

## Molecular distribution, $^{13}\text{C}$ -isotope, and enantiomeric compositions of carbonaceous chondrite monocarboxylic acids

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**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 16 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  $+27\%$ , 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  $^{13}\text{C}$ -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 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; Botta and Bada 2002; Sephton 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 meteorites, 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- ( $\leq 6$  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

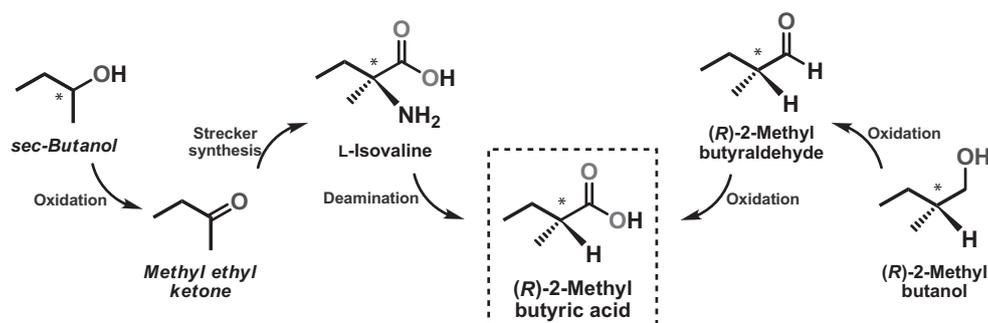


Fig. 1. Potential synthetic relationship between MCAs and meteoritic aliphatic alcohols, aldehydes, ketones, and amino acids. (\*) Indicates chiral center; we equate (*S*)- to *L*-enantiomers for consistency to the nomenclature used on previous meteoritic amino acid studies.

(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 (Fig. 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 in supporting information). 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; Shimoyama 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 microextraction (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; Hiltz 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. 2014b); 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 make 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 16 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 ( $\leq 6$  carbons). This chromatographic technique rests on the conversion of the MCAs into their corresponding esters (Fig. 2); chiral MCAs are converted into diastereomers, improving chromatographic separation on chiral GC columns without influencing the original enantiomeric and  $^{13}\text{C}$ -isotopic compositions of the studied MCAs (details on method development are discussed in the supporting information).

Table 1. Summary of the meteorite samples analyzed in this study.

Meteorite	Classification <sup>a</sup>	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 <sup>b</sup>	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	CV3.7	USNM 352916	2.79
LAP 02206	CV3.6	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

<sup>a</sup>Keller et al. (2012); Alexander et al. (2013, 2015); Lee et al. (2016); Davidson et al. (2015); Aponte et al. (2017).

<sup>b</sup>Further details about the classification of MIL 090001 are available in the supporting information.

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

## 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 MΩ, 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 (MgCl<sub>2</sub>·6H<sub>2</sub>O, ACS grade ≥99.0%), and (*S*)-(-)-2-methylbutanol (*S*-2-MeBuOH, 99%). Functionalized aminopropyl silica gel was from SiliCycle (*SiliaBond*<sup>®</sup>, 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<sup>®</sup> 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 μL of 2 M MgCl<sub>2</sub> 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 μL of DCM, then 20 μL of 6 M HCl, and 10 μL 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 PFTE-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 × 5 mm I.D.) to remove the excess of HCl used as reaction catalyst, rinsed using ~3 mL of DCM, dried with flowing N<sub>2</sub>, and enough DCM (10 to 100 μL) 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 (GC-MS/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 × 0.25 mm I.D. × 0.25 μm film thickness; Agilent), and two CP-Chirasil Dex CB (25 m length × 0.25 mm I.D. × 0.25 μm film thickness; Agilent) capillary columns connected in series using Press-Tight<sup>®</sup> connectors (Restek). The GC was coupled to a Thermo DSQII

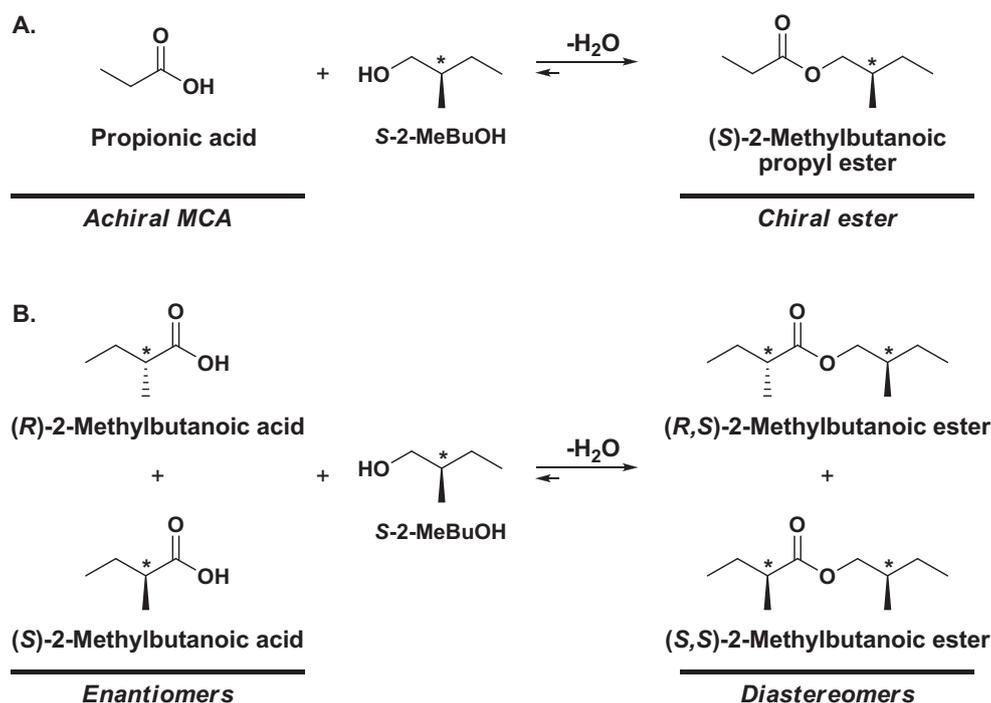


Fig. 2. Panel A shows the derivatization of achiral MCAs using (*S*)-2-methylbutanol (*S*-2-MeBuOH) as chiral derivatization reagent (\* indicates chiral center). Panel B shows the synthesis of diastereomeric 2-methylbutanoic acid esters by derivatization of a racemic mixture of the monocarboxylic acid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

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  $\geq C_6$  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<sup>-1</sup> to 86 °C and held for 50 min, ramped at 2 °C min<sup>-1</sup> to 130 °C, ramped at 20 °C min<sup>-1</sup> 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<sup>-1</sup> to 120 °C, ramped at 2 °C min<sup>-1</sup> to 140 °C and held for 5 min, ramped at 2 °C min<sup>-1</sup> to 160 °C and held for 5 min, ramped at 20 °C min<sup>-1</sup> 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<sup>-1</sup> 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 Fig. S1 in supporting information for molecular structures). Conditions for GC-MS/IRMS analysis and

measurement of  $\delta^{13}C$  values have been described in detail previously (e.g., Elsila et al. 2009, 2012; Aponte et al. 2014a, 2015). Briefly, six pulses of high-purity CO<sub>2</sub> gas ( $\delta^{13}C = -27.494$  ‰ Pee Dee Belemnite “PDB” standard) that had been precalibrated against two commercial reference CO<sub>2</sub> gases (Oztech Corporation,  $\delta^{13}C = -3.61$  PDB and  $\delta^{13}C = -40.740$  PDB) were injected into the IRMS for computation of the  $\delta^{13}C$  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  $\delta^{13}C$  value of  $-23.330$ ‰ (Iso-Analytical). The final  $\delta^{13}C$  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):

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

Table 2. Blank-corrected concentrations of MCA in hot-water extracts of chondrites studied here (values in  $\text{nmol g}^{-1}$  of meteorite), and MCA, carbonates, and IOM carbon weight percent (C wt%) for comparison.<sup>a</sup> Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al. 2012; Alexander et al. 2013, 2015; Davidson et al. 2015; Lee et al. 2016; Aponte et al. 2017).

#	MCA	ALH83100 (CM1.1)	LEW 90500 (CM1.6)	Murchison (CM1.6)	LON94101 (CM1.8)	EET96029 (CM2.7)	MIL 090001 (CR2.2)	GRA95229 (CR2.5)	LAP02342 (CR2.5)	MIL090657 (CR2.7)	DOM (CO3.00)	MIL 05013 (CO3.01)	Allende (CV3.6)	LAP (CV3.7)	GRA 06101 (CV3.7)	ALH 85002 (CK4.0)	EET 92002 (CK5.0)
1	Acetic	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	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	Isobutanoic	<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	<0.7	<0.7
4	2,2-Dimethylpropanoic	b	b	<0.7	b	b	b	<0.7	<0.7	b	b	b	b	b	b	b	b
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	b	b
6	(R)-2-Methylbutanoic	<0.7	9 ± 2	8 ± 2	<0.7	b	b	272 ± 26	382 ± 45	441 ± 16	b	b	b	b	b	b	b
7	(S)-2-Methylbutanoic	<0.7	9 ± 1	7 ± 2	<0.7	b	b	280 ± 32	413 ± 58	466 ± 26	b	b	b	b	b	b	b
8	Isopentanoic	<0.7	8 ± 4	10 ± 3	<0.7	<0.7	<0.7	<0.7	86 ± 20	86 ± 13	<0.7	<0.7	<0.7	b	b	b	b
9	2,2-Dimethylbutanoic	b	b	b	b	b	b	b	b	b	b	b	b	b	b	b	b
10	3,3-Dimethylbutanoic	b	b	b	b	b	b	b	b	b	b	b	b	b	b	b	b
11	Pentanoic	<0.7	19 ± 8	39 ± 8	6 ± 3	<0.7	<0.7	<0.7	133 ± 25	263 ± 48	<0.7	<0.7	50 ± 7	b	b	b	b
12	2-Ethylbutanoic	b	b	<0.7	b	b	b	b	b	b	b	b	b	b	b	b	b
13	(R)-2-Methylpentanoic	b	b	<0.7	b	b	b	<0.7	<0.7	<0.7	b	b	b	b	b	b	b
14	(S)-2-Methylpentanoic	b	b	<0.7	b	b	b	<0.7	<0.7	<0.7	b	b	b	b	b	b	b
15	(R,S)-3-Methylpentanoic	<0.7	5 ± 1	7 ± 2	1 ± 1	b	b	<0.7	<0.7	<0.7	b	b	b	b	b	b	b
16	4-Methylpentanoic	<0.7	2 ± 2	2 ± 2	<0.7	b	b	<0.7	<0.7	<0.7	b	b	b	b	b	b	b
17	Hexanoic	<0.7	6 ± 3	58 ± 11	1 ± 1	<0.7	b	<0.7	<0.7	<0.7	b	b	135 ± 16	b	b	b	b
18	Heptanoic	b	b	<0.7	b	b	b	b	b	b	b	b	33 ± 6	b	b	b	b
19	Octanoic	b	b	<0.7	b	b	b	b	b	b	b	b	53 ± 7	b	b	b	b
20	Nonanoic	b	b	<0.7	b	b	b	b	b	b	b	b	73 ± 10	b	b	b	b
	Total Abundance	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
	MCA's 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%	0.32	0.20	0.09	0.09	0.02	0.20	0.16	0.14	d	d	d	d	d	d	d	d
	IOM C wt%	0.76	d	0.83-1.06	1.05	d	0.38	0.68	d	0.24	d	d	0.18	d	d	d	d
	Bulk C wt%	1.90	1.84	2.08-2.22	2.06	1.51	0.70	1.09	1.13	1.25	1.19	0.65	0.12	d	d	d	d

<sup>a</sup>Compounds 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  $\text{nmol g}^{-1}$  meteorite are falling below our quantification limits.

<sup>b</sup>Values fell below our detection limits (0.01  $\text{nmol g}^{-1}$  meteorite).

<sup>c</sup>Values taken from: Alexander et al. (2007, 2010, 2012, 2015, 2018); Davidson et al. (2015).

<sup>d</sup>Not available in the scientific literature.

where  $n_{\text{MCA}}$  is the number of carbon atoms in the underivatized MCA, and  $n_{\text{d}}$  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):

$$\delta_{\text{sample MCA}}^2 = \delta_{\text{underivatized std}}^2 + [\delta_{\text{derivatized std}}^2 \times ((n_{\text{MCA}} + n_{\text{d}})/n_{\text{MCA}})^2] + [\delta_{\text{derivatized sample}}^2 \times ((n_{\text{MCA}} + n_{\text{d}})/n_{\text{MCA}})^2] \quad (2)$$

## RESULTS

Figure 3 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 (Figs. S2–S6 in supporting information). The concentrations in  $\text{nmol g}^{-1}$  of meteorite for the MCAs in CR chondrites (except in MIL 090001) were between 3 and 20 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; Fig. 4). 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 16 MCAs ranging from two to six carbon atoms ( $\text{C}_2$ – $\text{C}_6$ ). 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 ( $\text{C}_7$ ,  $\text{C}_8$ , and  $\text{C}_9$ ; 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 ( $\text{C}_2$ ) 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 (Fig. 4). 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 Fig. 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  $^{13}\text{C}$ -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 5 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 co-elutions 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

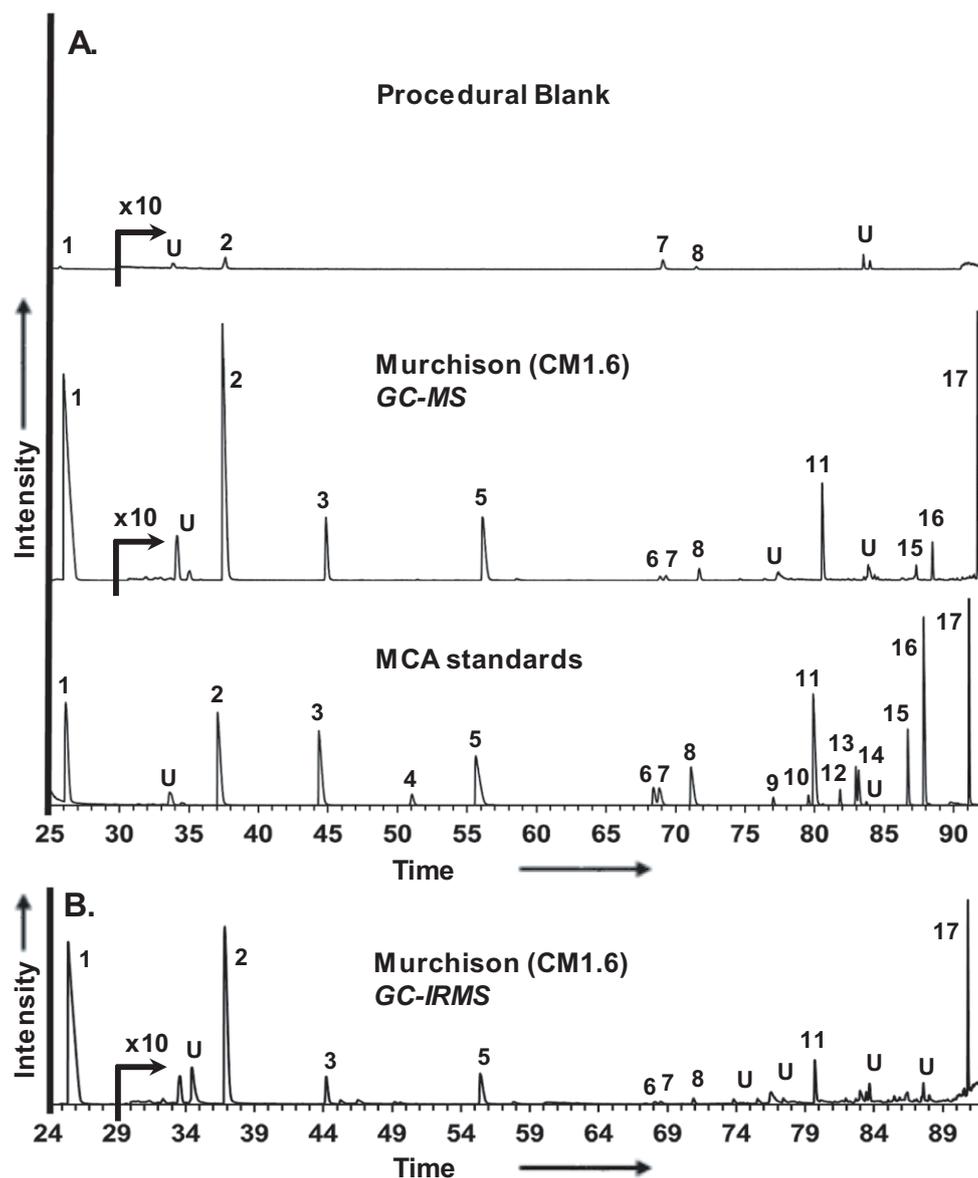


Fig. 3. Panel A shows a positive electron-impact GC-MS chromatogram (25–93 min region,  $m/z = 70 \pm 0.5$ ) of procedural blank, hot-water extracted derivatized MCAs from the Murchison meteorite, and commercially available MCAs standards (all traces excepting standards are on the same intensity scale). Panel B shows the GC-IRMS chromatogram obtained at  $m/z = 44$  ( $^{12}\text{CO}_2$  peak) 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 ( $\times 10$ ) for clarity. Similar chromatograms were obtained for other meteorites investigated in this work (see Figs. S2 to S6). The identities of the peaks and structures are presented in Table 2 and Fig. 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 provided in supporting information).

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. (2014b). 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 et al. 2011) is between 39 and 630 times

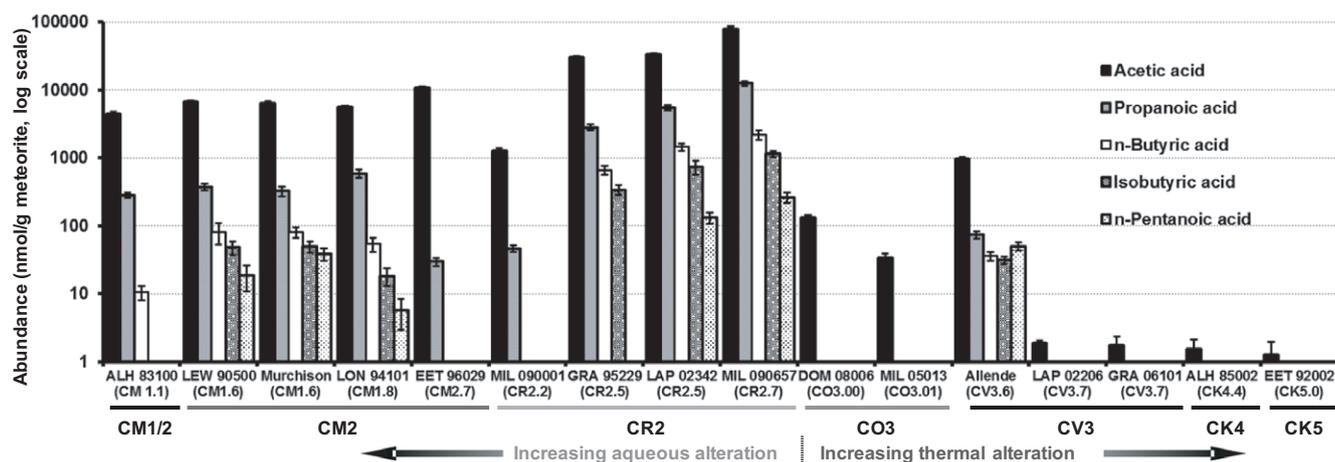


Fig. 4. Abundances of MCAs in hot-water extracts of the carbonaceous chondrites studied here (values taken from Table 2). Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al. 2012; Alexander et al. 2013, 2015; Davidson et al. 2015; Lee et al. 2016; Aponte et al. 2017).

lower than the total concentrations of MCAs we found in CR2 chondrites. Additionally, previous analyses of MCAs in CR2 chondrites showed concentrations of linear  $C_4$ - $C_8$  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 for details) 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 16 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 and/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

Table 3.  $\delta^{13}\text{C}$  values ( $\text{‰ VPDB}$ ) of MCAs (number of carbon atoms in molecule) in hot-water extracts of chondrites studied here.<sup>a</sup> Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al. 2012; Alexander et al. 2013, 2015; Davidson et al. 2015; Lee et al. 2016; Aponte et al. 2017).

#	MCA	ALH (CM1.1)	LEW 90500 (CM1.6)	Murchison (CM1.6)	LON 94101 (CM1.8)	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 ( $\text{C}_2$ )	$0 \pm 4$	$-9 \pm 1$	$-52 \pm 1$	$3 \pm 1$	$-17 \pm 3$	$-13 \pm 3$	$-13 \pm 2$	$3 \pm 2$	$14 \pm 2$	$-50 \pm 1$
2	Propanoic ( $\text{C}_3$ )	$4 \pm 2$	$14 \pm 2$	$-1 \pm 1$	$9 \pm 2$	$-11 \pm 3$	$-17 \pm 2$	$1 \pm 0$	$9 \pm 1$	$7 \pm 1$	$-35 \pm 2$
3	Isobutanoic ( $\text{C}_4$ )	b	$24 \pm 1$	$13 \pm 2$	b	b	b	$6 \pm 2$	$13 \pm 2$	$2 \pm 2$	$-37 \pm 2$
5	Butanoic ( $\text{C}_4$ )	$17 \pm 3$	$22 \pm 1$	$-4 \pm 3$	$6 \pm 3$	b	b	$-6 \pm 2$	$-7 \pm 3$	$-10 \pm 3$	$-32 \pm 2$
6	( <i>R</i> )-2-Methylbutanoic ( $\text{C}_5$ )	b	$5 \pm 3$	$6 \pm 2$	b	b	b	b	$27 \pm 2$	$-4 \pm 3$	b
8	Isopentanoic ( $\text{C}_5$ )	b	$12 \pm 2$	$-4 \pm 1$	b	b	b	b	$-9 \pm 2$	$-13 \pm 2$	b
11	Pentanoic ( $\text{C}_5$ )	b	$13 \pm 2$	$-9 \pm 2$	$9 \pm 1$	b	b	b	$0 \pm 1$	$-4 \pm 2$	$1 \pm 1$
16	4-Methylpentanoic ( $\text{C}_6$ )	b	$7 \pm 2$	$8 \pm 2$	b	b	b	b	b	b	b
17	Hexanoic ( $\text{C}_6$ )	b	$14 \pm 2$	$-17 \pm 2$	$12 \pm 1$	b	b	b	b	b	$-26 \pm 2$
18	Heptanoic ( $\text{C}_7$ )	b	b	b	b	b	b	b	b	b	$-20 \pm 1$
19	Octanoic ( $\text{C}_8$ )	b	b	b	b	b	b	b	b	b	$-19 \pm 1$
20	Nonanoic ( $\text{C}_9$ )	b	b	b	b	b	b	b	b	b	$-19 \pm 1$
	Average $\delta^{13}\text{C}$ MCAs	7	11	-7	8	-14	-15	-3	5	-1	-26
	$\delta^{13}\text{C}$ carbonates <sup>e</sup>	45	41	44	41	38	71	42	36	d	-7
	$\delta^{13}\text{C}$ IOM <sup>c</sup>	-10	d	-19	-15	d	-27	-22	d	-19	-17
	$\delta^{13}\text{C}$ bulk carbon <sup>c</sup>	-3	-2	-3	-2	-6	-10	0	-2	-2	-19

<sup>a</sup>Values are the average of three measurements; errors shown are standard deviations ( $n = 3$ ). GC-IRMS chromatograms are shown in Figs. S5 and S6.

<sup>b</sup>Value could not be determined due to co-eluting compounds and limited amount of sample.

<sup>c</sup>Values taken from: Grady et al. (1988); Alexander et al. (2007, 2010, 2012, 2013, 2015); Davidson et al. (2015).

<sup>d</sup>Not available in the scientific literature.

Table 4. Blank-corrected enantiomeric ratios and enantiomeric excess for 2-methylbutanoic acid extracted from CM2 and CR2 carbonaceous chondrites.<sup>a</sup>

Sample	2-Methylbutanoic acid	
	(R/S) <sup>a</sup>	<i>R</i> <sub>ee</sub>
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

<sup>a</sup>Values 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  $m/z = 69.5-70.5$ .

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 (Fig. 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 (-NH<sub>2</sub>) on a secondary carbon is typically higher than those of their corresponding isomer having the -NH<sub>2</sub> 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 co-elutes 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 and Moore 1993; Huang et al. 2005; Hiltz 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 <sup>13</sup>C-enriched water-soluble meteoritic organic compounds are indicative of an extraterrestrial origin, while lighter δ<sup>13</sup>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 δ<sup>13</sup>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‰ (Franks et al. 2001; Heuer et al. 2006), suggesting that the bulk of the MCAs δ<sup>13</sup>C values we measured would fall within the upper end of the terrestrial range (Table 3, Fig. 6). Given the airborne nature of MCAs and their ubiquitous presence in the terrestrial biosphere, the δ<sup>13</sup>C isotopic values reported here should be considered as the lower limit for meteoritic MCAs.

The δ<sup>13</sup>C values of MCAs we measured show variability in their carbon isotopic composition; for example, the δ<sup>13</sup>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 δ<sup>13</sup>C values are also seen within each evaluated meteorite, and no clear isotopic trend may be found between carbon number and meteorite petrology (Fig. S7 in supporting information). The exception for these

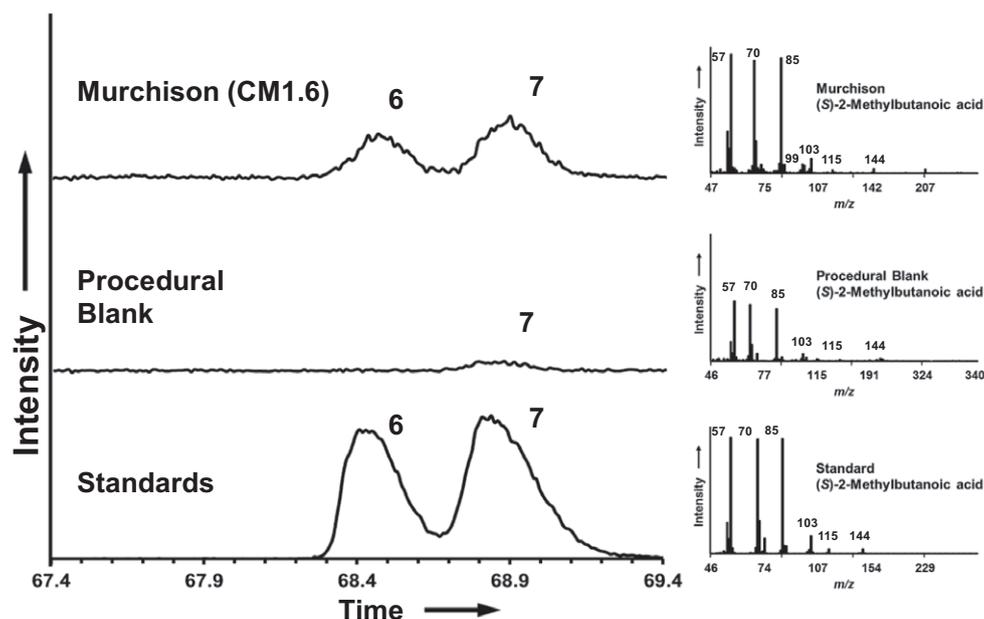


Fig. 5. Positive electron-impact GC-MS chromatogram (67.4–69.4 min region,  $m/z = 70 \pm 0.5$ ) of hot-water extracted derivatized (*R*)- and (*S*)-2-methylbutanoic acid (compounds 6 and 7) from the Murchison meteorite, procedural blank, and commercially available MCAs standards (all traces excepting 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 provided in supporting information).

observations, however, is the Murchison meteorite; straight-chain MCAs in Murchison ( $C_3$ – $C_6$ ) exhibit decreasing  $\delta^{13}C$  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  $\delta^{13}C$  values with those previously found for meteoritic carbonates and IOM (Table 3; Fig. 6) (Grady et al. 1988; Alexander et al. 2007, 2010, 2012, 2013, 2015; Davidson et al. 2015). Our results show that the average MCA  $\delta^{13}C$  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; Fig. 5). 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. 2014b), and with the racemic distributions of analogous aliphatic *sec*-butylamine found from meteorites from various petrologic types (Aponte et al. 2014a, 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;

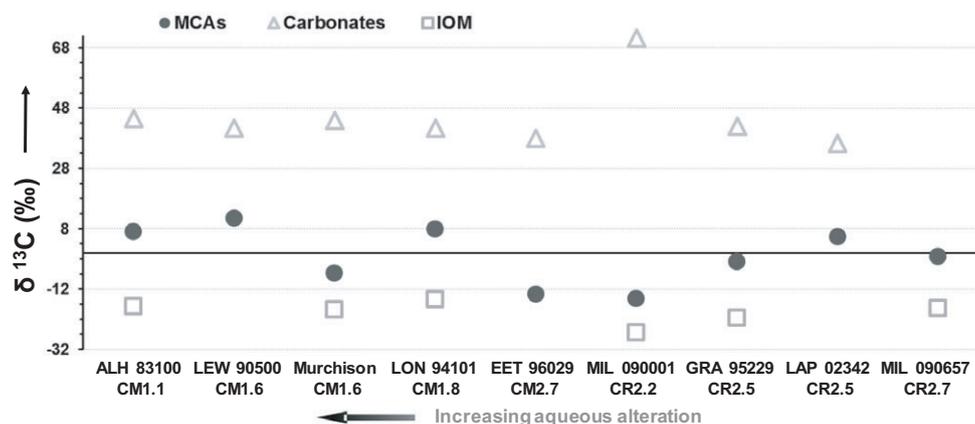


Fig. 6.  $\delta^{13}\text{C}$  isotopic values for the MCA, carbonates, and IOM in the meteorites we investigated. Values taken from Alexander et al. (2007, 2010, 2012, 2015, 2018); Davidson et al. (2015) (see Table 3).

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 (1) 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; (2) the deamination of enantioenriched isovaline (Fig. 1) was not a significant synthetic route capable of yielding enantioenriched 2-methylbutanoic acid; and/or (3) 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 preparent 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 MCA precursors such as alcohols and aldehydes (Fig. 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 16 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  $^{13}\text{C}$ -isotopic values measured fell within the upper range of terrestrial MCAs, and we did not observe strong linear correlations between  $^{13}\text{C}$ -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.

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## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

**Table S1.** Previous analyses of meteoritic MCAs.

**Fig. S1.** Structures of aliphatic monocarboxylic acids listed in Table 2.

**Fig. S2.** Positive electron-impact GC-MS chromatogram (25–93 min region,  $m/z = 70 \pm 0.5$ ) of procedural blank, hot-water extracted derivatized MCAs in CM carbonaceous chondrites, procedural blank, and standards (all traces except standards are on the same intensity scale). Compounds eluting after 29 min in the procedural blank and Murchison samples were magnified 10 times ( $\times 10$ ) for clarity. The identities of the peaks and structures are presented in Table 2 and Fig. S1, respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. U = Unknown compound, H: Aliphatic hydrocarbon (determined by MS fragmentation pattern).

**Fig. S3.** Positive electron-impact GC-MS chromatogram (25–93 min region,  $m/z = 70 \pm 0.5$ ) of procedural blank, hot-water extracted derivatized MCAs in CR carbonaceous chondrites, procedural blank, and standards (all traces excepting standards are on the same intensity scale). Compounds eluting after 29 min in the procedural blank and Murchison samples were magnified 2 times ( $\times 2$ ) for clarity. The identities of the peaks and structures are presented in Table 2 and Fig. S1, respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. U: Unknown compound.

**Fig. S4.** Positive electron-impact GC-MS chromatograms (24–42 min region,  $m/z = 70 \pm 0.5$ ) of hot-water extracted derivatized MCA in CO, CV, and CK carbonaceous chondrites, procedural blank, and standards, all traces excepting standards are on the same intensity scale, 10-time magnifications are indicated by ( $\times 10$ ). The chromatographic conditions for these analyses are slightly different to those used for CM and CR chondrites as described in the Methods section. The

identities of the peaks and structures are presented in Table 2 and Fig. S1, respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. U = Unknown compound.

**Fig. S5.** GC-IRMS chromatograms obtained at  $m/z = 44$  ( $^{12}\text{CO}_2$  peak) during carbon compound-specific isotope analysis of (*S*)-(-)-2-methylbutanol-MCAs esters from hot-water extracted derivatized MCA in CM1/2 and CM2 carbonaceous chondrites, a typical procedural blank, and standards (all traces excepting standards are on the same intensity scale). The identities of the peaks and structures are presented in Table 3 and Fig. S1, respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. U = Unknown compound; H = Aliphatic hydrocarbon (determined by MS fragmentation pattern).

**Fig. S6.** GC-IRMS chromatograms obtained at  $m/z = 44$  ( $^{12}\text{CO}_2$  peak) during carbon compound-specific

isotope analysis of (*S*)-(-)-2-methylbutanol-MCAs esters from hot-water extracted derivatized MCA in CR2 and Allende (CV3) carbonaceous chondrites and standards (all traces excepting standards are on the same intensity scale). The identities of the peaks and structures are presented in Table 3 and Fig. S1, respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. U = Unknown compound.

**Fig. S7.**  $\delta^{13}\text{C}$  isotopic data for the MCAs from hot-water extracts of CM1/2, CM2, CR2, and CV3 chondrites. MCAs are grouped within each meteorite by carbon number. Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al. 2012; Alexander et al. 2013, 2015; Davidson et al. 2015; Lee et al. 2016; Aponte et al. 2017).

**Data S1.** Method optimization for the analysis of meteoritic MCAs.

**Data S2.** Petrologic characterization of MIL 090001.

**Data S3.** Data points for figures.

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