MOLECULAR DISTRIBUTION OF MONOCARBOXYLIC ACIDS IN ASUKA CARBONACEOUS CHONDRITES FROM ANTARCTICA

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Abstract. Molecular distribution of low-molecular-weight monocarboxylic acids was studied in three CM2 Asuka carbonaceous chondrites (A-881280, A-881334 and A-881458), which were recovered from Antarctica by the 29th Japanese Antarctic Research Expedition in 1988. GC and GC/MS analyses identified more than 30 monocarboxylic acids in A-881458, including aliphatic and aromatic acids with various structural isomers. Isomeric phenolic compounds were also identified. The aliphatic carboxylic acids have straight-chain structures having 2 to 12 carbon atoms (C_2 to C_{12}), and branched-chain structures (C_4 to C_9). The quantities of straight-chain acids decrease logarithmically with increasing carbon number. At the same carbon number, a straight-chain isomer is always predominant compared to branched-chain isomers. All of the 14 possible C_4, C_5 and C_6 aliphatic monocarboxylic acids (not including optical isomers) have been identified, although all the isomers were not reported in Murchison and Y-791198 meteorites. Of the 17 possible isomeric C_7 acids, at least 14 isomers were tentatively identified by mass spectra (EI and CI mode). At C_8 or above, peaks of branched-chain isomers become obscure, probably due to the large number of isomers and small concentrations. Branched-chain monocarboxylic acids over C_6 have never been reported in Murchison. Although occurrence of aliphatic acids are similar between A-881458 and Murchison at C_4, C_5 and C_6 acids, a major difference is that A-881458 as well as Y-791198 have straight-chain predominance among isomers in contrast to Murchison being branched-chain predominant. In the case of isomeric aromatic compounds such as toluic acids and cresols, *m*-toluic acid and *p*-cresol are more abundant among their isomers, respectively. The molecular distribution may not reflect thermodynamic equilibrium but rather a kinetically controlled process for their formation mechanism. The other two CM2 chondrites (A-881280 and A-881334) were depleted in carboxylic acids in spite of similar carbon contents. The depletion is not due to weathering on ice, because the degrees of weathering are small and similar among the three chondrites. Probably those latter two chondrites may have been subjected to aqueous alteration or metamorphism on their meteorite parent bodies.

1. Introduction

Organic compounds in meteorites can provide useful information not only on chemical evolution in an extraterrestrial system but also on the chemical evolution and origins of life on the earth. To date, organic analyses in meteorites have focused mainly on the Murchison (CM2) meteorite. Various types of organic compounds

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have been identified in Murchison (Cronin *et al.*, 1988 and references therein). Antarctic meteorites give us new opportunities to examine the occurrence of organic compounds.

So far, four Antarctic CM2 chondrites were analyzed by the authors for solvent-extractable organic compounds such as amino acids (Shimoyama and Harada, 1984; Shimoyama *et al.*, 1979, 1985), carboxylic acids (Shimoyama *et al.*, 1986, 1989) and hydrocarbons (Naraoka *et al.*, 1988; Shimoyama *et al.*, 1989). Because mono-carboxylic acids are the most abundant solvent-extractable organic compounds in carbonaceous chondrites, their molecular distribution has a potential to infer inter-molecular relationships with other organic acids such as amino-, dicarboxylic- and hydroxy-acids. In addition, long-chain carboxylic acids may have been important in the formation of membrane-like structures under prebiotic conditions (Deamer *et al.*, 1994). In this study, we examined monocarboxylic acids in three Asuka CM2 chondrites collected from Antarctica in 1988.

It has been proposed that organic compounds in meteorites are produced by Fischer-Tropsch Type (FTT) reactions, i.e. a thermocatalytic reaction of CO, H_2 and NH_3 (Hayatsu and Anders, 1981). This model is based on the observation that straight-chain aliphatic hydrocarbons are predominant over branched-chain isomers. An alternative model is that organic acids are metastable thermodynamically under hydrothermal conditions (Shock and Schulte, 1990; Shock, 1995). Alternatively, in an isotope study of the Murchison meteorite, higher-molecular monocarboxylic acids were formed from lower molecular homologs by carbon extented reaction under kinetically controlled mechanisms (Yuen *et al.*, 1984). The formation mechanisms of organic compounds in carbonaceous chondrites are still controversial. In this study, we discuss the molecular distribution of carboxylic acids with respect to possible formation mechanisms; i.e. kinetically or thermodynamically controlled processes.

2. Samples and Experimental

Asuka (A-) meteorites were found during the Antarctic Meteorite Search Program by the 29th Japanese Antarctic Research Expedition. More than 2400 meteorite specimens were collected as individual stones or fragments on the blue ice field around the Sør Rondane Mountains (71–73°S; 21–29°E), Queen Maud Land, Antarctica. Detailed descriptions of this program and the recovered meteorites are given elsewhere (Yanai *et al.*, 1993). The collection contains several carbonaceous chondrites (Yanai and Kojima, 1995). Three CM2 chondrites, A-881280, A-881334 and A-881458, were collected at the Nansen Plateau located about 50 km south of the Sør Rondane Mountains. They were stored in Teflon bags, frozen and shipped to the National Institute of Polar Research (NIPR) in Tokyo, where they were defrosted in a clean cabinet under a stream of dry and pure nitrogen gas. Preliminary observation indicates that it is small and similar for these

TABLE I

Carbon concentrations and isotopic compositions in three Asuka CM2 chondrites used in this study

No.	Chondrite	C	$\delta^{13}C$ (‰ versus PDB)[b]		
		(wt %)[a]	bulk	after H_2O	after HCl/HF
1	A-881280	2.46	–13.4	–14.6	–15.1
2	A-881334	1.49	–6.9	–8.3	–9.0
3	A-881458	1.77	–2.6	–8.6	–13.2

[a] Average values for duplicate analyses.
[b] Carbon isotopic compositions were determined on bulk and residues of H_2O and HCl/HF treatments (Naraoka et al., 1997).

three chondrites to receive the terrestrial weathering on Antarctic ice (H. Kojima, personal communication).

Interior parts of each specimen were obtained by chipping on a clean bench at the NIPR. Part of each sample was pulverized using an alumina mortar and pestle on a clean bench set inside a clean room at Tsukuba. The alumina-ware were heated at 500 °C prior to use. Carbon contents were determined using a CHN analyzer (Perkin Elmer 240), ranging from 1.5 to 2.5 wt % (Table I), similar to carbon contents of other CM2 chondrites (Kerridge, 1985). Carbon isotopic compositions were determined on bulk and residues of H_2O and HCl/HF extraction (Table I) as reported by Naraoka et al. (1997).

The extractions of carboxylic acids were performed in a clean room. A powdered sample (0.5 g) was extracted with 5 mL of 1% KOH/methanol (w/v) by refluxing in a degassed and sealed glass tube at ∼80 °C for 3 h. The KOH pellet used was previously heated in an oven at 350 °C for 30 min on a platinum boat. After centrifugation the supernatant was removed, and 5 mL of water were added to the supernatant. The residue was further twice extracted by sonication with 2 mL of methanol. The combined solution was extracted with 3 mL of benzene three times. The water fraction (acid fraction) was evaporated to dryness and acidified with 0.2 mL of distilled HCl (azeotrope) at ice-water temperature. Finally, carboxylic acids were extracted with 1 mL of CH_2Cl_2 five times. A procedural blank was performed using 0.5 g of preignited sea sand (Figure 1d).

The extracted carboxylic acid fraction was analyzed by gas chromatography (GC; Shimadzu, GC-14A) with a flame ionized detector (FID), and gas chromatography/mass spectrometry (GC/MS; Shimadzu QP-1000) using both electron impact (EI) and chemical ionization (CI) with isobutane as a reaction gas. The CI method can selectively detect m/z signals of parent molecules (M) as M+1. A fused silica capillary column (PEG-20M, 50 m × 0.25 mm i.d.) was used for both analyses. Using a splitless injection, the oven was programmed from 30–80 °C at 10 °C min^{-1} and 80–200 °C at 2 °C min^{-1}. Mass spectra were acquired every 1 s over

the mass range 45–300. Molecular identification was based on retention times of carboxylic acids on GC and comparison with mass spectra obtained from authentic monocarboxylic acid standards. The concentration was generally determined using chromatographic areas on GC between standard and sample.

3. Results

More than 30 monocarboxylic acids were identified from A-881458, including aliphatic and aromatic structures (Figure 1). In addition to monocarboxylic acids, phenolic compounds and dimethylsulfone were also identified. The concentration of monocarboxylic acids recovered from A-881458 ranges from about 1.7 μmol to sub-nmol (or 100 μg to sub μg) per g of meteorite (Table II). The concentration is similar to that in Murchison meteorite (Lawless and Yuen, 1979; Yuen *et al.*, 1984) and up to two orders of magnitude higher than in Y-791198 meteorite (Shimoyama *et al.*, 1986). Carboxylic acids are about 20 times more abundant than amino acids in A-881458 (Naraoka *et al.*, 1990) and represent the most abundant solvent-extractable organic component in this chondrite, which is similar to recoveries from Murchison (Cronin *et al.*, 1988) and Y-791198 (Shimoyama *et al.*, 1986). However, A-881280 and A-881334 are depleted in carboxylic acids with small amounts of acetic acid and dimethylsulfone (peak No. 17 on Figure 1), in spite of a comparable carbon content to A-881458 (Table I). Dimethylsulfone, which was observed in similar amounts for the three chondrites, may be a terrestrial contaminant produced from dimethylsulfide by oxidation. Dimethylsulfide is highly volatile and one of the most abundant components in marine aerosol (Legrand *et al.*, 1991). Probable reasons for the acid-depletion are described in the following section. Conversely the possible terrestrial contamination of carboxylic acids in A-881458 is very low in this study, because these 3 chondrites have similar occurrence (i.e. small degree of weathering) on Antarctic ice and similar handling for analysis (i.e. collection, transportation, processing and so on).

Aliphatic acids have been identified with both straight-chain structures having 2 to 12 carbon atoms (C_2 to C_{12}), and branched-chain structures (C_4 to C_7). For the same carbon number, a straight-chain acid is always predominant compared to branched isomers. The concentration of straight acids decreases logarithmically with increasing carbon number except for C_{12} (Figure 2).

All of the 14 possible structural isomers of C_4, C_5 and C_6 aliphatic monocarboxylic acids (not including optical isomers) were identified in the chondrite, in contrast to that previous studies could not identify all the isomers in Murchison and Y-791198 (Yuen and Kvenvolden, 1973; Shimoyama et al, 1986). Peak No. 6 in Figure 1 contained two C_5 branched-chain acids (2- and 3-methylbutanoic acids; 2-MeC$_4$ and 3-MeC$_4$), where abundance ratio of 2-MeC$_4$/3-MeC$_4$ is ~4.8 (see Appendix). A straight-chain isomer is the most abundant of the C_6 acids, and three
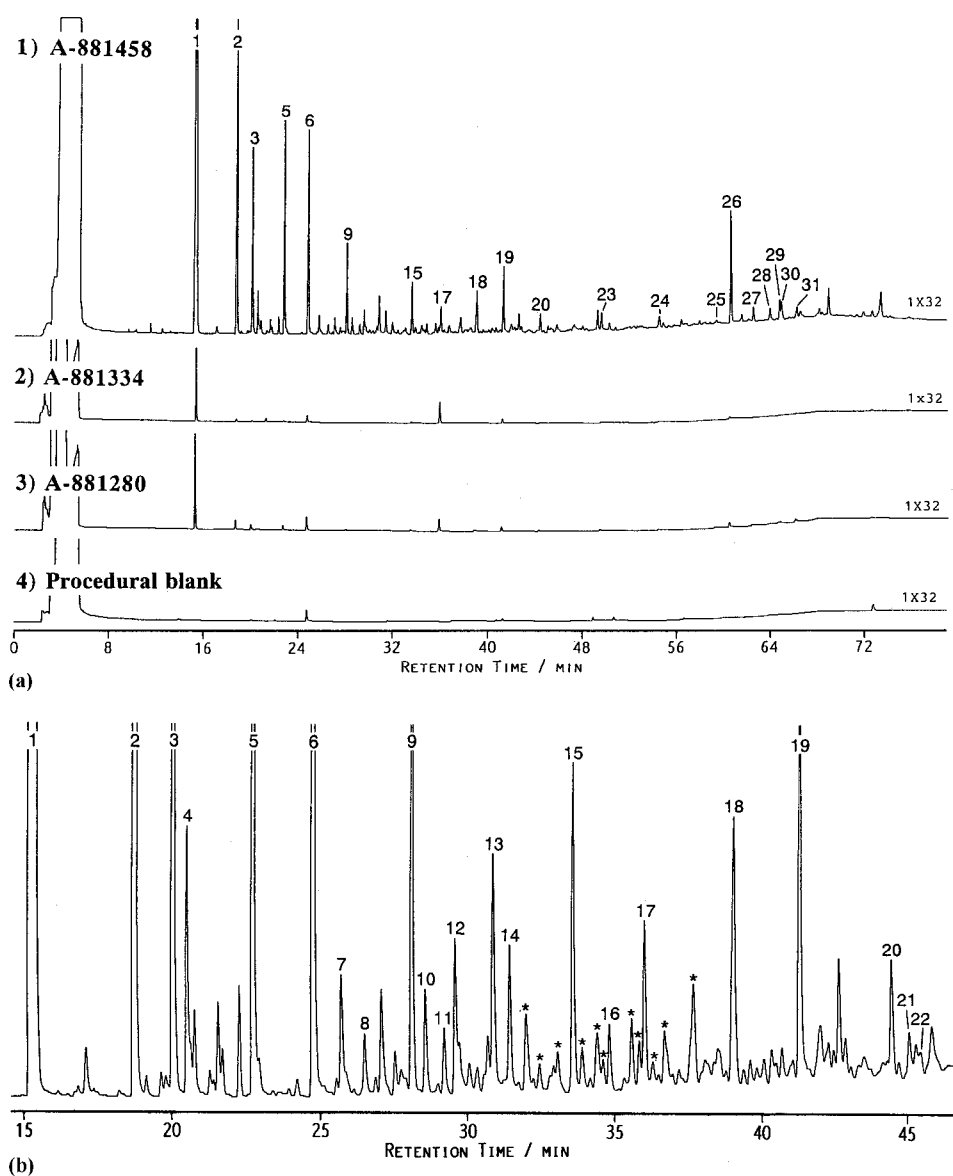
Figure 1. (a) Gas chromatograms of carboxylic acids from 1) A-881458, 2) A-881334, 3) A-881280, and 4) procedural blank. (b) An enlarged portion of Figure 1a for A-881458. 1. Acetic acid, 2. Propaonic acid, 3. 2-Methylpropionic acid, 4. 2,2-Dimethylpropanoic acid, 5. Butanoic acid, 6. 2- and 3-Methylbutanoic acid, 7. 3,3-Dimethylbutanoic acid, 8. 2,2-Dimethylbutanoic acid, 9. Pentanoic acid, 10. 2,3-Dimethylbutanoic acid, 11. 2-Ethylbutanoic acid, 12. 2-Methylpentanoic acid, 13. 3-Methylpentanoic acid, 14. 4-Methylpentanoic acid, 15. Hexanoic acid, 16. 2-Methylhexanoic acid, 17. Dimethylsulfone, 18. Heptanoic acid, 19. Phenol and *o*-Methylphenol, 20. Octanoic acid, 21. *p*-Methylphenol, 22. *m*-Methylphenol, 23. Nonanoic acid, 24. Decanoic acid, 25. Undecanoic acid, 26. Benzoic acid, 27. *o*-Toluic acid, 28. Dodecanoic acid, 29. *m*-Toluic acid, 30. *p*-Toluic acid, 31. Phenylacetic acid. *Branched-chain C$_7$ acids.

TABLE II

Amounts of carboxylic acids and related compounds in A-881458

No.	Peak no. in Figure 1	Compound[a]	Abbr.	Conc. (nmol g^{-1})	Relative abund. (%)[b]	n-C_m/2-MeC_m-l[c]	N/ΣBr[d]	Murchison[e] Conc. (nmol g^{-1})	N/ΣBr[d]
1	1	Acetic	C2	1680				1030	
2	2	Propanoic	C3	300				1830	
3	5	Butanoic	n-C4	95	55	1.2	1.2	380	0.76
4	3	2-Methylpropanoic	2-MeC3	79	45			500	
5	9	Pentanoic	n-C5	64	39	1.1	0.65	120	0.57
6	6	2-Methylbutanoic	2-MeC4	57	34			120	
7	6	3-Methylbutanoic	3-MeC4	12	9			90	
8	4	2,2-Dimethylpropanoic	2,2-diMeC3	29	18				
9	15	Hexanoic	n-C6	34	27	1.8	0.37	60	0.86
10	12	2-Methylpentanoic	2-MeC5	19	15				
11	13	3-Methylpentanoic	3-MeC5	22	17				
12	14	4-Methylpentanoic	4-MeC5	15	12			70	
13	11	2-Ethylbutanoic	2-EtC4	10	8				
14	8	2,2-Dimethylbulanoic	2,2-diMeC4	7	5				
15	7	3,3-Dimethylbutanoic	3,3-diMeC4	7	6				
16	10	2,3-Dimethylbutanoic	2,3-diMeC4	11	9				
17	18	Heptanoic	n-C7	19		4.2	0.32	30	
18	16	2-Methylhexanoic	2-MeC6	5					

TABLE II

(continued)

No.	Peak no. in Figure 1	Compound[a]	Abbr.	Conc. (nmol g^{-1})	Relative abund. (%)[b]	n-C_m/2-MeC_m-1[c]	N/ΣBr[d]	Murchison[e] Conc. (nmol g^{-1})	N/ΣBr[d]
19	20	Octanoic	n-C8	5				10	
20	23	Nonanoic	n-C9	4					
21	24	Decanoic	n-C10	3					
22	25	Undecanoic	n-C11	1					
23	28	Dodecanoic	n-C12	4					
24	26	Benzoic		90					
25	31	Phenylacetic		7					
26	27	*o*-Toluic		8.1	28				
27	29	*m*-Toluic		11.0	38				
28	30	*p*-Toluic		9.8	34				
29	19	Phenol		19					
30	19	*o*-Cresol		1.5	29				
31	22	*m*-Cresol		1.6	32				
32	21	*p*-Cresol		2.0	39				

[a] All compounds were identified by mass spectra using GC/MS (EI and CI) and retention times compared to those of standards except for 2,3-dimethylbutanoic acid (No. 16), which was identified by mass spectral interpretation (EI and CI).

[b] Relative abundances were determined among the isomers by GC or GC/MS (CI method).

[c] The abundance ratio of straight-chain (*n*-) to 2-methyl isomer at the same carbon number.

[d] The abundance ratio of straight-chain (*n*-) to total branched isomers at the same carbon number.
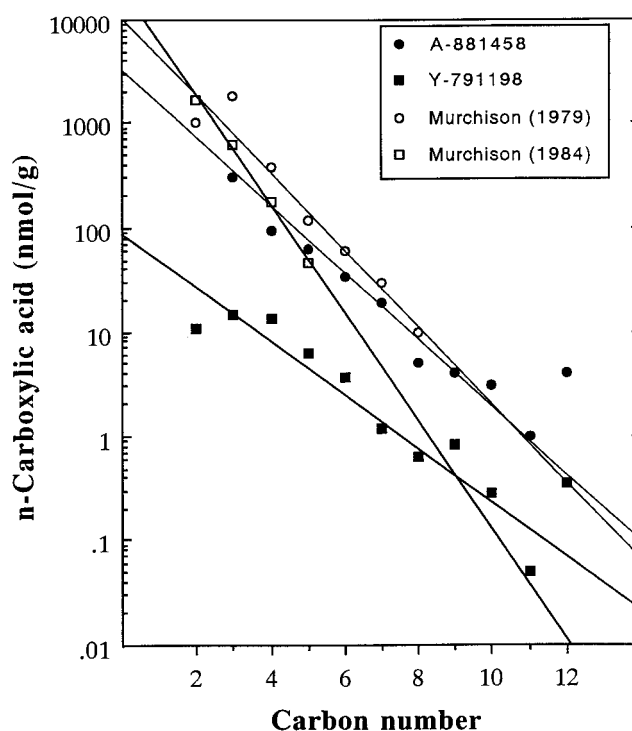
[e] Lawless and Yuen (1979).

Figure 2. Concentrations of straight-chain monocarboxylic acids depending on carbon number from Antarctic and Murchison carbonaceous chondrites. The concentrations decrease logarithmically with increasing carbon number. The Murchison data are from Lawless and Yuen (1979) and Yuen *et al.* (1984). The Antarctic data are from A-881458 (this study) and Y-791198 (Shimoyama *et al.*, 1986).

methylpentanoic acids (2-MeC$_5$, 3-MeC$_5$ and 4-MeC$_5$) are more abundant than dimethyl- and ethylbutanoic acids (Table II).

Of the 17 possible isomers at C$_7$, at least 14 isomers were tentatively identified using the CI mode (Figure 3f). Heptanoic and 2-methylhexanoic acids were identified using their standards, but peaks with an asterisk in Figure 1 are interpreted as C$_7$ acids on the basis of their mass spectra. At C$_8$ or above, peaks of branched-chain isomers become obscure, probably due to the large number of isomers and very small concentrations. Many structural isomers of the C$_8$ and C$_9$ acids are tentatively identified using the CI mode as shown in Figure 3g (C$_8$) and 3h (C$_9$), in which a straight-chain isomer is strongly predominant. This is the first report of branched-chain acids over C$_6$ in meteorites.

The most abundant aromatic carboxylic acid is benzoic acid (Figure 1). Methyl-benzoic acid (toluic acid) is also found as mixtures of *o*-, *m*- and *p*- isomers, and the structural isomer of phenylacetic acid is also identified. Among the three isomers of toluic acid, the *m*-isomer is more abundant (Table II). In addition to aromatic acids, phenol and methylphenol (cresol) are also present with *o*-, *m*- and *p*- isomers. In
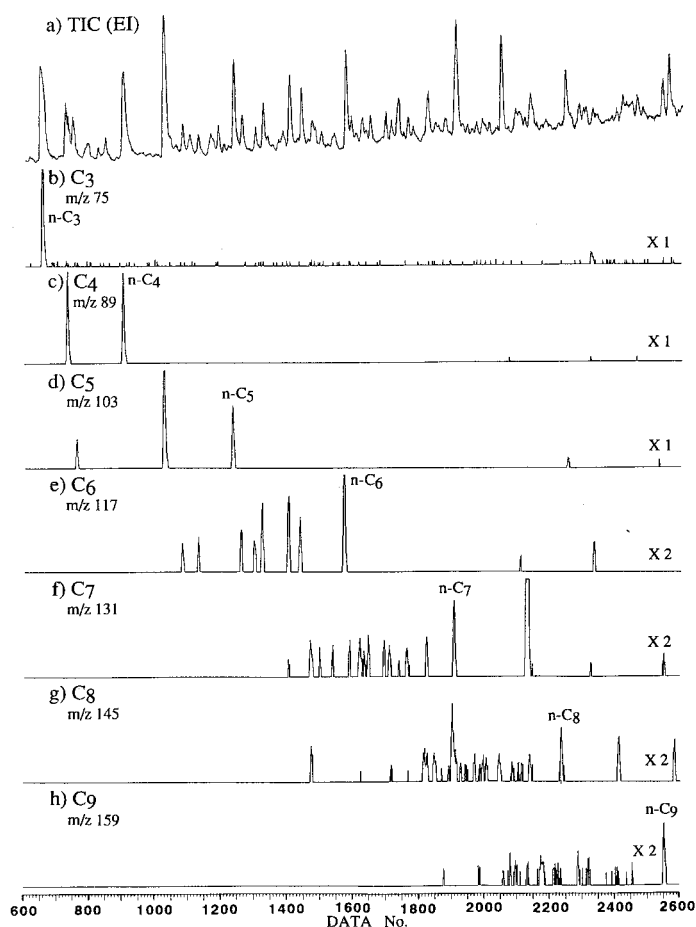
Figure 3. Mass chromatograms of selected ions of carboxylic acid fraction from A-881458 by GC/MS using a chemical ionization (CI) method. Selective m/z signals of parent molecules (M) are represented as M+1 by this method. Note that every branched-chain carboxylic acid always elutes prior to a straight-chain structure at the same carbon number. The straight-chain carboxylic acid is always predominant among the isomers.

the case of the three isomeric cresols, the *p*-isomer is more abundant than the other isomers (Table II).

4. Discussion

4.1. MOLECULAR ABUNDANCE PATTERNS OF CARBOXYLIC ACIDS IN A-881458

Monocarboxylic acids in A-881458 provide several insights into the molecular

distribution and offer a comparison with those in the Murchison and Y-791198 meteorites. This study further confirmed relatively long-chain (up to C_{12}) mono-carboxylic acids as in Y-791198 with no predominance of even- or odd-carbon, although only acids up to C_8 have been reported for Murchison (Lawless and Yuen, 1979). The concentration of straight-chain acids decreases logarithmically with increasing carbon number with correlations ($r^2 > 0.9$) (Figure 2). This was also observed for the carboxylic acids of Murchison (Lawless and Yuen, 1979; Yuen *et al*., 1984) as well as for Y-791198 (Shimoyama *et al*., 1986). Lawless and Yuen (1979) and Shimoyama *et al*. (1986) reported less abundant acetic acid than propanoic acid, which may be an experimental error due to the high volatility of acetic acid. A slight increase of n-C_{12} is observed in this study as well as in Y-791198, although the mechanism for this increase is not yet clear.

A difference of molecular distribution between Murchison and this study is the predominance in A-881458 of straight-chain acids relative to branched isomers. Whilst Lawless and Yuen (1979) and Yuen *et al*. (1984) reported a branched-isomer predominance over straight-chain acids between C_4 and C_6 in Murchison, the straight-chain predominance was observed in this study as well as Y-791198 (Shimoyama *et al*., 1986). For example, the abundance ratio of C_4 acids (n-C_4/2-MeC$_3$) is 0.76 for Murchison (Lawless and Yuen, 1979), whereas the same abundance ratios range from 1.20 (this study) to 1.66 (Y-791198) (Table II). The ratio of straight- to total branched-isomers ($N/\Sigma Br$) is similar in this study (0.65) and Murchison (0.57) at C_5, but lower (0.37, this study) than that of Murchison (0.86) at C_6 (Table II). This is because this study revealed more variety of structural isomers for C_6. In this study as well as Y-791198, however, a straight-chain acid is always the most abundant among the isomers at any carbon number.

One of the causes for the difference might be an artifact of the analytical procedure, i.e. differences in partition coefficients of carboxylic acids in the solvents used, as discussed by Lawless and Yuen (1979). For example, a difference in the partition coefficients of propanoic and hexanoic acids may be large enough to estimate abundances incorrectly. However, the difference is not so large between straight- and branched-chain isomers at the same carbon number. In addition, only straight-chain isomers have been reported for C_7 and C_8 in Murchison (Lawless and Yuen, 1979). Therefore, the molecular distribution in Murchison is somewhat inconsistent between carbon numbers above and below seven. Different formation mechanisms are unlikely among a series of carboxylic-acid homologs. The different molecular distributions may indicate different secondary processes such as degradation or partial equilibration, because branched carboxylic acids may be more stable thermodynamically than their straight-chain isomer as described in the following.

In earlier work fatty acids such as C_{16} and C_{18} were observed in some carbonaceous chondrites (Nagy and Bitz, 1963). Their existence, however, was critically reviewed as terrestrial biological contaminants based on the abundance patterns in which even carbon numbered (especially, C_{16} and C_{18}) acids were predominant,

as commonly occurs in organisms (Hayes, 1967). In this study the straight-chain acids become more prominent relative to branched isomers with increasing carbon number (Figures 1 and 3). The finding of carboxylic acids up to C_{12} in A-881458 as well as Y-791198 combined with their predominant straight-chain structures may be important to infer the presence of relatively long-chain acids, such as those may comprise boundary structures (Deamer *et al.*, 1994).

4.2. Mechanisms of carboxylic-acid synthesis in carbonaceous chondrites

Several mechanisms have been proposed to explain the origin of organic compounds in carbonaceous chondrites. A series of radical reactions of CH_4, H_2, NH_3 and H_2O could have taken place in electric discharges which might have occurred on meteorite parent bodies, and this mechanism explains well molecular distribution of amino acids (e.g. Miller *et al.*, 1976). However, this model cannot produce straight-chain-dominant molecules. Fischer-Tropsch Type (FTT) reactions, i.e. the thermocatalytic reactions of CO, H_2 and NH_3, may be the most favorable to explain the molecular distribution of dominant aliphatic straight-chain species (Hayatsu and Anders, 1981). Carbon isotopic compositions of individual carboxylic acids in Murchison (up to +22.7‰) were enriched in ^{13}C compared to terrestrial organic matter (–25 to –15‰; Deines, 1980). The $\delta^{13}C$ values decreased from +22.7 to +4.5‰ with increasing carbon number (C_2 to C_5) (Yuen *et al.*, 1984). Such an isotope distributions is attributable to a kinetically controlled carbon-chain formation, because ^{12}C could react with substrate kinetically faster than ^{13}C. In addition, high deuterium enrichment (300 to 700‰, relative to SMOW) of acid fraction in Murchison suggests that interstellar molecules might be involved in the synthesis of the acids (Epstein *et al.*, 1987; Krishnamurthy *et al.*, 1992). Alternatively, on the basis of considerations of the thermodynamic properties of aromatic hydrocarbons, CO_2, H_2, NH_3 and H_2O, it has been suggested that amino and carboxylic acids in meteorites may be thermodynamically present in a metastable state (Shock, 1990, 1995; Shock and Schulte, 1990). This model is based on aqueous alteration during hydrothermal processes on a meteorite parent body.

The structural varieties and abundances of monocarboxylic acids may provide an important clue for the elucidation of formation mechanisms. Such an approach may also provide an opportunity to infer formation mechanism of other organic compounds such as amino acids and dicarboxylic acids, since monocarboxylic acids constitute the major component in the solvent-extractable organic compounds of carbonaceous chondrites. If a thermodynamically controlled process is an important mechanism, it should result in an equilibrium of molecular distribution. Thermodynamic calculations might be consistent with the observation that the concentration of straight-chain acids decreases logarithmically with increasing carbon number (Shock, 1995). On the other hand, thermodynamic properties of various aliphatic branched-chain carboxylic acids are not yet known in detail. In the case of

aliphatic hydrocarbons, thermodynamic properties are reported for various isomers (Stull *et al*., 1969). Branched hydrocarbons are always more thermodynamically stable than the corresponding straight-chain components under the same conditions. If this signature is valid for carboxylic acid isomers as well, branched-chain carboxylic acids would be dominant species among the isomers at equilibrium. However, in A-881458 as well as in Y-791198, a straight-chain isomer is always predominant at the same carbon number. For example, in this study the ratio of n-C_m/2-MeC_{m-1} increases from 1.2 to 4.2 with increasing carbon number (m) from 4 to 7 (Table II). Above C_7, a straight-chain acid shows a strong predominance in both Antarctic and Murchison chondrites. It is unlikely that the energy difference thermodynamically between, e.g. n-C_7 and 2-MeC_6 is larger than that between n-C_4 and 2-MeC_3. Therefore, such molecular distributions of the aliphatic carboxylic acids cannot reflect a state of thermodynamic equilibrium.

The ratio of n-C_5/3-MeC_4 is high (4.6) compared to those of C_4 (1.2) and C_6 (2.2), and the 2-MeC_4/3-MeC_4 ratio is also higher (4.0) than those of 2-MeC_5/4-MeC_5 (1.3) and 3-MeC_5/4-MeC_5 (1.4). While the dimethyl-substituted acid (2,2-diMeC_3) is more abundant than 3-MeC_4 at C_5, dimethyl- and ethyl-substituted acids are less abundant than monomethyl-substituted acids at C_6. Such molecular distributions may be explained by a mechanism that invokes formation of a longer chain molecule from a shorter chain homolog by stepwise enlongated reaction using a single-carbon such as CH_3 radical or ion. A straight-chain predominance over branched-chain acids may be due to a stepwise reaction on a catalyst. Or the C-C bindings may be formed through carbon-cluster enlongation under a low pressure condition, because a linear carbon-cluster is preferentially formed under such a condition (Weltner Jr and Van Zee, 1989).

Isomeric aromatic compounds also provide information for formation mechanisms. In this study *o-, m-* and *p*-isomers were observed for toluic acid and cresol. Thermodynamic calculations indicate that *p*-toluic acid and *m*-cresol are favored among the various isomers (Stull *et al*., 1969; Shock, 1995). In this study, *m*-toluic acid and *p*-cresol are more abundant than their respective isomers (Table II), which is in conflict with the thermodynamic stabilities. However, the predominance of *m*-toluic acid and *p*-cresol is consistent with a nucleophilic CH_3 addition to benzoic acid and phenol, respectively. Both *o*-isomers are the least abundandant among the isomers, probably due to steric hindrance during CH_3 addition. These observations suggests that not only aliphatic but also aromatic compounds in the chondrite do not exhibit characteristics of thermodynamic equilibrium. This, in turn, may indicate that the kinetically controlled processes are important for their formation mechanism. The consideration is likely to be consistent with the isotope distributions in Murchison, where kinetically-controlled processing enriched the monocarboxylic acids in light carbon with increasing carbon number (Yuen *et al*., 1984).

4.3. CARBONACEOUS CHONDRITES DEPLETED IN CARBOXYLIC ACIDS

In contrast to A-881458, both A-881280 and A-881334 did not yield carboxylic acids except for small amounts of acetic acid, even though these 3 chondrites have similar carbon contents (1.5 to 2.5 wt %, Table I). Shimoyama and Harada (1984) first reported amino acid-depleted carbonaceous chondrites. At first, such depletion was thought to be due to leaching in Antarctic ice. Further studies also indicated the depletion of hydrocarbons, which are not soluble in water (Shimoyama *et al.*, 1988). If the leaching process might be important during weathering (including cryogenic weathering), hydrocarbons could be remain more than carboxylic and amino acids. However, molecular abundances show no evidence for such trends. Furthermore, Naraoka *et al.* (1997) determined carbon isotope ratios of bulk meteorite and residues after H_2O and HCl/HF treatments (Table I). A-881458 became rich in ^{12}C by 6‰ after the H_2O extraction. It implies that solvent-extractable organic matter is rich in ^{13}C, being consistent with previous studies (Becker and Epstein, 1982; Epstein *et al.*, 1987). On the other hand, the acid-depleted specimens (A-881280 and A-881334) did not change isotopically or only slightly rich in ^{12}C after the H_2O extraction (Table I). The bulk isotopic compositions are not so different as those of residues after HCl/HF treatment. Probably they lost solvent-extractable organic matter (rich in ^{13}C) such as carboxylic and amino acids on meteorite parent bodies during alteration. The carbon isotope signatures are consistent with mineralogical studies suggesting the alteration or thermal metamorphism on meteorite parent bodies (Kojima *et al.*, 1984; Akai, 1990; 1992).

To date, seven CM Antarctic carbonaceous chondrites were examined by the authors for solvent-extractable organic compounds. While three of these yielded appropriate amounts of organic compounds, the others are depleted in spite of similar carbon content ($\sim$1 to 2.5 wt %). This study may reveal the common occurrence of thermally altered specimens in carbonaceous chondrites.

5. Conclusions

Molecular distributions of monocarboxylic acids in A-881458 furthur confirmed a variety of structural isomers, and a predominance of a straight-chain over branched-chain isomers. The finding of carboxylic acids up to C_{12} in A-881458 as well as in Y-791198 combined with their predominant straight-chain structures is important to infer the presence of relatively long-chain acids which may comprise prebiotic membrane-like structures. Molecular distributions of carboxylic acids in carbonaceous chondrites suggest that a kinetically controlled process is dominant for their formation mechanism, in which carbon-chain is extented with straight-chains being favored, mediated on a catalyst or through carbon-cluster enlongation under a low pressure condition.

Acknowledgments

Appendix

Peak No. 6 in Figure 1 contained both 2-methylbutanoic (2-MeC$_4$) and 3-methyl-butanoic acid (3-MeC$_4$). The abundance ratio of 2-MeC$_4$/3-MeC$_4$ is determined by a calibration curve using areas of fragment ions (m/z 73 and 59) on the mass chromatograms of several standard mixtures of 2-MeC$_4$ and 3-MeC$_4$. Open circles denote ratios of fragment ions depending on the 2-MeC$_4$/3-MeC$_4$ ratios of standards. A filled square represents the abundance ratio of 2-MeC$_4$/3-MeC$_4$ (4.8) in A-881458. (See Appendix Figure)
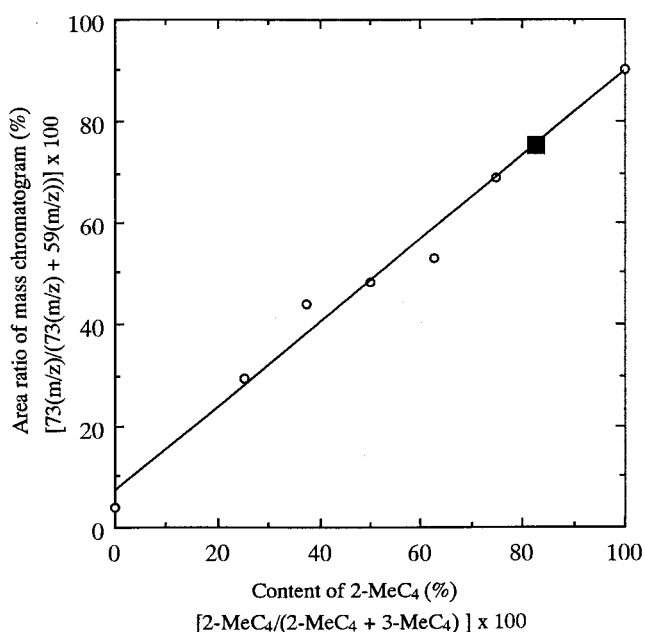
Appendix Figure.

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