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# Elemental and isotope behavior of macromolecular organic matter from CM chondrites during hydrous pyrolysis

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**Abstract**–A new insight into carbon and hydrogen isotope variations of insoluble organic matter (IOM) is provided from seven CM chondrites, including Murchison and six Antarctic meteorites (Y-791198, Y-793321, A-881280, A-881334, A-881458 and B-7904) as well as Murchison IOM residues after hydrous pyrolysis at 270–330 °C for 72 h. Isotopic compositions of bulk carbon ($\delta^{13}C_{bulk}$) and hydrogen ($\delta D$) of the seven IOMs vary widely, ranging from –15.1 to –7.6‰ and +133 to +986‰, respectively. Intramolecular carboxyl carbon ($\delta^{13}C_{COOH}$) is more enriched in $^{13}C$ by 7.5 –11‰ than bulk carbon. After hydrous pyrolysis of Murchison IOM at 330 °C, H/C ratio, $\delta^{13}C_{bulk}$, $\delta^{13}C_{COOH}$, and $\delta D$ values decrease by up to 0.31, 3.5‰, 5.5‰, and 961‰, respectively. The O/C ratio increases from 0.22 to 0.46 at 270 °C and to 0.25 at 300 °C, and decreases to 0.10 at 330 °C. $\delta^{13}C_{bulk}$-$\delta D$ cross plot of Murchison IOM and its pyrolysis residues shows an isotopic sequence. Of the six Antarctic IOMs, A-881280, A-881458, Y-791198 and B-7904 lie on or near the isotopic sequence depending on the degree of hydrous and/or thermal alteration, while A-881334 and Y-793321 consist of another distinct isotope group. A $\delta^{13}C_{bulk}$-$\delta^{13}C_{COOH}$ cross-plot of IOMs, including Murchison pyrolysis residues, has a positive correlation between them, implying that the oxidation process to produce carboxyls is similar among all IOMs. These isotope distributions reflect various degree of alteration on the meteorite parent bodies and/or difference in original isotopic compositions before the parent body processes.

## INTRODUCTION

Most organic carbon (>75%) in meteorites generally exists as a solvent-insoluble macromolecular organic matter (e.g., Cronin et al. 1987). This high-molecular organic material, now commonly known as insoluble organic matter (IOM), contains small amounts of hydrogen, nitrogen, oxygen and sulfur. The chemical structure of IOM has been investigated using a variety of techniques, such as chemical degradation (Hayatsu et al. 1977, 1980; Remusat et al. 2005a), pyrolysis (Komiya et al. 1993; Sephton and Gilmour 2000; Kitajima et al. 2002; Remusat et al. 2005b), hydrous pyrolysis (Sephton et al. 1998, 2000, 2003), hydropyrolysis (Sephton et al. 2004, 2005), solid-state $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy (Cronin et al. 1987; Gardinier et al. 2000; Cody et al. 2002; Cody and Alexander 2005; Yabuta et al. 2005), and high resolution transmission electron microscopy (HRTEM, Derenne et al. 2005). These investigations have revealed that more than 60% of the macromolecular carbon in Murchison is derived from aromatic structure up to ~7 rings with carboxyl and/or ester groups as well as ether and alkyl linkages between them. In addition, the aromatic structure in Murchison IOM is highly substituted with a H/C ratio of 0.53–0.70 (Cody et al. 2002; Naraoka et al. 2004; Yabuta et al. 2005; Alexander et al. 2007).

Organic fractions in carbonaceous chondrites can be largely subdivided into two types: solvent-extractable organic compounds such as amino acids, carboxylic acids and hydrocarbons, and solvent-insoluble IOM (e.g., Cronin and Chang 1993; Pizzarello et al. 2006). The IOM can be further subdivided into two types: thermally labile and refractory components (Sephton et al. 2003, 2004).

The IOM has been considered as a source of solvent-extractable organic compounds through aqueous alteration on meteorite parent bodies (Cronin and Chang 1993). For example, Sephton et al. (1998) suggest that the large part of solvent-extractable polycyclic aromatic hydrocarbons (PAHs) could be derived from the IOM because of the consistency in $\delta^{13}C$ values between solvent-extractable PAHs and those produced by hydrous pyrolysis of IOM. In addition, IOM has a potential to yield mono- and dicarboxylic acids during hydrous pyrolysis (Oba and Naraoka 2006a; Yabuta et al. 2007). Their studies suggest that some solvent-extractable organic compounds could be formed during hydrous activity on the meteorite parent bodies because most of the CM chondrites experienced either or both aqueous alteration and thermal metamorphism (e.g., Tomeoka et al. 1989). The generated compounds are closely related to the chemical structure of IOM containing relatively abundant aromatic and carboxyl carbon (Gardinier et al. 2000; Cody et al. 2002; Yabuta et al. 2005).

The labile part originally existed in IOM may have been removed during hydrous activities and/or thermal metamorphism. The labile component should be more enriched in hydrogen relative to refractory component, because the hydrogen to carbon ratio (H/C) of IOM could decrease toward to zero during the thermal event (Naraoka et al. 2004). This is consistent with the observation that aliphatic to aromatic carbon ratio of IOM decreases with the increase of thermal alteration (Yabuta et al. 2005). Thus, the chemical composition of IOM is a sensitive indicator to evaluate thermal history on the meteorite parent bodies (Kitajima et al. 2002; Naraoka et al. 2004).

Many studies into the isotopic compositions of IOM have been carried out to investigate meteoritic organic synthesis as well as its origin, in which the isotopic composition in carbonaceous chondrites is chemically and spatially heterogeneous (e.g., Kerridge et al. 1987; Sephton et al. 2003; Busemann et al. 2006; Remusat et al. 2006). For example, aliphatic chains of IOM are more D-enriched relative to aromatics implying more primitive signature in aliphatic chains (Remusat et al. 2006; Huang et al. 2007). In addition, the extreme D and $^{15}N$ enrichments of IOM (up to +19,400 and +3200‰, respectively) in CR and CM chondrites have been often inferred as indicators of interstellar origin (e.g., Busemann et al. 2006; Alexander et al. 2007). However, recent theoretical and analytical studies have proposed that such isotope enrichment could be caused by photochemical processes in a protosolar nebula (Aikawa and Herbst 2001; Remusat et al. 2006). Besides the original isotopic signature in interstellar and/or protosolar environment, planetary processes such as hydrous and thermal activities are expected to have influenced the isotope distributions of IOM (e.g., Robert and Epstein 1982; Sephton et al. 2003). For example, Yabuta et al. (2007) measured carbon and hydrogen isotopic compositions of Murray IOM before and after hydrothermal treatment, and showed that $^{13}C$- and D-enriched fraction was preferentially removed during this process. A recent bulk multi-isotope study on IOM from 75 carbonaceous, ordinary and enstatite chondrites suggests that all isotope variations are the result of parent body processing of a common precursor, and that the range of isotopic compositions within and between chondrite classes could be explained by the different degree and/or mechanism of parent-body processes (Alexander et al. 2007). However, there have been few examples to show isotope relationships of various IOMs between different meteorites caused by alteration processes.

In this study, we have measured elemental and bulk carbon ($\delta^{13}C_{bulk}$) and hydrogen ($\delta D$) isotopic compositions of IOM from seven CM2 chondrites to understand the evolution of meteoritic organic matter. In particular, with the hydrous pyrolysis experiment of Murchison IOM, elemental and isotopic systematics will be clarified with respect to its origins and alteration processes. Furthermore, the position-specific carbon isotope measurement of carboxyls (COOR, R = H and/or alkyl group; $\delta^{13}C_{COOH}$) is performed to investigate isotopic heterogeneity within IOM, since the intra-molecular isotope distribution has provided clues to alteration processes as well as organic origins (Kerridge et al. 1987).

## SAMPLES AND ANALYTICAL PROCEDURE

### Sample Preparation

Murchison meteorite and six Antarctic CM2 chondrites including Yamato (Y)-791198, Y-793321, Asuka (A)-881280, A-881334, A-881458, and Belgica Mountains (B)-7904 were used in this study. Powdered sample (0.5–1 g) of interior chunk of meteorite was extracted with water and organic solvents to analyze solvent-extractable (free) organic compounds such as amino acids, carboxylic acids, and polycyclic aromatic hydrocarbons (PAHs). The detailed analytical procedures and molecular distributions have been reported elsewhere (e.g., Shimoyama et al. 1979, 1989; Naraoka et al. 1999, 2000). After solvent extraction, the meteorite residue was treated with 6M HCl, and subsequently demineralized with a mixture of concentrated HF/HCl (1/1 by volume) in a Teflon$^{TM}$ bottle by shaking up to ~70 °C. After demineralization, the residue was washed with water until the pH was neutral and subsequently washed with a series of organic solvents decreasing in polarity (methanol followed by dichloromethane or benzene, then hexane and sometimes carbon disulfide) to remove free organic matter and elemental sulfur. The resultant solvent-insoluble organic matter (IOM) was subjected to an elemental analyzer (EA, FISONS NA-1500) to determine C-H-N concentrations. Oxygen concentration of IOM was separately determined as CO by pyrolysis at 1450 °C in the presence of graphite using a high temperature EA (ThermoQuest TC/EA). The C-H-N-O amounts were calibrated using organic standards: 2,5-Bis(5-tert-butyl-2-

benzoxazolyl)thiophene (BBOT) for C-H-N and benzoic acid for O. The analytical precision using the standards is generally better than 2–3%.

### Hydrous Pyrolysis of Murchison IOM

Hydrous pyrolysis of Murchison IOM (~7 mg) was conducted with 0.5 ml of distilled and deionized $H_2O$ ($H_2O$/IOM ~ 14 v/w) in a degassed and sealed tube at 270, 300, or 330 °C for 72 h. The three temperatures were selected in the present study in order to reveal temperature effect of hydrous pyrolysis on changes in elemental and isotopic composition, and were almost consistent with the most previous hydrous pyrolysis experiments using meteoritic IOM (e.g., Sephton et al. 1998; Yabuta et al. 2007). The δD value of $H_2O$ used in this study (δD = −75‰ versus VSMOW) is similar to that of hydrous minerals in Murchison (−88‰; Robert 2002). The detailed procedure has been reported by Oba and Naraoka (2006a). After removing the solution, the pyrolysis residue was washed with water and organic solvents, then dried under vacuum. The resultant IOM was subjected to $\delta^{13}C_{bulk}$, $\delta^{13}C_{COOH}$ and δD analyses as described below.

### Isotopic Analyses of IOM

The purified IOM (~200 to 1000 µg) was subjected to isotopic analyses. The $\delta^{13}C_{bulk}$ analysis was conducted as in Naraoka et al. (1997), namely, the sample was combusted at 900 °C and the $CO_2$ formed was subjected to an isotopic analysis. The $\delta^{13}C_{COOH}$ analysis was conducted using a high-temperature elemental analyzer equipped with a pyrolysis furnace (ThermoQuest TC/EA) coupled with an isotope ratio mass spectrometer (ThermoQuest DELTAplus XL). The carboxyls in IOM were converted to $CO_2$ through decarboxylation at 750 °C followed by GC separation with a 2 m PoraPLOT Q column at 50 °C using He (>99.9999% purity) as a carrier gas (90 ml/min). This analytical method was originally applied to carbon isotope analysis of carboxyls in aromatic carboxylic acids (Oba and Naraoka 2006b), being suitable for the meteoritic IOM because of the possible similarity in structure between aromatic carboxylic acid and IOM (e.g., Cody et al. 2002; Cody and Alexander 2005). $\delta^{13}C$ value was calculated with a $CO_2$ gas standard in per mil (‰) relative to the Vienna-Peedee Belemnite (VPDB). A standard deviation of the $\delta^{13}C_{COOH}$ analysis was better than 0.4‰ (Oba and Naraoka 2006b). The concentration of the $CO_2$ was calculated by comparing the mass 44 peak area with that of a standard reagent (benzoic acid) with the known amount. δD analysis was conducted under the same instrumental conditions as the $\delta^{13}C_{COOH}$ analysis except for the furnace and GC column conditions. The pyrolysis was conducted with graphite at 1450 °C followed by GC separation with a 0.6 m molecular-sieve column at 70 °C. δD value was calibrated with Vienna-Standard Mean Ocean Water (VSMOW), Greenland Ice Sheet Precipitation (GISP), and Standard Light Antarctic Precipitation (SLAP), and was calculated with $H_2$ gas standard in per mil (‰) relative to VSMOW. A standard deviation of δD analysis using an organic standard (benzoic acid) was better than 3‰.

## RESULTS

### Elemental Composition of IOM from CM2 Chondrites

Chemical and isotopic data of this study are summarized in Table 1. Multiple measurements are conducted for Y-793321, B-7904 and A-881458, showing that CHNO analyses have a good reproducibility (Table 1). Carbon content of 7 IOMs ranges from 47.6 to 64.7 wt%. As described in the previous study (Naraoka et al. 2004), hydrogen content ranges from 0.98 to 3.20 wt% with the H/C ratio of 0.18 to 0.71 (by atomic), while nitrogen content shows less variation from 2.17 to 3.00 wt% with N/C ratios of 0.029–0.041. Oxygen content is relatively similar, ranging from 12.1 to 18.4 wt% with an O/C ratio of 0.14 to 0.27. These CHNO contents are consistent with those of previous studies on CM chondrites (e.g., Hayatsu et al. 1980; Alexander et al. 2007). The amounts of the generated $CO_2$ range from 1.9 to 3.1mmol/g-C, consisting of 2.3–3.7% and 24.7–40.7% relative to total carbon and oxygen in IOM, respectively.

### Isotopic Composition of IOM from CM2 Chondrites

Figure 1 shows plots of $\delta^{13}C_{bulk}$ and δD of IOMs from CM2 chondrites. The $\delta^{13}C_{bulk}$ values range from −15.1 to −13.0‰ except for Y-793321 (−7.6‰) and A-881334 (−9.0‰). In this study, we define IOMs as $^{13}C$-depleted group (Murchison group; Murchison, Y-791198, A-881458, A-881280, and B-7904), and $^{13}C$-enriched group (Y-793321 group; Y-793321 and A-881334) on the basis of their carbon isotopic compositions. The Murchison group is compatible with some reports of Murchison IOM (e.g. −13.3‰; Robert and Epstein 1982), but slightly enriched in $^{13}C$ relative to other reports (e.g., −19.2‰; Sephton et al. 2003: −18.9‰; Alexander et al. 2007). Y-793321 group is also consistent with a previous study of Y-793321 (−8.4‰; Alexander et al. 2007). The intramolecular $\delta^{13}C_{COOH}$ values distribute from −7.6 to +3.0‰, being more enriched in $^{13}C$ relative to bulk carbon by up to 11‰. Y-793321 group also has $^{13}C$-enriched carboxyls (+3.0 ± 0.8‰ and +1.3‰ for Y-793321 and A-881334, respectively).

Bulk δD of IOM ranges widely from +133 to +986‰. Murchison IOM shows the most D-enrichment (+986‰), being similar (+945‰; Kerridge et al. 1987) or somewhat larger (+777‰; Alexander et al. 2007) relative to previous reports. In contrast to the extreme D-enrichment, this study reveals the common occurrence of less D-enriched IOM (Y-793321, +133‰; A-881334, +245‰), as well as confirming the low bulk δD of Y-793321 reported previously (~+95‰, Alexander et al. 2007). It should be noted that these less

Table 1. Elemental and isotopic compositions of purified macromolecular organic matter (IOM) from the CM2 chondrites and Murchison pyrolysis residues.

| Meteorites | C (wt%) | H (wt%) | N (wt%) | O (wt%) | Total (wt%) | H/C (atomic) | N/C (atomic) | O/C (atomic) | $\delta^{13}C_{bulk}$ (‰)[b] | $\delta D$ (‰)[c] | COOH (mmol/gC) | COOH-C /total C (%) | COOH-O /total O (%) | $\delta^{13}C_{COOH}$ (‰)[b] | Thermal metamorphism[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Y-791198[a] | 57.6 | 3.20 | 2.50 | 14.0 | 77.3 | 0.67 | 0.037 | 0.18 | −14.9 | 798 | 1.9 | 2.3 | 24.7 | −5.4 | Unheated |
| Y-793321 | 63.4 ± 0.7[e] | 2.11 ± 0.19 | 3.00 ± 0.09 | 15.4 ± 1.1 | 83.9 | 0.40 | 0.041 | 0.18 | −7.6 | 133 | 3.1 ± 0.2 | 3.7 | 40.7 | 3.0 ± 0.8 | Weakly heated |
| B-7904 | 64.7 ± 0.3 | 0.98 ± 0.21 | 2.22 ± 0.03 | 12.1 ± 1.0 | 80.0 | 0.18 | 0.029 | 0.14 | −13.9 | 450 | 2.0 ± 0.1 | 2.4 | 33.6 | −4.3 ± 1.8 | Strongly heated |
| A-881280[a] | 63.7 | 1.53 | 2.75 | 18.4 | 86.4 | 0.29 | 0.037 | 0.22 | −15.1 | 432 | 2.8 | 3.4 | 31.1 | −7.6 | Heated |
| A-881334 | 47.6 | 1.37 | 2.17 | 17.4 | 68.5 | 0.34 | 0.039 | 0.27 | −9.0 | 257 | 2.9 | 3.5 | 25.4 | 1.3 | Strongly heated |
| A-881458 | 57.4 ± 0.8 | 3.42 ± 0.07 | 2.75 ± 0.20 | 12.5 ± 0.0 | 76.1 | 0.71 | 0.041 | 0.16 | −13.2 | 903 | 2.1 ± 0.2 | 2.5 | 30.2 | −2.8 ± 0.2 | Very weakly heated |
| Murchison | 58.4 | 3.02 | 2.22 | 16.3 | 79.9 | 0.62 | 0.033 | 0.22 | −13.0 | 986 | 2.4 | 2.9 | 27.9 | −2.0 | Unheated |
| Murchison residues | | | | | | | | | | | | | | | |
| 270 °C | 38.5 | 1.34 ± 0.18 | 1.11 | 23.7 ± 1.1 | 67.7 | 0.41 | 0.025 | 0.46 | −15.7 | 307 ± 17 | 1.0 ± 0.1 | 1.2 | 3.2 | −6.9 ± 0.2 | |
| 300 °C | 53.0 | 1.74 ± 0.14 | 2.03 | 17.6 ± 3.1 | 74.4 | 0.39 | 0.033 | 0.25 | −16.2 | 64 ± 14 | 1.8 ± 0.1 | 2.1 | 5.6 | −7.4 ± 0.2 | |
| 330 °C | 70.8 | 1.83 | 2.43 | 9.5 | 84.6 | 0.31 | 0.029 | 0.10 | −16.1 | 25 | 0.6 | 0.8 | 2.0 | −7.3 | |

[a] C, H, N, and $\delta^{13}C_{bulk}$ are from Komiya et al. (1993), Naraoka et al. (1997, 2004).

[b] Relative to VPDB.

[c] Relative to VSMOW.

[d] From Kitajima et al. (2002), Naraoka et al. (2004), and references therein.

[e] Standard deviations are obtained from 2 to 4 measurements.

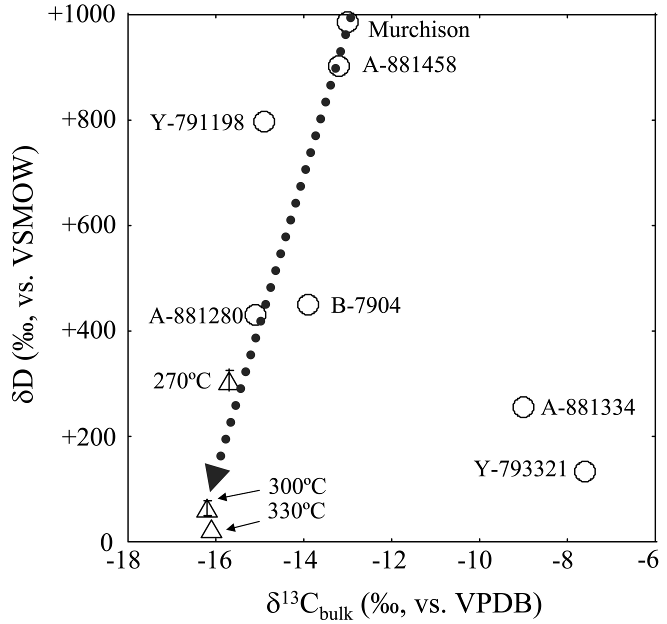

Fig. 1. A $\delta D$-$\delta^{13}C_{bulk}$ plot of the IOMs including Murchison hydrous pyrolysis residues. By hydrous pyrolysis, the changes in $\delta D$ and $\delta^{13}C_{bulk}$ of Murchison IOM is projected as a dashed arrow. Open triangles denote the plot of Murchison residues.

D-enriched meteorites belong to the $^{13}C$-enriched group as described above. Intermediate $\delta D$-bearing IOM is also characterized for B-7904 and A-881280 (~+450‰), being similar to that for Y-86720 (~+496‰, Alexander et al. 2007), while $\delta^{13}C$ are different between these meteorites.

## Changes in Elemental and Isotopic Compositions During Hydrous Pyrolysis

During hydrous pyrolysis of Murchison IOM, elemental C content decreases from 58.4 wt% (original) to 38.5 wt% at 270 °C, while the C content increases to 53.0 wt% and 70.8 wt% at 300 °C and 330 °C, respectively. This peculiar chemical behavior compensates for O incorporation into IOM from water at 270 °C (O: 23.7 ± 1.1 wt%) from original IOM (O: 16.3 wt%). Eventually, O/C ratio increases from 0.22 (original) to 0.46 at 270 °C and to 0.25 at 300 °C, while it decreases to 0.10 at 330 °C. H/C ratio is the highest for the original IOM (0.62), followed by 0.41, 0.39, and 0.31 at 270, 300, and 330 °C, respectively. On the other hand, N/C ratio changes little (0.033–0.025) under pyrolysis conditions in this study. Variations in H/C, O/C, and N/C of Murchison residues are summarized in Fig. 2. The amount of generated $CO_2$ from the residual IOM decreases from 2.4 mmol/g-C (original) to 1.0 ± 0.1 mmol/g-C at 270 °C (n = 2), 1.8 ± 0.1 mmol/g-C at 300 °C (n = 3), and 0.6 mmol/g-C at 330 °C, consisting of 0.8–2.1% C and 2.0–5.6% O relative to bulk C and O, respectively.

$\delta^{13}C_{bulk}$ of the original Murchison IOM (−13.0‰) becomes slightly $^{13}C$-depleted to −15.7‰ at 270 °C, −16.2‰ at 300 °C, and −16.1‰ at 330 °C after hydrous pyrolysis. Such a few ‰$^{13}C$-depletion is also observed after hydrous pyrolysis experiments of Murchison IOM at 320–330 °C by Sephton et al. (2003) and Murray IOM at 300 °C by Yabuta et al. (2007). These results are consistent with some previous reports that the evolved components are enriched in $^{13}C$ (Sephton et al. 1998, 2004), even though acetic acid generated during the pyrolysis is depleted in $^{13}C$ by more than 10‰ relative to bulk IOM (Oba and Naraoka 2006a).

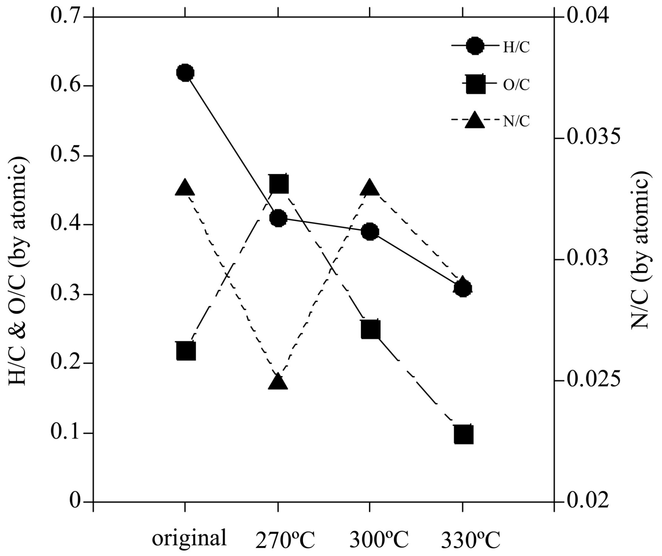

Fig. 2. Variations in H/C, O/C, and N/C ratio of Murchison IOM during hydrous pyrolysis at 270, 300, and 330 °C. Filled circles, squares, and triangles indicate H/C, O/C, and N/C, respectively.

$\delta^{13}C_{COOH}$ of the original Murchison IOM (−2.0‰) also changes to −6.9 ± 0.2‰ (n = 2) at 270 °C, −7.4 ± 0.2‰ (n = 3) at 300 °C, and −7.3‰ at 330 °C after hydrous pyrolysis. A change in $\delta^{13}C_{COOH}$ after hydrous pyrolysis (−4.9 to −5.4‰) is larger than that in $\delta^{13}C_{bulk}$ (−2.7 to −3.2‰).

Bulk $\delta D$ value changes dramatically from +986‰ (original) to +307 ± 17‰ (n = 2) at 270 °C, +64 ± 14‰ (n = 2) at 300 °C, and +25‰ at 330 °C, indicating labile hydrogen isotope behavior under hydrothermal conditions. A similar isotopic behavior is reported during hydrous pyrolysis for IOM of the Murray meteorite (Yabuta et al. 2007).

$\delta^{13}C_{bulk}$ and $\delta D$ of Murchison pyrolysis residues, together with those of the original Murchison and Antarctic IOMs, are shown in Fig. 1. A dashed line on the plot shows an isotopic change of Murchison IOM during hydrous pyrolysis.

## DISCUSSION

### Elemental Variations of IOM from CM2 Chondrites

H/C ratio of IOM is a sensitive indicator to evaluate thermal alteration and the metamorphic degree of carbonaceous chondrites, as a pyrolysis experiment confirms

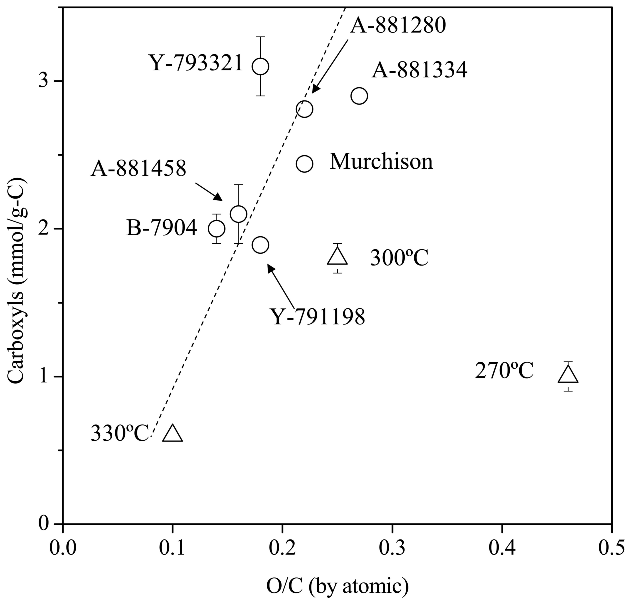

Fig. 3. An O/C-carboxyls plot of IOMs from 7 CM chondrites and Murchison residues. A dashed line indicates a positive correlation ($r^2$ = 0.61) between O/C and carboxyls concentration for the original Murchison and Antarctic IOMs.

preferential loss of H to C (Naraoka et al. 2004). The H/C ratio is in good agreement with the metamorphic grade defined by mineralogy and petrography. On the other hand, this study reveals that O content and O/C ratio do not apparently show a systematic trend. Thermally unaltered chondrites with the H/C of >0.6 (Murchison, Y-791198 and A-881458) have an O/C ratio of 0.16–0.22, which is not so different from thermally altered chondrites such as B-7904 (0.14) and Y-86720 (0.15; Alexander et al. 2007). Weakly thermally altered chondrites with H/C of 0.29–0.40 (A-881280, A-881334 and Y-793321) have slightly higher O/C ratios of 0.18–0.27, which indicate O incorporation into IOM during the alteration as described in the next section. Although the differences in O/C are small and subject to some uncertainty, such an O/C signature is consistent with the amount of carboxyls, in which the weakly thermally altered chondrites contain more carboxyls (2.8–3.1 mmol $CO_2$/gC) than thermally unaltered ones (1.8–2.4 mmol $CO_2$/gC) and thermally altered ones (B-7904; 2.0 mmol $CO_2$/gC). This co-variation indicates that the amount of carboxyls is an important factor for evaluating O content of IOM, which is supported by a positive correlation ($r^2$ = 0.61) between O/C and COOH amounts (Fig. 3). In addition, lower contents of carboxyls in Murchison, A-881458, and Y-791198 may be linked to the generation of solvent-extractable organic compounds during aqueous alteration, because the generation of solvent-extractable organics in carbonaceous meteorites could occur through aqueous reactions on the parent bodies (e.g., Bunch and Chang 1980).

The amount of carboxyls in IOM has been also estimated by $^{13}$C-NMR studies, in which carboxyls carbon occupies 6.8–7.4% of total carbon for Murchison (Cody et al. 2002). If this amount of carboxyls is applied to this study, stoichiometric calculation indicates carboxyls represent ~70% of total O in IOM, which is much higher than that measured directly in this study for Murchison (~28%). This difference may be attributable to different analytical methods. Or the carboxyls abundance measured in this study could be the minimum value for labile carboxyls, because less labile carboxyls such as phenol-containing carboxyls may not give $CO_2$. Further studies may be required to determine the correct amount of carboxlys in IOM.

## Elemental Changes of IOM During Hydrous Pyrolysis

Preferential loss of H relative to C is observed during pyrolysis without $H_2O$ (Naraoka et al. 2004). This study also confirms that H in IOM is preferentially lost relative to carbon during hydrous pyrolysis, even though much H is provided from environmental water. During the release of pyrolysis products, at least one C-C, C-O, or C-N bond must be cleaved, thus yielding organic radicals (Remusat et al. 2006). Then these radicals could be stabilized by intramolecular aromatization or incorporation of H (chemical reduction) or OH (chemical oxidation) into IOM from water. Because of the decrease in H/C (0.62 to 0.31) during hydrous pyrolysis, aromatization should preferentially occur relative to the H-addition, although the H or OH-addition actually occurs as discussed below. The H/C ratio of residual IOM (0.31–0.41) is comparable to that of A-881280 (0.29), A-881334 (0.34), and Y-793321 (0.36), which are depleted in solvent-extractable organic compounds (e.g. Shimoyama et al. 1989; Naraoka et al. 1999). However, this similarity in H/C does not necessarily indicate the similar degree of aqueous alteration because A-881280 might have been subjected to thermal alteration before hydrous activity (Naraoka et al. 2004). In addition, Y-793321 is highly dehydrated ($H_2O(+)$ = 6.5%; Yanai and Kojima 1995) probably due to the repeated impacts besides thermal metamorphism on the parent body (Nakamura 2006).

Although the preferential loss of N is also observed during thermal alteration (Sephton et al. 2003; Naraoka et al. 2004), N/C changes little in this study probably because of lower temperature. The little change in N/C in this study was consistent with the findings by Naraoka et al. (2004) and Yabuta et al. (2007), who imply that nitrogen mainly resides in the aromatic structure, not in substitutes such as amines or amides (Remusat et al. 2005b).

The O/C ratio increases from 0.22 (original) to 0.46 at 270 °C, and 0.25 at 300 °C, which strongly indicates that water-derived O is incorporated into IOM during hydrous pyrolysis. At higher temperature (330 °C), however, the O/C ratio decreases to 0.10, which is a similar value in O/C of thermally altered chondrites such as B-7904 (0.14) and Y-86720 (0.15; Alexander et al. 2007). Weakly thermally altered chondrites with H/C of 0.29–0.40 have slightly higher

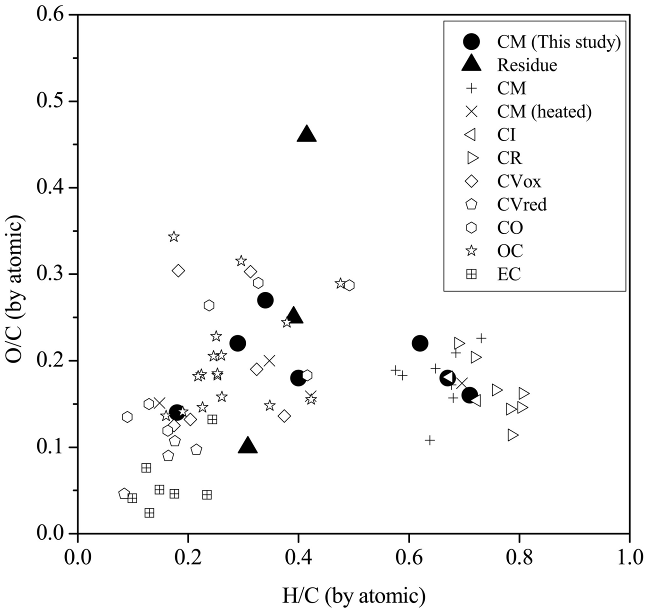

Fig. 4. A H/C-O/C plot of IOMs including Murchison hydrous pyrolysis residues. Filled circle and triangle denote CM and Murchison residues obtained in the present study. Other plots are from Alexander et al. (2007). Abbreviations CVox, CVred, OC, and EC indicate oxidized CV, reduced CV, ordinary chondrite, and enstatite chondrite, respectively.

O/C ratios of 0.18–0.27 (Fig. 4). The variations in H/C-O/C can be compared to those of various IOMs reported by Alexander et al. (2007), as shown in Fig. 4. Considering that some CO and oxidized CV IOMs have relatively higher O/C (~0.3) and lower H/C (< ~ 0.4) ratio compared to those of CMs, O/C-H/C plots of IOMs may have a potential to be an indicator to reflect the degree of chemical oxidation on their meteorite parent bodies. These observations suggest that more primitive (unaltered) IOM is subjected to chemical oxidation at up to ~300 °C under aqueous environments, followed by decarboxylation.

The change of carboxyls in amount is informative to consider this oxidation process. At 270 °C, the carboxyls amount decreases from 2.4 (original) to 1.0 mmol/gC, even though the O/C ratio increases much from 0.22 (original) to 0.46. Under this process, original carboxyl groups are lost from IOM by decarboxylation, while new O-containing groups such as hydroxyl and ketone are produced. This hypothesis is consistent with the carboxyls-O/C plot of Murchison residue at 270 °C in Fig. 3 because the residue does not follow a positive trend obtained from 7 IOMs and other residues. It is also likely that the high O/C of the residue is due to less acetic acid (i.e., O-rich) generation and/or the release of a variety of aromatic compounds during hydrous pyrolysis. Through the progressive chemical oxidation, the carboxyls amount increases again to 1.8 mmol/gC with continuous decarboxylation at 300 °C. Finally, further O-addition stops (O/C = 0.10) due to consumption of active sites (e.g., methylene carbon) with minor amounts of carboxyls (0.6 mmol/gC) at 330 °C. Under these reactions, IOM can release carboxylic acids, being consistent with abundant acetic acid production during hydrous pyrolysis (Oba and Naraoka 2006a).

## $\delta^{13}$C and $\delta$D Variations of IOM from CM2 Chondrites

With a few exceptions, most $\delta^{13}C_{bulk}$ values fall in the narrow range (−15.1 to −13.0‰) including Murchison (−13.0‰), which is more enriched in $^{13}$C by up to 6‰ compared to previous studies of Murchison (~−15‰, Yang and Epstein 1983; ~−19‰, Sephton et al. 2003; Alexander et al. 2007). Because the occurrence of organic matter is isotopically heterogeneous in carbonaceous chondrites, the $\delta^{13}C_{bulk}$ difference may be due to the heterogeneity of samples, and/or the difference of purification and measurement methods for IOM (Pizzarello et al. 2006; Alexander et al. 2007). However, IOM of Y-793321 (−7.6‰) and A-881334 (−9.0‰) is surely more enriched in $^{13}$C by 4–8‰ relative to that of most CM2 chondrites. Such a similar isotope difference is also observed in the carboxyls of IOM. The relatively high $\delta^{13}C_{bulk}$ values (~−8‰) of the Y-793321 group are also found in IOM from CO chondrites and enstatite chondrites (Alexander et al. 2007), the former being considered to have experienced high temperatures at 200–300 °C (Huss et al. 2006) and the latter at least 600–800 °C (Dodd 1981) on their meteorite parent bodies. Although B-7904 is also known to have suffered extensive thermal metamorphism (e.g., Akai 1988; Kojima et al. 1984), the $\delta^{13}C_{bulk}$ of B-7904 is not so high as that of Y-793321 group. The reason why Y-793321 group is enriched in $^{13}$C will be discussed later in more detail.

Intramolecular $\delta^{13}$C measurements demonstrate that carboxyls in IOM are enriched in $^{13}$C with positive delta values (~+3‰; Table 1). Comparing $\delta^{13}C_{COOH}$ with $\delta^{13}$C values of aliphatic side chains (–25 to –5‰; Huang et al. 2007) and $\delta^{13}$C of aromatic carbon in Murchison IOM (–28.8 to –5.8‰; Sephton et al. 1998), this study provides position-specific $\delta^{13}$C distribution in Murchison IOM: carboxyls > aliphatic ≥ aromatic. This $\delta^{13}$C distribution is in contrast to that of acetic acid generated from Murchison IOM through the hydrous pyrolysis, namely, carboxyl group of the generated acetic acid is $^{13}$C-depleted relative to the methyl group (Oba and Naraoka 2006a). This indicates that carboxyl carbon in acetic acid generated from the IOM is not derived from original carboxyls carbon but from oxidation of methylene carbon through a kinetic isotope effect during a hydrous pyrolysis experiment.

The bulk $\delta$D of IOM can be divided into 3 groups: D-enriched group (~+800–900‰: Murchison, Y-791198 and A-881458), intermediate group (~+450‰: B-7904 and A-881280), and D-depleted group (~+130–260‰: Y-793321 and A-881334). The D-enriched group consists of thermally unaltered chondrites, containing abundant solvent-soluble (free) organic compounds such as amino and carboxylic acids (Naraoka et al. 1997, 2004). Both free acids and aliphatic hydrogen of IOM in Murchison are extremely enriched in D up to ~+1300‰ (e.g., Epstein et al. 1987; Remusat et al. 2006; Huang et al. 2007). The other two groups have not only little free acids but also thermally altered signatures with H/C of 0.18–0.40, that is, much less aliphatic group as revealed by NMR study (Yabuta et al. 2005). However, the intermediate group has less H/C ratio (0.18–0.29) than the D-depleted group (0.34–0.40), being inconsistent with the amount of D-enriched aliphatic hydrogen. Hence, the δD of IOM is not dependent only on the degree of alteration.

## $\delta^{13}$C and δD Changes of IOM During Hydrous Pyrolysis

Although the $\delta^{13}C_{bulk}$ value decreases only by a few ‰ during hydrous pyrolysis, the δD value decreases much from +986‰ (original) to +25‰ (330 °C). Such a dramatic decrease cannot be expected under a kinetic control of C-H cleavage, where C-H is preferentially cleft relative to C-D. Preferential C-D cleavage and/or H-D isotope exchange must occur in IOM. Remusat et al. (2006) propose three types of hydrogen in IOM in Orgueil. Type 1 is benzylic H, i.e., H bound to α-carbon of an aromatic ring. Type 2 is non-benzylic aliphatic H. Type 3 is aromatic H. δD for each type of hydrogen is postulated to be +1250, +550, and +150‰ for type 1, 2, and 3, respectively. If the intramolecular δD distribution is applicable to Murchison IOM (up to +1283‰ for alkyl side chains, Huang et al. 2007), the D-enriched aliphatic H could be preferentially removed during hydrous pyrolysis, resulting in lower δD of the pyrolysis residues. This prediction is consistent with the H/C decrease of this study as well as aliphatic C/aromatic C changes (Yabuta et al. 2007) after hydrous pyrolysis. As the thermal alteration proceeds, the elimination of aliphatic group occurs in more cleavable sites such as C-O and C-N or through chemical oxidation of methylene (H/C = 2).

Another mechanism for the δD decreasing is H incorporation into IOM from $H_2O$ and/or H exchange of IOM with $H_2O$, even though this process could be a minor process (Yabuta et al. 2007). This process is highly dependent on the δD of the $H_2O$ source. As the δD value of $H_2O$ used in this study (δD = −75‰ versus VSMOW) is similar to that of hydrous minerals in Murchison (−88‰; Robert 2002), this experiment may simulate the hydrous activity isotopically to lower the δD of the original Murchison IOM (+986‰). Although the hydrous activity is an important process on meteorite parent bodies (e.g., Bunch and Chang 1980), the $H_2O$/IOM ratio and duration of this experiment cannot match the actual conditions. Nevertheless, α-hydrogen of organic compounds is easily exchangeable with ambient hydrogen (Fuller and Huang 2003), and aromatic H also exchanges with ambient $H_2O$ H under acidic conditions (Oba and Naraoka 2003). In addition, free-radical sites of pyrolysis products and residues should be stabilized by H addition (Remusat et al. 2006).

$\delta^{13}C_{COOH}$ of the original Murchison IOM (−2.0‰) decreases by up to 5.3‰ during hydrous pyrolysis. This $\delta^{13}$C decrease could be derived from a preferential release of $^{13}$C-enriched carboxyls and/or transformation of methylene carbon depleted in $^{13}$C to carboxyls through chemical oxidation during hydrous pyrolysis.

## $\delta^{13}$C-δD Relationship of IOM

As shown in Fig. 1, the data points of A-881458, Y-791198, B-7904, and A-881280 seem to make an isotopic sequence along the dashed line. This isotopic sequence implies that these five meteorites have originally a similar isotopic composition, and different degrees of hydrothermal alteration could have caused the different degree of $^{13}$C- and D-depletion. In contrast, the $\delta^{13}C_{buk}$-δD of A-881334 and Y-793321 do not lie nearby the isotopic sequence, being located at the high $\delta^{13}$C (~−8‰) and low δD (~+200‰) region. On the basis of $\delta^{13}C_{bulk}$-δD plot, CM chondrites used in this study are also distinguished into two groups: Murchison group and Y-793321 group. One of the possible explanations for the isotopic distribution of the Y-793321 group is that they may contain more of an extreme isotopic component such as carbides (e.g. $\delta^{13}$C ~ +1100‰; Zinner 1998; Sephton et al. 1998) than other groups. Stepwise combustion of Murchison IOM reveals that $\delta^{13}$C and δD decrease from −12.4‰ and ~+1200‰ down to −18.6‰ and ~+470‰, respectively, with increasing temperature until at 420 °C, followed by the extreme $\delta^{13}$C increase up to +220‰ and monotonic δD decrease down to ~+350‰ at higher temperature (Kerridge et al. 1987). This means that IOM suffering high temperature would lose parts of $^{13}$C-poor and D-rich phases. However, H/C of the Y-793321 group (~0.35) is not indicative of their extensive thermal alteration histories (Naraoka et al. 2004), which makes the case of the contribution from carbide less likely. In addition, not only bulk IOM but also intramolecular carboxyls are enriched in $^{13}$C for the Y-793321 group. Since the $\delta^{13}C_{COOH}$ should not be affected by such an extreme isotopic phase, the isotope distribution suggests that IOM of the Y-793321 group may be intrinsically different from that of the Murchison group.

A cross-plot of $\delta^{13}C_{bulk}$-$\delta^{13}C_{COOH}$ of IOMs including Murchison residues is shown in Fig. 5. An apparent positive correlation between $\delta^{13}C_{bulk}$ and $\delta^{13}C_{COOH}$ ($r^2$ = 0.93) could imply that these 7 IOMs may have experienced a similar oxidation process to produce the carboxyls. It should be noted that both $\delta^{13}C_{bulk}$ and $\delta^{13}C_{COOH}$ for Murchison IOM decrease after hydrous pyrolysis (Fig. 3). On the other hand, thermally more altered Y-793321 group is more $^{13}$C-enriched than thermally unaltered Murchison group, contradicting the isotope fractionations during hydrothermal alteration of this study.

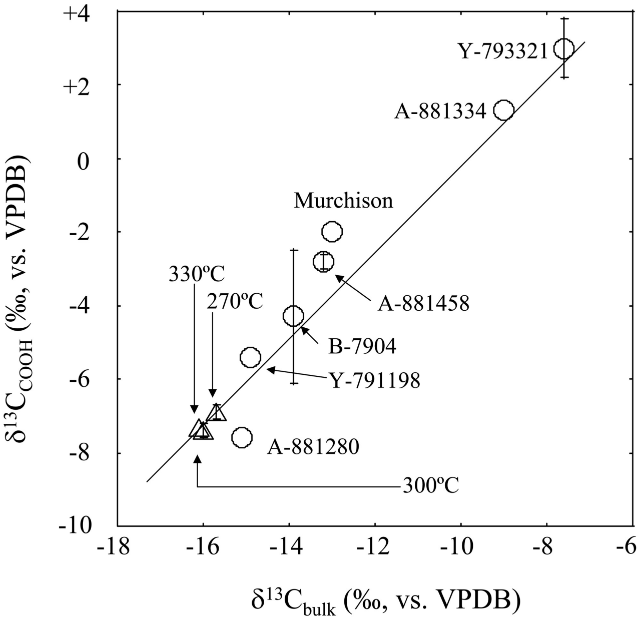

Fig. 5. A $\delta^{13}C_{COOH}$-$\delta^{13}C_{bulk}$ plot of IOMs including Murchison hydrous pyrolysis residues. Open triangles denote Murchison residues. Solid lines indicates a positive correlation ($r^2 = 0.93$) between $\delta^{13}C_{bulk}$ and $\delta^{13}C_{COOH}$ of 7 IOMs.

If distinct elemental and isotopic distributions are originated from a common IOM precursor, various mechanisms besides thermal and aqueous alterations should be inferred. As described above, Y-793321 is dehydrated probably due to repeated impacts on the parent body (Nakamura 2006). Such an impact process may induce different behavior of isotope fractionation, although A-881334 contains the appropriate amounts of $H_2O$ as a CM chondrite (13.9 wt%, Yanai and Kojima 1995). An alternative explanation is that IOM was already isotopically different between Murchison and Y-793321 groups when their parent bodies formed. This is consistent with an assumption that if IOM is solar, IOM that formed at different radial distance and times is likely to have different isotopic compositions (Alexander et al. 2007). Further studies are planned to investigate isotope fractionation mechanisms of IOM for various processes (impact, photolysis, etc.).

## SUMMARY

Bulk carbon ($\delta^{13}C_{bulk}$) and hydrogen (δD) as well as carboxyl carbon ($\delta^{13}C_{COOH}$) isotopic compositions have been determined for insoluble macromolecular organic matter (IOM) from seven CM chondrites and the hydrous pyrolysis residues of Murchison IOM. $\delta^{13}C_{bulk}$, $\delta^{13}C_{COOH}$, and δD of the seven CM IOMs distribute characteristically from −15.1 to −7.6‰, −7.6 to +3.0‰, and +133 to +986‰, respectively.

The H/C ratio of Murchison IOM changes from 0.62 to 0.41, 0.39, and 0.31 after hydrous pyrolysis at 270, 300, and 330°C, respectively. $\delta^{13}C_{bulk}$, $\delta^{13}C_{COOH}$, and δD of Murchison IOM also decrease after hydrous pyrolysis by up to 3.5‰, 5.5‰, and 961‰, respectively. These results suggest that preferential losses of $^{13}C$ and D within IOM could occur during hydrous activity on the meteorite parent bodies. The O/C ratio increases from 0.22 to 0.46 at 270 °C, and 0.25 at 300 °C, and decreases to 0.10 at 330 °C. The O/C variation indicates that both decarboxylation and oxygen incorporation from $H_2O$ progressively occur during hydrous pyrolysis.

The $\delta^{13}C_{bulk}$ and δD variations are shown for Murchison IOM and its residues after experimental hydrothermal alteration. A-881458, Y-791198, B-7904, and A-881280 lie on or near the isotopic sequences on the $\delta^{13}C_{bulk}$-δD plot. $\delta^{13}C_{COOH}$-$\delta^{13}C_{bulk}$ plots of the IOMs show a positive correlation, implying a similar oxidation process to produce carboxyls for 7 CM chondrites. However, A-881334 and Y-793321 cannot simply be explained isotopically by the hydrothermal isotope fractionation. If CM IOMs originate from a common precursor, the distinct carbon and hydrogen isotopic compositions of IOM from A-881334 and Y-793321 require other fractionation mechanism(s), or some isotopic heterogeneity in solar nebula before the formation of parent bodies. This study indicates that both difference of original isotopic compositions and degree of alteration on meteorite parent bodies could contribute to the elemental and isotopic distributions of IOM.

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