

## Free dicarboxylic and aromatic acids in the carbonaceous chondrites Murchison and Orgueil

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**Abstract**—We have analyzed an important fraction of the free carboxylic acids present in water extracts of the CM2 chondrite Murchison and the CI1 chondrite Orgueil using gas chromatography–mass spectrometry (GC-MS). The free nature of the carboxylic acids analyzed was ensured by employing a single-step water extraction. Analyses revealed the presence of a structurally diverse suite of both aliphatic and aromatic acids in Murchison, while Orgueil exhibits a simpler distribution of exclusively aromatic acids. Within the Murchison aromatic acids, there are previously unreported phthalic acids, methyl phthalic acids, and hydroxybenzoic acids. In Orgueil, benzoic acid and very small amounts of methylbenzoic acids and methylhydroxybenzoic acids were detected. For the aromatic acids in both Murchison and Orgueil, most structural isomers were identified, suggesting an origin by abiotic processes. Quantitative differences are evident between acids in the two meteorites; carboxylic acids are much more abundant in Murchison than in Orgueil. The data suggest that differing levels of aqueous alteration on the meteorite parent body(ies) has produced dissimilar distributions of carboxylic acids.

### INTRODUCTION

The analysis of organic compounds in carbonaceous meteorites provides information about chemical evolution in an extraterrestrial environment and the possible compounds that could have been present on the Earth before and during the origin of life. A less common approach for the study of organic compounds in meteorites is the use of these highly sensitive components as indicators of environmental conditions in the early solar system.

A wide range of soluble organic compounds is present in carbonaceous chondrites, including amino acids, N-heterocycles, hydrocarbons, and carboxylic acids (for a general overview see, e.g., Botta and Bada 2002; Sephton 2002, 2004). The carboxylic acids are of particular interest as they are the most abundant soluble compound class in meteorites. Numerous water extracts of carbonaceous chondrites have yielded carboxylic acids. Yuen and Kvenvolden (1973) were the first to detect straight and branched chain monocarboxylic acids, ranging from two to eight carbon atoms, in the CM2 carbonaceous chondrites

Murchison and Murray. Carboxylic acids were identified by gas chromatography–mass spectrometry (GC-MS), and the abundances ranged from 10 to 60  $\mu\text{g g}^{-1}$  per compound. Lawless et al. (1974) reported the presence of aliphatic dicarboxylic acids in Murchison, including branched and straight chain isomers with up to nine carbon atoms. Pizzarelli et al. (2001) detected carboxylic and dicarboxylic acids at concentrations of 40.0 and 17.5 ppm, respectively, in Tagish Lake, and >300 and >30 ppm, respectively, in Murchison. Most recently, the carboxylic acids content of the Antarctic C2 meteorite Elephant Moraine (EET) 96029.20 has been examined and an exceptionally high concentration of formic acid was detected (Huang et al. 2004).

Indigeneity of the meteoritic carboxylic acids has been provided by stable isotope measurements. Carbon isotopic measurements by Yuen et al. (1984) and isotopic compositions of hydrogen, nitrogen, and carbon of the Murchison acids (Epstein et al. 1987) provided unambiguous evidence that these compounds are of extraterrestrial origin. Furthermore, the carboxylic acids present in the meteorite were enriched in the heavy isotope of hydrogen (deuterium or D), which is

consistent with an interstellar origin or formation from interstellar precursors (Krishnamurthy et al. 1992). Compound-specific isotope data of monocarboxylic acids were first presented for Murchison straight and branched short chain monocarboxylic acids (Yuen et al. 1984) and were recently reported for carboxylic acids in Murchison and EET96029.20 (Huang et al. 2004). These studies indicate that a) the majority of compounds have isotope ratios outside the range of biological compounds, b) there is a general trend of decreasing  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values with chain length for straight chain acids, and c) the branched acids are enriched in  $\delta^{13}\text{C}$  and  $\text{D}$  relative to the straight chain acids. Huang et al. (2004) suggests that these data are in accord with an abiotic formation of monocarboxylic acids in the cold interstellar medium, or as suggested by Remusat et al. (2006) in the outer solar system, involving radical and ion-molecule reactions. Hydrogen and carbon isotopic compositions of individual aliphatic dicarboxylic acids in Tagish Lake were determined and reflect a nonterrestrial origin (Pizzarello and Huang 2002).

Carboxylic acids were first used as indicators of environmental conditions in the early solar system by Peltzer and Bada (1978) who identified seven hydroxycarboxylic acids in the water extract of Murchison at the same concentration as hydrolyzed amino acids ( $14.6 \mu\text{g g}^{-1}$  in total). The data suggested that the Strecker-cyanohydrin pathway is responsible for the synthesis of both hydroxyacids and amino acids in the parent body of the meteorites. Later, Cronin et al. (1993) found more than 50 hydroxydicarboxylic acids in Murchison. Cronin et al. (1993) also showed that the hydroxycarboxylic acids and the hydroxydicarboxylic acids had a chain structure that corresponded to  $\alpha$ -amino acids, supporting the hypothesis of Peltzer and Bada (1978) and Peltzer et al. (1984) that they share a common Strecker-cyanohydrin reaction pathway.

During Strecker-cyanohydrin reactions, hydrogen cyanide and aldehydes combine in aqueous solution to produce  $\alpha$ -hydroxycarboxylic acids, but if ammonia is also present, then  $\alpha$ -amino acids are formed. High pH also discourages the formation of  $\alpha$ -hydroxycarboxylic acids. Therefore, the ratio of  $\alpha$ -hydroxycarboxylic acids to  $\alpha$ -amino acids in meteorites can provide some indication as to the volatile content and pH of the asteroid parent body on which these compounds were synthesized (Peltzer et al. 1984). Carboxylic and dicarboxylic acids can also be formed from carboxamides upon hydrolysis, the latter compound class being present as numerous isomers and homologues in Murchison (Cooper and Cronin 1995). The ratio of carboxylic acids to structurally similar carboxamides, therefore, also presents the opportunity for constraining the extent of aqueous processing on the parent asteroid.

One class of carboxylic acids not currently utilized to provide environmental information from the early solar system are the aromatic carboxylic acids. Naraoka et al. (1999) reported the presence of both aliphatic and aromatic

acids in three CM2 Asuka carbonaceous chondrites from Antarctica. For the free aromatic acids, Naraoka et al. (1999) only reported the presence of benzoic acid, methylbenzoic acids (all three isomers), and phenylacetic acid. However, the aromatic acids reported by Naraoka et al. (1999) may not be "free" acids at all because the sample was refluxed with 0.18 M KOH and therefore saponification of bound acids cannot be ruled out. Carboxylated pyridines (nicotinic acid derivatives) were reported in the Murchison and Tagish Lake meteorites (Pizzarello et al. 2001). In addition, aromatic dicarboxylic acids were observed in benzene/methanol extracts as a series of imide derivatives of phthalic acid, homophthalic acid, and some alkyl homologues (Pizzarello et al. 2001). In the same study, carboxylic and dicarboxylic acids were identified in Tagish Lake and in Murchison.

In the present study, we extracted free carboxylic acids from the Murchison and Orgueil meteorites, subjected them to a derivatization procedure to ensure analytical amenability, and characterized their structure by GC-MS. Comparing data from these meteorites reveals a record of dissimilar levels of aqueous processing and further illustrates the utility of carboxylic acids as organic records of environmental conditions in the early solar system.

## MATERIALS AND METHODS

A chip of Murchison meteorite (5.103 g), provided by the Smithsonian National Museum of Natural History in Washington, D.C. (USNM 6550,1), and a large interior piece (7.76 g) of the Orgueil meteorite, provided by the Musée National in Paris, were crushed into powder using a ceramic mortar and pestle. A serpentine (hydrated magnesium silicate) sample from the Naturhistorisches Museum, Bern, precombusted at 500 °C for 3 h, was carried through the same procedure described for the meteorites, and used as a procedural blank.

All glassware and ceramics used for sample processing were heated at 500 °C for 3 h. Biopur tips (Fisherbrand) and Eppendorf microcentrifuge tubes (Sigma-Aldrich) were sterile.

## Extraction Procedure and GC-MS Analysis

Approximately 5 g of the Murchison and 5 g of Orgueil meteorite powder were placed inside Pyrex glass test tubes, 1 g per tube. Two ml of high performance liquid chromatography (HPLC) grade water (Sigma-Aldrich) were added to each tube, and then flame sealed. The extraction was performed in a heating block for 24 h at 100 °C. After extraction, the samples were centrifuged and the supernatant from each tube was transferred into new Pyrex test tubes. Meteorite sample residues contained in each tube were washed twice (1 ml each) with HPLC water and centrifuged,

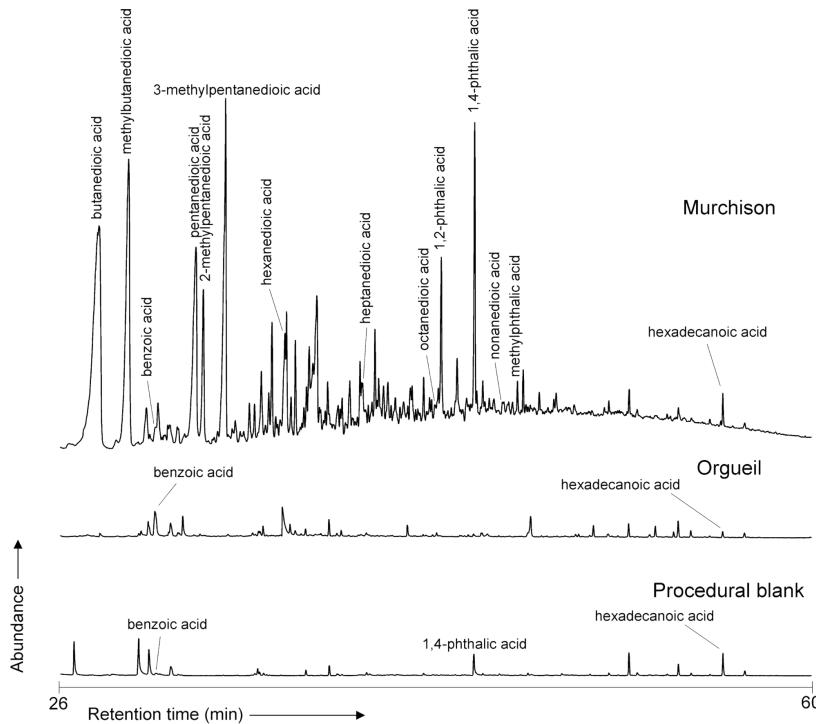


Fig. 1. A total ion chromatogram of the methylated water extracts from Murchison, Orgueil, and a full procedural blank, showing aliphatic dicarboxylic acids, benzoic acid, phthalic acids, and methyl phthalic acid (as methyl esters). All chromatograms are at the same scale.

and the water rinses were combined to the supernatants. The various water extracts for each meteorite were then combined and dried under vacuum.

For GC-MS analysis, quartz pyrolysis tubes were packed with quartz wool. The meteorite extracts were dissolved in 500  $\mu$ l of water, from which a 30  $\mu$ l aliquot was taken for analysis, adsorbed on the quartz wool and the water evaporated by heating to approximately 70 °C. To the loaded sample, 10  $\mu$ l of 25% tetramethylammonium hydroxide (TMAH) in methanol was added and the methanol was evaporated for 12 h. Samples were heated using a CDS Pyroprobe 1000 fitted with a 1500 valve interface (CDS Analytical, Oxford, PA) held at 250 °C. Following heating to 280 °C at a rate of 20 °C  $\text{ms}^{-1}$ , the sample was held at this temperature for 15 s in a flow of helium. The Pyroprobe was coupled to a GC-MS system comprising an Agilent Technology 6890 gas chromatogram (GC) combined with a 5973 mass spectrometer. Separation was performed on an S.G.E. (U.K.) BPX5 column (30 m length, 0.25 mm internal diameter, and 0.25  $\mu$ m film thickness). Helium at column flow rate of 1.1 ml  $\text{min}^{-1}$  (constant column flow rate) was used as the carrier gas. Injection was splitless and the injector temperature was 250 °C. The GC oven temperature was held for 15 min at 30 °C and then programmed at 4 °C  $\text{min}^{-1}$  to 300 °C, the final temperature was held for 9 min. Quantification was performed by comparing the GC-MS responses of derivatized acids to a known amount of benzoic acid subjected to the same analytical procedure. The values

for the aliphatic dicarboxylic acids (e.g., butanedioic acid) were further constrained by calculating their relative response factors.

## RESULTS AND DISCUSSION

### Carboxylic Acids Detected

A total ion chromatogram (TIC) of the methylated water extracts from Murchison and Orgueil is presented in Fig. 1, and the abundances of individual carboxylic acids are listed in Table 1. The most abundant carboxylic acids detected in Murchison were  $\alpha,\omega$ -dicarboxylic acids ( $\text{C}_4\text{--C}_9$ ), of which all structural isomers were found. In contrast to terrestrial biogenic aliphatic carboxylic acids, the meteoritic acids are short chained and display no even carbon number predominance. This observation is in accordance with earlier observations of dicarboxylic acids in Murchison (Cronin et al. 1993).

Dicarboxylic acids concentrations obtained by us in the Murchison water extract are consistent with the values reported by Peltzer et al. (1984). The 6.4  $\mu\text{g g}^{-1}$  for butanedioic acid, 2.6  $\mu\text{g g}^{-1}$  for methylbutanedioic acid, 0.2  $\mu\text{g g}^{-1}$  for pentanedioic acid, and 0.3  $\mu\text{g g}^{-1}$  for hexanedioic acid agree (or at least are on the same order of magnitude) with the 5.9  $\mu\text{g g}^{-1}$ , 5.3  $\mu\text{g g}^{-1}$ , 3.3  $\mu\text{g g}^{-1}$ , and 0.7  $\mu\text{g g}^{-1}$  obtained for the respective compounds by Peltzer et al. (1984). Dicarboxylic acid abundances in this study also

Table 1. Abundances of free dicarboxylic and aromatic acids in the Murchison and Orgueil meteorites and in a serpentine procedural blank.

Compound	Murchison (ng g <sup>-1</sup> )	Orgueil (ng g <sup>-1</sup> )	Serpentine (ng g <sup>-1</sup> )
Aliphatic dicarboxylic acids			
Butanedioic acid	6400	n.d.	n.d.
Methylbutanedioic acid	2600	n.d.	n.d.
Pentanedioic acid	170	n.d.	n.d.
2-methylpentanedioic acid	530	n.d.	n.d.
3-methylpentanedioic acid	1600	n.d.	n.d.
Hexanedioic acid	270	n.d.	n.d.
Heptanedioic acid	71	n.d.	n.d.
Octanedioic acid	29	n.d.	n.d.
Nonanedioic acid	28	n.d.	n.d.
Aromatic carboxylic acids			
Benzoic acid	47	100	4.9
2-methylbenzoic acid (+phenylacetic acid)	1.4	0.3	n.d.
3-methylbenzoic acid	0.8	0.4	n.d.
4-methylbenzoic acid	0.8	0.3	n.d.
2-hydroxybenzoic acid + 3-hydroxybenzoic acid	44	0.4	0.9
4-hydroxybenzoic acid	24	0.3	0.2
Methylhydroxybenzoic acids	40	0.4	n.d.
Aromatic dicarboxylic acids			
1,2-phthalic acid	320	6.9	n.d.
1,3-phthalic acid	46	n.d.	n.d.
1,4-phthalic acid	540	2.0	47
Methylphthalic acid	33	n.d.	n.d.

n.d. = not detected.

agree with other values previously observed in Murchison water extracts (Shimoyama and Shigematsu 1994). It is interesting to note that irrespective of the derivatization method used, the data obtained for the dicarboxylic acids are comparable between the various studies. Yet, in the context of our work, the application of a consistent method to a number of meteorites at least provides comparative data that reflect chemical constitution and past environmental conditions.

Aromatic acids detected in Murchison include benzoic and methylbenzoic acids, phthalic and methylphthalic acids as well as hydroxybenzoic acids (Table 1; Figs. 2–4). All possible structural isomers of phthalic acids and benzoic acids were detected, implying an origin by a random abiotic synthesis. In contrast, no ethylbenzoic acids or naphthoic acids were found in the Murchison meteorite. The abundant benzene-dicarboxylic acids (phthalic acids) will be, in part, indigenous but some contamination by phthalate esters (plasticizers) from terrestrial storage materials cannot be excluded, an assertion supported by the appearance of 1,4-phthalic acid in the procedural blank (Fig. 1; Table 1). However, the isomeric diversity suggests that most of the phthalate esters are likely to be extraterrestrial. Moreover, the most commonly used phthalate esters in polyvinylchloride (PVC) storage material are di(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DINP) and have chemical

structures that form only one of the isomers of phthalic acids (1,2-phthalic acid) when leached from PVC storage materials. Also, some phthalic acids (methyl phthalimide and dimethyl phthalimides) were detected previously by Pizzarelli et al. (2001).

The Orgueil carboxylic acids contain no abundant dicarboxylic acids, phthalic acids or hydroxybenzoic acids (Table 1) and, therefore, exhibit a much simpler distribution than those seen in Murchison (see Figs. 1–4). The only abundant acid present in Orgueil is benzoic acid. It is also possible to observe methylbenzoic acids (Fig. 2) with, as in the case of Murchison, all structural isomers represented, methylhydroxybenzoic acids, 1,2-phthalic, and 1,4-phthalic acid, all in very low abundances. The presence of these two phthalic acids in Orgueil may be explained (as referred to above) by the existence of 1,4-phthalic acid in the procedural blank, and additionally the presence of 1,2-phthalic acid by contamination by plasticizers from PVC storage materials.

To some extent, the data are incongruent with that of Pizzarelli and Huang (2002) who did detect dicarboxylic acids in Orgueil. The data could be explained by variable efficiencies for the different derivatization procedures or sample heterogeneity. Pizzarelli and Huang (2002) implied the possibility of terrestrial contamination as a source of these components because molecular  $\delta^{13}\text{C}$

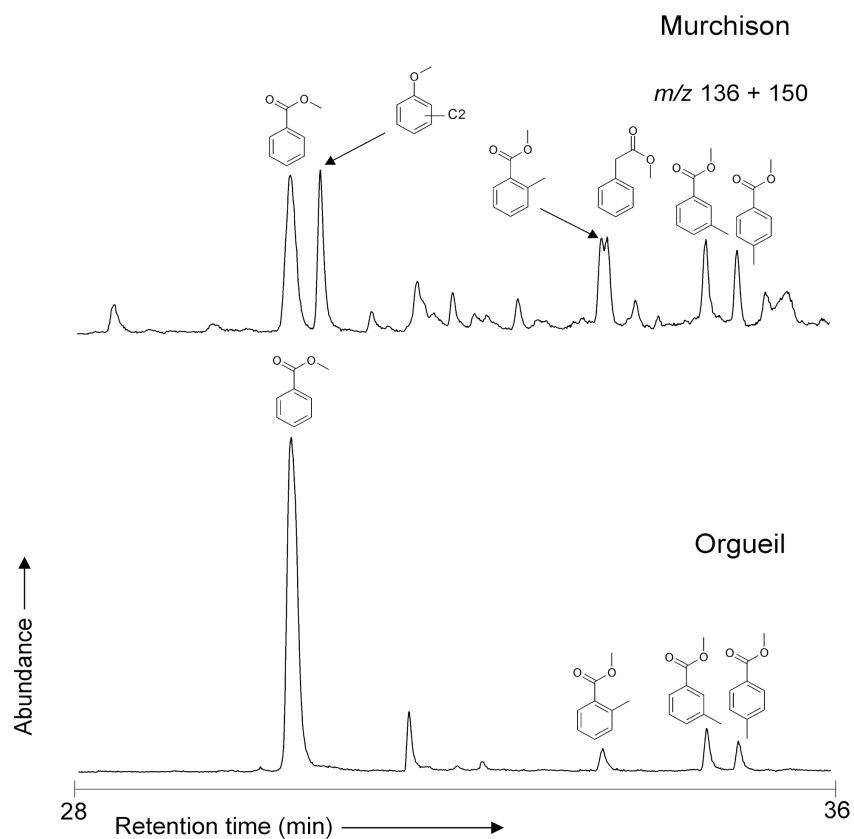


Fig. 2. A partially reconstructed mass chromatogram ( $m/z$  136 + 150) displaying benzoic acid and the methylbenzoic acids (as methyl esters) detected in Murchison and also in Orgueil. All structural isomers of the methylbenzoic acids are present.

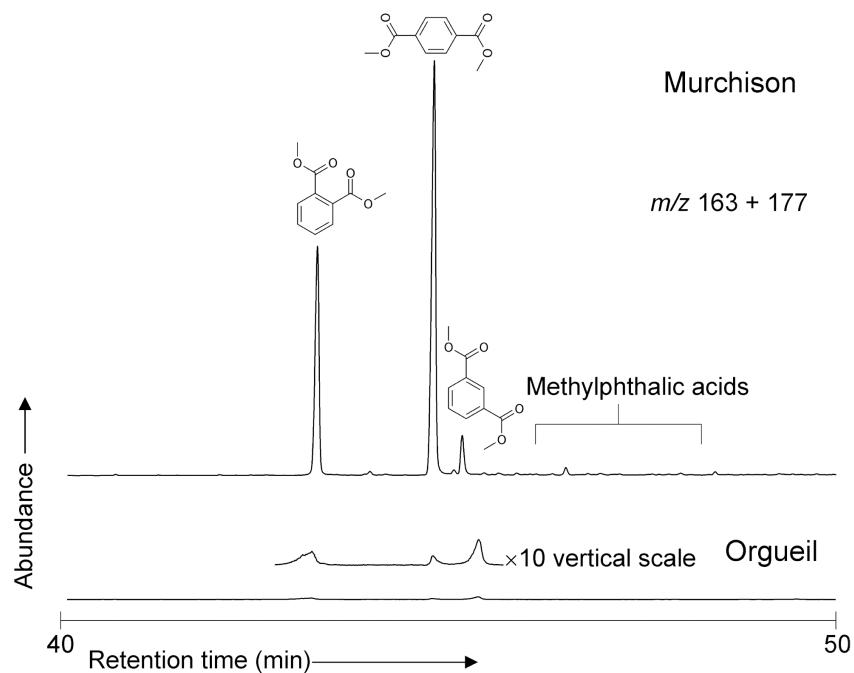


Fig. 3. A partially reconstructed mass chromatogram ( $m/z$  163 + 177) displaying the phthalic acids and methylphthalic acids (as methyl esters) from Murchison and Orgueil. The mass chromatogram from Orgueil is also shown magnified 10 $\times$  (vertical scale zoom).

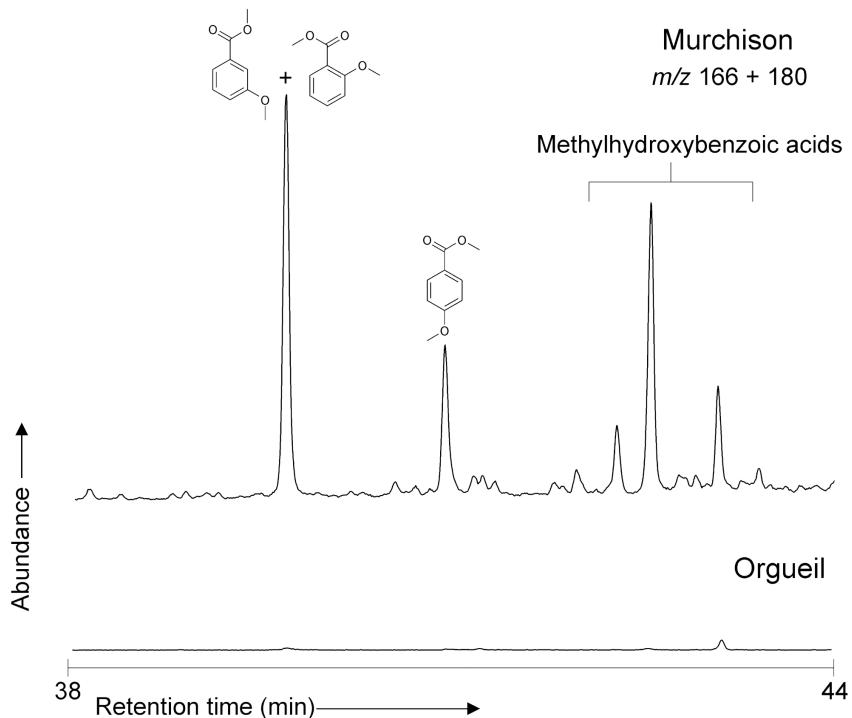


Fig. 4. A partially reconstructed mass chromatogram ( $m/z$  166 + 180) displaying the hydroxybenzoic acids and methylhydroxybenzoic acids (as methyl esters) from Murchison and Orgueil.

values for the Orgueil meteorite acids are in the terrestrial range (−23.8‰ for butanedioic acid, −19.5‰ for methylbutanedioic acid, −20.4‰ for pentanedioic acid, and −10.3‰ for 2-methylpentanedioic acid).

Numerous reports have identified free volatile aliphatic acids in Murchison and other meteorites (e.g., Yuen and Kvenvolden 1973; Yuen et al. 1984; Krishnamurthy et al. 1992; Cronin et al. 1993). In this study, the derivatization of the short chain aliphatic acids would have further increased their volatility and caused them to elute before the GC-MS solvent delay had finished. Furthermore, for larger carboxylic acids, it should be noted that water, when used as a solvent, discriminates against higher molecular weight carboxylic acids (owing to increased hydrophobic behavior with increasing molecule size). The previously reported free volatile aliphatic acids were not the object of this study and are not reflected in our data. Long chain acids present in Murchison are represented by small amounts of the biologically-common hexadecanoic acid (Fig. 1), which may indicate a low level of terrestrial contamination.

### Origin of Meteoritic Organic Acids

There are primarily two processes that could result in the formation of organic acids under space conditions. Acids could be formed in interstellar ices by irradiation with UV light or cosmic ray particles. Bernstein et al. (2002) presented

the first experimental evidence that ice photochemistry may have contributed to the formation of this class of compounds when  $\text{CO}_2$  was added to a polycyclic aromatic hydrocarbon (PAH) isolated in a  $\text{CO}_2$  ice matrix ( $\text{PAH}/\text{CO}_2 > 300$ ) at 15 K. Further support of an interstellar origin was provided when Wootten et al. (1992) and Mehringer et al. (1997) detected acetic acid in the interstellar medium. However, carboxylic acids, especially the aliphatic forms, were shown to be sensitive to UV radiation when in the gas phase or embedded in ices (Bernstein et al. 2004). Hence, radiation, shocks, and thermal processes may have destroyed most volatile carboxylic acids during solar system formation in the region where the meteorite parent bodies had formed.

A more likely process for the synthesis of carboxylic acids would be their formation during aqueous alteration on the meteorite parent body (Cronin and Chang 1993). In this environment, three possible pathways may be considered. First, the simple hydrolysis of precursor molecules would lead to acids. Precursors could include the corresponding nitriles, as is suggested for the amino acid synthesis as part of the Strecker-cyanohydrin pathway, or carboxamides and lactims (Cooper and Cronin 1995). Second, it may also be possible that cleavage and oxidation of hydrocarbons from the macromolecule or just oxidation of free hydrocarbons by oxidized fluids or minerals would lead, via alcohol and ketone intermediaries, to carboxylic acids. Third, evidence for organic synthesis may be forthcoming from the

Murchison phthalic acid data. The carboxyl substituent of benzoic acid has a deactivating effect on further substitution on the aromatic ring and promotes reactions at the *ortho*- (2) and *para*- (4) positions. The dominance of 1,2-phthalic acid and 1,4-phthalic acid support the possibility that phthalic acids are compounds produced by reactions on the parent body.

Irrespective of the ultimate origin of the carboxylic acids, a possible explanation of the different distributions of carboxylic acids in the two meteorites is the varying levels of parent body aqueous alteration experienced. For instance, oxidation reactions occurring during aqueous process would have selectively removed aliphatic material in free and macromolecular organic matter (Sephton et al. 2004). Hence, the loss of aliphatic carboxylic acids in the more extensively altered Orgueil meteorite can be attributed to the progressive carboxylation and decarboxylation of the hydrocarbon skeleton, eventually producing carbon dioxide and water. A similar process may have removed the methyl and methoxy substituents of benzoic and phthalic acid units to leave behind the more stable aromatic hydrocarbon cores.

## CONCLUSION

Two carbonaceous chondrites, Murchison and Orgueil, were analyzed for free dicarboxylic and aromatic acids. We report the first detection of free phthalic acids, methyl phthalic acids, and hydroxybenzoic acids in the Murchison meteorite. In Murchison, we observe both aliphatic ( $\alpha,\omega$ -dicarboxylic acids ranging from C<sub>4</sub> to C<sub>9</sub>) and aromatic acids (benzoic acids, phthalic acids, and hydroxybenzoic acids), while in Orgueil, only aromatic acids (benzoic acid being the most abundant) are present. This distinct distribution of carboxylic acids in different classes of meteorites can be explained by the different degrees of preterrestrial aqueous alteration. In Orgueil, a CI1 meteorite, extensive aqueous alteration may have oxidized hydrocarbons to form carboxylic acids which were then decarboxylated. Orgueil, therefore, has a much simpler distribution of these molecules in comparison to the CM2 Murchison meteorite that is thought to have undergone less extensive aqueous alteration on its parent body. A combination of interstellar and asteroidal processes may be responsible for the observed distribution of organic molecules in carbonaceous chondrites. Aqueous alteration appears to have had an important role in determining the abundance and organic composition of carbonaceous meteorites, which may have seeded the early Earth with important prebiotic organic compounds available for use by emerging life.

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**Editorial Handling**—Dr. Scott Sandford

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