Analyses of Aliphatic Aldehydes and Ketones in Carbonaceous Chondrites

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Abstract

Aliphatic aldehydes and ketones are essential building blocks for the synthesis of more complex organic compounds. In spite of their potentially key role as precursors of astrobiologically-important molecules, such as amino acids and carboxylic acids, this family of compounds has scarcely been evaluated in carbonaceous chondrites. The paucity of such analyses likely derives from the low concentration of aldehydes and ketones in the meteorites, and from the currently used chromatographic methodologies that have not been optimized for meteorite analysis. In this work, we report the development of a novel analytical method to quantify the molecular distribution and compound-specific isotopic analysis of 29 aliphatic aldehydes and ketones. Using this method, we have investigated the molecular distribution and ^{13}C-isotopic composition of aldehydes and ketones in ten carbonaceous chondrites from the CI, CM, CR and CV groups. The total concentration of carbonyl compounds ranged from 130 to 1000 nmolg^{-1} of meteorite, with formaldehyde, acetaldehyde, and acetone being the most abundant species in all investigated samples. The ^{13}C-isotopic values ranged from –67 to +64‰ and we did not observe clear relationships between ^{13}C-content and molecular weight. Accurately measuring the relative abundances, determining the molecular distribution, and isotopic composition of chondritic organic compounds is central in assessing both their formation chemistry and synthetic relationships.

1. INTRODUCTION

Carbonaceous chondrites represent roughly 4% of all meteorite falls on Earth.[1] Some of these carbon-rich meteorites (up to 3 wt.% of carbon) contain a diverse suite of organic compounds that hold a record of the chemical inventory and processes that occurred in the early Solar System and through parent body processing. Most of the organic carbon in carbonaceous meteorites is in the form of insoluble organic matter (IOM), while the rest is composed of a complex mixture of soluble organic compounds, including aliphatic amino acids, which are the most extensively studied types of meteoritic organics. More than ninety different amino acids, which represent a nearly complete structural diversity, have been identified from carbonaceous chondrites. The diversity of organics provides insight into the chemical nature of the meteorite parent bodies,[2-4] however although meteoritic amino acids have been studied for over 60 years using a variety of techniques,[5-10] their synthetic origins remain a subject of debate.[11]

Accurately measuring the molecular distributions of organic compounds and comparing the relative abundances of different compound types is key for understanding the effects of aqueous and thermal processing inside the parent body and the synthetic relationships between various classes of meteoritic organic compounds. Although aldehydes and ketones (collectively called “carbonyl compounds”) have been previously reported from carbonaceous chondrites,[12-17] and their potential synthetic relation to other organic compounds has been proposed (Scheme 1)[18-20], they remain a group of molecules whose meteoritic origins have not yet received much attention.

There are two main reasons that have likely hampered the study of carbonyl compounds in meteorites: 1) their low overall abundance in some of the most heavily studied carbonaceous chondrites such as Murchison; and 2) existing methods for meteorite extraction and workup may be detrimental to aldehydes and ketones. The Murchison meteorite is the most thoroughly studied carbonaceous chondrite with respect to its organic chemistry,[4,21-24] but its low carbonyl content may have discouraged further studies of these compounds. The low abundance of carbonyl compounds can result in the need for large sample sizes for analysis, which may be difficult to obtain for rare meteorites. Additionally, the gas chromatography-mass spectrometry (GC-MS) methodologies currently used for the analysis of meteoritic carbonyl compounds are designed for applications that do not necessarily require compound-specific stable isotope evaluations or chiral separations; thus, the extraction and workup methods applied previously were also not optimized for the exclusive analysis of aldehydes and ketones. Traditionally, these molecules have been quantified from aqueous extracts prepared with a focus on the extraction of amino acids, a process that may affect the measured abundance and isotopic composition of these compounds.[12-17]

To evaluate meteoritic carbonyl compounds, we have developed a novel GC-MS coupled to isotope ratios MS (IRMS) methodology, as well as a workup protocol suited to simultaneously measure the abundance and compound-specific isotopic analysis of short-chained meteoritic carbonyl compounds (≤ 6 carbons; Figure S1). This methodology derives from the conversion of aldehydes and ketones to their corresponding 1,4-dimethoxy-2,3-butane-acetals and ketals (hereafter DMB-derivatives; Scheme 2), simplifying the chromatographic analysis and eliminating the potential for isotopic fractionations occurring during derivatization. Here, we report the application of our methods to meteorites from the CI, CM, CR and CV groups (Table 1), with excellent efficiency, but without the capacity for enantiomeric quantitation (SI).

2. METHODS AND MATERIALS

2.1. Chemicals and reagents. Standards and reagents were purchased from Alfa Aesar or Sigma-Aldrich and used without further purification except as noted below. Compounds **26** and **27** were synthesized at NASA Goddard Space Flight Center; enantiopure forms of **15**, **17**, and **26** were synthesized at University College London (see Table 2 for compound identification, Figure S1 for structures, and Supporting Information for further details). 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. Boron trifluoride diethyl etherate (≥46.5% BF_3 basis) and (*S*,*S*)-(–)-1,4-dimethoxy-2,3-butanediol, ≥99.0% ((*S*,*S*)-DMB-Diol; sum of enantiomers, GC) were purchased from Sigma-Aldrich. We used HPLC grade dichloromethane (DCM) for sample extraction and derivatization.

2.2 Extraction of aliphatic aldehydes and ketones. Meteorite samples listed in Table 1 were obtained from interior chips that did not contain any visual evidence of fusion crust. The samples were provided from the meteorite collections at the Muséum National d'Histoire Naturelle (Paris, France), the Smithsonian National Museum of Natural History (Washington, DC, USA), and the NASA Johnson Space Center (Houston, TX, USA). All meteorites were individually crushed into fine powders and homogenized using a porcelain mortar and pestle in an ISO 5 positive pressure high efficiency particulate air-filtered laminar flow hood. Portions of each powdered meteorite sample (1.4 g or less) were flame sealed in glass ampoules containing 2 mL of DCM for the extraction of aldehydes and ketones, and then heated at 100 °C for 24 h. The liquid supernatants were collected after centrifugation and each residue was rinsed twice more using 1 mL of DCM; rinses were then combined with the initial extract (~4 mL total final volume). Dissolved sulfur was removed by adding freshly cleaned metallic copper beads (surface oxide was removed by rinsing in 6 M HCl, followed by water, methanol, and DCM cleaning). After filtration of the copper beads, the organic extracts were stored at –20 °C prior to derivatization. This entire extraction procedure was also carried out in parallel with a procedural blank.

2.3 Derivatization of aliphatic aldehydes and ketones. The acid-catalyzed acetalization of aldehydes and ketones with diols is one of the most common transformations in organic synthesis (see Supporting Information for further details); we modified previously reported methods for the formation of acetals and ketals starting from carbonyl compounds (Scheme 2).[25-27] The derivatization reaction was carried out by adding 20 μL of BF_3 and 50 μL of 0.1 mM (*S*,*S*)-DMB-Diol to the DCM meteorite extract, and heating the mixture at 110 °C for 1 h in sealed glass vials with PFTE-lined screw caps. Then, the reacted solution was concentrated to ~1 mL by flowing nitrogen gas (N_2), and extracted using 1 mL of water three times to remove the unreacted (*S*,*S*)-DMB-Diol and BF_3. After aqueous extraction, the organic layer was passed through a plug of anhydrous sodium sulfate (Na_2SO_4; 45 mm length × 5 mm I.D.), rinsed using 0.5 mL of DCM, and blown dry with N_2. Samples were dissolved in 70 or 100 μL of ethyl acetate for gas chromatography coupled with mass spectrometry and isotope ratio mass spectrometry (GC-MS/IRMS).

2.4 Compositional and isotopic analyses. Analyses of derivatized carbonyl compounds were performed using GC-MS/IRMS, which provides compound-specific identification and stable carbon isotopic ratios.[28] The gas chromatographic separation was accomplished using a Thermo Trace GC equipped with a 5 m length × 0.25 mm I.D. base-deactivated fused silica guard column (Restek) and four 25 m length × 0.25 mm I.D. × 0.25 μm film thickness CP-Chirasil Dex CB (Agilent) capillary columns connected in series using Press-Tight® connectors (Restek). Typically, samples were analyzed in triplicate. The oven program was set as follows: the initial temperature of 40 °C was held for 4 min, ramped at 5 $°C min^{-1}$ to 100 °C and held for 5 min, then ramped at 2 °Cmin^{-1} to 116 °C and held for 10 min, then ramped at 2 °Cmin^{-1} to 120 °C and held for 15 min, then ramped at 2 °Cmin^{-1} to 130 °C and held for 7 min, then ramped at 2 °Cmin^{-1} to 144 °C and held for 10 min, then ramped at 2 °Cmin^{-1} to 164 °C and held for 3 min, and finally ramped at 15 °Cmin^{-1} to 220 °C with a final hold of 15 min. The carrier gas used was ultrahigh purity (UHP) helium (5.0 grade) at 1.8 mLmin^{-1} flow rate. Triplicate injections of derivatized carbonyl compounds were made in splitless mode in aliquots of 1 μL. Approximately 10% of the sample eluting from the GC column was directed into a Thermo DSQII electron-impact quadrupole mass spectrometer (ion source set at 220 °C and 70 eV). The mass spectrum was used to identify and quantify the meteoritic carbonyl compounds by comparison to reference standards and applying a four-point calibration curve. Compounds **2** and **3** (Table 2) were extracted at *m/z* = 87; compounds **5-7**, **11**, **15**, **16**, **19**, **21-23**, **25-27**, and **29** were extracted at *m/z* = 161; compounds **1**, **4**, **8**, **9**, **12**, **13**, **17**, and **20** were extracted at *m/z* = 175; compounds **24** and **28** were extracted at *m/z* = 187; and compounds **10**, **14**, and **18** were extracted at *m/z* = 189. The remaining 90% of each eluting compound was directed through a Thermo GC-C III interface for oxidation of the compounds to carbon dioxide; the δ^{13}C stable isotopic measurement was then made on a Thermo MAT 253 IRMS. The δ^{13}C values of the eluting compounds were obtained after injection of three pulses of precalibrated CO_2 ($\delta^{13}C = –24.23‰$ VPDB) into the IRMS and computation using Thermo Isodat 2.5 software. In order to correct for the amount of carbon added by the derivatization reagent, underivatized standards were analyzed on a Costech ECS 4010 combustion elemental analyzer (EA) connected to the IRMS. The final δ^{13}C values of the meteoritic carbonyl compounds were calculated using equation 1. Given the high volatility and low stability of formaldehyde, which polymerizes over time in solution, we used formaldehyde diethyl acetal as substitute for formaldehyde; we used the average ^{13}C-isotope composition added by the derivatization agent in the other C_2-C_3 carbonyl compounds to calculate the δ^{13}C value of formaldehyde.

$$\delta^{13}C_{\text{sample carbonyl}} = [((n_{\text{carbonyl}} + n_{\text{d}})/n_{\text{carbonyl}}) \times (\delta^{13}C_{\text{derivatized sample carbonyl}} - \delta^{13}C_{\text{derivatized std carbonyl}})] + \delta^{13}C_{\text{underivatized std carbonyl}} \tag{1}$$

where n_{carbonyl} = number of carbon atoms in underivatized carbonyl and n_{d} = number of carbons added by derivatizing reagent. The precision (standard deviation) of the δ^{13}C values was obtained using equation 2.[29]

$$\sigma^2_{\text{sample carbonyl}} = \sigma^2_{\text{underivatized std}} + [\sigma^2_{\text{derivatized std}} \times ((_{\text{carbonyl}} + \mathrm{n_d})/\mathrm{n}_{\text{ carbonyl}})^2] + [\sigma^2_{\text{derivatized sample}} \times ((\mathrm{n}_{\text{ carbonyl}} + \mathrm{n_d})/\mathrm{n}_{\text{ carbonyl}})^2] \tag{2}$$

3. RESULTS

The total ion chromatogram from GC-MS of a procedural blank, the mixture of aldehyde and ketone standards, and the Murchison meteorite, as well as the GC-IRMS chromatogram of the Murchison injection are shown in Figure 1; similar chromatograms were obtained for other meteorites investigated in this work (Figures S2 and S3 in the Supporting Information). We were unable to fully assess the carbonyl compound content of LAP 02342 (CR2.5) due to experimental difficulties (after the first GC-MS/IRMS injection showed only acetone, acetaldehyde, and formaldehyde, we attempted to further concentrate the sample through solvent evaporation, but it was unfortunately lost during that process). The procedural blank contained detectable aldehydes and ketones suggesting that these compounds formed from the decomposition of DCM during extraction through yet-to-be-known mechanism (100 °C for 24 hours; see Supporting Information for further details).

The total concentrations of carbonyl compound we found ranged from 230 – 1000 nmolg^{-1} of meteorite (Table 2 and Figure 2). Given the potential for compounds losses during sample extraction, we consider the abundances shown in Table 2, as the minimum quantities of free aldehydes and ketones present in the carbonaceous chondrites we investigated. Aldehydes were more abundant than ketones, with formaldehyde and acetaldehyde being the most abundant aldehydes, and acetone the most abundant ketone across the different carbonaceous chondrites studied here. The total concentrations of carbonyl compounds in CI and CM chondrites ranged within similar values (230 to 350 nmolg^{-1} of meteorite), while those in CR chondrites seemed to be more dependent on the levels of parent body processing (total concentrations ranged from 130 to 1000 nmolg^{-1} of meteorite). We saw a lack of molecular diversity in the EET 96029 (CM2.7) which has only faced minimal levels of aqueous alteration. We also found that the overall concentration of carbonyl isomers decreased with increasing carbon number and branching; the exception to this was the higher concentrations of acetaldehyde compared to formaldehyde in Orgueil (CI1.1), ALH 83100 (CM1.1), LEW 90500 (CM1.6), Murchison (CM1.6), and LON 94101 (CM1.8). Aldehydes with the carbonyl moiety (–CHO) on a primary carbon were more abundant than their isomeric counterparts having the carbonyl group in the secondary and tertiary position (e.g., *n*-butanal vs. isobutanal, *n*-pentanal vs. isopentanal and pivaldehyde).

We interpreted that the aldehydes and ketones found in Allende (CV3) are product of terrestrial contamination based on the high concentrations of biological monocarboxylic acids we found ($\delta^{13}C$ values of monocarboxylic acids in Allende averaged to –26‰) in a previous analysis of the same material studied here for carbonyl species;[30] thus, the results of the analyses of carbonyl compounds found in Allende are shown in Table 3 but have been dismissed from further discussions in this report.

The $\delta^{13}C$ of carbonyl compounds ranged from –63 to +77‰. Figure 3 shows the $\delta^{13}C$ values of the most abundant carbonyl compounds; i.e., acetone, 2-butanone, formaldehyde, acetaldehyde, and propanal. Their corresponding chromatograms are shown in Figures S4 and S5, and the compound-specific $\delta^{13}C$ values of all compounds are plotted against carbon number by meteorite in Figure S6.

4. DISCUSSION

4.1 Molecular distribution of aliphatic carbonyl compounds in meteorites. The total concentration of aldehydes and ketones we found in the Murchison meteorite are 60% higher than those found by Pizzarello and Holmes (2009),[13] but only half of those extracted by Simkus et al. (2019)[17] from the same meteorite. The difference in the total concentrations we found with respect to those seen by Pizzarello and Holmes (2009)[13] may be the result of sample heterogeneity and/or sample processing as has been observed for other soluble organic compounds.[30,31-33] However, the lower concentrations we detected in comparison to Simkus et al. (2019)[17] are more likely explained by the different extraction protocol followed (see Supporting Information), given that the current work analyzed a portion of the same material used in that work (Murchison USNM 54512; Table 1). It is possible that aliphatic aldehydes and ketones remained trapped or adsorbed in mineral insoluble matrixes and clays where they were not fully accessible to the DCM solvent used for extraction,[13] or they could be forming insoluble adducts (e.g., bisulfite addition to carbonyl compound), that cannot be extracted in DCM. Nevertheless, some similarities in the molecular distributions among these three analyses are evident; for example, aldehydes are more abundant than ketones, with formaldehyde being less abundant than acetaldehyde, and acetone the most abundant ketone in all investigations of the Murchison meteorite. Similarly, the total concentration of aliphatic carbonyl compounds measured in the Antarctic CR chondrites studied here are within range of those concentrations (60-1000 nmolg^{-1} of meteorite) reported by Pizzarello and Holmes

(2009)[13] and Pizzarello et al. (2012)[15] in other CR chondrite species; furthermore, a higher concentration of formaldehyde compared to acetaldehyde (inverse to that seen in Murchison) was observed in these studied CR meteoritic samples, both here and in previous reports.

The total concentrations of carbonyl compounds among CI and CM chondrites ranged within similar values (220 to 340 $\mathrm{nmolg^{-1}}$ of meteorite), while those in CR chondrites seemed to be more dependent on the levels of aqueous alteration that occurred in the parent body (Figure 2). We saw a lack of molecular diversity for ketones, but not for aldehydes in the aqueously altered Orgueil (CI1.1) meteorite; we also observed a lack of molecular diversity of carbonyl compounds in the much less aqueously altered EET 96029 (CM2.7). These two observations suggest that parent body processes in addition to the as-yet-unknown organic-precursor budget of carbonaceous chondrites play an important and poorly understood role in the abundance and molecular distribution of soluble meteoritic aldehydes and ketones. The higher concentrations of carbonyl compounds in low aqueously altered CR meteorites, relative to those in CI and CM, is consistent with larger concentrations of aliphatic amino acids, amines, and MCAs previously seen in this chondrite class relative to CI and CM.[15,30,34-36] The higher abundance of soluble organic compounds in CR chondrites than in CI and CM chondrites may be related to the lower levels of aqueous alteration and thermal processing this chondrite class experienced, or it could be a signature of the original organic budget accreted in the CR parent body.

The complete structural diversity, higher abundance of primary-carbon bearing carbonyl isomers, and a trend of decreasing abundance with increasing molecular weight is similar to that seen in other compound classes such as meteoritic aliphatic amino acids, amines, and monocarboxylic acids (MCAs)[4,36,37-39]. These similarities in compound distributions may be indicative of potentially common origins and development throughout our Solar System. Aldehydes and ketones have been previously synthesized from UV irradiation and/or radiolysis of ices simulating interstellar environments and the presolar nebula,[40-42] and have been detected in comet 67P-Churyumov-Gerasimenko by the Rosetta spacecraft[43]. It is likely that the aldehydes and ketones we detected in carbonaceous chondrites may have been synthesized before the accretion of the different parent bodies and that the molecular diversity we observe now is the result of different processes occurred during parent body stage; further laboratory work is needed to fully understand the different potential sources of aldehydes, ketones, and their structurally related meteoritic organic compounds.

4.2 Compound-specific $\delta^{13}C$ analysis of meteoritic aliphatic carbonyl compounds. Carbon isotopic values are one way to distinguish terrestrial from extraterrestrial origins of organic compounds. Terrestrial carbonyl compounds that are present in the atmosphere, mainly produced by photo-oxidation of atmospheric aliphatic volatile organic compounds, have typical $\delta^{13}C$ values ranging from –46 to –17‰ (for formaldehyde, acetaldehyde, and acetone)[44-47]. The majority of the $\delta^{13}C$ values we measured for carbonyl species were ^{13}C-enriched relative to their terrestrial counterparts, supporting their extraterrestrial origin. The lower ^{13}C-enrichements for the compounds measured from Orgueil, EET 96029 and MIL 090001, may be attributable to their distinct parent body histories; it is reasonable that aqueous processing and short periods of parent body heating from impacts,[48-50] may have affected the isotopic composition of these compounds in an as-yet-unknown manner. Alternatively, a contribution from some volatile terrestrial carbonyl compounds impregnated in the surface of the analyzed samples cannot be completely ruled out. Given that possibility, the $\delta^{13}C$ values presented here should be considered as a lower limit for extraterrestrial carbonyl compounds.

The $\delta^{13}C$ composition of carbonyl compounds have only been previously evaluated for the Murchison meteorite.[17] In that work,[17] ^{13}C-isotopic values of six aldehydes and ketones extracted from the same meteorite piece we have studied here (Murchison USNM 54512) were reported. A comparison against those reported $\delta^{13}C$ values shows similar ^{13}C-compositions for 2-butanone and propanal, but $\delta^{13}C$ values that differ between 8 and 39‰ for acetone, acetaldehyde, and butanal (we were not able to measure the isotopic value of formaldehyde, Table 3). Even when insufficient or uneven sample mixing could be argued, sample heterogeneity may be unlikely in this case, thus, the isotopic differences we observed may be related to the extraction protocols used. The main difference between the method used by Simkus et al. (2019)[17] and that reported here is the use of DCM as extraction and derivatization solvent (see Supporting Information for details). As described in Section 4.1, it is possible that aldehydes and ketones may have not been accessible from insoluble minerals and clays or from insoluble adducts; all meteorites studied here were extracted and evaluated using the same methodology enabling comparisons between them without bringing into consideration the effects of the techniques used for analyses. Future efforts are needed to both understand the effects of different extraction solvents on the measured isotopic composition of meteoritic aldehydes and ketones and the use of the same extraction conditions when comparing different samples.

The most ^{13}C-depleted values of carbonyl compounds in the CM group is found in ALH 83100 and EET 96029 (Figure 3). ALH 83100 has experienced longer aqueous alteration processes than the other CM chondrites we analysed,[51-53] while there are suggestions that short periods of thermal processing occurred to EET 96029.[48-50] If all the CM chondrites arose from the same parent body, then the δ^{13}C differences observed between ALH 83100, EET 96029 and the rest of CM chondrites suggests a potential positive relationship between parent body aqueous and thermal processing and carbonyl δ^{13}C values. In addition, lower carbonyl ^{13}C-values were also seen in MIL 090001 in relation to rest of CR chondrites we studied here. MIL 090001 is more aqueously and thermally altered then GRA 95229 and MIL 090657;[54-56] suggesting again a link between ^{13}C-fractionation and parent body processing. However, future work remains to be done to fully understand this observation and its relationship to the original budget of carbonyl compounds accreted in the parent bodies and those that could potentially be synthesized after accretion or even during sample extraction.

The systematic addition of carbon monoxide (CO) under kinetic control has been proposed as the chain elongation mechanism during the synthesis of meteoritic aliphatic compounds.[57] This mechanism should lead to a pattern of decreasing ^{13}C enrichment with increasing chain length. In the samples we analysed, the relationship between increasing molecular weight with decreasing ^{13}C-content could only be observed for specific sets of compounds such ketones in Orgueil and the aldehydes in LON 94101. While more isotopic data is needed to draw conclusions about the relevance of kinetic control on the synthesis of meteoritic organics, the overall δ^{13}C values we found for carbonyl compounds reveal unclear correlations between carbon number and ^{13}C-contents (molecular weights) in the studied meteorites (Figure 3). These results would suggest that meteoritic aldehydes and ketones may have formed through mechanisms that did not mainly involve CO addition, or that their ^{13}C-content is the outcome of the synthesis/destruction through parent body processes that did not result in the conservation of a primordially existing relationship between increasing molecular weight and decreasing ^{13}C-content.

5. CONCLUSIONS

We developed a novel method for the identification, quantification, and stable-isotope evaluation of meteoritic aldehydes and ketones. We applied this methodology to meteorites with varying degrees of aqueous alteration, finding higher concentrations of aldehydes compared to ketones, with formaldehyde, acetaldehyde and acetone being the most abundant species in all investigated samples. The abundance of chondritic carbonyl compounds decreased with increasing carbon number, except for the higher concentrations of acetaldehyde compared to formaldehyde in more aqueously altered chondrites. In most of the meteorites the $\delta^{13}C$ values measured are ^{13}C-enriched relative to their terrestrial counterparts, and we did not observe correlations between ^{13}C-content and number of carbon atoms in the aliphatic chains. Further work aimed to understand the effects of parent body processing is needed to implement better constraints for the origins of meteoritic carbonyl compounds, their molecular distribution and isotopic composition.

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SUPPORTING INFORMATION

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

- Methodology used for analysis of aliphatic aldehydes and ketones.

- Methodology used for the syntheses of 3-methylpentanal (26) and 4-methylpentanal (27), and enantiopure standards (S)-2-methylbutanal, (S)-3-methylpentanone, and (S)-3-methylpentanal.

- Figure S1. Structures of aliphatic carbonyl compounds listed in Table 1.

- Figure S2. Electron impact ionization GC-MS chromatogram (40 - 95 min region, combined m/z = 87 ± 0.5, 161 ± 0.5, 175 ± 0.5) of procedural blank, hot-DCM extracted derivatized carbonyl compounds from the CI and CM carbonaceous chondrites studied here, procedural blank, and standards (all traces except standards are on the same intensity scale). The identities of the peaks and structures are presented in Table 2 and Figure S1 respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. B: reaction byproduct.

- Figure S3. Electron impact ionization GC-MS chromatogram (40 - 95 min region, combined m/z = 87 ± 0.5, 161 ± 0.5, 175 ± 0.5) of procedural blank, hot-DCM extracted derivatized carbonyl compounds from the CR and CV carbonaceous chondrites studied here, procedural blank, and standards (all traces except standards are on the same intensity scale). The identities of the peaks and structures are presented in Table 2 and Figure S1 respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. B: reaction byproduct.

- Figure S4. GC-IRMS chromatograms obtained at m/z = 44 (12CO2 peak) during carbon compound-specific isotope analysis of hot-DCM extracted derivatized carbonyl compounds in CI and CM carbonaceous chondrites, a typical procedural blank and standards (all traces except standards are on the same intensity scale). The identities of the peaks and structures are presented in Table 2 and Figure S1 respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. B: reaction byproduct.

- Figure S5. GC-IRMS chromatograms obtained at m/z = 44 (12CO2 peak) during carbon compound-specific isotope analysis of hot-DCM extracted derivatized carbonyl compounds in CR and CV carbonaceous chondrites (all traces except standards are on the same intensity scale). The identities of the peaks and structures are presented in Table 2 and Figure S1 respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity. B: reaction byproduct.

- Figure S6. δ13C isotopic data for meteoritic carbonyl compounds analyzed in this work. Carbonyl compounds are grouped within each meteorite by carbon number; squares are ketones and diamonds are aldehydes. Meteorite groups are arranged according to their aqueous and thermal alteration (Keller et al. 2012; Alexander et al. 2013, 2015; Lee et al. 2016; Davidson et al. 2015; Aponte et al. 2017).

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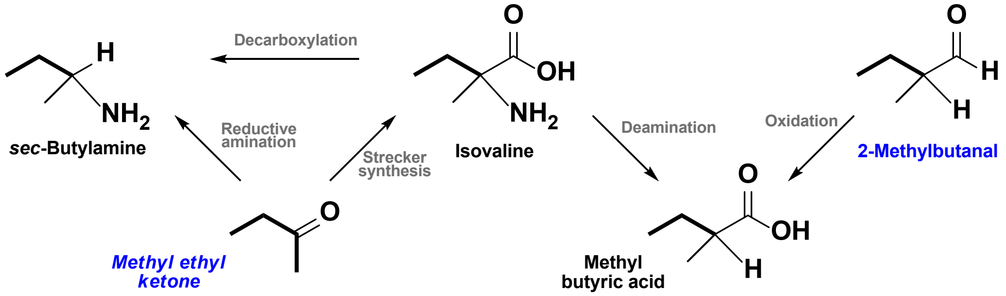
Scheme 1. Potential synthetic relationship between meteoritic aldehydes, ketones, amines, MCAs and amino acids (aldehydes and ketones names are listed in blue).



Scheme 2. Synthesis of carbonyl compound DMB-derivatives. (*S*,*S*)-DMB-Diol is: (*S*,*S*)-(–)-1,4-dimethoxy-2,3-butanediol.

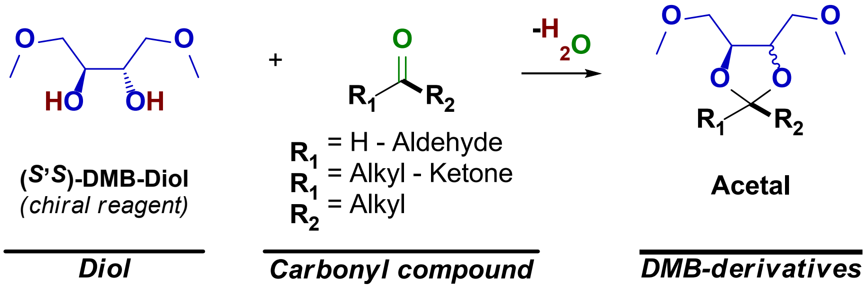


Table 1. Meteorites samples analyzed in this study.

Meteorite[a]	Classification[b]	Fragment	Mass extracted (g)
Orgueil	CI1.1	MNHN piece 234	1.01
ALH 83100	CM1.1	Specific 296, parent 22	2.84
LEW 90500	CM1.6	Specific 85, parent 2	1.22
Murchison	CM1.6	USNM 54512	2.50
LON 94101	CM1.8	Specific 99, parent 5	2.62
EET 96029	CM2.7	Specific 71, parent 68	2.00
MIL 090001	CR2.2	Specific 93, parent 48	2.30
LAP 02342	CR2.5	Specific 62, specific 0	0.10
GRA 95229	CR2.5	Specific 128, parent 35	0.09
MIL 090657	CR2.7	Specific 31, parent 25	0.22
Allende	CV3.6	USNM 352916	5.00

[a] Abbreviations: Allan Hills, ALH; Lewis Cliffs, LEW; Lonewolf Nunataks, LON; Elephant Moraine, EET; Graves Nunataks, GRA; La Paz Icefield, LAP.
[b] Keller et al., 2012; Alexander et al. 2013, 2015; Lee et al., 2016; Davidson et al., 2015.[49,51,58-61]

Table 2. Blank-corrected concentrations of carbonyl compounds in hot-DCM extracts of chondrites studied here; values in nmolg^{-1} of meteorite. Meteorite groups are arranged according to their aqueous and thermal alteration.[49,51,58-61]

#	**Compound[a]**	**Orgueil (CI1.1)**	**ALH 83100 (CM1.1)**	**LEW 90500 (CM1.6)**	**Murchison (CM1.6)**	**LON 94101 (CM1.8)**	**EET 96029 (CM2.7)**	**MIL 090001 (CR2.2)**	**LAP 02342 (CR2.5)**	**GRA 95229 (CR2.5)**	**MIL 090657 (CR2.7)**	**Allende (CV3.6)**
	Ketones											
1	Acetone	12.7 ± 0.8	43.1 ± 0.4	89.9 ± 1.9	32.0 ± 1.5	68.0 ± 5.1	67.4 ± 8.1	32.4 ± 2.0	16.6	18.8 ± 2.6	73.1 ± 2.5	10.6 ± 1.3
4	2-Butanone	3.2 ± 0.1	9.7 ± 0.1	23.7 ± 0.6	22.7 ± 2.4	22.8 ± 1.7	1.2 ± 0.1	4.5 ± 0.3	n.d.	21.5 ± 1.7	42.9 ± 1.5	0.64 ± 0.04
8	3-Methyl-2-butanone	[b]	[b]	[b]	[b]	[b]	[b]	[b]	n.d.	[b]	[b]	[b]
9	2-Pentanone	< 0.3	2.4 ± 0.1	4.8 ± 0.2	4.4 ± 0.4	4.0 ± 0.4	[b]	1.1 ± 0.1	n.d.	10.1 ± 0.4	9.1 ± 0.4	0.25 ± 0.05
10	3-Pentanone	[b]	0.6 ± 0.3	0.78 ± 0.02	1.3 ± 0.1	0.62 ± 0.04	[b]	0.34 ± 0.01	n.d.	2.84 ± 0.06	1.38 ± 0.01	[b]
12	3,3-Dimethyl-2-butanone	[b]	0.39 ± 0.03	0.94 ± 0.07	1.5 ± 0.1	0.84 ± 0.05	[b]	0.41 ± 0.03	n.d.	3.4 ± 0.3	1.40 ± 0.05	[b]
13	4-Methyl-2-pentanone	[b]	0.74 ± 0.05	1.60 ± 0.05	2.1 ± 0.3	1.1 ± 0.1	[b]	0.7 ± 0.2	n.d.	5.9 ± 0.1	3.1 ± 0.1	0.5 ± 0.1
14	2-Methyl-3-pentanone	[b]	[b]	[b]	[b]	[b]	[b]	[b]	n.d.	[b]	[b]	[b]
17	3-Methyl-2-pentanone	[b]	0.5 ± 0.1	1.24 ± 0.05	2.2 ± 0.2	1.1 ± 0.1	[b]	0.50 ± 0.03	n.d.	5.4 ± 0.4	2.6 ± 0.2	[b]
18	3-Hexanone	[b]	1.06 ± 0.01	2.03 ± 0.06	3.3 ± 0.5	2.1 ± 0.2	[b]	0.62 ± 0.03	n.d.	7.1 ± 0.4	3.1 ± 0.1	[b]
20	2-Hexanone	[b]	0.5 ± 0.1	1.1 ± 0.1	0.8 ± 0.1	1.0 ± 0.1	[b]	[b]	n.d.	2.7 ± 0.2	2.1 ± 0.1	[b]
24	Cyclopentanone	[b]	1.3 ± 0.1	2.07 ± 0.05	2.1 ± 0.2	1.8 ± 0.1	1.3 ± 0.1	0.7 ± 0.1	n.d.	6.8 ± 1.2	3.6 ± 0.2	[b]
28	Cyclohexanone	1.30 ± 0.04	0.55 ± 0.01	1.05 ± 0.01	[b]	0.66 ± 0.04	[b]	[b]	n.d.	2.9 ± 0.2	1.41 ± 0.01	0.192 ± 0.003
	Total ketones	17 ± 1	61 ± 1	129 ± 3	72 ± 6	104 ± 8	70 ± 8	41 ± 3	n.d.	87 ± 8	144 ± 5	12 ± 1
	Aldehydes											
2	Acetaldehyde	81.6 ± 4.7	92.4 ± 1.8	77.0 ± 2.7	86.6 ± 5.8	89.8 ± 6.7	102.0 ± 13.4	40.8 ± 2.7	49.1	5.1 ± 5.5	159.6 ± 8.1	37.0 ± 2.7
3	Formaldehyde	64.8 ± 13.8	47.1 ± 2.2	23.3 ± 10.0	66.8 ± 9.0	52.8 ± 5.4	127.4 ± 11.9	35.4 ± 7.5	120.4	323.6 ± 34.9	614.2 ± 29.2	221.7 ± 16.6
5	Propanal	44.5 ± 3.6	15.5 ± 8.4	31.1 ± 0.8	39.5 ± 3.8	19.9 ± 1.4	46.9 ± 7.8	4.1 ± 0.4	n.d.	3.1 ± 1.9	46.7 ± 1.8	5.0 ± 0.7
6	Isobutanal	10.2 ± 0.7	2.0 ± 1.1	3.5 ± 0.1	7.1 ± 0.6	3.6 ± 0.3	[b]	1.0 ± 0.1	n.d.	4.4 ± 0.3	8.0 ± 0.2	0.9 ± 0.1
7	Pivaldehyde	[b]	[b]	[b]	[b]	[b]	[b]	[b]	n.d.	[b]	[b]	[b]
11	Butanal	6.2 ± 0.3	8.4 ± 0.3	8.7 ± 0.2	13.2 ± 1.1	9.1 ± 0.8	[b]	2.4 ± 0.1	n.d.	8.0 ± 0.3	11.7 ± 0.3	2.7 ± 0.3
15	2-Methylbutanal	[b]	[b]	[b]	[b]	[b]	[b]	[b]	n.d.	[b]	[b]	[b]
16	Isopentanal	1.5 ± 0.1	1.47 ± 0.04	2.33 ± 0.05	2.8 ± 0.1	1.8 ± 0.2	[b]	0.79 ± 0.04	n.d.	3.3 ± 0.1	2.9 ± 0.1	0.25 ± 0.02
19	2,2-Dimethylbutanal	0.618 ± 0.004	0.32 ± 0.01	0.70 ± 0.01	0.95 ± 0.03	0.47 ± 0.02	< 0.3	0.37 ± 0.01	n.d.	2.16 ± 0.03	1.13 ± 0.02	[b]
21	3,3-Dimethylbutanal	0.761 ± 0.007	0.44 ± 0.01	0.82 ± 0.03	1.11 ± 0.05	0.51 ± 0.02	[b]	0.35 ± 0.01	n.d.	< 0.3	1.09 ± 0.01	[b]

22	Pentanal	3.1 ± 0.1	2.4 ± 0.1	3.30 ± 0.04	8.2 ± 0.6	2.6 ± 0.2	< 0.3	0.86 ±	n.d.	4.6 ± 0.1	4.1 ± 0.1	3.0 ± 0.4
23	2-Ethyl-butanal	[b]	[b]	[b]	[b]	[b]	[b]	[b]	n.d.	[b]	[b]	[b]
25	2-Methylpentanal	< 0.3	0.50 ± 0.01	0.75 ± 0.03	1.05 ± 0.02	0.56 ± 0.03	[b]	[b]	n.d.	< 0.3	1.39 ± 0.04	[b]
26	3-Methylpentanal	1.4 ± 0.1	0.97 ± 0.03	1.54 ± 0.03	1.9 ± 0.1	1.3 ± 0.1	[b]	0.56 ± 0.01	n.d.	2.81 ± 0.05	1.94 ± 0.04	[b]
27	4-Methylpentanal	1.5 ± 0.1	1.36 ± 0.04	2.18 ± 0.09	2.9 ± 0.2	1.7 ± 0.2	[b]	0.71 ± 0.03	n.d.	3.8 ± 0.1	2.8 ± 0.2	0.27 ± 0.01
29	Hexanal	2.8 ±0.2	1.2 ± 0.1	1.67 ± 0.01	5.0 ± 0.4	1.15 ± 0.05	[b]	0.52 ± 0.01	n.d.	3.1 ± 0.1	1.9 ± 0.1	1.3 ± 0.2
	Total aldehydes	219 ± 24	174 ± 14	157 ± 14	237 ± 22	185 ± 15	276 ± 33	88 ± 11	n.d.	364 ± 43	857 ± 40	272 ± 21
	Total ketones and aldehydes	236 ± 25	235 ± 15	286 ± 17	309 ± 28	289 ± 23	346 ± 41	129 ± 14	n.d.	451 ± 51	1001 ± 45	284 ± 22

[a] 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 Section 2.5; errors shown are standard deviations. Compounds at < 0.3 nmolg^{-1} meteorite are falling below our quantification limits

[b] Compound was searched for but not found or its concentration fell below our detection limits (0.01 nmolg^{-1} meteorite).

n.d.: Values could not be determined (see Results section for details).

Table 3. $\delta^{13}C$ values (‰VPDB) of carbonyl compounds in hot DCM extracts of chondrites studied here.[a] Meteorite groups are arranged according to their aqueous and thermal alteration. [49,51,58-61]

#	Compound	Orgueil (CI1.1)	ALH 83100 (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)	MIL 090657 (CR2.7)	Allende (CV3.6)
	Ketones										
1	Acetone	15 ± 3	–33 ± 5	–1 ± 3	3 ± 5	–4 ± 8	–26 ± 2	–64 ± 3	14 ± 4	3 ± 4	–28 ± 3
4	2-Butanone[b]	11 ± 2	–12 ± 4	30 ± 6	11 ± 6	20 ± 3	[c]	–15 ± 5	10 ± 4	–7 ± 3	[c]
	Average $\delta^{13}C$ ketones	13	–22	15	7	8	–26	–40	12	–2	–28
	Aldehydes										
2	Acetaldehyde	7 ± 5	–5 ± 6	60 ± 2	64 ± 1	37 ± 8	–9 ± 2	–51 ± 7	29 ± 8	9 ± 7	–19 ± 4
3	Formaldehyde[b]	1 ± 3	63 ± 8	[c]	[c]	93 ± 8	–58 ± 8	–67 ± 6	14 ± 9	3 ± 7	–45 ± 5
5	Propanal[b]	–17 ± 3	7 ± 4	43 ± 1	47 ± 6	35 ± 3	–19 ± 2	[c]	27 ± 8	10 ± 2	–12 ± 2
6	Isobutanal	20 ± 2	15 ± 5	49 ± 8	40 ± 2	41 ± 6	[c]	[c]	[c]	20 ± 3	–2 ± 3
11	Butanal[b]	[c]	[c]	[c]	3 ± 2	[c]	[c]	[c]	[c]	[c]	[c]
16	Isopentanal	–2 ± 4	15 ± 4	30 ± 7	36 ± 3	33 ± 8	[c]	[c]	[c]	[c]	[c]
22	Pentanal	–18 ± 3	–20 ± 7	1 ± 4	5 ± 5	6 ± 6	[c]	[c]	[c]	[c]	–30 ± 2
29	Hexanal	–33 ± 4	[c]	[c]	–1 ± 7	[c]	[c]	[c]	[c]	[c]	–21 ± 3
	Average $\delta^{13}C$ aldehydes	–6	12	37	28	41	–29	–59	23	11	–21
	Average $\delta^{13}C$ aldehydes and ketones	–2	4	30	23	33	–28	–49	19	6	–22

[a] Values are the average of three measurements; errors shown are standard deviations.

[b] Includes small contribution from coeluting unknown reaction byproduct.

[c] Value could not be determined due to low abundance, chromatographic coelution, or poor peak resolution.

Figure 1. (A) Electron impact ionization GC-MS chromatograms (40–95 min region, combined *m/z* = 87 ± 0.5, 161 ± 0.5, 175 ± 0.5, 189 ± 0.5) of the derivatized carbonyl compounds from hot-DCM extracts of the Murchison meteorite (top), a procedural blank (middle), and commercially available carbonyl compound standards (bottom). All traces except standards are on the same intensity scale. (B) GC-IRMS chromatogram obtained at *m/z* = 44 ($^{12}CO_2$ peak) obtained and measured during carbon compound-specific isotope analysis. Similar chromatograms were obtained for other meteorites investigated in this work (see Figures S2-S5 in the Supporting Information). The identities of the peaks and structures are presented in Table 1 and Figure S1 respectively. Unidentified peaks represent compounds that could not be adequately identified or analyzed because of co-elutions or insufficient sensitivity (x,y datasets for chromatograms are attached as Supporting Information); B: reaction byproduct. (C) Mass spectral fragmentation pattern for model DMB-derivatized aldehydes and ketones (see Section 2.4 for details).

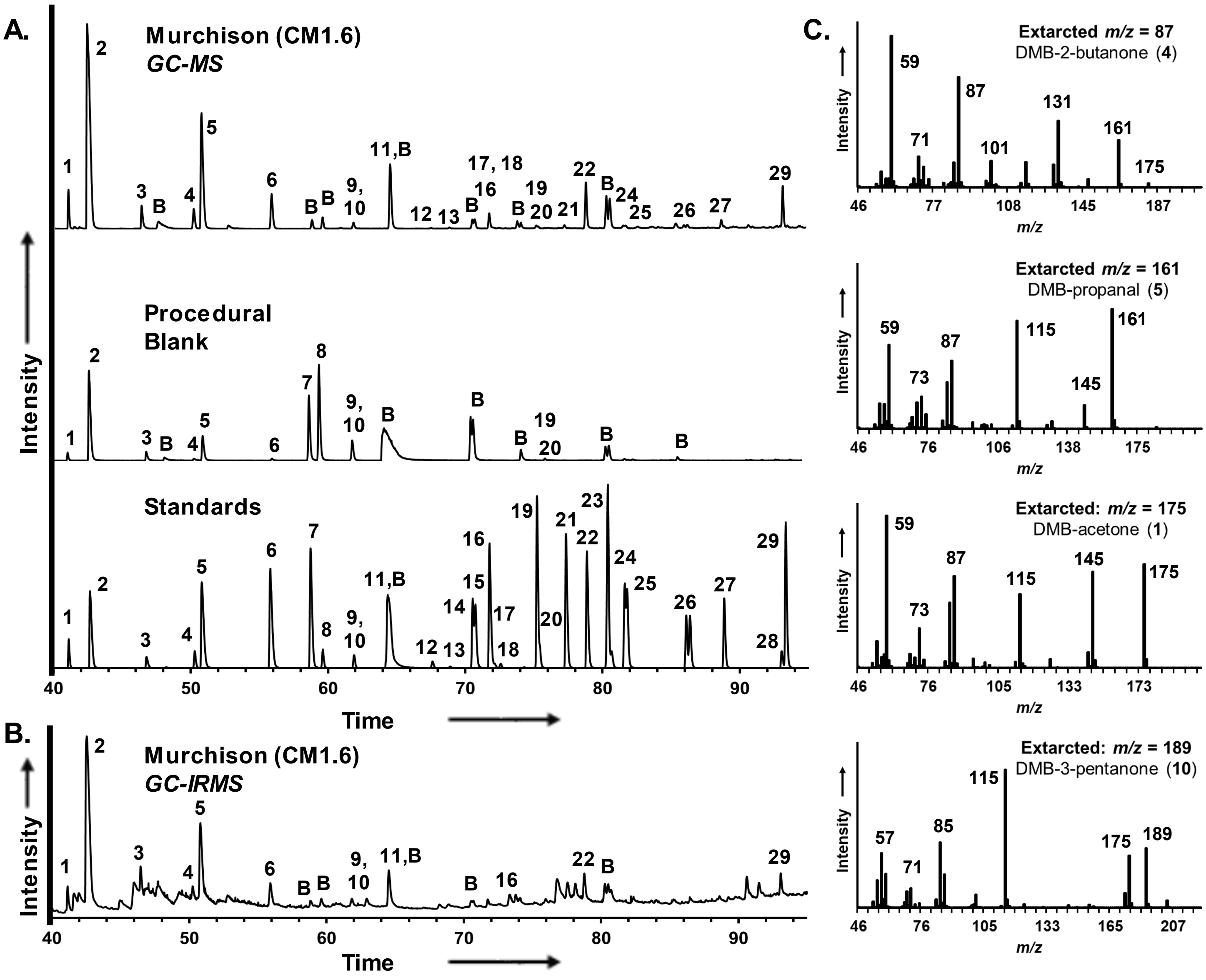

A.
Murchison (CM1.6)
GC-MS
Procedural Blank
Standards
Intensity
Time
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9, 10
11,B
12
13
14
15
16
17, 18
19
20
21
22
23
24
25
26
27
28
29
B
B.
Murchison (CM1.6)
GC-IRMS
Intensity
Time
C.
Extarcted m/z = 87
DMB-2-butanone (4)
Extarcted m/z = 161
DMB-propanal (5)
Extarcted: m/z = 175
DMB-acetone (1)
Extarcted: m/z = 189
DMB-3-pentanone (10)
Intensity
m/z
59
71
87
101
131
161
175
46
77
108
145
187
73
115
145
76
106
138
175
105
133
173
57
85
189
165
207

Figure 2. Abundances of carbonyl compounds extracted from CI, CM, CR and CV meteorites. Meteorite groups are arranged according to their level of parent body processing.[49,51,58-61]

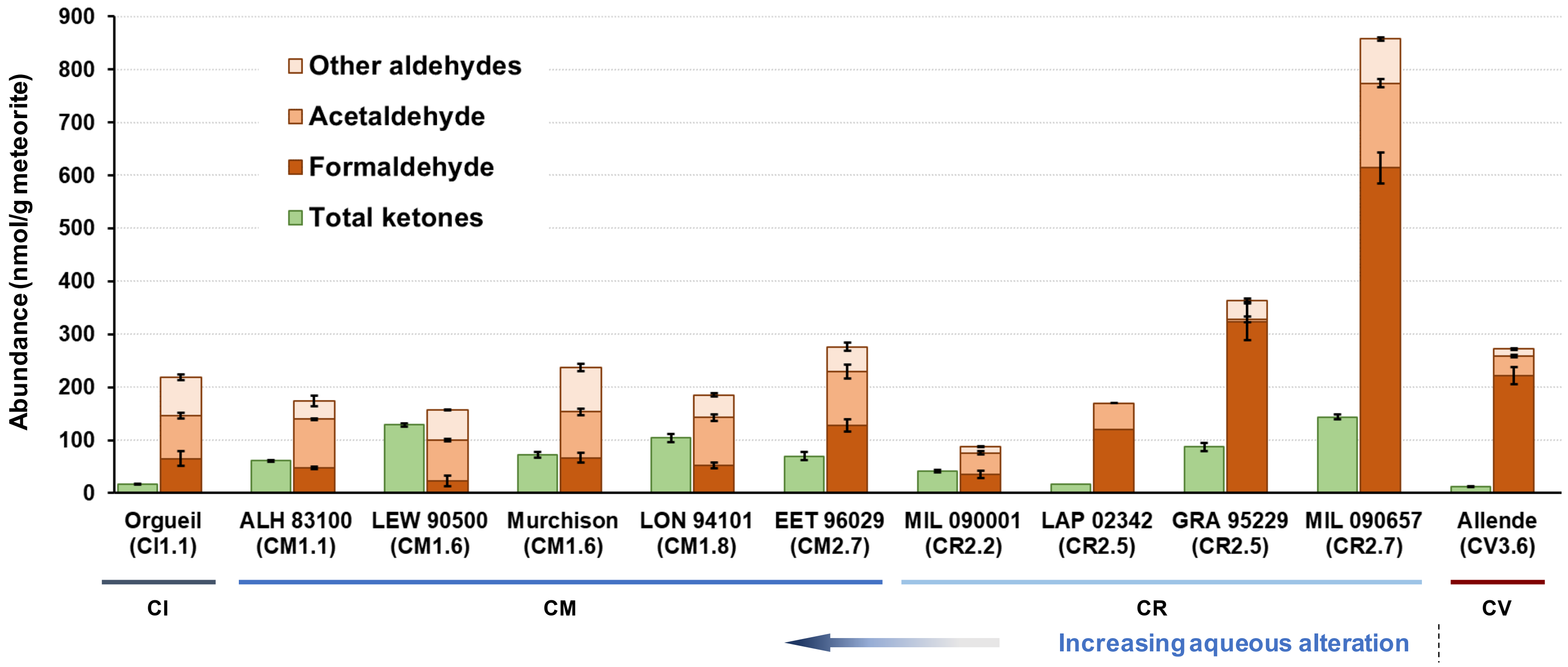
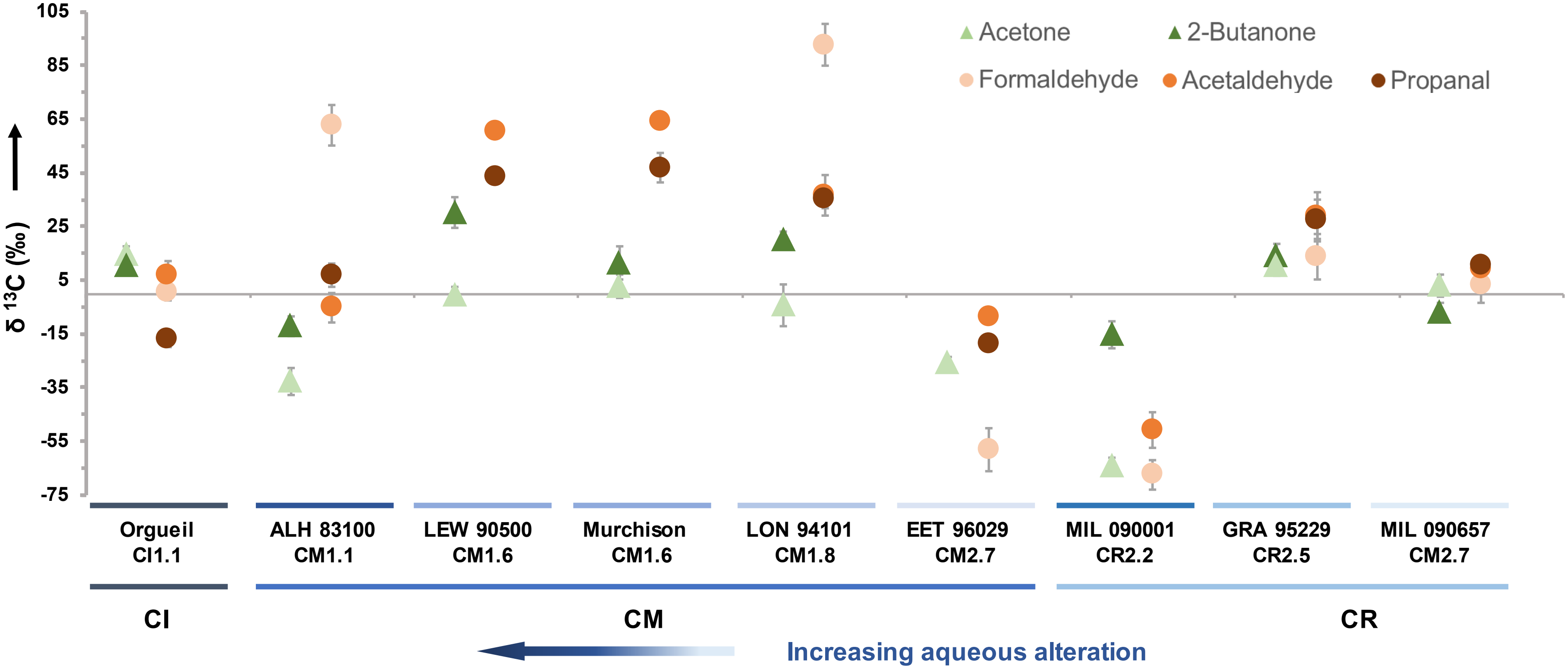


Figure 3. $\delta^{13}C$ isotopic data for selected carbonyl compounds from hot-DCM extracts of the chondrites studied here. Meteorites are arranged according to their aqueous and thermal alteration.[49,51,58-61]



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