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Pathways to Meteoritic Glycine and Methylamine

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Abstract

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

Graphical Abstarct

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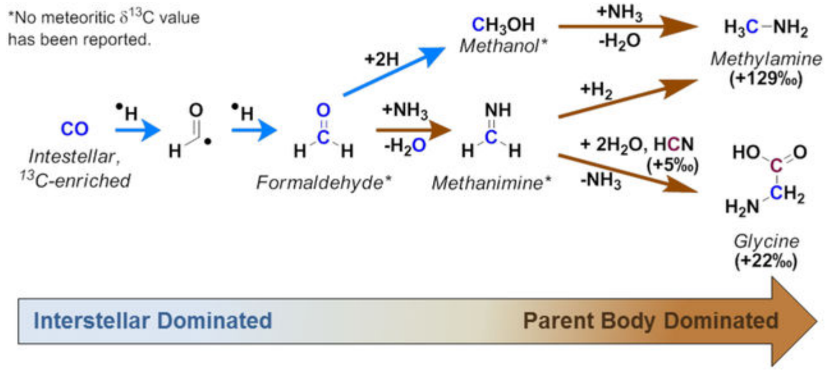

Keywords

Meteoritic organics; glycine; parent body processes; interstellar ice; methylamine

1. Introduction

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

Glycine ($NH_2CH_2CO_2H$) and methylamine (CH_3NH_2) are simple structurally analogous compounds related to each other by the presence or absence of the acid moiety (carboxyl group, - CO_2H; Scheme 1). Both compounds are common in the terrestrial biosphere. Both have also been detected in multiple extraterrestrial samples, including carbonaceous chondrites,[12–14] laboratory measurements of acid-hydrolyzed hot water extracts of comet-exposed materials from the Stardust sample return mission to comet 81P/Wild 2,[15–17] and direct *in situ* measurements of the coma of comet 67P/Churyumov-Gerasimenko by the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument.[18] Methylamine, but not glycine, was also identified by the Philae lander Cometary Sampling and Composition (COSAC) instrument shortly after Philae's first contact with the surface of Churyumov-Gerasimenko.[19] Additionally, glycine and methylamine have been produced from synthesis in gas-phase reactions,[20–23] UV-irradiated interstellar ice analogs,[24–32] and in Miller-Urey-type experiments,[33–34] representing potential abiotic syntheses in diverse environments.

Analysis of the ^{13}C isotopic compositions of meteoritic organics and their precursors may provide insights about their synthetic origins. The synthesis of meteoritic glycine and methylamine may have occurred in two broad cosmochemical regimes, the first dominated by gas- and ice-grain chemistry that occurred in the molecular cloud, the solar nebula, or the protoplanetary disk, and the second dominated by hydrothermal chemistry inside the meteorite parent body; thus, $\delta^{13}C$ values measured in the laboratory may result from isotopic fractionation inside various environments. Glycine and methylamine can be synthesized from common precursors such as carbon monoxide (CO), ammonia (NH_3), hydrogen cyanide (HCN), and carbon dioxide (CO_2); glycine and methylamine and their corresponding simpler building blocks may all have been incorporated during the accretion of Solar System bodies such as comets and asteroids, inside which further synthesis may have occurred.

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

Therefore, without being able to fully account for the level of fractionation that occurred through aqueous and thermal processing, it remains challenging to evaluate the synthetic routes leading to the origins of meteoritic glycine and methylamine. An additional challenge in using the $\delta^{13}C$ values of meteoritic glycine and methylamine as probes to their formation mechanisms is the unknown original concentration and isotopic values of their potential precursor molecules inside carbonaceous chondrites. Being mindful of these limitations and with the available data currently present in the literature, here we examine plausible diverse synthetic pathways that may have led to the origins of glycine and methylamine in meteorites. We consider those processes that occurred before the accretion of the meteorite parent body, but center our attention on those synthetic mechanisms that may have taken place much later during the parent body stage which are dominated by hydrothermal reactions. We focus on the Murchison meteorite because is the most thoroughly studied carbonaceous chondrite for amino acids,[7] as well as the only meteorite from which the stable carbon isotopic ratios ($\delta^{13}C$) of most of these potential precursor molecules have been reported. While other meteorites such as Orgueil (CI1), Lonewolf Nunataks (LON) 94101 (CM2), Lewis Cliff (LEW) 90500 (CM2), Allan Hills (ALH) 83100 (CM1/2), La Paz Icefield (LAP) 02342 (CR2), and Graves Nunataks (GRA) 95229 (CR2) contain glycine and methylamine,[9,10] the abundances and $\delta^{13}C$ of precursor molecules such as CO, CO_2, and HCN in these meteorites have not been reported. Isotopic analyses of precursor molecules in additional meteorites are needed to test and expand the hypotheses presented in this manuscript. We also evaluate the current knowledge of gas-phase reactions, irradiated ice grain chemistry, theoretical modeling, and telescopic observations of various interstellar regions for the synthesis of glycine, methylamine, and their corresponding precursor species.

2. The Pre-Parent body Phase

Inside interstellar environments, complex organic compounds may form in grain-surface and gas-phase reactions by hydrogen atom addition to CO and other unsaturated molecules, followed by carbon atom addition;[42–47] many of the predicted compounds such as formaldehyde and methanol, have been detected in the interstellar and circumstellar media, hot cores, interstellar clouds and circumstellar envelopes.[48–50] Several molecules of interest here, which may form in both surface- and gas-phase reactions (such as formaldehyde, methanimine, and methylamine) have been detected in interstellar and protostellar sources,[51–54] in comets,[19,55–57] and in carbonaceous chondrites.[12,14,35,58] Although glycine detection in the interstellar medium remains controversial,[59–61] possible formation pathways relevant to these environments have yet to be confirmed.[22,62–65] Similarly, even though methylamine and its structurally related compound, methanimine, are both observed in the interstellar medium,[66–69] their pre-solar formation mechanisms are not entirely understood. For example, Suzuki et al. (2016) have surveyed several star-forming cores for methanimine (CH_2NH) with the view that cores with the highest abundances would be the best places to conduct a subsequent glycine search.[70] Suzuki et al. (2016) also modeled the related gas-grain chemistry and concluded that interstellar methanimine formed in gaseous reactions.[70]

Recent observations of nearby young stellar objects (YSOs) in star forming regions with infrared absorption spectroscopy, have measured a discrepancy between gas-phase $^{12}CO/^{13}CO$ and solid-phase $^{12}CO/^{13}CO$ ratios.[71] The observed $^{12}CO/^{13}CO$ gas-phase ratios of the Solar System and local interstellar medium ranges from ~+290 to +370‰ which is higher,[72] (more ^{13}C enriched) than those measured in YSOs and nearby star-forming regions ranging at ~−460 to +47‰.[71] This leads to speculation that this effect may be due to isotopologue partitioning between the two reservoirs. Smith et al. (2015) ruled out isotope selective photo-dissociation for their results of gas-phase $^{12}CO/^{13}CO$, even though it is a significant effect for the oxygen isotopes.[71] The evolution of these objects through the prestellar disk and eventually planetary systems however, provides ample opportunity for further isotope effects to occur. Observational instrumentation is just reaching more complex molecular (and isotopic) detection limits, especially spatially, of these more evolved systems,[73] allowing for new detections and observational constraints to current theories. Models of disk chemistry suggest the fractionation to be dependent on the disk radius and height with some chemical dependence,[74] though the mid-plane results are consistent with current observations of comets.

In the cold interstellar medium, ^{13}C nuclei are effectively incorporated into ^{13}CO while expelling ^{12}C nuclei, through the following ion-molecule exchange reaction: $^{13}C^+ + {}^{12}CO \leftrightarrow {}^{13}CO + {}^{12}C^+$.[75] Therefore, it is expected that the carbon atoms and other C-bearing molecules (“CX”, also known as “the carbon isotope pool”) are depleted in ^{13}C and consequently have much higher $^{12}CX/^{13}CX$ ratios. Such depletion is therefore expected in other molecules formed primarily in gaseous reactions, such as HCN. Indeed, astronomical measurements using radio telescopes by Sakai et al. (2010)[76] and Yoshida et al. (2015)[77] have demonstrated the expected ^{13}C-depletions in interstellar acetylene radical (C≡C-H) and cyclopropenylidene ($c\text{-}C_3H_2$). Conversely, formaldehyde has been tentatively found to be more ^{13}C-enriched than CO in in some star-forming cores,[78] a result that is contrary to all theoretical predictions and that suggest that isotopic partitioning has not yet been demonstrated unequivocally for observations of a large suite of interstellar molecules. Large observational errors are obtained in $^{12}C/^{13}C$ ratios measurements,[79] which may not be very constraining on the ppm/ppb levels measured for organics in carbonaceous chondrites. Thus, a bulk isotope ratio cannot constrain the origin of meteoritic organics without extensively considering the chemistry and other isotope effects for each molecule present.

3. The Parent Body Phase

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

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

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

3.1 Synthesis of glycine and methylamine from formaldehyde.

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

The Strecker-cyanohydrin synthesis may be driven by parent-body aqueous processes, and is the most commonly invoked mechanism for the production of meteoritic α-amino acids such as glycine inside the parent body.[96,97] As shown in Scheme 2, one molecule of methanimine (formed from formaldehyde) reacts with one molecule of HCN to yield the α-aminonitrile. Again, it would be expected that formaldehyde and methanimine are ^{13}C-enriched relative to HCN (occurring from the carbon isotope pool; see Section 1) inside the parent body, and that the δ^{13}C composition of glycine before extended parent body processing would be the result of the combination of these two species. However, the preaccretionary abundance and δ^{13}C composition of formaldehyde, methanimine, and HCN upon accretion into the meteorite parent body, as well as the effects of parent body processing on the abundances and isotopic fractionation of these meteoritic species remains unknown. Without this information, it is impossible to confirm the roles of these proposed starting materials as glycine precursors; thus, both measurements of the δ^{13}C values of meteoritic formaldehyde and methanimine, as well as a more thorough understanding of the effects of parent body processing over the δ^{13}C composition of meteoritic organics are necessary future investigations to constrain the formation of meteoritic glycine.

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

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

3.2 Synthesis of glycine from CO_2 or HCN addition to methylamine.

An alternative route for the synthesis of meteoritic glycine is the addition of CO_2 (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 CO_2 to aliphatic amines has been demonstrated from photochemical and ion irradiation reactions (ices were composed of water and varying levels of CO_2 and an aliphatic amine)[102–105].

The meteoritic δ^{13}C value of methylamine is higher than that of free CO_2, 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 δ^{13}C values measured for these materials in meteorites are ^{13}C-enriched relative to their pre-accretionary values. The laboratory δ^{13}C values measured in meteorites are of the products and the remaining unreacted precursors and do not reveal the presolar $\delta^{13}C$ values of the reactants.

A close look at the reaction mechanisms involved in the addition of CO_2 and HCN to methylamine to synthesize glycine suggest that the likely products of these reactions may not result in the α-amino acid. Unlike photodissociation processes that result in bond cleavage, neutral- radical reactions, and radical-radical recombination, the addition of CO_2 to methylamine in aqueous media may only yield methylcarbamic acid (CH_3NHCO_2H).[106,107] Similarly, in the presence of an excess of amines, HCN reacts to form amidines (amines catalyze the polymerization of HCN if present in catalytic concentrations).[108,109] However, the synthesis of glycine from the addition of CO_2 or HCN to methylamine under meteoritic conditions is yet to be tested; it remains to be seen if in the presence of transition metals or mineral matrixes, carbamates and amidines are useful intermediates in, for example, transition metal-catalyzed reactions for the synthesis of amino acids.

3.3 Synthesis of glycine from NH_3 addition to acetic acid.

Similar to the addition of CO_2 to methylamine to form glycine, a source of nitrogen such as NH_3 may potentially add to acetic acid to produce glycine (Scheme 4). This reaction mechanism, however, has shown mixed results from experiments in the gas-phase;[22,23,110] the difficulty in obtaining glycine from these species is based on the acid nature of the carboxyl group and the basic nature of ammonia which result in proton transfer reactions only.[110] Therefore, to overcome this physicochemical barrier, Blagojevic et al. (2003) proposed the synthesis of glycine from the reaction of acetic acid with ionized and protonated hydroxylamine (NH_2OH^+ and NH_3OH^+ respectively) with successful results.[22,23] To the best of our knowledge, this gas-phase reaction has not been tested in ice-irradiated experiments containing acetic acid and hydroxylamine; however, it is very likely that glycine would form from the high energy processes and wide range of reactions mechanisms occurring in irradiated interstellar ice analogs.

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

Hydroxylamine in any of its forms has not been isolated nor identified from carbonaceous chondrites. However, this inorganic compound may be either present as its ammonia oxide isomer (NH_3O) or decomposed into nitrogen oxide species (water, ammonia, and hydrogen) as a result of catalytic effects of transition metals in water and thermal processing inside parent bodies.[120–122] The meteoritic $\delta^{13}C$ ratios of acetic acid have been measured twice from two different pieces of the Murchison meteorite showing contrasting values (Table 1);[35,88] thus, further $\delta^{13}C$ analysis of meteoritic acetic acid are needed in order to understand its potential meteoritic linkages to other organic species. The synthesis of glycine from acetic acid and hydroxylamine (either on its ionized or protonated form) is yet to be tested under meteoritic conditions; however, in the absence of highly energetic processes like those resulting in molecular photodissociation, it may prove challenging to propose the addition of hydroxylamine or any of its species to aliphatic moiety (sp^3 carbon) such as that in acetic acid, and to avoid side reactions such as proton transfer with the carbonyl group. Indeed, the more likely product may be acetamide formed from the dehydration of ammonium acetate.

3.4 Synthesis of glycine and methylamine from HCN and acetonitrile.

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

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

The measured $\delta^{13}C$ value of HCN from Murchison is ^{13}C-depleted relative to those found for CO_2, carbonates, methylamine, and glycine from the same meteorite (Table 1). As discussed before, these isotopic differences may not be representative of their composition upon accretion into the parent body; however, the $\delta^{13}C$ composition of HCN in Murchison may suggest it formed from the ^{13}C-depleted interstellar carbon pool. The isolation of HCN from the Murchison meteorite argues against its total decomposition through polymerization or oxidation, however, the hydrogenation of HCN under parent body conditions to form methanimine would need to be tested in order to consider the origins of glycine and methylamine from this species. Additionally, it would be worth investigating the kinetic isotope effect of the hydrogenation of $H^{12}CN$ and $H^{13}CN$, either through theoretical calculations or laboratory experiments in order to understand the expected isotopic relationship between HCN and its hydrogenation products. Along those lines, Huang and Sachtler (2000) found a strong D/H isotopic effect during hydrogenation of acetonitrile and deuterated acetonitrile (CH_3CN and CD_3CN respectively), showing that deuterium atoms add preferentially to the carbon atom, while hydrogen atoms added more selectively to the nitrogen atom.[127] The isolation of and $\delta^{13}C$ analysis of alkylnitriles is also necessary to fully understand these potential meteoritic connections; however, if the decomposition of these organic species is required to form the observed meteoritic glycine and methylamine, it is challenging to propose a scenario inside the parent body in which these decomposition products would not be quenched by water or other parent body constituents.

4. Synergistic Approaches

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

All the molecules serving as potential starting materials for the synthesis of glycine and methylamine discussed here, i.e., CO, HCN, CO_2, acetic acid, formaldehyde, methanol, methanimine, and acetonitrile have been detected in various interstellar regions. Further work needs to be done focused on measuring the isotopic composition of these species and in the identification of ever more complex organics in the interstellar medium. More accurate isotope measurement in comets and protoplanetary disks will also help constrain the origins of complex organics by determining the original isotope ratios in each species. These ambitious tasks, however, may remain as pending challenges for a new generation of telescopes like The Atacama Large Millimeter/submillimeter Array (ALMA).

While none of the discussed synthetic routes may be entirely discarded for the synthesis of glycine and methylamine until tested under simulated parent body conditions, the Strecker-cyanohydrin pathway (Scheme 2) is the only synthetic route that is compatible and complementary with the current knowledge of both interstellar processes and the meteoritic analyses. Addition of CO_2 (Scheme 3) to methylamine may result in the formation of methylcarbamic acid, while the addition of HCN (Scheme 3) may confer an alternative route but may result in the synthesis of amidines. The occurrence of methylcarbamic acid and amidines, however, may be necessary for other catalytic processes that increase the overall molecular diversity inside the parent body. Similarly, the addition of hydroxylamine to acetic acid to yield glycine (Scheme 4) seems unlikely given the high potential for proton transfer reactions. Indeed, both the addition of CO_2 to methylamine and the addition of hydroxylamine to acetic acid would need to occur through breaking a C-H sp^3 bond (present in methylamine or acetic acid), a process which may require high energetic input or highly reactive species such as radicals. Amino acids and amines may be generated from the formation of methanimine upon reduction or hydrogenation of HCN (Scheme 5); however, these processes may entirely depend on the nature of the reducing environment. Finally, acetonitrile may decompose to yield cyanide ion (CN^-), which may follow the same pathway as HCN discussed above.

Laboratory experiments simulating reactions occurring in the gas-phase and at the surface of interstellar ice particles provide powerful insights into the nature of the chemical processes inside cold molecular clouds and star forming regions. We now understand that that a plethora of complex organic molecules may result from the interaction of ionizing radiation (cosmic rays, UV photons, soft X-rays, etc.) and a mixture of volatile hydrogen, carbon, nitrogen and oxygen sources (H_2O, CO, CH_3OH, HCN, NH_3, etc.) in presolar and interstellar environments. However, greater effort should now be placed on quantitative analysis focused on measuring reaction rates, as well as the inherent molecular stability, abundance, isomeric distribution, and isotope effect of organic products.

In addition, relatively little attention has been paid to the identification of these volatile species from meteoritic sources and even fewer studies have been reported of their meteoritic isotopic values. Several families of complex organic molecules such as PAHs, amino acids, amines and carboxylic acid have been identified and isotopically characterized from carbonaceous chondrites,[10,88,89,128] however, much less is known about the abundance and isotopic distributions of free CO, CO_2, HCN and ammonia (Yuen et al. 1984; Pizzarello et al. 2011; Pizzarello and Williams 2012; Pizzarello 2014).[35,58,93,94] Furthermore, the Murchison meteorite has been found to contain a heterogeneous composition, meaning that different pieces analyzed may contain similar but not the same molecular and isotopic distributions;[89,129] therefore, it remains imperative to expand the stable isotopic studies of CO, HCN, CO_2, and acetic acid, as these measurements have only been performed on one meteorite for each compound. In addition, there are meteoritic organic compounds such as alcohols, aldehydes, and ketones (e.g. formaldehyde and methanol) which have been identified and quantified in Murchison and other meteorites, but without measurements of their corresponding isotopic values, and there are other plausible intermediates such as methanimine, alkylnitriles, aminonitriles, and hydroxynitrile that have not been searched for from any meteorite. Without a thorough assessment of the abundance and isotopic composition of these species, it remains difficult to investigate their potential synthetic relationship with more complex compounds. These should be high priority targets for study in meteorites as well as the large sample to be returned from asteroid Ryugu by JAXA’s Hayabusa2 sample return mission in 2020 and from asteroid Bennu by NASA’s OSIRIS-REx sample return mission in 2023.

5. Conclusion

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

We have evaluated the potential synthetic relationships between glycine and methylamine using their isotopic compositions and those of their potential precursor molecules from the Murchison meteorite. Our analysis aimed to evaluate various meteoritic species as probes into parent body chemistry and to link proposed formation mechanisms with data collected through astronomical observations, experiments in both the gas-phase and in irradiated ice interstellar analogs, and theoretical modeling. However, the main conclusion of this exercise is that there is still a large number of meteoritic and laboratory analyses, as well as telescopic observations, and theoretical modeling that must be performed before there is sufficient data to fully understand the synthesis of extraterrestrial organic compounds present in meteorites. Ideally, we would be able to draw phase diagrams for the synthesis of glycine and methylamine with respect to variables such as parent body temperatures and concentration of reactants for example; unfortunately, the original molecular concentrations and isotopic compositions of the precursor molecules remain unknown. Similarly we have only recently started to unveil the varying levels of aqueous and thermal effects occurred in different parent bodies, albeit, the magnitude of this processing on the organic composition of carbonaceous chondrites is still poorly understood, at least from a mechanistic standpoint. Therefore, future interdisciplinary efforts are needed to further our understanding of these and other meteoritic organic compounds.

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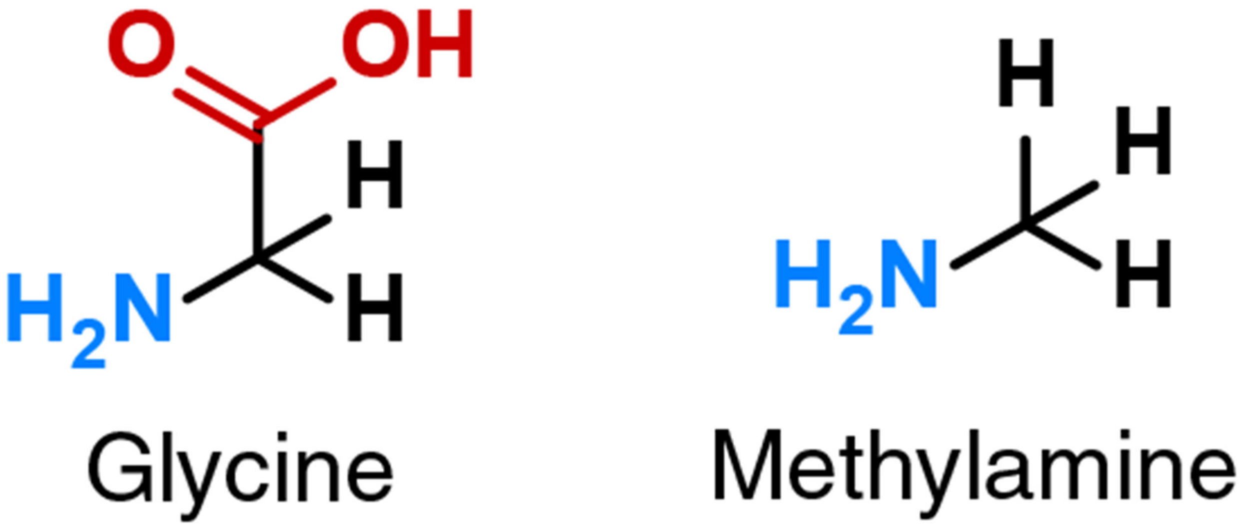
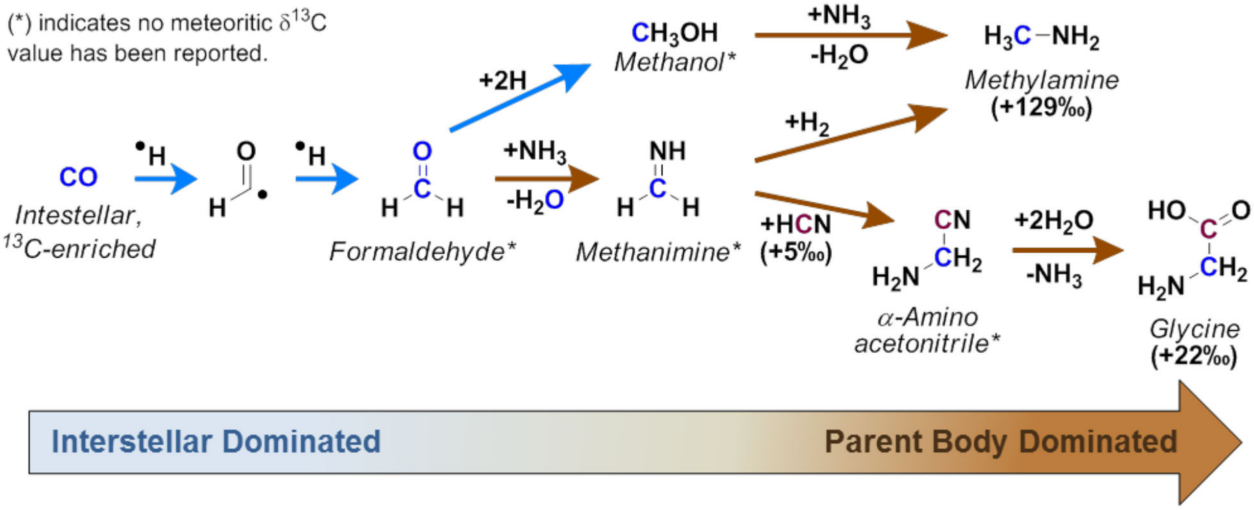


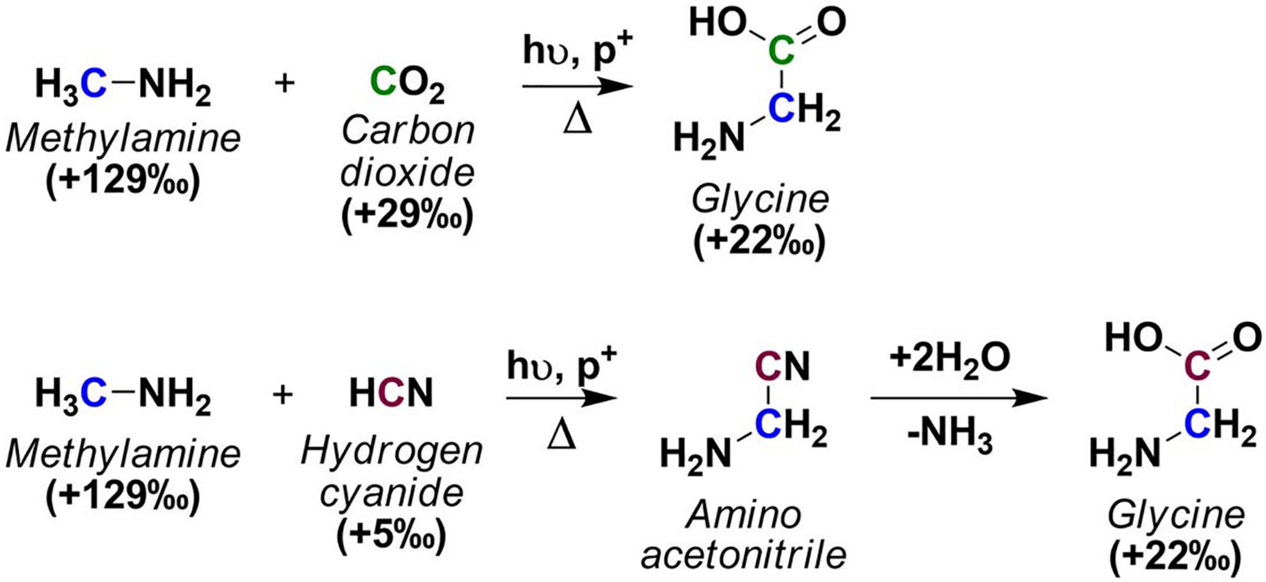
Scheme 1.

Structures of glycine and methylamine (color highlights the amine [blue, NH_2] and acid [red, CO_2H] functional groups).



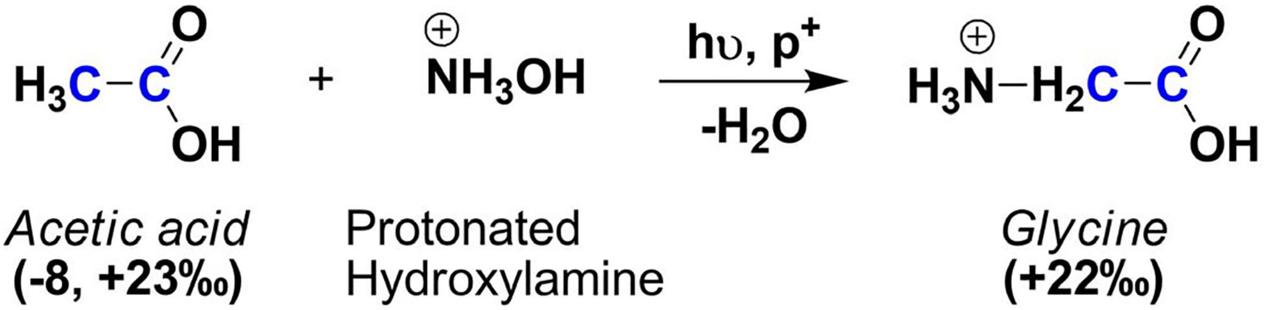
Scheme 2.

The Strecker-cyanohydrin synthesis and reductive amination of formaldehyde are potential synthetic routes for glycine and methylamine in the Murchison meteorite. Starting from ^{13}C-enriched CO, results in ^{13}C-enriched glycine and methylamine. These reactions may be dominant, but not exclusive inside the indicated environments.



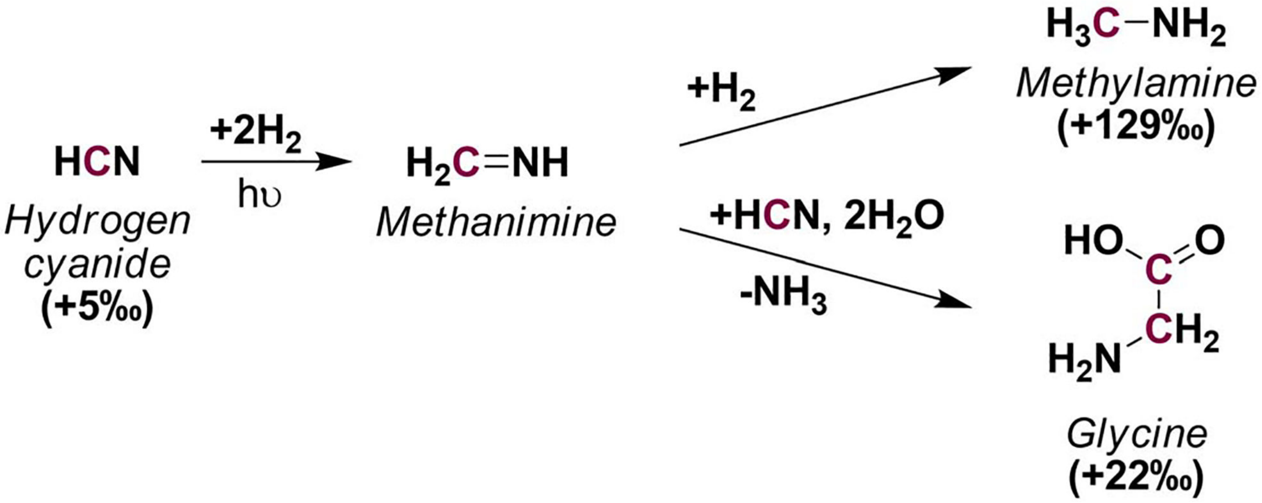
Scheme 3.

The synthesis of glycine from addition of meteoritic CO_2 or HCN to methylamine may occur in photochemical processes, but the likelihood of glycine formation glycine under aqueous hydrothermal conditions remains unknown.



Scheme 4.

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



Scheme 5.

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

Table 1.

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

Carbonaceous chondrite	**Type**	**$\delta^{13}C$ (‰)**						
		CO	**CO_2**	**CO_3^{2-}(carbonate)**	**HCN**	**CH_3CO_2H (acetic acid)**	**CH_3NH_2 (methylamine)**	**$NH_2CH_2CO_2H$ (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]

[35] Yuen et al. 1984. [82] Grady et al. 1988. [84] Alexander et al. 2015. [58] The value shown here is the average of four different samples measured by Pizzarello (2014). [88] Huang et al. 2005. [9] Aponte et al. 2015. [10] Aponte et al. 2016. [8] Aponte et al. 2014. [11] Pizzarello and Yarnes 2016. [85] Ehrenfreund et al. 2001. [89] Elsila et al. 2012. [90] Engel et al. 1990. [91] Pizzarello et al. 2004. [14] Pizzarello and Holmes 2009. [92] Martins et al. 2007.

Table 2.

Interstellar analogous synthesis of glycine and methylamine and their potential implications for their synthesis inside the parent body.

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.

[a] While ice analogs are usually a combination of CO, CO_2, 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.