

# Meteorite Parent Body Aqueous Alteration Simulations of Interstellar Residue Analogs

Danna Qasim,\* Hannah L. McLain, José C. Aponte, Daniel P. Glavin, Jason P. Dworkin, and Christopher K. Materese\*



Cite This: <https://doi.org/10.1021/acsearthspacechem.2c00274>



Read Online

ACCESS |



Metrics & More



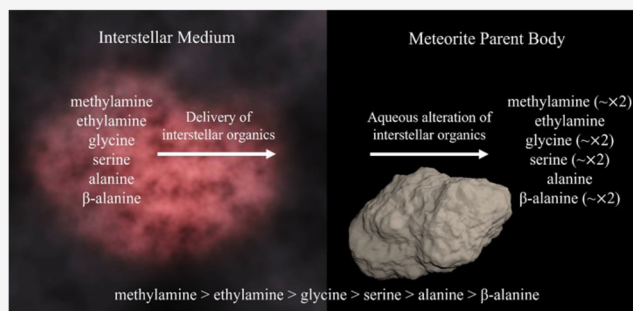
Article Recommendations



Supporting Information

**ABSTRACT:** Some families of carbonaceous chondrites are rich in prebiotic organics that may have contributed to the origin of life on Earth and elsewhere. However, the formation and chemical evolution of complex soluble organic molecules from interstellar precursors under relevant parent body conditions has not been thoroughly investigated. In this study, we approach this topic by simulating meteorite parent body aqueous alteration of interstellar residue analogs. The distributions of amines and amino acids are qualitatively and quantitatively investigated and linked to closing the gap between interstellar and meteoritic prebiotic organic abundances. We find that the abundance trend of methylamine > ethylamine > glycine > serine > alanine >  $\beta$ -alanine does not change from pre- to post-aqueous alteration, suggesting that certain parental cloud conditions have an influential role on the distributions of interstellar-inherited meteoritic organics. However, the abundances for most of the amines and amino acids studied here varied by about 2-fold when aqueously processed for 7 days at 125 °C, and the changes in the  $\alpha$ - to  $\beta$ -alanine ratio were consistent with those of aqueously altered carbonaceous chondrites, pointing to an influential role of meteorite parent body processing on the distributions of interstellar-inherited meteoritic organics. We detected higher abundances of  $\alpha$ - over  $\beta$ -alanine, which is opposite to what is typically observed in aqueously altered carbonaceous chondrites; these results may be explained by at least the lack of minerals, inorganic species, and insoluble organic matter-relevant materials in the experiments. The high abundance of volatile amines in the non-aqueously altered samples suggests that these types of interstellar volatiles can be efficiently transferred to asteroids and comets, supporting the idea of the presence of interstellar organics in solar system objects.

**KEYWORDS:** astrochemistry, astrobiology, interstellar ices, asteroids, meteorites, aqueous alteration, radiolysis, liquid chromatography



## 1. INTRODUCTION

The organic inventory of meteorites has been analyzed for decades, as it includes a variety of astrobiologically relevant organic compounds, such as amines and amino acids, that may have contributed to the origin of life on Earth and potentially elsewhere.<sup>1</sup> Substantial efforts have been taken to better understand the origins of these meteorites through direct collection of materials from carbon-rich asteroids, which are thought to be the parent bodies of some carbonaceous chondrites (e.g., OSIRIS-REx and Hayabusa2 sample-return missions). It is important to understand the processes that contributed to the formation and molecular distribution of prebiotic organics in meteoritic and sample-returned materials. Were meteoritic amino acids and amines formed primarily in the parent body, protoplanetary disk, or interstellar molecular cloud or do a combination of these dictate their distribution and abundances?<sup>2,3</sup> Understanding the origins of organic matter in meteoritic and sample-returned materials aids in elucidating the ubiquity of prebiotic molecules across our solar system and elsewhere.<sup>4–6</sup>

Laboratory experiments involving irradiated interstellar ice analogs have demonstrated the formation of refractory residues, which contain amines, amino acids, and other soluble organic compound classes, suggesting that the prebiotic organic matter found in meteorite parent bodies may have been (at least partially) inherited from interstellar materials.<sup>7–9</sup> Indeed, the work by Martins et al.<sup>10</sup> provided convincing evidence that the chemical contents of the Paris meteorite were strongly linked to interstellar precursors. However, the catalog and distribution of amines and amino acids in ice irradiation experiments have not always been consistent with what has been found in carbonaceous chondrites.<sup>11–13</sup> For example, some ice irradiation experiments have more  $\alpha$ - than

Received: September 5, 2022

Revised: November 30, 2022

Accepted: November 30, 2022

$\beta$ -alanine,<sup>7,8</sup> whereas the most aqueously altered chondrites, such as C1I, CM1, and CR1, typically contain more  $\beta$ - than  $\alpha$ -alanine, with the ratio reversing with decreasing aqueous alteration in the least altered CM2 and CR2 meteorites.<sup>9,14,15</sup> As such, these differences may be accounted for by aqueous alteration of the residues formed from ice irradiation experiments over a range of temperatures.

Recent laboratory experiments have sought to evaluate the effects of aqueous alteration of commercially available organics that are relevant to the constituents of interstellar materials.<sup>16–18</sup> Kebukawa et al.<sup>17</sup> followed a “bottom-up” approach by aqueously altering simple interstellar relevant molecules using calcium hydroxide under different temperature conditions. In contrast, Vinogradoff et al.<sup>18</sup> used a “top-down” approach by starting with hexamethylenetetramine (HMT), which is an abundant complex photoproduct of interstellar ice chemistry.<sup>19–22</sup> While these studies provide insight into some of the chemistry that may occur within meteorite parent bodies, there remain gaps in linking the studies to what has been found in aqueously altered meteorites, such as the differences in the  $\alpha$ - to  $\beta$ -alanine ratios. These gaps may be filled by processing of a more representative sample of interstellar-inherited meteoritic compounds, such as interstellar residue analogs.

This work investigates the effects of meteorite parent body aqueous alteration of interstellar residue analogs on the distribution of the formed amines and amino acids. Although aqueous alteration of the residues of irradiated ices has been performed in the laboratory by Danger et al.,<sup>23</sup> their study simulated the irradiation of ices at the edge of protoplanetary disks, which has higher temperatures and less volatiles available than interstellar ices. Additionally, the work by Danger et al.<sup>23</sup> utilized photons, whereas this work utilizes protons. Albeit, only small differences are found among chemical products of various radiation types.<sup>24</sup> In this article, we demonstrate the irradiation of a H<sub>2</sub>O:CO<sub>2</sub>:CH<sub>3</sub>OH:<sup>15</sup>NH<sub>3</sub> (20:4:2:1) ice mixture at 25 K and subsequently analyze its products when heated in aqueous solution at 50 and 125 °C for 2, 7, and 30 days. The ice mixture ratio was chosen to reflect the abundances detected toward low-mass young stellar objects (YSOs), where interstellar ices are warmed to temperatures above 20 K.<sup>25</sup> At that stage, ices are exposed to radiation from cosmic rays and the YSO and residue formation is expected to take place. A fraction of the interstellar ices and organic residues is transferred to the protoplanetary disk<sup>26,27</sup> and becomes incorporated into meteorite parent bodies, which then undergo aqueous alteration at various temperatures.<sup>28–30</sup> Temperatures of 50 and 125 °C and relatively short heating time scales were chosen for the experiments to reflect the processes in parent bodies that contain CI, CM, and CR chondrites and may account for the extended periods of time ( $\sim 10^4$ – $10^6$  years) when liquid water was present in the parent body, because they exhibit only moderate degrees of aqueous alteration.<sup>31–33</sup> Additionally, an experimental heating time scale that includes 2–30 days has been reported in the literature,<sup>18,23</sup> and therefore, the chemical changes observed in this study can be compared to that of related studies.

The amines and amino acids of interest for this study are methylamine, ethylamine, glycine, alanine,  $\beta$ -alanine, and serine, as they are the major products formed in these experiments. These compounds have been detected in meteorites<sup>34–36</sup> and, as a result of their relatively simple structures, may potentially be the more abundant amines and

amino acids in interstellar materials. This is supported by the detections of methylamine, ethylamine, and glycine around comet 67P/Churyumov-Gerasimenko<sup>37</sup> and in samples returned from comet 81P/Wild<sup>34,38</sup> and the detections of methylamine in the interstellar medium (ISM).<sup>39,40</sup> Notably, alanine,  $\beta$ -alanine, and serine have not been detected in comets or interstellar environments. Glavin et al.<sup>34</sup> detected L-alanine,  $\beta$ -alanine, D- and L-serine, and other amino acids in Stardust aerogels exposed to 81P/Wild, but these species can be explained as contamination by their appearance in various controls; thus, some or all of these compounds should be viewed as contamination. The near or total homochirality of alanine and serine reported by Glavin et al.<sup>34</sup> indicates that these amino acids are terrestrial contaminants, although as previously noted by Elsila et al.,<sup>38</sup> it is possible that some of the detected  $\beta$ -alanine may be cometary. However, the amino acids have been detected in numerous interstellar residue analog experiments, analyzed with and without hydrolysis of the synthesized ice residue.<sup>7,8,11</sup> Additionally, the relatively simple distribution of amino acids in the C1I meteorites Orgueil and Ivuna, dominated by glycine and  $\beta$ -alanine, was suggested by Ehrenfreund et al.<sup>41</sup> to be evidence that these C1I meteorites originated from a cometary parent body, and therefore, such amino acids are promising components of interstellar-inherited amino acids in meteorites.

## 2. METHODOLOGY

**2.1. Synthesis of Residues from Radiation Processing of Ices.** Ices and residues were created within a cryogenic high-vacuum chamber routinely used to investigate proton irradiation of ices (see studies by Hudson and Moore,<sup>42</sup> Gerakines and Hudson,<sup>43</sup> and Gerakines et al.<sup>44</sup> for more details). Briefly, the pressures of the chamber at room temperature and just before gas and vapor depositions were  $\sim 2$ – $3 \times 10^{-7}$  and  $\sim 5$ – $6 \times 10^{-8}$  Torr, respectively. A polished aluminum substrate (area of  $\sim 5$  cm<sup>2</sup>) was cooled to 25 K prior to deposition. On top of the substrate was a small sheet of clean aluminum foil (heated to 500 °C for 24 h in air) that was compressed to the substrate by a copper gasket.

Residues were synthesized starting from a H<sub>2</sub>O:CO<sub>2</sub>:CH<sub>3</sub>OH:<sup>15</sup>NH<sub>3</sub> (20:4:2:1) ice mixture. Note that <sup>15</sup>NH<sub>3</sub> was used to distinguish the results from contamination. Each gas or vapor was placed in its own line within a gas manifold before being simultaneously released into the chamber through calibrated leak valves. Leak valve calibrations and laser interferometry were jointly used; each leak valve was calibrated to a value that corresponded to a specific ice growth rate needed to acquire the desired ice mixture ratio. The deposition rate of each molecular species on the foil was monitored by laser interferometry. To determine the leak valve value that corresponded to the needed deposition rate, a large range of leak valve calibrations was performed to create calibration curves for three of the molecules (arbitrarily chosen), with the deposition rate of the remaining molecule as the independent variable. With laser interference data and data from the literature (Table 1), the following equation was used to determine the desired deposition rates to obtain a 20:4:2:1 ice mixture:

**Table 1. Values Used To Calculate the Deposition Rate for Each Molecule To Obtain the Chosen Ice Mixture Ratio**

molecule (brand and purity)	$n$	$\rho$	references for $n$ and $\rho$
H <sub>2</sub> O (Fisher Chemical, HPLC grade)	1.31	0.94	Weast et al. <sup>46</sup> and Narten et al. <sup>47</sup>
CO <sub>2</sub> (Matheson, 99.8%)	1.33	1.40	Loeffler et al. <sup>48</sup>
CH <sub>3</sub> OH (Sigma-Aldrich, HPLC grade)	1.26	0.64	Luna et al. <sup>49</sup>
<sup>15</sup> NH <sub>3</sub> (Cambridge Isotope Laboratories, 98%)	1.41 <sup>a</sup>	0.78 <sup>b</sup>	

<sup>a</sup> $n$  is the value for <sup>14</sup>NH<sub>3</sub> from Bouilloud et al.<sup>50</sup> <sup>b</sup>The value is estimated by multiplying  $\rho$  of <sup>14</sup>NH<sub>3</sub> (obtained from Bouilloud et al.<sup>50</sup>) by the molar mass ratio of <sup>15</sup>NH<sub>3</sub>/<sup>14</sup>NH<sub>3</sub>.

molecule X deposition rate

molecule Y deposition rate

$$= \frac{N_{\text{molecule X}}}{N_{\text{molecule Y}}} \times \frac{\rho_{\text{molecule Y}}}{\rho_{\text{molecule X}}} \times \frac{M_{\text{molecule X}}}{M_{\text{molecule Y}}} \times \frac{n_{\text{molecule X}}}{n_{\text{molecule Y}}} \quad (1)$$

where X and Y are arbitrary molecules,  $N$  is the number of molecules (or moles),  $\rho$  is the density (g cm<sup>-3</sup>),  $M$  is the molar mass (g mol<sup>-1</sup>), and  $n$  is the refractive index. Ices were grown for 3 h to reach a thickness of  $\sim 15$   $\mu$ m, in which the ice thickness can be determined by the following equation:

$$h = \frac{N_{\text{fr}} \lambda}{2\sqrt{n^2 - \sin^2 \theta}} \quad (2)$$

where  $h$  is the ice thickness,  $N_{\text{fr}}$  is the number of fringes,  $\lambda$  is the wavelength of the He–Ne laser (670 nm), and  $\theta$  is the incidence angle of the laser beam.<sup>45</sup> A thickness of  $\sim 15$   $\mu$ m was chosen, because it resulted in a detectable amount of product and is also below the penetration depth of  $\sim 25$   $\mu$ m for 0.9 MeV protons.

After the ices were formed, protons with an energy of 0.9 MeV at a current of  $1.5 \times 10^{-7}$  A were admitted into the vacuum chamber through an interfaced beamline that was connected to a Van de Graaff accelerator. Infrared (IR) spectra of the ices and residues were obtained *in situ* with a Nicolet Nexus 670 spectrometer. Ice and residue spectra were recorded as the average of 100 scans, with a resolution of 2 cm<sup>-1</sup>, from 5000 to 650 cm<sup>-1</sup>. Although IR spectroscopy was not used as the primary analytical technique, its purpose was to ensure consistency of the IR features between repeated experiments as well as to check for complex molecular structures in the residue. The ices experienced a radiation dose of 10 eV/molecule, which is roughly comparable to the dose received by interstellar icy grains in a dense cloud over the span of 10<sup>7</sup> years.<sup>51</sup> The radiation dose was calculated by the following equation:

$$\text{dose (MGy)} = SF \times (1.602 \times 10^{-22}) \quad (3)$$

where  $S$  is the proton stopping power (eV cm<sup>2</sup> g<sup>-1</sup> p<sup>+1</sup>),  $F$  is the proton fluence (p<sup>+</sup> cm<sup>-2</sup>) that is determined from the integrated current through the aluminum substrate sample, and the factor of  $1.602 \times 10^{-22}$  converts radiation dose units from eV g<sup>-1</sup> to MGy. The stopping power value of  $2.583 \times 10^8$  eV cm<sup>2</sup> g<sup>-1</sup> p<sup>+1</sup> was determined from the software package Stopping and Range of Ions in Matter.<sup>52</sup>

After irradiation, the samples were warmed to 300 K at 1.5 K/min to slowly release volatiles while keeping the residue intact within the foil. The cryostat was pulled out of the

vacuum chamber, and the residue-covered foils were pulled out by baked tweezers and carefully placed into 13  $\times$  110 mm baked tubes (Kimble). The tubes were then immediately stored in a  $-80$  °C freezer prior to preparation for the aqueous alteration experiments, as it was most effective to have a bulk of samples created before proceeding to the next steps. Thus, samples were frequently stored in the  $-80$  °C freezer throughout the entire experimental procedure. As the samples are eventually processed, storage of the samples at  $-80$  °C would have a negligible effect on the overall results.

**2.2. Preparation of Residues and Controls for Aqueous Alteration.** All glassware was cleaned by rinsing with Milli-Q ultrapure water (18.2 M $\Omega$ , <3 ppb of total organic carbon) and then baked in a muffle furnace at 500 °C in air overnight. To extract the samples from the foils, 850  $\mu$ L of methanol (Fisher Chemical, HPLC grade) was pipetted into each of the foil-containing tubes, and the tubes were subsequently sonicated for 10 min. After sonication, the resulting liquids were pipetted into 12  $\times$  32 mm baked vials (Supelco) that contained 10  $\mu$ L of 6 M HCl (Tama Chemicals Co., Ltd., ultrapure), used to avoid the loss of volatile amines. The acidified methanol solutions were split into four 200  $\mu$ L fractions placed in clean 13  $\times$  100 mm borosilicate tubes (Kimble): one tube was designated to not be aqueously processed; another tube was designated to be processed at 50 °C; another tube was designated to be processed at 125 °C; and the last tube was held in reserve as a spare. This process was repeated in triplicates to account for the three different processing time periods that we studied (2, 7, and 30 days). Following this procedure, the four tubes were placed into a Labconco CentriVap for  $\sim 24$  h to remove methanol. The dried tubes were then removed, and 200  $\mu$ L of ultrapure water were added to each of the samples. The pH of each water-filled tube was measured by spotting a drop of solution on universal pH paper to check for pH drift from  $\sim 7$  to 10 over the course of the experiment because the samples were unbuffered. The necks of the tubes were formed at approximately the top  $1/3$  of the tube with an oxy-propane torch to create an ampoule. The torch was affixed to a bracket, and the tube was manually rotated while held at both ends with nitrile-gloved hands to prevent potential sample contamination.<sup>53</sup> While the necks were formed, the solutions were not permitted to warm significantly, as verified by monitoring the glass tube by the sample while manually sealing by touch. The ampoules were liquid nitrogen freeze–pump–thaw degassed 3 times to remove volatile air contaminants and then flame-sealed *in vacuo* as described by Pavlov et al.<sup>54</sup>

**2.3. Aqueous Alteration.** The aqueous alteration samples were processed for a given temperature (50 or 125 °C) and duration (2, 7, or 30 days). To heat the samples, the tubes were placed within dry bath blocks, which were placed within a furnace or oven (Thermo Scientific). The tubes were processed uninterrupted during their 2, 7, or 30 days of duration. Note that the non-processed samples were placed in the freezer to preserve the products.

**2.4. Preparation of Aqueously Altered Samples for Analysis.** After aqueous alteration of the samples, the ampoule seals were carefully broken and the pH was measured and compared to the non-processed sample. All samples had a pH of  $\sim 7$ , except the sample processed at 125 °C for 30 days, which drifted to pH of  $\sim 8$  (this pH range is consistent with what has been modeled for CM asteroid fluids during aqueous alteration, with pH of  $\sim 7$ –10).<sup>28</sup> To obtain most of the

Table 2. Product Abundances of the Aqueously Altered Interstellar Residue Analogues<sup>a</sup>

compound	residue	abundances (nmol g <sup>-1</sup> )						
		initial	50 °C			125 °C		
			2 days	7 days	30 days	2 days	7 days	30 days
methylamine	A	2230 ± 130	2080 ± 190				3590 ± 390	
	B	900 ± 51		1410 ± 160				1970 ± 100
	C	1920 ± 210			2440 ± 280			923 ± 57
ethylamine	A	880 ± 29	842 ± 40				992 ± 10	
	B	663 ± 8		754 ± 25				824 ± 23
	C	826 ± 54			862 ± 23			790 ± 25
glycine	A	47.5 ± 3.7	43.3 ± 3.3				59.56 ± 0.51	
	B	14.8 ± 1.5		29.8 ± 4.5				48.9 ± 2.9
	C	64.5 ± 7.6			41.5 ± 4.5			96.9 ± 9.7
serine	A	6.10 ± 0.18	6.42 ± 0.29				8.53 ± 0.50	
	B	4.96 ± 0.13		6.71 ± 0.39				8.43 ± 0.2
	C	6.39 ± 0.27			8.22 ± 0.52			12.52 ± 0.89
alanine	A	3.82 ± 0.02	3.83 ± 0.03				4.83 ± 0.10	
	B	3.63 ± 0.02		3.82 ± 0.05				4.62 ± 0.07
	C	3.81 ± 0.02			4.10 ± 0.07			11.0 ± 1.1
$\beta$ -alanine	A	1.89 ± 0.01	2.05 ± 0.05				3.46 ± 0.12	
	B	1.73 ± 0.01		2.01 ± 0.05				3.50 ± 0.17
	C	1.91 ± 0.03			2.47 ± 0.12			2.29 ± 0.09

<sup>a</sup>Residues A, B, and C represent the same residue formed on different dates, hence having different initial values. Amino acid concentrations were determined from both ultraviolet (UV) fluorescence and single-ion mass peak areas and included background level correction using a procedural blank and a comparison of the peak areas to those of an amino acid standard run on the same day. The reported uncertainties ( $\delta x$ ) are based on the standard deviation of the average value of three separate measurements ( $n$ ) with a standard error,  $\delta x = \sigma x(n)^{1/2}$ , and take into account peak resolution quality.

aqueously altered samples, 400  $\mu$ L of ultrapure water was pipetted into the tubes. The liquids in the tubes were transferred into baked 12  $\times$  32 mm Total Recovery Autosampler Vials (Waters) that contained 20  $\mu$ L of 6 M HCl and dried in a centrifugal evaporator.

Samples were derivatized with AccQ•Tag reagents according to the protocol of the manufacturer (Waters). A total of 80  $\mu$ L of Waters AccQ•Tag sodium borate buffer and then 20  $\mu$ L of Waters AccQ•Tag derivatization agent were added. Samples and standards were heated for 10 min at 55 °C immediately following the addition of the derivatizing agent. Standards consisting of a set of nine calibrators (0.25–250  $\mu$ M) of the AccQ•Tag amino acid standard (purity of  $\geq 96.8\%$ ) along with  $\gamma$ -aminobutyric acid ( $\gamma$ -ABA), D,L- $\beta$ -aminoisobutyric acid ( $\beta$ -AIB), D,L- $\beta$ -amino-*n*-butyric acid ( $\beta$ -ABA), D,L- $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), and D,L- $\alpha$ -amino-*n*-butyric acid ( $\alpha$ -ABA) were prepared in water and treated the same way. The ultra-high performance liquid chromatography (UHPLC) solvents were prepared according to the protocol of the manufacturer (Waters).

**2.5. Analysis.** Separation of amino acids was accomplished by injecting 1  $\mu$ L of the AccQ•Tag derivatized sample onto an Acquity AccQ•Tag Ultra C18 column, 150  $\times$  2.1 mm column (1.7  $\mu$ m particle size) maintained at 55 °C. Chromatographic separation was achieved using 100  $\mu$ L of AccQ•Tag concentrate A with 900  $\mu$ L of ultrapure water as eluent A and Waters AccQ•Tag B as eluent B. Analytes were eluted using a flow rate of 700  $\mu$ L/min and the following gradient time in minutes (% B): 0.54 (0.1), 5.74 (10), 7.74 (21.2), 8.04 (59.6), 8.64 (59.6), 8.73 (0.1), and 10.00 (0.1). Waters Acquity UHPLC was equipped with a fluorescence detector set to  $\lambda_{\text{excitation}} = 266$  nm and  $\lambda_{\text{emission}} = 473$  nm.

AccQ•Tag measurements were conducted using a Xevo G2 XS with the electrospray capillary voltage set to 1.2 kV, the

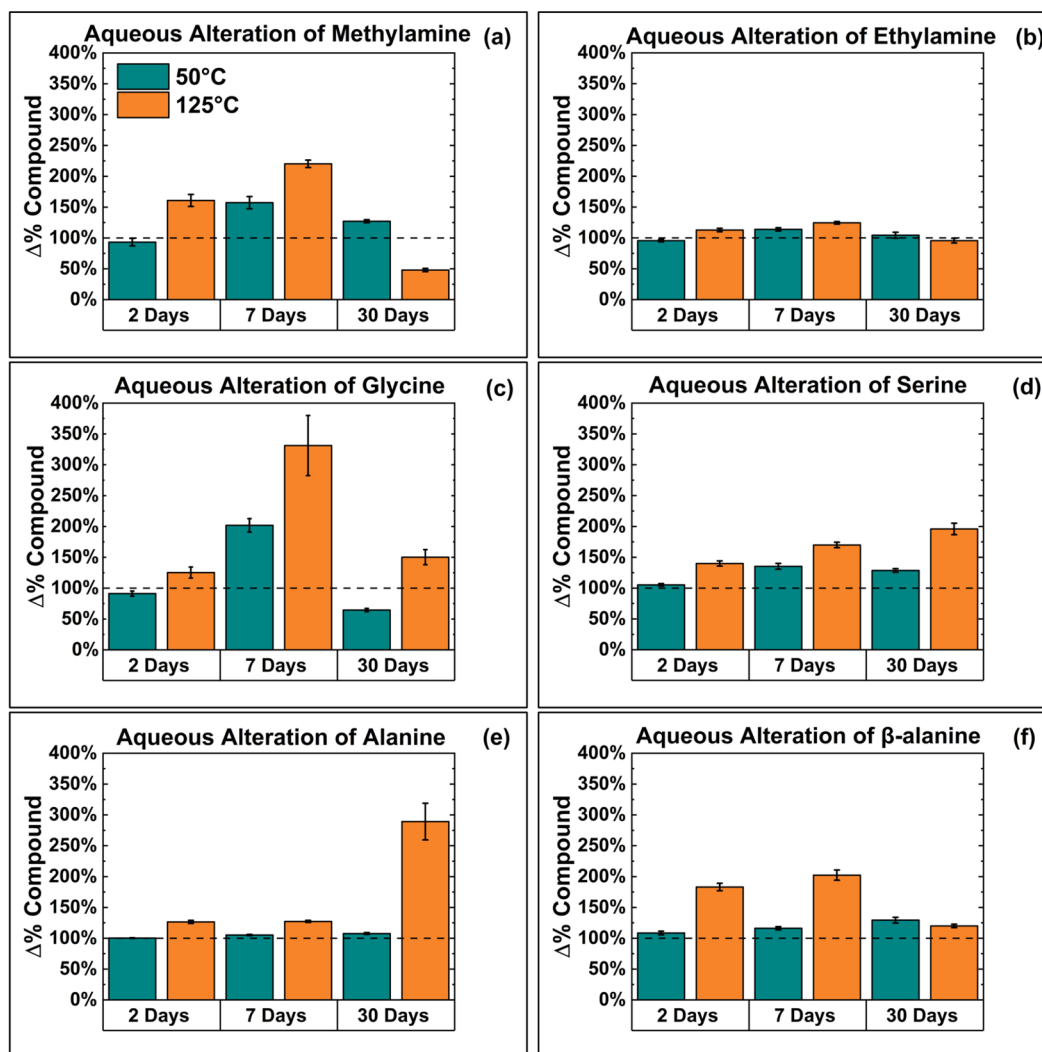
sample cone set to 40 V, the source temperature set to 120 °C, the cone gas flow set to 70 L h<sup>-1</sup>, the desolvation temperature set to 500 °C, and the desolvation gas flow set to 1000 L/h. The ToF-MS analyzer was operated in V-optics mode, which used a reflectron to achieve a full width at half maximum resolution of 22 000 based on the  $m/z$  value of leucine enkephalin. The  $m/z$  range over which data were collected was 100–600. For UHPLC analysis, a 100  $\mu$ L syringe and 15  $\mu$ L needle were used.

A set of 23 individual amino acids were prepared in water and analyzed at 9 different concentrations to generate a linear least squares model fit for each analyte (see the [Supporting Information](#)). A set of 16 individual amines were prepared in water and analyzed at 8 different concentrations to generate a linear least squares model for each amine analyte (see the [Supporting Information](#)). The abundance of amines and amino acids were 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.

No unexpected or unusually high safety hazards were encountered.

### 3. RESULTS

The major product abundances are shown in [Table 2](#). Minor product abundances include  $\gamma$ -aminobutyric acid,  $\beta$ -aminoisobutyric acid, isopropylamine, and propylamine (see the [Supporting Information](#)). Residues A, B, and C were formed by three separate, identical ice irradiations. These residues were either not processed (i.e., initial) or separately aqueously altered at temperatures of 50 and 125 °C for durations of 2 days (residue A), 7 days (residue B), and 30 days (residue C). Because each residue was formed on a different date, each one was exposed to unique conditions that contributed to



**Figure 1.** Change in product abundances after aqueous alteration of the residues for (a) methylamine, (b) ethylamine, (c) glycine, (d) serine, (e) alanine, and (f)  $\beta$ -alanine. Caution should be taken when analyzing the 30 days of duration, 125 °C sample (see the text). Columns below the dashed line indicate a decrease in abundance after aqueous alteration, and columns above the dashed line indicate an increase in abundance. The aqueously altered values are normalized to the non-aqueously altered values. Note that, because each duration represents a different residue, comparisons can only be made between data reflecting the same durations and between the aqueously altered and non-aqueously altered values.

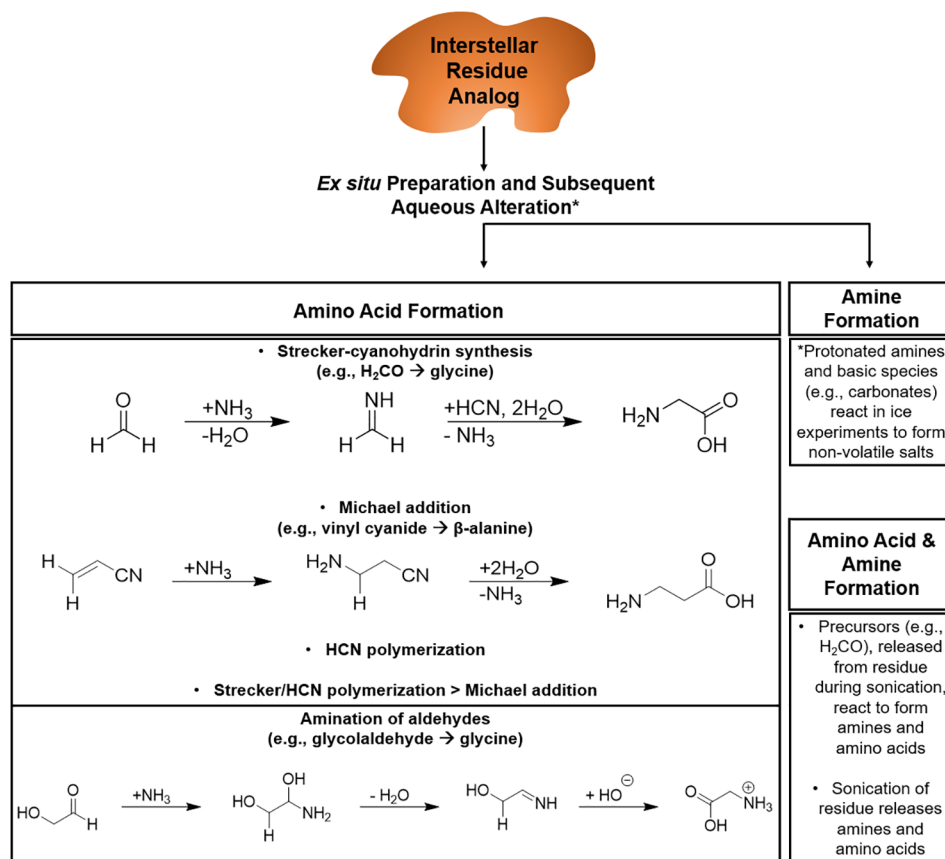
variations in the starting abundances. Figure 1 shows the  $\Delta\%$  in product abundances for (a) methylamine, (b) ethylamine, (c) glycine, (d) serine, (e) alanine, and (f)  $\beta$ -alanine as a function of the aqueous alteration duration and temperature to display aqueous alteration trends. Note that the aqueously altered values are normalized to the non-aqueously altered values.

#### 4. DISCUSSION

The non-aqueously altered abundances of amines and amino acids (i.e., samples from solely ice irradiation) varied between residues A, B, and C by up to  $\sim 4\times$ . However, product abundances followed the same trend, methylamine > ethylamine > glycine > serine > alanine >  $\beta$ -alanine, in all samples, including those for aqueously altered samples for all temperature and duration combinations (Table 2). These findings suggest that the set of conditions for forming the ice residues have a dominant role in the total concentrations of amines and amino acids formed pre-aqueous alteration, but because the abundance of the formed compounds decreased with

increasing molecular weight and because amines were found in higher concentrations than amino acids in all residues (even after hydrothermal processing), we found that slight variations of the conditions that we used to synthesize the interstellar residue analogs do not alter the absolute molecular distributions of amines and amino acids made.

The impact of aqueous alteration on the amine and amino acid distributions varied depending upon the alteration temperature and duration as well as the molecule. As shown in Figure 1, for durations of 2 and 7 days, the abundances were highest at 125 °C for all compounds studied. The 2 days of processing at 50 °C negligibly impacted the abundances. It is distinctly shown in the 7 days of duration that the abundances increased in a stepwise fashion (i.e., non-aqueously altered < 50 °C < 125 °C). The 30 days and 125 °C sample showed a modest pH drift from 7 to 8. It is possible that this was due to borate leaching from the glass or unknown contamination or a procedural error. This makes the data suspect and difficult to interpret the data points. However, observation of the 30 days and 50 °C data in comparison to the non-aqueously altered



**Figure 2.** Illustration summarizing how the amines and amino acids detected after aqueous alteration of the interstellar residue analogs were formed. Amine-containing salts were formed solely in the ice experiments, as noted by \*.

values shows no clear aqueous alteration trends. For the overall trend, ethylamine and alanine were the least impacted by aqueous alteration. The spike in the alanine abundance shown in Figure 1 appears to be an anomaly as a result of the potentially contaminated sample.

The observed aqueous alteration trends can be partially interpreted through consideration of synthesis routes. An illustration summarizing the synthesis routes as well as other pathways to forming the detected amines and amino acids is shown in Figure 2. Amines and amino acids could have been formed during the aqueous alteration process through precursors that were freed from the residue by the sonication extraction step. This is similar to what is observed during acid hydrolysis of meteorite extracts, where larger abundances of amines and amino acids are returned from the partial breakup of insoluble organic matter (IOM) and other structurally related species.<sup>55</sup>

From our aqueous alteration experiments, we did not observe a clear trend of consumption and production of amines and amino acids sharing the same aliphatic backbone when comparing data of the same durations for any of the experiments. For example, the abundance of ethylamine increases from ~842 to 992 nmol g<sup>-1</sup> when going from 50 to 125 °C for the 2 days of duration, and the abundance trend of β-alanine also shows an increase. Therefore, it was determined that the amine and amino acid products found here did not share parent–daughter synthetic relationships.

The abundances of methylamine and ethylamine were at least an order of magnitude higher than the amino acid abundances in the non-aqueously altered samples. As both

amines would desorb below room temperature in an ice experiment<sup>56</sup> and are volatile in ambient air, their substantial presence in the non-aqueously altered samples would occur if they were trapped by and subsequently released from the ice residue and/or synthesized from precursor molecules in the extraction step. It is also likely that basic species, like carbonates, may have formed during ice irradiation,<sup>57</sup> species that may have reacted with protonated methylamine and ethylamine to form non-volatile salts, thus rendering protection from volatilization after irradiation.

Synthesis routes that include nitriles may have a major role in influencing the aqueous alteration trends. Some key mechanisms, such as the Strecker cyanohydrin synthesis, the Michael addition to α–β-nitriles, and the polymerization of HCN, dictate the formation of α- and β-amino acids in aqueously altered environments, in which they include species like cyanide (CN<sup>-</sup>) and aliphatic nitriles (e.g., acrylonitrile).<sup>55</sup> In our experiments, cyanide and aliphatic nitriles could have formed in the ice starting from <sup>15</sup>NH<sub>3</sub>, as amines can be converted to nitriles through radiation processes.<sup>58,59</sup> Indeed, cyanide was found in the spare unprocessed samples. Interestingly, because CN<sup>-</sup> formed from the ice irradiation process, one would expect that they would participate in a number of chemical routes during aqueous alteration and, therefore, potentially change the product abundance trend. A possible explanation is that, under our experimental conditions, the efficiencies of the mechanisms that include cyanides or aliphatic nitriles changed similarly between each other under different durations and temperatures. However, that is difficult to determine considering that there is a variety of energy

barrier values for each mechanism.<sup>60,61</sup> As a result of the higher abundances of glycine and  $\alpha$ -alanine than  $\beta$ -alanine, it is proposed that Michael addition is a less dominant mechanism than Strecker/HCN polymerization reactions.

The observed aqueous alteration trends can also be interpreted through analysis of a potential degradation process of complex molecular structures formed during ice irradiation. Signatures of refractory organics and polymers were searched for in the IR data of the irradiated ice (25 K) and warmed residue (300 K). Species such as hexamethylenetetramine (HMT) along with variants and polymethylenimine (PMI) have been identified in the IR data of residues formed from the photolysis and irradiation of ices.<sup>19,20,22,62,63</sup> The identification of such molecules in the IR spectra of complex ices is not trivial, and we could not definitively identify any of the listed species in our samples. Regardless, the presence of refractory organics and polymers in the literature involving the irradiation of similar precursor ices makes their presence in our experiments likely.

As mentioned previously, an aqueous alteration trend was not observed for 30 days, suggesting a depletion of the initial precursor species at 30 days. However, it could also reflect the depletion of complex molecular structures in the aqueously altered environment that were sources of precursor molecules and/or the amines and amino acids themselves. In a related study by Vinogradoff et al.,<sup>18</sup> it was observed that HMT did not persist after 7 days of aqueous alteration at 150 °C and that the molecular size index and the aromatic/olefine/imine index dropped after 20 days of processing. Therefore, in our experiments, it is possible that polymers and/or other large molecular structures that acted as sources of precursor molecules and/or the products substantially depleted by 30 days of aqueous alteration. Note that thermal degradation was not considered, because the amino acids investigated in this study only start to decompose in the solid state at temperatures well above those used in this study.<sup>64,65</sup>

Our experiments showed an overabundance of glycine to alanine as well as the presence of  $\beta$ -alanine. In the work by Vinogradoff et al.,<sup>66</sup> the formose reaction, followed by the addition of  $\text{NH}_3$ , yielded glycine. The addition of  $\text{H}_2\text{CO}$  to glycine then yielded alanine; thus, alanine abundances were less than that of glycine. The presence of  $\beta$ -alanine originated from the addition of  $\text{NH}_3$  to glycolaldehyde formed in the formose reaction. However, unlike the study by Vinogradoff et al.,<sup>66</sup> our experiments were performed under neutral pH conditions (and with a potentially limited amount of  $\text{H}_2\text{CO}$ ), whereas the hydrothermal formose reaction is well-known to be base and divalent cation catalyzed.<sup>67,68</sup> Hence, the formose reaction is not expected to be a dominant reaction in our experiments. However, the slow step in the formose reaction is the formation of glycolaldehyde. If sufficient aldehydes were formed during the ice irradiation, as proposed to occur in irradiated methanol-containing ices<sup>69</sup> and observed to form from laboratory astrophysical ices,<sup>70,71</sup> it is possible that the amination could have occurred to these aldehydes in solution. There is some evidence that this mechanism could have been a minor component as a result of the formation of small amounts of  $\gamma$ -aminobutyric acid, which is not generated by Strecker or Michael addition but was observed by Vinogradoff et al.<sup>66</sup>

## 5. CONNECTION BETWEEN INTERSTELLAR AND METEORITE PARENT BODY ORGANICS

With and without aqueous alteration, the abundance trend of methylamine > ethylamine > glycine > serine > alanine >  $\beta$ -alanine did not change. Thus, the results from this study imply that interstellar cloud conditions and chemical inventories may have a highly influential role in the abundance trend of amines and amino acids in meteorite parent bodies, even after the parent body has been aqueously altered. These results parallel meteoritic studies, such as the work by Martins et al.,<sup>10</sup> that have demonstrated the strong connection between meteoritic and interstellar organic content. Additionally, the overall trend did not change, even though the non-aqueously altered abundances were different for each residue and cyanide was present, which is a significant reactant in aqueous alteration mechanisms. The resilience of the trend to the aqueous alteration and initial conditions of our experiments suggests that, for parent bodies experiencing aqueous alteration at temperatures of  $\leq 125$  °C, the amine and amino acid abundance trend can be somewhat linked to that from the parent molecular cloud, assuming that the molecules were interstellar-inherited. Albeit, a major caveat to this scenario is the absence of IOM-relevant materials, minerals and iron, magnesium, and aluminum, and other inorganic species with varying oxidation states, which were not used in our experiments and may be pivotal for the synthesis (and/or destruction) of chondritic amines and amino acids. However, it should be noted that dissimilarities in amino acid distributions have been found between CI-like chondrites and sample-returned materials.<sup>72</sup> Thus, progress is needed in both fields of study to better understand the interstellar–meteorite parent body connection.

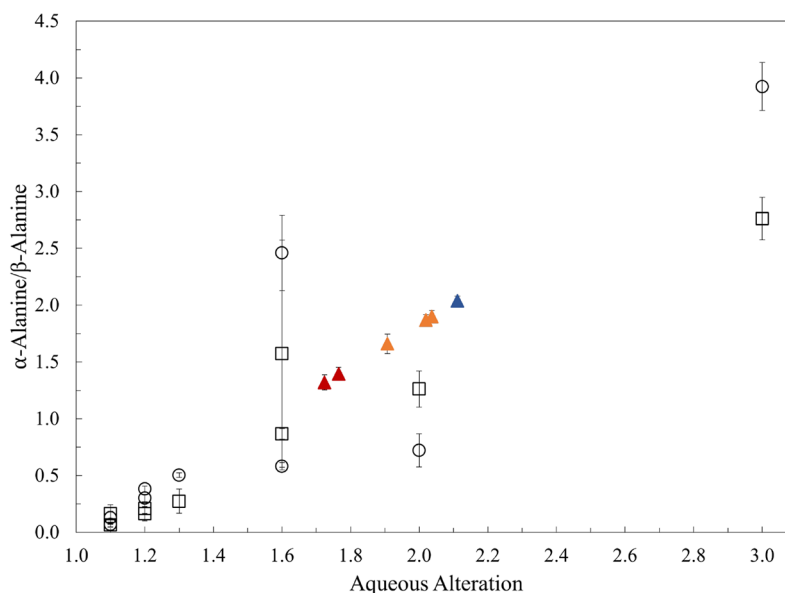
The aqueous alteration abundances of ethylamine and alanine remained close to that of the non-aqueous alteration abundances, also suggesting that the abundances of these molecules post-aqueous alteration may reflect the abundances delivered from the interstellar parental cloud. A major caveat includes the impact that parent body minerals would have on the abundances during aqueous alteration. Alternatively, methylamine, glycine, serine, and  $\beta$ -alanine abundances were altered by  $\sim 2$ -fold. Thus, when the abundances were analyzed in meteorites, it should be considered that the abundances of those molecules are likely not reflective of the distributions solely from interstellar clouds.

Similar to Modica et al.,<sup>9</sup> we found higher abundances of  $\alpha$ - than  $\beta$ -alanine in our synthetic interstellar ice residues. As mentioned previously, the most aqueously altered meteorites typically exhibit higher abundances of  $\beta$ - relative to  $\alpha$ -alanine.<sup>9,14,15</sup> In the aqueous alteration studies by Kebukawa et al.<sup>17</sup> and Vinogradoff et al.,<sup>66</sup> only ammonia or an amine was utilized as the N-bearing reactant, and in all cases, there was a greater abundance of  $\alpha$ - than  $\beta$ -alanine. A phyllosilicate was incorporated in the study by Vinogradoff et al.,<sup>66</sup> which still lead to more  $\alpha$ - than  $\beta$ -alanine, albeit cyanide and aliphatic nitriles were not used as reactants. These findings suggest that cyanide and aliphatic nitriles reacting with minerals in the parent body may be an influential piece of the puzzle in connecting interstellar abundances to the amine and amino acid abundances found in aqueously altered chondrites. Future experimental analyses, including representative meteoritic matrices and unoxidized mineral species, are needed to fully

**Table 3.** Ratio of  $\alpha$ -Alanine/ $\beta$ -Alanine from Table 2 with the Errors Propagated Compared to the Predicted Aqueous Alteration, Which Would Produce the Ratio as Described in the Text<sup>a</sup>

	$\alpha$ -alanine/ $\beta$ -alanine						
	initial	50 °C			125 °C		
		2 days	7 days	30 days	2 days	7 days	30 days
residue A	2.02 ± 0.02	1.87 ± 0.05			1.40 ± 0.06		
residue B	2.10 ± 0.02		1.90 ± 0.05			1.32 ± 0.07	
residue C	1.99 ± 0.02			1.66 ± 0.09			
alteration scale equivalent	2.1	2.0	2.0	1.9	1.8	1.7	

<sup>a</sup>The 30 days and 125 °C ratio is not shown as a result of the pH drift and uncertain data quality, as described in the text.

**Figure 3.** Ratio of  $\alpha$ -alanine/ $\beta$ -alanine in unhydrolyzed (circles) and hydrolyzed (squares) extracts of various carbonaceous chondrites versus aqueous alteration,<sup>73</sup> from unhydrolyzed and hydrolyzed amino acid data collected from the same hot water extract. The data from this study are plotted in the solid triangles along the empirical relationship between the alteration scale and the unhydrolyzed  $\alpha$ -alanine/ $\beta$ -alanine ratio, as described in the text. The initial  $\alpha$ -alanine/ $\beta$ -alanine in the three unheated residue samples is shown in the blue triangle. The orange and red triangles show the 50 °C and 2, 7, and 30 days and the 125 °C and 2 and 7 days heating experiments, respectively. Amino acid errors are propagated from the indicated sources. The meteorites plotted are hydrolyzed and unhydrolyzed CI1.1 Ivuna,<sup>35</sup> CI1.1 Orgueil,<sup>35,75</sup> CM1.2 SCO 06043<sup>35</sup> (Supporting Information), CM1.2 MET 01070<sup>35</sup> (Supporting Information), CR1.3 GRO 95577<sup>35</sup> (Supporting Information), CM1.6 Murchison,<sup>76</sup> CM1.6 LEW 90500,<sup>77</sup> C<sub>ung</sub>2.0 Tagish Lake (lithology Sb),<sup>78</sup> and CM3.0 Asuka-12236<sup>15,73</sup> for all meteorites with the exception of Tagish Lake Sb, which is described by Glavin et al.,<sup>15</sup> and Asuka-12236 from Nittler et al.<sup>79</sup>

understand the molecular distribution and abundance evolution during parent body aqueous alteration.

Looking at the ratio of  $\alpha$ - to  $\beta$ -alanine (Table 3), there is a trend toward a lower ratio as the aqueous alteration experiment progresses in both time and temperature. Furthermore, taking the aqueous alteration scale from Alexander et al.<sup>73</sup> for a variety of unhydrolyzed meteorites, there is an empirical relationship of  $\alpha$ -alanine/ $\beta$ -alanine = 1.85A – 1.88, where A is the Alexander et al.<sup>73</sup> alteration scale. A similar relationship for the Rubin et al.<sup>74</sup> scale can also be obtained (Figure S4 of the Supporting Information). A comparison of these scales and their use in amino acid analyses are discussed by Glavin et al.<sup>15</sup> (the relationship for the hydrolyzed amino acids is similar) and were also used by Modica et al.<sup>9</sup> to compare the amino acid molecular distribution in laboratory-irradiated ice analogs to that of CM chondrites with different degrees of aqueous alteration. Figure 3 shows the relationship between  $\alpha$ -alanine/ $\beta$ -alanine and the aqueous alteration of various carbonaceous chondrites from the CI, CM, and CR subgroups. The decrease in  $\alpha$ -

alanine/ $\beta$ -alanine with time and, to a greater extent, temperature follows the same trend observed in a range of increasingly aqueously altered carbonaceous chondrites. This appears to validate the applicability of the hydrothermal experiments.

The large presence of amines in the non-aqueously altered samples suggests that certain volatiles from the interstellar cloud can be efficiently transported to the protoplanetary disk, contributing to the inventory of aqueously altered interstellar-inherited species. In our experiments of the non-processed samples, amines from the ice experiments were trapped by and subsequently released from the residue, locked up into salts during the ice experiments, and/or synthesized by the extraction step from potentially even more volatile species. Indeed, salts have been abundantly detected in comet 67P/Churyumov-Gerasimenko,<sup>80,81</sup> in which their origin could be from irradiated interstellar ices. Therefore, in asteroids and comets and potentially other astrophysical bodies, it should be considered that, in addition to refractory materials, certain volatiles from the ISM may also be present.



## 6. CONCLUSION

Experimental simulations of meteorite parent body aqueous alteration of interstellar residue analogs were performed to understand the impact of interstellar-inherited residues on the amine and amino acid distributions measured in meteorites. The results from this work suggest that the conditions in and organics from the parental interstellar cloud have an appreciable role in the abundances of meteoritic soluble organic matter and that at least some of the interstellar organic abundances are likely altered in the meteorite parent body. This is supported by the following findings:

- (1) The abundance trend of methylamine > ethylamine > glycine > serine > alanine >  $\beta$ -alanine remained constant before and after aqueous alteration, even with the presence of aqueous alteration reactants, like cyanides, suggesting that the chemical inventory and conditions of the parental molecular cloud may be highly influential to the distribution of meteoritic amines and amino acids. Experiments with IOM-relevant materials, relevant minerals, and inorganic species need to be performed to further evaluate the evolution of soluble organics from the interstellar cloud to the parent body.
- (2) The abundances of ethylamine and alanine did not significantly change as a function of aqueous alteration, whereas the abundances of methylamine, glycine, serine, and  $\beta$ -alanine altered by  $\sim 2$ -fold. The varying sensitivities of each molecule to aqueous alteration may help explain the gap in linking interstellar to meteoritic abundances. The change in the ratio of  $\alpha$ -alanine/ $\beta$ -alanine with increasing aqueous alteration time and temperature was consistent with the trend observed in aqueously altered carbonaceous chondrites.
- (3) Processing for 7 days at 125 °C resulted in the most growth of product abundances after aqueous alteration.
- (4) The higher abundance of  $\alpha$ - than  $\beta$ -alanine matches well with results from aqueously processed commercial sample experiments but is in contrast with what has been typically found in aqueously altered chondrites. A comparison of our results to that of other experimental simulations suggests that at least cyanide/nitriles reacting with relevant minerals may be key to linking interstellar to aqueously altered meteoritic amine and amino acid abundances.
- (5) The relatively high abundances of volatile amines in the non-aqueously altered samples suggests that certain volatiles can be effectively delivered from the ISM to asteroids and comets, making a stronger case for the presence of interstellar organics beyond the ISM.
- (6) Progress is needed from both laboratory experiments and chondritic analyses to better understand the link between interstellar and meteoritic amines and amino acids.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00274>.

More details on materials (section S1), figures of amine and amino acid chromatograms (section S2), tables of LC–FD/ToF–MS detection metrics and parameters (section S3), table of unhydrolyzed meteorite amino

acid data (section S4), and figure of the ratio of  $\alpha$ -alanine/ $\beta$ -alanine as a function of aqueous alteration on the Rubin et al.<sup>74</sup> scale (section S5) (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Danna Qasim** – Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; Center for Research and Exploration in Space Science and Technology, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; Department of Physics and Astronomy, Howard University, Washington, D.C. 20059, United States; Present Address: Danna Qasim: Southwest Research Institute, San Antonio, Texas 78238, United States; [orcid.org/0000-0002-3276-4780](https://orcid.org/0000-0002-3276-4780); Email: [danna.qasim@nasa.gov](mailto:danna.qasim@nasa.gov)

**Christopher K. Materese** – Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; Email: [christopher.k.materese@nasa.gov](mailto:christopher.k.materese@nasa.gov)

### Authors

**Hannah L. McLain** – Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; Center for Research and Exploration in Space Science and Technology, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; Department of Physics, Catholic University of America, Washington, D.C. 20064, United States

**José C. Aponte** – Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; [orcid.org/0000-0002-0131-1981](https://orcid.org/0000-0002-0131-1981)

**Daniel P. Glavin** – Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; [orcid.org/0000-0001-7779-7765](https://orcid.org/0000-0001-7779-7765)

**Jason P. Dworkin** – Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, United States; [orcid.org/0000-0002-3961-8997](https://orcid.org/0000-0002-3961-8997)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsearthspacechem.2c00274>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the Emerging Worlds Program (Award 19-EW19\_2-0021), by NASA under Award 80GSFC21M0002, the NASA Astrobiology Institute through Award 13-13NAI7-0032 to the Goddard Center for Astrobiology (GCA), NASA's Planetary Science Division Internal Scientist Funding Program through the Fundamental Laboratory Research (FLaRe) Work Package at NASA Goddard Space Flight Center, and the Simons Foundation (SCOL Award 302497 to Jason P. Dworkin). Danna Qasim acknowledges Perry Gerakines for assistance with IR data analysis and Eric Parker for fruitful discussions. The authors acknowledge Stephen Brown, Eugene Gerashchenko, and Martin Carts for maintenance and operation of the Van de Graaff accelerator in the Radiation Effects Facility at the Goddard Space Flight Center (GSFC).

## REFERENCES

- (1) Glavin, D. P.; Alexander, C. M. O'D.; Aponte, J. C.; Dworkin, J. P.; Elsila, J. E.; Yabuta, H. The Origin and Evolution of Organic Matter in Carbonaceous Chondrites and Links to Their Parent Bodies. In *Primitive Meteorites and Asteroids: Physical, Chemical and Spectroscopic Observations Paving the Way to Exploration*; Abreu, N., Ed.; Elsevier: Amsterdam, Netherlands, 2018; Chapter 3, pp 205–271, DOI: 10.1016/B978-0-12-813325-5.00003-3.
- (2) Sandford, S. A.; Nuevo, M.; Bera, P. P.; Lee, T. J. Prebiotic astrochemistry and the formation of molecules of astrobiological interest in interstellar clouds and protostellar disks. *Chem. Rev.* **2020**, *120*, 4616–4659.
- (3) Materese, C. K.; Gerakines, P. A.; Hudson, R. L. Laboratory Studies of Astronomical Ices: Reaction Chemistry and Spectroscopy. *Acc. Chem. Res.* **2021**, *54*, 280–290.
- (4) Tachibana, S.; Abe, M.; Arakawa, M.; Fujimoto, M.; Iijima, Y.; Ishiguro, M.; Kitazato, K.; Kobayashi, N.; Namiki, N.; Okada, T.; Okazaki, R.; Sawada, H.; Sugita, S.; Takano, Y.; Tanaka, S.; Watanabe, S.; Yoshikawa, M.; Kuninaka, H. Hayabusa2: Scientific importance of samples returned from C-type near-Earth asteroid (162173) 1999 JU3. *Geochem. J.* **2014**, *48*, 571–587.
- (5) Lauretta, D. S.; Balram-Knutson, S. S.; Beshore, E.; Boynton, W. V.; Drouet d'Aubigny, C.; DellaGiustina, D. N.; Enos, H. L.; Golish, D. R.; Hergenrother, C. W.; Howell, E. S.; Bennett, C. A.; Morton, E. T.; Nolan, M. C.; Rizk, B.; Roper, H. L.; Bartels, A. E.; Bos, B. J.; Dworkin, J. P.; Highsmith, D. E.; Lorenz, D. A.; Lim, L. F.; Mink, R.; Moreau, M. C.; Nuth, J. A.; Reuter, D. C.; Simon, A. A.; Bierhaus, E. B.; Bryan, B. H.; Ballouz, R.; Barnouin, O. S.; Binzel, R. P.; Bottke, W. F.; Hamilton, V. E.; Walsh, K. J.; Chesley, S. R.; Christensen, P. R.; Clark, B. E.; Connolly, H. C.; Crombie, M. K.; Daly, M. G.; Emery, J. P.; McCoy, T. J.; McMahon, J. W.; Scheeres, D. J.; Messenger, S.; Nakamura-Messenger, K.; Righter, K.; Sandford, S. A. OSIRIS-REx: Sample return from asteroid (101955) Bennu. *Space Sci. Rev.* **2017**, *212*, 925–984.
- (6) Martins, Z.; Chan, Q. H. S.; Bonal, L.; King, A.; Yabuta, H. Organic matter in the solar system—Implications for future on-site and sample return missions. *Space Sci. Rev.* **2020**, *216*, 54.
- (7) Bernstein, M. P.; Dworkin, J. P.; Sandford, S. A.; Cooper, G. W.; Allamandola, L. J. Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature* **2002**, *416*, 401–403.
- (8) Muñoz Caro, G.; Meierhenrich, U. J.; Schutte, W. A.; Barbier, B.; Arcones Segovia, A.; Rosenbauer, H.; Thiemann, W.-P.; Brack, A.; Greenberg, J. M. Amino acids from ultraviolet irradiation of interstellar ice analogues. *Nature* **2002**, *416*, 403–406.
- (9) Modica, P.; Martins, Z.; Meinert, C.; Zanda, B.; d'Hendecourt, L. The amino acid distribution in laboratory analogs of extraterrestrial organic matter: A comparison to CM chondrites. *Astrophys. J.* **2018**, *865*, 41.
- (10) Martins, Z.; Modica, P.; Zanda, B.; d'Hendecourt, L. L. S. The amino acid and hydrocarbon contents of the Paris meteorite: Insights into the most primitive CM chondrite. *Meteorit. Planet. Sci.* **2015**, *50*, 926–943.
- (11) Elsila, J. E.; Dworkin, J. P.; Bernstein, M. P.; Martin, M. P.; Sandford, S. A. Mechanisms of amino acid formation in interstellar ice analogs. *Astrophys. J.* **2007**, *660*, 911.
- (12) Nuevo, M.; Auger, G.; Blanot, D.; d'Hendecourt, L. A detailed study of the amino acids produced from the vacuum UV irradiation of interstellar ice analogs. *Orig. Life Evol. Biosph.* **2008**, *38*, 37–56.
- (13) Aponte, J. C.; Dworkin, J. P.; Elsila, J. E. Assessing the origins of aliphatic amines in the Murchison meteorite from their compound-specific carbon isotopic ratios and enantiomeric composition. *Geochim. Cosmochim. Acta* **2014**, *141*, 331–345.
- (14) Botta, O.; Glavin, D. P.; Kminek, G.; Bada, J. L. Relative amino acid concentrations as a signature for parent body processes of carbonaceous chondrites. *Orig. Life Evol. Biosph.* **2002**, *32*, 143–163.
- (15) Glavin, D. P.; McLain, H. L.; Dworkin, J. P.; Parker, E. T.; Elsila, J. E.; Aponte, J. C.; Simkus, D. N.; Pozarycki, C. I.; Graham, H. V.; Nittler, L. R.; Alexander, C. M. O'D. Abundant extraterrestrial amino acids in the primitive CM carbonaceous chondrite Asuka 12236. *Meteorit. Planet. Sci.* **2020**, *55*, 1979–2006.
- (16) Kebukawa, Y.; Kilcoyne, A. L. D.; Cody, G. D. Exploring the potential formation of organic solids in chondrites and comets through polymerization of interstellar formaldehyde. *Astrophys. J.* **2013**, *771*, 19.
- (17) Kebukawa, Y.; Chan, Q. H. S.; Tachibana, S.; Kobayashi, K.; Zolensky, M. E. One-pot synthesis of amino acid precursors with insoluble organic matter in planetesimals with aqueous activity. *Sci. Adv.* **2017**, *3*, No. e1602093.
- (18) Vinogradoff, V.; Bernard, S.; Le Guillou, C.; Remusat, L. Evolution of interstellar organic compounds under asteroidal hydrothermal conditions. *Icarus* **2018**, *305*, 358–370.
- (19) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J.; Chang, S.; Scharberg, M. A. Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophys. J.* **1995**, *454*, 327.
- (20) Cottin, H.; Szopa, C.; Moore, M. Production of hexamethylenetetramine in photolyzed and irradiated interstellar cometary ice analogs. *Astrophys. J.* **2001**, *561*, L139.
- (21) Muñoz Caro, G. M.; Schutte, W. A. UV-photoprocessing of interstellar ice analogs: New infrared spectroscopic results. *Astron. Astrophys.* **2003**, *412*, 121–132.
- (22) Materese, C. K.; Nuevo, M.; Sandford, S. A.; Bera, P. P.; Lee, T. J. The Production and Potential Detection of Hexamethylenetetramine-Methanol in Space. *Astrobiology* **2020**, *20*, 601–616.
- (23) Danger, G.; Vinogradoff, V.; Matzka, M.; Viennet, J.-C.; Remusat, L.; Bernard, S.; Ruf, A.; Le Sergeant d'Hendecourt, L.; Schmitt-Kopplin, P. Exploring the link between molecular cloud ices and chondritic organic matter in laboratory. *Nat. Commun.* **2021**, *12*, 3538.
- (24) Hudson, R.; Moore, M. Radiation chemical alterations in solar system ices: An overview. *J. Geophys. Res.: Planets* **2001**, *106*, 33275–33284.
- (25) Boogert, A. A.; Gerakines, P. A.; Whittet, D. C. Observations of the icy universe. *Annu. Rev. Astron. Astrophys.* **2015**, *53*, 541–581.
- (26) Booth, A. S.; Walsh, C.; Terwisscha van Scheltinga, J.; van Dishoeck, E. F.; Ilee, J. D.; Hogerheijde, M. R.; Kama, M.; Nomura, H. An inherited complex organic molecule reservoir in a warm planet-hosting disk. *Nat. Astron.* **2021**, *5*, 684–690.
- (27) Brunken, N. G.; Booth, A. S.; Leemker, M.; Nazari, P.; van der Marel, N.; van Dishoeck, E. F. A major asymmetric ice trap in a planet-forming disk-III. First detection of dimethyl ether. *Astron. Astrophys.* **2022**, *659*, A29.
- (28) Zolensky, M. E.; Bourcier, W. L.; Gooding, J. L. Aqueous alteration on the hydrous asteroids: Results of EQ3/6 computer simulations. *Icarus* **1989**, *78*, 411–425.
- (29) Keil, K. Thermal alteration of asteroids: Evidence from meteorites. *Planet. Space Sci.* **2000**, *48*, 887–903.
- (30) Guo, W.; Eiler, J. M. Temperatures of aqueous alteration and evidence for methane generation on the parent bodies of the CM chondrites. *Geochim. Cosmochim. Acta* **2007**, *71*, 5565–5575.
- (31) Weisberg, M. K.; McCoy, T. J.; Krot, A. N. Systematics and evaluation of meteorite classification. In *Meteorites and the Early Solar System II*; Lauretta, D. S., McSween, H. Y., Eds.; University of Arizona Press: Tucson, AZ, 2006; Vol. 19, pp 19–52, DOI: 10.2307/j.ctv1v7zdm8.
- (32) Brearley, A. J. The action of water. In *Meteorites and the Early Solar System II*; Lauretta, D. S., McSween, H. Y., Eds.; University of Arizona Press: Tucson, AZ, 2006; Vol. 943, pp 587–624, DOI: 10.2307/j.ctv1v7zdm8.35.
- (33) Elsila, J. E.; Aponte, J. C.; Blackmond, D. G.; Burton, A. S.; Dworkin, J. P.; Glavin, D. P. Meteoritic amino acids: Diversity in compositions reflects parent body histories. *ACS Cent. Sci.* **2016**, *2*, 370–379.
- (34) Glavin, D. P.; Dworkin, J. P.; Sandford, S. A. Detection of cometary amines in samples returned by Stardust. *Meteorit. Planet. Sci.* **2008**, *43*, 399–413.

- (35) Burton, A. S.; Grunsfeld, S.; Elsila, J. E.; Glavin, D. P.; Dworkin, J. P. The effects of parent-body hydrothermal heating on amino acid abundances in CI-like chondrites. *Polar Sci.* **2014**, *8*, 255–263.
- (36) Aponte, J. C.; McLain, H. L.; Simkus, D. N.; Elsila, J. E.; Glavin, D. P.; Parker, E. T.; Dworkin, J. P.; Hill, D. H.; Connolly, H. C., Jr; Lauretta, D. S. Extraterrestrial organic compounds and cyanide in the CM2 carbonaceous chondrites Aguas Zarcas and Murchison. *Meteorit. Planet. Sci.* **2020**, *55*, 1509–1524.
- (37) Altwegg, K.; Balsiger, H.; Bar-Nun, A.; Berthelier, J.-J.; Bieler, A.; Bochsler, P.; Briois, C.; Calmonte, U.; Combi, M. R.; Cottin, H.; De Keyser, J.; Dhooghe, F.; Fiethe, B.; Fuselier, S. A.; Gasc, S.; Gombosi, T. I.; Hansen, K. C.; Haessig, M.; Jackel, A.; Kopp, E.; Korth, A.; Le Roy, L.; Mall, U.; Marty, B.; Mousis, O.; Owen, T.; Reme, H.; Rubin, M.; Semon, T.; Tzou, C.-Y.; Hunter Waite, J.; Wurz, P. Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko. *Sci. Adv.* **2016**, *2*, No. e1600285.
- (38) Elsila, J. E.; Glavin, D. P.; Dworkin, J. P. Cometary glycine detected in samples returned by Stardust. *Meteorit. Planet. Sci.* **2009**, *44*, 1323–1330.
- (39) Kaifu, N.; Morimoto, M.; Nagane, K.; Akabane, K.; Iguchi, T.; Takagi, K. Detection of interstellar methylamine. *Astrophys. J.* **1974**, *191*, L135–L137.
- (40) Bøgelund, E. G.; McGuire, B. A.; Hogerheijde, M. R.; van Dishoeck, E. F.; Ligterink, N. F. Methylamine and other simple N-bearing species in the hot cores NGC 6334I MM1–3. *Astron. Astrophys.* **2019**, *624*, A82.
- (41) Ehrenfreund, P.; Glavin, D. P.; Botta, O.; Cooper, G.; Bada, J. L. Extraterrestrial amino acids in Orgueil and Ivuna: Tracing the parent body of CI type carbonaceous chondrites. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 2138–2141.
- (42) Hudson, R.; Moore, M. Laboratory studies of the formation of methanol and other organic molecules by water + carbon monoxide radiolysis: Relevance to comets, icy satellites, and interstellar ices. *Icarus* **1999**, *140*, 451–461.
- (43) Gerakines, P. A.; Hudson, R. L. Glycine's radiolytic destruction in ices: First in situ laboratory measurements for Mars. *Astrobiology* **2013**, *13*, 647–655.
- (44) Gerakines, P. A.; Qasim, D.; Frail, S.; Hudson, R. L. Radiolytic Destruction of Uracil in Interstellar and Solar System Ices. *Astrobiology* **2022**, *22*, 233–241.
- (45) Heavens, O. S. *Optical Properties of Thin Solid Films*, 2nd ed.; Dover Publications: Mineola, NY, 2011; p 114.
- (46) Weast, R. C.; Suby, S.; Hodman, C. *Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1984.
- (47) Narten, A.; Venkatesh, C.-G.; Rice, S. Diffraction pattern and structure of amorphous solid water at 10 and 77 K. *J. Chem. Phys.* **1976**, *64*, 1106.
- (48) Loeffler, M.; Moore, M.; Gerakines, P. The effects of experimental conditions on the refractive index and density of low-temperature ices: Solid carbon dioxide. *Astrophys. J.* **2016**, *827*, 98.
- (49) Luna, R.; Molpeceres, G.; Ortigoso, J.; Satorre, M. A.; Domingo, M.; Maté, B. Densities, infrared band strengths, and optical constants of solid methanol. *Astron. Astrophys.* **2018**, *617*, A116.
- (50) Bouilloud, M.; Fray, N.; Bénilan, Y.; Cottin, H.; Gazeau, M.-C.; Jolly, A. Bibliographic review and new measurements of the infrared band strengths of pure molecules at 25 K: H<sub>2</sub>O, CO<sub>2</sub>, CO, CH<sub>4</sub>, NH<sub>3</sub>, CH<sub>3</sub>OH, HCOOH and H<sub>2</sub>CO. *Mon. Not. R. Astron. Soc.* **2015**, *451*, 2145–2160.
- (51) Moore, M.; Hudson, R.; Gerakines, P. Mid-and far-infrared spectroscopic studies of the influence of temperature, ultraviolet photolysis and ion irradiation on cosmic-type ices. *Spectrochim. Acta, Part A* **2001**, *57*, 843–858.
- (52) Ziegler, J. F.; Ziegler, M. D.; Biersack, J. P. SRIM—The stopping and range of ions in matter. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 1818–1823.
- (53) Dworkin, J. P.; Adelman, L. A.; Ajluni, T.; Andronikov, A. V.; Aponte, J. C.; Bartels, A. E.; Beshore, E.; Bierhaus, E. B.; Brucato, J. R.; Bryan, B. H.; Burton, A. S.; Callahan, M. P.; Castro-Wallace, S. L.; Clark, B. C.; Clemett, S. J.; Connolly, H. C.; Cutlip, W. E.; Daly, S. M.; Elliott, V. E.; Elsila, J. E.; Enos, H. L.; Everett, D. F.; Franchi, I. A.; Glavin, D. P.; Graham, H. V.; Hendershot, J. E.; Harris, J. W.; Hill, S. L.; Hildebrand, A. R.; Jayne, G. O.; Jenkens, R. W.; Johnson, K. S.; Kirsch, J. S.; Lauretta, D. S.; Lewis, A. S.; Loiacono, J. J.; Lorentson, C. C.; Marshall, J. R.; Martin, M. G.; Matthias, L. L.; McLain, H. L.; Messenger, S. R.; Mink, R. G.; Moore, J. L.; Nakamura-Messenger, K.; Nuth, J. A.; Owens, C. V.; Parish, C. L.; Perkins, B. D.; Pryzby, M. S.; Reigle, C. A.; Richter, K.; Rizk, B.; Russell, J. F.; Sandford, S. A.; Schepis, J. P.; Songer, J.; Sovinski, M. F.; Stahl, S. E.; Thomas-Keppta, K.; Vellinga, J. M.; Walker, M. S. OSIRIS-REX contamination control strategy and implementation. *Space Sci. Rev.* **2018**, *214*, 19.
- (54) Pavlov, A. A.; McLain, H. L.; Glavin, D. P.; Roussel, A.; Dworkin, J. P.; Elsila, J. E.; Yocum, K. M. Rapid Radiolytic Degradation of Amino Acids in the Martian Shallow Subsurface: Implications for the Search for Extinct Life. *Astrobiology* **2022**, *22*, 1099.
- (55) Simkus, D. N.; Aponte, J. C.; Elsila, J. E.; Parker, E. T.; Glavin, D. P.; Dworkin, J. P. Methodologies for analyzing soluble organic compounds in extraterrestrial samples: Amino acids, amines, monocarboxylic acids, aldehydes, and ketones. *Life* **2019**, *9*, 47.
- (56) Förstel, M.; Bergantini, A.; Maksyutenko, P.; Göbi, S.; Kaiser, R. I. Formation of methylamine and ethylamine in extraterrestrial ices and their role as fundamental building blocks of proteinogenic  $\alpha$ -amino acids. *Astrophys. J.* **2017**, *845*, 83.
- (57) Moore, M.; Khanna, R. Infrared and mass spectral studies of proton irradiated H<sub>2</sub>O + CO<sub>2</sub> ice: Evidence for carbonic acid. *Spectrochim. Acta, Part A* **1991**, *47*, 255–262.
- (58) Palumbo, M.; Strazzulla, G.; Pendleton, Y.; Tielens, A. ROC  $\equiv$ N Species Produced by Ion Irradiation of Ice Mixtures: Comparison with Astronomical Observations. *Astrophys. J.* **2000**, *534*, 801.
- (59) Danger, G.; Bossa, J.-B.; De Marcellus, P.; Borget, F.; Duvernay, F.; Theulé, P.; Chiavassa, T.; d'Hendecourt, L. Experimental investigation of nitrile formation from VUV photochemistry of interstellar ices analogs: Acetonitrile and amino acetonitrile. *Astron. Astrophys.* **2011**, *525*, A30.
- (60) Pardo, L.; Osman, R.; Weinstein, H.; Rabinowitz, J. R. Mechanisms of nucleophilic addition to activated double bonds: 1,2- and 1,4-Michael addition of ammonia. *J. Am. Chem. Soc.* **1993**, *115*, 8263–8269.
- (61) Magrino, T.; Pietrucci, F.; Saitta, A. M. Step by step strecker amino acid synthesis from ab initio prebiotic chemistry. *J. Phys. Chem. Lett.* **2021**, *12*, 2630–2637.
- (62) Briggs, R.; Ertem, G.; Ferris, J.; Greenberg, J.; McCain, P.; Mendoza-Gomez, C.; Schutte, W. Comet Halley as an aggregate of interstellar dust and further evidence for the photochemical formation of organics in the interstellar medium. *Orig. Life Evol. Biosph.* **1992**, *22*, 287–307.
- (63) Vinogradoff, V.; Fray, N.; Duvernay, F.; Briani, G.; Danger, G.; Cottin, H.; Theulé, P.; Chiavassa, T. Importance of thermal reactivity for hexamethylenetetramine formation from simulated interstellar ices. *Astron. Astrophys.* **2013**, *551*, A128.
- (64) Weiss, I. M.; Muth, C.; Drumm, R.; Kirchner, H. O. K. Thermal decomposition of the amino acids glycine, cysteine, aspartic acid, asparagine, glutamic acid, glutamine, arginine and histidine. *BMC Biophys.* **2018**, *11*, 2.
- (65) Rodante, F. Thermodynamics and kinetics of decomposition processes for standard  $\alpha$ -amino acids and some of their dipeptides in the solid state. *Thermochim. Acta* **1992**, *200*, 47–61.
- (66) Vinogradoff, V.; Remusat, L.; McLain, H.; Aponte, J.; Bernard, S.; Danger, G.; Dworkin, J.; Elsila, J.; Jaber, M. Impact of phyllosilicates on amino acid formation under asteroidal conditions. *ACS Earth Space Chem.* **2020**, *4*, 1398–1407.
- (67) Breslow, R. On the mechanism of the formose reaction. *Tetrahedron Lett.* **1959**, *1*, 22–26.
- (68) Kopetzki, D.; Antonietti, M. Hydrothermal formose reaction. *New J. Chem.* **2011**, *35*, 1787–1794.

(69) Hudson, R. L.; Moore, M. H.; Cook, A. M. IR characterization and radiation chemistry of glycolaldehyde and ethylene glycol ices. *Adv. Space Res.* **2005**, *36*, 184–189.

(70) de Marcellus, P.; Meinert, C.; Myrgorodska, I.; Nahon, L.; Buhse, T.; d'Hendecourt, L. L. S.; Meierhenrich, U. J. Aldehydes and sugars from evolved precometary ice analogs: Importance of ices in astrochemical and prebiotic evolution. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 965–970.

(71) Fedoseev, G.; Cuppen, H. M.; Ioppolo, S.; Lamberts, T.; Linnartz, H. Experimental evidence for glycolaldehyde and ethylene glycol formation by surface hydrogenation of CO molecules under dense molecular cloud conditions. *Mon. Not. R. Astron. Soc.* **2015**, *448*, 1288–1297.

(72) Parker, E.; Furusho, A.; Glavin, D.; Hamase, K.; Naraoka, H.; Takano, Y.; Dworkin, J. Amino Acid Analyses of a Sample of Ryugu by a Combination of Liquid Chromatography and High-Resolution Mass Spectrometry Techniques. *LPI Contrib.* **2022**, *2678*, 2651.

(73) Alexander, C. M.; Howard, K. T.; Bowden, R.; Fogel, M. L. The classification of CM and CR chondrites using bulk H, C and N abundances and isotopic compositions. *Geochim. Cosmochim. Acta* **2013**, *123*, 244–260.

(74) Rubin, A. E.; Trigo-Rodríguez, J. M.; Huber, H.; Wasson, J. T. Progressive aqueous alteration of CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **2007**, *71*, 2361–2382.

(75) Glavin, D. P.; Callahan, M. P.; Dworkin, J. P.; Elsila, J. E. The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteorit. Planet. Sci.* **2010**, *45*, 1948–1972.

(76) Glavin, D. P.; Elsila, J. E.; McLain, H. L.; Aponte, J. C.; Parker, E. T.; Dworkin, J. P.; Hill, D. H.; Connolly, H. C., Jr; Lauretta, D. S. Extraterrestrial amino acids and L-enantiomeric excesses in the CM2 carbonaceous chondrites Aguas Zarcas and Murchison. *Meteorit. Planet. Sci.* **2021**, *56*, 148–173.

(77) Glavin, D. P.; Dworkin, J. P.; Aubrey, A.; Botta, O.; Doty, J. H., III; Martins, Z.; Bada, J. L. Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography-time of flight-mass spectrometry. *Meteorit. Planet. Sci.* **2006**, *41*, 889–902.

(78) Glavin, D.; Freissinet, C.; Eigenbrode, J.; Miller, K.; Martin, M.; Summons, R.; Steele, A.; Franz, H.; Archer, D.; Brinckerhoff, W.; et al. Origin of Chlorobenzene Detected by the Curiosity Rover in Yellowknife Bay: Evidence for Martian Organics in the Sheepbed Mudstone? *Proceedings of the 45th Lunar and Planetary Science Conference (LPSC)*; The Woodlands, TX, March 17–21, 2014.

(79) Nittler, L.; Alexander, C.; Foustoukos, D.; Patzer, A.; Verdier-Paoletti, M. Asuka 12236, the most pristine CM chondrite to date. *Proceedings of the 51st Lunar and Planetary Science Conference (LPSC)*; The Woodlands, TX, March 16–20, 2020.

(80) Altwegg, K.; Balsiger, H.; Hänni, N.; Rubin, M.; Schuhmann, M.; Schroeder, I.; Sémon, T.; Wampfler, S.; Berthelier, J.-J.; Briois, C.; Combi, M.; Gombosi, T. I.; Cottin, H.; De Keyser, J.; Dhooche, F.; Fiethe, B.; Fuselier, S. A. Evidence of ammonium salts in comet 67P as explanation for the nitrogen depletion in cometary comae. *Nat. Astron.* **2020**, *4*, 533–540.

(81) Altwegg, K.; Combi, M.; Fuselier, S.; Hänni, N.; De Keyser, J.; Mahjoub, A.; Müller, D.; Pestoni, B.; Rubin, M.; Wampfler, S. Abundant ammonium hydrosulphide embedded in cometary dust grains. *Mon. Not. R. Astron. Soc.* **2022**, *516*, 3900–3910.

# Supporting Information

## Meteorite Parent Body Aqueous Alteration Simulations of Interstellar Residue Analogs

Danna Qasim,<sup>\*,†,‡,§</sup> Hannah L. McLain,<sup>†,‡,||</sup> José C. Aponte,<sup>†</sup> Daniel P. Glavin,<sup>†</sup>  
Jason P. Dworkin,<sup>†</sup> and Christopher K. Materese<sup>\*,†</sup>

<sup>1</sup> †*Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD  
20771, USA*

‡*Center for Research and Exploration in Space Science and Technology, NASA/GSFC,  
Greenbelt, MD 20771, USA*

¶*Department of Physics and Astronomy, Howard University, Washington, DC 20059, USA*

§*Current address: Southwest Research Institute, San Antonio, TX 78238, USA*

E-mail: [danna.qasim@nasa.gov](mailto:danna.qasim@nasa.gov); [christopher.k.materese@nasa.gov](mailto:christopher.k.materese@nasa.gov)

## S1 Materials: Chemicals and Reagents

For LC-MS analyses of aliphatic amino acids and amines, two eluents were used: A) AccQ•Tag A buffer and B) AccQ•Tag B buffer. Eluent A was prepared by mixing 10% AccQ•Tag A concentrate purchased directly from Waters Corporation with 90% Milli-Q water and Eluent B was purchased directly from Waters Corporation. Also used was a 0.5 M aqueous sodium formate solution to perform calibrations of the ToF-MS, and a 200  $\mu\text{g L}^{-1}$  leucine enkephalin solution to perform real-time lock mass corrections. These final two solutions were prepared as detailed in Glavin et al.<sup>1</sup>

All reagents used in this study were purchased from Sigma-Aldrich, Mann Research Labs, Acros Organics, Tama Chemicals Co., Ltd., Fisher Chemical, and Waters Corporation. Purchased, individual amino acid crystals [ $\beta$ -alanine ( $\beta$ -Ala),  $\gamma$ -amino-*n*-butyric acid ( $\gamma$ -ABA), D,L- $\beta$ -aminoisobutyric acid ( $\beta$ -AIB), D,L- $\beta$ -amino-*n*-butyric acid ( $\beta$ -ABA), D,L- $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), and D,L- $\alpha$ -amino-*n*-butyric acid ( $\alpha$ -ABA)] used to generate mixed amino acid standards all had purities  $\geq 96.8\%$ , while all other purchased reagents had purities  $\geq 95\%$ , unless stated otherwise. Individual amino acid stock solutions were prepared in ultrapure water at concentrations of 250 mM prior to mixing to generate mixed amino acid standards.

## S2 Liquid Chromatograms

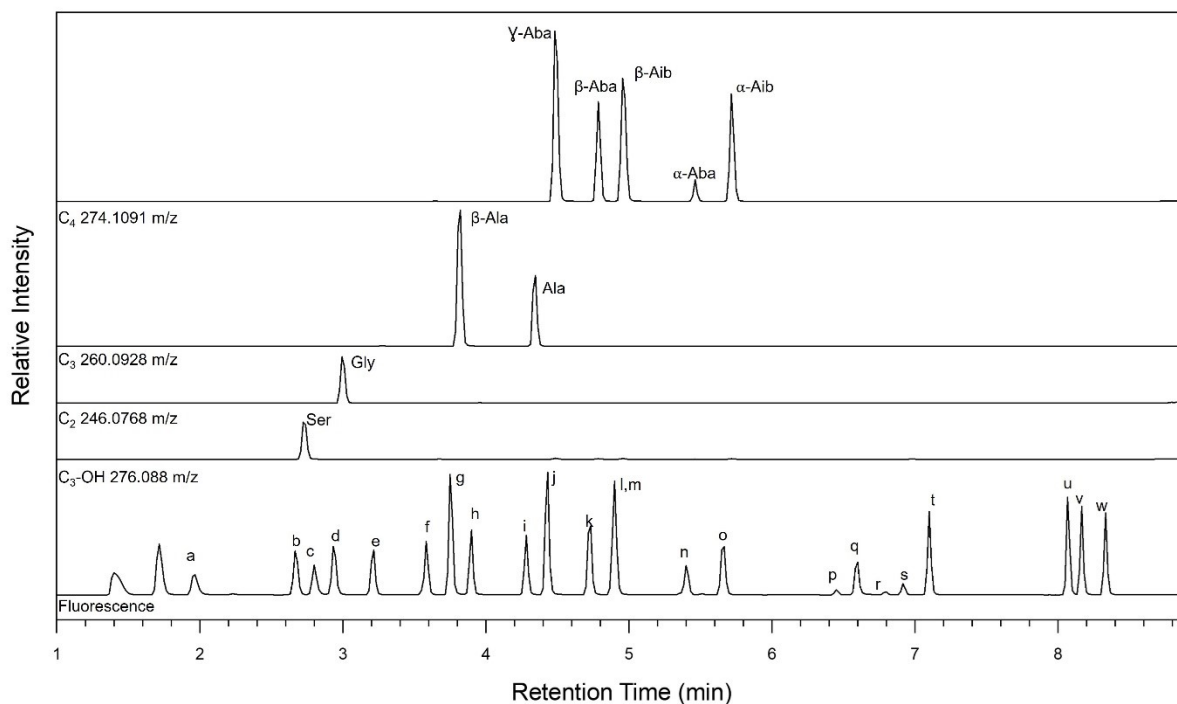


Figure S1: A mixed amino acid standard using the published amino acid gradient demonstrates chromatographic resolution of 23 amino acids. The 0 to 10 minute fluorescence chromatogram of a mixed amino acid standard is specifically shown. Chromatographic co-elution of target analytes was minimal, which facilitates accurate detection and quantitation of amino acids. Analyte identifications are as follows: a = histidine, b = serine, c = arginine, d = glycine, e = aspartic acid, f = glutamic acid, g =  $\beta$ -alanine, h = threonine, i = alanine, j =  $\gamma$ -aminobutyric acid, k =  $\beta$ -aminobutyric acid, l = proline, m =  $\beta$ -aminoisobutyric acid, n =  $\alpha$ -aminobutyric acid, o =  $\alpha$ -aminoisobutyric acid, p = cysteine, q = lysine, r = tyrosine, s = methionine, t = valine, u = leucine, v = isoleucine, w = phenylalanine.

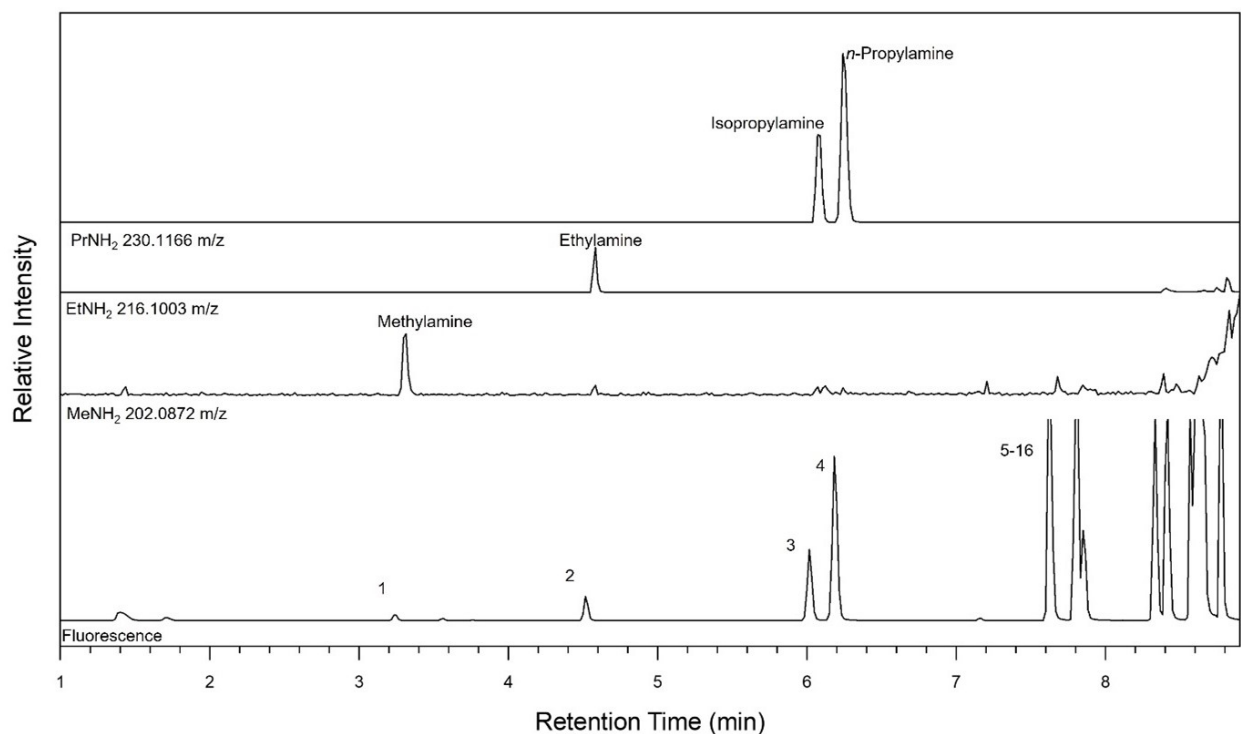


Figure S2: A mixed aliphatic amine standard comprised of 15 aliphatic amines was chromatographically resolved using the AccQ•Tag derivatization agent. The 1 to 9 minute region of a fluorescence chromatogram of a mixed aliphatic amine standard is shown. Analyte identifications are as follows: 1 = methylamine, 2 = ethylamine, 3 = propylamine, 4 = isopropylamine, 5 = sec-butylamine (does not fluoresce), 6 = isobutylamine, 7 = *n*-butylamine, 8 = *t*-butylamine, 9 = 3-aminopentane, 10 = 2-amino-3-methylbutane, 11 = sec-pentylamine, 12 = 2-methylbutylamine, 13 = tert-pentylamine, 14 = isopentylamine, 15 = pentylamine, and 16 = hexylamine.



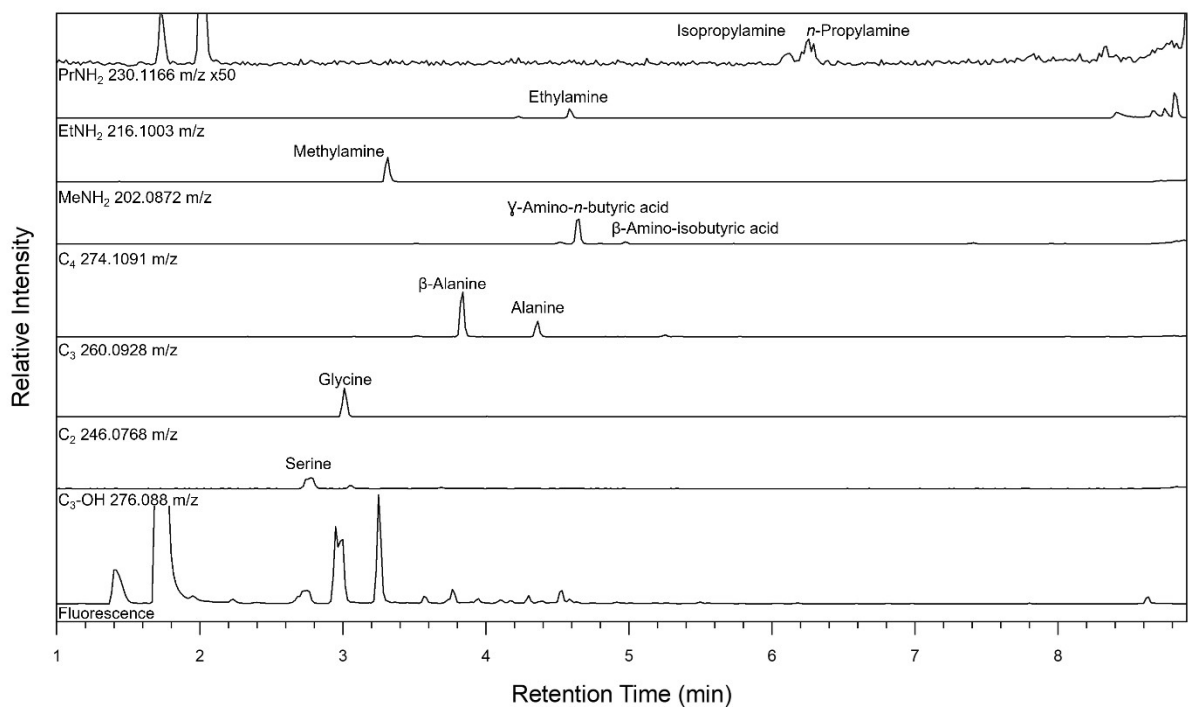


Figure S3: Amines and amino acids detected in the sample that were aqueously altered for 7 days at 125°C. Detected species: serine ( $m/z = 276.088$ ), glycine ( $m/z = 246.0768$ ), alanine and  $\beta$ -alanine ( $m/z = 260.0928$ ),  $\gamma$ -aminobutyric acid ( $m/z = 274.1091$ ),  $\beta$ -aminoisobutyric acid ( $m/z = 274.1091$ ), methylamine ( $m/z = 202.0872$ ), ethylamine ( $m/z = 216.1003$ ), isopropylamine ( $m/z = 230.1166$ ), and propylamine ( $m/z = 230.1166$ ).

20 **S3 Liquid Chromatography-Fluorescence Detection and**  
 21 **Time-of-Flight Mass Spectrometry (LC-FD/ToF-**  
 22 **MS) Detection Metrics and Parameters**

Table S1: Detection parameters for the isotopically labeled analytes – amino acids.

Amino acids	Chemical formula	m/z with $^{14}\text{N}$ from NIST	With AccQ•Tag	Number of nitrogens	m/z with $^{15}\text{N}$ (calculated)	With AccQ•Tag
Histidine	$\text{C}_6\text{H}_9\text{N}_3\text{O}_2$	155.1546	326.1546	3	158.1457	329.1457
Serine	$\text{C}_3\text{H}_7\text{NO}_3$	105.0926	276.0926	1	106.0896	277.0896
Arginine	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$	174.201	345.201	4	178.1891	349.1891
Glycine	$\text{C}_2\text{H}_5\text{NO}_2$	75.0666	246.0666	1	76.0636	247.0636
Aspartic Acid	$\text{C}_4\text{H}_7\text{NO}_4$	133.1027	304.1027	1	134.0997	305.0997
Glutamic Acid	$\text{C}_5\text{H}_9\text{NO}_4$	147.1293	318.1293	1	148.1263	319.1263
Threonine	$\text{C}_4\text{H}_9\text{NO}_3$	119.1192	290.1192	1	120.1162	291.1162
Alanine	$\text{C}_3\text{H}_7\text{NO}_2$	89.0932	260.0932	1	90.0902	261.0902
Proline	$\text{C}_5\text{H}_9\text{NO}_2$	115.1305	286.1305	1	116.1275	287.1275
Lysine	$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$	146.1876	581.06	2	148.1817	583.1000
Valine	$\text{C}_5\text{H}_{11}\text{NO}_2$	117.1463	487.14	1	118.1433	488.1400
Leucine	$\text{C}_6\text{H}_{13}\text{NO}_2$	131.1729	302.1729	1	132.1699	303.1699
Isoleucine	$\text{C}_6\text{H}_{13}\text{NO}_2$	131.1729	302.1729	1	132.1699	303.1699
Phenylalanine	$\text{C}_9\text{H}_{11}\text{NO}_2$	165.1891	336.1891	1	166.1861	337.1861
Tyrosine	$\text{C}_9\text{H}_9\text{NO}_3$	181.1885	352.1885	1	182.1855	353.1855
$\gamma$ -ABA	$\text{C}_4\text{H}_9\text{NO}_2$	103.1198	274.1198	1	104.1168	275.1168
$\beta$ -ABA	$\text{C}_4\text{H}_9\text{NO}_2$	103.1198	274.1198	1	104.1168	275.1168
$\beta$ -AIB	$\text{C}_4\text{H}_9\text{NO}_2$	103.1198	274.1198	1	104.1168	275.1168
$\alpha$ -ABA	$\text{C}_4\text{H}_9\text{NO}_2$	103.1198	274.1198	1	104.1168	275.1168
$\alpha$ -AIB	$\text{C}_4\text{H}_9\text{NO}_2$	103.1198	274.1198	1	104.1168	275.1168
$\beta$ -Alanine	$\text{C}_3\text{H}_7\text{NO}_2$	89.0932	260.0932	1	90.0902	261.0902

Table S2: Detection parameters for the isotopically labeled analytes – amines.

Amines	Chemical formula	m/z with $^{14}\text{N}$ from NIST	With AccQ•Tag	Number of nitrogens	m/z with $^{15}\text{N}$ (calculated)	With AccQ•Tag
Methylamine	$\text{CH}_5\text{N}$	31.0571	202.0571	1	32.0541	203.0541
Ethylamine	$\text{C}_2\text{H}_7\text{N}$	45.0837	216.0837	1	46.0807	217.0807
Isopropylamine	$\text{C}_3\text{H}_9\text{N}$	59.1103	230.1103	1	60.1073	231.1073
Propylamine	$\text{C}_3\text{H}_9\text{N}$	59.1103	230.1103	1	60.1073	231.1073
sec-Butylamine	$\text{C}_4\text{H}_{11}\text{N}$	73.1368	244.1368	1	74.1338	245.1338
Isobutylamine	$\text{C}_4\text{H}_{11}\text{N}$	73.1368	244.1368	1	74.1338	245.1338
<i>n</i> -Butylamine/ <i>t</i> -butylamine	$\text{C}_4\text{H}_{11}\text{N}$	73.1368	244.1368	1	74.1338	245.1338
3-Aminopentane	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
2-Amino-3methylbutane	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
sec-Pentylamine	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
2-Methylbutylamine	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
tert-Pentylamine	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
Isopentylamine	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
<i>n</i> -Pentylamine	$\text{C}_5\text{H}_{13}\text{N}$	87.1634	258.1634	1	88.1604	259.1604
<i>n</i> -Hexylamine	$\text{C}_6\text{H}_{15}\text{N}$	101.1900	272.19	1	102.1870	273.1870

23 **S4 Unhydrolyzed Meteorite Amino Acid Data**

24 Unhydrolyzed data was collected at the same time as hydrolyzed data<sup>2</sup> on CM1 meteorites  
 25 Meteorite Hills (MET) 01070, Scott Glacier (SCO) 06043, and CR1 meteorite Grosvenor  
 26 Mountains (GRO) 95577, but viewed as superfluous to the focus of that manuscript and

27 omitted. The previously unpublished data tables from that work are provided here. The  
28 method employed is described in detail in the original manuscript.

Table S3: Summary of the average blank-corrected amino acid concentrations in the non-hydrolyzed, hot-water extracts of three highly aqueously altered carbonaceous meteorites.

Amino acid	MET 01070	SCO 06043	GRO 95577
D-aspartic acid	12 ± 1	< 1.4	11 ± 2
L-aspartic acid	20 ± 2	5.7 ± 2.4	15 ± 1
D-glutamic acid	< 1.8	< 0.3	< 0.4
L-glutamic acid	10 ± 1	< 0.7	< 2.2
D-serine	< 1.3	< 0.8	< 1.8
L-serine	25 ± 2	5.4 ± 2.1	12 ± 2
D-threonine	< 1.3	< 1.4	< 1.3
L-threonine	< 3.6	< 1.2	< 1.6
glycine	90 ± 1	41 ± 1	175 ± 4
β-alanine	89 ± 2	58 ± 4	161 ± 5
γ-amino- <i>n</i> -butyric acid + D,L-β-aminoisobutyric acid*	21 ± 7	23 ± 3	66 ± 3
D-alanine	13 ± 1	8.4 ± 0.3	40 ± 2
L-alanine	21 ± 2	9.1 ± 1.3	41 ± 2
D-β-amino- <i>n</i> -butyric acid	9.5 ± 0.1	7.0 ± 0.6	32 ± 1
L-β-amino- <i>n</i> -butyric acid	12 ± 1	8.3 ± 0.6	38 ± 2
α-aminoisobutyric acid	29 ± 2	34 ± 3	145 ± 10
D,L-α-amino- <i>n</i> -butyric acid*	16 ± 7	2.6 ± 0.4	32 ± 15
D-norvaline	< 0.5	< 0.5	< 0.5
L-norvaline	< 0.4	< 0.3	< 0.4
D-isovaline	2.4 ± 0.3	2.3 ± 0.1	2.3 ± 0.3
L-isovaline	3.7 ± 0.6	3.1 ± 0.2	2.8 ± 0.1
D-valine	< 0.4	< 0.3	< 0.4
L-valine	3.9 ± 0.7	5.8 ± 0.3	3.6 ± 0.8
D,L-3-aminopentanoic acid <sup>†</sup>	9.0 ± 0.6	3.1 ± 0.2	3.1 ± 0.5
D,L- and allo-3-amino-2-methylbutanoic acid <sup>†</sup>	7.0 ± 0.4	1.4 ± 0.3	2.1 ± 0.1
3-amino-3-methylbutanoic acid <sup>‡</sup>	< 7	< 1	< 2
3-amino-2,2-dimethylpropanoic acid	7.9 ± 0.4	6.2 ± 0.6	12 ± 1
D,L-3-amino-2-ethylpropanoic acid*	12 ± 2	2.5 ± 0.2	6.9 ± 2.5
D,L-4-aminopentanoic acid <sup>†</sup>	16 ± 1	3.7 ± 0.7	4.6 ± 0.4
D,L-4-amino-2-methylbutanoic acid*	6.1 ± 0.2	4.0 ± 0.5	4.1 ± 0.1
D,L-4-amino-3-methylbutanoic acid*	29 ± 5	13 ± 4	14 ± 4
5-aminopentanoic acid	2.3 ± 0.3	5.3 ± 0.8	5.3 ± 0.8
ε-amino- <i>n</i> -caproic acid	59 ± 9	32 ± 4	133 ± 16

Values reported in parts-per-billion (ppb) on a bulk sample basis. Extracts were analyzed by OPA/NAC derivatization (15 minutes) and UHPLC separation with UV fluorescence and time of flight mass spectrometry (ToF-MS) detection. For the LC-ToF-MS data, the mono-isotopic masses of each protonated OPA/NAC amino acid derivative ( $M + H^+$ ) was used for quantification and final peak integrations included background level correction using a serpentine blank and a comparison of the peak areas with those of an amino acid standard run on the same day. Final values were normalized using the desalting and derivatization recoveries of an internal D,L-norleucine standard (recoveries ranged from 60-80% for the meteorite samples). Uncertainties ( $\delta x$ ) are based on the standard deviation of the average value of four separate measurements ( $n$ ) with a standard error,  $\delta x = \sigma x(n-1)^{1/2}$  \*Enantiomers could not be separated under the chromatographic conditions. <sup>†</sup>Enantiomers were separated but could not be identified due to the lack of optically pure standards. <sup>‡</sup>3-amino-3-methylbutanoic acid co-elutes with one of the enantiomers of D,L-4-aminopentanoic acid, therefore upper limits for 3-amino-3-methylbutanoic acid were estimated by taking the difference in peak areas of the two D,L-4-aminopentanoic acid enantiomers.

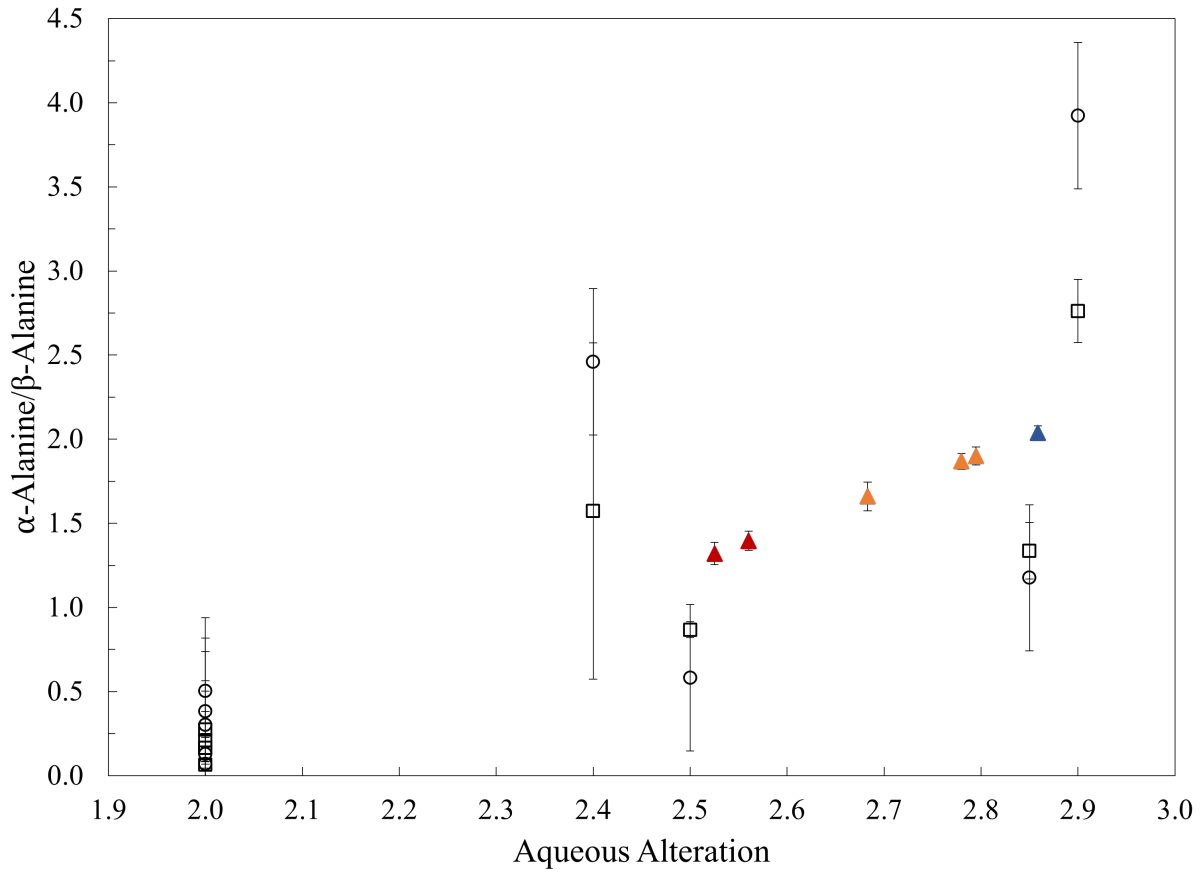


Figure S4: The ratio of  $\alpha$ -alanine/ $\beta$ -alanine in unhydrolyzed (circles) and hydrolyzed (squares) extracts of various carbonaceous chondrites versus aqueous alteration from unhydrolyzed and hydrolyzed amino acid data collected from the same hot water extract. The data from this study are plotted in the solid triangles along the empirical relationship between the alteration scale and the unhydrolyzed  $\alpha$ -alanine/ $\beta$ -alanine ratio, as described in the text. The initial  $\alpha$ -alanine/ $\beta$ -alanine in the three unheated residue samples is shown in the blue triangle. The orange and red triangles show the 50°C 2, 7, and 30 days and the 125°C 2 and 7 days heating experiments, respectively. Amino acid errors are propagated from the indicated sources. The meteorites plotted are hydrolyzed and unhydrolyzed CI2 Ivuna,<sup>4</sup> CI2 Orgueil,<sup>2,4</sup> CM2 SCO 06043,<sup>4</sup> CM2 MET 01070,<sup>4</sup> CR2 GRO 95577,<sup>4</sup> CM2.5 Murchison,<sup>5</sup> CM1.6 LEW 90500,<sup>1</sup> CM2.8/2.9 Paris,<sup>6</sup> and CM2.9 Asuka-12236.<sup>7</sup> Rubin et al.<sup>3</sup> for all meteorites with the exception of CI meteorites which is described in Glavin et al.,<sup>7</sup> Paris from Martins et al.,<sup>6</sup> and Asuka-12236 from Nittler et al.<sup>8</sup> On this scale, the empirical relationship is  $\alpha$ -alanine/ $\beta$ -alanine = 2.58R-4.87, where R is the Rubin et al.<sup>3</sup> alteration scale.

## References

- (1) Glavin, D. P.; Dworkin, J. P.; Aubrey, A.; Botta, O.; Doty III, J. H.; Martins, Z.; Bada, J. L. Amino acid analyses of Antarctic CM2 meteorites using liquid chromatography-time of flight-mass spectrometry. *Meteorit. Planet. Sci.* **2006**, *41*, 889–902.
- (2) Glavin, D. P.; Callahan, M. P.; Dworkin, J. P.; Elsila, J. E. The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteorit. Planet. Sci.* **2010**, *45*, 1948–1972.
- (3) Rubin, A. E.; Trigo-Rodríguez, J. M.; Huber, H.; Wasson, J. T. Progressive aqueous alteration of CM carbonaceous chondrites. *Geochim. Cosmochim. Acta.* **2007**, *71*, 2361–2382.
- (4) Burton, A. S.; Grunsfeld, S.; Elsila, J. E.; Glavin, D. P.; Dworkin, J. P. The effects of parent-body hydrothermal heating on amino acid abundances in CI-like chondrites. *Polar Sci.* **2014**, *8*, 255–263.
- (5) Glavin, D. P.; Elsila, J. E.; McLain, H. L.; Aponte, J. C.; Parker, E. T.; Dworkin, J. P.; Hill, D. H.; Connolly Jr, H. C.; Lauretta, D. S. Extraterrestrial amino acids and L-enantiomeric excesses in the CM 2 carbonaceous chondrites Aguas Zarcas and Murchison. *Meteorit. Planet. Sci.* **2020**, *56*, 148–173.
- (6) Martins, Z.; Modica, P.; Zanda, B.; d’Hendecourt, L. L. S. The amino acid and hydrocarbon contents of the Paris meteorite: Insights into the most primitive CM chondrite. *Meteorit. Planet. Sci.* **2015**, *50*, 926–943.
- (7) Glavin, D. P.; McLain, H. L.; Dworkin, J. P.; Parker, E. T.; Elsila, J. E.; Aponte, J. C.; Simkus, D. N.; Pozarycki, C. I.; Graham, H. V.; Nittler, L. R., et al. Abundant extraterrestrial amino acids in the primitive CM carbonaceous chondrite Asuka 12236. *Meteorit. Planet. Sci.* **2020**, *55*, 1979–2006.

55 (8) Nittler, L.; Alexander, C.; Foustoukos, D.; Patzer, A.; Verdier-Paoletti, M. Asuka 12236,  
56 The most pristine CM chondrite to date. Lunar and Planetary Science Conference. 2020;  
57 p 2276.