



Carbon isotopic composition of acetic acid generated by hydrous pyrolysis of macromolecular organic matter from the Murchison meteorite

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Abstract—Low molecular weight monocarboxylic acids, including acetic acid, are some of the most abundant organic compounds in carbonaceous chondrites. So far, the ¹³C- and D-enriched signature of water-extractable carboxylic acids has implied an interstellar contribution to their origin. However, it also has been proposed that monocarboxylic acids could be formed by aqueous reaction on the meteorite parent body. In this study, we conducted hydrous pyrolysis of macromolecular organic matter purified from the Murchison meteorite (CM2) to examine the generation of monocarboxylic acids with their stable carbon isotope measurement. During hydrous pyrolysis of macromolecular organic matter at 270–330 °C, monocarboxylic acids with carbon numbers ranging from 2 (C₂) to 5 (C₅) were detected, acetic acid (CH₃COOH; C₂) being the most abundant. The concentration of the generated acetic acid increased with increasing reaction temperature; up to 0.48 mmol acetic acid/g macromolecular organic matter at 330 °C. This result indicates that the Murchison macromolecule has a potential to generate at least ~0.4 mg acetic acid/g meteorite, which is about four times higher than the amount of water-extractable acetic acid reported from Murchison. The carbon isotopic composition of acetic acid generated by hydrous pyrolysis of macromolecular organic matter is ~–27‰ (versus PDB), which is much more depleted in ¹³C than the water-extractable acetic acid reported from Murchison. Intramolecular carbon isotope distribution shows that methyl (CH₃-)C is more enriched in ¹³C relative to carboxyl (-COOH)-C, indicating a kinetic process for this formation. Although the experimental condition of this study (i.e., 270–330 °C for 72 h) may not simulate a reaction condition on parent bodies of carbonaceous chondrite, it may be possible to generate monocarboxylic acids at lower temperatures for a longer period of time.

INTRODUCTION

Monocarboxylic acids, which contain only one carboxyl (-COOH) as a functional group in the molecular structure, are one of the abundant solvent-extractable (free) organic compound classes in carbonaceous chondrites. The occurrence of meteoritic monocarboxylic acid has been studied with respect to its origin and formation mechanism by many researchers (Yuen and Kvenvolden 1973; Lawless and Yuen 1979; Yuen et al. 1984; Epstein et al. 1987; Shimoyama et al. 1989; Krishnamurthy et al. 1992; Naraoka et al. 1999; Huang et al. 2005). Although the meteoritic monocarboxylic acid is comprised of compounds with aliphatic and aromatic structures, acetic acid (CH₃COOH) is the most abundant in

carbonaceous chondrites (up to ~100 ppm) (Yuen et al. 1984; Naraoka et al. 1999) for a single organic species. From the point of view of chemical evolution and origin of life, acetic acid has a central role in energy production for metabolism and lipid synthesis for membranes by all biological activities.

Historically, the formation of meteoritic organic matter was proposed by thermocatalytic reactions in the primordial solar nebula (Fischer-Tropsch type reaction; Anders et al. 1973), or by hydrothermal alteration of polycyclic aromatic hydrocarbons (PAHs) on the meteorite parent body (Shock and Schulte 1990). The similarity of organic products by Miller-Urey-type radical reactions was also discussed with respect to the occurrence of meteoritic organic matter (e.g., Hayatsu and Anders 1981; Mullie and Reisse 1987; Cronin

and Pizzarello 1988). However, none of these mechanisms by themselves can explain the molecular and isotopic occurrence in meteorites. The extreme D-enrichment of meteoritic organic matter suggests the contribution of interstellar precursor molecules followed by aqueous reactions such as the Strecker-cyanohydrin pathway on the meteorite parent body (e.g., Cronin and Chang 1993). Generally, the formation and alteration of meteoritic organic matters have been considered to be multistep processes in various different environments, from organic precursors in interstellar clouds to aqueous processes in the meteorite parent bodies (Cronin and Chang 1993; Kerridge 1999; Pizzarello 2004).

Similarly, origins and formation mechanisms of meteoritic monocarboxylic acids have not been understood. Although acetic acid has been found in molecular clouds (Mehring et al. 1997), its incorporation into the primordial solar nebula is unclear. In particular, the D-enrichment of meteoritic monocarboxylic acids (Krishnamurthy et al. 1992; Huang et al. 2005) may suggest that the interstellar processes may have played an important role in its occurrence in meteorites. However, the formation and alteration of monocarboxylic acids have not been clarified during the processes in the solar nebula and meteorite parent bodies.

Besides free organic compounds such as carboxylic acids and amino acids, a solvent-insoluble and high-molecular-weight macromolecule is the main component of total organic matter in carbonaceous chondrites. This macromolecular organic matter is extracted by demineralization of silicate matrix. Infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy have been applied to study the chemical structure of the macromolecule, consisting mainly of aromatics with minor aliphatic carbons and many functional groups such as carboxyl and carbonyl (Hayatsu et al. 1977; Cronin et al. 1987; Gardinier et al. 2000; Cody et al. 2002; Yabuta et al. 2005). Pyrolysis of macromolecular organic matter has been conducted, generating various PAHs ranging from one to seven rings with some alkyl-substituents (Komiya et al. 1993; Sephton et al. 1998, 2004). However, carboxylic acids (including monocarboxylic acid, dicarboxylic acid, and amino acid) generation from the meteoritic macromolecule has never been examined. Stable carbon isotopic composition of the carboxylic acid should provide important information on its origins and formation mechanisms. The free carboxylic acids in carbonaceous chondrite show ^{13}C - and D-enriched signature (Yuen et al. 1984; Epstein et al. 1987; Krishnamurthy et al. 1992; Huang et al. 2005). On the other hand, bulk macromolecular organic matter is depleted in ^{13}C relative to free organic matter (Robert and Epstein 1982; Kerridge et al. 1987; Krishnamurthy et al. 1992; Naraoka et al. 1997).

In this study, we have conducted hydrous pyrolysis of macromolecular organic matter purified from the Murchison meteorite to examine the generation of monocarboxylic acid, and also discuss the relationship between free monocarboxylic acid and macromolecular organic matter.

EXPERIMENTAL PROCEDURES

Hydrous Pyrolysis of Insoluble Organic Matter

A powdered aliquot of the Murchison meteorite (2.6 g), which was already extracted with water and organic solvent, was demineralized with 6M HCl and subsequently with a mixture of concentrated HF and HCl (1/1 by volume) in a closed Teflon bottle by shaking at temperatures up to $\sim 70^\circ\text{C}$ in a water bath. The residue was washed with H_2O several times until the pH was neutral. The acid treatment was totally repeated four times. Finally, the residue was successively washed with methanol, benzene, hexane, and CS_2 to remove solvent-extractable organic matter and elemental sulfur. The isolated macromolecule was dried (~ 35 mg) and a part of macromolecule was subjected to a CHNS elemental analyzer (FISONS NA-1500). It contained 58.4% carbon, 3.02% hydrogen, 2.22% nitrogen, and 10.6% sulfur (by weight). Bulk carbon isotopic composition of macromolecular organic matter ($\delta^{13}\text{C}_{\text{bulk}} = -13.0\text{‰}$) was determined using an isotope ratio mass spectrometer (Finnigan delta S) coupled with an elemental analyzer (FISONS NA-1500) in an on-line mode.

About 7 mg of the macromolecule was heated with 0.5 ml of H_2O in a sealed Pyrex tube (30×1.2 cm in diameter) after degassing at 270, 300, and 330 $^\circ\text{C}$ for 72 h. After heating followed by centrifugation, the solution (hydrous pyrolysate) was separated from the residue. The hydrous pyrolysate was made alkaline by adding 1.0 ml of 17 mM NaOH solution to prevent loss of volatile monocarboxylic acid, and evaporated to dryness under reduced pressure. The resulting residue was redissolved in 300 μl of H_2O and transferred to a glass tube in a two-way glass tube, where another glass tube contained ~ 200 μl of 85% H_3PO_4 . After the two-way glass tube was connected to another glass tube with a vacuum valve and the apparatus was evacuated, the alkaline solution was acidified with the H_3PO_4 followed by heating at $\sim 250^\circ\text{C}$ for distillation. The distillate containing volatile acid was transferred and trapped at liquid nitrogen temperature. Using a standard solution of acetic acid, propionic acid, and isobutyric acid, recovery through this analytical procedure was more than 90% (90–103%) for four measurements. A procedural blank was performed using 0.5 g of preheated (450°C for >3 h) sea sand at each temperature before actual hydrous pyrolysis of meteoritic macromolecule. The procedural blank contained small amounts of acetic acid (Fig. 1), showing 4.2% at 270 $^\circ\text{C}$, 0.3% at 300 $^\circ\text{C}$, and 7.0% at 330 $^\circ\text{C}$ of the total amount of acetic acid generated by each hydrous pyrolysis.

Quantification and Compound-Specific Carbon Isotope Analysis

The distilled aqueous solution containing monocarboxylic acids was analyzed by gas chromatography (GC). The GC analysis was conducted using an HP5890II GC

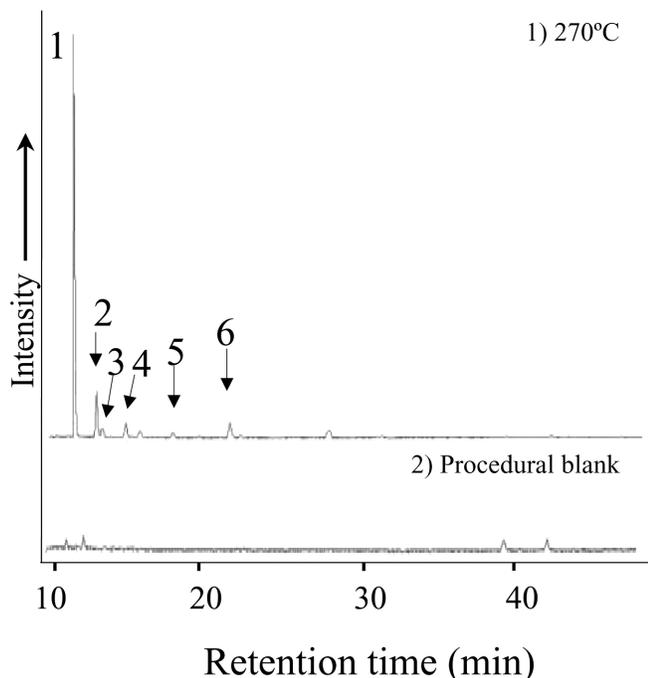


Fig. 1. Typical gas chromatograms of carboxylic acid (1) generated by hydrous pyrolysis of the Murchison macromolecular organic matter at 270 °C, and (2) from a procedural blank. 1 = acetic acid, 2 = propionic acid, 3 = 2-methylpropionic acid, 4 = 2- and 3-methylbutanoic acid, 5 = butanoic acid, and 6 = pentanoic acid.

equipped with a flame ionization detector using splitless injection. The GC column (DB-FFAP, 0.32 mm in diameter \times 30 m, 0.25 μ m in film thickness) was programmed at 40 °C for 2 min, followed by to 100 °C at 20 °C/min and to 200 °C at 2 °C/min. Quantification of acetic acid was performed by comparing the peak area of a standard.

Compound-specific carbon isotopic analysis was carried out by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) using a Finnigan delta S interfaced with an HP5890II GC. Intramolecular carbon isotope analysis of the carboxyl group (-COOH; carboxyl-C) in acetic acid was carried out by gas chromatography/pyrolysis/isotope ratio mass spectrometry (GC/pyrolysis/IRMS) using a Finnigan Delta plus XL interfaced with an HP6890GC (modified after Yamada et al. 2002). In this paper, $\delta^{13}\text{C}$ of acetic acid molecule is shown as “total” $\delta^{13}\text{C}$, while $\delta^{13}\text{C}$ of methyl (CH_3 -)C is calculated by isotopic mass balance using the following equation:

$$\delta^{13}\text{C}_{\text{CH}_3} (\text{‰}) = 2\delta^{13}\text{C}_{\text{total}} - \delta^{13}\text{C}_{\text{COOH}} \quad (1)$$

$\delta^{13}\text{C}$ of methyl- and carboxyl-C are denoted as $\delta^{13}\text{C}_{\text{CH}_3}$ and $\delta^{13}\text{C}_{\text{COOH}}$, respectively.

The combustion by GC/C/IRMS was performed in a microvolume ceramic tube with CuO, NiO, and Pt wires at 940 °C. The decarboxylation by GC/pyrolysis/IRMS was performed in a microvolume ceramic tube at 1000 °C (Yamada et al. 2002). The GC condition is identical to that

used for the GC analysis except for the column length (DB-FFAP, 0.32 mm in diameter \times 60 m in length, 0.25 μ m in film thickness). The $\delta^{13}\text{C}$ value was calibrated by working CO_2 gas standard, and given in per mil (‰) relative to Pee Dee belemnite (PDB). Standard deviations of $\delta^{13}\text{C}_{\text{total}}$ and intramolecular $\delta^{13}\text{C}$ analyses are better than 0.6‰ and 0.9‰, respectively. Isotope fractionation during the cryogenic distillation was examined using a solution of acetic acid standard ($-33.66 \pm 0.06\text{‰}$ by conventional measurement) to give $-34.0 \pm 0.4\text{‰}$ by GC/C/IRMS. The isotopic value indicates no substantial isotope fractionation during the analytical procedure. $\delta^{13}\text{C}_{\text{total}}$ of acetic acid in the procedural blank cannot be measured because of its low concentration. Using an isotopic mass balance calculation, $\delta^{13}\text{C}_{\text{total}}$ of the pyrolysate changes not more than 1.5‰, assuming that the $\delta^{13}\text{C}_{\text{total}}$ of the procedural blank ranges from -15 to -35‰ as a generally observed value for terrestrial acetic acid (Meinschein et al. 1974; Yamada et al. 2002; Dias et al. 2002a). However, high recovery (90–103%), no substantial isotope fractionation during the cryogenic distillation, and relatively low (0.3–7.0‰) background of acetic acid suggest minimal isotope change (<1‰) during the analytical procedure.

RESULTS AND DISCUSSION

Concentration of Carboxylic Acid Generated by Hydrous Pyrolysis

C_2 – C_5 monocarboxylic acids are produced during hydrous pyrolysis at 270–330 °C (Fig. 1). The acetic acid concentration increases with the increase of heating temperature (Table 1). The acetic acid constitutes more than 90% of total monocarboxylic acid detected in the hydrous pyrolysate fraction. The concentration of acetic acid ranges from 0.13 to 0.48 $\mu\text{mol}/\text{mg}$ of macromolecular organic matter (Table 1). Since Murchison is known to contain ~1.45 wt% macromolecular carbon (Mullie and Reisse 1987), this result indicates that the macromolecule has a potential to generate ~0.4 mg acetic acid/g meteorite. This amount is about four times higher than the amount of free acetic acid in Murchison (~100 ppm; Yuen et al. 1984).

About 0.5–2 wt% carbon of the macromolecular organic matter was converted to acetic acid. Because the carboxyl group constitutes 6.2–7.4 wt% of macromolecular organic matter in Murchison by NMR (Gardinier et al. 2000), all carboxyl groups may not be eliminated from macromolecular organic matter by hydrous pyrolysis at 270–330 °C. The proportion of acetic acid generated from macromolecular organic matter is close to that of monocarboxylic acids generated by hydrous pyrolysis of terrestrial kerogen at 250–350 °C (~1%) (Lundegard and Senftle 1987). The amount of acetic acid is probably the minimum value because acetic acid is partly decarboxylated at 300 °C, in which the amount decreases in half for 99 days at 300 °C (Kharaka et al. 1983).

Table 1. Concentration, relative carbon amounts, carbon isotopic composition of acetic acid, and bulk $\delta^{13}\text{C}$ of pyrolysis residue resulting from various heating temperatures.

	Abundance ($\mu\text{mol mg}^{-1}$)	Relative carbon amounts (%) ^a	$\delta^{13}\text{C}$ (% , versus PDB)			
			Bulk $\delta^{13}\text{C}$ after heating	CH_3COOH	CH_3-	$-\text{COOH}$
270 °C	0.13	0.52	-15.8	-20.8 ± 0.2	-19.1 ± 0.2	-22.5 ± 0.2
300 °C	0.25	1.02	-16.2	-26.7 ± 0.1	-20.1 ± 0.6	-32.6 ± 0.6
330 °C	0.48	1.97	-16.2	-27.0 ± 0.0	-25.7 ± 0.9	-28.3 ± 0.9

^aThe carbon amount of acetic acid generated by hydrous pyrolysis relative to that of bulk macromolecular organic matter.

Formation of monocarboxylic acid should involve cleavage of C-C bonding bound to the macromolecule under high temperature. In addition, ester, amide, and ether groups in the macromolecular organic structure may be hydrolyzed or cleft to generate carboxylic acid. So the generated monocarboxylic acid is considered to be derived from multiple functional groups in macromolecular organic matter. Acetic acid is the main product, because it is the simplest and most stable monocarboxylic acid.

Compound-Specific $\delta^{13}\text{C}$ of Acetic Acid

The $\delta^{13}\text{C}_{\text{total}}$ decreases from -20.8 to -27.0% with the increase of heating temperature (Table 1). The higher the heating temperature, the more ^{13}C -depleted acetic acid is generated by hydrous pyrolysis, indicating that the acetic acid precursor with more ^{13}C -depleted carbon occurs in the macromolecular organic matter. In contrast, in hydrous pyrolysis of terrestrial kerogen, the generated acetic acid becomes ^{13}C -enriched with increasing of thermal maturation (Dias et al. 2002a). This is because in a kinetically controlled process, more ^{13}C -depleted compounds are eliminated from the kerogen, resulting in a ^{13}C -enrichment of the remaining kerogen. This different isotopic behavior of meteoritic organic matter was also reported for PAH generation by hydrous pyrolysis (Sephton et al. 1998). The isotopic signature of meteoritic organic matter suggests heterogeneous isotope distribution in the macromolecular structure probably due to a multitude of formation pathways for the macromolecule. Because free acetic acid from Murchison is extremely enriched in ^{13}C ($\delta^{13}\text{C} = +22.4\%$) (Yuen et al. 1984), the ^{13}C -depleted and isotopically heterogeneous acetic acid precursors have different sources from the free acetic acid. The relatively ^{13}C -depleted acetic acid precursors were probably incorporated into macromolecular organic matter at the early stage of meteorite formation, followed by incorporation of the ^{13}C -enriched free acetic acid into the meteorite.

Intramolecular carbon isotope analysis shows that the methyl group of acetic acid is more enriched in ^{13}C than the carboxyl group at all temperatures (Table 1). This isotope distribution is in contrast to that of acetic acid generated by hydrous pyrolysis of terrestrial kerogen (Dias et al. 2002a, 2002b) and biologically synthesized acetic acid (Meinschein et al. 1974). Under a thermodynamic isotope equilibrium, carboxyl-C should be more enriched in ^{13}C than methyl-C

(e.g., Galimov 1985). Therefore, the isotope distribution of acetic acid generated from terrestrial kerogen is consistent with the thermodynamic equilibria. On the other hand, nonequilibrium isotope distribution of intramolecular carbon also indicates that the acetic acid generated in this study was formed under a kinetically controlled process, probably due to heterogeneous isotope distribution within the macromolecule. Although $\delta^{13}\text{C}_{\text{CH}_3}$ decreases as increasing heating temperature, the $\delta^{13}\text{C}_{\text{COOH}}$ value does not show a systematic trend (Fig. 2). This $\delta^{13}\text{C}_{\text{COOH}}$ variation may also suggest an isotopic heterogeneity of the macromolecule. Alternatively, the intramolecular isotope distribution may approach an equilibrium state (^{13}C -depleted CH_3 and ^{13}C -enriched COOH) with the prolonged reaction time under higher temperature at 330 °C (Fig. 2), which may accelerate carbon isotope exchange between CH_3 and COOH .

Comparison between Compound-Specific and Bulk $\delta^{13}\text{C}$

The bulk $\delta^{13}\text{C}$ of original macromolecular organic matter (-13.0%) changes to -15.8% at 270 °C, -16.0% at 300 °C, and -16.2% at 330 °C after pyrolysis. There is a large carbon isotopic difference between bulk macromolecular organic matter and the generated acetic acid by 7.8‰ at 270 °C, 13.7‰ at 300 °C, and 14.0‰ at 330 °C. Although the more ^{13}C -depleted acetic acid is generated by hydrous pyrolysis, the macromolecular organic matter becomes more depleted in ^{13}C by $\sim 3\%$ after heating (Table 1). This result indicates that ^{13}C -rich bearing species are generated simultaneously besides monocarboxylic acids. The large differences between compound-specific and bulk-isotopic compositions are not only observed in this study. For example, PAHs in hydrous pyrolysate display a wide range of $\delta^{13}\text{C}$ values, -5.6 to -24.6% (Sephton et al. 1998), being similar isotopic compositions to their free counterparts. In this study, however, the generated acetic acid is much more depleted in ^{13}C relative to its free counterpart (Yuen et al. 1984). Therefore, the formation mechanism is different between acetic acid and PAHs during hydrous pyrolysis.

This unusual isotope relationship between macromolecule and the generated low molecular weight compounds could be attributable to the kinetically controlled formation of low-molecular compounds and the isotopic heterogeneity of the macromolecule, as described above. The chemical structure of meteoritic macromolecule has been

clarified using solid-state NMR (Gardinier et al. 2000; Cody et al. 2002; Cody and Alexander 2005; Yabuta et al. 2005). The Murchison macromolecule is composed of extensively cross-linked, highly aromatic, and relatively lower content of aliphatic carbon with oxygen-containing functional groups, although some different relative abundances and functional carbon-type groups are reported under different measurement conditions (Gardinier et al. 2000; Cody et al. 2002). Oxygen-containing carbons such as alcohol, carboxyl, and carbonyl are relatively abundant up to ~20% of the total carbon in the macromolecule, which is partly because the hydrolysis during macromolecule purification could incorporate water-oxygen to the macromolecule. For example, nitrile, amide, and ester groups give carboxyl and alcohol groups after hydrolysis.

Because of the abundant carboxyl group, acetic acid could be generated easily after hydrous pyrolysis involved with C-C and/or C-O cleavage. Carbon isotope distribution within the macromolecule is as-yet unknown. If solvent-extractable ^{13}C -enriched amino and carboxylic acids (Yuen et al. 1984; Pizzarello et al. 2004) and ^{13}C -depleted PAHs (Naraoka et al. 2000) are applicable to aliphatic and aromatic carbons of the macromolecule, respectively, the ^{13}C -enriched methyl relative to carboxyl in this study may be explained. It is unlikely that the carboxyl group bound directly to the aromatic rings could generate the acetic acid. Further studies, especially on isotopic intramacromolecule composition, are needed to clarify the formation mechanism of acetic acid in this study. In addition, although the meteoritic macromolecule has been considered to contain a contribution partly from the interstellar environment based on its extreme D-enrichment (e.g., Kerridge et al. 1987), the ^{13}C -depleted acetic acid generated in this study cannot be distinctive isotopically from the acetic acid produced in solar nebula or terrestrial environment.

Relationship between Solvent-Extractable Acetic Acid and Hydrous Pyrolysate

In this study, acetic acid is the most abundant product in the hydrous pyrolysate fraction of macromolecular organic matter in Murchison, as described above. Acetic acid is also the most abundant free carboxylic acid in carbonaceous chondrites (Yuen et al. 1984; Shimoyama et al. 1989; Naraoka et al. 1999). The predominance of acetic acid is common, probably due to simple formation mechanisms and stability of this molecule.

It is well established that most carbonaceous chondrites have been subjected to aqueous alteration in the solar nebula and chondrite parent bodies (e.g., Clayton and Mayeda 1999; Benedix et al. 2003). Mineralogical and chemical studies have revealed that some CM chondrites have been subjected to various types of thermal alteration and metamorphism on their meteorite parent bodies (Akai 1988, 1990; Kojima et al. 1984). It might therefore be possible that solvent-extractable

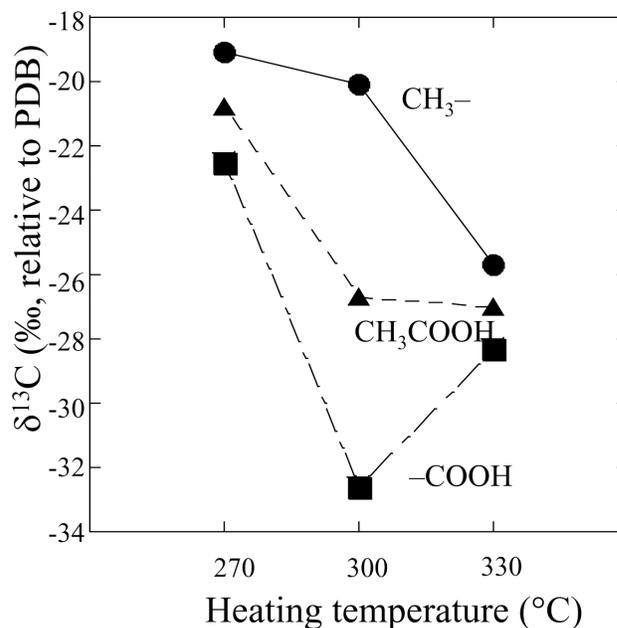


Fig. 2. Carbon isotopic compositions of “total” acetic acid, methyl-C, and carboxyl-C of acetic acid generated by hydrous pyrolysis of the Murchison macromolecular organic matter depending on heating temperature. The triangle, circle, and square symbols denote “total” acetic acid, methyl-C, and carboxyl-C, respectively.

acetic acid is derived from hydrous pyrolysis of macromolecular organic matter. However, the alteration temperature in Murchison is estimated to be 0–25 °C derived from oxygen isotopic fractionation between carbonates and phyllosilicates (Clayton and Mayeda 1999). Therefore, the temperature range of this hydrous pyrolysis experiment (270–330 °C for 72 h) cannot be applied directly to the occurrence of free monocarboxylic acid in Murchison. This discrepancy is also evident from the observation that free acetic acid in Murchison is extremely enriched in ^{13}C (+22.7‰) (Yuen et al. 1984) relative to acetic acid in this study (–20.8 to –27.0‰). Because the $\delta^{13}\text{C}$ of the bulk macromolecule is –13.0‰, the more ^{13}C -depleted acetic acid of this study is consistent with a kinetically controlled formation from macromolecule due to preferential cleavage of ^{12}C - ^{12}C relative to ^{13}C - ^{12}C . On the other hand, the ^{13}C -enriched free acetic acid could not be produced from the macromolecule, although heterogeneous carbon isotope distribution in the macromolecule has not been characterized yet. Such ^{13}C -enrichment of monocarboxylic acid combined with its D-enrichment could be inherited from an interstellar source (Huang et al. 2005).

This hydrous pyrolysis experiment (i.e., 270–330 °C for 72 h) may not accurately simulate a reaction condition on the parent bodies of carbonaceous chondrites. However, much longer duration at much lower temperatures could generate monocarboxylic acid from the macromolecule. Since the end-member isotopic composition has not been clarified for interstellar monocarboxylic acid, it should be noted that

monocarboxylic acid may be partly incorporated into a solvent-extractable form in carbonaceous chondrite by aqueous alteration of macromolecule. In addition, although the significance of solvent-extractable organic compounds in meteorites has been emphasized as source materials for the origin of life, macromolecular organic matter also has a potential to provide bio-related organic molecules to the Earth.

CONCLUSIONS

We have conducted hydrous pyrolysis of macromolecular organic matter purified from the Murchison meteorite to examine monocarboxylic acid formation. C₂-C₅ monocarboxylic acids are generated in the hydrous pyrolysate, where acetic acid constitutes more than 90% of total monocarboxylic acids. The amount of monocarboxylic acid increases with increasing of heating temperature. The Murchison macromolecule has a potential to generate acetic acid about four times higher than the amount of water-extractable acetic acid in the range of 270–330 °C. The carbon isotopic composition of the generated acetic acid decreases from –20.8 to –27.0‰ with increasing of heating temperature. Furthermore, we performed intramolecular δ¹³C measurement of the generated acetic acid, in which the methyl group is more enriched in ¹³C than the carboxyl group by up to 12.5‰, which suggests that the acetic acid formation during hydrous pyrolysis is predominantly controlled by a kinetic process.

The acetic acid generated in this study (–20.8 to –27.0‰) is significantly depleted in ¹³C relative to the free acetic acid reported in Murchison (+22.7‰). The large δ¹³C difference indicates that the free acetic acid is not apparently derived from macromolecule by aqueous alteration. The generated monocarboxylic acids are considered to be derived from multiple functional groups in isotopically heterogeneous macromolecular organic matter. Although the pyrolysis temperature of this study is much higher than the estimated alteration temperature of the Murchison meteorite, it may be possible to generate monocarboxylic acids from the macromolecular organic matter in meteorites under much longer duration at lower temperature.

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