sequence as an Indicator for Thermal Alteration of Macromolecules

An H/C-N/C plot of the nine purified macromolecules is shown in Fig. 1 using the data in Table 1. All the data points make a chemical sequence as shown along the solid line. The N/C ratio remains ~0.04 during a change of the H/C ratio from ~0.7 to ~0.3, however, N/C ratios drop markedly close to ~0 below an H/C ratio of ~0.3. Note that values close to H/C and N/C ratios of ~0 represent graphitic material. The macromolecules of Belgica Mountains (B-7904) and Y-86720 are depleted in N relative to C compared to other chondrites. This might imply a different mineralogy intrinsic to the nature of the solvent-insoluble fraction between the chondrites (i.e., abundant C-rich components such as SiC and diamond). However, the carbon isotopic composition of the solvent-insoluble fraction in B-7904 (−13.9‰) does not differ from that of Y-74662 (−15.2‰) and Y-791198 (−14.9‰). Because SiC and diamond in carbonaceous chondrites are known to have wide variations in  $^{13}\text{C}/^{12}\text{C}$  (e.g., Zinner 1998), this similar  $\delta^{13}\text{C}$  indicates that more abundant C-rich components such as SiC and diamond cannot account for the low N/C ratio of B-7904. Rather, the H/C-N/C sequence could indicate the degree of thermal alteration for macromolecules; an interpretation supported by the heated macromolecules of Y-74662 and Y-791198 plotting close to B-7904 (open small

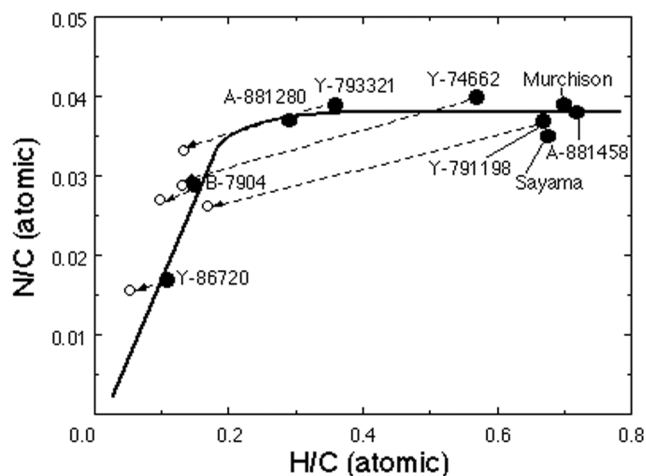


Fig. 1. An H/C-N/C plot of a macromolecule purified from the CM2 chondrites including the Murchison, Sayama, and seven Antarctic meteorites (large filled circles). The small open circle denotes the H/C-N/C plot after heating of the macromolecule up to 800 °C. By heating experimentation, the change in H/C and N/C ratios is projected as a dashed arrow.

circles in Fig. 1). The preferential loss of nitrogen from meteorite macromolecules during metamorphism is also reported (Sephton et al. 2003). Furthermore, previous mineralogical and chemical studies also support the proposal that Y-86720 and B-7904 have been subjected to significant amounts of thermal alteration (see below).

In comparison, a terrestrial sedimentary macromolecule (kerogen) is also composed mainly of carbon with minor amounts of H, N, O, and S and has been well-studied to evaluate thermal alteration (maturation) with respect to petroleum generation (e.g., Hunt 1995). Although an H/C-O/C plot of kerogen (termed a van Krevelen diagram) has been employed to clarify the thermal alteration, enrichment in carbon relative to other elements is also a common consequence of thermal maturation of terrestrial organic macromolecules. Therefore, most likely, the H/C-N/C curve is a sensitive and quantitative means to evaluate different degrees of thermal alteration of organic matter in meteorites. Of the nine CM chondrites in this study, Asuka- (A-) 881458, Murchison, Sayama, and Y-791198 are much less thermally altered, followed by Y-74662, Y-793321, A-881280, B-7904, and Y-86720.

The above thermal metamorphic degree can be discussed with the previous mineralogical and chemical studies, which are summarized in Table 2. Kojima et al. (1984) first pointed out unusual altered carbonaceous chondrites using seven Antarctic meteorites and classified them into four stages by examining chondrules and matrix. Of these, the degree of chondrule alteration changed from weak to intense: Y-793321 < Y-791198 < B-7904. B-7904 was considered to be thermally altered, while Y-791198 received aqueous alteration at low temperatures. Akai (1988, 1990, 1992) studied phyllosilicates

Table 2. Alteration or metamorphic degrees of the CM chondrites inferred from mineralogical or chemical studies.

Analytical technique	Alteration or metamorphic degree	Reference
Mineralogy		
Microscopy	Y-793321 <Y-791198 <Y-790003 <B-7904 <Y-791824	Kojima et al. (1984)
Transmission electron microscopy	Y-793321 <Y-82162 <Y-86720 ~B-7904	Akai (1990, 1992)
Inorganic geochemistry		
Mobile trace elements	Murchison <Y-793321 <A-881655 <B-7904 <Y-82162 <Y-86720	Lipschutz et al. (1999)
Organic geochemistry		
Differential thermal analysis-thermogravimetry-mass spectrometry	Y-74662 ~Y-791198 <Y-82162 <Y-793321 ~B-7904 <Y-86720	Shimoyama et al. (1991)
Flash pyrolysis-gas chromatography	Y-791198 <Murray <Y-793321 <A-881458 ~Cold Bokkeveld <B-7904 <A-881334 <Y-86695 ~Y-82054	Kitajima et al. (2002)
Organic macromolecule	A-881458 ~Murchison ~Sayama ~Y-791198 <Y-74662 <Y-793321 <A-881280 <B-7904 <Y-86720	This study

of the chondrites in detail by high-resolution electron microscopy and heating experiments. The peak metamorphic degree was estimated in the order of: Y-793321 <Y-82162 <Y-86720 ~B-7904 with an estimated peak temperature from ~300 to ~900 °C depending on the duration time. Lipschutz et al. (1999) also examined these chondrites by petrographic and mobile trace element studies, concluding a metamorphic order of: Y-793321 <(500 °C) <A-881655 <B-7904 <Y-82162 <Y-86720 <(700 °C). These metamorphic degrees can be comparable with the N/C-H/C sequence of this study, in which the Y-86720 is clearly subjected to the highest metamorphism.

A few organic geochemical studies were also carried out by a heating experiment. Shimoyama et al. (1991) quantified organic compounds released from these chondrites using DTA/TG-mass spectrometry. The amount of organic compounds was inferred to the alteration and/or metamorphism in the following order: Y-74662 ~Y-791198 <Y-82162 <Y-793321 ~B-7904 <Y-86720. Kitajima et al. (2002) proposed a graphitization index of macromolecules using organic compounds released by flash pyrolysis-gas chromatography. A metamorphic degree of the following order was suggested: Y-791198 <Y-793321 <A-881458 <B-7904. The relative alteration degrees are similar among these studies. A major difference is that A-881458 has been thermally altered more than Y-793321 in Kitajima et al. (2002), while the A-881458 chondrite was not much less altered in this study. The H/C ratio of the A-881458 macromolecule (0.72) is much larger than that of the Y-793321 macromolecule (0.36). In addition, the A-881458 yielded abundant indigenous solvent-extractable organic compounds such as carboxylic acid and polycyclic aromatic hydrocarbons (Naraoka et al. 1999, 2000), while Y-793321 was extremely depleted in these organic compounds (Shimoyama et al. 1989). The presence of these volatile organic compounds indicates that A-881458 has not been subjected to high temperatures (see below).

This study clearly shows that Y-86720 is more thermally altered than B-7904, and Y-793321 is more thermally altered than Y-791198 and A-881458. Indeed, besides thermal

alteration and metamorphism, aqueous activity on the parent body is another important factor of the alteration of a meteorite. For example, Y-7993321 contains only 6.5wt% H<sub>2</sub>O(+) by wet chemical analysis (Yanai and Kojima 1995), which is an extremely low H<sub>2</sub>O(+) concentration when compared to CM chondrites. Because the H<sub>2</sub>O(+) value of conventional wet chemical analysis includes volatile components such as carbon and sulfur, the Y-793321 was completely dehydrated. On the other hand, A-881280 contains as much as 17.6 wt% H<sub>2</sub>O(+) but is more thermally altered than Y-793321. Probably, A-881280 received aqueous alteration after thermal alteration.

### Solvent-Extractable Organic Matter Inferred from the H/C Ratio of Macromolecules

Cronin et al. (1988) summarized various molecular distributions from Murchison. The CM chondrites used in this study also have been examined for solvent-extractable organic matter by several authors (Shimoyama et al. 1979, 1984, 1985, 1986, 1989; Naraoka et al. 1988, 1999, 2000). Murchison, Y-74662, Y-791198, and A-881458 yielded appropriate amounts of solvent-extractable organic compounds, while B-7904, Y-793321, Y-86720, and A-881280 are extremely depleted in spite of comparable concentration of carbon (~1–2.5 wt%). The depletion is unlikely to be due to leaching by Antarctic water (Naraoka et al. 1997).

From a viewpoint of H/C ratios, as shown in Fig. 1, the chondrites with the H/C ratio >0.5 of macromolecules obviously contain solvent-extractable organic compounds, while the chondrites with the H/C ratio <0.4 are depleted in such molecules. This is a reasonable molecular feature because the H/C ratio of aliphatic compounds including amino acids, sugar-related compounds, and saturated hydrocarbons is ~2. Even more condensed PAH such as pyrene and fluoranthene, which are the most abundant PAHs in the CM chondrites, has the H/C ratio of ~0.6. The H/C ratio of <0.4, on average, indicates that organic matter in the meteorite is mostly graphitic in nature. Presumably, the thermally altered chondrites lost their solvent-extractable organic compounds,

even though these chondrites originally contained them. Although the solvent-extractable organic matters have been delivered from meteorites and have played an important role for the origins of life on the primitive Earth, the metamorphosed CM chondrites, such as Y-86720 and B-7904, could not be a direct source of the solvent-extractable organic matter on the Earth.

In the recent fall of the Tagish Lake CM chondrite, the macromolecule has an elemental composition of  $C_{100}H_{46}N_{10}O_{15}$  (Pizzarello et al. 2001). The H/C ratio of macromolecule in Tagish Lake (0.46) could suggest moderate thermal alteration on the basis of this study. However, Tagish Lake yielded a suite of solvent-extractable organic compounds such as mono- and dicarboxylic acids (Pizzarello et al. 2001). Apparently, a macromolecular H/C ratio of 0.46 may represent a minimum value for the occurrence of solvent-extractable organic compounds. Alternatively, Tagish Lake may be a peculiar CM chondrite—a suggestion supported by an unusually high N/C ratio (0.10) for its macromolecule.

The solvent-extractable organic compounds are thought to be associated with hydrous activity in the meteorite parent body (Bunch and Chang 1980). The organic precursors could have reacted with water to give amino and carboxylic acids (Cronin and Chang 1993). Also, the soluble organic compounds could be formed from the macromolecules during aqueous alteration (Sephton et al. 1998). In the case of this study, the chondrites rich in solvent-extractable organic compounds contain more than ~13 wt%  $H_2O(+)$  (Table 1), which is consistent with the above idea that natural hydrolytic transformation of macromolecules generates solvent-soluble compounds. However, even though A-881280 contains 2.46 wt% carbon and 17.6 wt%  $H_2O(+)$ , the solvent-extractable organic compounds are extremely depleted. As mentioned previously, this chondrite could have been subjected to thermal alteration before hydrous activity on the parent body. This result indicates that the final aqueous activity did not accompany organic synthesis using the metamorphosed carbon.

## CONCLUSIONS

The H/C ratio of well-purified macromolecules from nine CM chondrites varies widely from 0.11 to 0.72. The N/C ratio of the macromolecules remains ~0.04 between the H/C ratio of ~0.7 and ~0.3. However, under the H/C ratio of ~0.3, both H/C and N/C ratios get smaller close to ~0 (i.e., becoming more graphitic). The chemical sequence could be produced by laboratory heating of macromolecules depending on the maximum temperature and duration time. During thermal events on meteorite parent bodies, hydrogen is preferentially lost relative to nitrogen from the macromolecules. The H/C-N/C chemical sequence of well-purified macromolecules can be a sensitive indicator to evaluate thermal alteration and the metamorphic degree of carbonaceous chondrites. In addition, appropriate amounts of volatile organic compounds such as

amino acid, carboxylic acid, and PAHs were detected only in the CM chondrites with the H/C ratio  $> \sim 0.5$ . The solvent-extractable organic matter may not have survived during thermal alteration, which generated the H/C ratio  $< \sim 0.4$  of macromolecules on the meteorite parent body.

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**Editorial Handling**—Dr. Scott Sandford

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