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Pathways to Meteoritic Glycine and Methylamine

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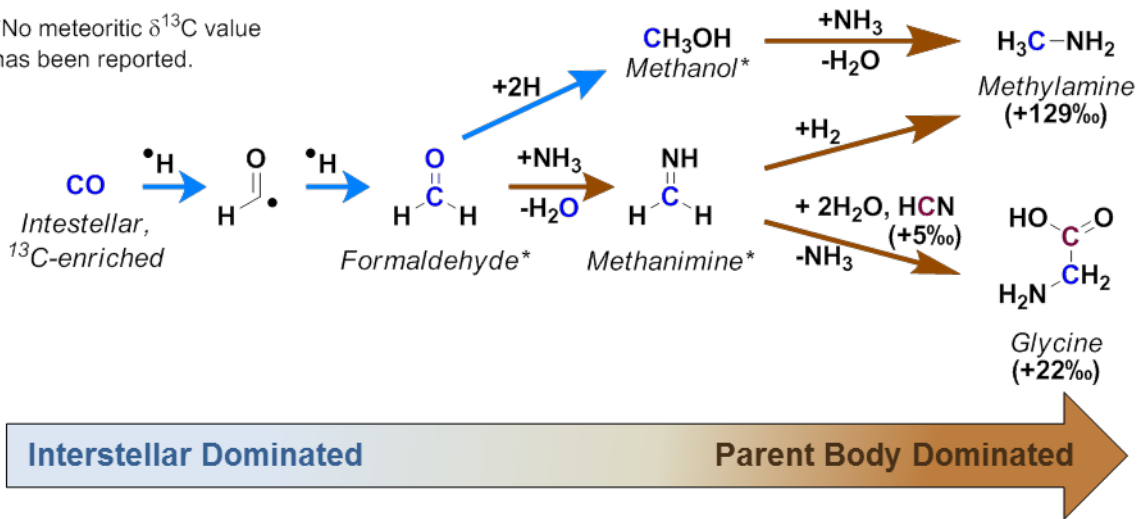
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*No meteoritic $\delta^{13}\text{C}$ value has been reported.



19

20 **Abstract**

21 Glycine and methylamine are meteoritic water-soluble organic compounds that provide
22 insights into the processes that occurred before, during, and after the formation of the Solar System.
23 Both glycine and methylamine and many of their potential synthetic precursors have been studied
24 in astrophysical environments via observations, laboratory experiments, and modeling. In spite of
25 these studies, the synthetic mechanisms for their formation leading to their occurrence in
26 meteorites remain poorly understood. Typical ^{13}C -isotopic values ($\delta^{13}\text{C}$) of meteoritic glycine and
27 methylamine are ^{13}C -enriched relative to their terrestrial counterparts; thus, analyses of their stable
28 carbon isotopic compositions ($^{13}\text{C}/^{12}\text{C}$) may be used not only to assess terrestrial contamination in
29 meteorites, but also to provide information about their synthetic routes inside the parent body.
30 Here, we examine potential synthetic routes of glycine and methylamine from a common set of
31 precursors present in carbonaceous chondrite meteorites, using data from laboratory analyses of
32 the well-studied CM2 meteorite Murchison. Several synthetic mechanisms for the origins of
33 glycine and methylamine found in carbonaceous chondrites may be possible, and the prevalence
34 of these mechanisms will largely depend on (a) the molecular abundance of the precursor
35 molecules and (b) the levels of processing (aqueous and thermal) that occurred inside the parent
36 body. In this work, we also aim to contextualize the current knowledge about gas-phase reactions
37 and irradiated ice grain chemistry for the synthesis of these species through parent body processes.
38 Our evaluation of various mechanisms for the origins of meteoritic glycine and methylamine from
39 simple species shows what work is still needed to evaluate both, the abundances and isotopic
40 compositions of simpler precursor molecules from carbonaceous chondrites, as well as the effects
41 of parent body processes on those abundances and isotopic compositions. The analyses presented
42 here combined with the indicated measurements will aid a better interpretation of quantitative
43 analysis of reaction rates, molecular stability, and distribution of organic products from laboratory
44 simulations of interstellar ices, astronomical observations, and theoretical modeling.

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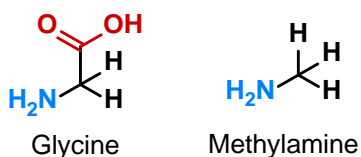
48 1. Introduction

49 Many carbonaceous chondrites, particularly the CI, CM, and CR groups that did not experience
50 extensive parent body thermal alteration, contain a rich suite of primordial organics that may
51 include compounds that formed before the Solar System, as well as compounds formed inside
52 asteroidal parent bodies from presolar precursors.¹⁻³ Amino acids are among the most well-studied
53 organic compounds in carbonaceous chondrites.⁴⁻⁷ Conversely, the molecular distribution and
54 isotopic composition of meteoritic amines have been only recently investigated,⁸⁻¹¹ and their
55 potential synthetic relationship with amino acids is not fully understood.

56 Glycine (NH₂CH₂CO₂H) and methylamine (CH₃NH₂) are simple structurally analogous
57 compounds related to each other by the presence or absence of the acid moiety (carboxyl group, –
58 CO₂H; Scheme 1). Both compounds are common in the terrestrial biosphere. Both have also been
59 detected in multiple extraterrestrial samples, including carbonaceous chondrites,¹²⁻¹⁴ laboratory
60 measurements of acid-hydrolyzed hot water extracts of comet-exposed materials from the Stardust
61 sample return mission to comet 81P/Wild 2,¹⁵⁻¹⁷ and direct *in situ* measurements of the coma of
62 comet 67P/Churyumov-Gerasimenko by the Rosetta Orbiter Spectrometer for Ion and Neutral
63 Analysis (ROSINA) instrument.¹⁸ Methylamine, but not glycine, was also identified by the Philae
64 lander Cometary Sampling and Composition (COSAC) instrument shortly after Philae's first
65 contact with the surface of Churyumov-Gerasimenko.¹⁹ Additionally, glycine and methylamine
66 have been produced from synthesis in gas-phase reactions,²⁰⁻²³ UV-irradiated interstellar ice
67 analogs,²⁴⁻³² and in Miller-Urey-type experiments,³³⁻³⁴ representing potential abiotic syntheses in
68 diverse environments.

69 **Scheme 1.** Structures of glycine and methylamine (color highlights the amine [blue, NH₂] and
70 acid [red, CO₂H] functional groups).

71



72

73 Analysis of the ¹³C isotopic compositions of meteoritic organics and their precursors may
74 provide insights about their synthetic origins. The synthesis of meteoritic glycine and methylamine
75 may have occurred in two broad cosmochemical regimes, the first dominated by gas- and ice-grain
76 chemistry that occurred in the molecular cloud, the solar nebula, or the protoplanetary disk, and

77 the second dominated by hydrothermal chemistry inside the meteorite parent body; thus, $\delta^{13}\text{C}$
78 values measured in the laboratory may result from isotopic fractionation inside various
79 environments. Glycine and methylamine can be synthesized from common precursors such as
80 carbon monoxide (CO), ammonia (NH_3), hydrogen cyanide (HCN), and carbon dioxide (CO_2);
81 glycine and methylamine and their corresponding simpler building blocks may all have been
82 incorporated during the accretion of Solar System bodies such as comets and asteroids, inside
83 which further synthesis may have occurred.

84 Analyses of meteoritic $\delta^{13}\text{C}$ values found for molecules regarded as precursors (CO, CO_2 , and
85 HCN), and those of larger species such as glycine and methylamine (so-called products) extracted
86 from carbonaceous meteorites suggest potential synthetic relationships between these
87 molecules.³⁵⁻³⁷ The ^{13}C -isotopic composition of the organic compounds found in carbonaceous
88 chondrites and analyzed in the laboratory is the result of various processes that occurred before
89 and after the accretion of the parent body. The degree of processing inside the parent body may
90 have greatly shaped the $\delta^{13}\text{C}$ signatures of the organic compounds evaluated in the laboratory.
91 Indeed, the varying levels of aqueous and thermal processing for different carbonaceous asteroids
92 and chondrite types and the conditions under which this processing occurred are currently poorly
93 understood.³⁸⁻⁴¹

94 Therefore, without being able to fully account for the level of fractionation that occurred
95 through aqueous and thermal processing, it remains challenging to evaluate the synthetic routes
96 leading to the origins of meteoritic glycine and methylamine. An additional challenge in using the
97 $\delta^{13}\text{C}$ values of meteoritic glycine and methylamine as probes to their formation mechanisms is the
98 unknown original concentration and isotopic values of their potential precursor molecules inside
99 carbonaceous chondrites. Being mindful of these limitations and with the available data currently
100 present in the literature, here we examine plausible diverse synthetic pathways that may have led
101 to the origins of glycine and methylamine in meteorites. We consider those processes that occurred
102 before the accretion of the meteorite parent body, but center our attention on those synthetic
103 mechanisms that may have taken place much later during the parent body stage which are
104 dominated by hydrothermal reactions. We focus on the Murchison meteorite because is the most
105 thoroughly studied carbonaceous chondrite for amino acids,⁷ as well as the only meteorite from
106 which the stable carbon isotopic ratios ($\delta^{13}\text{C}$) of most of these potential precursor molecules have
107 been reported. While other meteorites such as Orgueil (CI1), Lonewolf Nunataks (LON) 94101

108 (CM2), Lewis Cliff (LEW) 90500 (CM2), Allan Hills (ALH) 83100 (CM1/2), La Paz Icefield
109 (LAP) 02342 (CR2), and Graves Nunataks (GRA) 95229 (CR2) contain glycine and
110 methylamine,^{9,10} the abundances and $\delta^{13}\text{C}$ of precursor molecules such as CO, CO₂, and HCN in
111 these meteorites have not been reported. Isotopic analyses of precursor molecules in additional
112 meteorites are needed to test and expand the hypotheses presented in this manuscript. We also
113 evaluate the current knowledge of gas-phase reactions, irradiated ice grain chemistry, theoretical
114 modeling, and telescopic observations of various interstellar regions for the synthesis of glycine,
115 methylamine, and their corresponding precursor species.

116 **2. The Pre-Parent body Phase**

117 Inside interstellar environments, complex organic compounds may form in grain-surface and
118 gas-phase reactions by hydrogen atom addition to CO and other unsaturated molecules, followed
119 by carbon atom addition;⁴²⁻⁴⁷ many of the predicted compounds such as formaldehyde and
120 methanol, have been detected in the interstellar and circumstellar media, hot cores, interstellar
121 clouds and circumstellar envelopes.⁴⁸⁻⁵⁰ Several molecules of interest here, which may form in
122 both surface- and gas-phase reactions (such as formaldehyde, methanimine, and methylamine)
123 have been detected in interstellar and protostellar sources,⁵¹⁻⁵⁴ in comets,^{19,55-57} and in
124 carbonaceous chondrites.^{12,14,35,58} Although glycine detection in the interstellar medium remains
125 controversial,⁵⁹⁻⁶¹ possible formation pathways relevant to these environments have yet to be
126 confirmed.^{22,62-65} Similarly, even though methylamine and its structurally related compound,
127 methanimine, are both observed in the interstellar medium,⁶⁶⁻⁶⁹ their pre-solar formation
128 mechanisms are not entirely understood. For example, Suzuki et al. (2016) have surveyed several
129 star-forming cores for methanimine (CH₂NH) with the view that cores with the highest abundances
130 would be the best places to conduct a subsequent glycine search.⁷⁰ Suzuki et al. (2016) also
131 modeled the related gas-grain chemistry and concluded that interstellar methanimine formed in
132 gaseous reactions.⁷⁰

133 Recent observations of nearby young stellar objects (YSOs) in star forming regions with
134 infrared absorption spectroscopy, have measured a discrepancy between gas-phase ¹²CO/¹³CO and
135 solid-phase ¹²CO/¹³CO ratios.⁷¹ The observed ¹²CO/¹³CO gas-phase ratios of the Solar System
136 and local interstellar medium ranges from ~+290 to +370‰ which is higher,⁷² (more ¹³C enriched)
137 than those measured in YSOs and nearby star-forming regions ranging at ~-460 to +47‰.⁷¹ This
138 leads to speculation that this effect may be due to isotopologue partitioning between the two

139 reservoirs. Smith et al. (2015) ruled out isotope selective photo-dissociation for their results of gas-
140 phase $^{12}\text{C}/^{13}\text{C}$, even though it is a significant effect for the oxygen isotopes.⁷¹ The evolution of
141 these objects through the prestellar disk and eventually planetary systems however, provides ample
142 opportunity for further isotope effects to occur. Observational instrumentation is just reaching
143 more complex molecular (and isotopic) detection limits, especially spatially, of these more evolved
144 systems,⁷³ allowing for new detections and observational constraints to current theories. Models
145 of disk chemistry suggest the fractionation to be dependent on the disk radius and height with some
146 chemical dependence,⁷⁴ though the mid-plane results are consistent with current observations of
147 comets.

148 In the cold interstellar medium, ^{13}C nuclei are effectively incorporated into ^{13}CO while
149 expelling ^{12}C nuclei, through the following ion-molecule exchange reaction: $^{13}\text{C}^+ + ^{12}\text{CO} \leftrightarrow ^{13}\text{CO}$
150 $+ ^{12}\text{C}^+$.⁷⁵ Therefore, it is expected that the carbon atoms and other C-bearing molecules (“CX”,
151 also known as “the carbon isotope pool”) are depleted in ^{13}C and consequently have much higher
152 $^{12}\text{CX}/^{13}\text{CX}$ ratios. Such depletion is therefore expected in other molecules formed primarily in
153 gaseous reactions, such as HCN. Indeed, astronomical measurements using radio telescopes by
154 Sakai et al. (2010)⁷⁶ and Yoshida et al. (2015)⁷⁷ have demonstrated the expected ^{13}C -depletions in
155 interstellar acetylene radical ($\text{C}\equiv\text{C-H}$) and cyclopropenylidene ($c\text{-C}_3\text{H}_2$). Conversely,
156 formaldehyde has been tentatively found to be more ^{13}C -enriched than CO in in some star-forming
157 cores,⁷⁸ a result that is contrary to all theoretical predictions and that suggest that isotopic
158 partitioning has not yet been demonstrated unequivocally for observations of a large suite of
159 interstellar molecules. Large observational errors are obtained in $^{12}\text{C}/^{13}\text{C}$ ratios measurements,⁷⁹
160 which may not be very constraining on the ppm/ppb levels measured for organics in carbonaceous
161 chondrites. Thus, a bulk isotope ratio cannot constrain the origin of meteoritic organics without
162 extensively considering the chemistry and other isotope effects for each molecule present.

163 3. The Parent Body Phase

164 Chain-elongation reactions leading to the formation of more complex organic molecules may
165 preferentially yield ^{12}C -enriched products because breaking and creating $^{12}\text{C}\text{-}^{12}\text{C}$ bonds demands
166 slightly less energy than breaking and creating $^{12}\text{C}\text{-}^{13}\text{C}$ bonds.^{35,80,81} Thus, it is expected that larger
167 organic compounds will be ^{13}C -depleted relative to their molecular precursors; the remaining
168 unreacted starting materials would be ^{13}C -enriched relative to the newly formed products and to
169 their original compositions.

170 Table 1 shows the stable carbon isotopic measurements (in $\delta^{13}\text{C}$ notations) of several molecular
171 species that may serve as precursors or that share the same structural aliphatic backbone with
172 glycine and methylamine. The $\delta^{13}\text{C}$ values reported for HCN extracted from the Murchison
173 meteorite shows that meteoritic HCN is ^{13}C -rich relative to meteoritic CO extracted from the same
174 carbonaceous chondrite.⁵⁸ These results are difficult to understand based on interstellar
175 fractionation alone, unless the ^{12}CO and ^{13}CO molecules underwent isotopic-selective
176 photodissociation in the protosolar nebula producing a homogenous $^{12}\text{C}/^{13}\text{C}$ fractionation
177 pattern,⁷⁴ which is observed among the different meteoritic carbon species (Table 1). The $\delta^{13}\text{C}$ of
178 meteoritic organics shown in Table 1 average to $\delta^{13}\text{C} \sim 35\%$, this value is consistent with the Solar
179 System $\delta^{13}\text{C}$ value ($\sim +25\%$);⁷² however, it's worth noticing that large errors are present from
180 $^{12}\text{C}/^{13}\text{C}$ observational measurements (see Section 1). In the case of the isotopic difference between
181 meteoritic HCN and CO however, the ^{13}C nuclei could have been restored to the gas and eventually
182 take part in chemical reactions in gas phase that enriched molecules of the carbon isotope pool in
183 ^{13}C . However, it is also possible that CO in Murchison may have been more readily outgassed or
184 evaporated from nebular dust and planetesimals early in nebular evolution, and therefore further
185 fractionated than the comparably less volatile HCN.

186 Orgueil, one of the most aqueously altered carbonaceous chondrites, shows ^{13}C -enriched
187 carbonates relative to the other chondrite types (the origins of meteoritic carbonates are currently
188 poorly understood);⁸²⁻⁸⁴ aqueous processes have been linked to the destruction of meteoritic
189 organic species,^{85,86} which may potentially lead to isotopic fractionation. However, the different
190 measurements of meteoritic compounds do not show a simple and direct relationship between the
191 degrees of aqueous processing and the $\delta^{13}\text{C}$ values as shown in Table 1, suggesting that the
192 accretion of the parent body was highly heterogeneous. Indeed, CI, CM and CR meteorites likely
193 originate from distinct parent bodies, which may have accreted different abundances of water and
194 thus, may have resulted in different levels of processing and isotopic compositions (meteoritic
195 water contents have been found to follow the trend: $\text{CI1} > \text{CM1/2} > \text{CM2} > \text{CR2}$)⁸⁷. Regardless,
196 further $\delta^{13}\text{C}$ measurements of these and other carbon sources in carbonaceous chondrites and
197 experimental modeling mimicking conditions inside the parent body are needed to further our
198 understanding of the synthetic pathways for meteoritic amines and amino acids.

199 **Table 1.** $\delta^{13}\text{C}$ values of the molecular species evaluated here for the origins of glycine and methylamine in carbonaceous chondrites.

200

Carbonaceous chondrite	Type	$\delta^{13}\text{C}$ (‰)						
		CO	CO ₂	CO ₃ ²⁻ (carbonate)	HCN	CH ₃ CO ₂ H (acetic acid)	CH ₃ NH ₂ (methylamine)	NH ₂ CH ₂ CO ₂ H (glycine)
Orgueil	CI1	–	–	+60 ± 3 ⁸² , +59.2 ± 0.2 ⁸⁴ , +68.8 ± 0.2 ⁸⁴	–	–	+43 ± 10 ⁹	+22 ⁸⁵
ALH 83100	CM1/2	–	–	+44.5 ± 0.2 ⁸⁴	–	–	+41 ± 6 ¹⁰	+11 ⁸⁹ , +53 ± 3 ¹⁰
Murchison	CM2	-32 ± 2 ³⁵	+29.1 ± 0.2 ³⁵	+37 ± 3 ⁸² , +43.9 ± 0.2 ⁸⁴	+5 ± 2 ⁵⁸	+22.7 ± 0.2 ³⁵ , -7.7 ± 0.2 ⁸⁸	+129 ± 7 ⁸	+22 ⁹⁰ , +41 ± 2 ⁹¹ , +13 ± 3 ⁸⁹
LEW 90500	CM2	–	–	+41.3 ± 0.2 ⁸⁴	–	–	+59 ± 8 ¹⁰	+47 ± 10 ⁸⁹ , +47 ± 1 ¹⁰
LON 94101	CM2	–	–	+41.3 ± 0.2 ⁸⁴	–	–	+44 ± 6 ¹⁰	+38 ± 3 ⁸⁹ , +36 ± 4 ¹⁰
LAP 02342	CR2	–	–	+36.2 ± 0.2 ⁸⁴	–	–	+64.6 ± 1.6 ¹¹ , +10 ± 13 ¹⁰	+20.1 ± 0.1 ¹⁴
GRA 95229	CR2	–	–	+42.0 ± 0.2 ⁸⁴	–	–	+64.0 ± 2.1 ¹¹ , -1 ± 9 ¹⁰	+33.8 ± 1.6 ⁹² , +35 ± 9 ⁸⁹

³⁵Yuen et al. 1984. ⁸²Grady et al. 1988. ⁸⁴Alexander et al. 2015. ⁵⁸The value shown here is the average of four different samples measured by Pizzarello (2014).

⁸⁸Huang et al. 2005. ⁹Aponte et al. 2015. ¹⁰Aponte et al. 2016. ⁸Aponte et al. 2014. ¹¹Pizzarello and Yarnes 2016. ⁸⁵Ehrenfreund et al. 2001. ⁸⁹Elsila et al. 2012.

⁹⁰Engel et al. 1990. ⁹¹Pizzarello et al. 2004. ¹⁴Pizzarello and Holmes 2009. ⁹²Martins et al. 2007.

201

202 **3.1 Synthesis of glycine and methylamine from formaldehyde.** Two different synthetic
203 routes which may interconnect the synthetic origins of glycine and methylamine prior to and after
204 the formation of the asteroid parent body are shown in Scheme 2. The synthesis of interstellar
205 complex organics may start from the hydrogenation of interstellar CO to form formaldehyde;^{43,45,46}
206 this first step should occur prior to the accretion of the asteroid inside the interstellar medium and
207 later in the protosolar nebula and protoplanetary disk midplane, since the radical intermediate in
208 the hydrogenation of CO may react rapidly with surrounding water and mineral species present
209 inside the parent body, quenching or inducing the loss (via polymerization) of this intermediate
210 product. After interstellar formaldehyde is formed, it may have accreted into the parent body,
211 where it could react with surrounding ammonia to form methanimine. Ammonia has been reported
212 from various carbonaceous meteorites including Murchison (CM2) and the CR2 chondrites LAP
213 02342 and GRA 95229; those results indicated that ammonia is two orders of magnitude less
214 abundant in Murchison than in the CR2 chondrites.^{13,93} Indeed, the abundance of amino acids has
215 been found to be about ten times larger in CR2 chondrites than in the Murchison meteorite,
216 suggesting that larger concentrations of ammonia may be linked to larger amino acid abundances
217 in carbonaceous chondrites.^{14,94} Continuing with the synthesis of meteoritic glycine, methanimine
218 may readily react with meteoritic HCN and form α -aminoacetonitrile (Strecker-cyanohydrin
219 reaction), which yields the amino acid after aqueous hydrolysis (Scheme 2). Laboratory
220 simulations of the reactivity of aminoacetonitrile in ice analogs by Danger et al. (2011a) did not
221 find evidence for the formation of glycine at temperatures ranging from 20 to 300 °K, suggesting
222 that the formation of glycine would result after thermal activation inside the parent body.⁹⁵

223 The Strecker-cyanohydrin synthesis may be driven by parent-body aqueous processes, and is
224 the most commonly invoked mechanism for the production of meteoritic α -amino acids such as
225 glycine inside the parent body.^{96,97} As shown in Scheme 2, one molecule of methanimine (formed
226 from formaldehyde) reacts with one molecule of HCN to yield the α -aminonitrile. Again, it would
227 be expected that formaldehyde and methanimine are ¹³C-enriched relative to HCN (occurring from
228 the carbon isotope pool; see Section 1) inside the parent body, and that the $\delta^{13}\text{C}$ composition of
229 glycine before extended parent body processing would be the result of the combination of these
230 two species. However, the preaccretionary abundance and $\delta^{13}\text{C}$ composition of formaldehyde,
231 methanimine, and HCN upon accretion into the meteorite parent body, as well as the effects of
232 parent body processing on the abundances and isotopic fractionation of these meteoritic species

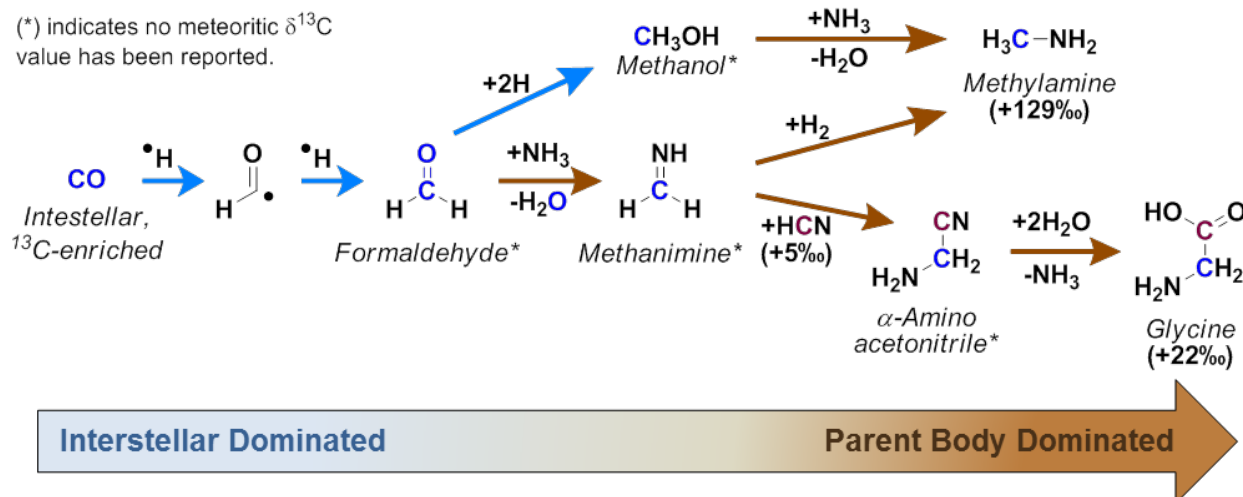
233 remains unknown. Without this information, it is impossible to confirm the roles of these proposed
234 starting materials as glycine precursors; thus, both measurements of the $\delta^{13}\text{C}$ values of meteoritic
235 formaldehyde and methanimine, as well as a more thorough understanding of the effects of parent
236 body processing over the $\delta^{13}\text{C}$ composition of meteoritic organics are necessary future
237 investigations to constrain the formation of meteoritic glycine.

238 Similar to glycine, methylamine may be synthesized from formaldehyde but through the
239 hydrogenation of methanimine (Scheme 2); indeed, the hydrogenation of methanimine to yield
240 methylamine has been experimentally tested in interstellar ice analogs with positive results.^{30,31} It
241 remains to be seen, however, whether this reaction would be viable inside an asteroid-like
242 environment. During the synthesis of glycine through this reaction, unreacted methanimine would
243 become ^{13}C -enriched relative to the produced glycine. Methylamine extracted from the acid-
244 hydrolyzed extract of the Murchison meteorite showed a $\delta^{13}\text{C}$ value which is ^{13}C -enriched relative
245 to the isotopic values reported for glycine (Table 1). Therefore, the $\delta^{13}\text{C}$ relationship between
246 meteoritic glycine and methylamine may suggest that methylamine could have formed from
247 hydrogenation of methanimine left unreacted from the synthesis of glycine (Scheme 2). Similar to
248 Murchison, methylamine was more ^{13}C -enriched than glycine in the LEW 90500, LON 94101,
249 and Orgueil meteorites, although opposite results were observed in the CM1/2 chondrite ALH
250 83100 and two CR2 chondrites (Table 1). Therefore, this synthetic pathway may have to be
251 reevaluated after future efforts to expand the $\delta^{13}\text{C}$ analyses of glycine and methylamine to other
252 carbonaceous chondrites from different petrologic types.

253 An alternative synthetic route for obtaining meteoritic methylamine may arise from the
254 formation of methanol after reduction of formaldehyde (Scheme 2). Through the reduction of
255 formaldehyde inside meteorites, protonated methanol would undergo dehydration upon reaction
256 with ammonia. The synthesis of aliphatic amines from the reaction of alcohols and ammonia has
257 been observed in high yields in the presence of transition metals, all of which may be present inside
258 the asteroid parent body, e.g., iron, nickel, phyllosilicates; however, the production of tertiary
259 amines as main products of this reaction may be a factor to consider.⁹⁸⁻¹⁰⁰ Still, evaluation of the
260 meteoritic $\delta^{13}\text{C}$ values of methanol and formaldehyde is needed to link their synthetic relationship
261 to meteoritic methylamine.

262 **Scheme 2.** The Strecker-cyanohydrin synthesis and reductive amination of formaldehyde are
263 potential synthetic routes for glycine and methylamine in the Murchison meteorite. Starting from

264 ^{13}C -enriched CO, results in ^{13}C -enriched glycine and methylamine. These reactions may be
 265 dominant, but not exclusive inside the indicated environments.
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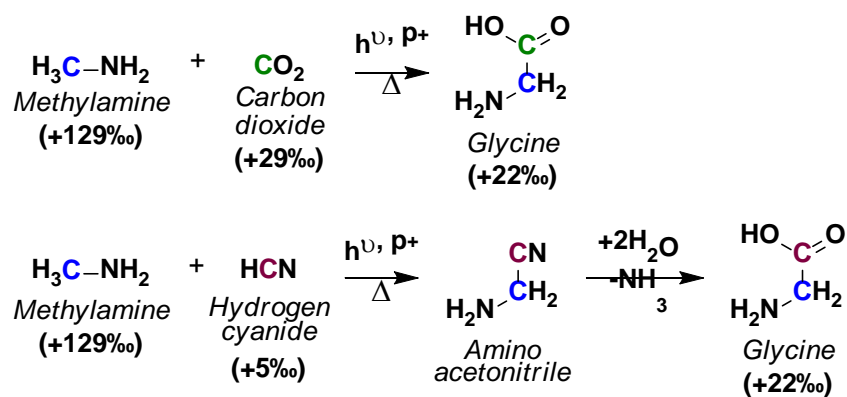
3.2 Synthesis of glycine from CO₂ or HCN addition to methylamine. An alternative route for the synthesis of meteoritic glycine is the addition of CO₂ (which may have nebular origins or may be generated from the reaction of carbonates and proton donors inside the parent body), or HCN to methylamine inside the parent body (Scheme 3). Experimental investigations of this ion/neutral reaction in the gas phase have been unsuccessful, yielding only proton transfer products rather than the amino acid;¹⁰⁰ however, the reaction may occur in ice chemistry. The synthesis of amino acids from the addition of CO₂ to aliphatic amines has been demonstrated from photochemical and ion irradiation reactions (ices were composed of water and varying levels of CO₂ and an aliphatic amine)¹⁰²⁻¹⁰⁵.

The meteoritic $\delta^{13}\text{C}$ value of methylamine is higher than that of free CO₂, carbonates, and HCN extracted from the Murchison meteorite (Table 1); these measured values, however, are the result of varying levels of processing on an unknown original concentration of molecules. Thus, given the faster reactivity and depletion of ^{12}C -bearing molecules, it may be possible that the $\delta^{13}\text{C}$ values measured for these materials in meteorites are ^{13}C -enriched relative to their pre-accretionary values. The laboratory $\delta^{13}\text{C}$ values measured in meteorites are of the products and the remaining unreacted precursors and do not reveal the presolar $\delta^{13}\text{C}$ values of the reactants.

A close look at the reaction mechanisms involved in the addition of CO₂ and HCN to methylamine to synthesize glycine suggest that the likely products of these reactions may not result

287 in the α -amino acid. Unlike photodissociation processes that result in bond cleavage, neutral-
 288 radical reactions, and radical-radical recombination, the addition of CO₂ to methylamine in
 289 aqueous media may only yield methylcarbamic acid (CH₃NHCO₂H).^{106,107} Similarly, in the
 290 presence of an excess of amines, HCN reacts to form amidines (amines catalyze the polymerization
 291 of HCN if present in catalytic concentrations).^{108,109} However, the synthesis of glycine from the
 292 addition of CO₂ or HCN to methylamine under meteoritic conditions is yet to be tested; it remains
 293 to be seen if in the presence of transition metals or mineral matrixes, carbamates and amidines are
 294 useful intermediates in, for example, transition metal-catalyzed reactions for the synthesis of
 295 amino acids.

296 **Scheme 3.** The synthesis of glycine from addition of meteoritic CO₂ or HCN to methylamine
 297 may occur in photochemical processes, but the likelihood of glycine formation glycine under
 298 aqueous hydrothermal conditions remains unknown.



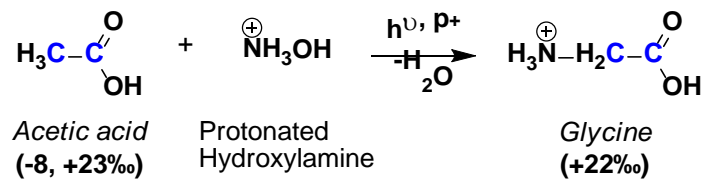
299
 300
 301 **3.3 Synthesis of glycine from NH₃ addition to acetic acid.** Similar to the addition of CO₂ to
 302 methylamine to form glycine, a source of nitrogen such as NH₃ may potentially add to acetic acid
 303 to produce glycine (Scheme 4). This reaction mechanism, however, has shown mixed results from
 304 experiments in the gas-phase,^{22,23,110} the difficulty in obtaining glycine from these species is based
 305 on the acid nature of the carboxyl group and the basic nature of ammonia which result in proton
 306 transfer reactions only.¹¹⁰ Therefore, to overcome this physicochemical barrier, Blagojevic et al.
 307 (2003) proposed the synthesis of glycine from the reaction of acetic acid with ionized and
 308 protonated hydroxylamine (NH₂OH⁺ and NH₃OH⁺ respectively) with successful results.^{22,23} To
 309 the best of our knowledge, this gas-phase reaction has not been tested in ice-irradiated experiments
 310 containing acetic acid and hydroxylamine; however, it is very likely that glycine would form from

311 the high energy processes and wide range of reactions mechanisms occurring in irradiated
312 interstellar ice analogs.

313 An astronomical constraint appears from the unsuccessful search for hydroxylamine from
314 interstellar localities;^{111,112} however, several synthetic pathways for interstellar hydroxylamine
315 have been proposed from various potential interstellar,¹¹³⁻¹¹⁵ including nitric oxide (NO)^{45,22} which
316 has been detected in the gas phase towards several dark and warm clouds in high concentrations
317 relative to molecular hydrogen.¹¹⁶⁻¹¹⁸ Furthermore, the theoretical stability of ionized and
318 protonated hydroxyl amine in the ISM suggested that this compound would not react with
319 molecular hydrogen, and thus may be available for the synthesis of larger molecular species such
320 as amino acids.¹¹⁹

321 Hydroxylamine in any of its forms has not been isolated nor identified from carbonaceous
322 chondrites. However, this inorganic compound may be either present as its ammonia oxide isomer
323 (NH₃O) or decomposed into nitrogen oxide species (water, ammonia, and hydrogen) as a result of
324 catalytic effects of transition metals in water and thermal processing inside parent bodies.¹²⁰⁻¹²²
325 The meteoritic $\delta^{13}\text{C}$ ratios of acetic acid have been measured twice from two different pieces of
326 the Murchison meteorite showing contrasting values (Table 1);^{35,88} thus, further $\delta^{13}\text{C}$ analysis of
327 meteoritic acetic acid are needed in order to understand its potential meteoritic linkages to other
328 organic species. The synthesis of glycine from acetic acid and hydroxylamine (either on its ionized
329 or protonated form) is yet to be tested under meteoritic conditions; however, in the absence of
330 highly energetic processes like those resulting in molecular photodissociation, it may prove
331 challenging to propose the addition of hydroxylamine or any of its species to aliphatic moiety (sp³
332 carbon) such as that in acetic acid, and to avoid side reactions such as proton transfer with the
333 carbonyl group. Indeed, the more likely product may be acetamide formed from the dehydration
334 of ammonium acetate.

335 **Scheme 4.** The synthesis of glycine from acetic acid and hydroxylamine may be more
336 challenging inside the asteroid parent body than in interstellar environments.



337
338

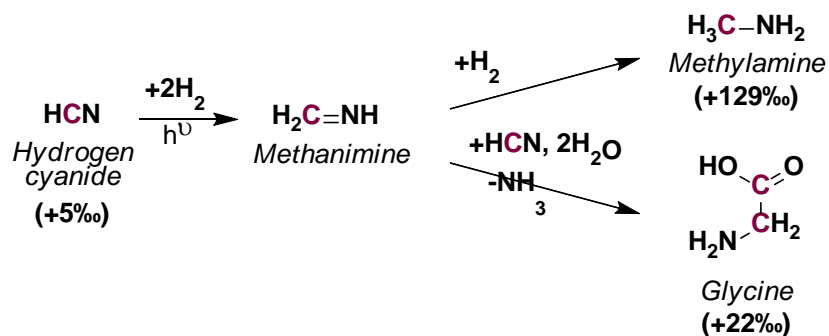
339 **3.4 Synthesis of glycine and methylamine from HCN and acetonitrile.** Scheme 5 shows the
340 synthesis of glycine and methylamine using HCN as starting material. HCN has been proposed as
341 a key starting material in interstellar ice chemistry for amino acids synthesis,^{24,27} the synthesis of
342 glycine from isotopically labeled methanol and HCN in UV-irradiated ices suggested that only
343 low amounts of glycine may form from the oxidation of methanol to formaldehyde in Strecker-
344 type synthesis, and that the majority of glycine (~60%) will preferentially form from HCN when
345 present.²⁷ Similarly, HCN may also be an important precursor of methylamine; Theulé et al.
346 (2011)³⁰ and Kim and Kaiser (2011)³¹ demonstrated the experimental hydrogenation of HCN
347 through the formation of methanimine as a stable intermediate to yield methylamine in ice-
348 irradiated interstellar analogs.

349 Amino acids may also be generated from alkylnitriles; Hudson et al. (2008) proposed the
350 synthesis of amino acids from a proton-irradiated interstellar ice analog composed of acetonitrile
351 and water only. This experiment suggested that the decomposition of acetonitrile would generate
352 HCN and other radical species which could serve as starting materials for the amino acids
353 observed.¹²³ Danger et al. (2011a,b) demonstrated the potential interconversion and synthesis of
354 various species including acetonitrile, α -aminoacetonitrile (a glycine precursor through acid
355 hydrolysis), HCN, and methanimine through thermal activation and VUV irradiation
356 respectively;^{95,124} suggesting that HCN and acetonitrile may be relevant species for the origins of
357 precursor molecules of glycine and methylamine prior to the formation of the parent body.
358 Although acetonitrile has been observed in interstellar environments,^{125,126} and could have
359 therefore been incorporated into asteroids, no aliphatic nitrile has yet been extracted and identified
360 from carbonaceous chondrites.

361 The measured $\delta^{13}\text{C}$ value of HCN from Murchison is ^{13}C -depleted relative to those found for
362 CO_2 , carbonates, methylamine, and glycine from the same meteorite (Table 1). As discussed
363 before, these isotopic differences may not be representative of their composition upon accretion
364 into the parent body; however, the $\delta^{13}\text{C}$ composition of HCN in Murchison may suggest it formed
365 from the ^{13}C -depleted interstellar carbon pool. The isolation of HCN from the Murchison meteorite
366 argues against its total decomposition through polymerization or oxidation, however, the
367 hydrogenation of HCN under parent body conditions to form methanimine would need to be tested
368 in order to consider the origins of glycine and methylamine from this species. Additionally, it
369 would be worth investigating the kinetic isotope effect of the hydrogenation of H^{12}CN and H^{13}CN ,

370 either through theoretical calculations or laboratory experiments in order to understand the
 371 expected isotopic relationship between HCN and its hydrogenation products. Along those lines,
 372 Huang and Sachtler (2000) found a strong D/H isotopic effect during hydrogenation of acetonitrile
 373 and deuterated acetonitrile (CH₃CN and CD₃CN respectively), showing that deuterium atoms add
 374 preferentially to the carbon atom, while hydrogen atoms added more selectively to the nitrogen
 375 atom.¹²⁷ The isolation of and δ¹³C analysis of alkylnitriles is also necessary to fully understand
 376 these potential meteoritic connections; however, if the decomposition of these organic species is
 377 required to form the observed meteoritic glycine and methylamine, it is challenging to propose a
 378 scenario inside the parent body in which these decomposition products would not be quenched by
 379 water or other parent body constituents.

380 **Scheme 5.** The hydrogenation of HCN has been tested through irradiation of interstellar-ice
 381 analogs. This synthetic model however, may need to be tested under parent body conditions to be
 382 considered as a plausible synthetic route for meteoritic glycine and methylamine.



383

384 4. Synergistic Approaches

385 In order to thoroughly understand and constrain the various chemical routes associated with
 386 the formation of meteoritic glycine and methylamine to a common set of molecular precursors, a
 387 multipronged approach that combines astronomical searches, theoretical modeling, and
 388 experimental work on reactions in the gas-phase and in interstellar ice analogs, together with the
 389 isolation and isotopic analysis of meteoritic species is needed. Organics that formed in the gas
 390 phase or in icy grains and their volatile precursors may have been incorporated into the protosolar
 391 nebula and later into solar bodies where synthetic and destructive processes also occurred.
 392 However, a potential linkage between the formation mechanisms of glycine and methylamine
 393 inside interstellar locations, their predicted isotopic outcomes, and their isotopic values registered
 394 from meteoritic analyses may provide novel constraints for the likelihood of one synthetic route
 395 over the other as summarized in Table 1.

396 All the molecules serving as potential starting materials for the synthesis of glycine and
 397 methylamine discussed here, i.e., CO, HCN, CO₂, acetic acid, formaldehyde, methanol,
 398 methanimine, and acetonitrile have been detected in various interstellar regions. Further work
 399 needs to be done focused on measuring the isotopic composition of these species and in the
 400 identification of ever more complex organics in the interstellar medium. More accurate isotope
 401 measurement in comets and protoplanetary disks will also help constrain the origins of complex
 402 organics by determining the original isotope ratios in each species. These ambitious tasks,
 403 however, may remain as pending challenges for a new generation of telescopes like The Atacama
 404 Large Millimeter/submillimeter Array (ALMA).

405 **Table 2.** Interstellar analogous synthesis of glycine and methylamine and their potential
 406 implications for their synthesis inside the parent body.

407

Synthesis from/by	Gly/methylamine seen in gas-phase reactions?	Gly/methylamine seen in irradiated ice analogs?	Possibility of reaction inside the asteroid parent body
CO and/or formaldehyde (Scheme 2)	n.d.	Yes ^{a,24-27}	Glycine may form through the Strecker synthesis
CO ₂ addition to methylamine (Scheme 3)	No ^a	Yes ¹⁰¹⁻¹⁰²	May produce methylcarbamic acid instead of glycine
HCN addition to methylamine (Scheme 3)	n.d.	n.d.*	May yield amidines or polymerization of HCN depending on abundances instead of glycine
NH ₃ /hydroxylamine addition to acetic acid (Scheme 4)	No ¹⁰⁹ /Yes ^{22,23}	n.d.*	May result in proton transfer reactions instead
HCN hydrogenation (Scheme 5)	n.d.	Yes ^{30,31}	Would depend on the reduction potential of the molecular environment

n.d: Experiment has not been performed or reported in the literature.

^aWhile ice analogs are usually a combination of CO, CO₂, methanol, HCN, and ammonia in water, it has been suggested that at least a portion of glycine and methylamine would form from the hydrogenation of CO to formaldehyde and subsequent Strecker reaction and nucleophilic substitution respectively (Scheme 2)²⁴⁻²⁷.

*This experiment may have not been performed or reported in the literature; however, it is very likely that glycine and methylamine will form from the molecular photodissociation of acetic acid and hydroxylamine to yield highly reactive radical/ionic species inside ice irradiated experiments.

408

409 While none of the discussed synthetic routes may be entirely discarded for the synthesis of
 410 glycine and methylamine until tested under simulated parent body conditions, the Strecker-
 411 cyanohydrin pathway (Scheme 2) is the only synthetic route that is compatible and complementary
 412 with the current knowledge of both interstellar processes and the meteoritic analyses. Addition of
 413 CO₂ (Scheme 3) to methylamine may result in the formation of methylcarbamic acid, while the

414 addition of HCN (Scheme 3) may confer an alternative route but may result in the synthesis of
415 amidines. The occurrence of methylcarbamic acid and amidines, however, may be necessary for
416 other catalytic processes that increase the overall molecular diversity inside the parent body.
417 Similarly, the addition of hydroxylamine to acetic acid to yield glycine (Scheme 4) seems unlikely
418 given the high potential for proton transfer reactions. Indeed, both the addition of CO₂ to
419 methylamine and the addition of hydroxylamine to acetic acid would need to occur through
420 breaking a C–H sp³ bond (present in methylamine or acetic acid), a process which may require
421 high energetic input or highly reactive species such as radicals. Amino acids and amines may be
422 generated from the formation of methanimine upon reduction or hydrogenation of HCN (Scheme
423 5); however, these processes may entirely depend on the nature of the reducing environment.
424 Finally, acetonitrile may decompose to yield cyanide ion (CN⁻), which may follow the same
425 pathway as HCN discussed above.

426 Laboratory experiments simulating reactions occurring in the gas-phase and at the surface of
427 interstellar ice particles provide powerful insights into the nature of the chemical processes inside
428 cold molecular clouds and star forming regions. We now understand that that a plethora of complex
429 organic molecules may result from the interaction of ionizing radiation (cosmic rays, UV photons,
430 soft X-rays, etc.) and a mixture of volatile hydrogen, carbon, nitrogen and oxygen sources (H₂O,
431 CO, CH₃OH, HCN, NH₃, etc.) in presolar and interstellar environments. However, greater effort
432 should now be placed on quantitative analysis focused on measuring reaction rates, as well as the
433 inherent molecular stability, abundance, isomeric distribution, and isotope effect of organic
434 products.

435 In addition, relatively little attention has been paid to the identification of these volatile species
436 from meteoritic sources and even fewer studies have been reported of their meteoritic isotopic
437 values. Several families of complex organic molecules such as PAHs, amino acids, amines and
438 carboxylic acid have been identified and isotopically characterized from carbonaceous
439 chondrites,^{10,88,89,128} however, much less is known about the abundance and isotopic distributions
440 of free CO, CO₂, HCN and ammonia (Yuen et al. 1984; Pizzarello et al. 2011; Pizzarello and
441 Williams 2012; Pizzarello 2014).^{35,58,93,94} Furthermore, the Murchison meteorite has been found to
442 contain a heterogeneous composition, meaning that different pieces analyzed may contain similar
443 but not the same molecular and isotopic distributions;^{89,129} therefore, it remains imperative to
444 expand the stable isotopic studies of CO, HCN, CO₂, and acetic acid, as these measurements have

445 only been performed on one meteorite for each compound. In addition, there are meteoritic organic
446 compounds such as alcohols, aldehydes, and ketones (e.g. formaldehyde and methanol) which
447 have been identified and quantified in Murchison and other meteorites, but without measurements
448 of their corresponding isotopic values, and there are other plausible intermediates such as
449 methanimine, alkylnitriles, aminonitriles, and hydroxynitrile that have not been searched for from
450 any meteorite. Without a thorough assessment of the abundance and isotopic composition of these
451 species, it remains difficult to investigate their potential synthetic relationship with more complex
452 compounds. These should be high priority targets for study in meteorites as well as the large
453 sample to be returned from asteroid Ryugu by JAXA's Hayabusa2 sample return mission in 2020
454 and from asteroid Bennu by NASA's OSIRIS-REx sample return mission in 2023.

455 **5. Conclusion**

456 Meteoritic glycine and methylamine may have formed in pre-solar environments and/or inside
457 meteorite parent bodies. Separating synthetic processes that may have occurred before the
458 formation of the parent body from those that occurred through aqueous and thermal processes
459 inside the parent body is challenging. Even more challenging is assessing the synthesis/destruction
460 of an original compound pool and the level of ^{13}C -fractionation experienced over different periods
461 of time and physicochemical conditions. Therefore, we face two main challenges which may be
462 solved through a future systematic quantification and experimental modeling. Evaluating the
463 effects of aqueous and thermal processing on the abundance and isotopic compositions of
464 meteoritic organic compounds may lead to a more comprehensive evaluation of the origins of
465 meteoritic organic compounds. Estimating the magnitude of fractionation expected during
466 synthesis and parent body processing remains highly challenging and much work is needed to fully
467 understand the kinetics and reaction efficiencies, as well as the pre-parent body molecular
468 abundances and isotopic compositions of these molecules.

469 We have evaluated the potential synthetic relationships between glycine and methylamine
470 using their isotopic compositions and those of their potential precursor molecules from the
471 Murchison meteorite. Our analysis aimed to evaluate various meteoritic species as probes into
472 parent body chemistry and to link proposed formation mechanisms with data collected through
473 astronomical observations, experiments in both the gas-phase and in irradiated ice interstellar
474 analogs, and theoretical modeling. However, the main conclusion of this exercise is that there is
475 still a large number of meteoritic and laboratory analyses, as well as telescopic observations, and

476 theoretical modeling that must be performed before there is sufficient data to fully understand the
477 synthesis of extraterrestrial organic compounds present in meteorites. Ideally, we would be able to
478 draw phase diagrams for the synthesis of glycine and methylamine with respect to variables such
479 as parent body temperatures and concentration of reactants for example; unfortunately, the original
480 molecular concentrations and isotopic compositions of the precursor molecules remain unknown.
481 Similarly we have only recently started to unveil the varying levels of aqueous and thermal effects
482 occurred in different parent bodies, albeit, the magnitude of this processing on the organic
483 composition of carbonaceous chondrites is still poorly understood, at least from a mechanistic
484 standpoint. Therefore, future interdisciplinary efforts are needed to further our understanding of
485 these and other meteoritic organic compounds.

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490 **REFERENCES**

- 491 (1) Oró, J. Comets and the formation of biochemical compounds on the primitive Earth.
492 *Nature* **1961**, *190*, 389-390.
- 493 (2) Anders, E. Pre-biotic organic matter from comets and asteroids. *Nature* **1989**, *342*, 255-
494 257.
- 495 (3) Chyba, C.; Sagan, C. Endogenous production, exogenous delivery and impact-shock
496 synthesis of organic molecules: an inventory for the origins of life. *Nature* **1992**, *355*, 125-
497 132.
- 498 (4) Botta, O.; Glavin, D. P.; Kminek, G.; Bada, J. L. Relative amino acid concentrations as a
499 signature for parent body processes of carbonaceous chondrites. *Orig. Life Evol. Biosph.*
500 **2002**, *32*, 143-163.
- 501 (5) Burton, A. S.; Stern, J. C.; Elsila, J. E.; Glavin, D. P.; Dworkin, J. P. Understanding
502 prebiotic chemistry through the analysis of extraterrestrial amino acids and nucleobases in
503 meteorites. *Chem. Soc. Rev.* **2012**, *41*, 5459-5472.
- 504 (6) Cobb, A. K.; Pudritz, R. E. Nature's starships. I. Observed abundances and relative
505 frequencies of amino acids in meteorites. *Astrophys. J.* **2014**, *783*, 140 (12pp).
- 506 (7) Elsila, J. E.; Aponte, J. C.; Blackmond, D. G.; Burton, A. S.; Dworkin, J. P.; Glavin, D. P.
507 Meteoritic amino acids: Diversity in compositions reflects parent body histories. *ACS*
508 *Cent. Sci.* **2016**, *2*, 370-379.
- 509 (8) Aponte, J. C.; Dworkin, J. P.; Elsila, J. E. Assessing the origins of aliphatic amines in the
510 Murchison meteorite from their compound-specific carbon isotopic ratios and
511 enantiomeric composition. *Geochim. Cosmochim. Acta* **2014**, *141*, 331-345.
- 512 (9) Aponte, J. C.; Dworkin, J. P.; Elsila, J. E. Indigenous aliphatic amines in the aqueously
513 altered Orgueil meteorite. *Meteorit. Planet. Sci.* **2015**, *50*, 1733-1749.
- 514 (10) Aponte, J. C.; McLain, H. L.; Dworkin, J. P.; Elsila, J. E. Aliphatic Amines in Antarctic
515 CR2, CM2 and CM1/2 Carbonaceous Chondrites. *Geochim. Cosmochim. Acta* **2016**, *189*,
516 296-311.
- 517 (11) Pizzarello, S.; Yarnes, T. Enantiomeric excesses of chiral amines in ammonia-rich
518 carbonaceous meteorites. *Earth Planet. Sci. Lett.* **2016**, *443*, 176-184.
- 519 (12) Jungclaus, G. A.; Cronin, J. R.; Moore, C. B.; Yuen, G. U. Aliphatic amines in the
520 Murchison meteorite. *Nature* **1976**, *261*, 126-128.
- 521 (13) Pizzarello, S.; Feng, X.; Epstein, S.; Cronin, J. R. Isotopic analyses of nitrogenous
522 compounds from the Murchison meteorite: ammonia, amines, amino acids, and polar
523 hydrocarbons. *Geochim. Cosmochim. Acta* **1994**, *58*, 5579-5587.

- 524 (14) Pizzarello, S.; Holmes, W. Nitrogen-containing compounds in two CR2 meteorites: ¹⁵N
525 composition, molecular distribution and precursor molecules. *Geochim. Cosmochim. Acta*
526 **2009**, *73*, 2150-2162.
- 527 (15) Sandford, S. A.; Aléon, J.; Alexander, C. M. O'D.; Araki, T.; Bajt, S.; Baratta, G. A.; Borg,
528 J.; Brucato, J. R.; Burchell, M. J.; Busemann, H.; Butterworth, A.; Clemett, S. J.; Cody, G.;
529 Colangeli, L.; Cooper, G.; D'Hendecourt, L.; Djouadi, Z.; Dworkin, J. P.; Ferrini, G.;
530 Fleckenstein, H.; Flynn, G. J.; Franchi, I. A.; Fries, M.; Gilles, M. K.; Glavin, D. P.;
531 Gounelle, M.; Grossemy, F.; Jacobsen, C.; Keller, L. P.; Kilcoyne, D.; Leitner, J.; Matrajt,
532 G.; Meibom, A.; Mennella, V.; Mostefaoui, S.; Nittler, L. R.; Palumbo, M. E.; Robert, F.;
533 Rotundi, A.; Snead, C. J.; Spender, M. K.; Steele, A.; Stephan, T.; Tyliszczak, T.; Westphal,
534 A. J.; Wirick, S.; Wopenka, B.; Yabuta, H.; Zare, R. N.; Zolensky, M. Organics captured
535 from comet Wild 2 by the Stardust spacecraft. *Science* **2006**, *314*, 1720-1724.
- 536 (16) Glavin, D. P.; Dworkin, J. P.; Sandford, S. A. Detection of cometary amines in samples
537 returned by Stardust. *Meteorit. Planet. Sci.* **2008**, *43*, 399-413.
- 538 (17) Elsila, J. E.; Glavin, D. P.; Dworkin, J. P. Cometary glycine detected in samples returned
539 by Stardust. *Meteorit. Planet. Sci.* **2009**, *44*, 1323-1330.
- 540 (18) Altwegg, K.; Balsiger, H.; Bar-Nun, A.; Berthelier, J.-J.; Bieler, A.; Bochler, P.; Briois,
541 C.; Calmonte, U.; Combi, M. R.; Cottin, H.; De Keyser, J.; Dhooghe, F.; Fiethe, B.; Fuselier,
542 S. A.; Gasc, S.; Gombosi, T. I.; Hansen, K. C.; Haessig, M.; Jäckel, A.; Kopp, E.; Korth,
543 A.; Le Roy, L.; Mall, U.; Marty, B.; Mousis, O.; Owen, T.; Rème, H.; Rubin, M.; Sémon,
544 T.; Tzou, C.-Y.; Waite, J. H.; Wurz, P. Prebiotic chemicals -amino acid and phosphorus- in
545 the coma of comet 67P/Churyumov-Gerasimenko. *Sci. Adv.* **2016**, *2*, e1600285.
- 546 (19) Goesmann, F.; Rosenbauer, H.; Bredehöft, J. H.; Cabane, M.; Ehrenfreund, P.; Gautier, T.;
547 Giri, C.; Krüger, H.; Le Roy, L.; MacDermott, A. J.; McKenna-Lawlor, S.; Meierhenrich,
548 U. J.; Muñoz-Caro, G. M.; Raulin, F.; Roll, R.; Steele, A.; Steininger, H.; Sternberg, R.;
549 Szopa, C.; Thiemann, W.; Ulamec, S. Organic compounds on comet 67P/Churyumov-
550 Gerasimenko revealed by COSAC mass spectrometry. *Science* **2015**, *349*, aab0689.
- 551 (20) Gardner, E. P.; McNesby, J. R. Methylamine formation in the vacuum ultraviolet photolysis
552 of methane and ammonia mixtures. *J. Photochem.* **1980**, *113*, 353-356.
- 553 (21) Ogura, K.; Migita, C. T.; Yamada, T. Photochemical formation of methylamine and
554 ethylenediamine from gas mixtures of methane, ammonia, and water. *Chem. Lett.* **1988**,
555 1563-1566.
- 556 (22) Blagojevic, V.; Petrie, S.; Bohme, D. K. Gas-phase syntheses for interstellar carboxylic and
557 amino acids. *Mon. Not. Astron. Soc.* **2003**, *339*, L7-L11.
- 558 (23) Snow, J. L.; Orlova, G.; Blagojevic, V.; Bohme, D. K. Gas-phase ionic syntheses of amino
559 acids: β versus α . *J. Am. Chem. Soc.* **2007**, *129*, 9910-9917.
- 560 (24) Bernstein, M. P.; Dworkin, J. P.; Sandford, S. A.; Cooper, G. W.; Allamandola, L. J.
561 Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature*
562 **2002**, *416*, 401-403.
- 563 (25) Muñoz-Caro, G. M.; Meierhenrich, U. J.; Schutte, W. A.; Barbier, B.; Segovia, A. A.;
564 Rosenbauer, H.; Thiemann, W. H.-P.; Brack, A.; Greenberg, J. M. Amino acids from
565 ultraviolet irradiation of interstellar ice analogues. *Nature* **2002**, *416*, 403-406.
- 566 (26) Nuevo, M.; Meierhenrich, U. J.; Muñoz-Caro, G. M.; Dartois, E.; D'Hendecourt, L.;
567 Deboffle, D.; Auger, G.; Blanot, D.; Bredehöft, J.-H.; Nahon, L. The effects of circularly
568 polarized light on amino acid enantiomers produced by the UV irradiation of interstellar ice
569 analogs. *Astron. Astrophys.* **2006**, *457*, 741-751.

- 570 (27) Elsila, J. E.; Dworkin, J. P.; Bernstein, M. P.; Martin, M. P.; Sandford, S. A. Mechanisms
571 of amino acid formation in interstellar ice analogs. *Astrophys. J.* **2007**, *660*, 911-918.
- 572 (28) Takano, Y.; Takahashi, J.; Kaneko, T.; Marumo, K.; Kobayashi, K. Asymmetric synthesis
573 of amino acid precursors in interstellar complex organics by circularly polarized light. *Earth*
574 *Planet Sci. Lett.* **2007**, *254*, 106-114.
- 575 (29) De Marcellus, P.; Meinert, C.; Nuevo, M.; Filippi, J.-J.; Danger, G.; Deboffle, D.; Nahon,
576 L.; Le S. d'Hendecourt, L.; Meierhenrich, U. J. Non-racemic amino acid production by
577 ultraviolet irradiation of achiral interstellar ice analogs with circularly polarized light.
578 *Astrophys. J. Lett.* **2011**, *727*, L27 (6pp).
- 579 (30) Theulé, P.; Borget, F.; Mispelaer, F.; Danger, G.; Duvernay, F.; Guillemin, J. C.; Chiavassa,
580 T. Hydrogenation of solid hydrogen cyanide HCN and methanimine CH₂NH at low
581 temperature. *Astron. Astrophysics.* **2011**, *534*, A64 (6pp).
- 582 (31) Kim, Y. S.; Kaiser, R. I. On the formation of amines (RNH₂) and the cyanide anion (CN⁻)
583 in electron-irradiated ammonia–hydrocarbon interstellar model ices. *Astrophys. J.* **2011**,
584 *829*, 68 (7pp).
- 585 (32) Modica, P.; Meinert, C.; De Marcellus, P.; Nahon, L.; Meierhenrich, U. J.; Le S.
586 d'Hendecourt, L. Enantiomeric excesses induced in amino acids by ultraviolet circularly
587 polarized light irradiation of extraterrestrial ice analogs: A possible source of asymmetry
588 for prebiotic chemistry. *Astrophys. J. Lett.* **2014**, *788*, 79 (11pp).
- 589 (33) Miller, S. L. A production of amino acids under possible primitive Earth conditions. *Science*
590 **1953**, *117*, 528-529.
- 591 (34) Parker, E. T. ; Cleaves, H. J.; Dworkin, J. P.; Glavin, D. P. ; Callahan, M.; Aubrey, A.;
592 Lazcano, A.; Bada, J. L. Primordial synthesis of amines and amino acids in a 1958 Miller
593 H₂S-rich spark discharge experiment. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 5526-5531.
- 594 (35) Yuen, G.; Blair, N.; Des Marais, D. J.; Chang, S. Carbon isotopic composition of individual,
595 low molecular weight hydrocarbons and monocarboxylic acids from the Murchison
596 meteorite. *Nature* **1984**, *307*, 252-254.
- 597 (36) Sandford, S. A.; Bernstein, M. P.; Dworkin, J. P. Assessment of the interstellar processes
598 leading to deuterium enrichment in meteoritic organics. *Meteor. Planet. Sci.* **2001**, *36*, 1117-
599 1133.
- 600 (37) Robert, F. The D/H ratio in chondrites. *Space Sci. Rev.* **2003**, *106*, 87-101.
- 601 (38) Le Guillou, C.; Bernard, S.; Brearley, A. J.; Remusat, L. Evolution of organic matter in
602 Orgueil, Murchison and Renazzo during parent body aqueous alteration: In situ
603 investigations. *Geochim. Cosmochim. Acta* **2014**, *131*, 368-392.
- 604 (39) Beck, P.; Garenne, A.; Quirico, E.; Bonal, L.; Montes-Hernandez, G.; Moynier, F.; Schmitt,
605 B. Transmission infrared spectra (2–25 μm) of carbonaceous chondrites (CI, CM, CV-CK,
606 CR, C2 ungrouped): Mineralogy, water, and asteroidal processes. *Icarus* **2014**, *229*, 263-
607 277.
- 608 (40) McAdam, M. M.; Sunshine, J. M.; Howard, K. T.; McCoy, T. M. Aqueous alteration on
609 asteroids: Linking the mineralogy and spectroscopy of CM and CI chondrites. *Icarus* **2015**,
610 *245*, 320-332.
- 611 (41) Kaluna, H. M.; Masiero, J. R.; Meech, K. J. Space weathering trends among carbonaceous
612 asteroids. *Icarus* **2016**, *264*, 62-71
- 613 (42) Tielens, A. G. G. M.; Hagen, W. Model calculations of the molecular composition of
614 interstellar grain mantles. *Astron. Astrophys.* **1982**, *114*, 245-260.

- 615 (43) Charnley, S. B. On the Nature of Interstellar Organic Chemistry, in *Astronomical and*
616 *Biochemical Origins and the Search for Life in the Universe*, eds. C.B. Cosmovici, S.
617 Bowyer & D. Werthimer, Editrice Compositori, Bologna, p. 89, 1997.
- 618 (44) Ehrenfreund, P.; Charnley, S. B. Organic molecules in the interstellar medium, comets, and
619 meteorites: A voyage from dark clouds to the early Earth. *Annu. Rev. Astron. Astrophys.*
620 **2000**, *38*, 427-483.
- 621 (45) Charnley, S. B. The Bridge between the Big Bang and Biology, ed. F. Giovannelli,
622 Consiglio Nazionale delle Ricerche, Italy, p. 139, 2001.
- 623 (46) Charnley, S. B.; Rodgers, S. D. Clouds, clumps, cores and comets– a cosmic chemical
624 connection? *Adv. Geosci.* **2009**, *15*, 211.
- 625 (47) Taquet, V.; Wirström, E.; Charnley, S. B. Formation and recondensation of complex organic
626 molecules during protostellar luminosity outbursts. *Astrophys. J.* **2016**, *821*, 46 (12pp).
- 627 (48) Ziurys, L. M. The chemistry in circumstellar envelopes of evolved stars: Following the
628 origin of the elements to the origin of life. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 12274-
629 12279.
- 630 (49) Herbst, E.; van Dishoeck, E. F. Complex organic interstellar molecules. *Annu. Rev. Astro.*
631 *Astrophys.* **2009**, *47*, 427-480.
- 632 (50) Öberg, K. I.; Fayolle, E. C.; Reiter, J. B.; Cyganowski, C. Complex molecule formation
633 around massive young stellar objects. *Farad. Discuss.* **2014**, *168*, 81-101.
- 634 (51) Turner, B. E. Detection of doubly deuterated interstellar formaldehyde (D₂CO) - an
635 indicator of active grain surface chemistry. *Astrophys. J. Lett.* **1990**, *362*, L29-L33.
- 636 (52) Latter, W. B.; Walker, C. K.; Maloney, P. R. Detection of the carbon monoxide ion (CO⁺)
637 in the interstellar medium and a planetary nebula. *Astrophys. J.* **1993**, *419*, L97-L100.
- 638 (53) Ohishi, M.; Ishikawa, S.-I.; Amano, T.; Oka, H.; Irvine, W. M.; Dickens, J. E. Detection of
639 a new interstellar molecular ion, H₂COH⁺ (protonated formaldehyde). *Astrophys. J. Lett.*
640 **1996**, *471*, L61-L64.
- 641 (54) Bacmann, A.; García-García, E.; Faure, A. Detection of protonated formaldehyde in the
642 prestellar core L1689B. *Astron. Astrophys.* **2016**, *588*, L8.
- 643 (55) Jehin, E.; Manfroid, J.; Hutsemékers, D.; Arpigny, C.; Zucconi, J.-M. Isotopic ratios in
644 comets: Status and perspectives. *Earth Moon Planet* **2009**, *105*, 167-180.
- 645 (56) Mumma M. J.; Charnley, S. B. The chemical composition of comets-emerging taxonomies
646 and natal heritage. *Annu. Rev. Astron. Astrophys.* **2011**, *49*, 471-524.
- 647 (57) A'Hearn, M. F.; M. Feaga, L.; Keller, H. U.; Kawakita, H.; Hampton, D. L.; Kissel, J.;
648 Klaasen, K. P.; McFadden, L. A.; Meech, K. J.; Schultz, P. H.; Sunshine, J. M.; Thomas, P.
649 C.; Veverka, J.; Yeomans, D. K.; Besse, S.; Bodewits, D.; Farnham, T. L.; Groussin, O.;
650 Kelley, M. S.; Lisse, C. M.; Merlin, F.; Protopapa, S.; Wellnitz, D. D. Cometary volatiles
651 and the origin of comets. *Astrophys. J.* **2012**, *758*, 29 (8pp).
- 652 (58) Pizzarello, S. The nitrogen isotopic composition of meteoritic HCN. *Astrophys. J. Lett.*
653 **2014**, *796*, L25 (4pp).
- 654 (59) Kuan, Y.-J.; Charnley, S. B.; Huang, H.-C.; Tseng, W.-L.; Kisiel, Z. Interstellar glycine.
655 *Astrophys. J.* **2003**, *593*, 848-867.
- 656 (60) Ceccarelli, C.; Loinard, L.; Castets, A.; Faure, A.; Lefloch, B. Search for glycine in the solar
657 type protostar IRAS 16293-2422. *Astron. Astrophys.* **2000**, *362*, 1122-1126.
- 658 (61) Snyder, L. E.; Lovas, F. J.; Hollis, J. M.; Friedel, D. N.; Jewell, P. R.; Remijan, A.; Ilyushin,
659 V. V.; Alekseev, E. A.; Dyubko, S. F. A rigorous attempt to verify interstellar glycine.
660 *Astrophys. J.* **2005**, *619*, 914-930.

- 661 (62) Woon, D. E. Pathways to glycine and other amino acids in ultraviolet-irradiated
662 astrophysical ices determined via chemical modeling. *Astrophys. J.* **2002**, *571*, L177-L180.
- 663 (63) Largo, L.; Redondo, P.; Rayón, V. M.; Largo, A.; Barrientos, C. The reaction between NH_3^+
664 and CH_3COOH : A possible process for the formation of glycine precursors in the interstellar
665 medium. *Astron. Astrophys.* 2010, **516**, A79-A86.
- 666 (64) Pilling, S.; Baptista, L.; Boechat-Roberty, H. M.; Andrade, D. P. P. Formation routes of
667 interstellar glycine involving carboxylic acids: Possible favoritism between gas and solid
668 phase *Astrobiology* **2011**, *11*, 883-893.
- 669 (65) Nhlabatsi, Z. P.; Bhasi, P.; Sitha, S. Possible interstellar formation of glycine from the
670 reaction of $\text{CH}_2=\text{NH}$, CO and H_2O : Catalysis by extra water molecules through the
671 hydrogen relay transport. *Phys. Chem. Chem. Phys.* **2016**, *18*, 375-381.
- 672 (66) Kaifu, N.; Morimoto, M.; Nagane, K.; Akabane, K.; Iguchi, T.; Takagi, K. Detection of
673 interstellar methylamine. *Astrophys. J.* **1974**, *191*, L135-L137.
- 674 (67) Fourikis, N.; Takagi, K.; Saito, S. Probable detection of interstellar methylamine-D
675 (CH_3NHD). *Astrophys. J.* **1977**, *212*, L33-L37.
- 676 (68) Dickens, J. E.; Irvine, W. M.; DeVries, C. H.; Ohishi, M. Hydrogenation of interstellar
677 molecules: A survey for methylenimine (CH_2NH). *Astrophys. J.* **1997**, *479*, 307-312.
- 678 (69) Halfen, D. T.; Ilyushin, V. V.; Ziurys, L. M. Insights into surface hydrogenation in the
679 interstellar medium: Observations of methanimine and methyl amine in Sgr B2(N). The
680 *Astrophys. J.* **2013**, *797*, 66 (11pp).
- 681 (70) Suzuki, T.; Ohishi, M.; Hirota, T.; Saito, M.; Majumdar, L.; Wakelam, V. Survey
682 observations of a possible glycine precursor, methanimine (CH_2NH). *Astrophys. J.* **2016**,
683 *825*, 79 (14pp).
- 684 (71) Smith, R. L.; Pontoppidan, K. M.; Young, E. D.; Morris M. R.. Heterogeneity in $^{12}\text{CO}/^{13}\text{CO}$
685 abundance ratios toward solar-type young stellar objects. *Astrophys. J.* **2015**, *813*, 120
686 (16pp).
- 687 (72) Scott, P. C.; Asplund, M.; Grevesse, N.; Sauval, A. J. Line formation in solar granulation.
688 VII. CO lines and the solar C and O isotopic abundances. *Astron. Astrophys.* **2006**, *456*,
689 675-688.
- 690 (73) Qi, C.; D'Alessio, P.; Öberg, K. I.; Wilner, D. J.; Hughes, A. M.; Andrews, S. M.;
691 Ayala, S. Resolving the CO snow line in the disk around HD 163296. *Astrophys. J.* **2011**,
692 *740*, 84 (18pp).
- 693 (74) Woods, P. M.; Willacy, K. Carbon isotope fractionation in protoplanetary disks. *Astrophys.*
694 *J.* **2009**, *693*, 1360-1378.
- 695 (75) Langer, W. D.; Graedel, T. E.; Frerking, M. A.; Armentrout, P. B. Carbon and oxygen
696 isotope fractionation in dense interstellar clouds. *Astrophys. J.* **1984**, *277*, 581-604.
- 697 (76) Sakai, N.; Saruwatari, O.; Sakai, T.; Takano, S.; Yamamoto, S. Abundance anomaly of the
698 ^{13}C species of CCH. *Astron. Astrophys.* **2010**, *512*, A31 (10pp).
- 699 (77) Yoshida, K.; Sakai, N.; Tokudome, T.; López-Sepulcre, A.; Watanabe, Y.; Takano, S.;
700 Lefloch, B.; Ceccarelli, C.; Bachiller, R.; Caux, E.; Vastel, C.; Yamamoto, S. Abundance
701 anomaly of the ^{13}C isotopic species of c- C_3H_2 in the low-mass star formation region L1527.
702 *Astrophys. J.* **2015**, *807*, 66 (9pp).
- 703 (78) Wirström, E. S.; Charnley, S. B.; Geppert, W. D.; Persson, C. M. Observations of carbon
704 isotopic fractionation in interstellar formaldehyde (abstract #1161). 43rd Lunar and
705 Planetary Science Conference 2012, CD-ROM.

- 706 (79) Milam, S. N.; Savage, C.; Brewster, M. A.; Ziurys, L. M.; Wyckoff, S. The $^{12}\text{C}/^{13}\text{C}$ isotope
707 gradient derived from millimeter transitions of CN: The case for galactic chemical
708 evolution. *Astrophys. J.* **2005**, *634*, 1126-1132.
- 709 (80) Des Marais, D. J.; Donchin, J. H.; Nehring, N. L.; Truesdell, A. H. Molecular carbon
710 isotopic evidence for the origin of geothermal hydrocarbons. *Nature* **1981**, *292*, 826-828.
- 711 (81) Chang, S.; Des Marais, D. J.; Mack, R.; Miller, S. L.; Strathearn, G. Earth's Earliest
712 Biosphere: Its Origin and Early Evolution. ed. J. W. Schopf. Princeton University Press,
713 1983.
- 714 (82) Grady, M. M.; Wright, I. P.; Swart, P. K.; Pillinger, C. T. The carbon and oxygen isotopic
715 composition of meteoritic carbonates. *Geochim. Cosmochim. Acta* **1988**, *52*, 2855-2866.
- 716 (83) Cody, G. D.; Alexander, C. M. O'D. NMR studies of chemical structural variation of
717 insoluble organic matter from different carbonaceous chondrite groups. *Geochim.*
718 *Cosmochim. Acta* **2005**, *69*, 1085-1097.
- 719 (84) Alexander, M. O'D.; Bowden, R.; Fogel, M. L.; Howard, K. T. Carbonate abundances and
720 isotopic compositions in chondrites. *Meteorit. Planet. Sci.* **2015**, *50*, 523-849.
- 721 (85) Ehrenfreund, P.; Glavin, D. P.; Botta, O.; Cooper, G.; Bada, J. L. Extraterrestrial amino
722 acids in Orgueil and Ivuna: Tracing the parent body of CI type carbonaceous chondrites.
723 *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 2138-2141.
- 724 (86) Glavin, D. P.; Callahan, M. P.; Dworkin, J. P.; Elsila, J. E. The effects of parent body
725 processes on amino acids in carbonaceous chondrites. *Meteorit. Planet. Sci.* **2010**, *45*, 1948-
726 1972.
- 727 (87) Alexander, C. M. O'D.; Bowden, R.; Fogel, M. L.; Howard, K. T.; Herd, C. D. K.; Nittler,
728 L. R. The provenances of asteroids, and their contributions to the volatile inventories of the
729 terrestrial planets. *Science* **2012**, *337*, 721-723.
- 730 (88) Huang, Y.; Wang, Y.; Alexandre, M. R.; Lee, T.; Rose-Petruck, C.; Fuller, M.; Pizzarello,
731 S. Molecular and compound-specific isotopic characterization of monocarboxylic acids in
732 carbonaceous meteorites. *Geochim. Cosmochim. Acta* **2005**, *69*, 1073-1084.
- 733 (89) Elsila, J. E.; Charnley, S. B.; Burton, A. S.; Glavin, D. P.; Dworkin, J. P. Compound-specific
734 carbon, nitrogen, and hydrogen isotopic ratios for amino acids in CM and CR chondrites
735 and their use in evaluating potential formation pathways. *Meteor. Planet. Sci.* **2012**, *47*,
736 1517-1536.
- 737 (90) Engel, M. H.; Macko, S. A.; Silfer, J. A. Carbon isotope composition of individual amino
738 acids in the Murchison meteorite. *Nature* **1990**, *348*, 47-49.
- 739 (91) Pizzarello, S.; Huang, Y.; Fuller, M. The carbon isotopic distribution of Murchison amino
740 acids. *Geochim. Cosmochim. Acta* **2004**, *68*, 4963-4969.
- 741 (92) Martins, Z.; Alexander, C. M. O'D.; Orzechowska, G. E.; Fogel, M. L.; Ehrenfreund, P.
742 Indigenous amino acids in primitive CR meteorites. *Meteorit. Planet. Sci.* **2007**, *42*, 2125-
743 2136.
- 744 (93) Pizzarello, S.; Williams, L. B. Ammonia in the early Solar System: An account from
745 carbonaceous meteorites. *Astrophys. J.* **2012**, *749*, 161 (6pp).
- 746 (94) Pizzarello, S.; Williams, L. B.; Lehman, J.; Holland, G. P.; Yarger, J. L. Abundant ammonia
747 in primitive asteroids and the case for a possible exobiology. *Proc. Natl. Acad. Sci. USA*
748 **2011**, *108*, 4303-4306.
- 749 (95) Danger, G.; Borget, F.; Chomat, M.; Duvernay, F.; Theulé, P.; Guillemin, J.-C.;
750 d'Hendecourt, L. L. S.; Chiavassa, T. Experimental investigation of aminoacetonitrile
751 formation through the Strecker synthesis in astrophysical-like conditions: Reactivity of

- 752 methanimine (CH₂NH), ammonia (NH₃), and hydrogen cyanide (HCN). *Astron. Astrophys.*
753 **2011a**, 535, A47 (9pp).
- 754 (96) Peltzer, E. T.; Bada, J. L.; Schlesinger, G.; Miller, S. L. The chemical conditions on the
755 parent body of the Murchison meteorite: some conclusions based on amino, hydroxy and
756 dicarboxylic acids. *Adv. Space Res.* **1984**, 4, 69-74.
- 757 (97) Lerner, N. R.; Peterson, E.; Chang, S. The Strecker synthesis as a source of amino acids in
758 carbonaceous chondrites—Deuterium retention during synthesis. *Geochim. Cosmochim.*
759 *Acta* **1993**, 57, 4713-4723.
- 760 (98) Gunanathan, C.; Milstein, D. Selective synthesis of primary amines directly from alcohols
761 and ammonia. *Angew. Chem. Int. Ed.* **2008**, 47, 8661-8664.
- 762 (99) Shimizu, K.; Kon, K.; Onodera, W.; Yamazaki, H.; Kondo, J. N. Heterogeneous Ni catalyst
763 for direct synthesis of primary amines from alcohols and ammonia. *ACS Catal.* **2013**, 3,
764 112-117.
- 765 (100) Yan, T.; Feringa, B. L.; Barta, K. Iron catalysed direct alkylation of amines with alcohols.
766 *Nature Commun.* **2014**, 5, 5602.
- 767 (101) Jackson, D. M.; Stibrich, N. J.; Adams, N. G.; Babcock, L. M. A selected ion flow tube
768 study of the reactions of a sequence of ions with amines. *Int. J. Mass Spectrom.* **2005**, 243,
769 115-120.
- 770 (102) Holtom, P. D.; Bennett, C. J.; Osamura, Y.; Mason, N. J.; Kaiser, R. I. A combined
771 experimental and theoretical study on the formation of the amino acid glycine
772 (NH₂CH₂COOH) and its isomer (CH₃NHCOOH) in extraterrestrial ices. *Astrophys. J.* **2005**,
773 626, 940-952.
- 774 (103) Hudson, R. L.; Lewis, A. S.; Moore, M. H.; Dworkin, J. P.; Martin, M. P. Enigmatic
775 isovaline: Investigating the stability, racemization, and formation of a non-biological
776 meteoritic amino acid. *Astron. Soc. Pacific Conf. Series* **2009**, 420, 157-162.
- 777 (104) Bossa, J.-B.; Duvernay, F.; Theulé, P.; Borget, F.; d'Hendecourt, L.; Chiavassa, T.
778 Methylammonium methylcarbamate thermal formation in interstellar Ice analogs: a glycine
779 salt precursor in protostellar environments. *Astron. Astrophys.* **2009**, 506, 601-608.
- 780 (105) Lee, C.-W.; Kim, J.-K.; Moon, E.-S.; Minh, Y. C.; Kang, H. Formation of glycine on
781 ultraviolet-irradiated interstellar ice-analog films and implications for interstellar amino
782 acids. *Astrophys. J.* **2009**, 697, 428-435.
- 783 (106) Murphy, L. J.; Robertson, K. N.; Kemp, R. A.; Tuononen, H. M.; Clyburne, J. A. C.
784 Structurally simple complexes of CO₂. *Chem. Commun.* **2015**, 51, 3942-3956.
- 785 (107) Mohammed, F. S.; Kitchens, C. L. Reduced reactivity of amines against nucleophilic
786 substitution via reversible reaction with carbon dioxide. *Molecules* **2016**, 21 (11pp).
- 787 (108) Erickson, J. G. Reactions of some amines with hydrogen cyanide. *J. Org. Chem.* **1955**, 20,
788 1569-1572.
- 789 (109) Wang, J.; Xu, F.; Cai, T.; Shen, Q. Addition of amines to nitriles catalyzed by ytterbium
790 amides: An efficient one-step synthesis of monosubstituted *n*-arylamidines. *Org. Lett.* **2008**,
791 10, 445-448.
- 792 (110) Jackson, D. M.; Stibrich, N. J.; McLain, J. L.; Fondren, L. D.; Adams, N. G.; Babcock, L.
793 M. A selected ion flow tube study of the reactions of various nitrogen containing ions with
794 formic acid, acetic acid, and methyl formate. *Int. J. Mass Spectrom.* **2005**, 247, 55-60.
- 795 (111) Pulliam, R. L.; McGuire, B. A.; Remijan, A. J. A search for hydroxylamine (NH₂OH)
796 toward select astronomical sources. *Astrophys. J.* **2012**, 751, 1 (7pp).

- 797 (112) McGuire, B. A.; Carroll, P. B.; Dollhopf, N. M.; Crockett, N. R.; Corby, J. F.; Loomis, R.
798 A.; Burkhardt, A. M.; Shingledecker, C.; Blake, G. A.; Remijan, A. J. CSO and CARMA
799 observations of L1157. I. A deep search for hydroxylamine (NH₂OH). *Astrophys. J.* **2015**,
800 *812*, 76 (9pp).
- 801 (113) Nishi, N.; Shinohara, H.; Okuyama, T. Photodetachment, photodissociation, and
802 photochemistry of surface molecules of icy solids containing NH₃ and pure H₂O ices. *J.*
803 *Chem. Phys.* **1984**, *80*, 3898-3910.
- 804 (114) Zheng, W.; Kaiser, R. I. Formation of hydroxylamine (NH₂OH) in electron-irradiated
805 ammonia-water ices. *J. Phys. Chem. A* **2010**, *114*, 5251-5255.
- 806 (115) He, J.; Vidali, G.; Lemaire, J.-L.; Garrod, R. T. Formation of hydroxylamine on dust grains
807 via ammonia oxidation. *Astrophys. J.* **2015**, *799*, 49 (9pp).
- 808 (116) Liszt, H. S.; Turner, B. E. Microwave detection of NO. *Astrophys. J.* **1978**, *224*, L73-L76.
- 809 (117) McGonagle, D.; Ziurys, L. M.; Irvine, W. M.; Minh, Y. C. Detection of nitric oxide in the
810 dark cloud L134N. *Astrophys. J.* **1990**, *359*, 121-124.
- 811 (118) Gerin, M.; Viala, Y.; Pauzat, F.; Ellinger, Y. The abundance of nitric oxide in molecular
812 clouds. *Astron. Astrophys.* **1992**, *266*, 463-478.
- 813 (119) Largo, L.; Rayón, V. M.; Barrientos, C.; Largo, A.; Redondo, P. Stability of protonated and
814 ionized hydroxylamine in the interstellar medium. *Chem. Phys. Lett.* **2009**, *476*, 174-177.
- 815 (120) Iwata, Y.; Koseki, H. Decomposition of hydroxylamine/water solution with added iron ion.
816 *J. Hazard. Mater.* **2003**, *104*, 39-49.
- 817 (121) Wang, Q.; Wei, C.; Pérez, L. M.; Rogers, W. J.; Hall, M. B.; Mannan, M. S. Thermal
818 decomposition pathways of hydroxylamine: Theoretical investigation on the initial steps. *J.*
819 *Phys. Chem. A* **2010**, *114*, 9262-9269.
- 820 (122) Adamopoulou, T.; Papadaki, M. I.; Kounalakis, M.; Vazquez-Carretero, V.; Pineda-Solano,
821 A.; Wang, Q.; Mannan, M. S. *J. Hazard. Mater.* **2013**, *254-255*, 382-389.
- 822 (123) Hudson, R. L.; Moore, M. H.; Dworkin, J. P.; Martin, M. P.; Pozun, Z. D. Amino acids from
823 ion-irradiated nitrile-containing ices. *Astrobiology* **2008**, *8*, 771-779.
- 824 (124) Danger, G.; Bossa, J.-B.; de Marcellus, P.; Borget, F.; Duvernay, F.; Theulé, P.; Chiavassa,
825 T.; d'Hendecourt, L. Experimental investigation of nitrile formation from VUV
826 photochemistry of interstellar ices analogs: Acetonitrile and amino acetonitrile. *Astron.*
827 *Astrophys.* **2011b**, *525*, A30 (6pp).
- 828 (125) Bell, M. B.; Avery, L. W.; MacLeod, J. M.; Matthews, H. E. The excitation temperature of
829 HC₉N in the circumstellar envelope. *Astrophys. J.* **1992**, *400*, 551-555.
- 830 (126) Öberg, K. I.; Guzman, V. V.; Furuya, K.; Qi, C.; Aikawa, Y.; Andrews, S. M.; Loomis, R.;
831 Wilner, D. J. The comet-like composition of a protoplanetary disk as revealed by complex
832 cyanides. *Nature* **2015**, *520*, 198-201.
- 833 (127) Huang, Y.; Sachtler, W. M. H. Intermolecular hydrogen transfer in nitrile hydrogenation
834 over transition metal catalysts. *J. Catal.* **2000**, *190*, 69-74.
- 835 (128) Engel, M. H.; Macko, S. A. Isotopic evidence for extraterrestrial non-racemic amino acids
836 in the Murchison meteorite. *Nature* **1997**, *389*, 265-268.
- 837 (129) Pizzarello, S.; Zolensky, M.; Turk, K. A. Non racemic isovaline in the Murchison meteorite:
838 Chiral distribution and mineral association. *Geochim. Cosmochim. Acta* **2003**, *67*, 1589-
839 1595.