Extraterrestrial organic compounds and cyanide in the CM2 carbonaceous chondrites Aguas Zarcas and Murchison

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Abstract–Evaluating the water-soluble organic composition of carbonaceous chondrites is key to understanding the inventory of organic matter present at the origins of the solar system and the subsequent processes that took place inside asteroid parent bodies. Here, we present a side-by-side analysis and comparison of the abundance and molecular distribution of aliphatic amines, aldehydes, ketones, mono- and dicarboxylic acids, and free and acid-releasable cyanide species in the CM2 chondrites Aguas Zarcas and Murchison. The Aguas Zarcas meteorite is a recent fall that occurred in central Costa Rica and constitutes the largest recovered mass of a CM-type meteorite after Murchison. The overall content of organic species we investigated was systematically higher in Murchison than in Aguas Zarcas. Similar to previous meteoritic organic studies, carboxylic acids were one to two orders of magnitude more abundant than other soluble organic compound classes investigated in both meteorite samples. We did not identify free cyanide in Aguas Zarcas and Murchison; however, cyanide species analyzed after acid digestion of the water-extracted meteorite mineral matrix were detected and quantified at slightly higher abundances in Aguas Zarcas compared to Murchison. Although there were differences in the total abundances of specific compound classes, these two carbonaceous chondrites showed similar isomeric distributions of aliphatic amines and carboxylic acids, with common traits such as a complete suite of structural isomers that decreases in concentration with increasing molecular weight. These observations agree with their petrologic CM type-2 classification, suggesting that these meteorites experienced similar organic formation processes and/or conditions during parent body aqueous alteration.

INTRODUCTION

Carbonaceous chondrites represent the oldest solid materials in the solar system available for laboratory analysis. Contained within the mineral matrices of these bodies is a rich history dating from the birth of our solar system (Anders 1989). The water-soluble organic compounds present in these extraterrestrial samples constitute a record of presolar chemical reactions, and also of those chemical reactions that occurred in the early solar system and those resulting from parent body aqueous and thermal processing. Several classes of soluble organic compounds have been identified in carbonaceous chondrites, including amino acids, hydroxy amino acids, diamino acids, imino acids, monocarboxylic- and dicarboxylic acids, hydroxy acids, aldehydes and ketones (collectively called carbonyl compounds), aliphatic and aromatic hydrocarbons, amines, amides, alcohols, *N*-heterocycles, sulfonic acids, phosphonic acids, and polyols (Sephton 2002; Burton

et al. 2012; Elsila et al. 2016; Glavin et al. 2018). Some of these organic compound classes are structurally related, and therefore, they may share common synthetic origins in extraterrestrial samples. Additionally, this inventory of organic compounds may represent a potential important source of prebiotic molecules needed for the origins and/or early evolution of life on Earth (Oró 1961; Chyba and Sagan 1992). Thus, accurately measuring the molecular distributions of soluble meteoritic organics is critical, not only for understanding the effects of aqueous and thermal processing inside the asteroid parent body but also to shed light on the prebiotic synthetic relationships between various compound classes. The understanding of pre-accretionary compounds in carbonaceous chondrites would be greatly benefited from a clear assessment of the influence of parent body processes over these species. Additionally, these analyses are also important when evaluating the organic composition of materials from sample return missions such the Apollo lunar samples and asteroidal samples to be brought to the Earth by the Hayabusa2 and OSIRIS-REx missions.

The Aguas Zarcas meteorite was a witnessed fall that occurred on April 23, 2019 circa 9:09 p.m. local time in the town of San Carlos, Alajuela province, in central Costa Rica. The approximate total mass recovered of this meteorite was 27 kg, which makes Aguas Zarcas not only the second meteorite ever registered in Costa Rican history (Lücke et al. 2019) but also the second largest CM (Mighei-like) chondrite ever recovered (Meteoritical Bulletin Database 2020; Takir et al. 2020). At least 11 kg of Aguas Zarcas meteorite fragments was quickly recovered during the first 6 days after its fall; this portion of recovered meteorite is commonly referred to as "pre-rain Aguas Zarcas" and constitutes material which has experienced only minimal terrestrial weathering. Based on its mineralogy, elemental abundances, and O-isotope composition, the Aguas Zarcas meteorite was classified as a petrographic type 2 CM chondrite (Meteoritical Bulletin Database 2020; Takir et al. 2020), and like other more studied CM2 chondrites such as Murchison and Murray, it is rich in water and soluble organic compounds, offering a unique opportunity to expand our knowledge of the organic inventory in the early solar system (Glavin et al. 2020).

The only previous study of water-soluble organic compounds in two different pre-rain Aguas Zarcas fragments focused on the abundance, molecular distribution (including enantiomeric measurements), and $\delta^{13}C$-isotopic compositions of amino acids (Glavin et al. 2020). The origins of meteoritic amino acids continue to be a subject of debate, although they likely formed from precursor molecules such as amines, aldehydes, cyanide, and/or other precursors in the interstellar medium and

during aqueous processes inside the meteorite parent body (Oró 1961; Peltzer et al. 1984; Aponte et al. 2017). Evaluating the molecular compositions of these basic building blocks may, therefore, provide valuable insights into the origins of meteoritic amino acids. Here, we have studied the concentration of aliphatic amines, carbonyl compounds, carboxylic acids, and free (water-soluble) and acid-releasable (water-insoluble) forms of cyanide contained in one fragment of pre-rain Aguas Zarcas; moreover, to put these measurements into context, we have contrasted these values against those found in a pristine fragment of Murchison, which was analyzed in parallel to Aguas Zarcas.

Analyses of multiple compound classes from a single meteorite sample have been reported previously (Pizzarello et al. 2008; Monroe and Pizzarello 2011); however, there are few reports comparing multiple organic compound classes in different meteorites using the same methodologies. This is important, because when different methods are used, it can be difficult to fully understand whether reported differences between meteorites are intrinsic or reflect methodological biases. In cases where evaluation of methods does occur, the differences in the resulting analyses can be substantial (Simkus et al. 2019a). Often, different methods have been used in different laboratories (or even in subsequent years in the same research groups), making it difficult to draw conclusions from any comparisons. This often goes unrealized or undiscussed and there is little published evaluation of how different analytical methodologies and techniques compare to each other (Simkus et al. 2019a). Therefore, direct comparison of the composition of various soluble organic compound classes in Aguas Zarcas and Murchison, using identical preparative methods on both meteorites, should be a more robust way to evaluate the organic composition of these two CM2 chondrites.

MATERIALS AND METHODS

Materials and Reagents

All glassware and sample handling tools used for the meteorite samples were rinsed with Millipore Direct Q3 UV ultrapure water (18.2MΩ, 3 ppb total organic carbon; hereafter referred to as "water"), wrapped in aluminum foil, and then pyrolyzed in air at 500 °C overnight. Standards and reagents were purchased from Sigma Aldrich, Alfa Aesar, and Fisher Scientific and used without further purification, with the exception of 6 M hydrochloric acid (HCl), which was double-distilled. Semi-conductor grade sodium hydroxide (NaOH), HPLC grade dichloromethane (DCM), (±)-2-pentanol (99%), O-(2,3,4,5,6-pentafluorobenzyl)

hydroxylamine hydrochloride (PFBHA, ≥99.0%), potassium cyanide (KCN), naphthalene-2,3-dicarboxaldehyde (NDA), and glycine (Gly) ≥99.0% purity were used. Functionalized aminopropyl silica gel was from SiliCycle (Silia*Bond*®, 40–63 µm particle size) and cleaned using methanol and DCM rinses followed by drying under vacuum.

Meteorite Samples and Controls

In this study, we analyzed pre-rain Aguas Zarcas (CM2, UA 2741-1, also named "UA 2741 (0.08 g)" in Glavin et al. 2020; extracted mass: 0.08 g) and Murchison (CM2, also named "Chicago Field Museum, Murchison (0.08 g)" in Glavin et al. 2020; extracted mass: 0.08 g) for aliphatic amines, carbonyl compounds, carboxylic acids, and free and acid-releasable forms of cyanide. The amino acid results from these two meteorite fragments were reported in Glavin et al. (2020). The Aguas Zarcas and Murchison samples were both obtained from interior chips that did not contain any visual evidence of fusion crust and were provided by the University of Arizona and the Chicago Field Museum, respectively (further details about the source and known curation histories of these meteorites can be found in Glavin et al. 2020). Aguas Zarcas and Murchison 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 located in an ISO 8 white room. Each powdered sample was extracted with 1 mL of water in a flame-sealed glass ampule at 100 °C for 24 h. After extraction, the residual meteorite solids were rinsed three times using 0.5 mL of water for each rinse; the aqueous supernatant and rinses were combined into one fraction (~2.4 mL of each hot water extract) and split by volume for analyses of amino acids (40%; Glavin et al. 2020), amines (10%), carbonyl compounds (20%), carboxylic acids (10%), and free cyanide (20%). A procedural water blank was carried through an identical extraction procedure. In addition, we analyzed for acid-releasable cyanide in the dried water-extracted residues of two other pre-rain Aguas Zarcas meteorite samples (UA 2741, mass: 0.49 g and UA 2746, mass: 0.52 g), and one soil sample collected from the Aguas Zarcas meteorite fall site (UA 2745, mass: 0.56 g) which were previously extracted and analyzed for amino acids only (Glavin et al. 2020).

Analyses of Aliphatic Amines

The portions of the aqueous extract allocated for amine analysis were acidified with 40 µL of 6 M HCl,

dried under vacuum, and then derivatized with the AccQ•Tag protocol for analysis (Boogers et al. 2008; see supporting information for further details). We detected and quantified the concentrations of aliphatic amines in the meteorite samples and procedural blank by ultrahigh-performance liquid chromatography with UV fluorescence and quadrupole time-of-flight mass spectrometry detection (hereafter LC-FD/Q-ToF-MS) using a Waters ACQUITY H Class UPLC with a Waters fluorescence detector and a Waters Xevo G2-XS. The amine derivatization and subsequent LC-FD/Q-ToF-MS analysis used for this study were modeled after the amino acid method used by Dworkin et al. (2018). C_1–C_6 amines were chromatographically resolved using an AccQ•Tag Ultra reversed phase column (2.1 × 100 mm, 1.7 µm bead), which was maintained at constant 55 °C. For LC analysis, a 250 µL syringe and 15 µL needle were used, with a total injection volume of 1 µL. Eluent A was 10:90 v/v (AccQ•Tag Ultra A concentrate: water), Eluent B was 100% AccQ•Tag Ultra solvent B. The mobile phase conditions for amine separations were as follows: flow rate, 700 µL min^{-1}; gradient, time in minutes (% B): 0.00 (0), 2.49 (10), 7.00 (20), 7.99 (50), 8.00 (100), 8.99 (100), 9.00 (0), 10.00 (0). AccQ•Tag amine derivatives were monitored by LC-FD (λ_{ex} = 340 nm, λ_{em} = 450 nm), and peak identification confirmation was provided by accurate mass measurements using a match tolerance of 10 ppm (centered at 202.0908, 216.1056, 230.1211, 244.1385, 258.1559, and 272.1693 Da). The Xevo G2-XS parameter included: electrospray ionization of the capillary voltage at 1.2 keV, sample cone at 40 V, source temperature at 120 °C, cone gas (N_2) flow se to 50 L h^{-1}, and desolvation gas (N_2) flow at 1000 L h^{-1}. A set of amine standards was prepared in water and analyzed at 10 different concentrations to generate a linear least-square model fit for each analyte. The abundance of amines was quantified from peak areas generated from the mass chromatogram of their AccQ•Tag derivatives. The abundances are defined as the average of three separate measurements of the same extracted sample.

Analyses of Aliphatic Carbonyl Compounds and Carboxylic Acids

The portions of the water extract allocated for analysis of carbonyl compounds were derivatized using PFBHA as previously described (Simkus et al. 2019b). Briefly, 1 mL of 0.2 mg mL^{-1} PFBHA was added to the sample aqueous extract. After reaction for 24 h at room temperature, the solution was quenched with 100 µL of 0.4 M HCl. The PFBHA-derivatives were separated from the aqueous solution using DCM

(2 × 2 mL), carried through an acid wash step (3 mL of 0.4 M HCl), and concentrated for analysis. The portions of the water extract allocated for analysis of carboxylic acids were acidified with 40 µL 2 M NaOH, dried under vacuum, and then derivatized with 2-pentanol using previously described methods (Aponte et al. 2019; see supporting information for further details). The dry residues were suspended in 50 µL of 6 M HCl, 20 µL of 2-pentanol, 100 µL of DCM, and heated at 100 °C for 15 h 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.), rinsed using ~3 mL of DCM, dried with flowing N_2, and dissolved in 100 µL of DCM for analysis. We quantified the concentrations of carbonyl compounds and carboxylic acids in the samples and procedural blank by gas chromatography coupled to triple-quadruple mass spectrometry detection (GC-QqQ-MS). The abundances of carbonyl compounds and carboxylic acids were quantified from the peak areas generated using the average value of three separate GC-QqQ-MS measurements on the same sample.

The derivatized carbonyl compounds and carboxylic acids were analyzed using a Thermo Trace 1310 GC equipped with a 5 m base-deactivated fused silica guard column (Restek, 0.25 mm I.D.), two Rxi-5ms (30 m length × 0.25 mm I.D. × 0.5 µm film thickness; capillary columns connected in series using SilTite µ-union connectors, Restek), and coupled to a Thermo TSQ8000 electron-impact triple-quadrupole mass spectrometer (ion source set at 220 °C and 70 eV). The oven program used for the analyses of carbonyl compounds was: initial temperature was 40 °C, ramped at 10 °C min^{-1} to 160 °C, then ramped at 5 °C min^{-1} to 190 °C, then ramped at 20 °C min^{-1} to 310 °C, with a final hold time of 5 min. The oven program used for the analyses of carboxylic acids was: the initial temperature was held at 40 °C for 1 min, then ramped at 15 °C min^{-1} to 110 °C, ramped at 10 °C min^{-1} to 140 °C, and held for 2 min, ramped at 10 °C min^{-1} to 145 °C, and finally ramped at 30 °C min^{-1} to 300 °C with a final hold time of 5 min. The carrier gas used was ultrahigh purity grade helium (5.0 grade) at 2.5 mL min^{-1} flow rate for carbonyl compounds and 4.8 mL min^{-1} for carboxylic acids. Triplicate injections of derivatives were made in split mode (split flow: 5 mL min^{-1}, held for 1 min) in aliquots of 1 µL. The mass spectra were used to identify and quantify the meteoritic carbonyl compounds and carboxylic acids by comparison to reference standards and application of calibration curves as described elsewhere (Aponte et al. 2019; Simkus et al. 2019b, 2019c).

Analyses of Free and Acid-Releasable Cyanide

Cyanide ions (CN$^-$) were evaluated from the hot water extract and from the mineral residues left after aqueous extraction; both types of samples (liquid or solid) were acid-digested using a MicroDIST distillation apparatus (Lachat Instruments) using previously published methods (Smith et al. 2019). Samples were placed into a micro-distillation tube with 5 mL of water, 750 µL of 9 M sulfuric acid used as a releasing agent for cyanide, and 1.5 mL of 0.08 M NaOH as a trapping solution for gaseous hydrogen cyanide (HCN); the acid digestion proceeded at 135 °C for 30 min. After distillation, 200 µL of 2 M NaOH was added to each distillate sample to raise the pH above 12; the total final volume of the distillate was measured by mass (3–4 g of distillates were typically collected). An aliquot of 50 µL of free and acid-releasable cyanide distillate solutions was derivatized using 50 µL of 10 mM sodium borate buffer (pH = 9), 50 µL of 1 mM naphthalene-2,3-dicarboxaldehyde (NDA) solution in methanol, and 50 µL of 0.1M Gly in water, reacted at room temperature for 30 min, and analyzed via LC-FD/ToF-MS.

Free and acid-releasable cyanide species were quantified using a Waters ACQUITY Classic UPLC coupled to a fluorescence detector and a Waters LCT Premier time of flight mass spectrometer (LC-FD/ToF-MS). For LC analyses, 250 µL syringe, 50 µL loop, and 15 µL needle were used, with a total injection volume of 1 µL. The NDA-cyanide derivative was chromatographically resolved using an ACQUITY UPLC CSH Phenyl Hexyl column (2.1 × 150 mm, 1.7 µm bead), an ACQUITY UPLC CSH C18 column (2.1 × 100 mm, 1.7 µm bead), and an ACQUITY UPLC CSH Phenyl Hexyl column (2.1 × 150 mm, 1.7 µm bead) attached in series. All columns were maintained at 30 °C. Eluent A was an ammonium formate buffer that was prepared via NH$_4$OH titration of a 50 mM formic acid solution to pH 9 and Eluent B was methanol. The mobile phase conditions for the separation of the NDA-cyanide derivative were as follows: flow rate, 100 µL min^{-1}; gradient, time in minutes (% B): 0.00 (70), 4.00 (90), 14.00 (90), 14.01 (100), 18.00 (100), 18.01 (70), 20.00 (70). The optical absorbance of NDA-derivative analytes was monitored by LC-FD (λ_{ex} = 252 nm, λ_{em} = 483 nm), and peak identification confirmation was provided by accurate mass using a match tolerance of 10 ppm (251.0815 Da). The ToF-MS electrospray ionization capillary voltage was set to 3.5 kV, the sampling cone to 50 V, the source temperature to 120 °C, the cone gas (N$_2$) flow to 70 L h^{-1}, and the desolvation gas (N$_2$) to 700 L h^{-1}. Cyanide standards (potassium cyanide, KCN) were

prepared in water and analyzed at 10 different concentrations to generate a linear least-square model fit for this analyte. The abundances of cyanide were quantified from peak areas generated from the mass chromatograms of the NDA-derivative, which is given as the average of three separate measurements of the same extracted sample.

RESULTS AND DISCUSSION

Abundance and Molecular Distribution of Amines

Figure 1 shows the LC-Q-ToF-MS chromatograms of representative injections from Aguas Zarcas, Murchison, a procedural blank, and a mixture of amine standards. Table 1 presents the procedural blank-corrected concentrations of amines in Aguas Zarcas and Murchison (structures are shown in Fig. S1 in supporting information). The total amounts of aliphatic amines in Murchison are 1.5 times higher than those in Aguas Zarcas; however, this difference in concentrations is mainly due to the larger abundances of methylamine and ethylamine in Murchison than in Aguas Zarcas, as the majority of the other amines are present in similar abundances in the two meteorites (Table 1). The total concentration of amines in Murchison reported here is about 2.5 times higher than those previously reported for Murchison (Aponte et al. 2014); this higher total amine abundance is also due to higher amounts of methylamine and ethylamine detected in this sample compared to previous reports. These contrasting amine abundances in Murchison may be related to differences in extraction efficiencies, derivatization yields, and/or sample heterogeneity (Simkus et al. 2019a), as well as curation conditions. However, a notable similarity is apparent in the molecular distribution of aliphatic amines in Aguas Zarcas and Murchison, whereby both meteorites show a full suite of C_1–C_5 amine isomers which decrease in concentration with increasing molecular weight (Table 1). This may point to a common synthetic mechanism for amine aliphatic chains in Aguas Zarcas and Murchison, suggesting that there is the possibility that aliphatic amines in these two meteorites may have formed through similar ion and radical reactions in the gas phase of the interstellar medium (Kaifu et al. 1974; Fourikis et al. 1977; Halfen et al. 2013), and the subsequent synthesis/destruction experienced in analogous levels by processing in the CM parent body.

Abundance and Molecular Distribution of Carbonyl Compounds

The GC-QqQ-MS chromatograms of representative injections from Aguas Zarcas, Murchison, a procedural blank, and a mixture of carbonyl standards are shown in Fig. 2. The corresponding procedural blanks for both meteorite analyses contain a similar distribution of carbonyl compounds in trace levels. Despite the small meteorite sample sizes, a suite of carbonyl compounds was detected above background levels in both Aguas Zarcas and Murchison. Table 1 presents the blank-corrected concentrations of carbonyl compounds in Aguas Zarcas and Murchison (structures are shown in Fig. S1). The total aliphatic carbonyl content of Murchison is 12-fold higher than that of Aguas Zarcas. Unlike the aliphatic amines, where only methylamine and ethylamine are present in notably higher abundances in Murchison, all of the individual carbonyl compounds in Murchison are more abundant than in Aguas Zarcas by at least threefold. Although the total concentration of aliphatic carbonyl compounds in Murchison is similar to that previously reported in a different Murchison piece, which was studied using the same extraction and derivatization protocol (Simkus et al. 2019b), an eight-fold increase in the concentration of formaldehyde is evident from the Murchison sample used in this work. The main difference between this study and other previous analyses of carbonyl compounds in Murchison is the substantially lower amount of sample used in this work; after splitting the meteorite hot water extract, the amount allocated for studying carbonyl compounds was equivalent to only 16 mg of meteorite, which may have resulted in greater formaldehyde extraction efficiencies or stability in solution. Aside from that, the larger amounts of formaldehyde in this work than in the sample used by Simkus et al. (2019b) may also be related to differences in curation histories and meteorite heterogeneity.

The use of lower amounts of extracted sample hampered our ability to screen the full molecular diversity of carbonyl compounds in Aguas Zarcas and Murchison. Based on our previous experiences analyzing meteoritic carbonyl compounds (Simkus et al. 2019b, 2019c), if larger meteorite samples would have been extracted, additional carbonyl compounds present in relatively low abundances would have been detectable above background levels; as the background levels would have likely remained the same as the present study given that the analytical protocol would have remained unchanged. Formaldehyde is the most abundant aldehyde in Aguas Zarcas, making up ~88% of the aldehyde content, while acetaldehyde is the most abundant aldehyde in Murchison, comprising ~45% of the aldehyde (Table 1). Aside from the respective dominant aldehyde species in Aguas Zarcas and Murchison, both meteorites show similarities such as a decrease in aldehyde and ketone concentrations with increasing molecular weight, and acetone being the most
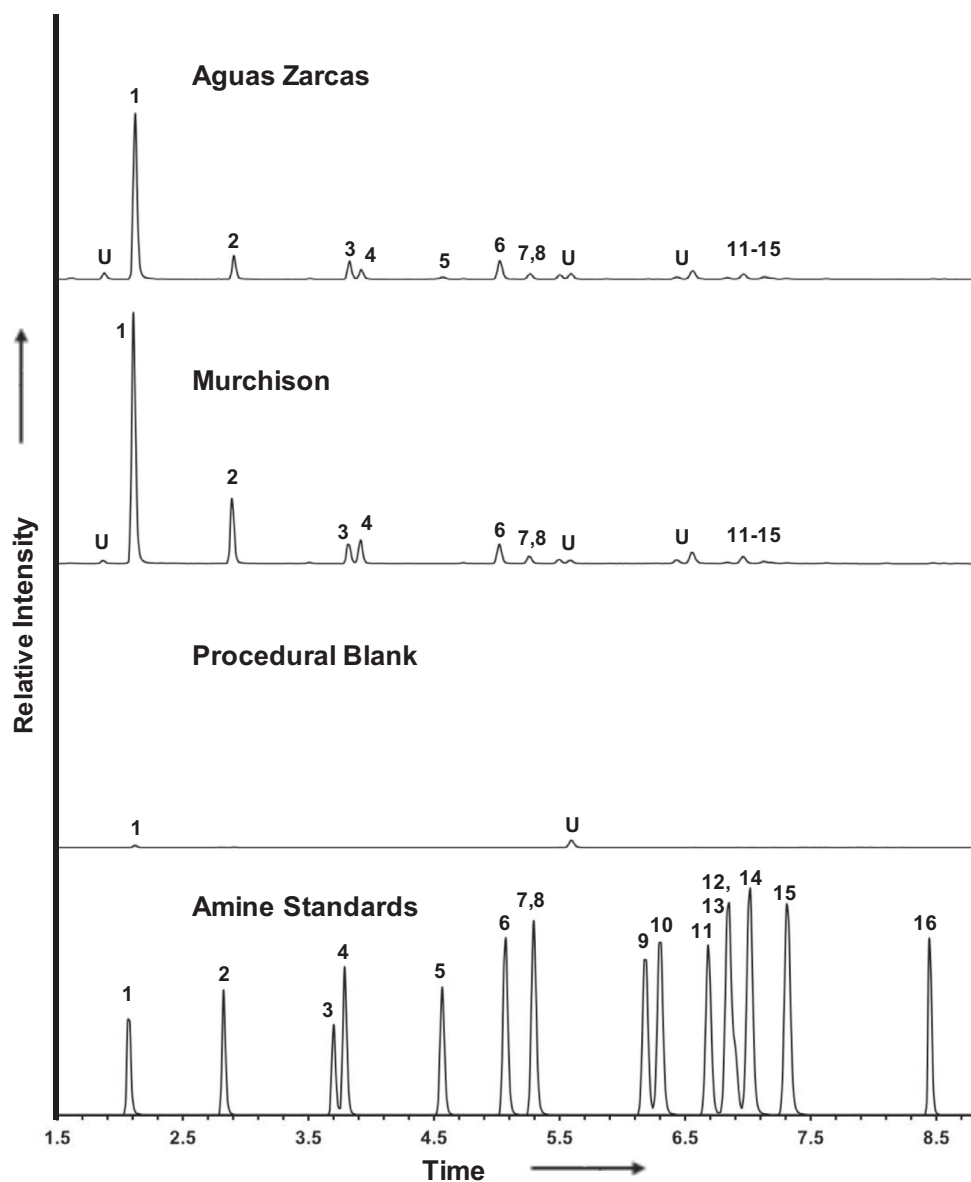
Fig. 1. Positive electrospray LC-FD/ToF-MS chromatogram (1.5–8.5 min region, 10 ppm centered at 202.0908, 216.1056, 230.1211, 244.1385, 258.1559, and 272.1693 Da) of hot water extracted derivatized amines from the Aguas Zarcas, Murchison, procedural blank, and commercially available standards (all traces are on the same intensity scale, except for the standard trace). Compound identifications: **1**, methylamine; **2**, ethylamine; **3**, isopropylamine; **4**, propylamine; **5**, *sec*-butylamine; **6**, isobutylamine; **7,8** *n*-butylamine/*t*-butylamine; **9**, 3-aminopentane; **10**, 2-amino-3-methylpentame; **11**, *sec*-pentylamine; **12**, 2-methylbutylamine; **13**, *tert*-pentylamine; **14**, isopentylamine; **15**, *n*-pentylamine; **16**, hexylamine. U: unknown compound.

abundant ketone in both samples. The differences in carbonyl concentrations and molecular diversity in Aguas Zarcas and Murchison may be due to (1) inherited characteristics from their pre-accretion and parent body processing, (2) volatile loss of different sized meteors when crossing Earth's atmosphere, or (3) differences in collection and curation histories. Because we evaluated unheated interior samples of these meteorites, the hypothesis of losing carbonyl compounds during atmospheric entry may not constitute the main explanation for the differences in concentrations we saw here; however, it is worth mentioning that in contrast to amino acids, amines, and carboxylic acids, meteoritic carbonyl compounds may not be present as ionic nonvolatile compounds (salt species) inside the meteorite mineral matrix; therefore, these neutral volatile compounds could be lost as gases while inside the parent body (Schaefer and Fegley 2007; Thompson et al. 2020) or during transit through Earth's atmosphere if the size of the bolide and fusion crust is

Table 1. Blank subtracted abundances of free amines, carbonyl compounds, carboxylic acids, and total free amino acids in the hot water extracts of Aguas Zarcas (UA 2741-1) and Murchison (values in nmol g^{-1} of meteorite).[a] Structures of the studied compounds are shown in Fig. S1

	Aguas Zarcas UA 2741-1	Murchison
Amines		
Methylamine	158.1 ± 1.3	228.3 ± 0.7
Ethylamine	4.0 ± 0.5	27.5 ± 0.1
Isopropylamine	4.0 ± 0.1	3.60 ± 0.02
Propylamine	1.2 ± 0.1	2.28 ± 0.02
sec-Butylamine	0.18 ± 0.02	0.15 ± 0.02
Isobutylamine	0.88 ± 0.02	1.02 ± 0.01
n-Butylamine/t-butylamine	0.49 ± 0.01	0.33 ± 0.02
3-Aminopentane	0.34 ± 0.01	0.38 ± 0.01
2-Amino-3-methylbutane	1.19 ± 0.02	1.07 ± 0.03
sec-Pentylamine	0.24 ± 0.01	0.74 ± 0.01
2-Methylbutylamine	0.45 ± 0.01	0.22 ± 0.01
tert-Pentylamine	≤0.01	≤0.01
Isopentylamine	0.34 ± 0.01	0.07 ± 0.01
n-Pentylamine	0.07 ± 0.01	0.06 ± 0.01
n-Hexylamine	≤0.01	≤0.01
Total free amines (this work)	171 ± 2	266 ± 1
Total free amines (Aponte et al. 2014b)	–	106 ± 10
Carbonyl (aldehydes and ketones)		
Formaldehyde	44.9 ± 7.4	156.3 ± 13.7
Acetaldehyde	≤0.01	280.1 ± 23.2
Acetone	3.3 ± 2.3	119.2 ± 18.9
Propionaldehyde	2.5 ± 0.5	35.8 ± 2.7
Butyraldehyde	≤0.01	26.9 ± 2.4
Total carbonyl (this work)	51 ± 10	618 ± 61
Total carbonyl (Simkus et al. 2019b)	–	626 ± 105
Monocarboxylic acids		
Formic acid	2885.3 ± 85.7	3383.0 ± 549.0
Acetic acid	1174.9 ± 46.6	3368.1 ± 541.4
Propanoic acid	213.2 ± 9.1	313.1 ± 52.2
Isobutyric acid	59.6 ± 3.9	61.4 ± 11.1
2,2-Dimethylpropanoic acid	8.4 ± 0.5	13.0 ± 2.1
Butyric acid	77.6 ± 1.0	113.7 ± 20.2
2-Methylbutyric acid	20.9 ± 1.1	18.4 ± 2.4
Isopentanoic acid	17.5 ± 1.2	20.2 ± 3.8
2,2-Dimethylbutyric acid	1.7 ± 0.8	2.6 ± 0.5
3,3-Dimethylbutyric acid	3.7 ± 0.1	8.5 ± 5.7
Pentanoic acid	19.1 ± 1.3	29.9 ± 6.0
2-Ethylbutyric acid/2-Methylpentanoic acid	≤0.01	≤0.01
3-Methylpentanoic acid	9.2 ± 0.7	11.6 ± 1.7
4-Methylpentanoic acid	7.2 ± 0.3	7.8 ± 0.8
Hexanoic acid	15.4 ± 1.5	19.3 ± 4.7
Benzoic acid	26.7 ± 8.2	109.4 ± 35.4
Total monocarboxylic acids (this work)	4541 ± 162	7480 ± 1237

Table 1. Continued. Blank subtracted abundances of free amines, carbonyl compounds, carboxylic acids, and total free amino acids in the hot water extracts of Aguas Zarcas (UA 2741-1) and Murchison (values in nmol g^{-1} of meteorite).[a] Structures of the studied compounds are shown in Fig. S1.

	Aguas Zarcas UA 2741-1	Murchison
Total monocarboxylic acids (Aponte et al. 2019)	–	7038 ± 482
Dicarboxylic acids		
Malonic acid	28.1 ± 3.2	173.7 ± 36.1
Succinic acid	97.8 ± 11.9	287.1 ± 64.7
Fumaric acid	13.9 ± 1.5	62.7 ± 16.5
Total dicarboxylic acids (this work)	140 ± 17	524 ± 117
Total carboxylic acids (this work)	4680 ± 179	8003 ± 1354
Total free amino acids (Glavin et al. 2020)	135 ± 8 (90)[b]	50 ± 3
Total free amino acids (Glavin et al. 2006)	–	63 ± 8

[a]Compounds identified by comparison of elution time and mass spectra to that of standards. Values are the average of three measurements; errors shown are standard deviations.
[b]Shown in parentheses is the approximate total amount of free amino acids, correcting for terrestrial contamination.

not sufficiently large to protect gases from escaping the mineral matrix (Sears 1975; Shingledecker 2014; Mehta et al. 2018). Additionally, it could be possible that the Aguas Zarcas meteorite chip we obtained for this work was from a more degassed portion of the Aguas Zarcas parent body. Future analyses of carbonyl compounds using larger amounts of the Aguas Zarcas meteorite are needed to better understand their molecular abundance and distribution.

Abundance and Molecular Distribution of Mono- and Dicarboxylic Acids

Figure 3 shows the GC-QqQ-MS chromatograms of representative injections from Aguas Zarcas, Murchison, a procedural blank, and a mixture of carboxylic acid standards (combination of mono- and dicarboxylic acids). Table 1 presents the blank-corrected concentrations of carboxylic acids in Aguas Zarcas and Murchison (structures are shown in Fig. S1). The total amounts of aliphatic carboxylic acids in Murchison are 1.7 times higher than those in Aguas Zarcas; however, this difference in concentrations is largely due to the higher concentrations of formic acid and acetic acid observed in Murchison compared to Aguas Zarcas, as the concentrations of most of the other carboxylic acids
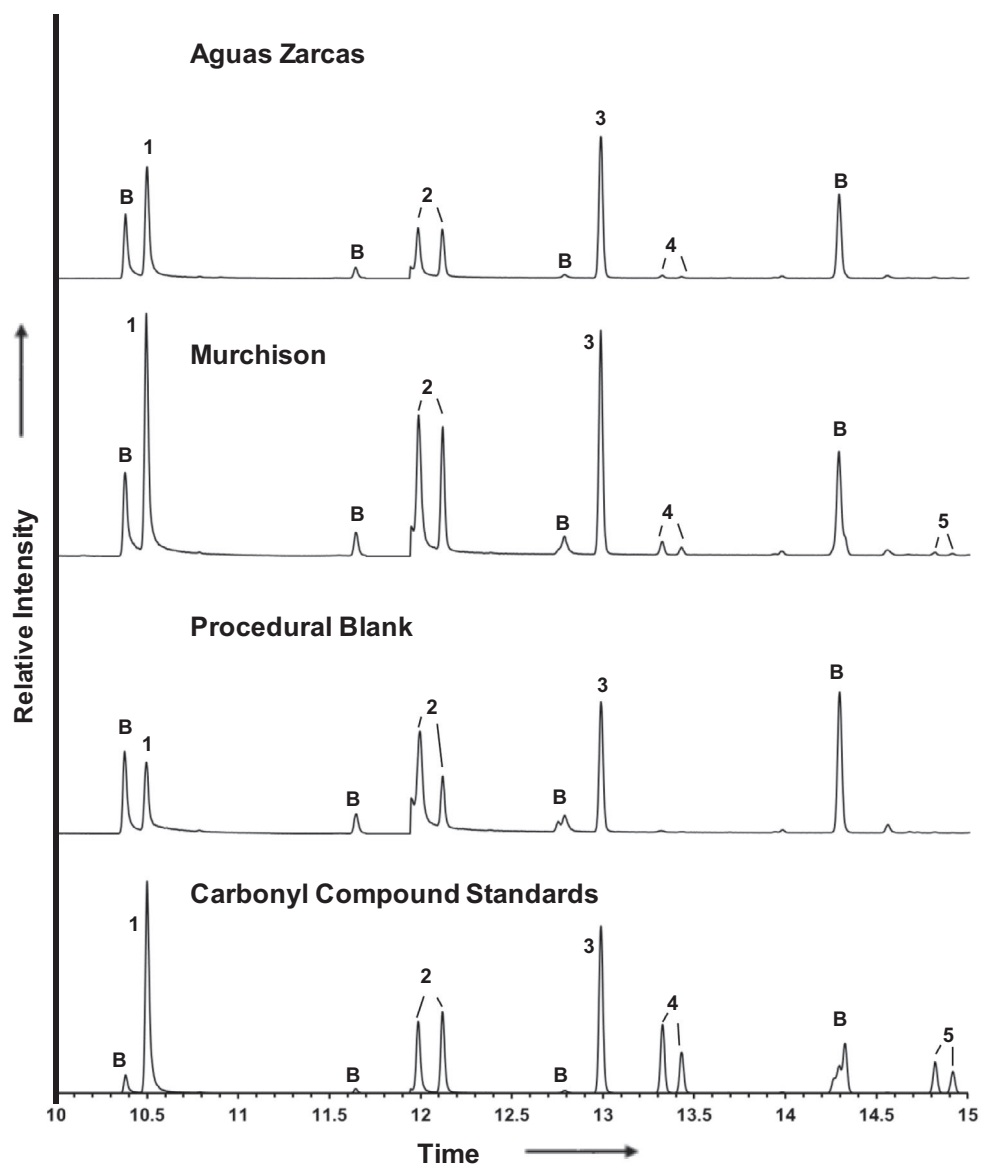
Fig. 2. Positive electron-impact GC-QqQ-MS chromatogram (10–15 min region, $m/z = 181$) of hot water extracted derivatized carbonyl compounds from the Aguas Zarcas, Murchison, procedural blank, and commercially available standards (all traces excepting standards are on the same intensity scale; full TIC chromatograms are shown in Fig. S2 in supporting information). Compound identifications ([E]- and [Z]-isomers are produced during derivatization for those carbonyl compounds with asymmetrical chemical structures): **1**, formaldehyde; **2**, (E)-, (Z)-acetaldehyde; **3**, acetone; **4**, (E)-, (Z)-propionaldehyde; **5**, (E)-, (Z)-butyraldehyde. **B**: reaction byproduct. A large peak representing unreacted derivatizing reagent eluted between 11.7 and 11.9 min (mass spec dominated by characteristic $m/z = 181$ ion). The scan was set to single ion mode ($m/z = 61$) between 11.7 and 11.9 minutes in order to eliminate this peak.

are relatively similar in both meteorites (Table 1). The total abundances of carboxylic acids in Murchison reported here are similar to those previously reported (Aponte et al. 2019); however, the abundance of acetic acid in the Murchison fragment studied here is about half that reported by Aponte et al. (2019). Like the differences seen in concentrations for specific amines and carbonyl compounds, the differences in acetic acid

concentration in Murchison could be related to derivatization efficiencies and/or sample heterogeneity (Simkus et al. 2019a). Similar to the amines, Aguas Zarcas and Murchison show a full suite of C_1–C_6 monocarboxylic acid isomers which decrease in concentration with increasing molecular weight. Contrary to aliphatic amines, however, aliphatic carboxylic acids are unlikely to be produced from the
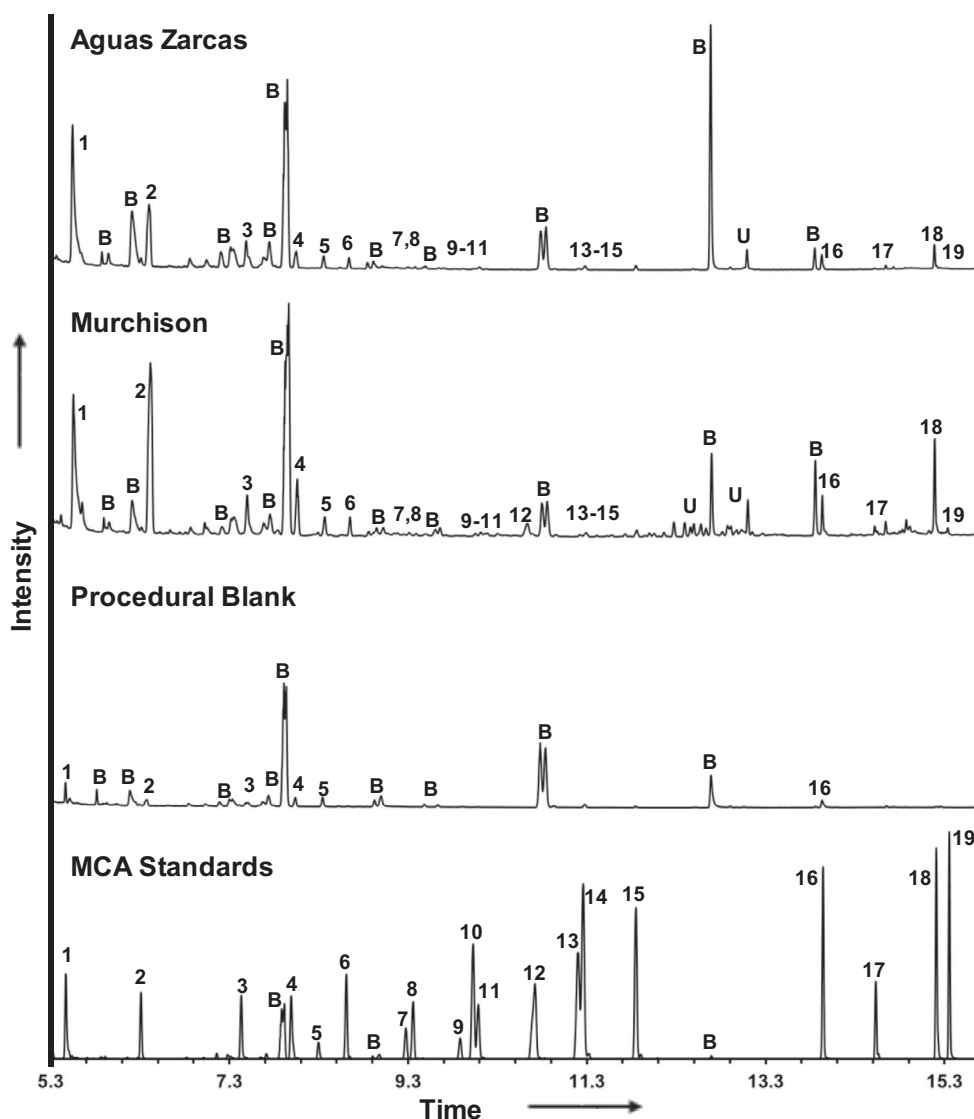
Fig. 3. Positive electron-impact GC-QqQ-MS chromatogram (5.3–15.7 min region, $m/z = 55+60 + 70+81 + 89+99 + 101+105 + 169$) of hot water extracted derivatized carboxylic acids from the Aguas Zarcas, Murchison, procedural blank, and commercially available standards (all traces excepting standards are on the same intensity scale; full TIC chromatograms are shown in Fig. S3 in supporting information). Acid identifications: **1**, formic; **2**, acetic; **3**, propanoic; **4**, isobutyric; **5**, 2,2-dimethylpropanoic; **6**, butyric; **7**, 2-methylbutyric; **8**, isopentanoic; **9**, 2,2-dimethylbutyric; **10**, 3,3-dimethylbutyric; **11**, pentanoic; **12**, 2-ethylbutyric and 2-methylpentanoic; **13**, 3-methylpentanoic; **14**, 4-methylpentanoic; **15**, hexanoic; **16**, benzoic; **17**, malonic; **18**, succinic; **19**, fumaric. **B**: reaction byproduct (ethers formed from the excess alcohol used for esterification); **U**: unknown compound.

decomposition of amino acids (Pietrucci et al. 2018). Thus, it is expected that less oxidized aliphatic organic compounds such as nitriles, aldehydes, and/or alcohols, and more oxidized species such as sugar acids or even organic macromolecular material (i.e., insoluble organic matter) would readily oxidize or reduce to yield carboxylic acids through parent body processes. This observation implies that even though the molecular distribution of aliphatic chains in carboxylic acids and amines may share common characteristics, they may not necessarily share the same synthetic pathways and/or precursor molecules.

The molecular distribution of monocarboxylic acids in Aguas Zarcas and Murchison does not show a predominance of straight chain over branched isomers (Table 1). This observation may help evaluate potential formation mechanisms. For example, the molecular distribution of aliphatic organic compounds formed through Fischer–Tropsch type (FTT) reactions shows a predominant formation of straight over branched chain

isomers (Friedel and Sharkey 1963; Anders et al. 1973). In 1979, Lawless and Yuen observed similar distributions to what we report here and concluded that FFT reactions, alone, may not have led to the observed isomeric distribution of the aliphatic chains of monocarboxylic acids in Murchison. In turn, they hypothesized that FTT reactions followed by partial equilibration through parent body processing (Lawless and Yuen 1979) may be responsible for the isomeric distribution of monocarboxylic acids in meteorites. This hypothesis, however, may need to be expanded to include a plethora of synthetic/destructive processes that, together with FTT reactions, may have been reshaped through parent body aqueous and thermal processes. Future synthetic experiments, models, and theories are needed to implement constraints on our understanding of the abiotic origins of these and other meteoritic organic compounds.

The few dicarboxylic acids we saw in Murchison do not show the same full isomeric distribution seen for monocarboxylic acids; it is worth noting that we have not verified that our method is capable of detecting oxalic and maleic acids. Martins et al. (2006) evaluated the molecular distribution of dicarboxylic acids in Murchison and other meteorites using tetramethylammonium hydroxide-derivatization followed by pyrolysis-GC-MS. In that work, in addition to oxalic and maleic acids, malonic and fumaric acids were also not detected, and succinic acid (butanedioic acid) was detected in concentrations 22 times higher than those observed here (Table 1). However, these dicarboxylic acids have been detected in previous analyses of Murchison by Lawless et al. (1974) and Peltzer et al. (1984). Similarly, concentrations of benzoic acid in Murchison varying by up to an order of magnitude per gram of meteorite have been measured in this work and by Huang et al. (2005), Martins et al. (2006), and Aponte et al. (2011). This observation suggests that more than sample heterogeneity, the detection of these dicarboxylic acids may be highly dependent on the specific extraction and analytical protocol used (Simkus et al. 2019a).

Abundance of Free and Acid-Releasable Cyanide Species

Figure 4 shows the LC-ToF-MS chromatograms of representative injections from hot water extracts and the water-extracted residues of Aguas Zarcas, Murchison, a procedural blank, and a cyanide standard. Table 2 presents the procedural blank-corrected concentrations of cyanide in these samples, as well as in additional samples of Aguas Zarcas residues and an unextracted Murchison sample. As discussed in detail by Smith et al. (2019), cyanide (CN^-) in meteorites may be extracted as soluble species such as hydrogen cyanide (HCN) and water-soluble cyanide salts, or they could be present as bound or insoluble CN^- species such as HCN-polymers, ferrocyanide, cyanocarbonyl complexes, and other related cyanometallates potentially formed through aqueous alteration in the meteorite parent body (Smith et al. 2019). In this work, we first looked for free forms of cyanide (CN^-) that could be separated from the mineral by hot water extraction. Our analyses of the hot water extracts of Aguas Zarcas and Murchison did not show detectable amounts of free CN^- (Table 2). In contrast to Smith et al. (2019), in this work, we analyzed the hot water extracts rather than bulk meteorite samples. The absence of free CN^- we found was, therefore, not surprising given that only trace amounts of free CN^- are expected after meteorite aqueous extraction at high temperatures (i.e., after extracting a meteorite sample for 17 h at room temperature, Smith et al. [2019] found that only about 7% of meteoritic CN^- would be present as soluble or in its free form). It is possible that free CN^- could have either been trapped in organometallic complexes or decomposed to form CN-polymers and/or carboxylic acids in the parent body or through our hot water extraction.

Next, we evaluated the concentrations of acid-releasable CN^- in the previously water-extracted mineral residues. As shown in Table 2, acid-releasable CN^- was found in Murchison and Aguas Zarcas samples UA 2741-1 and UA 2741, while negligible concentrations were measured in Aguas Zarcas UA 2746 and Aguas Zarcas soil. Larger amounts of acid-releasable CN^- were found in Aguas Zarcas 2741-1 than Murchison, albeit the amounts of acid-releasable CN^- varied greatly between different Aguas Zarcas and Murchison samples (Table 2). The amounts of acid-releasable CN^- found here and those reported by Smith et al. (2019) were measured using the same methodologies with the exception that the piece of Murchison used here was water extracted before acid digestion. Thus, the lower amounts of acid-releasable CN^- measured in this study can be explained by a combination of water extraction before mineral distillation and potential sample heterogeneity. The larger amount of acid-releasable CN^- in Aguas Zarcas UA 2741-1 than in Murchison may suggest that Aguas Zarcas UA 2741-1 experienced slightly lower levels of aqueous alteration than Murchison, a hypothesis that is consistent with the lower ratio of the amino acid β-alanine to glycine in Aguas Zarcas (Modica et al. 2018; Glavin et al. 2020) and with petrographic observations and in situ geochemical analyses of Aguas Zarcas (Martin and Lee 2020). However, more analyses are needed to fully understand the origins, forms, and abundances of CN^- in carbonaceous chondrites as this
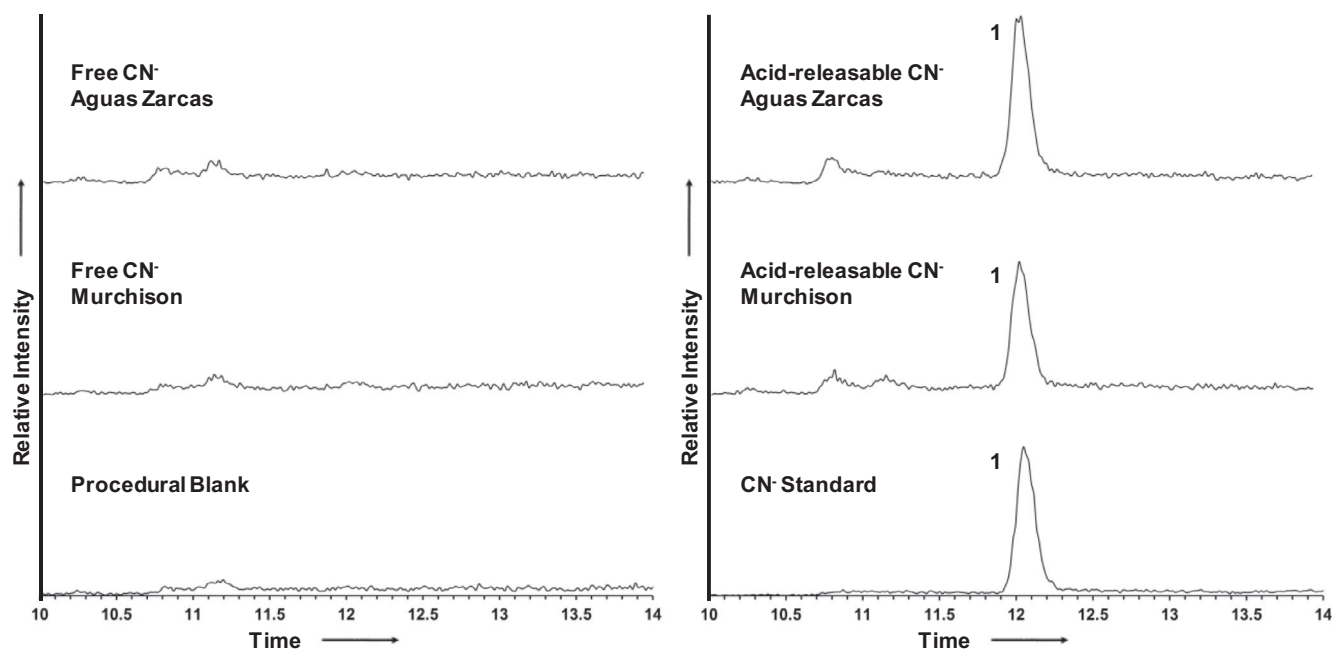
Fig. 4. Positive electrospray LC-FD/ToF-MS chromatogram (10–14 min region, 10 ppm centered on m/z = 251.0815) of free and acid-releasable CN^- from the Aguas Zarcas, Murchison, procedural blank, and commercially available standard (all traces excepting standards are on the same intensity scale). Peak identification: **1**, NDA-cyanide derivative.

Table 2. Blank subtracted abundances of free and acid-releasable cyanide species in the hot water extract and mineral solid residues of the Aguas Zarcas meteorites (UA 2741-1, UA 2741, and UA 2746), Aguas Zarcas landing site soil (UA 2745), and Murchison; values in nmol g^{-1} of meteorite.

Sample	Free CN^-	Acid-releasable CN^-
Aguas Zarcas UA 2741-1 (0.08 g)[a]	<0.1	62.4 ± 1.3
Murchison (0.08 g)[a]	<0.1	45.1 ± 1.1
Aguas Zarcas UA 2741 (0.5 g)[a]	n.d.	7.8 ± 0.2
Aguas Zarcas UA 2746[a]	n.d.	<0.1
Aguas Zarcas UA 2745 (soil)[a]	n.d.	<0.1

	Bulk
Murchison[b]	95 ± 1

n.d. = not determined.
[a]Sample previously extracted for amino acids (Glavin et al. 2020).
[b]Value taken from Smith et al. (2019). Sample analyzed as bulk (without hot water extraction).

and previous analyses suggest that CN^- was more readily available in the meteorites and thus the early Earth, than previously thought.

The fusion crust of Aguas Zarcas can have a strong blue color (Fig. 5). We had hypothesized that the color could be a result of Prussian blue (ferric ferrocyanide, $Fe^4[Fe(CN)^6]^3$) formed by HCN liberated during atmospheric heating reacting with meteoritic iron. Although no blue fusion crust Aguas Zarcas samples were available for this study for destructive analysis, the modest concentration of acid-releasable cyanides relative to the non-blue Murchison suggests another source of the color is likely. It is also interesting to note that the blue-colored aromatic compound azulene has been detected (Tunney et al. 2020), though postulated as a contaminant.

Comparison of Organic Compounds in Aguas Zarcas and Murchison

Aguas Zarcas UA 2741-1 and Murchison both belong to the CM2 carbonaceous chondrite subgroup (Meteoritical Bulletin Database 2020; Takir et al. 2020), and thus, as discussed above, the organic compounds extracted from these meteorite specimens should share common molecular traits. Figure 6 illustrates that although Murchison contained higher abundances of the organic compounds studied here, the bulk compositions of the organics studied here in these two meteorites are largely normalized by the similar relative proportions of carboxylic acids detected. Carboxylic acids are the most abundant organic species in both meteorites, while amino acids, amines, carbonyl compounds, and cyanide comprised only between 8% and 11% of the total organics we investigated in this

Fig. 5. Sample of Aguas Zarcas fusion crust can present a strong blue color (photo by: Robert Ward; April 23, 2019). Note, this particular sample was not analyzed for this study and is obviously contaminated by handling. (Color figure can be viewed at wileyonlinelibrary.com.)

work. Carboxylic acids have been observed as one of the most abundant organic compounds in the CM2 chondrite subtype (Epstein et al. 1987; Krishnamurthy et al. 1992; Huang et al. 2005; Aponte et al. 2011, 2019). It is possible, however, that other aliphatic species not studied here could be even more abundant than carboxylic acids in Aguas Zarcas, Murchison, or other carbonaceous chondrites. One main difference between the organic composition of Aguas Zarcas and Murchison is the substantially higher concentration of volatile neutral (non-ionic) carbonyl compounds in Murchison compared to Aguas Zarcas (Figure 6). These results may be explained by exposure to different degrees of aqueous alteration inside the parent body or to a heterogeneous accretion of precursor compounds such as carbonyl compounds in Murchison and Aguas Zarcas (Findlay et al. 2020). Therefore, while Aguas Zarcas and Murchison could come from the same parent body, further quantifications of these and other organic compounds in a larger suite of carbonaceous chondrites (especially using the same analytical tools and techniques) are needed to fully understand the potential synthetic relationships between them and the originally accreted meteoritic species.

The seemingly complete suites of molecular isomers of aliphatic amines and monocarboxylic acids, which both decrease in concentration with increasing molecular weight and do not show a strong predominance of straight chain over branched compounds, are consistent with ion/radical mechanisms for the production of aliphatic compounds, as suggested by Cronin and Chang (1993). This hypothesis is supported by reaction intermediates that are stabilized preferentially at highly substituted carbon centers even at low temperatures (10–100 K; Herbst 1995), and by the low levels of chain elongation reaction products expected if in competition with isomerization and dissociation processes (Duffy et al. 1995), such as those in interstellar environments. These factors suggest a scenario where ion/radical reactions may have played a more preponderant role than other reactions such as FTT when it comes to the synthesis of the aliphatic chains in amines and monocarboxylic acids. This conclusion, however, requires an understanding of the molecular diversity derived from reactions other than ion/radical syntheses and the reshaping of the molecules generated that would occur inside the parent body. Nevertheless, it is possible that ion/radical reactions may have been the predominant synthetic pathway in cold interstellar regions and before the accretion of asteroids (and other solar system bodies, including comets) inside which aqueous and thermal processes may have had an even greater impact on the molecular diversity we see now in carbonaceous chondrites. More laboratory work is needed to understand the yields and molecular diversities in different simulated environments where organic syntheses could have occurred and the effects of processing the organic material produced may have faced in our solar system.

CONCLUSION

We used analytical protocols that enabled a direct comparison of the abundance and molecular distribution of aliphatic amines, aldehydes, ketones, carboxylic acids, and free and acid-releasable cyanide species in the CM2 chondrites Aguas Zarcas and Murchison. Using identical preparative methods on both meteorites, we were able to directly compare their molecular distributions and exclude methodological uncertainties. We observed higher abundances of aliphatic amines, carbonyl compounds, and carboxylic acids in Murchison than Aguas Zarcas. We did not find free cyanide in the aqueous extract of both meteorites; however, larger amounts of acid-releasable cyanide were seen in Aguas Zarcas than in Murchison after acid distillation of their mineral matrixes. Although we observed higher concentrations of aliphatic organic
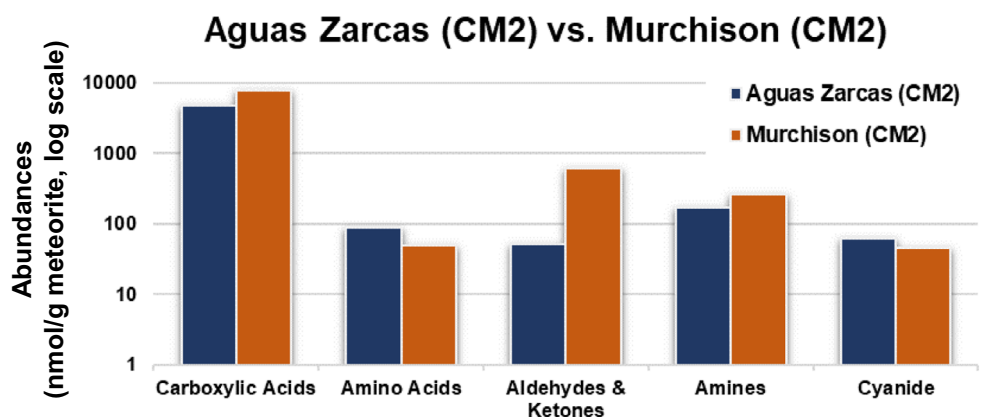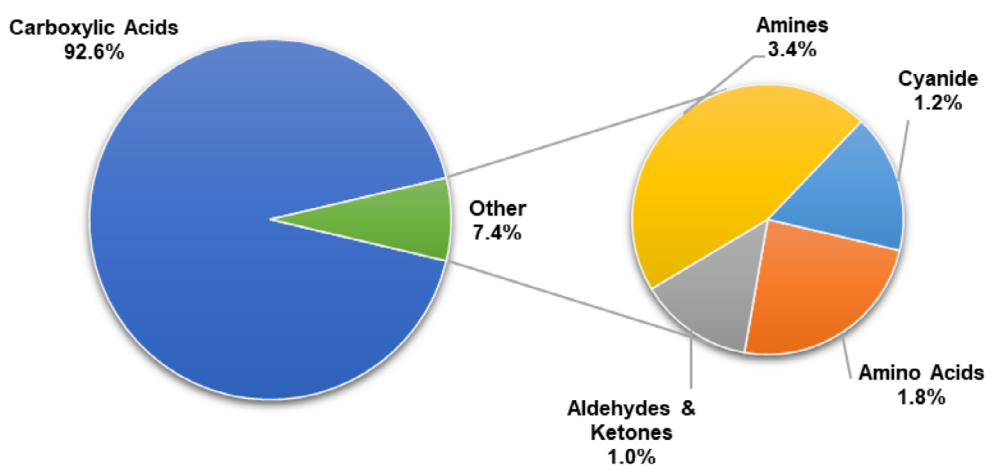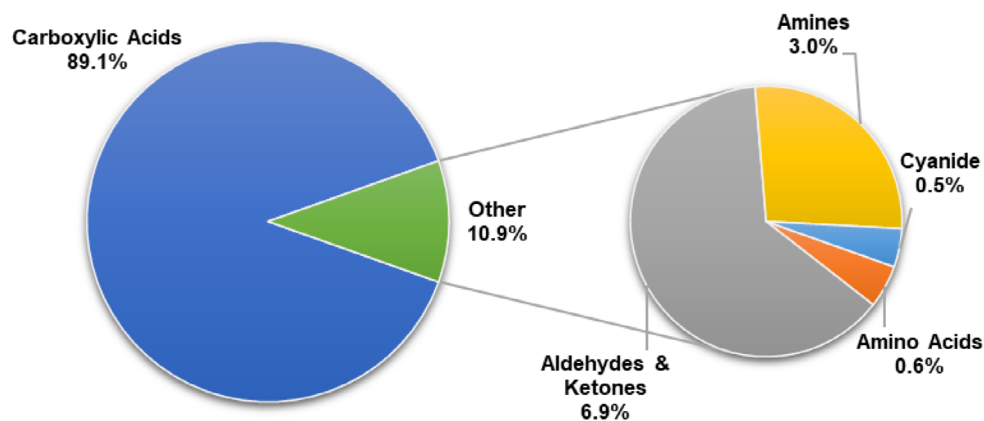
Fig. 6. Comparison of organic compounds in Aguas Zarcas (UA 2741-1) and Murchison (values taken from Table 1). (Color figure can be viewed at wileyonlinelibrary.com.)

compounds in Murchison than in Aguas Zarcas, both samples showed a similar molecular distribution of aliphatic amines and monocarboxylic acids, suggesting that the concentrations we found were shaped by similar aqueous and thermal processes that likely occurred inside the same asteroid parent body. Ion/

radical reactions that occurred before the accretion of the parent body and other reactions such as FTT have been suggested to be responsible for the synthesis and molecular distribution of the aliphatic chains in meteoritic amines and monocarboxylic acids; however, additional work is needed to understand how these and other reactions and their molecular yields would be reshaped during parent body processing. Aside from the meteoritic results reported here, these type of analyses are also important for understanding the organic content of other extraterrestrial materials such as the Apollo lunar samples, the Stardust cometary sample, and the asteroidal samples to be brought to the Earth by the Hayabusa2 and OSIRIS-REx missions.

Editorial Handling—Dr. Scott Sandford

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SUPPORTING INFORMATION

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

Fig. S1. Structures of aliphatic amines, carbonyl compounds, and carboxylic acids studied in this work as shown in Fig. 1, 2, and 3.

Fig. S2. Positive electron-impact GC-QqQ-MS chromatogram (9 - 23 min region, total ion chromatogram) of hot-water extracted derivatized carbonyl compounds from the Aguas Zarcas, Murchison, procedural blank, and commercially available standards (all traces excepting standards are on the same intensity scale). Compound identifications ((E)- and (Z)-isomers are produced during derivatization for those carbonyl compounds with asymmetrical chemical structures): **1**, formaldehyde; **2**, (E)-, (Z)-acetaldehyde; **3**, acetone; **4**, (E)-, (Z)-propionaldehyde; **5**, (E)-, (Z)-butyraldehyde.

Fig. S3. Positive electron-impact GC-QqQ-MS chromatogram (5.3 - 21.3 min region, total ion chromatogram) of hot-water extracted derivatized carboxylic acids from the Aguas Zarcas, Murchison, procedural blank, and commercially available standards (all traces excepting standards are on the same intensity scale). Acid identifications: **1**, formic; **2**, acetic; **3**, propanoic; **4**, isobutyric; **5**, 2,2-dimethylpropanoic; **6**, butyric; **7**, 2-methylbutyric; **8**, isopentanoic; **9**, 2,2-dimethylbutyric; **10**, 3,3-dimethylbutyric; **11**, pentanoic; **12**, 2-ethylbutyric and 2-methylpentanoic; **13**, 3-methylpentanoic; **14**, 4-methylpentanoic; **15**, hexanoic; **16**, benzoic; **17**, malonic; **18**, succinic; **19**, fumaric.

Data S1. Data points for Figures 1, 2, 3, and 4.

Supporting Information

Extraterrestrial Organic Compounds and Cyanide in the CM2 Carbonaceous Chondrites Aguas Zarcas and Murchison

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26   **AccQ•Tag analysis of aliphatic amines.** This is the first report of amines from the Aguas

27   Zarcas and Murchison meteorites using Water's AccQ•Tag liquid chromatographic protocol

28   (Boogers et al. 2008). We elected to use this methodology over the OPA/NAC approach (Glavin

29   et al., 2006, 2010) because the AccQ•Tag-amine derivatization product (see Scheme S1; Cohen

30   and Michaud, 1993) is more stable than the OPA/NAC-amine derivative products, which allows

31   for automated sequential analyses; additionally, the AccQ•Tag derivatization method does not

32   require desalting of the meteorite extracts because it is not susceptible to multivalent cation

33   interference.

34   **Scheme S1.** AccQ•Tag-amine derivatization reaction (R, R' = alkyl or H).

6-Aminoquinolyl-*N*-hydroxysuccinimidyl carbamate   Amine   **AccQ•Tag-amine derivative**   *N*-Hydroxysuccinimide
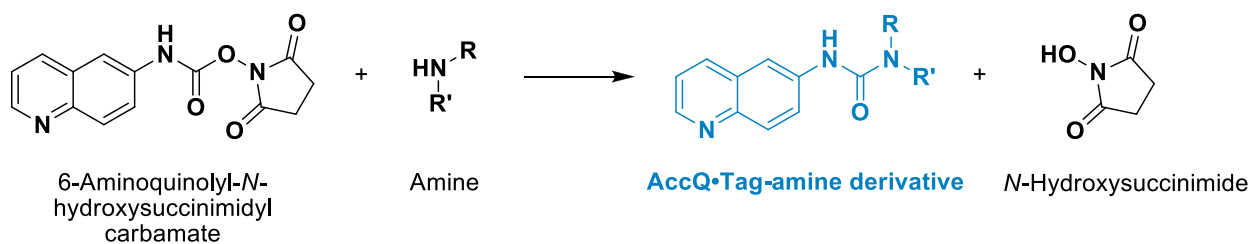
36   The fluorescent AccQ•Tag LC-method is not only significantly faster (each run is 10

37   minutes, compared to 60 minutes for OPA/NAC), but also offers higher sensitivities than gas

38   chromatographic methods. The amount of material used in this study was equivalent to 8 mg of

39   each meteorite. According to our previous amine meteoritic analyses using gas chromatography

40   (Aponte et al., 2014, 2016), we expect that using that same amount of sample (8 mg), but applying

41   a GC method, we would not be able to evaluate the molecular diversity of C_3-C_6 amines. It is worth

42   mentioning, however, that AccQ•Tag does not facilitate chromatographic separation of chiral

43   amines into their corresponding enantiomers (e.g., (*R*)- and (*S*)-*sec*-butylamine).

44

45   **Analysis of aliphatic carboxylic acids.** We have slightly modified our previous

46   esterification protocol (Aponte et al., 2019) for the analysis of aliphatic meteoritic carboxylic

47   acids. In the method we used for the present work, we dried the meteorite hot-water extract in

48   sufficient aqueous NaOH to bring the pH of the solution above 12 instead of using magnesium

49   chloride as an acid chelating agent, and we changed to a more volatile secondary alcohol (2-

50   pentanol) for acid derivatization. We tested alcohols of different molecular weights and boiling

51   points for derivatization (isopropanol, isobutanol, butanol, pentanol, 2-methylbutanol, and 2-

52   pentanol), to improve the chromatographic separation of the formic acid ester derivative, which

could not be quantified using our previous method. We found that 2-pentanol was the best suited

for quantifying formic acid using GC in split mode (see Materials and Methods section for further

details). Nevertheless, using this alcohol for derivatization and chromatographic conditions results

in an inability to separate carboxylic acid-ester derivatives into enantiomers (e.g., (*R*)- and (*S*)-2-

methylbutyrate), and this method may not be well-suited for analyses designed to circumvent

sample isotopic fractionation using GC in splitless mode.

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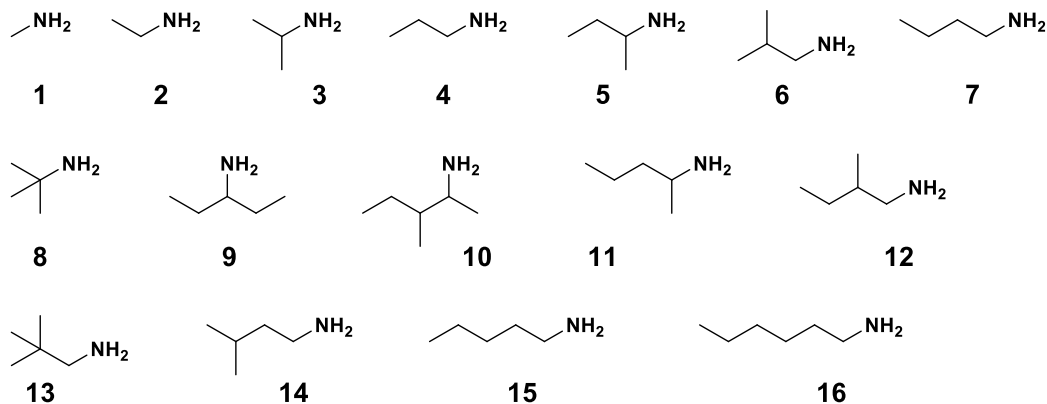
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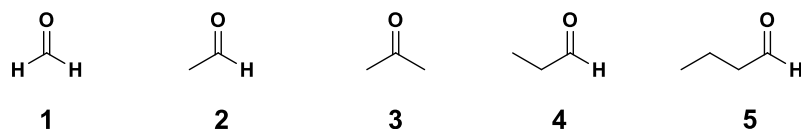
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Figure S1. Structures of aliphatic amines, carbonyl compounds, and carboxylic acids studied in
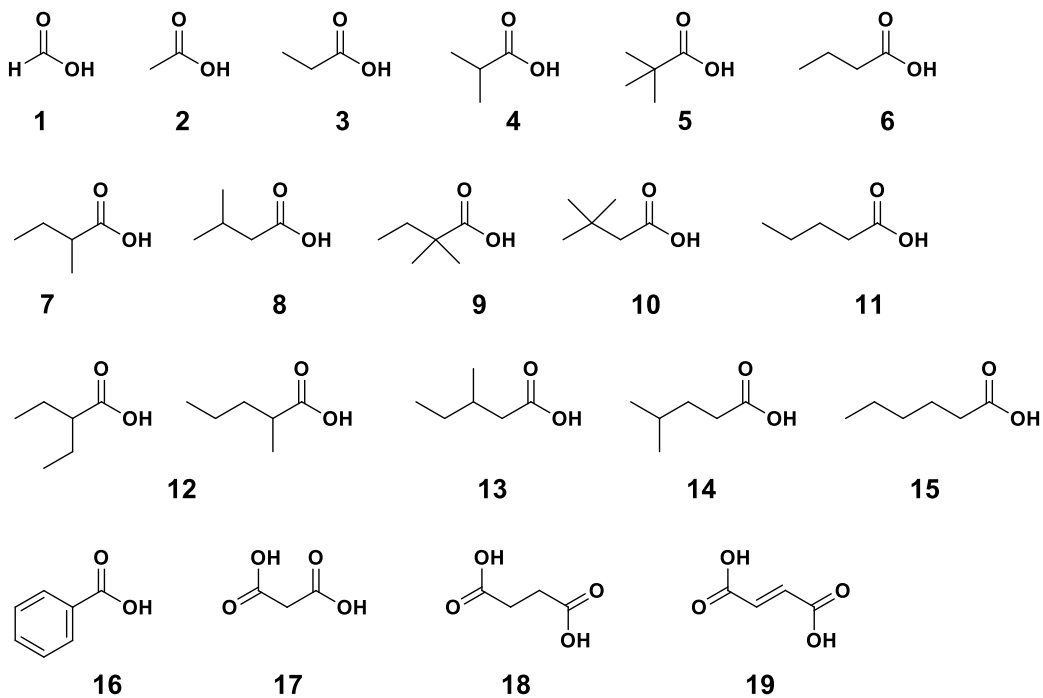this work as shown in Figures 1, 2 and 3.
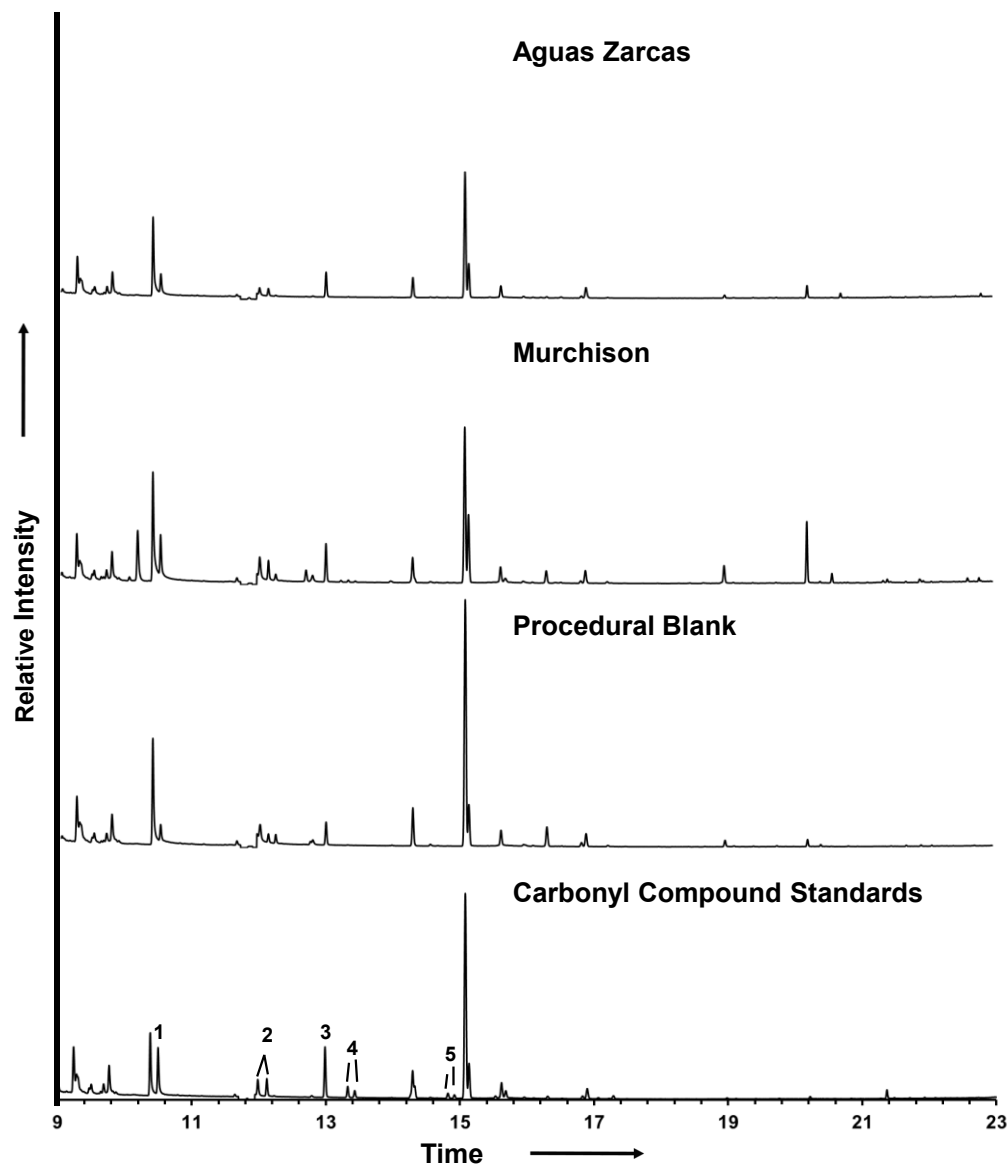
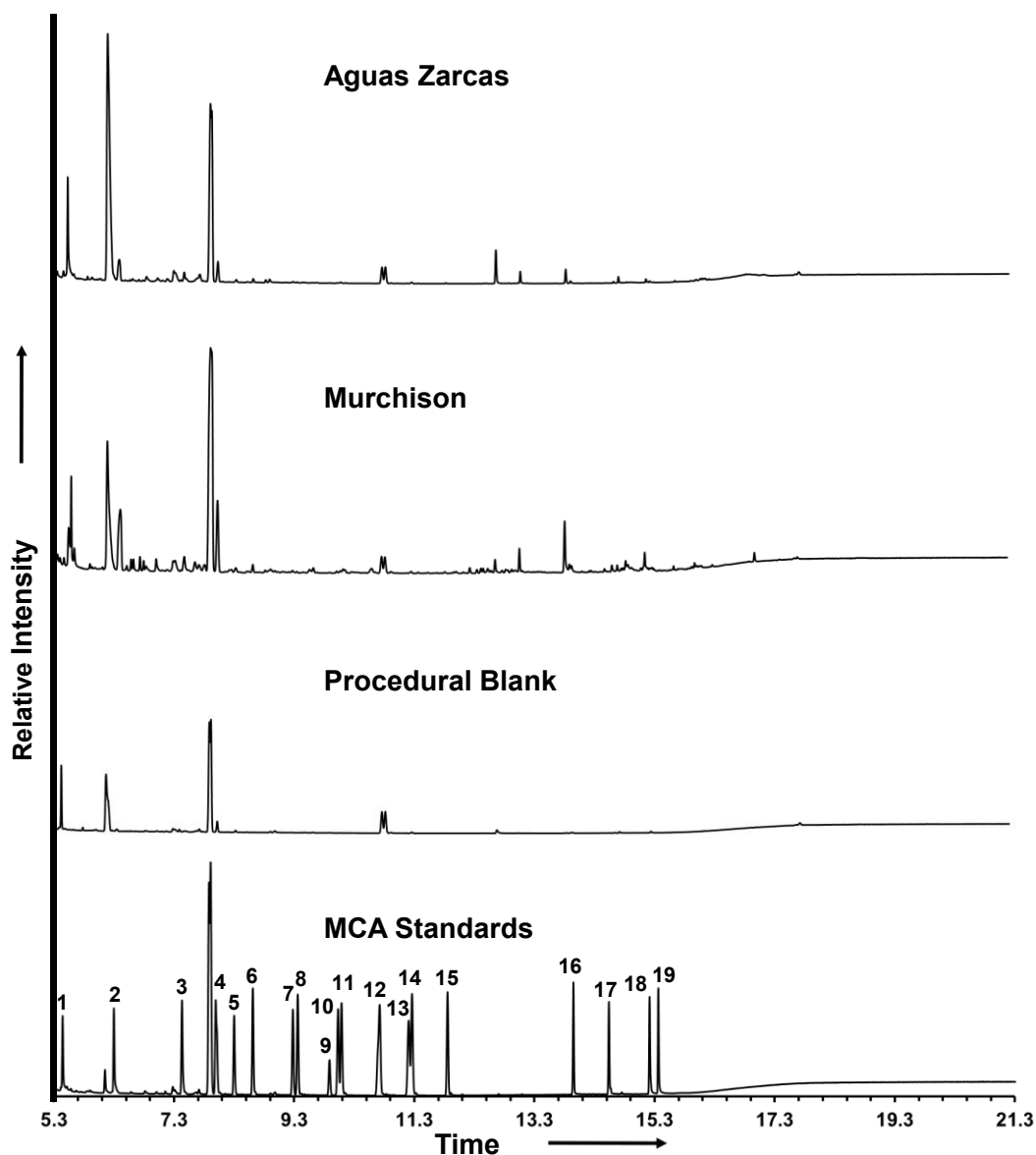**Amines:**

Carbonyl Compounds:

Carboxylic Acids:

94

95

Figure S3. Positive electron-impact GC-QqQ-MS chromatogram (5.3 - 21.3 min region, total ion
chromatogram) of hot-water extracted derivatized carboxylic acids from the Aguas Zarcas,
Murchison, procedural blank, and commercially available standards (all traces excepting standards
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malonic; **18**, succinic; **19**, fumaric.

106   **Data S1.** Data points for Figures 1, 2, 3 and 4.

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