Relative proportion of prebiotic amino acids: part 4—the case for the primitive atmosphere having been weakly reducing

Royal Truman, Boris Schmidtgall, and Chris Basel

Evolutionary geochemists believe the prebiotic atmosphere consisted almost entirely of CO_2, N_2, and H_2O, with trace amounts of CO, CH_4, H_2, NH_3, and H_2S. The evidence for this view enjoys wide support from the literature, such as analysis of the oxidation state of zirconium silicates (ZrSiO4) and ancient terrestrial magma. CH_4, NH_3, and H_2 would have been destroyed by fierce UV photolysis. Especially H_2 would have escaped at the predicted mean temperature of >1,400 K predicted for the uppermost atmosphere, helped through acceleration of H ions by the earth's magnetic field. Experiments based on realistic gas mixtures using spark discharge and proton irradiation typically produced proteinogenic amino acids (AAs) consisting of >99% glycine + alanine and 5–10 times more contaminating carboxylic acids, which would have also reacted with AAs. The resulting peptide-like substances would have had no resemblance to those used in OoL chemical experiments.

Most evolutionists believe that abiotic AAs originated primarily from molecules produced by high-energy reactions in the ancient atmosphere, based on the Miller-type experiments, which began in the 1950s.[1] The results of key Miller-type studies based on reduced gas mixtures were discussed in part 1[2] and part 2[3] of this series. The results using oxidized gas mixtures discussed in part 3[4] with spark discharge or proton irradiation as energy sources are summarized in table 1.

Products from non-reducing gas mixtures

Evolutionary geochemists believe the most realistic prebiotic atmospheric composition would have consisted almost entirely of $N_2/CO_2/H_2O$ with a proportion of $CH_4:CO_2$ <5%. However, the entries in table 1 reveal that the focus has not been on realistic mixtures (including perhaps trace amounts of CH_4, H_2, NH_3, and CO). Chemists knew in advance that such mixtures would only produce an insignificant amount of AAs. Furthermore, minimal or no effort was invested in reporting the trace amounts of other products. Irrespective of the energy source used, a gas mixture of N_2/CO consistently produced almost only glycine from among the proteinogenic AAs.[8] Even experiments conducted in 2002 by Miyakawa *et al.* using high energy 2.5–3.0 MeV protons with 1:1 mixture of CO and N_2 with H_2O produced no AAs.[9]

An exception are experiments by Cleaves *et al.*, shown in rows 3 and 4 in table 1 in which a high concentration of the powerful biologically produced ascorbate was used.[6] Potentially relevant prebiotic oxidation inhibitors were also tested in large excess: $FeCl_2$, Na_2S, Na_2SO_3, $FeSO_4$, pyrites, and sodium formate, of which only pyrites and $FeSO_4$ seemed to have a small anti-oxidation effect. Unfortunately, the yields of AAs were not reported, nor were prebiotically reasonable molar proportions tested. The highest amount of AAs was obtained in the presence of high concentrations of $CaCO_3$ and ascorbate (a biochemical antioxidant). According to figure 2 of ref. 6, only Gly, Ala, Asp, Glu, and Ser, were produced, of which Gly and Ala jointly represented ⅔. The other chemicals produced, which would have interfered with forming proper peptides, were unfortunately not reported.

An important result of all attempts to produce high AA concentrations and of wider variety was also revealed by what Cleaves *et al.* found; namely, that such optimizing conditions inevitably *increased the yield of non-proteinogenic AAs and other substances* which would have interfered with forming suitable peptides for OoL purposes. In these experiments, typically less than half the AAs produced were proteinogenic.

Products from slightly reducing gas mixtures

In order to obtain AAs at all with highly oxidized CO_2/N_2 mixtures researchers usually included a high proportion of the reducing gases H_2 or CH_4. The consensus within the OoL community is that these experiments do not reflect a prebiotic atmosphere (for example row 2 with H_2 being, by

Table 1. Summary of AAs identified in key Miller-type experiments using oxidized gas mixtures. Data extracted from Schlesinger and Miller (1983)[5], Cleaves *et al.* (2008)[6], Bada (2013)[7], Hirose *et al.* (1990)[8], Miyakawa *et al.* (2002)[9]. All mixtures included water vapour. The ratios are reported on a molar basis. Prot. = proteinogenic AAs; Gly = glycine; Ala = alanine.

Year	Gas mixture	Energy source	Prot. AA [a]	Prot. AA among non-AA [b]	Prot. AA overall	(Gly+Ala) / Prot.	Number AA	Comments	Ref
1983	CO_2, N_2, H_2 (1:1:0.5)	Spark	99.9%	—	—	99.4%	5	Continuous spark discharge 48 h at 25°C; aqueous phase equilibrated 48 h.	5
1983	CO_2, N_2, H_2 (1:1:3)	Spark	99.9%	—	—	99.6%	4	Continuous spark discharge 48 h at 25°C; aqueous phase equilibrated 48 h.	5
2008	CO_2, N_2 (1:1)	Spark	48%	—	—	13%	5	With antioxidant (ascorbate); without $CaCO_3$. 1.3% AA based on N_2 input.	6
2008	CO_2, N_2 (1:1)	Spark	47%	—	—	65%	5	With antioxidant (ascorbate); with $CaCO_3$. 2.5% yield based on N_2 input.	6
2013	CO_2, NH_3, CH_4, H_2S (0.33:0.97:1:0.39)	Spark	61.1%	—	—	83.8%	9	Only 2-6 carbon AA and 1-2 carbon amines identified; no carboxylic acids, etc.	7
1990	CO, N_2 (2:1)	Spark	99.3	—	—	96.7%	4	Irradiated ~15 kV, 6 months; 37 °C. CO_2 absorbent $Ca(OH)_2$; H_2 generated 0.2-0.6 Torr.	8
1999	CO, N_2 (1:1)	H+ irrad.	—	0%	0%	—	0	2.5–3.0 MeV protons from an accelerator for 3 h.	9
1983	CO, N_2, H_2, (1:1:0.5)	Spark	99.9%	—	—	99.9%	4	Continuous spark discharge 48 h at 25°C; aqueous phase equilibrated 48 h.	5
1983	CO, N_2, H_2, (1:1:3)	Spark	99.9%	—	—	99.8%	6	Continuous spark discharge 48 h at 25°C; aqueous phase equilibrated 48 h.	5

[a] Proteinogenic AAs / all AA

[b] Proteinogenic AAs / (Proteinogenic AAs + other interfering chemicals)

far, the major gas component). Nevertheless, an extensive study in 2003 of 11 standard high school biology textbooks showed that their discussion on the Urey-Miller experiments either did not mention that irrelevant gas mixtures had been used or implied that this was not a serious problem.[10] (We have not examined the latest editions of the current standard textbooks.) However, as discussed below, some scientists have tried recently to find conditions where the atmosphere might have been temporarily slightly or highly reduced. Therefore, the results from these older experiments may be discussed again in the future.

Sparking $CO_2/N_2/H_2$ mixtures with high proportions of H_2 produced virtually no proteinogenic AAs,[5] of which about 99.5% was only glycine + alanine, as shown in rows 1 and 2 of table 1, consistent with the other mixtures mentioned below.

In row 5, N_2 was replaced by NH_3, and very high proportions of CH_4 and H_2S were included, mimicking, in a very unrealistic manner, lightning discharges near a volcanic eruption (of volcanic gases, CO_2 should have been the major, not the minor, component!).[7] Unsurprisingly, a wider variety of AAs was obtained, but once again the principle held, that when the proportion of glycine + alanine to all proteinogenic AAs decreased, this was accompanied by a much higher amount and variey of non-proteinogenic AAs.

In rows 6–9, CO_2 was replaced by CO, a slightly reducing gas, in various experiments.[5,8,9] Under these conditions, CO would have oxidized to CO_2 in the presence of water vapour, so an atmosphere devoid of CO_2 would not have existed. Using a CO_2 absorbent led to a slightly lower proportion of Gly + Ala vs all four proteinogenic AAs formed (96.7%, see row 6), but, otherwise, the Gly + Ala proportion was about 99.9%.

Assuming a less oxidized atmosphere in order to obtain a wider variety and yield of AAs has a serious drawback: the biosphere would have been flooded almost entirely with Gly and some Ala, *making it ever more difficult to obtain peptides with a rich variety of AAs* as assumed for OoL purposes.

Table 2. Carboxylic acids from proton irradiation and spark discharge experiments from gas mixtures of $CO_2/N_2/CH_4$ in 5 mL H_2O, using a range of methane ratios (rCH_4). Data estimated from the values in figure 6 of Kobayashi *et al.*[11] Concentrations are expressed in nanomoles; nd = not determined. Calculation available in file Supplementary Materials, sheet ('Kobayashi').

	rCH_4	0%	5%	25%	0%	5%	25%
Torr	CH_4:	0	35	175	0	35	175
	CO_2:	350	315	175	350	315	175
	N_2:	350	350	350	350	350	350
Carboxylic acid	**No.of C atoms**	**Proton irradiation**			**Spark discharge**		
formic acid	1	1,500	17,000	17,000	1,300	3,200	15,000
acetic acid	2	35	8,000	9,000	15	80	4,000
propanoic acid	3	4	1,100	5,000	4	10	180
isobutyric acid	4	1	50	400	2	3	2
isovaleric acid	5	50	100	600	20	20	2
oxalic acid	2	80	500	550	180	320	4,000
malonic acid	3	18	180	180	10	12	10
succinic acid	4	4	35	150	9	7	60
glutaric acid	5	<1	<1	2	1	1	3
	Carboxylic acids:	1,693	26,966	32,882	1,541	3,653	23,257

Atmospheric chemistry as the dominant source of amino acids

In 2023, Kobayashi *et al.* published a comprehensive study covering the major potential sources of AAs and carboxylic acids between 4.5 and 3.8 Ga based on evolutionary assumptions.[11] This is when life was supposed to have arisen, including DNA-based organisms. To their credit, they selected the atmospheric composition believed to be relevant, CO_2/N_2 with water,[12–15] and tested a wide range of added CH_4.

They estimated that carbonaceous chondrites would only have delivered about 1 kg/yr glycine (and, by implication, far less of the other proteinogenic AAs).[11] The effects of lightning were simulated using spark discharge experiments, but they concluded that at *least 15% methane* would have been required to form any detectable amount of AAs—an unrealistic requirement.

This is consistent with the results from the Miller-type experiments mentioned above.[5,16–18] For example, Schlesinger and Miller reported an AA yield of 0.0006% (based on the available carbon) using $CO_2/N_2/H_2O$ mixtures.[5] Even the paltry yields obtained might have been a laboratory artefact through catalysis of the borosilicate found in the glass vessels used.[19]

Different sources of energy would have had very different abilities to form organic compounds. Kobayashi and 14 other scientists analyzed these energy sources carefully, as will be reviewed next.[11]

UV radiation

The highest energy flux during the prebiotic period would have been delivered by UV radiation. However, this would have been inadequate to convert N_2 into a chemically usable form. NH_3 is believed to have hardly been present in the atmosphere, and N_2 would have only been dissociated by low-frequency wavelengths of <110 nm,[11,20] a minor portion of the radiation. Therefore, solar UV would not have provided efficient energy to synthesize AAs.

Lightning

Some have claimed that lightning flashes might have provided the second-largest energy flux.[16] However, these occur about 30 times more frequently over land than over oceans, and <1% of the earth would have been continental during the Hadean period.[21,22] The paucity of large land mass also implies that relatively little lightning caused by the electrification of volcanic plumes would have existed.[22,23] Kobayashi *et al.* used spark discharges to simulate lightning, using a Tesla coil for 24 h, alternating on/off for 1-minute periods. Very few proteinogenic AAs were obtained, and in very low concentrations, as discussed below.

Solar energetic particles (SEP)

Kobayashi *et al.* concluded that the major effective energy source to produce organic chemicals would have been solar energetic particles caused by occasional massive solar superflares.[11]

Galactic cosmic rays (GCR)

Kobayashi *et al.* also concluded that the second most effective energy source would have been from galactic cosmic rays.[11] Simulations for these latter two energy sources will be reviewed next.

Table 3. Amino acids from proton irradiation and spark discharge experiments using gas mixtures of $CO_2/N_2/CH_4$, in 5 mL H_2O (~20 Torr) across a range of methane ratios (rCH_4). Concentrations in 10^9 moles. Data estimated from the values in figures 1–4 of Kobayashi *et al.* (2023).[11]

	rCH$_4$	0%	5%	10%	20%	30%	50%	0%	5%	20%	30%	50%
Torr	CH$_4$:	0	35	70	140	210	350	0	35	140	210	350
	CO$_2$:	350	315	280	210	140	0	350	315	210	140	0
	N$_2$:	350	350	350	350	350	350	350	350	350	350	350
Amino acid		**Proton irradiation [a)]**						**Spark discharge [b)]**				
Glycine		0	6,000	6,500	9,500	8,500	15,000	0	0	1,000	3,000	37,000
		Proton irradiation [c)]						**Spark discharge [d)]**				
Serine		0	30 [e)]	–	112 [e)]	–	180 [g)]	0	0	–	–	120 [h)]
Aspartic acid		0	0	–	11 [f)]	–	0	0	0	–	–	120 [h)]
Glutamic acid		0	0	–	0	–	0	0	0	–	–	12 [i)]
Sum proteinogenic:		0	6,030		9,623		15,180	0	0	1,000	3,000	37,252
		Proton irradiation [a)]						**Spark discharge [b)]**				
α-amino butyric acid		0	250	450	450	400	1,050	0	0	20	500	1,650
β-alanine		0	30	118	112	60	18	0	0	5	350	120
γ-aminobutyric acid		0	0	5	22	17	6	0	0	0	12.5	13
Sum non-proteinogenic:		0	280	573	584	477	1,074	0	0	25	863	1,783

a) From fig. 4 in Kobayashi *et al.* (2003)[11]
b) From fig. 3 in Kobayashi *et al.* (2003)[11]
c) From fig. 2 in Kobayashi *et al.* (2003)[11] All these AAs have primary amine groups that were derivatized with o-phthalaldehyde (OPA) and N-acetyl-L-cysteine (NAC) to form fluorescent isoindole derivatives. Since the AAs themselves don't absorb, the peak sizes reflect the molar concentration of the chromophore attached to each AA.
d) From fig. 1 in Kobayashi *et al.* (2003)[11]
e) [Serine] ≈ [β-ala] from fig 2 in Kobayashi *et al.* (2003)[11] See footnote c) which explains why the relative peak sizes reflect the relative molar concentration.
f) [Aspartic acid] ≈ 10% of [β-ala] from fig. 2 in Kobayashi *et al.* (2003)[11]
g) [Serine] ≈ 10 × [β-alanine] from fig. 2 in Kobayashi *et al.* (2003)[11]
h) [Serine] ≈ [β-alanine] from fig. 1 in Kobayashi *et al.* (2003)[11]
i) [Glutamic acid] ≈ 10% of [β-alanine] from fig. 1 in Kobayashi *et al.* (2003)[11]

Simulation of solar energetic particles and galactic cosmic rays

Very little effort has been devoted by the OoL community into examining CO_2/N_2 mixtures, knowing that AAs don't form using spark discharges, but Kobayashi *et al.* used a very high energy source.[11] SEP and GCR would have split N_2 in a primitive atmosphere, permitting AAs to be produced. Kobayashi *et al.* simulated these energy sources using a 2.5 MeV proton beam generated by a Tandem accelerator, as SEP and GCR consist mainly of charged particles, particularly protons. The proton flux lasted about 1–2 h, comparable to the energy delivered by a superflare.

The methane ratio (rCH_4), i.e., the proportion of CH_4 to $CH_4 + CO_2 + N_2$ in the early earth's atmosphere, has been estimated by various researchers to have been very low, less than 5%.[24,25] CH_4 is a very minor component of volcanic eruptions, and the other highly reducing gas, H_2, can readily escape from the atmosphere.[24] UV and x-ray irradiation would have destroyed atmospheric CH_4 and also NH_3.[26,27]

Kobayashi *et al.* tested several $CO_2/N_2/CH_4$ ratios (with H_2O), using 0%–50% CH_4. The AAs obtained are summarized in table 2. One concern they did not address involves the Pyrex glass tubes used since Criado-Reyes have shown that the borosilicate surface catalyzes formation of AAs.[19]

Kobayashi *et al.* did not carry out an extensive search for all the chemicals produced, such as for amines, which would have interfered with forming peptides. The data summarized in table 3 show that the major chemicals found were carboxylic acids, which would have interfered with forming peptides.

For rCH_4 between 0%-5% the proportion of proteinogenic AA:carboxylic acids varied between 0 and 0.2, depending of the energy source used; and for around rCH_4 = 25% (prebiotically unrealistic) the proportion of proteinogenic AA:carboxylic acids was between around 0.04 and 0.3. This would have severely limited the size of peptides formed.

Table 4 summarizes key conclusions extracted from tables 6 and 7.

Several important conclusions can be drawn from the data summarized in tables 1–4:

Table 4. Proportion of proteinogenic AAs, glycine + alanine, and proteinogenic AAs:carboxylic acids produced for different mixtures of CO_2, N_2, CH_4 with water using proton irradiation and spark discharge as energy sources. Data extracted from Kobayashi *et al.* (2023).[11]

A

	Proton irradiation			Spark discharge		
rCH_4:	0%	5%	25%	0%	5%	25%
Proteinogenic AAs / carboxylic acids:	0%	22.4%	29.3% $^{a)}$	0%	0%	8.6% $^{b)}$

B

	Proton irradiation			Spark
rCH_4:	5%	20%	50%	50%
(Gly+Ala) / proteinogenic AAs:	99.5%	98.7%	98.8% $^{a)}$	99.3%
Proteinogenic AAs / all AAs:	95.6%	94.3%	93.4%	67.6%

a) The AAs weren't measured at rCH_4 = 25%, so the value for rCH_4 = 20% was used.
b) The AAs weren't measured at rCH_4 = 25%, so the average from rCH_4 = 20% and 30% was used.

- The proton irradiation experiments (simulating SEPs and GCRs) produced only Gly (with possibly trace amounts of Ala) from among the proteinogenic AAs when rCH_4 <5% (see table 2). Across the range rCH_4 = 0%–50%, Gly + Ala represented from 98.7% to 100% of the AA yield (see table 4-B).
- The spark discharge experiments (simulating lightning) also produced only Gly (with possibly trace amounts of Ala) even when rCH_4 was as high as about 50% (see table 2). Across the range rCH_4 = 0%–50%, Gly + Ala represented from 99.3% to 100% of the AA yield (see table 4-B).
- These two observations are consistent with the range of 99.4%–99.6% for the $CO_2/N_2/H_2$ mixtures in proportions (1/1/0.5) and (1/1/3) reported by other researchers, see rows 1 and 2 of table 1.
- Both proton irradiation and spark discharge experiments produced far more proteinogenic than non-proteinogenic AAs (see table 4-B).
- Under all conditions and gas mixtures, several times more carboxylic acid was produced than proteinogenic AAs; when $rCH_4 \leq 5\%$, about 5 times more carboxylic acid was produced using proton irradiation, and only carboxylic acids were produced using spark discharge (see table 4-A). With rCH_4 = 25%, the spark discharge did produce some AAs but less than ⅒ as much as carboxylic acids (see table 4-A).
- Kobayashi *et al.* did not report the concentration of other substances, such as amines, alcohols, or aldehydes.

Probable prebiotic atmospheric composition

The relevance of reported Miller-type experiments depends on what the composition of a prebiotic atmosphere might have been. The evolutionary reasoning about a primitive atmosphere will be reviewed next to clarify which gas mixtures and resulting products would have existed.

The case for a weakly reducing or non-reducing atmosphere

Virtually all paleo-geoscientists believe the early earth did not possess an H_2/CH_4-rich atmosphere, based on data such as analysis of zircons. Zircons (crystals of zirconium silicate, $ZrSiO_4$) are created when rocks are modified under high temperature and pressure. They are commonly associated with igneous and metamorphic rocks and are often used to deduce putative prebiotic environments.[28,29] According to Trail *et al.*, chemical analyses of ancient zircons have indicated that the oxidation state of the early mantle resembled that found today.[30] This implies that the atmosphere would not have contained significant proportions of reducing gases which would have permitted production of AAs through lightning discharges. Although photochemical reactions could have produced some atmospheric HCN, the necessary gases, like CH_4 and C_2H_2, would have been almost completely absent.

In 2020, a large international team concluded that around 4.5 Ga ago the original atmosphere contained very little O_2 and no CH_4, based on the oxidation state of terrestrial magma.[31] CH_4 and NH_3 would have been destroyed by UV photolysis and have been present transiently, at best,[32–36] with a small minority believing CH_4 and NH_3 might have been present.[37]

Sometime after ~4.3 Ga it is thought that the earth's atmosphere had cooled, resembling the atmosphere of Venus: mostly CO_2 (~80 bars) and some N_2 (~2 bars).[32] Eventually, enough of the atmospheric CO_2 allegedly dissolved in oceans until the major composition became N_2. One carbonate–silicate climate model predicted a CO_2 concentration of 7×10^{-2} – 0.1 bar between 3.5–4.0 Ga.[24,38]

Most evolutionists believe the prebiotic atmosphere was very *weakly reducing* around when life is supposed to have arisen, consisting primarily of CO_2 and N_2, with only minor proportions of reducing gases such as CO, H_2, CH_4, and some H_2S in the lower atmosphere in contact with the earth surface.[6,15,32,39,40] One extensive modelling study suggested that CO_2 was roughly 20 times higher in the prebiotic atmosphere than the preindustrial modern value (280 ppm).[41] (The current global average concentration of CO_2 in the atmosphere has increased to 421 ppm as of May 2022.)[42]

The amount of N_2 is believed to have been within a factor of 2 of the modern levels, and vanishingly low amounts of O_2 would have been present.[15,24,43–47] Noble gases and photochemical products of the dominant species should also have been present in small quantities.[48]

Domagal-Goldman argued that there is no evidence for an atmosphere containing high levels of CH_4, since models indicated that for CH_4:CO_2 ratios > 0.1, global glaciations would have resulted; also, analysis of ancient minerals indicated that the redox state of the mantle has not changed much throughout Earth's history.[49] A biogeochemical model coupled to photochemistry estimated, for the period between 3.5–4.0 Ga, a partial pressure of $5 \times 10^{-4} - 2 \times 10^{-3}$ bar for CH_4.[24,50] Comparing this to the values above for CO_2 leads to ratios of CH_4:CO_2 ≈ 0.7% around 3.5 Ga, and ≈ 2% around 4.0 Ga. Another study used a model for fractionation of xenon isotopes and predicted that around 3.5 Ga the overall proportion of CH_4 in the atmosphere may have been ~ 0.5%.[24,51] It is important to recall from table 3, that when rCH_4 <5% glycine was almost the only AAs formed.

Almost all researchers agree that very little H_2 would have been present when life is assumed to have arisen. Atmosphere chemist Catling described several mechanisms for how H_2 would have been lost, including acceleration of H ions by the earth's magnetic field to cause collisions leading to fast-moving neutral atoms.[52] A multigas model predicted a mean temperature >1,400 K in the uppermost region of the atmosphere, which would have facilitated rapid hydrogen escape.[52] Also, extreme ultraviolet (EUV) fluxes would have split H_2 and the resulting radicals would have escaped even more easily than H_2. As Catling opined,[52]

> "... data suggest that hydrogen actually did escape from early Earth at rates close to its upper limit. The isotopic mass fractionation of atmospheric xenon is consistent with the idea that hydrogen escaped so strongly that it dragged even xenon, the heaviest gas in the atmosphere, to space."

Various photochemical models led to the conclusion that H_2 would have been effectively depleted from the upper atmosphere.[53,54]

In 2017 Catling *et al.* estimated the H_2 abundance in the prebiotic atmosphere, taking into account the contribution of volcanically outgassed H_2 and the rate of loss to space, concluding that the atmosphere H_2 abundance may have been around 400 ppm.[15]

A very weakly reducing primitive atmosphere renders most of the Miller-type experiments irrelevant. SciTechDaily noted correctly, in 2020, that[31]

> "… a popular theory on the emergence of life on Earth now seems much less likely. This so-called 'Miller–Urey experiment', in which lightning strikes interact with certain gases (notably ammonia and methane) to create amino acids—the building blocks of life—*would have been difficult to realize. The necessary gases were simply not sufficiently abundant* [emphasis added]."

The case for a more reducing atmosphere

When Miller performed his experiments in the 1950s it was believed that the prebiotic atmosphere consisted mostly of CH_4, NH_3, H_2O, and H_2.[1]

The publications referred to in the bottom half of table 1 showed that gas mixtures containing extremely high proportions of CH_4 and/or H_2 produced a wider variety of chemical substances and at higher concentrations than when using realistic mixtures of CO_2/N_2. Unwilling to bow to the evidence, some evolutionists have argued that strongly reducing comets or asteroids might have fleetingly led to highly reducing atmospheres.[55,56] It is claimed that many impactors in the early solar system might have delivered highly reduced minerals, such as metallic iron and various reduced compounds, into the atmosphere as a gas which would have reacted with CO_2 and N_2.[27]

The various models, involving a single massive impact or multiple large impactors, were critiqued in part 2 of this series. They were only invoked since, otherwise, virtually no AAs or key chemicals would have been available from atmospheric reactions.

Discussion

Some evolutionists attempt to downplay how irrelevant gas mixtures had been used in early Miller-type experiments, and how this has misled countless students.

Intelligent Design critic Gishlick stated that

> "… scientists working on the origin and early evolution of life are well aware of the current theories of the earth's early atmosphere and have found that *the revisions have little effect on the results of various experiments* [emphasis added]."[57]

It would be advantageous if agreement could be reached on what proportion of AAs would have been present, since then it would be easy to show that most of the polymeric products would have consisted of glycine attached to non-AAs and non-proteinogenic AAs. The details depend on the specific gas mixture assumed.

Which peptide sequences would have formed abiotically would have depended on the proportion of AAs present, since there would be relatively little difference in the rate of condensation of different AAs. This is because the portion of the side chains which could affect the nucleophilic character of the amino end and the electrophilic character of the carbonyl at the carboxyl end are too far away to transfer partial charge through the carbon chain. As shown in figure 1, the first carbon atom of the side chain group, R, is already two carbons away for all cases except glycine, for which R = H. In 14 cases, the R group has an additional CH_2, which further dilutes electronic influence at the reaction site, and in 3 cases a similar $CHCH_3$ portion forms part of the side chain.

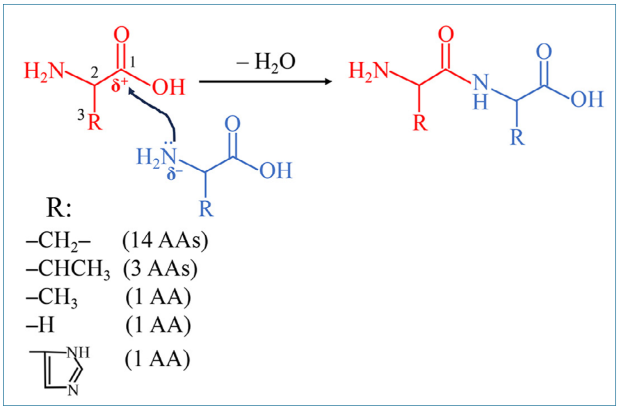

Figure 1. Condensation reaction of AAs to form peptides. The portions of the side chains (R) closest to the reacting $-NH_2$ and $-COOH$ ends are mostly either identical or similar and thus affect the nucleophilic and electrophilic natures of the end portions of AAs to a similar degree.

Chemicals which prevent peptides forming

The same experiments reported by Criado-Reyes *et al.* also indicated that only about 58% of the AAs were proteinogenic,[19] see table 1 in part 2 of this series.[3] Unfortunately, comparable analyses could not be found in the literature for highly oxidized gas mixtures; e.g., combinations of CO_2/N_2.

The data in table 2 also shows that high concentrations of carboxylic acids (which hinder formation of peptides) resulted for all high energy sources using CO_2/N_2 mixtures. Detailed studies were not found where similar analysis had been conducted using highly reducing gas mixtures. Other kinds of interfering chemicals were not systematically analyzed using different gas mixtures either, as discussed below.

Could proteinogenic AAs and carboxylic acids have separated due to different solubilities; for example, by repeated evaporation and concentration? This is not a reasonable expectation, since the variety of carboxylic acids produced included high concentrations of very soluble and slightly soluble compounds, mimicking the solubilities of the AAs. Contamination would have been unavoidable.

Many kinds of chemicals formed abiotically in addition to AAs would have also been able to integrate into peptides or terminate AA condensation by reacting with the terminal amino or carboxyl group, as shown in figure 2.

Peptide bonds using D-enantiomer AAs were not included in figure 2; neither were the variety of reactions involving AA side chains. Figure 2 shows how the end groups of the 20 proteinogenic AAs react. However, several other classes of compounds produced in chemical abiotic simulations can also react with AAs. Some kinds of reactions that would also have occurred at the end positions of AAs include:

- *With both the $-NH_2$ and $-COOH$ group of AAs*: non-proteinogenic AAs (including α-, β-, and γ-AAs) to form amide bonds, see figure 2-D; and α-hydroxy acids (which are analogous to AAs, with the $-NH_2$ replaced by –OH) to form amide and ester bonds, see figure 2-F.
- *With the $-NH_2$ group of AAs*: carboxylic acids can react to form amides, see figure 2-B; alcohols can react to form esters,[58,59] see figure 2-F; and aldehydes can lead to decarboxylation and deamination products,[59] see figure 2-E. High concentrations of carboxylic acids can also transfer a proton to the $-NH_2$ and form unreactive AA salts.[60]

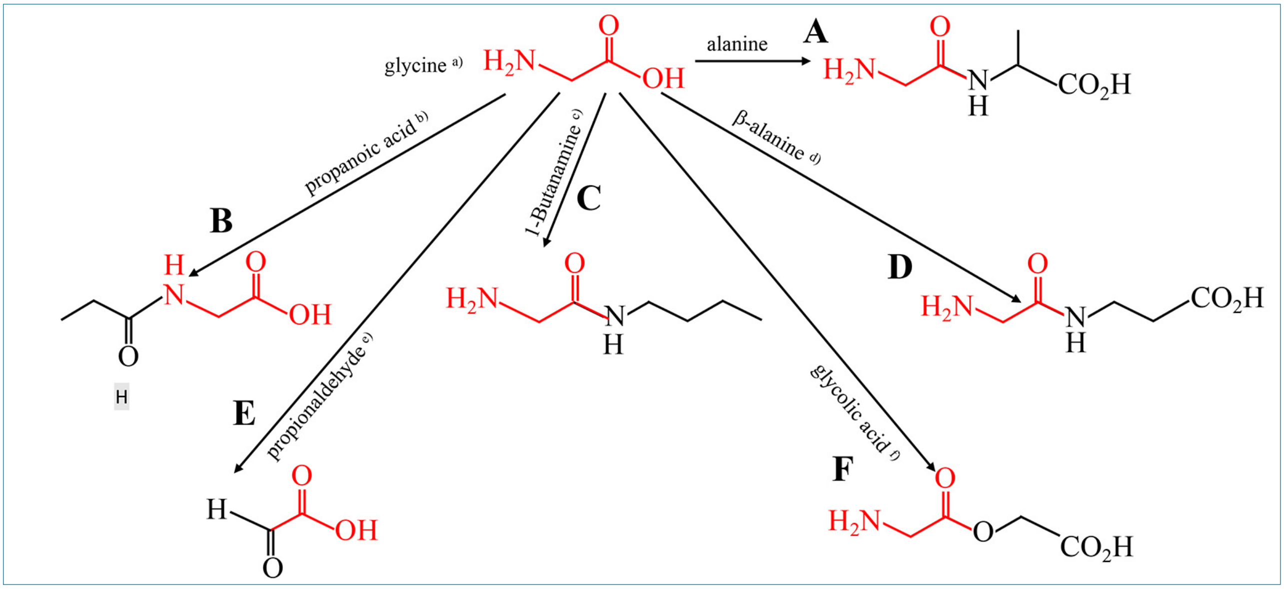

Figure 2. A: Biologically relevant peptides and proteins can form when proteinogenic AAs polymerize. Many kinds of chemicals prevent forming proper peptides. B: Carboxylic acids. C: Amines. D: Non-proteinogenic AAs. E: Aldehydes[58]; and F: Alcohols, including α-hydroxy acids[58].

- *With the –COOH group of AAs*: amines can react to form amides,[59] see figure 2-C. However, amines can also accept a proton from the –COOH group, leading to unreactive salts, especially at high concentrations of amines.

This list is not exhaustive, but clarifies why the yields of AAs from Miller-type reactions are often less than 1% of the carbon consumed. Side-chain reactions, such as those involving the sulfhydryl group (-SH) of cysteine, could also occur, and various reactions which produce cyclic products. The importance of each reaction is affected by pH and temperature.

All these chemicals formed would have thoroughly mixed in terrestrial water: multiple meteors would have raised the temperature of oceans for long periods of time, ensuring that virtually all these chemicals would have been soluble at some time; and violent tides several times daily about 30 times higher than current tides would have resulted from a moon ⅓ as far away.[61,62]

There is an important aspect to the argument that many classes of chemicals would also have reacted with AAs. Amino acids do not spontaneously condense in water to form amide bonds (the reaction is endergonic; i.e., $\Delta G > 0$, and thus unfavourable). Therefore, OoL experiments invariably first chemically alter (i.e., 'activate') the end –COOH and/or end NH_2 group. If this is assumed to have been prebiotically plausible, then these kinds of activations should also be assumed for the potential interfering chemicals.

Final comments

Instead of admitting that the most popular theory for the origin of key organic building blocks lacks substance, Gishlick from the National Center for Science Education employed the 'endless other possibilities' argument, writing that

> "The Miller–Urey experiment only showed one possible route by which the basic components necessary for the origin of life could have been created, not how life came to be."[57]

This weakest of logic is often used by evolutionists and can be illustrated by an absurd example: "We know Mr Jones murdered X because we can show scenarios where someone could have murdered X."

Using evolutionary presuppositions, in the weakly reducing prebiotic atmosphere assumed to have existed almost only glycine and alanine would have been produced, using any available energy source. Attempts to increase the variety of proteinogenic AAs by optimizing the experimental gas mixtures concurrently increased the amounts of carboxylic acids, non-proteinogenic AAs, and other chemicals. These would have interfered with suitable peptides being formed.

Clearly, chemists have not become evolutionists due to the strength of the scientific evidence for abiogenesis.

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***Royal Truman** has bachelor's degrees in chemistry and computer science, an M.B.A., a Ph.D. in organic chemistry, and a two-year post-graduate* Fortbildung *in bioinformatics. After working 40 years for the world's largest chemical firm he retired, and is currently a visiting scientist at a German university.*

***Boris Schmidtgall** obtained his M.S. (German Diploma) and Ph.D. in chemistry from the University of Göttingen, followed by postdoctoral work in biochemistry in Strasbourg, France. Since 2018 he has been employed by the German creation research group Wort und Wissen. He has published extensively in secular international chemistry journals and also on origin of life research and biomolecular chemistry from a creation science perspective.*

***Chris Basel** has a bachelor's degree in chemistry from William Jewell College, a master's degree in analytical chemistry from the University of Kansas, and a certificate in ADMET Process (pharmacology) from the University of California-San Diego. He worked as a research manager in the pharmaceutical industry for 30 years and now serves as an associate professor of chemistry and department chair at a Christian university in Missouri.*