The insoluble carbonaceous material of CM chondrites: 
A possible source of discrete organic compounds under hydrothermal conditions

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Abstract—We report on the molecular analyses of the water- and solvent-soluble organic compounds released from the insoluble organic material (IOM) of the Murray meteorite upon treatment with weight-equivalent amounts of water and under conditions of elevated temperature and pressure. A varied suite of compounds was identified by gas chromatography–mass spectrometry (GC-MS). C3-C17 alkyl dicarboxylic acids and N- and O-containing hydroaromatic and aromatic compounds were found in the water extracts. The solvent extracts contained N-, O-, and S-containing aromatic compounds, a large number of their isomers and homologs, and a series of polycyclic aromatic hydrocarbons (PAHs) of up to five rings, together with noncondensed aromatic species such as substituted benzenes, biphenyl, and terphenyls as well as their substituted homologs, and hydrated PAHs. Isotopic analyses showed that residue IOMs after hydrothermal treatment had lower deuterium and 15N content than the untreated material (ΔD = −833‰ and Δ15N = −24.1) but did not differ from it in 13C composition. The effect of the hydrothermolytic release was recorded in significant differences between the NMR spectra of untreated and residue IOM. A possible relation to common precursors for the dicarboxylic acids found in the IOM and bulk extracts is discussed.

INTRODUCTION

The larger portion of the organic carbon in carbonaceous chondrites (70–99% of the total) is present as a complex and heterogeneous macromolecular material whose structure and molecular composition are not yet known in detail. In broad terms, the plausible structure we can postulate for this insoluble organic material (IOM) from spectroscopic and decomposition analyses is that of condensed aromatic, hydroaromatic, and heteroaromatic macromolecules that contain alkyl branching, functional groups such as OH and COOH, and are bridged by alkyl chains, ether, and sulfide linkages, as first proposed by Hayatsu et al. in 1977 (see Pizzarello et al. 2006 for a review).

Additional details have been attained for IOM aromatic and alkyl constituents. 1H and 13C nuclear magnetic resonance (NMR) spectroscopic studies have indicated that the aromatic component mainly comprises rather small (smaller than C24 coronene) and highly substituted ring aggregates (Gardinier et al. 2000; Cody et al. 2002; Cody and Alexander 2005), where larger unprotonated structures make up, at most, only 10% of total aromatics (Cody et al. 2002). This general outline seems confirmed by the analyses of the solvent-soluble compounds released from the IOM via hydrous-pyrolysis (Sephton et al. 2002 and references therein) and hydro-pyrolysis (Sephton et al. 2004), where the major decomposition products consisted of either small aromatic units such as benzene, C1-C4 alkylbenzenes, naphthalene, and C1 alkyl naphthalenes (in the case of hydrous pyrolysis), or of polycyclic aromatic compounds from phenanthrene to coronene in various degree of alklylation. These pyrolytic processes expose the IOM to liquid water or constant flow of H2 at high temperature and pressure in the presence of a catalyst; they lead to the nonoxidative cleavage of a substantial percent of the material (35% and up to 85%, respectively) and allow the plausible inference that compounds directly comparable to the pyrolytic products were part of the IOM structure.

By studying the carbon isotopic differences between soluble, pyrolysable, and residual material, Sephton et al.
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(1998) postulated that the carbonaceous chondrite’s macromolecular carbon comprises at least two components: a more labile portion which can be solubilized from the IOM under pyrolytic conditions (and presumably may have generated soluble compounds in the meteorite’s parent body under comparable exposure to temperature and pressure), and a refractory material. Although the authors’ findings related expressly to the aromatic compounds, this hypothesis of diverse IOM phases agrees with isotopic data (Kerridge et al. 1987) that showed a two-temperature release of carbonaceous components from the IOM (at ~250–350 °C and over 400 °C, respectively) where the more labile phase was enriched in deuterium (δD ≥ +1165‰). The δ15N values measured by step combustion of several carbonaceous chondrite IOMs (Alexander et al. 1998) also showed a two-component distribution for this element up to 500 °C, with a third component of heavier nitrogen (δ15N ≥ +260‰) released above that temperature. The finding was later expanded by Sepphton et al. (2003) and would indicate that the make-up of the IOM residue left after hydrous pyrolysis is itself heterogeneous.

The molecular structure of the IOM alkyl component has also been the focus of recent analyses. Remusat et al. (2005) treated Orgueil and Murchison IOM with ruthenium tetroxide, a selective oxidant for aromatic units, and analyzed the alkyl compounds left from the aromatic decomposition. They found relatively short aliphatic di-acids and tri-acids and interpreted the result as an indication that alkyl links in the IOM are short and substituted. This work was significantly expanded by Huang et al. (2006), who were able to analyze the monocarboxylic acids produced by the same treatment and described a large suite of the acids that are highly branched and range from C2-C10. The latter finding demonstrates that a considerable portion of the IOM alkyl component consists of free branching of significant chain length and complexity.

In spite of much progress, to date some major questions remain unanswered as to the detailed composition of the IOM, its overall origin, and the kind of relationship, if any, existing between the insoluble material and the soluble compounds of meteorites. For example, we do not know whether the IOM consists of one or more molecular domains. Microscopic observations have already shown that individual globular entities are embedded in chondritic IOM (e.g., Garvie and Buseck 2004 and references therein). Are there other distinct molecular phases in the core IOM structure? Other questions include the contribution that the IOM might have made to soluble organic compounds within various meteorites or on the early Earth and, were such exogenous delivery significant, whether it also could have been relevant to prebiotic chemical evolution. Oba and Naraoka (2006) have addressed these questions in part by analyzing the monocarboxylic acids produced by hydropyrolytic treatment of Murchison IOM, as well as their carbon isotopic composition. They found that, under such conditions, a suite of C2 to C5 acids is produced; the predominant component is acetic acid that is present at a concentration four times higher and with a different 13C composition than the acetic acid in the water extracts of whole meteorite powders.

We report here on more general molecular analyses of the water- and solvent-soluble organic compounds released from the IOM under conditions of elevated temperature and pressure in water. These conditions were selected to be in a range where diagenesis of clays is known to ensue in nature, and to plausibly mimic within laboratory time scales the hydrothermal activity in asteroidal parent bodies (e.g., Zolensky et al. 1997) and the early Earth (e.g., Kelley et al. 2002). The overall effect of this treatment on the IOM powders was also recorded by NMR to allow for a comparison of spectral features with molecular distribution.

**MATERIALS AND METHODS**

**Sample Preparation**

The Murray sample used in this study consisted of 16 g of meteorite powders that had been extracted with water for a previous study (Pizzarello and Huang 2005). The powders were further extracted with 20 mL of dichloromethane/methanol (DCM/MeOH) (9:1, v:v), at 100 °C for 24 h and, upon decanting of the extract and drying, with 10 mL of 6N HCl at room temperature for 24 h with stirring. The extracted residue was demineralized by the method of Cronin et al. (1987); the powders were briefly washed with an 8N HF/3N HCl solution in water, in Teflon containers at room temperature for 24 h with stirring, and followed by 6N HCl rinses. The process was repeated several times until powders showed a stable weight upon drying, and was followed by several water rinses and one last MeOH rinse. About 280 mg of IOM were obtained (1.75% by weight of the starting powders); of these, ~50 mg were set aside for NMR analyses and the remainder used for hydrothermal experiments.

Water and 6N HCl used in the procedure were triple and double distilled, respectively, and the HF solution (48%, double distilled, PPB/Teflon grade) was purchased from Aldrich; DCM and MeOH were twice distilled. All glassware was heated to 565 °C in air before use.

**Hydrothermal Treatment**

The pure gold tubes for the hydrothermal treatment (HT) experiments measured 5 mm in diameter (0.125 mm wall) by 300 mm and were annealed at 500 °C in air overnight before use. Before the powders were loaded, one side of the tube was sealed by an Auto Arc TIG 50A Precision Welder. The chosen aliquots of IOM powders (15–20 mg) were extracted before each HT experiment with 2 mL of water at 100 °C for 24 h and, after drying, with 2 mL of DCM/MeOH at room
temperature for 2 h; the extracts were then decanted and analyzed. After drying, the IOM powders were loaded into the Au tubes and degassed water was added in equal proportion by weight (15–20 μL) with a syringe; the tubes were kept at about 0 °C and sealed by arc welding under argon atmosphere. The sealed Au tubes were then placed in a stainless-steel pressure vessel sealed with a Teflon Bridgman seal (Williams et al. 2001) and pressurized with distilled deionized water; the vessel has an inside diameter of 1.90 cm and a length of 54 cm. The experiments were conducted at 300 °C and 100 MPa for 6 days. The temperature was measured by two internal thermocouples placed in the center of the long axis of the vessel at each end of the Au tubes, with a measured gradient of ±5 °C. Pressure was monitored using a Bourdon-tube gauge with an accuracy of ±5 MPa.

After the treatment, the hydrothermal vessel was quenched in ice and Au tubes were removed, weighed to certify no weight loss or gain, and rinsed with water and solvents. The Au tubes were opened by slicing their midsection with a razor blade, which had also been cleaned. The IOM powders were rinsed out of the tube into a beaker with water employing a pipette; the suspensions were subsequently centrifuged and the extracts were decanted and dried by rotary evaporation. The powders were then dried and extracted with 4 mL of DCM/MeOH. The solvent extracts were also centrifuged, decanted, and dried by rotary evaporation.

The IOM residues were dried under vacuum and a portion set aside for NMR analyses. Their weight loss after each experiment was not measured, due to the fact that the powder amounts were very small and their weight could have been significantly altered by incomplete recovery from the tubes.

Gas Chromatography–Mass Spectrometry Analyses

The dry HT IOM water extracts were reacted in succession with isopropanol, 3N HCl and TFAA using the procedure commonly employed to obtain the amino acid O-ipropyl N-TFA derivatives (e.g., Pizzarello and Cronin 2000); derivatized samples were dissolved in DCM. Gas chromatography–mass spectrometry (GC-MS) analyses were performed with an Agilent 6890N GC-5973N Mass Selective Detector Network System equipped with either of two chiral columns: a CP Chirasil-dex CB (CHROMPACK), 25 m × 0.25 mm, 0.25 μm df, or a Chirasil-val (ALLTECH ASS. INC), 50 m × 0.25 mm, 16 μm df. The GC oven temperature programs were, respectively: 70 °C initial, 5 min hold, 70–85 °C at 1 °C min⁻¹, 85–200°C at 5 °C min⁻¹, and 45 min hold; 70 °C initial, 1 min hold, 70–100 °C at 2 °C min⁻¹, 100–200 °C at 4 °C min⁻¹, and 45 min hold.

The HT IOM solvent extracts were dried and the residues redissolved in DCM; their GC-MS analyses were performed utilizing a DB-17 capillary column (J & W Scientific, 60 m × 0.25 mm, 0.25 μm df). The GC oven temperature program was 70 °C initial, 1 min hold, 70–100 °C at 2 °C min⁻¹, from 100–300 °C at 4 °C min⁻¹, and 60 min hold. Aliquots from all the sample solutions were injected into the GC by Solids Injector (SGE Inc.).

Identification of compounds was made by comparison of their peak retention times and mass spectra with those of standard compounds. For unknowns, identification was made by comparison of the mass spectra with library data (NIST98) and individual examination of the suggested match reliability.

Solid State ¹³C NMR Spectroscopic Analyses

For a general account of NMR spectroscopy, please see Cody et al. (2002). The IOM residues were analyzed before and after the hydrothermal treatment; all NMR spectra were obtained on a Varian-Chemagnetics Infinity 300 nuclear magnetic resonance spectrometer at a static field of ~7.05 T, corresponding to resonance frequencies of 75.6 MHz. For each ¹³C NMR experiment, samples were packed into zirconia rotors of 5 mm OD, sandwiched between boron nitride inserts. The variable amplitude (VA) experimental parameters for VA-cross polarization (CP) experiments had been previously optimized using various aromatic standards (Cody and Alexander 2005). VACP MAS (magic angle spinning) was applied with a contact time of 4.5 ms, a spinning speed of 12 kHz, a pulse delay of 1s, 90° ¹H pulse width of 4 us, 75 kHz decoupling field, and acquisition involving 78,000 free induction decays (FIDs) per contact time. Identification of the spectral peaks and deconvolution with Gaussian peaks were performed according to Cody et al. (2002) and references therein. Solid-state ¹³C single pulse (SP) (Bloch decay) MAS experiments were performed at MAS = 12 kHz, a 30° tip angle, and ¹³C excitation pulse with RF power equivalent to achieve a 4.5 us 90 °C pulse width, and 75 kHz decoupling field. All ¹³C spectra are referenced to the methyl resonance of tetramethyl silane (defined as equal to 0 ppm).

TCEA-IRMS Analyses

Prior to analysis, samples were stored in a dry N₂ flushed oven held at 50 °C for at least 24 h. The samples were weighed just before analysis. Carbon, H, and N contents and bulk ¹³C/¹²C, D/H, and ¹⁵N/¹⁴N ratios in the IOM residues before and after the hydrothermal treatment were determined using a thermal conversion elemental analyzer coupled to a Thermo Finnigan MAT Delta+–XL isotope ratio mass spectrometry (IRMS).

RESULTS

A total of nine samples of hydrothermally treated Murray IOM were prepared for this study and all extracts analyzed showed the presence of water- and solvent-soluble organic compounds. Their amounts was found to vary between samples, with the most variability seen in the water-soluble
organic yields. Because we strived to assure a reproducible methodology for both the hydrothermal treatment and the recovery of the samples, it would be tempting to invoke heterogeneity of the IOM to explain such differences; however, the demineralization treatment was prolonged, involved stirring, and should have thoroughly mixed the material. It is more likely, therefore, that the observed differences resulted from subtle changes in experimental conditions. The data reported in the following sections are representative of samples that showed the higher yields of soluble organics; they are not averages of all yields. All compounds were identified either by comparison to standards (when so indicated in the tables), or by unequivocal matching with library spectra. Some examples of the latter are shown in Fig. 2.

The Water-Soluble Compounds Released from the IOM

Various organic compounds were identified in the water extracts of Murray HT IOM. They include alkyl dicarboxylic acids, nitrogen- and oxygen-containing hydroaromatic and aromatic compounds, and several unknowns. The linear dicarboxylic acids make up a series of compounds of C3 to C17 chain length (Fig. 1) with C9 (azelaic acid) being the larger, with an estimated abundance in the range of 9.5 ± 1.5 pmol/mg of IOM. Their distribution differs from that seen for these acids in the bulk extracts, where succinic acid was the largest species (~40 nmol/g of meteorite) and abundances decreased with increasing chain length (azelaic ≤ 1 nmol/g). C4 and C5 unsaturated diacids were searched for but not found; peaks displaying mass fragments belonging to C6, C7, and C8 mono-unsaturated diacids were found in abundances that were comparable to the linear series of corresponding chain length, but they could not be positively identified for the lack of standards or library references spectra. Benzoic acid was detected in an amount comparable to that of azelaic acid.

The methodology we used did not allow for the retention of volatile monocarboxylic acids; however, we did observe C15 to C18 long chain acids. These acids have also been described by Remusat et al. (2005) and are likely of biological origin, possibly freed from bacterial contaminants by hydrolysis during the demineralization process. Tricarboxylic acids were searched for but not detected.

The heteroatom-containing aromatic compounds found in water extracts comprise: 2-methyl benzimidazole plus several of the C2H5, C3H7, and C4H9 higher alkyl homologs (at least three, four, and two species for each series, respectively), 6-hydroxy quinoline, several methyl hydroxyquinolines isomers, benzothiazolone, and morpholine (Scheme 1; Fig. 2). Mass spectra with good matches for those of methyl- and dimethylbenzimidazoles and methyl hydroxyquinoline were also observed.

Fig. 1. A GC-MS analysis of the dicarboxylic acids with general formula: HOOC-R-COOH, where -R- represents (-CH2-)n, found in the water extract of hydrothermally treated Murray IOM. Single ion trace chromatogram of isopropyl ester derivative base peaks.

The Solvent-Soluble Compounds

A large suite of over two hundred compounds was observed in the DCM/MeOH extracts of the HT IOM powders (Fig. 3). They include a series of PAHs of up to five rings (Table 1); N-, O-, and S-containing aromatic compounds (Table 2); and a large number of their isomers and homologs. Noncondensed aromatic species such as substituted benzenes (C4 and C5), biphenyl and substituted biphenyls (four C1 and eight C2 species), and terphenyls and substituted terphenyls as well as hydrated PAHs were also detected (e.g., Scheme 2 and Fig. 2).

Scheme 1.

Scheme 2.
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(e.g., by silica gel separation) was attempted because of the small size of the samples. This entailed some inevitable chromatographic co-elutions, which did not compromise identification of the compounds by single ion analyses but prevented the precise attribution of their abundance in several occasions. Therefore, Tables 1 and 2 report only relative abundances except for the larger compounds and/or those whose GC elution was unquestionably unhindered. Based on these measurements and the estimation of the total ion chromatographic area, we can set the approximate total yield for soluble compounds extracted from HT IOM by solvents to be ≥1 nmol/mg IOM. Also with some uncertainty, because several of the water-soluble compounds have yet to be identified, these yields appear to be at least an order of magnitude larger than those of compounds obtained by water extraction.

Fig. 2. Matches between spectra of some of the unknown peaks seen in GC-MS chromatogram of HT IOM water and solvent extracts and library spectra. a) 2-methylbenzimidazole; b) dimethylbenzimidazole; c) methyl-hydroxyquinoline; d) 5-methylindan; e) 2-ethyl-5,7-dimethylbenzo[b]thiophene; f) o-therphenyl.
Fig. 3. A total ion chromatogram of an HT IOM solvent extract analysis corresponding to ~1.4 mg of the material using a DB-17 capillary column (60 m × 0.25 mm).
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NMR Spectroscopic Analyses

The VACP MAS NMR spectroscopic analyses of untreated and HT-treated Murray IOM powders are presented in Fig. 5; the VACP MAS NMR spectrum of Tagish Lake IOM is included for comparison. In each case, the spectra are normalized to the intensity of aromatic (and olefinic) peak at 129 ppm. The distribution of oxygen-substituted and protonated aromatic and aliphatic moieties in the untreated Murray IOM is very similar to that observed in previous analyses of the Murchison meteorite (e.g., Cody and Alexander 2005). The specific distribution of the aromatic, -CO, -CH$_2$O, and -CH$_x$ functionalities (F) of the two Murray samples obtained by VACP MAS and SP MAS NMR are listed in Table 3. The spectrum of the HT-treated IOM differs considerably from that of the untreated material; most significantly there is complete loss of spectral intensity spanning the range from 35 to 85 ppm, the region of the chemical shift that is attributed to aliphatic CH$_3$(O, N), acetylenic (C≡CR), and methyne (CH) functional groups. The remaining saturated carbon lies at a frequency centered at 20 ppm, typical of phenyl linked methyl groups. There also is a reduction in the carbonyl compounds, e.g., ketones and carboxyls in the heated Murray IOM relative to the intensity of aromatic carbon. A comparison with Tagish Lake IOM is interesting: whereas both Tagish Lake and heated Murray IOM have relatively low abundances of saturated (sp$^3$ bonded) carbon, in the case of Tagish Lake this carbon is dominated by CH$_x$O moieties. The highly aromatic character of Tagish Lake has been interpreted to be the result of low-temperature chemical oxidation that occurred during parent body aqueous alteration (Cody and Alexander 2005). The distinct differences in the aliphatic chemistry between Tagish Lake and heated Murray IOM indicates that very different chemical mechanisms are involved in altering the respective IOM.

<table>
<thead>
<tr>
<th>Table 1. The aromatic compounds extracted from Murray IOM after hydrothermal treatment.</th>
<th>Table 2. The heteroatom-containing aromatic compounds extracted from Murray IOM after hydrothermal treatment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs (n)$^a$ (pmol/mg)</td>
<td>Relative$^b$ Also by</td>
</tr>
<tr>
<td></td>
<td>abundance</td>
</tr>
<tr>
<td>C$_1$-indanes (2)</td>
<td>++</td>
</tr>
<tr>
<td>C$_2$-indanes (5)</td>
<td>++</td>
</tr>
<tr>
<td>C$_3$-indanes (3)</td>
<td>++</td>
</tr>
<tr>
<td>Naphthalene,$^d$ 96 ± 43</td>
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</tr>
<tr>
<td>C$_1$-naphthalenes (2) 117 ± 52</td>
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<td>C$_2$-naphthalenes (11) 72 ± 28</td>
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<td>C$_1$-naphthalenes (15) 19 ± 8</td>
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<tr>
<td>C$_2$-naphthalenes (6) 7 ± 3</td>
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<tr>
<td>Biphenyl</td>
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<tr>
<td>C$_1$-biphenyl (4)</td>
<td>++</td>
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<tr>
<td>C$_2$-biphenyl (8)</td>
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</tr>
<tr>
<td>Acenaphthenes</td>
<td>+++</td>
</tr>
<tr>
<td>Fluorene$^d$</td>
<td>+++</td>
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<tr>
<td>C$_1$-fluorene (4)</td>
<td>++</td>
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<tr>
<td>C$_2$-fluorene (11)</td>
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<td>Phenanthrene$^d$ 21 ± 7</td>
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<td>Antracene$^d$ 4 ± 1.5</td>
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<td>C$_1$-phenanthrene/antracenes (6)</td>
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<tr>
<td>Fluoranthenes (fl) 16 ± 5</td>
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<tr>
<td>Pyrene$^d$ 22 ± 6.5</td>
<td>+++</td>
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<tr>
<td>C$_1$-fluor/pyrene/benzo(10)</td>
<td>+++</td>
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<tr>
<td>C$_2$-fluor/terphenyls (8)</td>
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<tr>
<td>Benz[a]anthracene$^d$</td>
<td>++</td>
</tr>
<tr>
<td>Chrysene$^d$(chr)</td>
<td>++</td>
</tr>
<tr>
<td>C$_1$-chrysene/benzopenthanthrenes (11)</td>
<td>+</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>++</td>
</tr>
</tbody>
</table>

$^a$Number of compounds within the group.
$^b$++++ > 50pm/mg; +++ > 10 pm/mg; ++ > 1pm/mg, + > 0.1pm/mg.
$^c$Hydrous pyrolysis (Sephton et al. 1998).
$^d$Identified with standards.

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Isotopic Analyses

As shown in Table 4, the isotopic compositions of HT and untreated IOM were found to be different—the δD and δ15N values of the Murray HT IOM were significantly lower than those of the untreated material. The δ13C values were in the negative range in both materials, and only slightly lighter in the HT IOM.

DISCUSSION

The hydrothermolytic treatment of Murray IOM material produced novel results in the release of several compounds. To understand such release of a selected group of soluble organic compounds—several of which were not seen previously in the extracts of whole meteorite powders—and to properly construe the original structure of the IOM from which they were freed, we need to attempt to reconcile the unambiguous spectroscopic data available for the material with a realistic interpretation of possible decomposition pathways.

Dicarboxylic Acids

The freeing of a suite of dicarboxylic acids with far larger molecular range than that found in bulk CM2 chondrite water extracts is particularly intriguing and challenging. In bulk extracts, C_{10} is the maximum chain length for these compounds (Pizzarello and Huang 2002) and even the subsequent extraction of the powders with ethanol, in which higher dicarboxylic acids could be more soluble, did not produce longer acids (Pizzarello, unpublished results). In contrast, their range extended to C_{17} in Murray HT IOM extracts. Because previous analyses of CM2 IOM NMR spectra do not support the presence of a substantial quantity of predominantly methylenic carbon consistent with substantial quantities of long alkyl chain aliphatic compounds in the material (Cody et al. 2002; Cody and Alexander 2005) and the HT IOM spectra showed an unambiguous reduction of a localized NMR feature, it would be reasonable to suggest that the two findings are related and could point to precursor macromolecules not described before.

Dicarboxylic acids were described following the chemical oxidation of the IOM (Hayatsu et al. 1977) and interpreted as the oxidation products of alkyl or ether linkages between the aromatic moieties. Such an interpretation appeared to be confirmed by the targeted oxidative decomposition of the IOM aromatic structures, which released di- and tricarboxylic acids (Remusat et al. 2005) that were also interpreted as the residual products of linear and branched alkyl chains linking aromatic structures. In the case of the HT-produced dicarboxylic acids, however, the predominance of linear-chain species and the length of their chains (up to C_{17}) make the previous interpretation somewhat unlikely from a chemical standpoint. In fact, the subcritical temperatures employed in our experiments, the degassing of the water we used, which would have lead to loss of most of the dissolved O_{2}, as well as model experiments with simple molecules under these conditions (e.g., see Siskin and Katritzky 2001 and Katritzky et al. 2001 for reviews on the reactivity of organic compounds in superheated water), suggest that the cleavage of mono-alkyl branching and di- and tri-alkyl bridges would not have resulted in their oxidation to carboxylic functions. In fact, monocarboxylic acids were not found in the HT IOM extracts (although volatile, they could have been detected at chain lengths of C_{6} and above) and, as mentioned, nor were tricarboxylic acids detected. The only other carboxylated species in the extract was benzoic acid.

On the other hand, the increase in temperature from 25 to 300 °C dramatically changes the properties of water, with a decreased dielectric constant that gives water solvent properties comparable to those of acetone and an increased...
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ionic constant (dissociation constant) that would favor ionic reactions of dissolved organics. If, as expected, decarboxylation and hydrolysis of labile groups in peripheral chains of the material occurred during the first stages of the hydrothermal treatment, mild acid-catalyzed reactions could have been possible through the release of CO₂. For example, we can hypothesize that IOM 1,2-diaerylethane bridges, which are known to be thermally labile unlike methylene cross-links that are stable and unreactive in water (Siskin and Katrizky 2001), may have cleaved and oxidized in the presence of CO₂ to give the abundant acetic acid observed in Murchison by Oba and Naraoka (2005). The abundance of phenols would attest to the possibility of oxidation during the hydrothermal treatment (see below).

However, the hydrothermal formation of linear dicarboxylic acids as long as C₁₇ in this manner is unlikely because cleavage of alkyl chains and bridges, which could lead to disproportionation and recombination reactions possibly followed by oxidation, are not favored in water at subcritical temperature and in the absence of catalysts (Henderson et al. 1968). In the absence of clues from model experiments or related kerogen literature, therefore, we take a literal interpretation of the decreased (CHₓO) feature in the HT IOM NMR spectra and suggest that this feature may include alkyl poly-methylene bridges connected to the aryl clusters by either di-esters, di-ethers, or limited olefinic features (C=C=CR) that would be amenable to hydrolysis and/or oxidation to give linear dicarboxylic acids in the HT IOM extracts.

It cannot be excluded that the precursors to the dicarboxylic acids found in the HT IOM extracts comprise a distinct molecular phase, whether directly bonded to the aromatic network or independent from it. Again on the basis of the NMR spectra, this phase could have olefinic regions, perhaps branched, amenable to cleavage and/or oxidation. Were this the case, we could also consider the possibility that the free dicarboxylic acids found in several types of carbonaceous chondrites may have common precursor in similar labile material. The interpretation would agree with the findings of similar dicarboxylic acid suites in meteorites of diverse hydrothermal history and organic composition, such as the Murchison and Tagish Lake meteorites. In view of the high δ¹³C and δD values determined for these acids in both meteorites (Pizzarello and Huang 2002), we should expect these precursors to be mainly presolar in origin, perhaps long chain nitrile and di-nitrile circumstellar species that had already undergone partial saturation with D-rich H₂ gas in the cold interstellar or nebular environments.

**Water Soluble Heteroaromatics**

The water-soluble heteroaromatic compounds, as well as the solvent soluble compounds observed in the extracts after the hydrothermal treatment, can be more easily understood than the dicarboxylic acids as the products of cleavage from larger aromatic structures, possibly due to the nature of their linkages. Compounds as large as coronene are solubilized by the HT treatment and most aromatic species are accompanied in the HT IOM extracts by a large number of branched homologs, multi-methyl as well as longer alkyl substituted in the case of the smaller PAHs. This could be indicative of their peripheral position in the macromolecular structure, but also that noncondensed aromatic species could be more abundant in the labile portion of CM2 chondrite IOM. Phenols are the only abundant O-containing aromatic compounds released from HT IOM, while quinones such as anthraquinone that are observed in the whole extracts of the bulk meteorites were not detected. In view of a possible relationship between insoluble and soluble organic material in meteorites, the absence of larger oxidized PAHs after HT treatment of the IOM would indicate that, if such a relation existed, larger PAHs released from the labile IOM material were later exposed to parent body oxidation processes.

Fig. 5. A normalized comparative VACP MAS NMR spectra of untreated Murray, HT-treated Murray, and Tagish Lake IOM.
Changes in IOM Isotopic Composition by HT Treatment

The overall D-enrichment of the organic compounds released from Murray IOM, as estimated by the difference between untreated and treated material δD values, is higher than that determined for the combined aromatic and heteroaromatic fractions of bulk Murchison extracts (~+400 and +950‰, respectively; Krishnamurthy et al. 1992). The δ15N value of the untreated material agrees well with the mean value (+19‰) found by Alexander et al. (1998) for the Murray IOM, although it is lower than those detected upon combustion of the material between 200–300 °C.

In general terms, the finding that the IOM after the HT treatment is less enriched in deuterium and 15N appears to support the presence in the IOM of isotopically distinct material held to the remaining macromolecular structure by labile chemical bonds or chemisorption because, were the compounds released by the HT treatment the products of partial decomposition of larger macromolecular units, the isotopic composition of the residual material would be expected to be heavier instead of lighter.

In the absence of compound-specific isotopic analyses of the HT products, however, it is not possible to determine with certainty whether the compounds released upon HT were, as it appears, the main repositories of deuterium enrichment in the IOM or the observed compositional differences between materials for this isotope were, to an unknown extent, due to exchange with experimental water. 15N enrichment, on the other hand, seems indigenous to the compounds and indication of their presolar origin.

The δ13C values of both the HT and untreated IOM are slightly lower than that averaged for alkyl, aromatic, and heteroaromatic compounds extracted from the bulk Murchison (Krishnamurty et al. 2002). They are close to the average value found by Sephton et al. (2000) for a mixture of twelve substituted benzenes, naphthalenes, and phenol produced by hydrous pyrolysis of Murchison IOM. Of all the Murchison soluble organic compounds analyzed so far, a somewhat similar composition (D-enrichment coupled to less enhanced 13C) has been observed only for some of the amino acids (the 2-amino-2H- and 2-amino-2-methyl amino acids (Pizzarello et al. 2004; Pizzarello and Huang 2005), and the lower molecular weight carboxylic acids (Yuen et al. 1984; Huang et al. 2005). The mechanism proposed for this isotopic distribution is a synthetic process involving the building of homologous suites through sequential addition of carbon moieties (Yuen et al. 1984). It is possible that precursors to IOM macromolecules were similarly built up via kinetically controlled additions that resulted in their 13C depletion.

CONCLUSIONS

The release from the IOM of a sizable suite of water-soluble organic compounds under hydrothermal conditions, as well as the likelihood that they could be freed by prolonged exposure to water under milder conditions, suggest that the IOM might have made an important contribution to the organic pool of the early Earth. We know carbonaceous chondrites delivered 1–3% of their weight in carbon during the early impact period; a very conservative estimate (Pizzarello 2004) of just the soluble compounds delivered at today’s impacts rates to the Earth is ≤8 10^4 Kg/yr. Because the IOM represents at least 70% of the organic carbon in carbonaceous chondrites, even a small percent release of soluble compounds from the material would have increased their total delivery several fold.

The chemical pathways that lead to the emergence of life are unknown and the potential influence that abiotic organic material might have had on life’s origin can only be guessed. With this constraint, we can speculate that the long-chain dicarboxylic acids could have been helpful in molecular evolution by aiding in the formation of vesicles for the encapsulation of early genetic material and the efficient concentration of compounds and catalysts in reactions.
chiral assessment of the IOM before and after treatment indicated that the IOM lost a statistically significant level of asymmetry upon hydrothermalysis (Kawasaki et al. 2006). Consequently, some compounds released from the IOM may be nonracemic and would have increased the extent of molecular asymmetry available to the early Earth for possible stereospecific reactions (Pizzarello and Weber 2004; Pizzarello 2006).

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