Published in final edited form as:

Meteorit Planet Sci. 2019 February ; 54(2): 415–430. doi:10.1111/maps.13216.

Molecular Distribution, ^{13}C -Isotope, and Enantiomeric Compositions of Carbonaceous Chondrite Monocarboxylic Acids

José C. Aponte^{1,2,*}, Hannah K. Woodward^{2,3}, Neyda M. Abreu⁴, Jamie E. Elsila¹, Jason P. Dworkin¹

¹Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

²Department of Chemistry, Catholic University of America, Washington, DC 20064, USA.

³Department of Chemistry, University of Reading, Reading RG6 6UA, UK.

⁴Earth Science Program, Pennsylvania State University – Du Bois Campus, Du Bois, Pennsylvania 15801, USA.

Abstract

The water-soluble organic compounds in carbonaceous chondrite meteorites constitute a record of the synthetic reactions occurring at the birth of the solar system and those taking place during parent body alteration and may have been important for the later origins and development of life on Earth. In this present work, we have developed a novel methodology for the simultaneous analysis of the molecular distribution, compound-specific $\delta^{13}\text{C}$ and enantiomeric compositions of aliphatic monocarboxylic acids (MCA) extracted from the hot-water extracts of sixteen carbonaceous chondrites from CM, CR, CO, CV and CK groups. We observed high concentrations of meteoritic MCAs, with total carbon weight percentages which in some cases approached those of carbonates and insoluble organic matter. Moreover, we found that the concentration of MCAs in CR chondrites is higher than in the other meteorite groups, with acetic acid exhibiting the highest concentration in all samples. The abundance of MCAs decreased with increasing molecular weight and with increasing aqueous and/or thermal alteration experienced by the meteorite sample. The $\delta^{13}\text{C}$ isotopic values of MCAs ranged from -52 to $+27\text{‰}$, and aside from an inverse relationship between $\delta^{13}\text{C}$ value and carbon straight-chain length for $\text{C}_3\text{-C}_6$ MCAs in Murchison, the ^{13}C -isotopic values did not correlate with the number of carbon atoms per molecule. We also observed racemic compositions of 2-methylbutanoic acid in CM and CR chondrites. We used this novel analytical protocol and collective data to shed new light on the prebiotic origins of chondritic MCAs.

INTRODUCTION

Carbonaceous chondrites are among the oldest and most primitive materials in the Solar System. These extraterrestrial natural samples carry within their mineral matrices the

*Corresponding author: jose.c.aponte@nasa.gov; tel.: +1.301.614.6916; fax: +1.301.286.1683.

chemical inventory available at the birth of the solar system. The organic content of meteorites can be used to decipher the history of prebiotic organic chemistry, the processes that occurred inside a meteorite's parent body, and how these organics may have contributed to the development of life on Earth. Several types of organic compounds have been identified in carbonaceous chondrites, including aliphatic monocarboxylic acids (MCA) and other structurally related aliphatic molecules, such as alcohols, aldehydes, ketones, and amino acids (see reviews and references therein: Cronin and Chang, 1993; Sephton, 2002; Botta and Bada, 2002; Pizzarello et al., 2006). MCAs constitute the most abundant class of water-soluble organic compounds in one of the most organics-rich and extensively studied meteorite, the CM2 Murchison meteorite (Epstein et al., 1987; Krishnamurthy et al., 1992; Huang et al., 2005; Aponte et al., 2011). Thus, MCAs may have influenced the synthesis of other meteoritic organic species. Both short- (6 carbons) and long-chain MCAs may also be of potential astrobiological importance, as short-chain MCAs are important in central metabolism and long-chain MCAs (fatty acids) are found in biological membranes and may therefore be important for the origins of life on Earth (Deamer et al., 2002).

Meteoritic MCAs may form from the oxidation of alcohols and aldehydes and from the deamination of amino acids (Scheme 1); these mechanisms may occur under aqueous and/or thermal processing inside the asteroid parent body. Like some amino acids, some MCAs are chiral. The delivery of enantiomerically enriched amino acids inside meteorites and comets to the early Earth may have contributed to the development of Earth's homochirality (Engel and Macko 1997; Pizzarello and Cronin, 2000; Glavin and Dworkin, 2009; Burton et al., 2013); thus, understanding the relationship between amino acids and other structurally analogous organic compounds may shed light on their prebiotic break in symmetry. Additionally, in carbonaceous chondrites, water-soluble organic meteoritic compounds often show distinctive isotopic compositions (e.g., D/H, $^{13}\text{C}/^{12}\text{C}$) compared to those of their terrestrial analogs (Kvenvolden et al. 1970; Yuen et al., 1984; Krishnamurthy et al., 1992). Therefore, the study of meteoritic MCA isotopic compositions can provide information about the prebiotic synthesis of organic compounds present in meteorites, and about the processes that occurred inside their asteroid parent bodies.

There have been multiple techniques used in previous analyses of meteoritic MCAs (Table S1). Gas chromatographic (GC) analyses of MCAs based on the simultaneous extraction and derivatization of these compounds as their corresponding methyl esters have been commonly reported (Yuen and Kvenvolden, 1973; Lawless and Yuen, 1979; Shimoya et al., 1986, 1989; Naraoka et al., 1999; Monroe and Pizzarello, 2011). This method, however, appears to result in the loss of low molecular weight acids, as shown by comparison with liquid ion chromatography analyses of underivatized meteoritic MCAs (Yuen et al., 1984; Briscoe and Moore, 1993). Given the large abundance of MCAs in meteorites and their volatile nature, several analyses using solid phase micro-extraction (SPME) were performed in carbonaceous chondrites belonging to various petrologic groups (Huang et al., 2005; Aponte et al., 2011; Herd et al., 2011; Dillon et al., 2013; Hilts et al., 2014); the use of SPME, however, may induce some unavoidable degree of isotopic fractionation if not applied carefully (Dias and Freeman, 1997). More recently, the molecular distribution and enantiomeric composition of chondritic MCAs were determined after chiral derivatization (Aponte et al., 2014a); this method, however, resulted in the formation of a large suite of

reaction byproducts which makes it unsuitable for GC isotopic analyses. In this report, we analyzed carbonaceous chondrites belonging to five different groups using the same methodology, allowing us to draw comparisons and conclusions across our data set. However, differences in fractionation and other bias effects between methods used in previous studies makes it difficult to fully compare published meteoritic results.

In this study, we developed a novel method for the simultaneous GC enantiomeric and isotopic analyses of meteoritic MCAs and applied it to the analysis of sixteen carbonaceous chondrites from seven carbonaceous subtypes (Table 1): CM (ALH 83100, LEW 90500, Murchison, LON 94101, and EET 96029), CR (MIL 090001, GRA 95229, LAP 02342, and MIL 090657), CO (DOM 08006 and MIL 05013), CV (Allende, GRA 06101 and LAP 02206), and CK (ALH 85002 and EET 92002). Our developed GC method was optimized for the simultaneous measurement of the abundance, enantiomeric composition, and compound-specific isotopic analysis of short-chained MCAs (< 6 carbons). This chromatographic technique rests on the conversion of the MCAs into their corresponding esters (Scheme 2); chiral MCAs are converted into diastereomers, improving chromatographic separation on chiral GC columns without influencing the original enantiomeric and ^{13}C -isotopic compositions of the studied MCAs (details on method development are discussed in the Supporting Information).

MATERIALS AND METHODS

Materials.

Standards and reagents were purchased from Alfa Aesar or Sigma-Aldrich and used without further purification except as noted below. All glassware and sample handling tools used for the meteorite samples were rinsed with Millipore Direct Q3 UV water (18.2 M Ω , 3 ppb total organic carbon; hereafter referred to as “water”) wrapped in aluminum foil, and then heated in a muffle furnace at 500 °C overnight. We used HPLC grade dichloromethane (DCM), semiconductor grade NaOH, doubly distilled 6 M HCl, magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ACS grade 99.0%), and (*S*)-(-)-2-methylbutanol (*S*-2-MeBuOH, 99%). Functionalized aminopropyl silica gel was from SiliCycle (SiliaBond®, 40–63 μm particle size) and cleaned using methanol and DCM followed by drying under vacuum.

Meteorite extraction procedure.

Meteorite samples, obtained from interior chips that did not contain any visual evidence of fusion crust, were provided from the Antarctic meteorite collection at the NASA Johnson Space Center and the Smithsonian National Museum of Natural History, Washington, D.C.; specific details for each sample, including petrologic classifications and extracted masses are given in Table 1. The meteorites studied here were classified using the petrologic scale proposed by Alexander et al. (2013, 2015; Table 1). All meteorites were individually crushed and homogenized using a porcelain mortar and pestle in an AirClean® Systems ISO 5 positive pressure high efficiency particulate (HEPA) air-filtered laminar flow hood. Portions of each powdered meteorite sample (no more than 0.35 g at a time) were flame sealed in glass ampoules containing 1 mL of water for the extraction, and then heated at 100 °C for 24 h. A procedural water blank, analogous to the aqueous solution obtained after

meteorite extraction (used to quantify the concentration of MCAs present in the derivatization reagent prior to sample analyses and other potential contaminants) was carried through the identical extraction procedure as the meteorites.

Processing and derivatization for MCA analysis.

After aqueous extraction, the supernatants were separated by centrifugation and the meteorite residues were rinsed three times using 0.5 mL of water each time. The extract and rinses were combined, and 50 μ L of 2 M MgCl_2 was added to each extract to avoid the evaporation of volatile acids after extraction and to improve sample solubility and reactivity (see Supporting Information for details on method optimization). Next, the samples were filtered and dried overnight under reduced pressure. The residues were suspended in 100 μ L of DCM, then 20 μ L of 6 M HCl, and 10 μ L of 0.1 M *S*-2-MeBuOH, the derivatizing alcohol, in DCM were added. Next, the mixtures were heated at 80 °C for 30 min in sealed PTFE-lined screw cap vials in a heating block. After cooling to room temperature, the derivatized samples were passed through a plug of aminopropyl silica gel (45 mm length $\times$ 5 mm I.D.) to remove the excess of HCl used as reaction catalyst, rinsed using $\sim$ 3 mL of DCM, dried with flowing N_2 , and enough DCM (10 to 100 μ L) was added to dissolve the sample for analyses.

Compositional and isotopic analyses.

The derivatized MCAs were analyzed by GC coupled with parallel mass spectrometry and combustion isotope ratio mass spectrometry (GCMS/IRMS). The Thermo Trace GC was equipped with a 5 m base-deactivated fused silica guard column (Restek, 0.25 mm ID), two DB-5MS (30 m length $\times$ 0.25 mm I.D. $\times$ 0.25 μ m film thickness; Agilent), and two CP-Chirasil Dex CB (25 m length $\times$ 0.25 mm I.D. $\times$ 0.25 μ m film thickness; Agilent) capillary columns connected in series using Press-Tight® connectors (Restek). The GC was coupled to a Thermo DSQII electron-impact quadrupole mass spectrometer and to a Thermo MAT 253 isotope-ratio mass spectrometer via a Thermo GC-C III oxidation interface. Given that we did not expect the presence of 2-methylbutanoic acid and other C_6 chiral acids in organic-depleted chondrites (CO, CV and CK), we used two different GC-oven ramps for the analysis of MCAs, saving time and consumables when enantiomeric GC-resolution was not a critical step. The oven program used for the analyses of MCAs extracted from CM and CR chondrites was: initial temperature was 40 °C, ramped at 2 °C/min to 86 °C and held for 50 min, ramped at 2 °C/min to 130 °C, ramped at 20 °C/min to 190 °C with a final hold of 15 min. For MCAs in CV, CO and CK chondrites, the oven program was set as follows: initial temperature was 60 °C, ramped at 5 °C/min to 120 °C, ramped at 2 °C/min to 140 °C and held for 5 minutes, ramped at 2 °C/min to 160 °C and held for 5 minutes, ramped at 20 °C/min to 190 °C with a final hold of 15 min. The carrier gas used was UHP helium (5.0 grade) at 2.9 mL/min flow rate. Targeted ion mass-to-charge ratio ($m/z = 70 \pm 0.5$) was used to identify and quantify compounds through comparison to individual reference standards and the application of a 5-point calibration curve (concentrations ranged from 0.01 to 7 nM, $R^2 > 0.79$; see Table 2 for compound identifications and Figure S1 for molecular structures). Conditions for GC-MS/IRMS analysis and measurement of $\delta^{13}\text{C}$ values have been described in detail previously (e.g., Elsila et al., 2009, 2012; Aponte et al., 2014b, 2015). Briefly, six pulses of high-purity CO_2 gas ($\delta^{13}\text{C} = -27.494$ ‰ Pee Dee Belemnite “PDB” standard) that

had been precalibrated against two commercial reference CO₂ gases (Oztech Corporation, $\delta^{13}\text{C} = -3.61$ PDB and $\delta^{13}\text{C} = -40.740$ PDB) were injected into the IRMS for computation of the $\delta^{13}\text{C}$ values of the eluting derivatized standard and sample compounds. Analysis of the MAT 253 data was performed with Thermo Isodat 2.5 software. Peaks were integrated using the BaseFit background method. Stock solutions of individual MCA standards were combined to make a standard mixture that was carried through the derivatization process and run daily on the GC-MS/IRMS. The individual, underivatized stock solutions were also analyzed on a Costech ECS 4010 combustion elemental analyzer (EA) connected to the MAT 253 IRMS and compared to terrestrial L-alanine with a known $\delta^{13}\text{C}$ value of -23.330‰ (Iso-Analytical). The final $\delta^{13}\text{C}$ values of the meteoritic MCAs were obtained by correcting for the carbon added during derivatization using Equation 1 (rearranged from O'Brien et al. 2002):

$$\delta^{13}\text{C}_{\text{sample MCA}} = \left[\left((n_{\text{MCA}} + n_d) / n_{\text{MCA}} \right) \times \left(\delta^{13}\text{C}_{\text{derivatized sample MCA}} - \delta^{13}\text{C}_{\text{derivatized std MCA}} \right) \right] + \delta^{13}\text{C}_{\text{underivatized std MCA}} \quad (1)$$

where n_{MCA} is the number of carbon atoms in the underivatized MCA, and n_d is the number of carbons added by the *S*-2-MeBuOH. The $\delta^{13}\text{C}$ value for the carbon added by derivatization is thus determined empirically for each individual MCA, accounting for kinetic isotope effects during derivatization (Silfer et al. 1991). The precision of the calculated value also depends on the precision of the three measurements described above (i.e., derivatized sample, derivatized standard, underivatized standard) and can be calculated using Equation 2 (Docherty et al. 2001):

$$\delta^2_{\text{sample MCA}} = \delta^2_{\text{underivatized std}} + \left[\delta^2_{\text{derivatized std}} \times \left((n_{\text{MCA}} + n_d) / n_{\text{MCA}} \right)^2 \right] + \left[\delta^2_{\text{derivatized sample}} \times \left((n_{\text{MCA}} + n_d) / n_{\text{MCA}} \right)^2 \right] \quad (2)$$

RESULTS

Figure 1 presents the total ion chromatogram from GC-MS of a procedural blank, the mixture of MCA standards, and the Murchison meteorite, as well as the GC-IRMS chromatogram of the Murchison injection, illustrating the application of our analytical protocol to a meteorite extract. Similar chromatograms were obtained for other meteorites investigated in this work (Figures S2–S6 in the Supporting Information). The concentrations in nmol/g of meteorite for the MCAs in CR chondrites (except in MIL 090001) was between three and twenty times higher than those found in CM chondrites. The relatively lower abundances and diversity of compounds seen in MIL 090001 may have resulted from the fact that it is an anomalous CR chondrite (see Supporting Information; Keller, 2011; Keller et al., 2012; Alexander et al., 2013; Noronha and Friedrich, 2014; Harju et al., 2014; Abreu, 2016). The total abundances of MCAs in CO, CV, and CK carbonaceous chondrites were a minimum of 3 – 4 orders of magnitude lower than those seen in the CM and CR chondrites studied here. We observed decreasing concentrations of MCAs with increasing aqueous and thermal processing and little variability in their concentration among samples belonging to the same petrologic type (Table 2, Figure 2). Additionally, we found that the carbon weight

percentages (C wt.%) of MCAs are within the same orders of magnitude as that of carbonates and insoluble organic matter (IOM) in CR chondrites (again excluding MIL 090001), but more depleted in CM chondrites.

Our investigation focused on sixteen MCAs ranging from two to six carbon atoms (C₂–C₆). Throughout our analyses, we interpret the MCAs analyzed in the Allende (CV3.6) meteorite as dominated by terrestrial contamination. Therefore, the results of the analyses of MCAs found in Allende are shown but have been excluded from discussions in this report. We based this conclusion on the high total concentration of MCAs we found in Allende which is in sharp contrast to other thermally altered CV3 meteorites analyzed here and before (Aponte et al. 2011). Specifically, Allende contained high concentrations of heptanoic, octanoic, and nonanoic acids (C₇, C₈, and C₉; Table 2), MCAs that are very common in the terrestrial biosphere (Cork and Park, 1996; Bernier et al., 2000), but are only detected in trace amounts in other meteorites analyzed here (Table 2). Thus, given the potential for Allende contamination in particular and the anomalous results, the most parsimonious explanation is to assume contamination.

Acetic acid (C₂) was the most abundant acid found in each sample, constituting between 79 and 100% of the total amount of MCAs in all meteoritic samples studied. A consistent trend of decreasing MCA abundances with increasing carbon number was observed (Figure 2). MCAs with the carboxyl group on a primary carbon were consistently more abundant than their isomeric counterparts having the carboxyl moiety in the secondary and tertiary position (e.g., *n*-butanoic acid vs. isobutanoic acid, *n*-pentanoic acid vs. methylbutanoic and 2,2-dimethylpropanoic acid). Table 3 shows the $\delta^{13}\text{C}$ isotopic values for MCAs in CM, CR, and Allende (CV3) and their corresponding chromatograms are shown in Figure S6. The $\delta^{13}\text{C}$ isotopic values of MCAs in the studied meteorites range from –52 to +27‰. Excepting MIL 090001 (CR2.2), MIL 090657 (CR2.7), and LAP 02342 (CR2.5), acetic acid is the most ^{13}C -depleted MCA in each of the analyzed samples, with $\delta^{13}\text{C}$ isotopic values ranging from –52 to +3‰ (Table 3).

We measured the enantiomeric composition (*R/S* and *ee*) of 2-methylbutanoic acid in the CM and CR chondrites studied here (Table 4). Figure 3 shows the gas chromatogram of (*R*)- and (*S*)-2-methylbutanoic acid (compounds **6** and **7**) monitored at $m/z = 70 \pm 0.5$ and the mass spectra of these peaks in the analyzed extracts of the Murchison meteorite, procedural blank, and standards. Comparison of the mass spectra fragmentation patterns obtained for samples and standards showed that there are no significant coelutions or contaminants (except for that added by the derivatization reagent) present in the analyzed samples that would affect enantiomeric quantitation. All investigated chiral MCAs showed enantiomeric ratios consistent with racemic compositions within experimental error (Table 4).

DISCUSSION

MCA abundances and comparisons with previous studies.

Here, we compare the results of our current analyses with those previously reported. The total abundance of MCAs in the Murchison meteorite we measured are 1.2, 2.5 and 1.7 times higher than those reported by Lawless and Yuen (1979), Yuen et al. (1984), and Huang

et al. (2005) respectively, but a factor of 2.5 and 27.2 times lower than those found by Briscoe and Moore (1993) and Aponte et al. (2014a). In addition, previous GC-MS analyses of MCAs in Murchison found that acetic acid constitutes between 13 and 28% of the total MCA content in meteorites; in our analysis, however, the concentration of acetic acid accounted for 91% of the total concentration of MCAs in Murchison. The total abundance of MCAs in CR2 chondrites previously analyzed (Pizzarello et al. 2008, 2012; Aponte 2011), are between 39 and 630 times lower than the total concentrations of MCAs we found in CR2 chondrites. Additionally, previous analyses of MCAs in CR2 chondrites showed concentrations of linear C₄-C₈ MCAs (namely *n*-butanoic, *n*-pentanoic, *n*-hexanoic, *n*-heptanoic, and *n*-octanoic acids) that are within a similar range or in higher concentrations than acetic acid (Pizzarello et al. 2008, 2012), in contrast with our results which place acetic acid as the most abundant MCAs in CR2 chondrites.

Total MCA variability, including acetic acid concentration across different Murchison analyses could be attributed to sample heterogeneity. However, it seems likely that the multiple preparatory and analytical methods (e.g., multi-stepped extraction, purification methods; see Table S1) as well as the use of different analytical instrumentation used in different laboratories exert a significant bias which contributes to the difficulty in cross-comparison (Glavin et al. 2011). There is little discussion and published evaluation of how the methodology used may bias the analytical results; thus, to allow for a comparison across meteorites, it is critical to apply the same method.

Abundance and molecular distribution of MCAs in this study.

We analyzed sixteen carbonaceous chondrites across five groups, allowing us to distinguish between the abundances and distributions of MCAs that arose from (1) residence in different parent bodies and (2) those that resulted from various levels of aqueous or thermal alteration in the same parent body. MCAs may originate from the oxidation of aliphatic alcohols, aldehydes, or nitriles; thus, assuming a homogeneous accretion of these organic species across different parent bodies, it would be expected that more oxidized carbonaceous chondrites would contain higher levels of MCAs. CR chondrites are the least oxidized sample studied here (Krot et al. 2005). However, our results show that CR chondrites contain higher concentrations of MCAs than CM, CO, CV and CK chondrites. These results suggest that the accretion of aliphatic precursors of MCAs was not homogeneous throughout different parent bodies, or that the abundance of MCAs was mostly affected by parent body processes. Independently of the level of aqueous and/or thermal processing experienced by the meteorites studied here, we observed a decrease in the abundance of MCAs with increasing molecular weight. We also observed decreasing total concentrations of MCAs with increasing levels of aqueous alteration (Table 2); for example, the abundances in the CM chondrites increase in the order ALH 83100 (CM1.1) < Murchison ~ LEW 90500 ~ LON 94101 (CM 1.6–1.8) < EET 96029 (CM 2.7), while in the CR chondrites MIL 090001 contains lower abundances than the less altered GRA 95229, LAP 02342, and MIL 090657. This suggests that aqueous processing may reduce the abundance of MCAs within CM and CR chondrites.

In thermally altered chondrites, the low abundances of MCAs in CV and CK chondrites may be related to the extensive degree of thermal metamorphism experienced in their corresponding parent bodies. CO chondrites represent a unique case; although some CO chondrites record extensive signs of thermal metamorphism, the specific samples we analyzed (DOM 08006 and MIL 05013) only show limited evidence for thermal metamorphism and their primordial matrix mineralogy may be intrinsically similar to that of CM and CR meteorites (Keller and Buseck, 1990; Davidson et al., 2014; Leroux et al., 2015; Abreu, 2016). Thus, the low concentration of MCAs in the CO3 meteorites DOM 08006 and MIL 05013 may not be the result of parent body processing but may suggest that MCAs and/or their precursors were not present at the time or in the environment where the accretion of their parent body took place.

Our results on the abundance and molecular distribution of MCAs essentially follow the same overall trends as those observed previously for aliphatic amino acids and monoamines in chondrites: decreasing concentration with increasing molecular weight, and the total concentration of water-soluble MCAs, amino acids and monoamines in the order of CR2 > CM2 > CM1/2 >> CO3 ≈ CV3 ≈ CK4–5 (e.g., Martins et al. 2008; Glavin et al., 2011; Burton et al., 2012, 2015; Elsila et al., 2016; Aponte et al., 2017). These similarities may suggest that meteoritic MCAs, amino acids and amines may have shared similar synthetic processes before the accretion of the parent body (Cronin and Pizzarello, 1983, 1986; Huang et al., 2005; Aponte et al., 2011, 2016). The lower molecular diversity and the presence of less oxidized compounds (aliphatic hydrocarbons) seen in the weakly aqueously altered meteorite EET 96029 (CM2.7) but not in other CM chondrites (Figure S2), may suggest that aqueous alteration increases the MCA molecular diversity while decreasing overall abundances. Further analyses of meteorites with low levels of aqueous processing are needed to confirm the relationship between level of aqueous alteration and molecular diversity.

Previous reports have shown that the abundance of chondritic monoamines and amino acids having the amino moiety (–NH₂) on a secondary carbon is typically higher than those of their corresponding isomer having the –NH₂ group on a primary or tertiary carbon (Martins et al. 2008; Glavin et al., 2011; Aponte et al. 2016). In contrast, in our study, the most abundant MCAs were those that contained the carboxylic group (–COOH) on a primary carbon (e.g., butanoic acid and pentanoic acid) rather than on a secondary carbon (e.g., isobutanoic acid and 2-methylbutanoic acid). Synthetic processes for the original synthesis of MCAs, or processes that may have occurred inside the parent body (i.e., decomposition of macromolecules and IOM) that resulted in the formation of MCAs, may have favored the occurrence of primary MCAs over the rest of their isomeric structures. Future synthetic experiments and *in silico* modeling may be able to provide insights about the abiotic synthesis of MCAs and their structurally related amines and amino acids.

Our results do not include abundances for formic acid, because we were unable to optimize chromatographic resolution for this compound (the formic acid ester derivative coelutes at the tail of unreacted *S*-2-MeBuOH used as derivatization reagent). Undoubtedly, quantitation of formic acid or other MCAs such as aromatic acids (not searched here) would increase the total MCA abundances, as previous reports have unsurprisingly shown

substantial amounts of formic acid in various carbonaceous chondrites (Briscoe et al., 1993; Huang et al., 2005; Hilt et al., 2014). Even neglecting these compounds, the high abundance of MCAs represents an important fraction of the total carbon inventory, with abundances that can approach those in some carbonaceous chondrite carbonates and IOM (Table 2).

MCA compound-specific carbon isotopic analyses.

It is generally the case that ^{13}C -enriched water-soluble meteoritic organic compounds are indicative of an extraterrestrial origin, while lighter $\delta^{13}\text{C}$ values suggest contamination, since their terrestrial biological counterparts often exhibit enrichments of the lighter isotope (Yuen et al., 1984; Cronin and Chang, 1993; Pizzarello et al., 2004). However, when evaluating the compound-specific isotopic values of meteoritic MCAs, it is important to note that the $\delta^{13}\text{C}$ composition of biologically produced MCAs and those reported from sedimentary and oilfield waters typically extracted in the petrochemical industry have an extraordinarily large range from -89 to $+9\text{‰}$ (Franks et al., 2001; Heuer et al., 2006), suggesting that the bulk of the MCAs $\delta^{13}\text{C}$ values we measured would fall within the upper end of the terrestrial range (Table 3, Figure 4). Given the airborne nature of MCAs and their ubiquitous presence in the terrestrial biosphere, the $\delta^{13}\text{C}$ isotopic values reported here should be considered as the lower limit for meteoritic MCAs.

The $\delta^{13}\text{C}$ values of MCAs we measured show variability in their carbon isotopic composition; for example, the $\delta^{13}\text{C}$ value of acetic acid (the most abundant MCA in all analyzed samples) exhibits a median value of -9‰ with a standard deviation of 17‰ across all of the evaluated meteorites. Additionally, variabilities of the MCA $\delta^{13}\text{C}$ values are also seen within each evaluated meteorite, and no clear isotopic trend may be found between carbon number and meteorite petrology (Figure S7). The exception for these observations however, is the Murchison meteorite; straight chain MCAs in Murchison ($\text{C}_3\text{-C}_6$) exhibit decreasing $\delta^{13}\text{C}$ values with increasing molecular weight, which suggests synthesis on the parent body occurred under kinetic control, as originally proposed by Yuen et al. (1984).

Given the large abundance of MCAs in CM and CR chondrites, we compared their $\delta^{13}\text{C}$ values with those previously found for meteoritic carbonates and IOM (Table 3, Figure 4; Grady et al., 1988; Alexander et al., 2007, 2010, 2012, 2013, 2015; Davidson et al., 2015). Our results show that the average MCA $\delta^{13}\text{C}$ values are ^{13}C -enriched relative to those found in IOM, but ^{13}C -depleted in relation to those found in meteoritic carbonates. These results evoke three scenarios for the prebiotic origins of MCAs found in meteorites: (1) MCAs, IOM and carbonates formed from isotopic pools or meteoritic precursors having distinct isotopic values; thus, these carbon-bearing species exhibit different isotopic compositions; (2) MCAs and IOM may have formed from the same set of less oxidized precursors (e.g. alcohols, aldehydes and/or nitriles) and were fractionated through parent body processes so that MCAs became ^{13}C -enriched relative to the IOM; one potential mechanism for MCA ^{13}C -enrichment through parent body processing may have been an exchange between the MCA carboxyl moiety and ^{13}C -carbonates present in solution (Seewald and Boekelheide, 2005; Glein and Cody, 2013); and/or (3) IOM decomposed through parent body aqueous and thermal alteration, and/or during meteorite extraction to produce MCAs that are ^{13}C -

enriched relative to its parent source. Future analyses of potential meteoritic MCA molecular precursors (e.g., carbon monoxide/dioxide, aliphatic alcohols, aldehydes and nitriles), and modeling of the isotopic fractionation of meteoritic organics (and IOM) facing varying levels of aqueous and thermal processing are needed to unveil the origins of the isotopic compositions of these meteoritic species.

Racemic composition of chiral 2-methylbutic acid.

Our analyses indicate that 2-methylbutanoic acid is present as a racemic mixture in all the meteorite samples we analyzed (Table 4 and Figure 3). The racemic composition of 2-methylbutanoic acid agrees with those previously found for the same compound in Murchison (CM2), LON 94101 (CM2) and EET 87770 (CR2) (Aponte et al., 2014a), and with the racemic distributions of analogous aliphatic *sec*-butylamine found from meteorites from various petrologic types (Aponte et al., 2014b, 2015, 2016). However, the racemic composition of 2-methylbutanoic acid contrasts with the L-*ee* found for meteoritic isovaline, its analogous amino acid, in several carbonaceous chondrites, including Murchison and LEW 90500 (e.g., Pizzarello et al., 2003; Glavin and Dworkin, 2009; Burton et al., 2013). There are several potential factors that may explain the enantiomeric discrepancy between the amino acid and the MCA: (a) there was no substantial enantioenrichment (values below our current detection limit) of 2-methylbutanoic acid prior to the accretion of the parent body, or it was lost due to racemization of the acid in the parent body; (b) the deamination of enantioenriched isovaline (Scheme 1) was not a significant synthetic route capable of yielding enantioenriched 2-methylbutanoic acid, and/or (c) the creation of a small break in symmetry and its subsequent amplification resulting in the enantioenrichment seen for meteoritic L-isovaline occurred through processes that did not create the same effects for 2-methylbutanoic acid.

Recent studies of the anisotropy spectra of isovaline and 2-methylbutanoic acid indicate that exposures of these compounds to circularly polarized light would result in a break in symmetry for isovaline, but not for 2-methylbutanoic acid (Meinert et al. 2014, 2016; Myrgorodska et al., 2017). Therefore, interstellar or pre-parent body 2-methylbutanoic acid exposed to the same circularly polarized light is expected to be racemic, and the subsequent addition of ammonia to 2-methylbutanoic acid inside the parent body or other processes capable of yielding isovaline from 2-methylbutanoic acid would result in the racemic amino acid. Future efforts aimed to understand the complex synthetic relationship between various meteoritic organic compounds that can be MCAs precursors such as alcohols and aldehydes (Scheme 1) and the process occurred inside the parent body are needed to implement further constraints on the origins of L-isovaline *ee*.

CONCLUSIONS

Using a newly developed GC-chromatographic methodology, we have determined molecular abundances, compound-specific $\delta^{13}\text{C}$ isotopic distributions and enantiomeric compositions of aliphatic MCAs from hot-water extracts of sixteen carbonaceous chondrites. We observed higher abundances of MCAs in CR meteorites relative to all other carbonaceous chondrite subtypes. The abundance of MCAs decreased with increasing carbon number, with acetic

acid being the most abundant MCA in all investigated samples. Abundances also decreased with increasing aqueous and/or thermal processing experienced on the parent body. Most of the ^{13}C -isotopic values measured fell within the upper range of terrestrial MCAs, and we did not observe strong linear correlations between ^{13}C -content and number of carbon atoms. We also found a racemic composition of 2-methylbutanoic acid in CM and CR chondrites. The racemic nature of 2-methylbutanoic acid may suggest that this compound may have been racemic prior to the formation of the parent body or that the processes that resulted in the L-enantioenrichments seen for its structurally analogous amino acid isovaline did not have a significant effect on the acid. Experimental and theoretical analyses of aliphatic MCAs and their potential precursor molecules in the context of meteoritic aqueous and thermal alteration are needed to understand the abiotic origins of these and related organic building blocks.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGEMENTS

US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and NASA and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Curation Office at NASA Johnson Space Center. The authors thank T. McCoy, J. Hoskin, and the Smithsonian National Museum of Natural History—Division of Meteorites for providing meteorite samples used in this study, and Y. Kebukawa and an anonymous reviewer for insightful criticism and suggestions to improve the manuscript quality. This research was supported by the NASA Astrobiology Institute and the Goddard Center for Astrobiology, and a grant from the Simons Foundation (SCOL award 302497 to J.P.D.).

REFERENCES

- Abreu NM 2016 Why is it so difficult to classify Renazzo-type (CR) carbonaceous chondrites? – Implications from TEM observations of matrices for the sequences of aqueous alteration. *Geochimica et Cosmochimica Acta* 194:91–122.
- Alexander CMO'D, Fogel M, Yabuta H, and Cody GD 2007 The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochimica et Cosmochimica Acta* 71: 4380–4403.
- Alexander CMO'D, Newsome SD, Fogel ML, and Cody GD 2010 Deuterium enrichments in chondritic macromolecular material: Implications for the origin and evolution of water, organics, and asteroids. *Geochimica et Cosmochimica Acta* 74:4417–4437.
- Alexander CMO'D, Bowden R, Fogel ML, Howard KT, Herd CDK, and Nittler LR 2012 The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets. *Science* 337: 721–723. [PubMed: 22798405]
- Alexander CMO'D, Howard KT, Bowden R, and Fogel ML 2013 The classification of CM and CR chondrites using bulk H, C and N abundances and isotopic compositions. *Geochimica et Cosmochimica Acta* 123: 244–260.
- Alexander CMO'D, Bowden R, Fogel ML, and Howard KT 2015 Carbonate abundances and isotopic compositions in chondrites. *Meteoritics & Planetary Science* 50:810–833.
- Alexander CMO'D, Greenwood RC, Bowden R, Gibson JM, Howard KT, and Franchi IA 2018 A multi-technique search for the most primitive CO chondrites. *Geochimica et Cosmochimica Acta* 221:406–420.
- Aponte JC, Alexandre MR, Wang Y, Brearley AJ, Alexander CMO'D, and Huang Y 2011 Effects of secondary alteration on the composition of free and IOM-derived monocarboxylic acids in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 75, 2309–2323.

- Aponte JC, Taroza R, Alexandre MR, Alexander CMO'D, Charnley SB, Hallmann C, Summons R, and Huang Y 2014a Chirality of meteoritic free and IOM-derived monocarboxylic acids and implications for prebiotic organic synthesis. *Geochimica et Cosmochimica Acta* 131:1–12.
- Aponte JC, Dworkin JP, and Elsila JE 2014 Assessing the origins of aliphatic amines in the Murchison meteorite from their compound-specific carbon isotopic ratios and enantiomeric composition. *Geochimica et Cosmochimica Acta* 141:331–345.
- Aponte JC, Dworkin JP, and Elsila JE 2015 Indigenous aliphatic amines in the aqueously altered Orgueil meteorite. *Meteoritics & Planetary Science* 50:1733–1749.
- Aponte JC, McLain HL, Dworkin JP, and Elsila JE 2016 Aliphatic amines in Antarctic CR2, CM2 and CM1/2 carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 189:296–311.
- Aponte JC, Abreu NM, Glavin DP, Dworkin JP, and Elsila JE 2017 Distribution of aliphatic amines in CO, CV, and CK carbonaceous chondrites and relation to mineralogy and processing history. *Meteoritics & Planetary Science* 52:2632–2646. [PubMed: 32440083]
- Bernier UR, Kline DL, Barnard DR, Schreck CE, and Yost RA 2000 Analysis of human skin emanations by gas chromatography/mass spectrometry. 2. Identification of volatile compounds that are candidate attractants for the yellow fever mosquito (*Aedes aegypti*). *Analytical Chemistry* 72:747–756. [PubMed: 10701259]
- Botta O and Bada JL 2002 Extraterrestrial organic compounds in meteorites. *Surveys in Geophysics* 23:411–467.
- Briscoe JF and Moore CB 1993 Determination of formic acid and acetic acid in chondritic meteorites. *Meteoritics* 28:330.
- Burton AS, Elsila JE, Callahan MP, Martin MG, Glavin DP, Johnson NM, and Dworkin JP 2012 A propensity for *n*- ω -amino acids in thermally altered Antarctic meteorites. *Meteoritics & Planetary Science* 47:374–386.
- Burton AS, Elsila JE, Hein JE, Glavin DP, and Dworkin JP 2013 Extraterrestrial amino acids identified in metal-rich CH and CB carbonaceous chondrites from Antarctica. *Meteoritics & Planetary Science* 48:390–402.
- Burton AS, McLain H, Glavin DP, Elsila JE, Davidson J, Miller KE, Andronikov AV, Lauretta D, and Dworkin JP 2015 Amino acid analyses of R and CK chondrites. *Meteoritics & Planetary Science* 50:470–482.
- Cork A and Park KC 1996 Identification of electrophysiologically-active compounds for the malaria mosquito, *Anopheles gambiae*, in human sweat extracts. *Medical and Veterinary Entomology* 10:269–276. [PubMed: 8887339]
- Cronin JR and Pizzarello S 1983 Amino acids in meteorites. *Advances in Space Research* 3:5–18. [PubMed: 11542462]
- Cronin JR and Pizzarello S 1986 Amino acids of the Murchison meteorite. III. Seven carbon acyclic primary α -amino alkanolic acids. *Geochimica et Cosmochimica Acta* 50:2419–2427. [PubMed: 11542028]
- Cronin JR and Chang S 1993 Organic matter in meteorites: Molecular and isotopic analysis of the Murchison meteorite In *The chemistry of life's origins*, edited by Greenberg JM, Mendoza CX, and Pirronelle V Dordrecht: Kluwer Academic Publishers pp. 209–258.
- Davidson J, Nittler LR, Alexander CMO'D, and Stroud RM 2014 Petrography of very primitive CO3 chondrites: Dominion Range 08006, Miller Range 07687, and four others. 45th Lunar and Planetary Science Conference, held 17–21 March, 2014 at The Woodlands, Texas LPI Contribution No. 1777.
- Davidson J, Alexander CMO'D, Schrader DL, Nittler LR, and Bowden R 2015 Miller Range 090657: A very pristine Renazzo-like (CR) carbonaceous chondrite. 46th Lunar and Planetary Science Conference, held 16–20 March, 2015 at The Woodlands, Texas LPI Contribution No. 1603.
- Deamer D, Dworkin JP, Sandford SA, Bernstein MP, and Allamandola LJ 2002 The first cell membranes. *Astrobiology* 2:371–381. [PubMed: 12593777]
- Dias RF and Freeman KH 1997 Carbon isotope analyses of semivolatile organic compounds in aqueous media using solid-phase microextraction and isotope ratio monitoring GC/MS. *Analytical Chemistry* 69:944–950. [PubMed: 21639231]

- Dillon J, Tarozo R, Yin Q, and Huang Y 2013 Analysis of carboxylic acid compounds in the Sutter's Mill meteorite. 44th Lunar and Planetary Science Conference, held 18–22 March, 2013 at The Woodlands, Texas LPI Contribution No. 2916.
- Docherty G, Jones V, and Evershed RP 2001 Practical and theoretical considerations in the gas chromatography/combustion/isotope ratio mass spectrometry $\delta^{13}\text{C}$ analysis of small polyfunctional compounds. *Rapid Communications in Mass Spectrometry* 15:730–738 [PubMed: 11319796]
- Elsila JE, Glavin DP, and Dworkin JP 2009 Cometary glycine detected in samples returned by Stardust. *Meteoritics & Planetary Science* 44:1323–1330.
- Elsila JE, Charnley SB, Burton AS, Glavin DP, and Dworkin JP 2012 Compound-specific carbon, nitrogen, and hydrogen isotopic ratios for amino acids in CM and CR chondrites and their use in evaluating potential formation pathways. *Meteoritics & Planetary Science* 47:1517–1536.
- Elsila JE, Aponte JC, Blackmond DG, Burton AS, Dworkin JP, and Glavin DP 2016 Meteoritic amino acids: Diversity in compositions reflects parent body histories. *ACS Central Science* 2:370–379. [PubMed: 27413780]
- Engel MH and Macko SA 1997 Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite. *Nature* 389:265–268. [PubMed: 9305838]
- Epstein S, Krishnamurthy RV, Cronin JR, Pizzarello S, and Yuen GU 1987 Unusual stable isotope ratios in amino-acid and carboxylic-acid extracts from the Murchison meteorite. *Nature* 326:477–479. [PubMed: 11540894]
- Franks SG, Dias RF, Freeman KH, Boles JR, Holba A, Fincannon AL, and Jordan ED 2001 Carbon isotopic composition of organic acids in oil field waters, San Joaquin Basin, California, USA. *Geochimica et Cosmochimica Acta* 65:1301–1310.
- Glein CR and Cody GD 2013 Rapid carbon-carbon bond formation and cleavage revealed by carbon isotope exchange between the carboxyl carbon and inorganic carbon in hydrothermal fluids. American Geophysical Union Fall Meeting. Abstract id. B13B-0459.
- Glavin DP and Dworkin JP 2009 Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies. *Proceedings of the National Academy of Sciences of the United States of America* 106:5487–5492. [PubMed: 19289826]
- Glavin DP, Callahan MP, Dworkin JP, and Elsil JE 2011 The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteoritics & Planetary Science* 45:1948–1972.
- Grady MM, Wright IP, Swart PK, and Pillinger CT 1988 The carbon and oxygen isotopic composition of meteoritic carbonates. *Geochimica et Cosmochimica Acta* 52:2855–2866.
- Harada K 1999 Molecular distributions of monocarboxylic acids in Asuka carbonaceous chondrites from Antarctica. *Origins of Life and Evolution of Biospheres* 29:187–201.
- Harju ER, Rubin AE, Ahn I, Choi B-G, Ziegler K, and Wasson JT 2014 Progressive aqueous alteration of CR carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 139:267–292.
- Herd CDK, Blinova A, Simkus DN, Huang Y, Tarozo R, Alexander CMO'D, Gyngard F, Nittler LR, Cody GD, Fogel ML, Kebukawa Y, Kilcoyne ALD, Hilts RW, Slater GF, Glavin DP, Dworkin JP, Callahan MP, Elsil JE, De Gregorio BT, and Stroud RM 2011 Origin and evolution of prebiotic organic matter as inferred from the Tagish Lake meteorite. *Science* 332:1304–1307. [PubMed: 21659601]
- Heuer V, Elvert M, Tille S, Krummen M, Prieto Mollar X, Hmelo LR, and Hinrichs K-U 2006 Online $\delta^{13}\text{C}$ analysis of volatile fatty acids in sediment/porewater systems by liquid chromatography-isotope ratio mass spectrometry. *Limnology and Oceanography: Methods* 4:346–357.
- Hilts RW, Herd CDK, Simkus DN, and Slater GF 2014 Soluble organic compounds in the Tagish Lake meteorite. *Meteoritics & Planetary Science* 49:526–549.
- Huang Y, Wang Y, Alexandre MR, Lee T, Rose-Petrucci C, Fuller M, and Pizzarello S 2005 Molecular and compound-specific isotopic characterization of monocarboxylic acids in carbonaceous meteorites. *Geochimica et Cosmochimica Acta* 69:1073–1084.
- Keller LP and Buseck PR 1990 Matrix mineralogy of the Lancé CO3 carbonaceous chondrite: A transmission electron microscope study. *Geochimica et Cosmochimica Acta* 54:1155–1163.

- Keller LP. Mineralogy and petrography of MIL 090001, a highly altered CV chondrite from the reduced sub-group. 42nd Lunar and Planetary Science Conference; 7–11 March, 2011; The Woodlands, Texas. 2011. heldatLPI Contribution No. 2409.
- Keller LP, McKeegan KD, and Sharp ZD 2012 The Oxygen Isotopic Composition of MIL 090001: A CR2 Chondrite with Abundant Refractory Inclusions. 43rd Lunar and Planetary Science Conference, held 19–23 March, 2012 at The Woodlands, Texas LPI Contribution No. 2065.
- Krishnamurthy RV, Epstein S, Cronin JR, Pizzarello S, and Yuen GU 1992 Isotopic and molecular analyses of hydrocarbons and monocarboxylic acids of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 56:4045–4058. [PubMed: 11537206]
- Krot AN, Keil K, Goodrich CA, Scott ERD, and Weisberg MK 2005 Classification of Meteorites In *Meteorites, Comets, and Planets : Treatise on Geochemistry, Second Edition, Volume 1* (ed. Davis AM), pp 83–128. Elsevier Science & Technology.
- Kvenvolden K, Lawless J, Pering K, Peterson E, Flores J, Ponnamperna C, Kaplan IR, and Moore C 1970 Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite. *Nature* 228:923–926. [PubMed: 5482102]
- Lawless JG and Yuen GU 1979 Quantification of monocarboxylic acids in the Murchison carbonaceous meteorite. *Nature* 282:396–398.
- Lee MR, Lindgren P, King AJ, Greenwood RC, Franchi IA, and Sparkes R 2016 Elephant Moraine 96029, a very mildly aqueously altered and heated CM carbonaceous chondrite: Implications for the drivers of parent body processing. *Geochimica et Cosmochimica Acta* 187:237–259.
- Leroux H, Cuvillier P, Zanda B, and Hewins RH 2015 GEMS-like material in the matrix of the Paris meteorite and the early stages of alteration of CM chondrites. *Geochimica et Cosmochimica Acta* 170:247–265.
- Martins Z, Botta O, Fogel ML, Sephton MA, Glavin DP, Watson JS, Dworkin JP, Schwartz AW, and Ehrenfreund P 2008 Extraterrestrial nucleobases in the Murchison meteorite. *Earth and Planetary Science Letters* 270:130–136.
- Meinert C, Hoffmann SV, Cassam-Chenai P, Evans AC, Giri C, Nahon L, and Meierhenrich UJ 2014 Photonenergy-controlled symmetry breaking with circularly polarized light. *Angewandte Chemie International Edition* 53:210–214. [PubMed: 24227543]
- Meinert C, Jones NC, Hoffmann SV, Meierhenrich UJ 2016 Anisotropy spectroscopy of chiral alcohols, amines, and monocarboxylic acids: Implications for the analyses of extraterrestrial samples. *Journal of Photochemistry and Photobiology A: Chemistry* 331:130–137.
- Monroe AA and Pizzarello S 2011 The soluble organic compounds of the Bells meteorite: Not a unique or unusual composition. *Geochimica et Cosmochimica Acta* 75:7585–7595.
- Myrgorodska I, Meinert C, Hoffmann SV, Jones NC, Nahon L, and Meierhenrich UJ 2016 Light on chirality: Absolute asymmetric formation of chiral molecules relevant in prebiotic evolution. *ChemPlusChem* 82:74–87. [PubMed: 31961503]
- Noronha BA and Friedrich JM 2014 Chemical compositions and classification of five thermally altered carbonaceous chondrites. *Meteoritics & Planetary Science* 49:1494–1504.
- Pizzarello S, and Cronin JR 2000 Non-racemic amino acids in the Murray and Murchison meteorites. *Geochimica et Cosmochimica Acta* 64:329–338. [PubMed: 11543420]
- Pizzarello S, Zolensky M, and Turk KA 2003 Non-racemic isovaline in the Murchison meteorite: chiral distribution and mineral association. *Geochimica et Cosmochimica Acta* 67:1589–1595.
- Pizzarello S, Huang Y, and Fuller M 2004 The carbon isotopic distribution of Murchison amino acids. *Geochimica et Cosmochimica Acta* 68:4963–4969.
- Pizzarello S, Cooper GW, and Flynn GJ 2006 The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles In *Meteorites and the Early Solar System II* (eds. Lauretta DS and McSween HY), pp 625–651. University of Arizona Press: Tucson, AZ.
- Pizzarello S, Huang Y, and Alexandre MR 2008 Molecular asymmetry in extraterrestrial chemistry: Insights from a pristine meteorite. *Proceedings of the National Academy of Sciences of the United States of America* 105:3700–3704. [PubMed: 18310323]
- Pizzarello S, Schrader DL, Monroe AA and Lauretta DS 2012 Large enantiomeric excesses in primitive meteorites and the diverse effects of water in cosmochemical evolution. *Proceedings of*

the National Academy of Sciences of the United States of America 109:11949–11954. [PubMed: 22778439]

Seewald JS and Boekelheide N 2005 Experimental investigation of organic acid carboxyl carbon exchange with aqueous CO₂. *Geochimica et Cosmochimica Acta* 69:supplement, A558.

Sephton MA 2002 Organic compounds in carbonaceous meteorites. *Natural Product Reports* 19:292–311. [PubMed: 12137279]

Silfer JA, Engel MH, Macko SA, and Jumeau EJ 1991 Stable carbon isotope analysis of amino acid enantiomers by conventional isotope ratio mass spectrometry and combined gas chromatography/isotope ratio mass spectrometry. *Analytical Chemistry* 63:370–374.

Shimoyama A, Naraoka H, Yamamoto H, and Harada K 1986 Carboxylic Acids in the Yamato-791198 Carbonaceous Chondrites from Antarctica. *Chemistry Letters* 15:1561–1564.

Shimoyama A, Naraoka H, Komiya M, and Harada K 1989 Analyses of Carboxylic Acids and Hydrocarbons in Antarctic Carbonaceous Chondrites, Yamato-74662 and Yamato-793321. *Geochemical Journal* 23:181–193.

Yuen GU and Kvenvolden KA 1973 Monocarboxylic acids in Murray and Murchison carbonaceous meteorites. *Nature* 246:301–303.

Yuen G, Blair N, Des Marais DJ, and Chang S 1984 Carbon isotopic composition of individual, low molecular weight hydrocarbons and monocarboxylic acids from the Murchison meteorite. *Nature* 307:252–254. [PubMed: 11536574]

Figure 1.

Panel A shows a positive electron-impact GC-MS chromatogram (25 – 93 min region, $m/z = 70 \pm 0.5$) of procedural blank, hot-water extracted derivatized MCAs from the Murchison meteorite, and commercially available MCAs standards (all traces excepting standards are on the same intensity scale). Panel B shows the GC-IRMS chromatogram obtained at $m/z = 44$ ($^{12}\text{CO}_2$ peak) obtained and measured during carbon compound-specific isotope analysis of Murchison. Compounds eluting after 29 min in the procedural blank and Murchison samples were magnified 10 times (x10) for clarity. Similar chromatograms were obtained for other meteorites investigated in this work (see Figures S2 to S6 in the Supporting Information). The identities of the peaks and structures are presented in Table 2 and Figure S1 respectively. Unidentified peaks represent compounds that could not be adequately

identified or analyzed because of co-elutions or insufficient sensitivity; U: Unknown compound (x and y axis for chromatograms are attached as Supporting Information).

Figure 2.

Abundances of MCAs in hot water extracts of the carbonaceous chondrites studied here (values taken from Table 2). Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al., 2012; Alexander et al. 2013, 2015; Lee et al., 2016; Davidson et al., 2015; Aponte et al., 2017).

Figure 3.

Positive electron-impact GC-MS chromatogram (67.4 – 69.4 min region, $m/z = 70 \pm 0.5$) of hot-water extracted derivatized (*R*)- and (*S*)-2-methylbutanoic acid (compounds **6** and **7**) from the Murchison meteorite, procedural blank, and commercially available MCAs standards (all traces excepting standards are on the same intensity scale). Similar chromatograms were obtained for other meteorites investigated in this work (x and y axis for chromatograms are attached as Supporting Information).

Figure 4.
 $\delta^{13}\text{C}$ isotopic values for the MCA, carbonates, and IOM in the meteorites we investigated. Values taken from Alexander et al., 2007, 2010, 2012, 2015, 2018; Davidson et al., 2015 (see Table 3).

Scheme 1.

Potential synthetic relationship between MCAs and meteoritic aliphatic alcohols, aldehydes, ketones and amino acids. (*) Indicates chiral center; we equate (*S*)- to L-enantiomers for consistency to the nomenclature used on previous meteoritic amino acid studies.

Scheme 2.

Panel A shows the derivatization of achiral MCAs using (*S*)-2-methylbutanol (*S*-2-MeBuOH) as chiral derivatization reagent (* indicates chiral center). Panel B shows the synthesis of diastereomeric 2-methylbutanoic acid esters by derivatization of a racemic mixture of the monocarboxylic acid (*R/S*)-2-methylbutanoic acid with *S*-2-MeBuOH.

Table 1.

Summary of the meteorites samples analyzed in this study.

Meteorite ^a	Classification ^b	Fragment	Mass extracted (g)
ALH 83100	CM1.1	Specific 296, parent 22	1.49
LEW 90500	CM1.6	Specific 85, parent 2	0.91
Murchison	CM1.6	USNM 54512	1.81
LON 94101	CM1.8	Specific 99, parent 5	1.20
EET 96029	CM2.7	Specific 71, parent 68	1.21
MIL 090001	CR2.2 ^c	Specific 93, parent 48	1.50
GRA 95229	CR2.5	Specific 128, parent 35	0.06
LAP 02342	CR2.5	Specific 62, specific 0	0.08
MIL 090657	CR2.7	Specific 31, parent 25	0.13
DOM 08006	CO3.00	Specific 77, parent 32	0.48
MIL 05013	CO3.01	Specific 25, parent 3	0.54
Allende	CV3.6	USNM 352916	2.79
LAP 02206	CV3.7	Specific 66, parent 50	0.53
GRA 06101	CV3.7	Specific 75, parent 58	0.60
ALH 85002	CK4.0	Specific 115, parent 85	0.51
EET 92002	CK5.0	Specific 67, parent 53	0.61

^aAbbreviations: Allan Hills, ALH; Lewis Cliffs, LEW; Lonewolf Nunataks, LON; Elephant Moraine, EET; Graves Nunataks, GRA; La Paz Icefield, LAP; Dominion Range, DOM.

^bKeller et al., 2012; Alexander et al. 2013, 2015; Lee et al., 2016; Davidson et al., 2015; Aponte et al., 2017.

^cFurther details about the classification of MIL 090001 are available in the Supporting Information.

Table 2.

Blank-corrected concentrations of MCA in hot-water extracts of chondrites studied here (values in nmol/g of meteorite), and MCA, carbonates and IOM carbon weight percent (C wt.%) for comparison.^a Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al., 2012; Alexander et al. 2013, 2015; Lee et al., 2016; Davidson et al., 2015; Aponte et al., 2017).

#	MCA	ALH 83100 (CML1)	LEW 90500 (CML6)	Murchison (CML6)	LON 94101 (CML8)	EET 96029 (CML7)	MIL 09001 (CR2.2)	GRA 95229 (CR2.5)	LAP 02342 (CR2.5)	MIL 090657 (CR2.7)	DOM 08006 (CO3.00)	MIL 05013 (CO3.01)	Allende (CV3.6)	LAP 02206 (CV3.7)	GRA 06101 (CV3.7)	ALH 85002 (CK4.0)	EET 92002 (CK5.0)
1	Meteoritic	4455 ± 383	6725 ± 337	6449 ± 374	5675 ± 235	10992 ± 421	1278 ± 120	30657 ± 1271	33637 ± 1428	80007 ± 6386	133 ± 10	34 ± 5	972 ± 71	1.9 ± 0.2	1.7 ± 0.6	1.5 ± 0.6	1.3 ± 0.7
2	2-Propanoic	281 ± 24	375 ± 46	327 ± 54	590 ± 79	30 ± 4	47 ± 5	2820 ± 277	5508 ± 443	12520 ± 944	<0.7	<0.7	74 ± 9	<0.7	<0.7	<0.7	<0.7
3	3-Butanoic	<0.7	48 ± 11	49 ± 10	18 ± 5	<0.7	<0.7	339 ± 57	734 ± 168	1158 ± 113	<0.7	<0.7	32 ± 4	<0.7	<0.7	<i>b</i>	<i>b</i>
4	2-Methylpropanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<0.7	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
5	Butanoic	11 ± 2	82 ± 29	82 ± 14	54 ± 12	<0.7	<0.7	661 ± 96	1454 ± 174	2198 ± 350	<0.7	<0.7	36 ± 5	<0.7	<0.7	<i>b</i>	<i>b</i>
6	(R)-2-Methylbutanoic	<0.7	9 ± 2	8 ± 2	<0.7	<i>b</i>	<i>b</i>	272 ± 26	382 ± 45	441 ± 16	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
7	(S)-2-Methylbutanoic	<0.7	9 ± 1	7 ± 2	<0.7	<i>b</i>	<i>b</i>	280 ± 32	413 ± 58	466 ± 26	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
8	5-Pentanoic	<0.7	8 ± 4	10 ± 3	<0.7	<0.7	<0.7	<0.7	86 ± 20	86 ± 13	<0.7	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
9	2-Methylbutanoic	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
10	3-Methylbutanoic	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
11	Pentanoic	<0.7	19 ± 8	39 ± 8	6 ± 3	<0.7	<0.7	<0.7	133 ± 25	263 ± 48	<0.7	<i>b</i>	50 ± 7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
12	2-Ethylbutanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
13	(R)-2-Methylpentanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<0.7	<0.7	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
14	(S)-2-Methylpentanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<0.7	<0.7	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
15	(R,S)-3-Methylpentanoic	<0.7	5 ± 1	7 ± 2	1 ± 1	<i>b</i>	<i>b</i>	<0.7	<0.7	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
16	4-Methylpentanoic	<0.7	2 ± 2	2 ± 2	<0.7	<i>b</i>	<i>b</i>	<0.7	<0.7	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

#	MCA	ALH 83100 (CML1)	LEW 90500 (CML6)	Murchison (CML6)	LON 94101 (CML8)	EET 96029 (CML2.7)	MIL 090001 (CR2.2)	GRA 95229 (CR2.5)	LAP 02342 (CR2.5)	MIL 090657 (CR2.7)	DOM 08006 (CO3.00)	MIL 05013 (CO3.01)	Allende (CV3.6)	LAP 02206 (CV3.7)	GRA 06101 (CV3.7)	ALH 85002 (CK4.0)	EET 92002 (CK5.0)
17	Hexanoic	<0.7	6 ± 3	58 ± 11	1 ± 1	<0.7	<i>b</i>	<0.7	<0.7	<0.7	<i>b</i>	<i>b</i>	135 ± 16	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
18	Heptanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	33 ± 6	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
19	Octanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	53 ± 7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
20	Nonanoic	<i>b</i>	<i>b</i>	<0.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	73 ± 10	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
<i>Total Abundance</i>		4747 ± 410	7289 ± 445	7038 ± 482	6345 ± 337	11024 ± 425	1325 ± 125	35029 ± 1756	42349 ± 2360	97138 ± 7897	133 ± 10	34 ± 5	1298 ± 112	2 ± 0.2	2 ± 1	2 ± 1	1 ± 1
MCAs C wt.%		0.012	0.018	0.018	0.016	0.027	0.003	0.092	0.117	0.261	0.00032	0.00008	0.006	0.000005	0.000004	0.000004	0.000003
Carbonate C wt.% ^c		0.32	0.20	0.09	0.09	0.02	0.20	0.16	0.14	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
IOM C wt.% ^c		0.76	<i>d</i>	0.83–1.06	1.05	<i>d</i>	0.38	0.68	<i>d</i>	0.24	<i>d</i>	<i>d</i>	0.18	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
Bulk C wt.% ^c		1.90	1.84	2.08–2.22	2.06	1.51	0.70	1.09	1.13	1.25	1.19	0.65	<i>d</i>	0.12	<i>d</i>	<i>d</i>	<i>d</i>

^aCompounds identified by comparison with elution time and mass spectra of standards. Values are the average of three measurements from single-ion gas chromatograms as detailed in the Methods section; errors shown are standard deviations. Compounds at <0.7 nmol/g meteorite are falling below our quantification limits

^bValues fall below our detection limits (0.01 nmol/g meteorite).

^cValues taken from: Alexander et al., 2007, 2010, 2012, 2015, 2018; Davidson et al., 2015.

^dNot available in the scientific literature.

Table 3.

$\delta^{13}\text{C}$ values (‰ VPDB) of MCAs (number of carbon atoms in molecule) in hot-water extracts of chondrites studied here.^a Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al., 2012; Alexander et al. 2013, 2015; Lee et al., 2016; Davidson et al., 2015; Aponte et al., 2017).

#	MCA	ALH 83100 (CML1.1)	LEW 90500 (CML6)	Murchison (CML6)	LON 94101 (CML8)	EET 96029 (CM2.7)	MIL 090001 (CR2.2)	GRA 95229 (CR2.5)	LAP 02342 (CR2.5)	MIL 090657 (CR2.7)	Allende (CV3.6)
1	Acetic (C_2)	0 ± 4	-9 ± 1	-52 ± 1	3 ± 1	-17 ± 3	-13 ± 3	-13 ± 2	3 ± 2	14 ± 2	-50 ± 1
2	Propanoic (C_3)	4 ± 2	14 ± 2	-1 ± 1	9 ± 2	-11 ± 3	-17 ± 2	1 ± 0	9 ± 1	7 ± 1	-35 ± 2
3	Isobutanoic (C_4)	<i>b</i>	24 ± 1	13 ± 2	<i>b</i>	<i>b</i>	<i>b</i>	6 ± 2	13 ± 2	2 ± 2	-37 ± 2
5	Butanoic (C_4)	17 ± 3	22 ± 1	-4 ± 3	6 ± 3	<i>b</i>	<i>b</i>	-6 ± 2	-7 ± 3	-10 ± 3	-32 ± 2
6	(<i>R</i>)-2-Methylbutanoic (C_5)	<i>b</i>	5 ± 3	6 ± 2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	27 ± 2	-4 ± 3	<i>b</i>
8	Isopentanoic (C_5)	<i>b</i>	12 ± 2	-4 ± 1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	-9 ± 2	-13 ± 2	<i>b</i>
11	Pentanoic (C_5)	<i>b</i>	13 ± 2	-9 ± 2	9 ± 1	<i>b</i>	<i>b</i>	<i>b</i>	0 ± 1	-4 ± 2	1 ± 1
16	4-Methylpentanoic (C_6)	<i>b</i>	7 ± 2	8 ± 2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
17	Hexanoic (C_6)	<i>b</i>	14 ± 2	-17 ± 2	12 ± 1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	-26 ± 2
18	Heptanoic (C_7)	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	-20 ± 1
19	Octanoic (C_8)	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	-19 ± 1
20	Nonanoic (C_9)	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	-19 ± 1
<hr/>											
Average $\delta^{13}\text{C}$ MCAs		7	11	-7	8	-14	-15	-3	5	-1	-26
$\delta^{13}\text{C}$ carbonates ^c		45	41	44	41	38	71	42	36	<i>d</i>	-7
$\delta^{13}\text{C}$ IOM ^c		-10	<i>d</i>	-19	-15	<i>d</i>	-27	-22	<i>d</i>	-19	-17
$\delta^{13}\text{C}$ bulk carbon ^c		-3	-2	-3	-2	-6	-10	0	-2	-2	-19

^aValues are the average of three measurements; errors shown are standard deviations ($n = 3$). GC-IRMS chromatograms are shown in Figures S1 and S2.

^bValue could not be determined due to coeluting compounds and limited amount of sample.

^cValues taken from: Grady et al., 1988; Alexander et al., 2007, 2010, 2012, 2013, 2015; Davidson et al., 2015.

Not available in the scientific literature.

NASA Author Manuscript

NASA Author Manuscript

NASA Author Manuscript

Table 4.

Blank-corrected enantiomeric ratios and enantiomeric excess for 2-methylbutanoic acid extracted from CM2 and CR2 carbonaceous chondrites.^a

Sample	2-Methylbutanoic acid	
	(<i>R/S</i>) ^a	<i>R</i> _{ee}
LEW 90500 (CM1.6)	1.05 ± 0.09	0.32 ± 2.32
Murchison (CM1.6)	1.07 ± 0.11	0.49 ± 1.73
GRA 95229 (CR2.5)	0.97 ± 0.04	−0.22 ± 1.69
LAP 02342 (CR2.5)	0.94 ± 0.15	−0.60 ± 2.12
MIL 090657 (CR2.7)	0.95 ± 0.06	−0.42 ± 1.29

^aValues have been corrected against injections of racemic standards to account for instrument response. Enantiomeric ratios and standard deviations of 2-methylbutanoic acid are based on three separate measurements from single ion gas chromatograms extracted at *m/z* = 69.5–70.5.