Relative proportion of prebiotic amino acids: part 2—models to form highly reduced atmospheres

Royal Truman, Boris Schmidtgall, and Chris Basel

Most Miller-type experiments have used highly reduced gas mixtures no longer considered to reflect the composition of a prebiotic atmosphere. Speculative models have been reviewed for evolutionary mechanisms to produce favourable reducing atmospheres. These involved enormous theoretical impactors able to deliver gases such as CH_4, NH_3, CO, and H_2, and/or also a high iron content able to convert all, or most, terrestrial water into reducing H_2. The resulting less oxidized atmospheres would have produced primarily only the proteinogenic amino acids (AAs) glycine and alanine, and a high yield of chemicals which would have interfered with forming peptides. Adjustment of model parameters to increase the variety and concentration of AAs inevitably led to more contaminating non-proteinogenic AAs.

In part 1 of this five-part series, ten properties were identified which peptides and proteins must fulfil to be relevant for prebiotic studies.[1] The focus of this series is on properties number 4 and 5:

No. 4: *Precise sequences composed of various amino acid residues must form to perform useful functions*.

No. 5: *Other molecules, including non-biological amino acids, must be avoided in the peptides.*

Proteins contain 50 or more amino acids and have a distinct complex three-dimensional structure. When the term 'peptide' is used here, simple chains of about four or more amino acids (AAs) are meant, but all the statements refer to proteins also.

The *proportion* of AAs present in water would have determined which peptides formed, and origin of life (OoL) theories require precise sequences, for example, to form amyloids according to the amyloid world hypothesis.[2,3] In fact, *a vast number of identical peptides* would have been necessary at the same location to form amyloids, all generated abiotically without a cellular system, including the genetic code.[4]

The purpose of this series is to demonstrate that under realistic abiotic conditions:

- Only some of the AAs formed would have been proteinogenic (i.e., among the 20 used to form proteins).
- Usually, glycine and alanine comprise almost the entire yield of the proteinogenic AAs formed.
- Other chemicals also formed would have interfered with the formation of suitable peptides.

In part 1, the key Miller-type experiments were reviewed, which used highly reduced gases mixtures (CH_4, NH_3, and H_2, with H_2O). These results have been summarized in table 1.

Most of the early Miller-type experiments used highly reducing mixtures of gases over water, composed of CH_4 and NH_3 (or N_2 occasionally) and usually also H_2, as summarized in rows 1–8 of table 1. These gas mixtures produce 4–10 proteinogenic AAs. The ninth row in table 1 used Teflon reaction vessels and will be discussed below. However, in 1971 Lasaga pointed out that ultraviolet radiation would have formed methyl and methylene radicals in a methane-rich atmosphere leading to polymerization and an oil slick 1 to 10 metres thick.[10] Later, OoL researchers concluded that CH_4 and NH_3 would not have been present at all in the early atmosphere.[11]

Caution must be exercised when interpreting these mostly older experiments, since the goal had only been to identify as many proteinogenic AAs as possible, and chemicals such as α-hydroxy acids, amines, carboxylic acids, and large non-proteinogenic AAs were of minor or no interest but would have prevented forming suitable biologically relevant peptides.

The results from CH_4/N_2 mixtures have been summarized in rows 1–3. In the first two experiments, a very small amount of NH_3 was also included, and in the third experiment H_2 was the major gas. The proportion of Gly + Ala to all proteinogenic AAs found ranged from about 94%–97%. Unlike almost all other gas mixtures, the proportion of Ala was considerably greater than Gly in 2 of the experiments and about the same in one of them. This is difficult to explain, but an independent study confirmed this; row 4, using a $CH_4/N_2/NH_3$ (2:1:2) mixture, produced almost twice as much Ala as Gly on a molar basis. However, in all the realistic gas mixtures dominated by CO_2, almost only Gly was formed with virtually no Ala, as reviewed in part 3[12] and part 4[13].

According to rows 1–3, the proportion of proteinogenic AAs ranged from 73%–90%.

The results summarized in rows 5–8 used gas mixtures of $CH_4/NH_3/H_2$ (2:2:1), and 4–7 proteinogenic AAs were

Table 1. Summary of AAs identified in key Miller-type experiments using highly reducing gas mixtures. The ratios are reported on a molar basis. Prot. = proteinogenic amino acids; Gly = glycine; Ala = alanine. The data was calculated from the references given in the last column.

No.	Gas mixture	Energy source	Proteinogenic/ all AAs a)	Proteinogenic/ non-AA b)	Proteinogenic/ interfering c)	(Gly+Ala) / Proteinogenic d)	No. of AAs	Comments	Reference
1	CH_4, N_2 (1:1), trace NH_3	Spark	73%	—	—	93.6%	10	0.05 M NH4Cl, pH 8.7. Only amino acids were reported.	f)
2	CH_4, N_2, NH_3 (1:1:0.001)	Spark	89.9%	—	—	97.2%	6	Continuous spark discharge 48 h at 25°C; aqueous phase equilibrated 48 h.	g)
3	CH_4, N_2, H_2, (1:1:3)	Spark	86.9%	—	—	96.4%	6	Continuous spark discharge 48 h at 25°C; aqueous phase equilibrated 48 h.	g)
4	CH_4, N_2, NH_3 (2:1:2) e)	Spark	90.3%	21.3%	20.8%	59.9%	11	Usual Pyrex (borosilicate) reactor used in Miller-type experiments.	h)
5	CH_4, NH_3, H_2 (2:2:1)	Spark	79%	21%	~19.9%	99%	4	Repeat of the original 1953 experiment using better analytical techniques.	i)
6	CH_4, NH_3, H_2 (2:2:1)	Spark	99.4%	99.3%	98.8%	99.9%	7	Only the primary-substituted AAs were identified.	j)
7	CH_4, NH_3, H_2 (2:2:1)	Spark	86.0%	99.8%	85.9%	99.9%	7	Gas forced into the spark. Only the primary amines were identified.	j)
8	CH_4, NH_3, H_2 (2:2:1)	Spark	68.8%	97.1%	67.4%	99.7%	7	Silent discharge instead of electrode. Only primary amines identified.	j)
9	CH_4, N_2, NH_3, (2:1:2)	Spark	23.4%	3.6%	3.2%	0%	4	Teflon reactor. Proteinogeinic AAs: only His, Lys, Pro, Asn.	h)

a) Proteinogenic AAs / all AAs. (AA[s] = amino acid[s])
b) Proteinogenic AAs / (proteinogenic + non-AA compounds able to react with COOH or NH_2)
c) Proteinogenic AAs / (all compounds able to react with COOH or NH_2)
d) (Gly + Ala) / all proteinogenic AAs
e) Data from Supplementary Materials Table S2
f) Ring (1972)[5]
g) Schlesinger and Miller (1983)[6]
h) Criado-Reyes *et al.* (2021)[7]
i) Miller and Urey (1959)[8]
j) Johnson *et al.* (2008)[9]

identified. The proportion of Gly + Ala to all proteinogenic AAs ranged from 99% to 99.9%, where now [Gly] >> [Ala]. In these four experiments, the proportion of proteinogenic AAs ranged from 79% to 99.4%, and the proportion of proteinogenic AAs to all competing substances able to interfere (i.e., react) with AAs ranged from 21%–99.8%. Although all four experiments had been executed by Miller in the 1950s, the analyses were performed in 2008 on the stored samples. Uncertainty arises since Miller could have easily performed a TLC (thin layer chromatography) analysis on these samples after having gone through the trouble of running the time-consuming experiments, so there are doubts concerning what laboratory processing had been involved. Repeating the experiments would not make much sense since it is now not believed by the OoL community that an atmosphere consisting of only these three highly reducing gases (plus water) existed in the supposed prebiotic world.

In part 1 we also reported that Criado-Reyes *et al.* concluded, in 2021, that the borosilicate glass used in probably all Miller-type experiments was catalyzing the formation of organic compounds.[7] The yields of organic compounds using a Teflon reactor, shown in the last row of table 1, were much lower: only four proteinogenic AAs were obtained (His, Lys, Pro, and Asn), and the ratio of proteinogenic AAs to chemicals able to react with AAs was only about 5.4%. This is a disastrous finding for the OoL community, especially since the unrealistic gas mixture of $CH_4/N_2/NH_3$ (2:1:2) plus water vapour had been selected to facilitate the formation of AAs and other organic compounds.

It remains to be seen how other researchers respond to this stunning discovery, since these catalysts (borosilicate glass) would not have been present in the atmosphere where the high-energy source was primarily located. A key experiment would be to test some realistic CO_2/N_2 gas mixtures in a borosilicate-free reactor to determine what chemicals form. It is likely that essentially no AAs would be produced.

The comprehensive range of gas mixtures, summarized in table 1, led to an overwhelming overabundance of glycine and alanine, a serious problem for OoL speculations. In part 5 of this series,[14] it will be shown that other potential sources of AAs would not have contributed to a more balanced proportion of proteinogenic AAs.

As will be discussed in parts 3 and 4 of this series, most geochemists believe the prebiotic atmosphere would have consisted primarily of CO_2 and N_2, along with H_2O and trace amounts of CH_4. A minority of researchers have attempted to show that the Miller-type experiments using highly reduced gases might still be relevant if special temporary atmospheric conditions could be construed. This will be reviewed next.

Reduced atmosphere due to a hypothetical huge impactor

Some evolutionists theorize that a short-lived strongly reduced atmosphere, containing gases like CH_4, HCN, and perhaps NH_3, resulted from a single huge impact.[15,16]

Zahnle *et al.* reasoned that the earliest atmosphere would have resembled volcanic gas compositions, but the problem was that H_2, CH_4, and ammonia would have been far too dilute for Miller-type chemistry to produce biologically useful chemicals in relevant concentrations.[17] In principle, metallic iron could have reduced CO_2 to CH_4, but almost all terrestrial iron would have already been transferred deep into the earth's core.[18] What could a new source of iron have been? A minority of meteorites contain metallic iron, but the amount would have had to be sufficient to reduce virtually all of the volatile material created from the explosive crash to produce a reduced overall atmospheric composition. A small excess of iron would have only had a small effect, considering the vast amounts of atmospheric CO_2 assumed to have been present.

Benner *et al.* recognized the difficulty of obtaining nitrogen in a reactive form to produce key chemicals like cyanoacetylene and cyanamide to make RNA, without which the RNA world hypothesis would be unviable.[19] Therefore, they hypothesized, in 2019, that a massive impact may have occurred about 4.35 Gyr ago and created a temporarily reducing terrestrial surface lasting for about 15 Myr.

The impactor would need to have been massive to provide enough metallic iron to scavenge oxygen by the reaction

$$Fe + H_2O \leftrightharpoons FeO + H_2 \qquad (1)$$

Zahnle *et al.* modelled the effects of a hypothetical massive 2.5×10^{24} g impactor (i.e., about 20% the mass of Pluto), assuming a terrestrial atmosphere containing 5 bar CO_2 and 1 bar N_2 over 1.85 oceans of water. Optimally, if all of the iron produced from the explosion would have reacted with water and CO_2, most of the CO_2 would have been converted into 0.4 bar of CH_4.[17] However, an impactor this size would have released enough energy to vapourize 20 oceans of water, melted the crust tens of kilometres deep, and blanketed the Earth in impact ejecta tens of kilometres deep. Consequently, much of the iron would have been buried before it could react with water.

This impact, however, would have heated the surface far above the boiling point of water and remained very hot for a long time due to greenhouse effects, conditions too hot for any relevant prebiotic chemistry.[17]

Alternatively, the more frequent, but much smaller, impactors would not have fully vapourized the oceans and would not have produced enough CH_4 or NH_3 to affect the overall atmospheric composition significantly.[17] Zahnle et al. recognized the contradictory trade-offs:

> "But if the primary requirements for life are methane, ammonia, HCN, and their photochemical derivatives, only the biggest impacts or as of yet unknown chemistry will do."[17]

Zahnle *et al.* needed impactors of just the right size. Using evolutionary reasoning, such as the amount of cratering on the moon, they thought that >10 impactors would have been massive enough to fully vapourize the ocean but would not have been large enough to deliver enough iron to reduce all of the H_2O to H_2. The debris would still have been thicker than the ocean was deep.[17]

Therefore, their model required impacts massive enough to vapourize the oceans entirely and generate as much H_2, CH_4, and NH_3 as possible but without generating too much heat. Noteworthy is that H_2 would easily escape into space[16,17] helped by radiative heating of the atmosphere[20], and CH_4 lost through photolysis[17], both irreversible processes.

According to Zahnle *et al.*, after the putative impact that created the moon, there may have been 1–4 impacts of objects of the 'right' mass, comparable in size to Ceres, the largest object in the asteroid belt (i.e., 9.4×10^{20} kg, representing >1% the mass of Earth's moon) and 2–10 impacts of objects of size comparable to Vesta, the second largest object in the asteroid belt (i.e., 2.6×10^{20} kg).[17]

We find the scenario favoured by Zahnle *et al.* to be problematic for many reasons. The researchers had an outcome in mind when selecting the parameters to model the atmospheric chemical processes. For example, to avoid a dried-out world they assumed the primordial oceans contained 1.85 times more water than today. And there are other concerns.

They estimated that an impact about the size of Vesta would have evaporated two oceans worth of water, leaving little water behind where life could have arisen. Assuming a pre-impact atmosphere of 5 bar CO_2, 1 bar N_2, and 500 bar H_2O, if 100% of the assumed Fe delivered had been used effectively, then their model predicted a post-impact atmospheric content of 4.955 bar CO_2, 1 bar N_2, ≈500 bar H_2O, 3.9 bar H_2, and 0.045 bar CH_4,[17]; i.e., at best, a modestly reducing atmosphere.

Studies reviewed in part 3 revealed that a relative proportion (rCH_4) ≈ 10% produced almost only glycine.[13] In any event, the proposed temporary atmosphere would not have remotely resembled the exclusively $CH_4/H_2/NH_3$ Miller mixtures (which also produced almost only glycine and alanine!).

However, not all the deleterious potential consequences were considered by Zahnle *et al.* Just one very large impact would have evaporated all terrestrial water, or a sequence of smaller impactors could have removed all, or most, of the water stepwise, producing a dried-out earth. Why would only one impact of just the right size and iron content have occurred?

For comparison purposes, the Mistastin asteroid which crashed in Labrador, Canada, conventionally dated to 36 Ma ago, was 'only' about 5 kilometres in diameter and believed to have heated rocks to at least 2,370°C and produce an 80-m-thick impact melt sheet.[21,22] The products resulting from meteor impacts include high-pressure forms of shocked quartz, like coesite or stishovite, unsuitable for life-like chemistry,[23] and Vesta-size impactors would have been about a million times more massive.[24] The resulting extremely thick, hard, glassy melt sheet, probably several km thick, would not have been a hospitable environment for life.

More than 95% of meteorites observed to fall to Earth are composed mostly of silicate, with only small-scattered grains of iron. Less than 2% of all known meteorites are stony-iron meteorites, which contain about equal proportions of silicate material with iron bound in iron–nickel alloys, like kamacite (5–12 wt% Ni) and taenite (20% to 65% nickel).[25] Some of the iron in meteorites is often found already oxidized, especially as magnetite (Fe_3O_4) (a combination of Fe(II) and Fe(III) ions).[26–28] In addition, the most abundant element in the earth's crust is oxygen (46.1%), whereas there is only about 5.5% iron, with the concentration decreasing towards the surface.[29]

Therefore, it is not self-evident why most of the impactors would not have *released pre-existing oxygen from the crust, while also adding oxygen* to the total inventory from their own silicates. It would also seem that the much higher momentum of denser iron-rich impactors would have embedded their content deeper after impact than the lighter and more fragile silicate-based impactors, which would not have provided reducing potential and probably much oxygen instead.

For OoL purposes, one must not overlook that any impact large enough to heat the ocean above a mere 80°C or so for just a few years would have ensured complete racemization of amino acids and sugars.[30] However, pre-biology models like the RNA world or the amyloid world require large enantio-pure polymers. The products plus their precursors would instead have racemized in hot water very rapidly.

Reduced atmosphere due to several large impactors

Several OoL researchers have focused on the effect of less massive asteroids of 100–250 km in diameter instead of the largest ones, as in the section above.[16,17,31] Reducing gases, such as H_2, CH_4, and NH_3 would have been released, in some cases with enough iron to deplete some of the oxidants on the earth's surface,[17,32] and HCN may have been formed photochemically.[19,32] Each impact would have strongly heated the earth's surface and produced a steam atmosphere >100°C, lasting ~ 1 to 100 years.[33]

In 2023, Zhang *et al.* published a thermodynamic analysis of various organic compounds over a temperature range of 100–340°C and pH 2–12.[33] Their calculations were based on a hypothetical atmosphere of water (at saturation pressure) plus CO_2 (1 bar), CO (10^{-3} bar), H_2 ($10^{0.9}$ bar, i.e., ≈ 8 bar), NH_3 ($10^{-2.5}$ bar) and N_2 (1 bar). This mixture was selected based on a model by Zahnle *et al.*, who claimed that this would have resulted from a ~1,000 km impactor *assumed to have contained enough metallic iron* to reduce all the H_2O in the ocean to H_2.[17,34] The *assumed* 8:1 highly reducing molar proportion of H_2:CO_2 (!) for the thermodynamic analysis would have been close to optimal to produce a variety of organic chemicals. For comparison, the H_2:CO_2 ratio in the atmosphere is currently <0.0013 (i.e., 0.000055% H_2[35] vs 0.0417% CO_2).[36]

Zhang *et al.* defined a *positive synthesis affinity* as when there is a thermodynamical tendency to form >10^{-6} molal (m) of a particular molecule from the above gas mixture in the surface seawater. The selection of the 10^{-6} m was arbitrary and intended to reflect that chemicals in lower concentrations would usually not be considered relevant for OoL purposes.[33] They concluded that methane, methanol, and carboxylic acids would have had positive synthesis affinity over a wide range of temperatures, whereas other *key building blocks for prebiotic chemistry, like cyanide and formaldehyde, would have had overall negative affinities at all temperatures*, and would have hydrolyzed rapidly. Indeed, other workers have shown that HCN has a half-life <1 day at >100°C at relevant pH values.[37]

Zhang *et al.* found that, even with these high assumed gas concentrations in a very favourable proportion, the equilibrium concentration of HCN in the surface water would have been <10^{-9} molal at 100°C and pH = 6 and <10^{-13} molal at 200°C and pH = 6. They admitted that this posed a challenge for many OoL models:

> "Although life relies on liquid water, polymerization reactions that lead to functional biomolecules (e.g., polynucleotides, polypeptides) are largely dehydration processes. That is one major challenge for the origin of life studies as one usually *needs very high reactant concentrations* for chemical evolution to happen in simulative experiments–for example, molar level of HCN used in synthesis reactions [emphasis added]."[33]

Their calculations contradicted many claims by other evolutionists (which they extensively referenced), *denying that formaldehyde would have been readily available*. They concluded:

> "However, according to our calculations, it is thermodynamically unfavourable to synthesize/

> accumulate appreciable levels (>10^{-6} molal) of HCN and HCHO, beneath a steam atmosphere after the impacts in the reference atmospheric composition."[33]

Most of the 18 investigated proteinogenic AAs had positive affinities only at temperature <220°C (i.e., concentrations of 10^{-6} m could have been theoretically achieved at equilibrium) but the concentration would have decreased with increasing temperature in almost all cases at >220°C. Serine, histidine, and arginine had negative synthesis affinities across almost the entire temperature range. Formation of nucleosides and nucleobases was also thermodynamically unfavourable. They concluded:

> " … our results agree roughly with the early proposal that amino acids are not thermodynamically favorable to accumulate to levels higher than 10^{-8} molal in natural hydrothermal fluids (Amend and Shock, 1998)."[33]

Several conclusions can be made, based on the reported calculations.

- As discussed above, Schlesinger and Miller used a $CO_2/N_2/H_2$ (1:1:3) mixture, which produced only four proteinogenic AAs, where Gly + Ala represented about 99.6% of the yield.[6] This does not contradict the thermodynamic expectation that more than four AAs could have formed at a concentration ≥10^{-6} M at lower temperatures. But *absent a feasible pathway like the Strecker reaction* (shown in figure 3 of part 1 of this series), which requires HCN *formation of AAs, would only have been energetically but not factually feasible*. To illustrate, the thermodynamically most stable form of carbon is diamond, but this is present in very low concentrations on Earth.
- Other more thermodynamically stable isomers were not considered. For example, the reaction of methylamine + CO_2 can produce several $C_2H_5NO_2$ isomers of glycine of which N-methylcarbamic acid, methyl carbamate, and 2-hydroxyacetamide have lower Gibbs free energy.[38]
- Many molecules not considered could also form from this gas mixture, which would have been able to react with AAs and prevent long peptides from forming.

To summarize this section, some proposals for how the atmosphere might have been somewhat reducing temporarily assume a single massive impactor,[19,39] and other proposals, a series of large ones.[40,41] These putative impactors would have produced the excess of siderophile ('iron-loving') elements (the so-called 'late veneer') on the earth's surface compared to what models expected to have been present. Others who accept the hypothesis of a veneer have argued that it could have arisen from the core material of only Theia, the putative moon-forming impactor, and they disagreed with the speculations of the researchers mentioned above.[42,43]

A wide range of gas mixtures could be hypothesized during a particular period of time. In the above sections, CO_2 concentrations were claimed to range from about 20 bar to a small fraction of a bar. The pre-impact CO_2 concentration assumed by a scientist would lead to a very large difference in the assumed resulting $CO_2:H_2$ ratio post-impact (i.e., how much CO_2 was reduced to other gases). The amount of reducing Fe supposedly exploded into the atmosphere would also make a big difference. It is important not to lose sight of the fact that these are merely proposals with a veneer (pun intended) of plausibility; there is no hard evidence a moderately or strongly reducing atmosphere ever existed.

Discussion and suggestions

The Miller experiment, in 1953, drew much attention, because it seems that 70 years ago chemists were unsure whether AAs would be produced from simple gases using spark discharges. Few modern chemists would have been surprised if the same results had just been published. Unfortunately, there is now the vague perception that all the AAs necessary to form proteins abiotically would have been available, based on the Miller-type experiments discussed in part 1. The current view that the highly reduced gas mixtures used did not reflect the prebiotic atmospheric content has been countered by creative models to produce temporarily reduced atmospheres. This does not change the findings reported in part 1, namely that virtually only glycine and alanine were produced in almost all these experiments, *along with non-proteinogenic AAs in higher concentrations than all the other proteinogenic AAs combined*.

If any OoL researchers believe a temporarily reduced atmosphere may have existed, new Miller-type experiments should realistically be dominated by CO_2 and N_2 along with only minor proportions of H_2S, H_2, NH_3, and CO. But all the products able to react with AAs and their concentrations *must now also be determined*. The reactors should exclude irrelevant catalysts, the pH must be controlled, and only relevant antioxidants should be included. Only then would it become possible to discuss the kinds of peptides that may have formed prebiotically under specific new scenarios.

In part 3, Miller-type key experiments using neutral or slightly reducing gas mixtures are reviewed.[12]

References

1. Truman, R., Schmidtgall, B., and Basel, C., Relative proportion of prebiotic amino acids: part 1—experiments using reduced gas mixtures, *J. Creation* **38**(3):87–98, 2024.
2. Rout, S.K., Friedmann, M.P., Riek, R., and Greenwald, J., A prebiotic template-directed peptide synthesis based on amyloids, *Nat. Commun.* **9**:234–242, 2018.
3. Maury, C.P.J., Amyloid and the origin of life: self-replicating catalytic amyloids as prebiotic informational and protometabolic entities, *Cell. Mol. Life Sci.* **75**:1499–1507, 2018.
4. Truman, R., Basel, C., and Schmidtgall, B., Amyloid world—the impossible requirement for identical prebiotic peptides in high concentration, *J. Creation* **38**(3):72–80, 2024.
5. Ring, D., Wolman, Y., Friedmann, N., and Miller, S.L., Prebiotic synthesis of hydrophobic and protein amino acids, PNAS **69**(3):765–768, 1972.
6. Schlesinger, G. and Miller, S.L., Prebiotic synthesis in atmospheres containing CH4, CO, and CO2. I. Amino acids, *J. Mol. Evol.* **19**:376–382, 1983.
7. Criado-Reyes, J., Bizzarri, B.M., García-Ruiz, J.M., Saladino, R., and Di Mauro, E., The role of borosilicate glass in Miller–Urey experiment, *Sci. Rep.* **11**:21009, 2021.

8. Miller, S.L. and Urey, H.C., Organic compound synthesis on the primitive earth, *Science* **130**:245–251, 1959.
9. Johnson, A.P., Cleaves, H.J., Dworkin, J.P., Glavin, D.P., Lazcano, A, and Bada, J.L., The Miller volcanic spark discharge experiment, *Science* **322**(5900):404, 2008.
10. Lasaga, A.C., Holland, H.D., and Dwyer, M.J., Primordial oil slick, *Science* **174**:53–55, 1971.
11. Kasting, J.F., Earth's early atmosphere, *Science* **259**:920–926, 1993.
12. Truman, R., Schmidtgall, B., and Basel, C., Relative proportion of prebiotic amino acids: part 3—experiments using reduced gas mixtures, *J. Creation* **38**(3):105–111, 2024..
13. Truman, R., Schmidtgall, B., and Basel, C., Relative proportion of prebiotic amino acids: part 4—the case for the primitive atmosphere having been oxidizing, *J. Creation* (in press).
14. Truman, R., Schmidtgall, B., and Basel, C., Relative proportion of prebiotic amino acids: part 5—amino acids from non-atmospheric reaction, *J. Creation* (in press).
15. Zahnle, K., Arndt, N., Cockell, C. *et al.*, Emergence of a habitable planet, *Space Sci. Rev.* **129**:35–78, 2007.
16. Schaefer, L. and Fegley, B., Redox states of initial atmospheres outgassed on rocky planets and planetesimals, *Astrophysical J.* **843**(2):120, 2017.
17. Zahnle, K.J., Lupu, R., Catling, D.C., and Wogan, N., Creation and evolution of impact-generated reduced atmospheres of early earth, *Planet. Sci. J.* **1**:11, 2020.
18. Astromaterials research & exploration science: meteorite falls, ares.jsc.nasa.gov, accessed 24 Jan 2024.
19. Benner, S.A., Bell, E.A., Biondi, E. *et al.*, When did life likely emerge on earth in an RNA-first process? *ChemSystemsChem* **2**:e1900035, 2020.
20. Yoshida, T. and Kuramoto, K., Hydrodynamic escape of an impact-generated reduced proto-atmosphere on Earth, *Monthly Notices of the Royal Astronomical Society* **505**(2):2941–2953, 2021.
21. O'Datle, C., Mistastin impact crater, craterexplorer.ca, accessed 24 Jan 2024.
22. Chung, E., Ancient Canadian meteor strike created hottest rock on earth, cbc.ca, accessed 24 Jan 2024.
23. Ohtani, E., *et al.*, Coesite and stishovite in a shocked lunar meteorite, Asuka-881757, and impact events in lunar surface, PNAS **108**(2):463–466, 2010.
24. Assume, for estimating purposes, that this 5-km diameter impactor was a chondritic type having a density of about 2,600 kg/m³ to compare with a much larger Vesta-size object.
25. Zolensky, M.E., Abreu, N.M., Velbel, M.A., Rubin, A., Chaumard, N., Noguchi, T., and Michikami, T., Physical, chemical, and petrological characteristics of chondritic materials and their relationships to small solar system bodies, chap. 2; in: Abreu, N. (Ed.), *Primitive Meteorites and Asteroids*, Elsevier, pp. 59–204, 2018.
26. Jarosewich, E., Chemical analysis of meteorites: a compilation of stony and iron meteorite analyses, *Meteoritics* **25**:323–327, 1990.
27. Chemical composition of meteorite, sites.wustl.edu, accessed 24 Jan 2024.
28. Frost, D.J. and McCammon, C.A., The redox state of earth's mantle, *Annual Rev. Earth Planet. Sci.* **36**:1, 389–420, 2008.
29. 2.2: The Elements—LibreTexts; in: Lide, D.R. (Ed.), *CRC Handbook of Chemistry and Physics*, 89th edn, CRC Press, Boca Raton, FL, pp. 14–17, 2008–2009.
30. Truman, R., Racemization of amino acids under natural conditions: part 2—kinetic and thermodynamic data, *J. Creation* **36**(2):72–80, 2022.
31. Parkos, D., Pikus, A., Alexeenko, A., and Melosh, H.J., HCN production via impact ejecta reentry during the late heavy bombardment, *J. Geophys. Res. Planets* **123**:892–909, 2018.
32. Pearce, B.K.D., Molaverdikhani, K., Pudritz, R.E., Henning, T., and Cerrillo, K.E., Toward RNA life on early earth: from atmospheric HCN to biomolecule production in warm little ponds, *Astrophys. J.* **932**:939, 2022.
33. Zhang, Z., Jiang, H., Ju, P., Pan, L., Rouillard, J., Zhou, G., Huang, F., and Hao, J., Evaluating the abiotic synthesis potential and the stability of building blocks of life beneath an impact-induced steam atmosphere, *Front. Microbiol.* **14**:03, Apr 2023.
34. 1 atmosphere pressure ≈ 1.01 bars.
35. Novelli, P.C., Crotwell, A.M., and Hall, B.D., Application of gas chromatography with a pulsed discharge helium ionization detector for measurements of molecular hydrogen in the atmosphere, *Environmental Science and Technology* **43**(7):2431–2436. A value of 0.53 ppm was reported for 2009 but has been slowly increasing. Most current estimates are 0.55 ppm, for example Atmosphere of Earth.
36. Atmospheric carbon dioxide, U.S. Global Change Research Program. The CO_2 value was reported for 2022.
37. Miyakawa, S., James Cleaves, H., and Miller, S.L., The cold origin of life: a. implications based on the hydrolytic stabilities of hydrogen cyanide and formamide, *Orig. Life Evol. Biosph.* **32**:195–208, 2002. Based on their figure 1 and also pointed out in ref. 33.
38. Szőri, M., Jójárt, B., Izsák, R., Kornél, S., Csizmadia, I.G., and Viskolcz, B., Chemical evolution of biomolecule building blocks. Can thermodynamics explain the accumulation of glycine in the prebiotic ocean? *Phys. Chem. Chem. Phys.* **13**(16):7449–7458, 2011.
39. Genda, H., Brasser, R., and Mojzsis, S.J., Earth planet, the terrestrial late veneer from core disruption of a lunar-sized impactor, *Sci. Lett.* **480**:25–32, 2017.
40. Chou, C.L., Fractionation of siderophile elements in the earth's upper mantle, *Proc. 9th Lunar Planet. Sci. Conf.* **9**:219–230, 1978.
41. Albarede, F., Ballhaus, C., Blichert-Toft, J., Lee, C.-T., Marty, B., Moynier, F., and Yin, Q.-Z., Asteroidal impacts and the origin of terrestrial and lunar volatiles, *Icarus* **222**:44–52, 2013.
42. Mrnjavac, N., Wimmer, J.L.E., Brabender, M., Schwander, L., and Martin, W.F., The moon-forming impact and the autotrophic origin of life, *ChemPlusChem* **88**:e2023002, 2023.
43. Sleep, N.H., Asteroid bombardment and the core of Theia as possible sources for the earth's late veneer component, *Geochem. Geophys. Geosyst.* **17**:2623–2642, 2016.

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.*