Solid-state $^{13}$C NMR characterization of insoluble organic matter from Antarctic CM2 chondrites: Evaluation of the meteoritic alteration level

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Abstract—Chemical structures of the insoluble organic matter (IOM) from the Antarctic CM2 chondrites (Yamato [Y-] 791198, 793321; Belgica [B-] 7904; Asuka [A-] 881280, 881334) and the Murchison meteorite were analyzed by solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. Different types of carbons were characterized, such as aliphatic carbon (Ali-C), aliphatic carbon linked to hetero atom (Hetero-Ali-C), aromatic carbon (Aro-C), carboxyls (COOR), and carbonyls (C=O). The spectra of the IOM from Murchison and Y-791198 showed two major peaks: Ali-C and Aro-C, while the spectra from the other meteorites showed only one major peak of Aro-C. Carbon distribution was determined both by manual integration and deconvolution. For most IOM, the Aro-C was the most abundant (49.8–67.8%) of all carbon types. When the ratios of Ali-C to Aro-C (Ali/Aro) were plotted with the atomic hydrogen to carbon ratio (H/C), a correlation was observed. If we use the H/C as a parameter for the thermal alteration event on the meteorite parent body, this result shows a different extent of thermal alteration. In addition, IOM with a lower Ali/Aro showed a lower ratio of Ali-C to COOR plus C=O (Ali / (COOR + C=O)). This result suggests that the ratio of CO moieties to aliphatic carbon in IOM might reflect chemical oxidation that was involved in hydrothermal alteration.

INTRODUCTION

Carbonaceous chondrites retain volatile elements that record the history of their chemical evolution in the universe. The chondrites also contain a significant amount of organics, most of which (70–99%) are complex macromolecular matter that is insoluble in water, acids, or any organic solvent, and is thus defined as insoluble organic matter (IOM). A number of investigations have indicated that IOM is structurally uncharacterized and isotopically heterogeneous (see Sephton et al. 2002 for a recent review). The chemical structures of IOM have been investigated by chemical degradation (Hayatsu et al. 1977, 1980), various pyrolytic experiments (Komiya et al. 1993; Sephton et al. 1998a, 1998b, 2000, 2003, 2004; Kitajima et al. 2002), solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy (Cronin et al. 1987; Gardinier et al. 2000; Cody et al. 2002), Allende (CV) (Cronin et al. 1987), Orgueil (CI) (Cronin et al. 1987; Gardinier et al. 2000; Cody and Alexander 2005), Tagish Lake (C2) (Pizzarello et al. 2001; Cody and Alexander 2005), and Elephant Moraine (EET) 92042 (CR2) (Cody and Alexander 2005). The origin and history of IOM are still being discussed. The similarity of chemical compositions between IOM and interstellar organic matter (Ehrenfreund et al. 1991) and significant excesses of D and $^{15}$N in IOM (e.g., Kerridge et al. 1987; Alexander et al. 1998) indicate that IOM was possibly
formed in the interstellar environment and afterward experienced thermal metamorphism and/or aqueous alteration on the meteorite parent body. The chemical constituents of IOM could have been affected by those events. Komiya et al. (1993) performed laboratory heating experiments with IOM from several CM2 chondrites and revealed that IOM from some chondrites possessed the thermally labile organic fraction and that those from the other chondrites did not; this may be related to meteoritic alteration events. Sephton et al. (1998a, 1998b, 2000) carried out hydrous (H2O-) pyrolysis of IOM considering hydrous activity on the meteorite parent body and identified a variety of polycyclic aromatic hydrocarbons (PAHs) with their carbon isotopic compositions. Recently, they applied a new advanced technique, hydro- (H2-) pyrolysis, for the further characterization of IOM (Sephton et al. 2004). Kitajima et al. (2002) used pyrolysis-gas chromatography coupled with mass spectrometry (pyr-GC/MS) to analyze the pyrolyzates of IOM from CM chondrites and determined their degrees of graphitization during thermal metamorphism. Naraoka et al. (2004) proposed an organic parameter of thermal alteration of IOM using solid-state 13C-NMR spectroscopy. The chemical structures of IOM could be related to alteration event. Carbon, H, and N contents in the IOM were determined using a CHN analyzer (Peklin Elmer 240 or Carlo Erba EA-1180). The results of the elemental analysis are summarized in Table 1, including information on C and H2O (+) contents and extractable organic compounds in bulk samples.

**Elemental Analyses**

Carbon, H, and N contents in the IOM were determined using a CHN analyzer (Peklin Elmer 240 or Carlo Erba EA-1180). The results of the elemental analysis are summarized in Table 1, including information on C and H2O (+) contents and extractable organic compounds in bulk samples.

**Solid-State 13C NMR**

Solid-state 13C-NMR spectra were obtained on a Chemagnetics CMX-300 spectrometer at a field strength corresponding to 75.6 MHz for 13C and 300.5 MHz for 1H. Each sample was packed into a zirconium rotor 5 mm in diameter and spun at the magic angle (54° 44'). The cross polarization (CP) and magic angle spinning (MAS) method was applied in order to obtain spectra with a higher signal to noise ratio in a short period. To accomplish effective CP transfer and reduce the exhibition of spinning side bands (SSB) that could interfere other peaks, the variable amplitude cross polarization (VACP) experiment with MAS was applied with a contact time of 1 msec, a spinning speed of 10 kHz, a pulse delay of 4 sec, and a 90° 1H pulse width of 4 μsec. The contact time was determined by our previous study, which has conducted variable contact time experiments in a range of 0.1–5 msec for coals and several organic standards such as hexamethylbenzene, glyicine, polystyrene, poly-(methyl methacrylate), and poly-2-vinylpyrrolidene. It has been confirmed that the signal intensities were maximum and the relative proportions of functional groups were correctly obtained for each sample around at 1 msec. The acquisitions on each sample were performed in the range of 2172–84107 (Table 1), depending on the strength of the signal. The spectral peaks were identified and integrated in two methods: manual integration and deconvolution. Manual integration was applied for the following ranges (Kidena et al. 1996): 0–60 ppm (aliphatic carbon; Ali-C), 60–80 ppm (aliphatic carbon linked to hetero atom (O and/or N); Hetero-Ali-C), 80–150 ppm (aromatic carbon; Aro-C), 150–180 ppm (carboxyls; COOR, R=H and/or alkyl group), and 180–200 ppm (carbons; C=O). Deconvolution was performed on the basis of Gardinier et al. (2000) and Cody et al. (2002). The Gaussian peak heights and widths were carefully adjusted so that the spectrum combining those peaks could fit the original spectrum for all the samples.

**MATERIAL AND METHODS**

**Samples**

Five Antarctic CM2 chondrites (Yamato [Y-] 791198 and 793321, Belgica Mountains [B-] 7904, and Asuka [A-] 881280 and 881334) and the Murchison meteorite were analyzed. The Antarctic meteorites were collected by the Japanese Antarctic Research Expeditions and were classified mineralogically by Yanai and Kojima (1995).

**Preparation of IOM**

Each powdered meteorite sample (1.0–2.6 g) that had previously been extracted with boiling water and organic solvent was rinsed with 6 M HCl at room temperature for 12 hr. The extracted residue was shaken with 8 M HF/3 M HCl in a Teflon container at room temperature to 70 °C for more than 48 hr, followed by washing with 6 M HCl. This process was repeated several times. The demineralized residue was washed with water, methanol, dichloromethane, hexane, and CS2, in that order, and was dried under vacuum.

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Table 1. Sample weights, C, H, and N contents, and NMR acquisition numbers for the IOM, C, and H₂O (+) contents in bulk samples, and characteristics on soluble organic compounds from the Antarctic CM2 chondrites and Murchison meteorite.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight (mg)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>H/C</th>
<th>N/C</th>
<th>¹³C NMR acquisition number</th>
<th>C⁺ (%)</th>
<th>H₂O (+) (%)</th>
<th>Soluble organic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-791198</td>
<td>28.9</td>
<td>57.6</td>
<td>3.20</td>
<td>3.20</td>
<td>0.67</td>
<td>0.037</td>
<td>28200</td>
<td>2.29</td>
<td>12.8</td>
<td>Abundant</td>
</tr>
<tr>
<td>Y-793321</td>
<td>34.7</td>
<td>64.2</td>
<td>1.90</td>
<td>1.90</td>
<td>0.36</td>
<td>0.039</td>
<td>24880</td>
<td>1.68</td>
<td>6.5</td>
<td>Depleted</td>
</tr>
<tr>
<td>B-7904</td>
<td>17.8</td>
<td>64.3</td>
<td>0.79</td>
<td>0.79</td>
<td>0.15</td>
<td>0.029</td>
<td>63400</td>
<td>1.13</td>
<td>2.1</td>
<td>Depleted</td>
</tr>
<tr>
<td>A-881280</td>
<td>34.0</td>
<td>63.7</td>
<td>1.53</td>
<td>2.75</td>
<td>0.29</td>
<td>0.037</td>
<td>21726</td>
<td>2.46</td>
<td>17.6</td>
<td>Depleted</td>
</tr>
<tr>
<td>A-881334</td>
<td>17.6</td>
<td>47.6</td>
<td>1.37</td>
<td>2.17</td>
<td>0.34</td>
<td>0.039</td>
<td>84107</td>
<td>1.49</td>
<td>n.d.</td>
<td>Depleted</td>
</tr>
<tr>
<td>Murchison</td>
<td>33.0</td>
<td>56.9</td>
<td>3.30</td>
<td>2.60</td>
<td>0.70</td>
<td>0.039</td>
<td>25265</td>
<td>1.6–2.5</td>
<td>n.d.</td>
<td>Abundant</td>
</tr>
</tbody>
</table>

³Naraoka et al. (1997); Kerridge (1985).

RESULTS AND DISCUSSION

Structural Characterization

The CP/MAS ¹³C-NMR spectra of the IOM of five Antarctic chondrites and Murchison meteorite are shown in Fig. 1. The spectra of Murchison showed two major signals of Aro-C at 130 ppm and Ali-C at 30 ppm. The peak of Aro-C includes protonated (~100 to ~130 ppm), non-protonated (~130 to ~150 ppm), phenolic, and methoxyl substituted aromatic carbons (~145 to ~160 ppm). The peak of Ali-C is due to methylene (CH₂) and CH₃ groups. The width at the range of 60–80 ppm corresponds to Hetero-Ali-C. The shoulders at the ranges of 150–180 ppm and 180–200 ppm indicate the presence of COOR and C=O, respectively. The ranges of ~20–0 and 200–250 ppm are SSBs derived from the signal of Aro-C. This identification result is very similar to those of Cronin et al. (1987), Gardinier et al. (2000), and Cody et al. (2002). The spectrum of Y-791198 is very similar to that of Murchison and each type of carbon was identified as well. The signals of CH₂ and CH₃ are separated a little more clearly than those of Murchison. On the other hand, the spectra of Y-793321 and A-881280 show one sharp signal of Aro-C and are very similar to each other. The total signal of Ali-C, including shoulders and their widths, are depleted in these spectra compared to those of Murchison and Y-791198. A-881334 shows an intermediate spectrum between Murchison type and Y-793321 type. The intensity of the spectra of B-7904 is very weak. The weak spectra of B-7904 occurs possibly because the sample amounts were low (17.8 mg) and/or because these samples contained predominant aromatic carbon non-detectable by CP/MAS, such as quaternary carbon atoms distant from ¹H in the condensed aromatic structure. Nevertheless, the broad peaks of Aro-C for the samples arose at 130 ppm by taking longer acquisition time. Considering the low signal to noise ratio of this spectrum, their baselines were adjusted manually for precise quantification.

Carbon Functional Group Distribution

Figures 2a and 2b show the relative abundances of different types of carbons in the IOM of Antarctic chondrites and the Murchison meteorite, which were estimated by manual integration (Fig. 2a) and deconvolution with Gaussian peaks (Fig. 2b) for the ¹³C-NMR spectra of the IOM. In Fig. 2a, variations of percentages of Ali-C, Hetero-Ali-C, Aro-C, COOR, and C=O for those samples were in a range of 8.2–27.6, 2.8–7.9, 49.8–67.8, 11.2–22.2, and 2.4–6.6%, respectively. For all the IOM samples, the relative abundance of Aro-C was higher than any other carbon type, supporting prior investigations that have indicated a highly aromatic nature of meteoritic IOM (e.g., Hayatsu et al. 1977; Sephton et al. 2000). The relative abundance of Aro-C is also referred to the aromaticity factor (fₐ) when the relative abundance of Aro-C is 100%, fₐ is equal to 1). In this study, the fₐ of Murchison IOM was 0.50, a value that is similar to those reported by Cronin et al. (1987) and Gardinier et al. (2000) (~0.40 and 0.52, respectively). It has been suggested that the aromaticity factor may depend on the contact time for the CP/MAS method. Cronin et al. (1987) applied a contact time of 1 msec. Gardinier et al. (2000) indicated the f₂ value via variable contact time experiments and fitting of the variation of intensity with contact time for each type of carbon. Cody et al. (2002) revealed that a contact time of 4.5 msec is needed for a complete magnetization transfer to the aromatic carbon by variable contact time experiments. They reported an f₂ between 0.61 and 0.66 for Murchison. Using the longer contact time, the intensity of spectra of B-7904 in this study (Fig. 1) might be increased. On the other hand, Derenne et al. (2003) showed that even much longer contact time (9.6 msec) could not hold for Orgueil IOM and suggested that only single pulse (SP) spectra could lead to quantitative data on polyaromatic macromolecules like IOM. Cody and Alexander (2005) also presented the quantitative data from both of VACP-MAS and SP-MAS NMR spectra of IOM from Murchison, Orgueil, Tagish Lake, and EET 92042,
Fig. 1. Solid-state CP/MAS $^{13}$C NMR spectra of the insoluble organic matter of the Antarctic CM2 chondrites and the Murchison meteorite. The spectra were identified for the following ranges: 0–60 ppm (aliphatic carbon; Ali-C), 60–80 ppm (aliphatic carbon linked to hetero atom [O and/or N]; Hetero-Ali-C), 80–150 ppm (aromatic carbon; Aro-C), 150–180 ppm (carboxyls; COOR, $R=H$ and/or alkyl group), and 180–200 ppm (carbonyls; C=O). The ranges of −20–0 and 200–250 ppm were spinning side bands (*) derived from the signal of Aro-C.
and described that the differences observed between the two methods derived aromaticities likely reflected preferential signal enhancement of protonated organic compounds in VACP, rather than due to SP detecting additional nonprotonated aromatic moieties. They concluded that the two methods cannot be compared to indicate significant quantities of large polyaromatic moieties in IOM. In this study, we did not use SP consciously, since our sample amounts (Table 1) could be unsuitable for the method involving low signal to noise caused from signal limitation by the $^{13}$C spin lattice relaxation. In addition, an enormously long time would be needed for the $^{13}$C spin lattice relaxation in the SP experiment and an even longer time for low amounts of the sample. Here, the most important thing is that a consistent contact time is chosen as described in methods. Even if an artificially low estimate of $f_a$ occurred at the contact time of 1 msec, the $f_a$ values and ratios of aliphatic to aromatic carbons determined for each IOM still enable a relative comparison among meteorites and they do not change the conclusions in this study. The $f_a$ value of the IOM of Y-791198 (0.50) showed similar levels to that of Murchison. Those of Y-793321 (0.68), A-881280 (0.65), A-881334 (0.57), and B-7904 (0.62) were $\sim$10–20% higher than those of Murchison and Y-791198. Of the relative

Fig. 2. Relative abundances of different functional groups of carbons in the insoluble organic matter of the Antarctic CM2 chondrites and the Murchison meteorite derived in (a) manual integration and (b) deconvolution with Gaussian peaks for solid-state $^{13}$C-NMR spectra of IOM. The percentage of aliphatic carbon (Ali-C) is shown as white, aliphatic carbon linked to hetero atom (Hetero-Ali-C) is shown as shaded, aromatic carbon (Aro-C) is shown as black, carboxyls (COOR) are shown as cross-hatching, and carbonyl (C=O) is shown as light gray.
abundances of Ali-C, the second highest were for Murchison (27.6%) and Y-791198 (21.9%). Those of Y-793321, A-881280, and A-881334 were ~10 ± 2%. The relative abundances of Hetero-Aro-C, COOR, and C=O showed nearly the same values respectively for all the samples. In Fig. 2b, percentage variations of Ali-C, Hetero-Ali-C, Aro-C, COOR, and C=O for the same samples were 3.5–25.1, 2.1–27.1, 47.4–61.2, 8.1–23.2, and 0–8.6%, respectively. The results were roughly similar to those in Fig. 2a. However, deconvolution might have brought some errors, particularly to weak spectra of IOM of B-7904 and a minor signal of Hetero-Ali-C. The relative abundances of some carbons in such spectra and signal were likely overestimated compared to those by manual integration. For example, the relative abundances of Hetero-Ali-C were estimated very high in B-7904 (27.1%), which brought very low abundances of Ali-C (3.7%). In such cases, manual integration could be more reliable.

**Carbon Functional Group Distributions of IOM and Alteration Event on the Meteorite Parent Body**

Naraoka et al. (2004) showed a changing sequence of the hydrogen to carbon (H/C) and nitrogen to carbon (N/C) ratios by heating the IOM of several CM2 chondrites. In particular, the H/C decreased significantly, from ~0.7 to ~0.3, after heating the IOM up to 800°C. They suggested that hydrogen could have been lost from the IOM during thermal events on meteorite parent bodies and proposed the chemical sequence as a new parameter for the thermal alteration extent of carbonaceous chondrites. According to this hypothesis, the H/C could reflect the IOM chemical structures consisting of different carbon types.

In this study, the ratio of aliphatic carbon to aromatic carbon in each IOM, Ali/Aro, was obtained from the NMR spectra and is shown in Fig. 3 to investigate the relationships with H/C for each IOM. The Ali/Aro ratios which are derived both in manual integration and deconvolution (as reflected by error bars) showed similar values in most of IOM. As expected, a correlation was observed between Ali/Aro ratios and H/C values. This relationship indicates that the H/C variation reflects the distributions of aliphatic and aromatic carbons in IOM. Therefore, it can be suggested that Ali/Aro of IOM shows different extents of thermal alteration on the meteorite parent body as well as H/C; lower Ali/Aro (lower H/C) implies higher alteration levels. Based on these results, the order of alteration level is shown as follows (weak < intense): Murchison (Ali/Aro = 0.46–0.55) ~ Y-791198 (0.37–0.44) < Y-793321 (0.17–0.19) ~ A-881334 (0.16–0.19) ~ A-881280 (0.15–0.16) < B-7904 (0.06–0.13) (the ranges count the values derived both in manual integration and deconvolution). This order was similar to those estimated by the other methods such as Si-Mg-Fe ratios of chondrules and matrixes (Kojima et al. 1984), phyllosilicate analyses (Akai 1990, 1992; Akai and Tari 1997; Lipschutz et al. 1999), and pyrolysis of IOM (Shimoyama et al. 1991; Kitajima et al. 2002).

Figure 3 shows that the aliphatic structures of the IOM could be modified in some way during thermal alteration, by being aromatized, graphitized, or lost. Wdowiak et al. (1988) heated Orgueil IOM under vacuum at different temperatures and found that new weak aromatic features appeared along with the decrease of the aliphatic content by infrared spectroscopy. They argued that the aliphatic components were removed by C-C bond cracking and that aromatic ones were formed by heating. A study by Kitajima et al. (2002) on pyrGC/MS used a model in which labile portions in IOM were released and primary large polyaromatic moieties remained as graphite sheet during thermal alteration. Recently, Cody and Alexander (2005) compared 13C NMR spectra of IOM belonging to different meteorite classes (CR, CI1, CM2, and C2) and clearly showed that the progressive loss of intensity in aliphatic moieties was compensated for by increases in aromatic carbon and carboxyl carbon. They pointed out that the conversion of aliphatic moieties to aromatic ones would be unlikely during the low temperature hydrothermal alteration, and suggested that the final modifications from low to moderate temperatures involving chemical oxidation during aqueous alteration on the parent body resulted in partial conversion of aliphatic carbons (including carbons bound with hetero atoms) to CO moieties (COOR and C=O).

In order to examine their hypothesis, the ratio of Ali-C to the sum of COOR and C=O, Ali/(COOR + C=O), was obtained from the NMR spectra and is shown in Fig. 4 to investigate the relationship with Ali/Aro for each IOM. Both ratios are derived both in manual integration and deconvolution (as reflected by error bars). A rough correlation was seen between the two ratios, indicating that the ratio of CO moieties to aliphatic carbon was abundant in highly altered IOM. According to the values of Ali/(COOR + C=O), the order of alteration level is shown as follows (weak < intense): Murchison (1.37–1.67) < Y-791198 (0.56–0.92) ~ Y-793321 (0.52–0.93) < A-881280 (0.50–0.55) ~ A-881334 (0.31) ~ B-7904 (0.37–0.43) (the ranges count the values derived both in manual integration and deconvolution). This order was similar to those estimated by Fig. 3. Based on the discussion by Cody and Alexander (2005) and on Fig. 4, thermal alteration might result in chemical oxidation in addition to hydrothermal alteration. Remusat et al. (2005) suggested that the oxygen contents in IOM reflected oxidation levels of the meteoritic organic matter upon the hydrothermal event, which also supports the interpretation in this study. Note that the plot of Y-793321 was located between Murchison (and Y-791198) and A-881334 (A-881280 and B-7904) in Fig. 4. It is known that Y-793321 is classified to the weakly (moderate) altered CM2 chondrites by several investigations described above. Figure 4 appears to
Insoluble organic matter from Antarctic CM2 chondrites

show that Y-793321 experienced relatively intense thermal alteration, but also slight degrees of chemical oxidation during hydrous activity in its parent body. Also, Y-793321 has been known to have heterogeneity due to its solar–noble gas enrichment and impact features (Nakamura et al. 2000) and a variety of clasts exhibiting different degrees of aqueous alteration (Tonui et al. 2002).

Naraoka et al. (2004) have shown that the chondrites with higher H/C (Murchison and Y-791198) contain a variety of soluble organic molecules, but that those with lower H/C (Y-793321, A-881281, A-881334, and B-7904) do not (Table 1). They assumed that the thermally altered chondrites lost their soluble organic compounds. Many have considered that some of the soluble organic compounds may have been produced by aqueous alteration of IOM (Bunch and Chang 1980; Cronin and Chang 1993; Sephton et al. 1998). Moreover, Cody and Alexander (2005) suggested that the progressive oxidation of IOM preferentially targeted the aliphatic carbon and led hydroxylation to yield water-soluble organic compounds such as carboxylic acids. As we can see from Figs. 3 and 4 in this study, the modification of aliphatic carbon of IOM is likely related to the presence or formation of soluble organic compounds in the CM2 chondrites. However, the chondrites with lower Ali/Aro and Ali/(COOR + C=O) values (Y-793321, A-881281, A-881334, and B-7904) do not contain soluble organic compounds. Possible explanations are that thermal alteration after the aqueous alteration could have lost such compounds, or that long duration with hydrous activity may lose them (Naraoka et al. 1997).

CONCLUSIONS

For structural classification of IOM belonging to the same meteorite classes, solid-state $^{13}$C-NMR analyses were performed for IOM from five Antarctic CM2 chondrites and the Murchison meteorite. Five carbon types, Ali-C, Hetero-Ali-C, Aro-C, COOR, and C=O, were identified for each IOM. Their relative abundances varied among the IOM: 8.2–27.6% (Ali-C), 2.8–7.9% (Hetero-Ali-C), 49.8–67.8% (Aro-C), 11.2–22.2% (COOR), and 2.4–6.6% (C=O). Ali/Aro showed a correlation with H/C that is related to the thermal alteration event on the meteorite parent body. Also, lower Ali/Aro (highly altered IOM) included lower Ali/(COOR + C=O), which could support the hypothesis of the partial conversion of aliphatic carbons to CO moieties during hydrothermal alteration. This study showed that the chemical structures of the IOM could be related to the alteration level of the meteorites. In particular, modification of aliphatic carbon of IOM during the alteration events was likely related to formation of soluble organic compounds in the carbonaceous chondrites. Further studies are necessary to elucidate relationships between IOM constituents and soluble organic compounds.

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