Part One
Origins of Amino Acids

Amino Acids, Peptides and Proteins in Organic Chemistry. Vol.1 – Origins and Synthesis of Amino Acids.
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Extraterrestrial Amino Acids

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1.1
Introduction

The space between the stars, the interstellar medium (ISM), is composed of gas-phase species (mainly hydrogen and helium atoms) and submicron dust grains (silicates, carbon-rich particles, and ices). The ISM has many different environments based on its different temperatures (T_k), hydrogen density (n_H), and ionization state of hydrogen (for reviews, see [1–3]); it includes the diffuse ISM ($T_k \sim 100$ K, $n_H \sim 10$–$300\,cm^{-3}$), molecular clouds ($T_k \sim 10$–100 K, $n_H \sim 10^3$–$10^4\,cm^{-3}$; e.g., [4]) [molecular clouds are not uniform but instead have substructures [5] – they contain high-density clumps (also called dense cores; $n_H \sim 10^3$–$10^5\,cm^{-3}$), which have higher densities than the surrounding molecular cloud; even higher densities are found in small regions, commonly known as "hot molecular cores", which will be the future birth place of stars], and hot molecular clouds ($T_k \sim 100$–300 K, $n_H \sim 10^6$–$10^8\,cm^{-3}$; e.g., [6]). Observations at radio, millimeter, submillimeter, and infrared frequencies have led to the discovery of numerous molecules (currently more than 151) in the interstellar space, some of which are organic in nature (Table 1.1; an up-to-date list can be found at www.astrochemistry.net). The collapse of a dense cloud of interstellar gas and dust leads to the formation of a so-called solar nebula. Atoms and molecules formed in the ISM, together with dust grains are incorporated in this solar nebula, serving as building blocks from which future planets, comets, asteroids, and other celestial bodies may originate. Solar system bodies, such as comets (e.g., [7] and references therein; [8]), meteorites (e.g., [9, 10]), and interplanetary dust particles (IDPs [11, 12]) are known to contain extraterrestrial molecules, which might have a heritage from interstellar, nebular, and/or parent body processing. Delivery of these molecules to the early Earth and Mars during the late heavy bombardment (4.5–3.8 billion years ago) may have been important for the origin of life [13, 14]. Among the molecules delivered to the early Earth, amino acids may have had a crucial role as they are the building blocks of proteins and enzymes, therefore having implications for the origin of life. In this chapter we describe different extraterrestrial environments where amino acids may be present and

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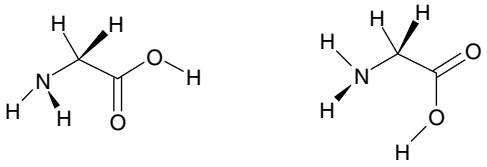
Table 1.1 Summary of molecules identified in the interstellar and circumstellar medium[a].

Number of atoms											
2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
H_2	H_3^+	CH_3	CH_4	C_2H_4	CH_3NH_2	CH_3CH_3	C_2H_5OH	CH_3CH_2CHO	CH_3C_6H	C_6H_6	$HC_{11}N$
CH	CH_2	NH_3	NH_4^+	CH_3OH	CH_3CCH	C_3H_4O	CH_3OCH_3	CH_3COCH_3	HC_9N		
CH^+	NH_2	H_3O^+	CH_2NH	CH_3CN	c-C_2H_4O	CH_2OHCHO	CH_3CH_2CN	$HOCH_2CH_2OH$			
NH	H_2O	C_2H_2	H_3CO^+	CH_3NC	CH_3CHO	CH_3COOH	CH_3CONH_2	NH_2CH_2COOH			
OH	H_2O^+	H_2CN	SiH_4	NH_2CHO	CH_2CHCN	$HCOOCH_3$	CH_3C_4H				
OH^+	C_2H	$HCNH^+$	c-C_3H_2	CH_3SH	C_6H	CH_2CCHCN	C_8H				
HF	HCN	H_2CO	H_2CCC	H_2CCCC	C_6H^-	CH_3C_3N	C_8H^-				
C_2	HNC	c-C_3H	CH_2CN	HCCCCH	HC_5N	C_6H_2	HC_7N				
CN	HCO	l-C_3H	H_2CCO	$H_2C_3N^+$		HCCCCCCH					
CN^+	HCO^+	HCCN	NH_2CN	c-H_2C_3O		C_7H					
CO	HN_2^+	HNCO	HCOOH	HC_2CHO							
CO^+	HOC^+	$HNCO^-$	C_4H	C_5H							
N_2^+	HNO	$HOCO^+$	C_4H^-	HC_4N							
SiH	H_2S	H_2CS	HC_3N	C_5N							
NO	H_2S^+	C_3N	HCCNC	SiC_4							
CF^+	C_3	C_3O	HNCCC								
HS	C_2O	HNCS	C_5								
HS^+	CO_2	SiC_3									
HCl	CO_2^+	C_3S									
SiC	N_2O										
SiN	HCS^+										
CP	NaCN										
CS	MgCN										

SiO	MgNC
PN	c-SiC_2
AlF	AlNC
NS	SiCN
SO	SiNC
SO^+	C_2S
NaCl	OCS
SiS	SO_2
AlCl	
S_2	
FeO	
KCl	

[a]Observations suggest the presence of polycyclic aromatic hydrocarbons in the interstellar gas (e.g., [244]).



I II

Figure 1.1 Molecular structures of conformers I and II of glycine in the gas phase (adapted from [21, 29]).

detected, their proposed formation mechanisms, and possible contribution to the origin of life on Earth.

1.2 ISM

The search for amino acids, in particular for the simplest amino acid glycine (NH_2CH_2COOH), in the ISM has been carried on for almost 30 years [15–28]. While in theory glycine may have several conformers in the gas phase [29], astronomical searches have only focused on two (Figure 1.1, adapted from [21, 29]). Conformer I is the lowest energy form, while conformer II has a higher energy, larger dipole moment, and therefore stronger spectral lines [30]. Only upper limits of both conformers were found in the ISM until Kuan *et al.* [25] reported the detection of glycine in the hot molecular cores Sgr B2(N-LMH), Orion-KL, and W51 e1/e2. This detection has been disputed by Snyder *et al.* [26], who concluded that the spectral lines necessary for the identification of interstellar glycine have not yet been found. In addition, they argued that some of the spectral lines identified as glycine by Kuan *et al.* [25] could be assigned to other molecular species. Further negative results include the astronomical searches of Cunningham *et al.* and Jones *et al.* [27, 28], who claim that their observations rule out the detection of both conformers I and II of glycine in the hot molecular core Sgr B2(N-LMH). They conclude that it is unlikely that Kuan *et al.* [25] detected glycine in either Sgr B2(N-LMH) or Orion-KL. No other amino acid has been detected in the ISM. Despite these results, amino acids were proposed to be formed in the ISM by energetic processing on dust grain surfaces, which will then be evaporated, releasing the amino acids into the gas phase (solid-phase reactions), or synthesized in the gas phase via ion–molecule reactions (gas-phase reactions). These two processes will now be described in more detail (for a review, see, e.g., [31]).

1.2.1 Formation of Amino Acids in the ISM via Solid-Phase Reactions

Several mechanisms have been proposed for amino acid formation in the ISM. These include solid-phase reactions on interstellar ice grains by energetic processing,

Table 1.2 Abundances of interstellar ices (normalized to H_2O) in the high-mass protostellar objects W33A and NGC758:IRS9, in the low-mass protostellar object Elias 29, and the field star Elias 16.

Ice specie	W33A high-mass protostar	NGC758:IRS9 high-mass protostar	Elias 29 low-mass protostar	Elias 16 field star
H_2O	100	100	100	100
CO	9	16	5.6	25
CO_2	14	20	22	15
CH_4	2	2	<1.6	—
CH_3OH	22	5	<4	<3.4
H_2CO	1.7–7	5	—	—
NH_3	3–15	13	<9.2	<6
OCS	0.3	0.05	<0.08	—
C_2H_6	<0.4	<0.4	—	—
HCOOH	0.4–2	3	—	—
O_2	<20	—	—	—
OCN^-	3	1	<0.24	<0.4

Adapted from [31, 32, 52].

which may occur in cold molecular clouds (e.g., [32] and references therein). In these regions of the ISM, in which temperatures are very low (<50 K), atoms and molecules in the gas phase will be accreted onto the surface of dust grains leading to the formation of ice mantles [33, 34]. Diffusion of accreted atoms leads to surface reactions, forming additional species in the ice mantles. These interstellar ices are mainly composed of H_2O, CO, CO_2, CH_4, CH_3OH, and NH_3, with traces of other species (Table 1.2; [32, 34–38]). Once these ice grains are formed, energetic processes [e.g., cosmic rays and ultraviolet (UV) irradiation] may change the ice mantle composition.

A range of interstellar ice analogs have been irradiated at low temperatures (~10 K) to produce a variety of amino acids. Holtom *et al.* [39] used galactic cosmic ray particles to irradiate an ice mixture containing carbon dioxide (CO_2) and methylamine (CH_3NH_2), which produced hydroxycarbonyl (HOCO) and aminomethyl (CH_2NH_2) radicals. The recombination of these radicals would then form glycine and its isomer ($CH_3NHCOOH$). Briggs *et al.* [40] UV-irradiated a mixture of $CO : H_2O : NH_3$ (5 : 5 : 1) at 12 K for 24 h. This resulted in the formation of an organic residue, which included among other organic compounds, 0.27% of glycine. Ice mixtures containing $H_2O : CH_3OH : NH_3 : CO : CO_2$ (2 : 1 : 1 : 1 : 1 molar composition; [41]), and H_2O with NH_3, CH_3OH, and HCN (0.5–5% NH_3, 5–10% CH_3OH, and 0.5–5% HCN, relative to H_2O [42]) were UV-irradiated in high vacuum at below 15 K. While Bernstein *et al.* [42] obtained glycine and racemic mixtures ($D/L \sim 1$) of alanine and serine, a large variety of amino acids were found by Munõz Caro *et al.* [41]. These results were confirmed by Nuevo *et al.* [43, 44].

The exact formation pathway of amino acids in interstellar ices is unknown, but the Strecker synthesis ([42]; for more details, see Section 1.4), reactions on the surface of

polycyclic aromatic hydrocarbon flakes [45], and radical–radical reactions [46, 47] have been proposed. As radical–radical reactions can occur with almost no activation energy [47], theoretical modeling suggests that glycine may be formed in interstellar ice mantles via the following radical–radical reaction sequence:

$$CO + OH \rightarrow COOH \tag{1.1}$$

$$CH_3 + COOH \rightarrow CH_3COOH \tag{1.2}$$

$$NH_2 + CH_3COOH \rightarrow NH_2CH_2COOH + H \tag{1.3}$$

Quantum chemical calculations indicate that amino acids may also be formed by recombination of the radicals COOH and CH_2NH_2, which are produced by dehydrogenation of H_2O and CH_3OH, and hydrogenation of HCN, respectively [47]. However, all radical–radical reactions described above require the radicals to diffuse into and/or onto the ice mantle which, as noted by Woon [47], may only occur at temperatures of 100 K or higher, much higher than the temperature in molecular clouds. Furthermore, Elsila *et al.* [48] used isotopic labeling techniques to test whether Strecker synthesis or radical–radical reactions were responsible for amino acid formation in interstellar ice analogs. Their results show that amino acid formation occurs via multiple routes, not matching the previously proposed Strecker synthesis or radical–radical mechanisms. Ultimately, the need for high UV flux to produce amino acids in ice mantles contrasts with the low expected efficiency of UV photolysis in dark molecular clouds [4]. This, together with the fact that amino acids have low resistance to UV photolysis [49], raises concerns about the amino acid formation in interstellar ices by UV photolysis.

1.2.2
Formation of Amino Acids in the ISM via Gas-Phase Reactions

Potential mechanisms alternative to solid-phase reactions include gas-phase formation of interstellar amino acids via ion–molecule reactions. Amino acids, once formed, could potentially survive in the gas phase in hot molecular cores, because the UV flux is sufficiently low (i.e., 300 mag of visual extinction) [31]. Alcohols, aminoalcohols, and formic acid evaporated from interstellar ice grains (Table 1.2; [50–53]) may produce amino acids in hot molecular cores through exothermic alkyl and aminoalkyl cation transfer reactions [52]. Aminoalkyl cation transfer from aminomethanol and aminoethanol to HCOOH can produce protonated glycine and β-alanine, respectively via the following reactions [52]:

$$NH_2CH_2OH_2^+ + HCOOH \rightarrow NH_2CH_2COOH_2^+ + H_2O \tag{1.4}$$

$$NH_2(CH_2)_2OH_2^+ + HCOOH \rightarrow NH_2(CH_2)_2COOH_2^+ + H_2O \tag{1.5}$$

An electron recombination will then produce the neutral amino acids. Further alkylation may produce a large variety of amino acids through elimination of a water molecule [31, 52].

Alternatively, Blagojevic *et al.* [54] have experimentally proven the gas-phase formation of protonated glycine and β-alanine, by reacting protonated hydroxylamine with acetic and propanoic acid, respectively:

$$NH_2OH^+ + CH_3COOH \rightarrow NH_2CH_2COOH^+ + H_2O \quad (1.6)$$

$$NH_2OH^+ + CH_3CH_2COOH \rightarrow NH_2(CH_2)_2COOH^+ + H_2O \quad (1.7)$$

Neutral amino acids could then be produced by dissociative recombination reactions [54].

Independently of the mechanism of synthesis (solid-phase or gas-phase reactions), once formed, amino acids would need to be resistant and survive exposure to cosmic rays and UV radiation in the ISM. The stability of amino acids in interstellar gas and on interstellar grains has been simulated [49]. Different amino acids [i.e., glycine, L-alanine, α-aminoisobutyric acid (α-AIB), and β-alanine] were irradiated in frozen argon, nitrogen, or water matrices to test their stability against space radiation. It was shown that these amino acids have very low stability against UV photolysis. Therefore, amino acids will not survive in environments subject to high UV flux, such as the diffuse ISM. This does not eliminate formation of amino acids in the ISM, but instead requires that amino acids are incorporated into UV-shielded environments such as hot molecular cores, in the interior of comets, asteroids, meteorites, and IDPs.

1.3 Comets

Comets are agglomerates of ice, organic compounds, and silicate dust, and are some of the most primitive bodies in the solar system (for reviews about comets, see, e.g., [55–57]). Comets were first proposed to have delivered prebiotic molecules to the early Earth by Chamberlin and Chamberlin [58]. Since then, space telescopes (such as the Hubble Space Telescope, Infrared Space Observatory, and Spitzer Space Telescope; e.g., [59–66]), ground-based observations (e.g., [67–69]), cometary fly-bys (Deep Space 1 mission, and Vega1, Vega2, Suisei, Sakigake, ICE, and Giotto spacecraft missions; e.g., [70–76]), impacts (Deep Impact mission, which impacted into the 9P/Tempel comet's nucleus; e.g., [77–79]), collection of dust from the coma of a comet (Stardust mission to comet Wild-2; e.g., [80–84]), and rendezvous missions (such as the Rosetta mission, which will encounter the comet 67P/Churyumov–Gerasimenko in 2014) advanced our knowledge about these dirty snowballs.

Several organic compounds have been detected in comets (Table 1.3; for reviews, see, e.g., [7, 8, 85]). Fly-by missions have suggested the presence of amino acids on comet Halley [71], but their presence could not be confirmed due to the limited resolution of the mass spectrometers on board the Giotto and Vega spacecrafts. In addition, only an upper limit of less than 0.15 of glycine relative to water has been determined in the coma of Hale–Bopp using radio telescopes (Table 1.3; [69]). Although several amino acid precursors (see Section 1.4), including ammonia,

Table 1.3 Molecular abundances of ices for comets Halley, Hyakutake, and Hale–Bopp.

Molecule	Halley	Hyakutake	Hale–Bopp
H_2O	100	100	100
H_2O_2		<0.04	<0.03
CO	15	6–30[a]	20[a]
CO_2	3	<7[b]	6[b]
CH_4	0.2–1.2	0.7	0.6
C_2H_2	~0.3	0.5	0.1
C_2H_6	~0.4	0.4	0.3
CH_3C_2H			<0.045
CH_3OH	1.3–1.7	2	2.4
H_2CO	0–5	0.2–1[a]	1.1[a]
HCOOH			0.08
CH3COOH			<0.06
$HCOOCH_3$			0.08
CH_3CHO			0.025
H_2CCO			<0.032
C_2H_5OH			<0.05
CH_3OCH_3			<0.45
CH_2OHCHO			<0.04
NH_3	0.1–2	0.5	0.7
HCN	~0.2	0.1	0.25
HNCO		0.07	0.10
HNC		0.01[a]	0.04[a]
CH_3CN		0.01	0.02
HC_3N			0.02
NH_2CHO			0.01
NH_2CH_2COOH			<0.15
C_2H_5CN			<0.01
CH_2NH			<0.032
HC_5N			<0.003
N_2O			<0.23
NH_2OH			<0.25
H_2S	0.04	0.8	1.5
OCS		0.1[a]	0.3[a]
SO			0.2–0.8[a]
CS_2		0.1c	0.2[c]
SO_2			0.23
H_2CS			0.02
S_2		0.005	
NaCl			<0.0008
NaOH			<0.0003

Abundances are normalized to H_2O and were measured at around 1 AU from the Sun. Adapted from [8, 32, 69, 86, 245].

[a]Extended sources (the abundance is model dependent).

[b]Measured at 2.9 AU from the Sun.

[c]Abundance deduced from CS.

HCN, formaldehyde, and cyanoacetylene, have been observed in the Hyakutake and Hale–Bopp comets [7], only a very limited number of carbonyl compounds necessary for the synthesis of amino acids were detected in comets [7, 32, 86]. The ultimate proof for the presence of amino acids in comets is a sample return mission such as Stardust, which collected dust from the coma of the Wild-2 comet using a lightweight material called aerogel [80]. Analyses of comet-exposed aerogel samples show a relative molar abundance of glycine that slightly exceeds that found in control samples, suggesting a cometary origin for this amino acid [83]. Compound-specific isotopic analyses of glycine present in comet-exposed aerogel samples have not yet been performed and therefore it has not been possible to ultimately constrain its origin. Other amino acids present in the comet-exposed aerogel samples included ε-amino-*n*-caproic acid, β-alanine, and γ-amino-*n*-butyric acid (γ-ABA). The similarity in the distribution of these amino acids in the comet-exposed sample, the witness tile (which witnessed all the terrestrial and space environments as the comet-exposed samples, but did not "see" comet Wild-2), and the Stardust impact location soil indicates a terrestrial origin (contamination) for these amino acids [83].

1.4 Meteorites

Meteorites are extraterrestrial objects that survived the passage through the Earth's atmosphere and the impact with the Earth's surface. Excepting the lunar and Martian meteorites [87–91], all meteorites are thought to have originated from extraterrestrial bodies located in the asteroid belt (e.g., [92–98]). Although unproven, it was also suggested that they could have originated from comets ([99–102] and references therein). Meteorites can be divided into iron, stony-iron, and stony meteorites. They can be further divided into classes according to their chemical, mineralogical, and isotopic composition (for reviews, see, e.g., [103–105]). A very primitive class of stony meteorites, named carbonaceous chondrites, has not been melted since their formation early in the history of the solar system, around 4.6 billion years ago (for reviews, see, e.g., [9, 10]). Within the class of carbonaceous chondrites, there are the CI-, CM-, CK-, CO-, CR-, CV-, CH-, and CB-type chondrites. Chondrites are also classified and grouped into petrographic types. This refers to the intensity of thermal metamorphism or aqueous alteration that has occurred on the meteorite parent body, ranging from types 1 to 6. A petrologic type from 3 to 1 indicates increasing aqueous alteration. A petrologic type from 3 to 6 indicates increasing thermal metamorphism.

Carbonaceous chondrites have a relatively high carbon content and can contain up to 3 wt% of organic carbon. More than 70% of it is composed of a solvent-insoluble macromolecular material, while less than 30% is a mixture of solvent-soluble organic compounds. Carbonaceous chondrites, as revealed by extensive analyses of the Murchison meteorite, have a rich organic inventory that includes organic compounds important in terrestrial biochemistry (Table 1.4). These include amino acids (e.g., [106–108]), carboxylic acids (e.g., [109, 110]), purines and pyrimidines

Table 1.4 Abundances (in ppm) of the soluble organic matter found in the Murchison meteorite.

Compounds	Concentration
Carboxylic acids (monocarboxylic)	332
Sulfonic acids	67
Amino acids	60
Dicarboximides	>50
Dicarboxylic acids	>30
Polyols	24
Ketones	17
Hydrocarbons (aromatic)	15–28
Hydroxycarboxylic acids	15
Hydrocarbons (aliphatic)	12–35
Alcohols	11
Aldehydes	11
Amines	8
Pyridine carboxylic acid	>7
Phosphonic acid	1.5
Purines	1.2
Diamino acids	0.4
Benzothiophenes	0.3
Pyrimidines	0.06
Basic *N*-heterocycles	0.05–0.5

Adapted from [9, 10, 161, 246].

(e.g., [111–113]), polyols [114], diamino acids [115], dicarboxylic acids (e.g., [116–119]), sulfonic acids [120], hydrocarbons (e.g., [121, 122]), alcohols (e.g., [123]), amines and amides (e.g., [124, 125]), and aldehydes and ketones [123].

The first evidence of extraterrestrial amino acids in a meteorite was obtained by Kvenvolden *et al.* [121], after analyzing a sample of the Murchison meteorite which had recently fallen in Australia in 1969. These authors detected several amino acids in this meteorite, including the nonprotein amino acids α-AIB and isovaline, which suggested an abiotic and extraterrestrial origin for these compounds. Since then, Murchison has been the most analyzed carbonaceous chondrite for amino acids, with more than 80 different amino acids identified, the majority of which are rare (or nonexistent) in the terrestrial biosphere (for reviews, see, e.g., [107, 108]). These amino acids have carbon numbers from C_2 through C_8, and show complete structural diversity (i.e., all isomers of a certain amino acid are present). They can be divided into two structural types, monoamino alkanoic acids and monoamino dialkanoic acids, which can occur as *N*-alkyl derivatives or cyclic amino acids, with structural preference in abundance order $\alpha > \gamma > \beta$. Branched-chain amino acid isomers predominate over straight ones and there is an exponential decline in concentration with increasing carbon number within homologous series.

Amino acids have also been reported in several other carbonaceous chondrites besides Murchison (Table 1.5). Within the CM2 group the total amino acid abundances and distributions are highly variable; Murray [126], Yamato (Y-) 74 662 [127, 128], and Lewis Cliff (LEW) 90 500 [129, 130] show an amino acid distribution and

Table 1.5 Summary of the average blank corrected amino acid concentration (in ppb) in the 6 M HCl acid-hydrolyzed hot-water extracts of carbonaceous chondrites.

	CM2									
Amino acid	**Murchison**	**Murray**	**Y-74 662**	**LEW 90 500**	**Y-791 198**	**Essebi**	**Nogoya**	**Mighei**	**ALHA 77 306**	**ALH 83 100**
D-Aspartic acid	100 ± 15	51 ± 31	160[a]	127 ± 24	226	72 ± 33	163 ± 135	105 ± 62	186[a]	29 ± 4
L-Aspartic acid	342 ± 103	65 ± 16	[a]	151 ± 73	280	134 ± 12	418 ± 106	145 ± 22	[a]	43 ± 6
D-Glutamic acid	537 ± 117	135 ± 50	532[a]	317 ± 55	530	49 ± 21	211 ± 74	111 ± 48	177[a]	21 ± 7
L-Glutamic acid	801 ± 200	261 ± 15	[a]	316 ± 55	588	130 ± 83	1003 ± 110	279 ± 24	[a]	23 ± 6
D-Serine	436 ± 227[a]	92 ± 32[a]	21[a]	<219	84	<62[a]	327 ± 84[a]	68 ± 23[a]	42[a]	<4
L-Serine	[a]	[a]	[a]	<235	126	[a]	—	—	[a]	<5
Glycine	2919 ± 433	2110 ± 144	2553	1448 ± 682	14 130	495 ± 6	1118 ± 729	788 ± 66	548	300 ± 75
β-Alanine	1269 ± 202	1063 ± 268	1247	442 ± 238	1425	1396 ± 157	796 ± 97	897 ± 72	160	338 ± 31
γ-ABA	1331 ± 472	717 ± 192	1753[e,f]	164 ± 21[d]	495	6425 ± 645	1548 ± 187	1136 ± 351	309	308 ± 68[d]
D,L-β-AIB[c]	343 ± 102	147 ± 88	ND	[d]	1836	ND	<124	ND	124	[d]
D-Alanine	720 ± 95	617 ± 79	1158[a]	343 ± 171	2895	128 ± 13	125 ± 92	240 ± 18	160[a]	110 ± 44
L-Alanine	956 ± 171	647 ± 58	[a]	352 ± 161	2913	113 ± 10	332 ± 120	347 ± 57	[a]	134 ± 19
D-β-ABA	708 ± 171[a]	424 ± 18[a]	[e,f]	155 ± 16	<1753	389 ± 180[a]	283 ± 144[a]	487 ± 50[a]	134[a]	33 ± 8
L-β-ABA	[a]	[a]	[e,f]	172 ± 40	1495	[a]	[a]	[a]	[a]	33 ± 12
α-AIB	2901 ± 328	1968 ± 350	381	2706 ± 377	22 630	208 ± 26	458 ± 346	740 ± 219	144	250 ± 40
D-α-ABA	295 ± 111	463 ± 68[a]	691[a]	431 ± 159[a]	907	<11	<151[a]	100 ± 70	93[a]	19 ± 5[a]
L-α-ABA	347 ± 98	[a]	[a]	[a]	907	<18	[a]	101 ± 78	[a]	[a]
D-Isovaline	350 ± 183	2834 ± 780[a]	ND	1306 ± 83[a]	4075[a]	<11	<72[a]	136 ± 49	ND	<10[a]
L-Isovaline	458 ± 209	[a]	ND	[a]	[a]	<18	[a]	159 ± 136	ND	[a]
Total	14 800	12 600	8500	8400	55 600	9500	6800	5800	2100	1600

(*Continued*)

Table 1.5 (*Continued*)

	CM2		CM1			CI1		CV3	C2
Amino acid	**Y-79 331**	**B-7904**	**ALH 88 045**	**MET 01 070**	**LAP 0227**	**Orgueil**	**Ivuna**	**Allende**	**Tagish Lake**
D-Aspartic acid	10[a]	20[a]	68 ± 18	106 ± 27	10 ± 1	28 ± 16	30 ± 2	<7	11 ± 1
L-Aspartic acid	[a]	[a]	99 ± 39	201 ± 61	29 ± 13	54 ± 18	146 ± 8	100 ± 42	83 ± 8
D-Glutamic acid	ND	ND	33 ± 9	54 ± 14	24 ± 3	15 ± 6	8 ± 1	<7	16 ± 2
L-Glutamic acid	ND	ND	174 ± 50	274 ± 74	64 ± 10	61 ± 31	372 ± 11	329 ± 41	306 ± 48
D-Serine	11[a]	25[a]	<174[a]	147 ± 52[a]	101 ± 13[a]	51 ± 26[a]	217 ± 12[a]	241 ± 149[a]	ND
L-Serine	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	ND
Glycine	7	19	369 ± 117	575 ± 159	55 ± 17	707 ± 80	617 ± 83	457 ± 121	147 ± 17
β-Alanine	4	1	197 ± 21	169 ± 39	16 ± 6	2052 ± 311	1401 ± 146	317 ± 28	64 ± 10
γ-ABA	ND	ND	168 ± 35	259 ± 61	95 ± 10	628 ± 294	~600	307 ± 129	77 ± 10
D,L-β-AIB[c]	ND	ND	ND	ND	ND	148 ± 70	84 ± 12	<6	ND
D-Alanine	[g]	2[a]	389 ± 87	630 ± 135	201 ± 14	69 ± 9	82 ± 22	<4	20 ± 5
L-Alanine	[g]	[a]	605 ± 149	1028 ± 239	228 ± 45	69 ± 9	157 ± 14	127 ± 92	75 ± 18
D-β-ABA	ND	ND	ND	ND	ND	332 ± 99[a]	438 ± 142[a]	<6[a]	<26[a]
L-β-ABA	ND	ND	ND	ND	ND	[a]	[a]	[a]	[a]
α-AIB	ND	ND	380 ± 97	881 ± 280	28 ± 10	39 ± 37	46 ± 33	<10	<27
D-α-ABA	ND	ND	ND	ND	ND	13 ± 11[a]	12 ± 7[a]	<4[a]	84 ± 40[a]
L-α-ABA	ND	ND	ND	ND	ND	[a]	[a]	[a]	[a]
D-Isovaline	ND	ND	ND	ND	ND	<194[a]	<163[a]	<35[a]	<56 ± [a]
L-Isovaline	ND	ND	ND	ND	ND	[a]	[a]	[a]	[a]
Total	30	70	2500	4300	850	4300	4200	1900	890

	CR2				CR1
Amino acid	**EET 92 042**	**GRA 95 229**	**Renazzo**	**Shişr 033**	**GRO 95 577**
D-Aspartic acid	409 ± 41	551 ± 75	49 ± 12	57 ± 5	13 ± 2
L-Aspartic acid	465 ± 24	576 ± 51	173 ± 80	189 ± 23	19 ± 4
D-Glutamic acid	3090 ± 422	3489 ± 389	<26	124 ± 7	16 ± 6
L-Glutamic acid	4468 ± 503	4209 ± 415	856 ± 188	489 ± 34	40 ± 3
D-Serine	742 ± 42[a]	1807 ± 84[a]	195 ± 112[a]	32 ± 11	50 ± 11[a]
L-Serine	[a]	[a]	[a]	140 ± 34	[a]
Glycine	24 975 ± 608	40 496 ± 1028	875 ± 188	417 ± 55	136 ± 14
β-Alanine	3046 ± 50	3143 ± 495	223 ± 55	62 ± 10	122 ± 6
γ-ABA	1512 ± 66	1914 ± 398	1092 ± 243	49 ± 23	54 ± 6
D,L-β-AIB[c]	1429 ± 333	2091 ± 405	<40	<2	30 ± 2
D-Alanine	21 664 ± 1009	52 465 ± 6860	<38	274 ± 14	74 ± 22
L-Alanine	22 297 ± 1583	51 141 ± 6272	<132	330 ± 59	96 ± 20
D-β-ABA	1327 ± 33	3903 ± 377	534 ± 24[a]	<6	49 ± 5[a]
L-β-ABA	1458 ± 99	4239 ± 494	[a]	<4	[a]
α-AIB	50 210 ± 870	30 257 ± 1226	<73	34 ± 5	48 ± 3
D-α-ABA	1123 ± 54	2956 ± 125	<89[a]	<5[a]	ND
L-α-ABA	1244 ± 28	2955 ± 120	[a]	[a]	ND
D-Isovaline	22 806 ± 459[a]	29 245 ± 2229[a]	349 ± 33[a]	<3	<131[a]
L-Isovaline	[a]	[a]	[a]	<5	[a]
Total	162 000	235 000	4300	2200	750

The associated errors are based on the standard deviation of the average value. Adapted from [126–128, 130–133, 136–138, 140–142].
[a]Enantiomers could not be detected individually, so the total (D + L) abundance of the amino acids is reported in the row for the D-enantiomer.
[b]Tentative identification.
[c]Optically pure standard not available for enantiomeric identification.
[d]γ-ABA and D,L-β-AIB could not be separated under the chromatographic conditions used, so the total abundance is reported in the cell corresponding to γ-ABA.
[e]γ-ABA and D,L-β-ABA could not be separated under the chromatographic conditions used, so the total abundance is reported in the cell corresponding to γ-ABA.
[f]The value corresponds mostly to γ-ABA.
[g]Detected but too small to estimate.
ND = not determined.

abundance similar to the CM2 Murchison. While the CM2 Y-791 198 has an extremely high total amino acid concentration (71 ppm [131, 132]), which is about 5 times as high as Murchison (15 ppb), the CM2s Essebi, Nogoya, Mighei [133], Allan Hills (ALHA) 77 306 [134–136], ALH 83 100 [130], Y-79 331, and Belgica (B-) 7904 [137] have much lower amino acid abundances, some being depleted in amino acids (Table 1.5). For Essebi, Botta *et al.* [133] consider that the high abundances (relative to glycine) of γ-ABA and β-alanine are derived from terrestrial contamination at the fall site.

CM1s chondrites were analyzed for the first time for amino acids by Botta *et al.* [138]. ALH 88 045, MET (Meteorite Hills) 01 070, and LAP (La Paz) 0227 have total amino acid concentration much lower than the average of the CM2s. According to Botta *et al.* [138], these results and the similar relative amino acid abundances between the CM1 class meteorites and the CM2 Murchison are explained by decomposition of a CM2-like amino acid distribution during extensive aqueous alteration in the CM1s meteorite parent body.

The CI1 chondrites Orgueil and Ivuna have total amino acid abundances of about 4.2 ppm, with β-alanine, glycine, and γ-ABA as the most abundant amino acids, while glycine and α-AIB are the most abundant amino acids in the CM2 chondrites Murchison and Murray [136]. The CV3 Allende [133, 139] and the ungrouped C2 Tagish Lake meteorites [133, 140] are essentially free of amino acids (total amino acid abundances of 2 and 1 ppm, respectively), with most of the amino acids probably being terrestrial contaminants.

The highest amino acid abundances ever measured in a meteorite were found on the CR2s EET 92 042 and GRA 95 229, with total amino acid concentrations of 180 and 249 ppm, respectively [141]. The most abundant amino acids present in these meteorites are the α-amino acids glycine, isovaline, α-AIB and alanine. The high $\delta^{13}C$ results together with the racemic enantiomeric ratios determined [141] for most amino acids indicate an extraterrestrial origin for these compounds (see Section 1.4.1). In addition, these authors analyzed the CR1 GRO 95 577, which was found to be depleted in amino acids (1 ppb). Other CRs analyzed include the CR2 chondrites Renazzo [133] and Shişr 033 [142]. Renazzo has a total amino acid abundance of only 4.8 ppm, which is similar to the CI chondrites Orgueil and Ivuna. This meteorite has a distinct amino acid distribution, with γ-ABA, glycine, and L-glutamic acid as the most abundant amino acids. Only upper limits for alanine and α-AIB were reported for Renazzo, while isovaline was tentatively identified [133]. The most abundant amino acids in the Shişr 033 meteorite are glycine, L-glutamic acid, L-alanine, and L-aspartic acid. In addition to this, Shişr 033 D/L protein amino acid ratios are smaller than 0.4 and in agreement with the D/L amino acid ratios of Shişr 033 fall-site soil. These results suggest extensive amino acid contamination of the meteorite (see Section 1.4.1). However, Shişr 033 contains a small fraction of extraterrestrial amino acids, as indicated by the presence of α-AIB [142].

Apart from carbonaceous chondrites, amino acid analyses have also been carried out on Martian meteorites. As our present knowledge of amino acids potentially present in Mars may be accessed from these meteorites (see also Section 1.6), amino

acid analyses have been performed in the Martian meteorites EET 79 001 [143], ALH 84 001 [144], and Miller Range (MIL) 03 346 [145]. In all three samples, the meteoritic amino acid distribution was similar to the one in the Allan Hills ice, which suggested that the ice meltwater was the source of the amino acids in these meteorites. In addition, analysis of the Nakhla meteorite, which fell in Egypt, shows that the amino acid distribution (including the D/L ratios) is similar to the one in the sea-floor sediment from the Nile Delta [146].

1.4.1 Sources of Meteoritic Amino Acids (Extraterrestrial versus Terrestrial Contamination)

In order to determine if the amino acids present in carbonaceous chondrites are indigenous to the meteorites, four approaches are generally applied: (i) detection of amino acids that are unusual in the terrestrial environment, (ii) comparison of the absolute abundances of amino acids in the meteorites to the levels found in the fall-site environment (soil or ice), (iii) determination of enantiomeric ratios (D/L ratios), and (iv) determination of compound specific stable isotope ratios of hydrogen, carbon, and nitrogen.

1.4.1.1 Detection of Amino Acids that are Unusual in the Terrestrial Environment

The majority of the more than 80 different amino acids identified in carbonaceous meteorites are nonexistent (or rare) in terrestrial proteins (for a review, see, e.g., [108]). Extraterrestrial meteoritic nonprotein amino acids such as α-AIB, isovaline, β-ABA, and β-AIB have concentrations usually in the order of a few hundred parts per billion maximum (Table 1.5). However, Murchison [126] has a higher abundance of α-AIB (2901 ppb), while Murray and LEW90 500 [126, 129, 130] contain higher abundances of both α-AIB (1968 and 2706 ppb, respectively) and isovaline (2834 and 1306 ppb, respectively). The highest abundances of α-AIB, isovaline, β-ABA, and β-AIB were detected in the CR2 chondrites EET92 042 and GRA95 229 [141]. The CM2 Y791 198 ([131, 132]) contained similar abundances of α-AIB, β-ABA, and β-AIB as EET92 042 and GRA95 229, but lower abundance of isovaline (Table 1.5).

1.4.1.2 Determination of the Amino Acid Content of the Meteorite Fall Environment

Samples collected from meteorite fall sites have been analyzed for amino acids and their distribution compared to the one from the carbonaceous chondrites. Ice from the Antarctic regions of Allan Hills [143, 144] and La Paz [130, 147] contained only trace levels of aspartic acid, serine, glycine, alanine, and γ-ABA (less than 1 ppb of total amino acid concentration). No isovaline or β-ABA was detected above detection limits. Only an upper limit of α-AIB (<2 ppt) was detected in the Allan Hills ice [144], while a relatively high abundance (ranging between 25 and 46 ppt) of α-AIB was detected in the La Paz Antarctic ice [130, 147].

Soil samples from the Shişr 033 fall site show that the most abundant amino acids are L-glutamic acid, L-aspartic acid, glycine, and L-alanine, with nonprotein amino acids absent from the soil [142]. In addition, comparison of the protein

amino acid enantiomeric ratios of Shişr 033 to those of the soil (D/L < 0.4) shows agreement, indicating that most of the amino acids in this meteorite are terrestrial in origin. On the other hand, a soil sample collected close to the fall site of the Murchison meteorite showed much smaller amino acid relative concentrations (glycine = 1) when compared to the Murchison meteorite, indicating that the majority of the amino acids present in this meteorite are extraterrestrial in origin [133].

1.4.1.3 Determination of Enantiomeric Ratios

Chirality is a useful tool for determining the origin (biotic versus abiotic) of amino acids in meteorites. On Earth most proteins and enzymes are made of only the L-enantiomer of chiral amino acids; however, abiotic synthesis of amino acids yields racemic mixtures (D/L ~ 1). If we assume that meteoritic protein amino acids were racemic (D/L ~ 1) prior to the meteorite fall to Earth, then their D/L ratios can be used as a diagnostic signature to determine the degree of terrestrial L-amino acid contamination they have experienced. In fact, racemic amino acid ratios for protein (and nonprotein) amino acids in carbonaceous chondrites indicate an abiotic synthetic origin. Although racemic mixtures have been observed for most nonprotein chiral amino acids (Table 1.5), small L-enantiomeric excess for some nonprotein amino acids has been reported in the Murchison and Murray meteorites [148–150]. Six α-methyl-α-amino acids unknown or rare in the terrestrial biosphere (both diastereomers of α-amino-α,β-dimethyl-pentanoic acid, isovaline, α-methylnorvaline, α-methylnorleucine, and α-methylvaline) had L-enantiomeric excesses ranging from 2.8 to 9.2% in Murchison and from 1.0 to 6.0% in Murray [148, 149]. More specifically, Murchison has shown to have an L-enantiomeric excess of isovaline ranging from 0 to 15.2% with significant variation both between meteorite stones and even within the same meteorite stone [150]. The meteoritic enantiomeric excess of α-methyl-α-amino acids and the absence for the α-H-α-amino acids may be explained by the resistance to racemization of α-methyl-α-amino acids during aqueous alteration in the meteorite parent body, due to their lack of an α-hydrogen [149, 151, 152]. Another explanation could be a different amino acid formation process, namely pre-solar formation for the α-methyl-α-amino acids and subsequent incorporation into the parent body, followed by parent body formation of the α-H-α-amino acids [149, 152].

1.4.1.4 Determination of Compound-Specific Stable Isotope Ratios of Hydrogen, Carbon, and Nitrogen

For meteoritic nonchiral amino acids, such as glycine, α-AIB, β-ABA, and β-alanine, compound-specific stable isotope measurements are the only means to establish their origin. The abundances of stable isotopes are expressed in δ values. These indicate the difference in per mil (‰) between the ratio in the sample and the same ratio in the standard, as shown by:

$$\delta(‰) = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \times 1000 \tag{1.8}$$

where R represents $D/^1H$ for hydrogen, $^{13}C/^{12}C$ for carbon, and $^{15}N/^{14}N$ for nitrogen. The standards usually used are standard mean ocean water for hydrogen, Pee Dee Belemnite for carbon, and air for nitrogen.

Stable isotope analyses of the total amino acid fractions of the Murchison meteorite showed $\delta D = +1370‰$, $\delta^{15}N = +90‰$, and $\delta^{13}C = +23.1‰$ [153], which were later confirmed by Pizzarello *et al.* [154, 155], who obtained $\delta D = +1751‰$, $\delta^{15}N = +94‰$, and $\delta^{13}C = +26‰$. Stable isotope analyses were obtained for individual amino acids in different meteorites (Table 1.6; [126, 141, 150, 156–159]). These values (with a few exceptions, in which there is terrestrial contribution) are clearly outside the amino acid terrestrial range (from -70.5 to $+11.25‰$; [160]) and fall within the range of those measured for other indigenous polar organic compounds present in meteorites [161]. The highly enriched δD, $\delta^{15}N$, and $\delta^{13}C$ values determined for the meteoritic amino acids indicate primitive extraterrestrial organic matter.

The deuterium enrichment of amino acids is thought to be the result of interstellar chemical reactions (e.g., gas-phase ion–molecule reaction and reactions on interstellar grain surfaces) which formed the amino acid precursors. These reactions occur in the low temperatures of dense clouds ($T < 50$ K) in which deuterium fractionation is efficient (e.g., [162–164]). Meteoritic amino acids would have then been formed from their deuterium-enriched interstellar precursors and deuterium-depleted water ([165] and references therein) by synthesis (aqueous alteration) in the meteorite parent body (see Section 1.4.2). However, α-amino acids are more deuterium (and ^{13}C)-enriched than α-hydroxy acids [117], which is inconsistent with a Strecker-cyanohydrin-type synthesis from a common precursor [116, 166]. Differences may be explained by different reaction paths leading to different isotopic distributions [164]. The ^{15}N enrichment of amino acids is also thought to be due to chemical fractionation in interstellar ion–molecule exchange reactions [167, 168].

The hydrogen isotope composition of meteoritic amino acids follows a relatively simple pattern, in which δD varies more with the structure of their carbon chains (δD is higher for amino acids having a branched alkyl chain) than with the chain length [159]. On the other hand, $\delta^{13}C$ of α-amino acids (α-methyl-α- and α-H-α-amino acids) decreases with increasing carbon chain length (with the α-methyl-α-amino acids more ^{13}C-enriched than the corresponding α-H-α-amino acids), while $\delta^{13}C$ for non-α-amino acids remains unchanged or increases with increasing carbon chain length [158]. This suggests diverse synthetic processes for meteoritic amino acids, in particular that the amino acid carbon chain elongation followed at least two synthetic pathways [158, 159].

1.4.2
Synthesis of Meteoritic Amino Acids

Meteoritic amino acids are thought to be formed by a variety of synthetic pathways. Namely, it is suggested that α-amino acids form by a two-step process, in which the α-amino acid precursors (carbonyl compounds, ammonia, and HCN) were present (or formed) in a proto-solar nebula and were later incorporated into an asteroidal parent

Table 1.6 Compound-specific stable isotope composition (in ‰) of individual amino acids in carbonaceous chondrites.

Amino acid	Murchison			Murray		GRA 95 229	EET 92 042	Orgueil
	δD	$\delta^{13}C$	$\delta^{15}N$	δD	$\delta^{13}C$	$\delta^{13}C$	$\delta^{13}C$	$\delta^{13}C$
D,L-Aspartic acid[a]			+61					
D-Aspartic acid		+25				+35	+34	
L-Aspartic acid		–6				+33	+23	
D-Glutamic acid	+473	+29	+60			+47	+46	
L-Glutamic acid	+292	+7	+58			–18	–19	
Glycine		+22; +41	+37	+399		+34	+32	+22
β-Alanine	+461	+5	+61	+1063				+18
γ-ABA	+599	+19		+763				
D,L-β-AIB[a,]	+967							
D-Alanine	+429	+22; +52	+60	+614		+42	+45	
L-Alanine	+360	+27; +39	+57	+510		+41	+50	
D,L-β-ABA[a]	+20.7							
α-AIB	+3058	+5; +43	+184	+3097		+32		
D-α-ABA	+1338	+29		+1633				
L-α-ABA	+1225	+28						
D,L-Isovaline[a]	+3419	+16; +22	+66	+3181		+51		
D-Isovaline		+11 to +20			+19			
L-Isovaline		+17 to +22		+3283	+20			
D-Norvaline		+15		+1505				
D-Valine				+2432				
L-Valine				+2266				
L-Leucine			+60					
D,L-α-Methylnorvaline[a]	+2686	+7		+3021				

D,L-α-Amino-α,β-dimethylbutyric acid[a]	+3318			+3604
L-α-Amino-α,β-dimethylbutyric acid[a]		+23		
D-*allo*-isoleucine				+2251
L-*allo*-isoleucine				+2465
L-isoleucine				+1819
D,L-γ-Aminovaleric acid[a]	+367	+29		+965
δ-Aminovaleric acid	+362	+24		+552
β-Amino-α,α-dimethylpropionic acid		+25		+2590
β-Amino-β-methylbutyric acid				+1141
D,L-γ-Amino-α-methylbutyric acid[a] + D,L-γ-amino-β-methylbutyric acid[a]	+1164			+1164
D,L-α-Aminoadipic acid[a]	+181			+619
L-α-Aminoadipic acid		+35		
D,L-β-Aminoadipic acid[a]		+37		
D,L-α-Methylglutamic acid[a]	+2049	+32		+1563
D,L-*threo*-β-Methylglutamic acid		+32		
D- or L-*threo*-β-Methylglutamic acid[b]				+1255
D- or L-*threo*-β-Methylglutamic acid[b]	+1352			+1408
D,L-*threo*-γ-Methylglutamic acid[a]		+36		
D,L-Proline[a]		+4	+50	+478
Cycloleucine	+425	+24		+850
Sarcosine	+962	+53	+129	+1337
D,L-*N*-Methylalanine[a]				+1267
N-Methyl-α-AIB				+3446

Adapted from [126, 141, 142, 150, 157–159].
[a]Isotopic value corresponds to the combined enantiomeric peaks.
[b]The chromatographic order of elution for the two enantiomers could not be established for lack of standards.

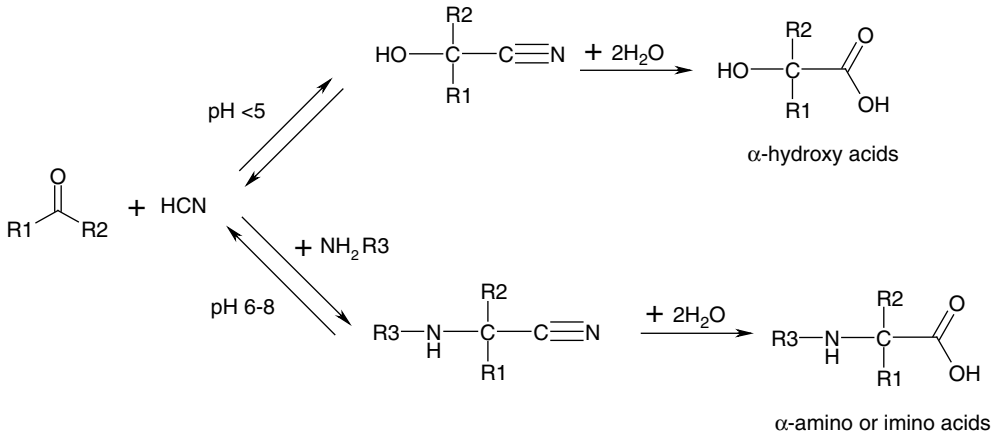


Figure 1.2 The Strecker-cyanohydrin synthetic pathway for the formation of α-amino α-hydroxy and imino acids (adapted from [116, 133, 171, 247]). R_1 and R_2 correspond to H or C_nH_{2n+1}. If R_3 corresponds to H then α-amino acids are produced; if R_3 is an amino acid then imino acids are produced.

body [169]. During aqueous alteration on the asteroidal parent body, Strecker-cyanohydrin synthesis would have taken place to form α-amino acids (Figure 1.2; [108, 116, 163, 166]). Since the carbonyl precursors (aldehydes and ketones) are thought to be synthesized by the addition of a single-carbon donor to the growing alkane chain, a decrease of the α-amino acid abundances with increasing chain length is expected. Also, synthesis of branched carbon chain analogs is expected to be favored over straight-carbon chain analogs (e.g., [108]), and this trend is observed in the EET 92 042 and GRA 95 229 meteorites [141]. Additional support for this hypothesis is the finding of α-amino acid, α-hydroxy acids [116, 117, 166], and imino acids [170] in carbonaceous meteorites. However, non-α-amino acids cannot be produced by the Strecker-cyanohydrin synthesis. Alternatively, meteoritic β-amino acids are thought to be synthesized by Michael addition of ammonia to α,β-unsaturated nitriles, followed by reduction/hydrolysis (Figure 1.3; e.g., [108] and references therein). These precursor molecules have been detected in the ISM (Table 1.1 and reference therein) and also in comets (Table 1.3 and references therein). A chemical reaction such as a Michael addition could occur on the parent body of meteorites. For example, the extensively aqueous altered CI chondrites Orgueil and Ivuna are rich in β-alanine, but depleted in α-amino acids. As suggested [138], this might indicate that the CI parent body was depleted in carbonyl compounds (aldehydes and ketones) necessary for the Strecker-cyanohydrin synthesis to occur. Additional synthetic pathways in the meteorite parent body have been proposed for non-α-amino acids (for a review, see, e.g., [108]). For example, hydrolysis of lactams and carboxy lactams, which have been detected in carbonaceous meteorites [125], gives the corresponding β-, γ-, and δ-amino acids, and dicarboxylic amino acids, respectively.

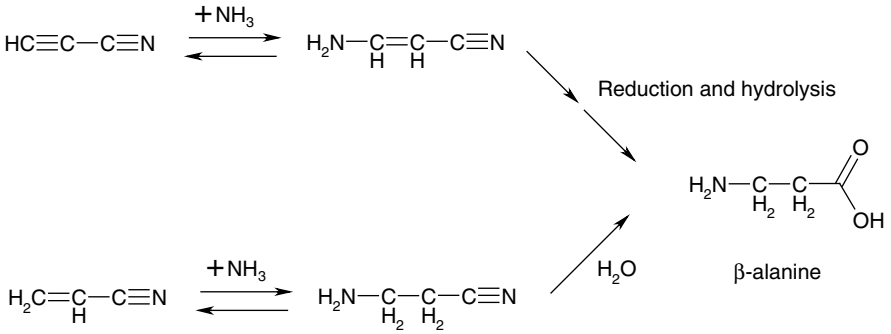


Figure 1.3 Michael-addition of ammonia to a α,β-unsaturated nitrile to form a β-amino alkylnitrile that is then hydrolyzed to form a β-amino acid (β-alanine) (adapted from [133]).

1.5 Micrometeorites and IDPs

Micrometeorites (MMs) and IDPs are thought to be the remains of comets and asteroids (for reviews, see, e.g., [171–176]). MMs are small extraterrestrial dust particles, typically in the range 50 μm to 2 mm [177], that have survived atmospheric entry. They are collected in deep-sea sediments [171, 178], Antarctic ice [179–181], and Greenland lake deposits [182–184]. On the other hand, IDPs are extraterrestrial particles (usually measuring less than 30 μm in size), which are collected from the Earth's stratosphere (at an altitude of ~20 km) by NASA aircraft (e.g., [171, 185, 186]).

Several organic molecules have been found in IDPs and MMs, such as ketone and aliphatic hydrocarbons [12, 187–189], and polycyclic aromatic hydrocarbons [11, 190]. Antarctic micrometeorites (AMMs) have also been analyzed for amino acids [191–193]. Most AMMs analyzed by Brinton *et al.* [191] had very low abundances of amino acids and high L-enantiomeric excess, with a distribution similar to that found in the Antarctic ice. One set of samples containing around 30 MMs was found to contain α-AIB at high levels (~280 ppm). However, the identification of α-AIB was tentative and needs further confirmation [191]. In addition, Glavin *et al.* [192] studied 455 AMMs and none of them contained α-AIB. A third study by Matrajt *et al.* [193] analyzed 300 AMMs and found α-AIB in around 100 MMs. These authors calculated that only around 14% of AMMs analyzed so far contained α-AIB.

1.6 Mars

The possibility of Mars harboring alien life (presently and/or in the past) is the focus of future space missions planned to the Red Planet. Their target compounds indicative of life include, among others, amino acids [194–196]. These are key biomolecules on Earth, but are also produced by abiotic reactions such as those

occurring in the parent body of meteorites (see Section 1.4.2). Amino acids synthesized elsewhere in the solar system may therefore be delivered intact into the surface of Mars. In fact, large amounts of carbonaceous material are thought to be delivered to the surface of Mars by IDPs and meteorites every year [14, 197, 198]. However, in 1976 the Viking landers found no organic molecules above the parts per billion to parts per million levels on the surface of Mars (e.g., [199, 200]), even though they should have been able to detect amino acids on the order of tens of parts per million [201, 202]. This might be explained by chemical reactions occurring in the surface of Mars, leading to the destruction of organic molecules. For example, oxidant molecules may react with any potential organic compound present in the surface of the Martian soil, leading to their destruction. These oxidizing molecules may be formed by UV photolysis of the Martian atmosphere [203–207], interaction of Martian minerals with atmospheric H_2O_2 [208] or UV radiation [209], or by chemical weathering of silicates by low-temperature frost and adsorbed water in the Martian soil [210, 211]. In addition, amino acids directly exposed to Mars-like UV radiation are rapidly degraded [212–214]. For example, thin films of glycine and D-alanine have half-lives in the order of 10^4–10^5 s when irradiated under simulated noon-time Mars equatorial surface conditions [213].

If present, amino acids should therefore be in the subsurface of the Red Planet, shielded from exterior radiation. As shown by Kminek and Bada [215], amino acids can survive up to 3 billion years at a depth of more than 2 m. In particular, Aubrey *et al.* [216] found that the amino acids glycine and alanine have a half-life of up to 1.1 billion years, if buried under simulated Martian conditions. Similar results had previously been obtained by Kanavarioti and Mancinelli [217], based on amino acid decomposition rates in aqueous solutions. They found that a fraction of the amino acids phenylalanine, alanine, and pyroglutamic acid would have been preserved buried beneath the surface of Mars up to 3.5 billion years.

The mineralogical composition of Martian soils may also have an influence on the amino acid stability [216, 218, 219]. Peeters *et al.* [218, 219] have shown that different mineralogical compositions of Mars soil analogs lead to differences in amino acid stability (for a review about Mars soil analogs, see [220]); in particular, clay mineral matrices seem to have a shielding effect, protecting amino acids against destruction. In addition, Aubrey *et al.* [216] determined that amino acids can be preserved for geologically long periods (billions of years) in sulfate mineral matrices. These results suggest that locations on Mars containing clay and/or sulfate minerals (for a review, see, e.g., [221]) should be the prime targets for future missions with the goal to search for life, in particular for its amino acid constituents.

1.7 Delivery of Extraterrestrial Amino Acid to the Earth and its Importance to the Origin of Life

Independently of the environment where extraterrestrial amino acids were formed, these molecules were exogenously delivered to the early Earth during the period of

late heavy bombardment 4.5–3.8 billion years ago. In fact, comets, meteorites, MMs, and IDPs are thought to have delivered tons of organic carbon per year to our planet during this period of time [13, 14, 222], just before life emerged (e.g., [223–225]). Although we do not know what the production rates of different organic compounds were on the early Earth (i.e., impact-shock synthesis, endogenous production by UV light or electrical discharge, and synthesis in submarine hydrothermal vents), the higher the content of key molecules in primitive extraterrestrial materials, the more likely it is that exogenous material played a role in the origin of life. As noted by Chyba and Sagan [14], the heavy bombardment may have delivered or produced organic molecules in the early Earth in quantities comparable to other sources, possibly playing an important role for the origin of life.

The survival rate of amino acids in extraterrestrial bodies under simulated Earth atmospheric entry has been studied by several authors. Amino acids present in the interior of meteorites bigger than 1 mm survive atmospheric deceleration ([226]; see also Section 1.4), as the meteorite only experiences pyrolytic temperatures (>600 °C) and melting on the surface (<1 mm depth [227]). This does not happen with smaller particles such as MMs and IDPs, which are uniformly heated. In fact, it is estimated that most MMs and IDPs are heated for a few seconds to peak temperatures of up to 1700 °C during atmospheric entry [228–230]. However, a small percentage of dust (MMs and IDPs) enters the atmosphere at temperatures below 700 °C [173, 228, 231–233]. Glavin and Bada [234] investigated the sublimation of amino acids from sub-100 μm Murchison meteorite grains to test the survival of amino acids in MMs during atmospheric entry. They found that under vacuum (800 mT) and at 550 °C, only glycine survived. All other amino acids (including α-AIB and isovaline) were completely destroyed, which is not surprising if we consider that, with a few exceptions, pure amino acids suffer thermal decomposition in the range of 200–600 °C [235]. Glavin and Bada [234] also found that methylamine and ethylamine, which are the α-decarboxylation products of glycine and alanine, respectively, were not detected. This indicates that α-decarboxylation did not occur or that these amines were also decomposed during the experiments. Although amino acids are expected to have a higher atmospheric entry survival in smaller cosmic dust particles (<50 μm) [228, 231], Matrajt *et al.* [236] found similar results to Glavin and Bada [234] using activated alumina with grain sizes ranging from 5 to 9 μm, which suggests that the amino acid survival is not greatly dependent on the grain size. On the other hand, Matrajt *et al.* [236] demonstrated that the combination of porosity and heatshield effect (i.e., ablative cooling) of extraterrestrial dust particles during atmospheric heating results in poor heat transfer to the particle's interior, providing thermal protection and allowing organic compounds to survive. This reinforces the idea that IDPs, which are around 10% organic carbon by mass, can decelerate in the atmosphere and deliver organic compounds intact [222], and might have been the major source of exogenous organics in the early Earth as suggested by Chyba and Sagan [14].

Nonprotein amino acids, α-AIB and racemic isovaline, have been detected within around 1 m above and below the sediments of the iridium-rich Cretaceous/Tertiary boundary at Stevns Klint, Denmark by Zhao and Bada [237]. These authors suggested that the sediments represented components of a large bolide (i.e., a comet), which

collided with the Earth 65 million years ago. These results are not in agreement with xenon measurements at the Cretaceous/Tertiary boundary [238, 239] or with two-dimensional smoothed particle hydrodynamics simulations of cometary organic pyrolysis by impacts [13]. However, Chyba *et al.* [13] noted the lack of relevant kinetic data for high-temperature pyrolysis of organic molecules. Further work on amino acid survival in simulated large asteroidal and cometary shock impacts has been performed [240–243]. Peterson *et al.* [240] conducted a series of shock impact experiments over a pressure range of 3.5–32 GPa using powdered Murchison and Allende meteorite samples. These were previously extracted to eliminate their original amino acid content and subsequently doped with known amino acids. The results show that amino acids diminished substantially with increasing high pressures and new "daughter" amino acids were formed, in particular β-alanine, glycine, alanine, γ-ABA, and β-AIB. At 30 GPa, the abundances of the daughter compounds exceeded those of the remaining initial amino acids. However, as noted by Blank *et al.* [242], these authors did not refer to the porosity of the starting material or the temperature conditions of the experiments. Further shock experiments in the range 5–21 GPa and 139–597 °C and using aqueous amino acid solutions were performed by Blank *et al.* [242]. In all the experiments a large fraction of amino acids survived, supporting the hypothesis that organic compounds could survive impact processes. In addition, high-resolution hydrocode simulations of comet impacts, over different projectile radii, impact velocities, and angles, show that significant amounts of amino acids can be delivered intact to the Earth via kilometer-sized comet impacts [241, 243].

1.8 Conclusions

To date, extraterrestrial amino acids have only been unequivocally identified in meteorites and a few AMMs. However, the potential precursors of these prebiotic molecules are abundant in a variety of extraterrestrial environments, including the ISM and comets. This suggests that meteoritic amino acids may have a contribution from interstellar, nebular and/or parent body processing. The delivery of these prebiotic molecules to the early Earth during the period of heavy bombardment (4.5–3.8 billion years ago) may have provided the necessary feedstock for the evolution of emergent life systems.

Laboratory analyses of meteoritic material together with future missions (including sample return missions) to solar system planets (e.g., Mars Science Laboratory, ExoMars), satellites, asteroids, and comets may expand our inventory of amino acids in extraterrestrial environments.

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