Is Random Formation of Nucleosides Possible?

Derek Marshall

B.A. Physics, 2006. Michigan State University

http://www.CreationFunction.com.

East Lansing, MI

dmarshal@mtu.edu

Abstract

Proponents of evolution and abiogenesis explain that the Earth is 4.6 Billion years old, and that this time span was sufficient for life to spontaneously appear on Earth. Further analysis of the popular Miller-Urey type experiments suggests that its generation of proteogenic material had a maximum cutoff molecular weight of 180 - 183 Daltons, with an increase of approximately 147 - 149 Daltons above its largest precursor reagent, hydrogen sulfide. A probabilistic binary model helps explain this cutoff and further predicts that to chemically increase the molecular weight of any precursor materials by over 200 Daltons, and to randomly create a targeted proteogenic substance, or to even create a series of recursive reactions to build such a molecule would require more than 4.6 billion years via abiogenic processes, even under the most favorable conditions. This prediction is affirmed by extra-terrestrial sources and the most recent laboratory efforts to produce nucleosides of 227 Daltons and greater. This cutoff creates an insurmountable gap between the proteogenic compounds formed by Miller-Urey and nucleosides which are the very smallest among the necessary building blocks for RNA and DNA.

Introduction

The feasibility and application of the results of the Miller-Urey (MU) experiments to an abiogenic terrestrial beginning of life on Earth have been largely debated by researchers (Ferus, et al., 2017). However, this idea still captures the imagination of lay people and is a ready source of false inspiration that this is how life first began on the Earth (Bergman, 2000). Even now, articles meant for the consumption of the general public still "tip their hat" to this idea because of how easy it is to assimilate. These articles always tout MU's formation of "amino acids" and "nucleobases", the latter which are the

canonical building blocks of RNA and DNA. With these, it is easy to make the leap of thought that this is enough to seed the formation of life. However, what is usually glossed over, or not mentioned at all is that it is not the nucleobases themselves that form the RNA or DNA polymer. In the case of RNA, A nucleobase must first obtain a ribose sugar to allow it to be structurally a part of the spiral staircase structure of the genetic material. In the case of DNA, a deoxyribose sugar must be attached the nucleobase. Either way, with its sugar backbone, the nucleobase becomes a nucleoside. It is this very first step in becoming RNA or DNA that befuddles all observation made from laboratory experimentation, including amino compounds isolated from extra-terrestrial (ET) objects, such as meteorites. To date, no nucleosides or nucleotides have ever been isolated from MU-type experiments attempting to duplicate early conditions on Earth (Stout, 2019). In addition, no nucleosides or nucleotides have been obtained via biochemical analysis of ET materials found on Earth or in space. Whenever they are reported as having been isolated, it is always a designed laboratory experiment which starts with precursor materials, seeking a pathway from precursor material supposed present in early Earth chemistry. The difficulties bridging this gap between the nucleobases found and the monomeric compounds needed to form DNA and RNA have been the topic of research. One reason we don't see these larger molecules formed is because as the MU experiments proceed, formic acid is produced as a by-product (DeMassa and Boudreaux, 2013). This acid would break down these larger nucleosides before they would have a chance to go to the next step. And, even if you do get two nucleotide monomers together to start forming a RNA/DNA polymer, they cannot remain active to bond in the presence of water (Sharp, 1977). Water, as this "life-giving" substance, suddenly becomes the

enemy of this generative process. Statistical and probabilistic barriers to form RNA and DNA molecules and proteins have been put forth in the literature. These are impressive and very real deterrents to the abiotic generation of proteins, the building blocks of life. But, for some reason, these uses of probability have fallen flat in the minds of the general public. The idea that persists is "sometime in the billions of years, somewhere in the infinite universe, anything can and will happen, no matter how improbable." This paper seeks to use another approach to the use of probability. It will use the MU results and three other constraints to which evolutionists must adhere. We will invoke the longest period of time, 4.6 billion years and the shortest amount of time, known as Planck's Time (Thornton and Rex, 2002). We will also invoke the existence of "chemical space" (Reymond, et al., 2010). We will show that there just "isn't enough time" to go from nucleobase, which is less than 151 Dalton (Da) molecular weight (MW) to a nucleoside which is greater than 227 Da MW. The MU results are a "two-edged sword" of sorts. True, they do produce some proteogenic material, but they also show the limitations to what can be produces in a short amount of time, or recursively over a large amount of time. Further, we will look at several examples of what is produced abiotically in billions or years by looking at several ET objects' results. It will be shown that the larger a proteogenic molecule is, it is exponentially harder to make. We will see that there is a MW cutoff of around 183 Da (Daltons) that is backed up statistically as well as by the MU results themselves as it pertains to how much of each proteogenic material was produced. We will also see that the more complex a particular compound is, the less likely it will be produced and therefore less of it will be produced in a given time frame. ET results will back this idea up by showing that given billions of years, the 183 Da

cutoff is present for proteogenic compounds, while many other less complex but larger compounds are produced and present in the ET samples. This means even though there was the opportunity for large proteogenic compounds to be formed over billions of years, we just don't see any when we analyze the samples. Also, we will examine the most recent laboratory efforts to produce nucleosides abiotically and show that it can only be done over several small steps in MW, again demonstrating the efficacy of the statistical model.

A Probabilistic Model for the Formation of Larger Targeted Molecules

The thesis of this paper is rather intuitive: The larger the molecule, the more difficult it is to produce, and the more time it takes to form. This idea is not new, it was expressed by Dr. Emmett Williams in 1967: "It should be obvious that if it is difficult to form simpler compounds, it would be almost impossible to form more complex compounds" (Williams, 1967). His was from a thermodynamic and kinetics standpoint which are quantitative measures of how a chemical process will proceed. In the same paper he gives an example reaction from the work of Hull: the formation of glycine from methane, ammonia, and water, the MU reagents. This reaction was supposed to be not so favorable, with a calculated yield of only 10^{-27} moles per liter (Hull,1960). However, we will see that Miller-Urey did produce Glycine, and in enough abundance that it can be used as the relative measure for all of the other interesting reaction products. But to employ these tools to evaluate the Miller-Urey experiment would be to check every possible reaction for its favorability, or lack thereof. This would be a daunting undertaking, and with potentially arbitrary results as we saw above with glycine. I know

from my own background that thermodynamic processes that be modelled statistically. Also, my background in programming automated machinery inspired me to approach the problem from another angle. Modern machinery has many levels of safety built into each motion the equipment will make, the first level being the interlock. At this level, several condition must be met to enable a given machine motion to be made. Also, any single other interlock condition can prevent the motion from happening at all—An absolutely necessary condition for machines that are hand-loaded to preclude motions when a person's hand is inside the machine. The favorable conditions for a given motion are binary (GO/NO-GO) and are AND-ed together to form a string of logic that can be evaluated probabilistically with the form $1/2^n$, with n-number of pre-conditions for motion. Therefore, if there is only 1 condition for motion, the probability for motion is ½ or 50-50, motion or no motion, and as long as there are no active interlocks. I apply this idea to successful formation of molecules. For a molecule to form, the constituent atoms must be present at the reaction site. If they are all present, the molecule will form, unless there is a condition that prevents the same from happening. Although there many, many conditions that prevent any reaction from proceeding (interlock condition), this will not be the primary focus of this paper. I theorize that even under the best conditions, it is still difficult to get all of the reagents together at the reaction site at the same time, and this difficulty increases exponentially with the increase of the MW of the targeted end-product.

The Miller-Urey Experimental Setup: Four Experiments

I examined 4 MU results here for this paper. Three of the actual experiments where done in 1950's, and after Miller's death in 2007, the materials from these experiments were re-

examined using state-of-the-art chemical analyses (Johnson et al, 2008). The fourth was done more recently by researchers in Europe. The first MU result was from the "classic" experiment. This was analyzed alongside another trial referred to as the "volcanic" experiment which attempted to simulate the conditions found near the volcanos suspected to be prevalent on the surface of a young Earth. The third experiment added hydrogen sulfide to the MU precursor materials, again trying to simulate which compounds may have been available for an abiotic chemical reaction in the early stages of Earth development 3.5 Billion years ago (Parker et al, 2011). The fourth experiment we looked at was recent and focused on the production of the 4 canonical nucleobases (Ferus et al, 2017). All four MU experiments produced amino acids which are necessary for life. When the "classic" experimental results were published in 1953, it was big news. We are still living under the shadow of that discovery, even though most researchers do not believe that the experimental design was applicable to early Earth. We will examine the results of each and show that these results wield a "two-edged sword" when it comes to showing what is possible abiotically under random circumstances and what is not. I believe that it is important to note that Dr Stanley Miller said of his famous experiment "In this apparatus an attempt was made to duplicate a primitive atmosphere of the earth, and not to obtain the optimum conditions for the formation of amino acids" (Miller,1953). It was believed at the time that an early Earth atmosphere could have been anaerobic, i.e. without oxygen gas, and therefore, reducing (Oparin, 1953).
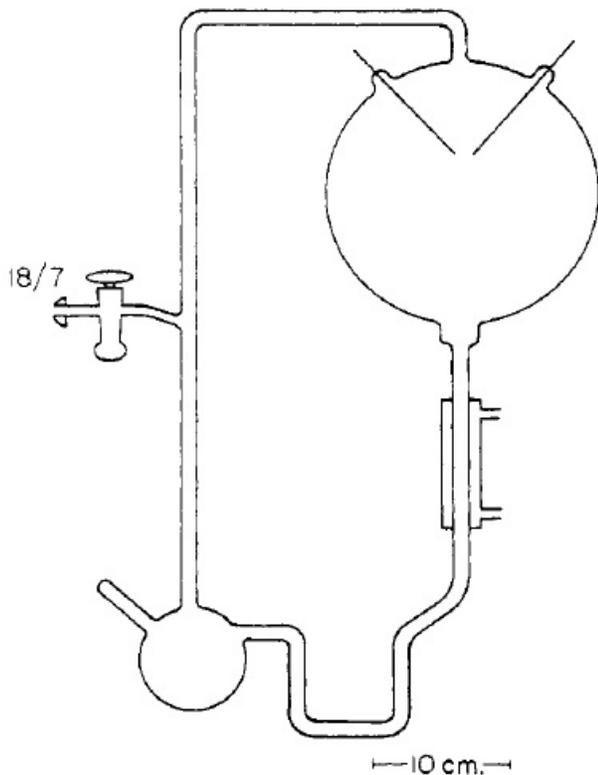
Fig. 1.—Apparatus no. 1.

Figure 1: The 1958 Miller-Urey "Classic" electric-discharge experimental apparatus. Boiling chamber shown in lower left, the spark chamber is upper right. The middle right item is the condenser. Image taken directly from the Miller paper.

Simplicity seemed to be key with the apparatus in Figure 1 being comprised of a 5-liter reaction flask, fitted with electrodes for an electric spark from a Tesla coil, a boiling flask to hold and boil liquid water, and a condenser (Miller,1955). The "primitive Earth atmosphere" included hydrogen gas, gaseous ammonia and methane. The main ingredient of the experiment was 200 mL of water in the boiling flask which was to be brought to boiling to produce enough steam to mix with the other gases in the presence of the spark. The water vapor would proceed in a clockwise direction into the condenser

and rejoin the liquid water at the bottom of the smaller water flask. Any products formed

by the spark reaction would deposit on the surface of the reaction flask, condense and

flow back down into the boiling flask via the "U-tube". After one day of operation, the

water in the boiling flask turned noticeably pink, and the end of a week the mixture was

"deep red and turbid" (Miller, 1953). The reaction was then stopped and product streams

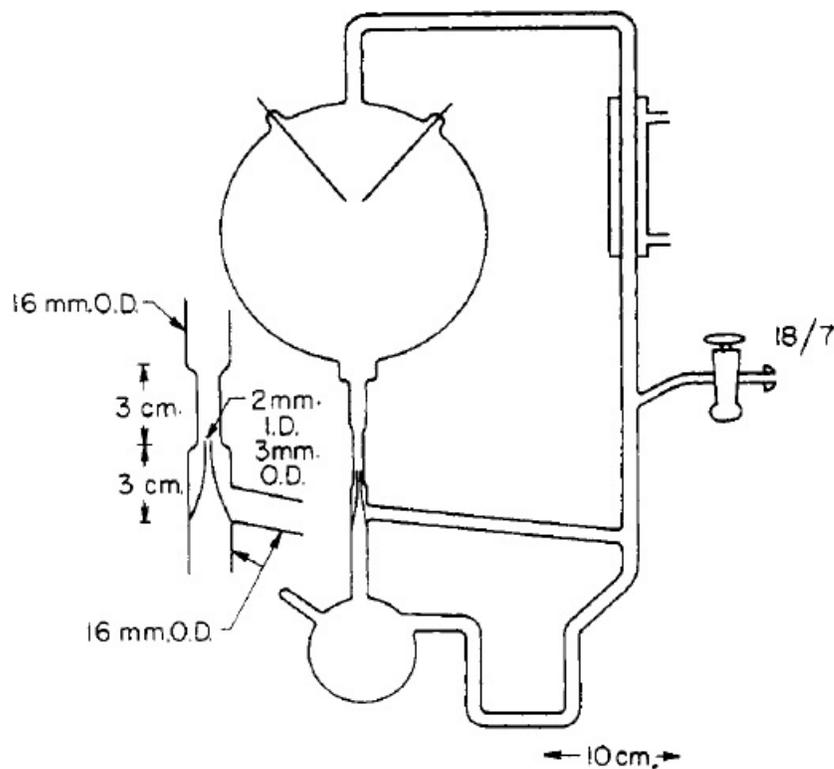were carefully isolated by various chemical means (Miller, 1955).

Fig. 2.—Apparatus no. 2.

Figure 2: The 1958 Miller-Urey "Volcanic" and "H$_2$S" electric-discharge experimental apparatus. Boiling chamber shown in lower left, the spark chamber is upper left. The upper right item is the condenser. Center tube from right to left leads to aspirator directly underneath the spark chamber to simulate steam from volcano. Additional information on aspirator is shown to the left of the reactor. Image taken directly from the Miller paper.

Originally, the quantitative analysis of the effluent was done using paper

chromatography, method of choice in the 1950's. Several proteogenic amino acids were

isolated and the results were promptly reported in a short paper in 1953. The second MU reactor shown in Figure 2 switched things around somewhat and added an aspirator above the boiling flask in order to concentrate a blast of steam towards the electrodes in the adjacent reaction vessel. An application of this was to simulate how nearby volcano would affect the reactions (Johnson, et al, 2008). The results of volcanic "Run 2" with the aspirator were reported alongside the detailed report of the classic "Run 1" without the aspirator in Miller's 1955 paper. Being limited to the analysis techniques of 1955, not much separation was achieved between the results of Run 1 and 2. Run 3 of the 1955 paper was the "silent" method of introducing an electrical discharge to the gaseous mixture and is not of interest to this paper. However, a substitute Run 3 is offered by this paper: It is the H_2S-rich experiment later performed by Miller in 1958, which went unreported until 2011. This trial also used the "volcanic" apparatus described above and shown in Figure 2. It introduced an additional H_2S gas component often found in volcanic plumes (Parker, et al, 2011). The fourth experiment I examine was not performed by Miller, but by researchers in the Czech Republic This setup was a "prototype" of the MU experiment with a laser glow discharge emission cell acting as a lightning simulation at 650K. The reducing atmosphere was made up of H20 + NH3 + CO fed into a chamber at 10 torr. The products were then isolated in a liquid-nitrogen trap (Ferus et al, 2017).

Table 1: Amino Acids and Nucleobases Targeted in Four Miller-Urey Type Experiments

MW (Da)	Name	H₂S	Classic	Volcanic	Lightning
75	Glycine	Y	Y	Y	Y
77	Cysteamine	Y	--	--	--
89	β-Alanine	Y	Y	Y	--
89	α-Alanine	Y	Y	Y	--
103	β-Aminobutyric acid	Y	Y	Y	--
103	α-Aminobutyric acid	Y	Y	Y	--
103	α-Aminoisobutyric acid	Y	Y	Y	--
103	γ-Aminobutyric acid	Y	Y	Y	--
103	β-Aminoisobutyric acid	Y	Y	Y	--
105	Serine	Y	Y	Y	--
105	Isoserine	Y	X	Y	--
111	Cytosine	--	--	--	Y
112	Uracil	--	--	--	Y
115	Proline	X	X	X	--
117	Norvaline	X	Y	Y	--
117	Valine	Y	Y	Y	--
117	Isovaline	Y	Y	Y	--
119	Homoserine	X	X	Y	--
119	2-Methylserine	X	X	Y	--
119	Threonine	Y	X	X	--
121	Cysteine	N	--	--	--
131	Leucine	Y	X	X	--
131	Isoleucine	Y	X	X	--
132	Ornithine	X	X	Y	--
132	Asparagine	X	X	X	--
133	Aspartic acid	Y	Y	Y	--
135	S-methylcysteine	Y	--	--	--
135	Adenine	--	--	--	Y
146	Glutamine	X	X	X	--
146	Lysine	X	X	X	--
147	Glutamic acid	Y	Y	Y	--
149	Methionine	Y	--	--	--

149	β-Hydroxyaspartic acid	N	N	Y	--
151	Guanine	--	--	--	Y
155	Histidine	N	N	N	--
161	α-Aminoadipic acid	N	N	Y	--
161	2-Methylglutamic acid	N	N	Y	--
163	Ethionine	Y	--	--	--
165	Methionine sulfoxide	Y	--	--	--
165	Phenylalanine	N	N	Y	--
174	Arginine	N	N	N	--
181	Tyrosine	N	N	N	--
181	Methionine sulfone	Y	--	--	--
183	Homocysteic acid	Y	--	--	--
204	Tryptophan	N	N	N	--

Legend: Y = Species Found   N=Species Not Found
"—" = Species not Targeted

The Analysis of Four Miller-Urey Experimental Results Shows a Molecular Weight Cutoff

Refer to Figures 1 and 2. Where the analytical methods of 1955 did not offer much difference between Runs 1 and 2, the HPLC, UV Florescence and TOF-LCMS technology employed in 2008 on these reconstituted samples showed that the volcanic apparatus produced more amino acids species than the classic apparatus (Johnson, et al, 2008, Supplemental Material). It is believed that the steam directed into the electrical discharge generated hydroxide ion which could have additionally reacted with amino compounds formed (Johnson, et al., 2008). Of particular interest is that the abundances of the amino products reported decrease exponentially with increase of MW.
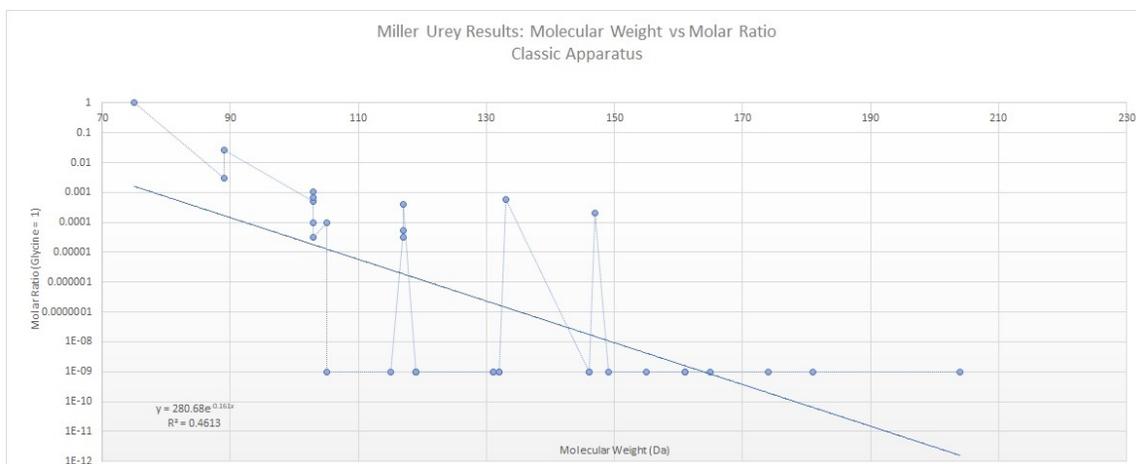
Figure 3: Chart of the Miller-Urey "Classic" results. The largest amino acid found was Glutamic acid with a MW of 147 Da. The data shows an exponential trendline which extrapolates a 10nmol cutoff of 149 Da. The 1 nmol "zero" crossing is 164 Da.

Refer to Figure 3. The highest amino compound formed in the classic experiment was Glutamic acid with a MW of 147 Da. The trendline obtained from the experimental data had an R-squared value of 0.46 which I believe is appropriate for the following reasons: I used a very low molar ratio value, 10-9 to represent compounds "not found" in comparison to the volcanic apparatus results, since there is no "zero" in a logarithmic plot. And I include "not found" data to enhance the trend's response to the difficulty in forming these "targeted" amino acids. The "not found" data points will upset the R-squared value, as will the fact that these unique products of reactions are subject to their individual chemistry, and will not necessarily follow a mathematical curve based upon yield. Another reason I am comfortable with the trend lines in all these experiments shown is that one can see the trend in each case. The Classic trendline predicts a cutoff MW of 149 Da, with a MW increase of 131 Da above the largest precursor reagent, water. This cutoff is based upon a molar fraction 10-8 well below the detectable threshold implied by the results reported, and well below any useful amount of substance.

The classical setup produced 7 of the 20 canonical amino acids along with 7 other amino compounds. Using the volcanic apparatus, the largest proteogenic compound formed was phenylalanine with a MW of 165 Da, with a MW increase over yield of 147 Da above the MW of water, 18 Da.

Figure 4: Chart of the Miller-Urey "Volcanic" results. The largest amino acid found was phenylalanine with a MW of 165 Da. The data shows an exponential trendline which extrapolates a 10nmol cutoff of 166 Da. The 1 nmol "zero" crossing is 181 Da. The MW increase from precursor reagent (water) was 147 Da, close to the proposed "maximum" for "one-pot" electric discharge experiments with a Tmin of 9.6 seconds.
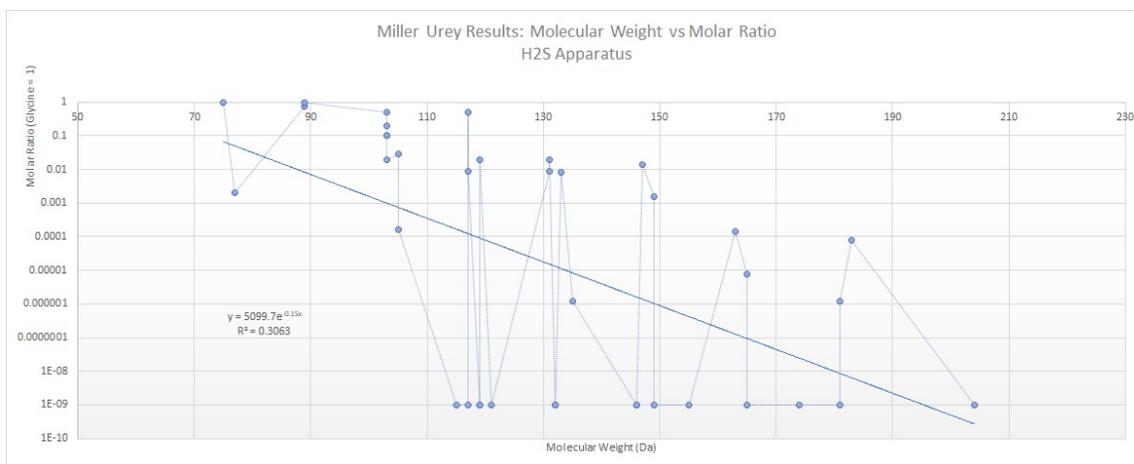
Figure 5: Chart of the Miller-Urey "H2S" results. The largest amino acid found was homocysteic acid with a MW of 183 Da. The data shows an exponential trendline which extrapolates a 10nmol cutoff of 180 Da. The 1 nmol "zero" crossing is 195 Da. The MW increase from precursor reagent (water) was 149 Da, the proposed "maximum" for "one-pot" electric discharge experiments with a **T**min of 38 seconds.

Figure 4 shows a trendline predicting a 166 Da cutoff. The volcanic setup produced 7 of the 20 canonical amino acids along with 15 other amino compounds. Figure 5 displays the H_2S experimental result, using the same type of reactor as the volcanic run, produced 10 of the 20 canonical amino acids along with 14 other amino and amino/sulfurous compounds. The largest amino substance reported for the H_2S was Homocysteic acid with a MW of 183 Da. This trendline for the H_2S has a lower R-squared value of 0.31, much for the same reason stated earlier. This data has more "not found" substances to keep the list of species targeted the same across the 3 experiments. Refer to Figure 8 to see a 3-D "stick and ball" model of some of the targeted amino acids to see the complexity increase required to get to the larger "not found" species. The H_2S experiment included sulfide gas whereas the other two experiments did not. Therefore, I did not list sulfuric compounds as "not found" in the two runs which did not have sulfur. The addition of H_2S as a precursor reagent was significant in the final product MW. But

taking H_2S with MW of 34 Da into account as the largest precursor, and a trendline predicting a cutoff of 180 Da. In this case the actual largest MW molecule produced was 183 Da, a MW increase of 149 above H_2S, very similar to the 147 Da increase over the heaviest molecule found in the volcanic reactor. The similarity and repeatability of this reactor to produce such a similar increase in complexity of molecules, even though the experiments were done years apart and with a different set of reagents, is noteworthy. The 4th MU experiment was somewhat different that the first three because it was targeted for production of nucleobases in a reducing environment. In Figure 7, the yield of these products was in the part-per-million range, they used "GC-MS with volatilization of biomolecules using silylation agent in the derivatization process" (Ferus et al, 2017, Supplemental Material). The results are shared in Figure 7 under the "Lightning" heading. Also, for reference I included Figure 6 to show the complexity of these chemical compounds. These were included because we wanted to show that nucleobases are produced in a MU-type reducing atmosphere, but in very low amounts. And among those produced, the largest of the canonical nucleobases found was Guanine, having a MW of 151 Da. We also see the trend of smaller molecules having larger yields, except Uracil was the least produced, although it is not the smallest molecule. Still, this is well within the cutoff established by the other three MU-type experiments and is a similar to the "Classic" MU results.
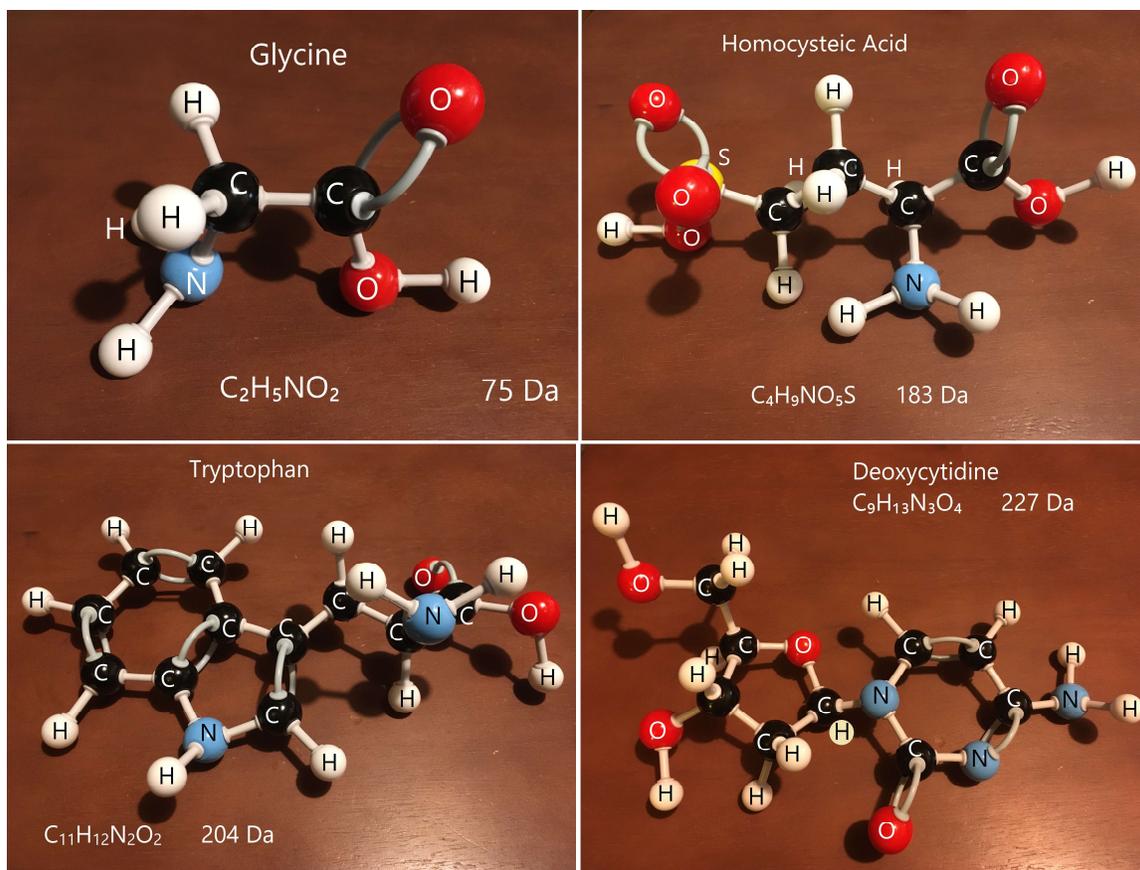
Figure 6: "Stick and Ball" models of the amino acids targeted for the Miller-Urey experiments. The figure shows the increasing stereochemical complexity of the molecules, especially as MW increases. Glycine was the smallest species found. Homocysteic Acid was the largest. Tryptophan was not found in the Miller-Urey results, and is the largest canonical amino acid, shown here for comparison. Deoxycytidine is the smallest nucleoside at 227 Da, and is shown here directly below Homocysteic Acid for comparison purposes to show the complexity increase of the largest molecule found at 183 Da.
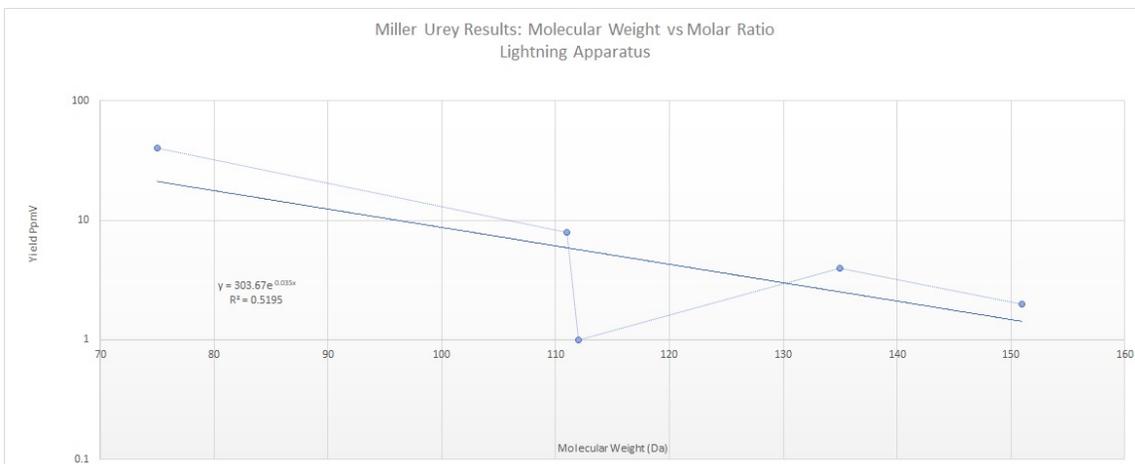
Figure 7: Chart of the Miller-Urey "Lightning" results. The largest nucleobase found was guanine with a MW of 151 Da. The data shows an exponential trendline which extrapolates a 1ppmV cutoff of 163 Da. The extrapolated MW increase from precursor reagent (water) was 147 Da, the proposed "maximum" for "one-pot" electric discharge experiments with a **T**min of 9.6 seconds. The extrapolated value of MW increase is highlighted here due to the limited number of "targeted" molecules and the relatively high R-squared value obtained.
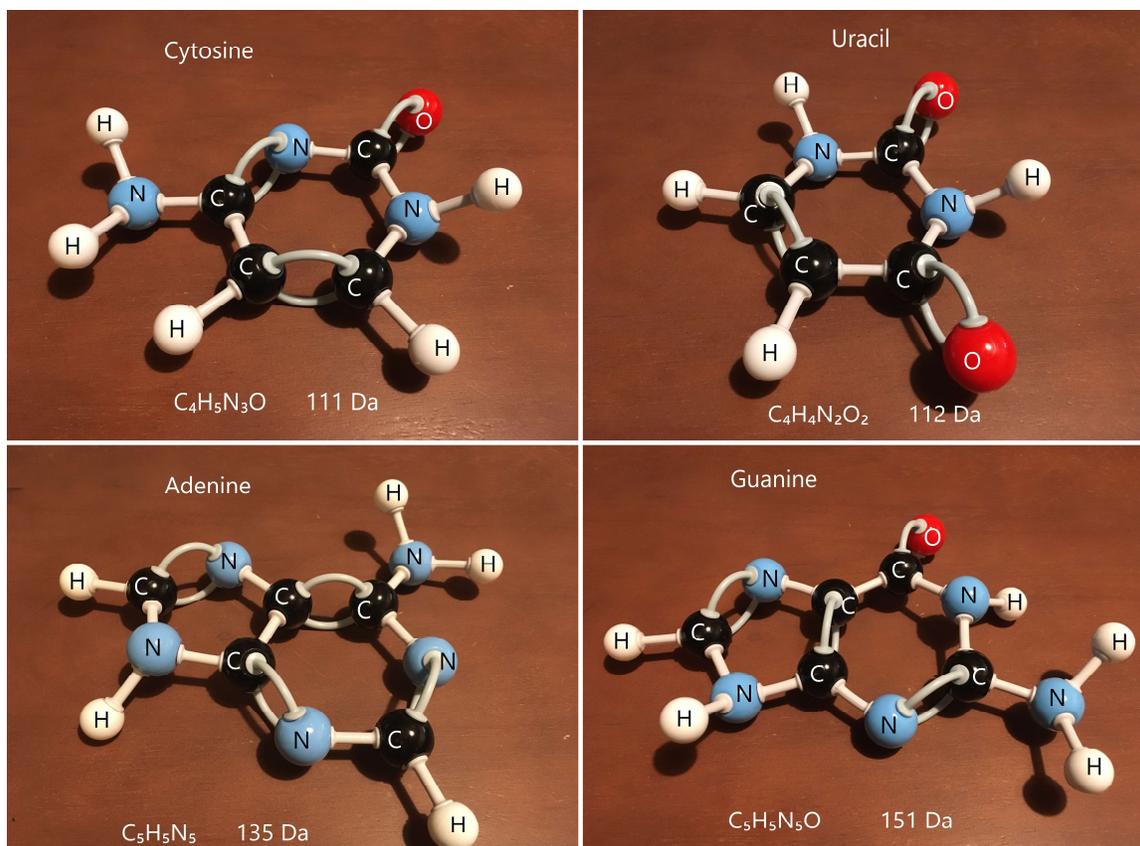
Figure 8: "Stick and Ball" models of the canonical nucleobases show the increasing complexity of the molecules, especially as MW increases. All four molecule exhibit aromatic ring structures which require specialized non-destructive chemical analysis techniques to isolate.

Very Recent "One Pot" Experiments to Produce Nucleosides

In the spirit of MU, researchers are still looking for a "one-pot" solution to get small molecules to organize into large, complex macro-molecules, especially those directly responsible for the construction of DNA and RNA. This paper has chosen to focus on the synthesis of nucleosides from the small precursor materials of MU. In October 2019, just last month from the time of this writing, a Science article was published claiming a "unified prebiotically plausible synthesis of pyrimidine and purine RNA nucleotides" in a "one pot" manner (Becker, et al, 2019). The difficulties they are trying to overcome is

the prebiotic, "one-pot" and, "simultaneous" generation of pyrimidines and purines into nucleosides and further nucleotides. They submit several pathways to accomplish such and submit impressive lab results having successfully abiotically produced nucleosides cytidine and uridine. In one scenario, their starting materials in the pot are cyanoacetylene and hydroxylamine. These are given as "acceptable prebiotic" materials because cyanoacetylene forms from electric discharge under CH4-N2 (Muchowska, et al., 2019) and hydroxylamine, while they freely admit it is unclear where it comes from, can arise prebiotically also from lightning with N2 and CO2 after several steps including the formation of anions nitrate and nitrite, the addition of sulfuric acid, and a subsequent hydrolysis to purify the targeted amine. This reasoning is troublesome. So far, we need one pot to create cyanoacetylene, and 3 pots to get hydroxylamine. Then, we need a pot to put the two together to form 3-aminoisoxazole, MW of 84 Da. Then Urea, MW 60 Da, is added to form a large N-isoxazole-urea complex. Another pot is brought in for a reaction with added boric acid, MW 62 Da and added ribose, MW 150 Da to produce a large ribosylated product of MW 293. This intermediate product needs another pot to react with borates to isolate the furanosides. Then "the final step" is "reductive opening of the isoxazole N-O bond, followed by tautomerization, intramolecular cyclization, and water elimination in a cascade-like fashion. We found that this reaction occurred rapidly with Fe2+ in the presence of thiols" (Becker, et al, 2019). With this final step being actually 5 steps, we have a total of at least 12 pots. Also, we see a maximum MW increase cutoff of 143 Da during their recursive experiments, going from the large N-isoxazole-urea complex to the large ribosylated product. Their explanation of how this is a "one pot" reaction is that during early Earth, there were wet and dry cycles, cyclic water

currents and weather, with cyclic heat and cold with natural changes of pH and natural serial addition of "prebiotic" chemicals e.g. Urea and many others to form this nucleoside abiotically. Everyone knows that complex chemicals can be synthesized, but to put together such a wild story of how this is "plausible" with no guidance or observer on the ground is not science. Cyclic dry and wet, high temperature, low temperature, high pressure, low pressure, high and low voltage cycles are all forms of information. If this is what the "Earth" was doing when these compounds were formed, then one must accept that there was a source of this information given and stored in the Earth, somehow extracted out of the chaos of early Big-Bang space. Invoking an Earth imbued with information, or an "Informed Earth", is not a random process, and by definition not a true abiogenic or abiotic process. This logic likens to Earth to a large catalytic machine, an oversized biotic enzyme, that is taking small separate molecules and forming pure organic macromolecules and sequestering them to later continue form large continuous polymeric proteins while at the same time, selecting only the left-handed ones to form RNA and DNA. The problem we have with stopping this rampant, non-scientific form of inquiry is that the Earth is full of information at all levels of complexity and scale. Atoms are full of information of how they combine with relative sizes so neatly arranged that we can tabulate them, a.k.a. The Periodic Table of the Elements. Molecules themselves contain, and once formed, retain information such as phase, temperature, pressure and relative mass. The point here is that we bring all this information into our experiments as simple and pure as they may seem. Therefore, on one hand we say that a process is random, when it really isn't. An on the other hand, we say a process is guided by the Earth alone, when it really isn't to the point to which we believe. But what we can

say is that there exist physical constraints and our assumptions can be tested within these constraints.

Comparing the Volcanic, H₂S Rich Miller-Urey Experimental Results and "One Pot" to the Proposed Statistical Model

A simple binary probabilistic model is given, likened to flipping up to $n = MW$ coins at one time, and repeating every 10^{-43} seconds, expecting to get all "heads" after a prescribed minimum time "Tmin" has elapsed. "All heads" means successful molecule of n MW. The model estimates the absolute minimum time (Tmin) required to generate a compound of any given molecular weight (MW) using $Tmin=2^{(MW-Pmax)}*Tp$, where Tp is Planck Time, 5.4e-44 (s). It is the smallest amount of time applicable to physical chemistry, used here as a Universal Clock Cycle counting through the binary number obtained from $2^{(MW-Pmax)}$. The Tmin result is how long would it take to overflow the binary counter in seconds, since the singular favorable outcome is represented by the overflow (maximum) value of "all 1's", meaning all of the reagents are in position. Pmax represents the largest precursor material in the reaction, usually water (18 Da) in MU, except for the H₂S version in which we must use 34 Da for Pmax to account for the advantage of adding ready-made and purified compounds to an abiogenic experiment. It was reported that some of the amino acids produced by this type of experiment form immediately upon turning the reactor on. In a 1996 interview, Stanley Miller stated: "Just turning on the spark in a basic pre-biotic experiment will yield 11 out of 20 amino acids" (Access Interview, 2008). A computer-simulation of MU modelled some reactions as favorable to occur within 1 pico-second (Saita and Saija,2014). Of note one example is aspartic acid, being 133 Da. This is one of the amino acids readily identified by Miller in

1953 by paper chromatography. This compound has a Tmin value of 2^(133-18)*5.4e-44 = 2.2 nanoseconds. This is not the formation time, but the absolute minimum time it should take to form from a probabilistic standpoint. Therefore, the smaller compounds not only form in greater abundance, but also form more rapidly. It is interesting to note here that rapid formation of molecules is more fitting for a young-earth scenario in which materials were formed on the order of seconds, minutes and hours of a day. In the cases of the "volcanic" and "H2S" experiments, the MW increase cutoff of 147 – 149 Da computes to a Tmin of 9.6 – 38 seconds. Both are long times of formation, but not in the context of an experiment that ran one week. In addition, multi-step, recursive reactions must also follow the statistical model but to their detriment in that each trial now being on the order of seconds having to select against the 10^60 possible C,N,O,S, organic compounds in the chemical space below 500 Da (Reymond, et al., 2010). There are 1.5e17 seconds in 4.6 billion years, not enough time to create all the possible organics to arrive at any one targeted.

ET Results: Many Large Compounds Formed, but Those Macromolecules Needed for Life Conspicuously Absent.

With our probabilistic model being strengthened by what we observe in our laboratory experiments in regards to what can be produced in a short amount of time, we need to see if the model holds up in actual "ET experiments" outside of human control that have persisted over the maximum amounts of time in question, i.e. billions of years. Extraterrestrial objects, such as meteorites and comets are such objects with the "carbonaceous" variety being among the most interesting. These space rocks are found on the surface of the Earth, either long after they have landed, or more desirably after

eyewitness accounts of an object landing and immediately being taken and analyzed with a known proper chain of custody to insure purity. A specific famous example of a carbonaceous meteorite is that of the one found in Murchison, New Zealand. Much research and analysis has been done on the Murchison Meteorite (MM) in order to ascertain if contains organic substances. If proteogenic species can be isolated from MM, this could support the idea that the Earth was seeded from an ET source. However, this just puts the problem on another planet.
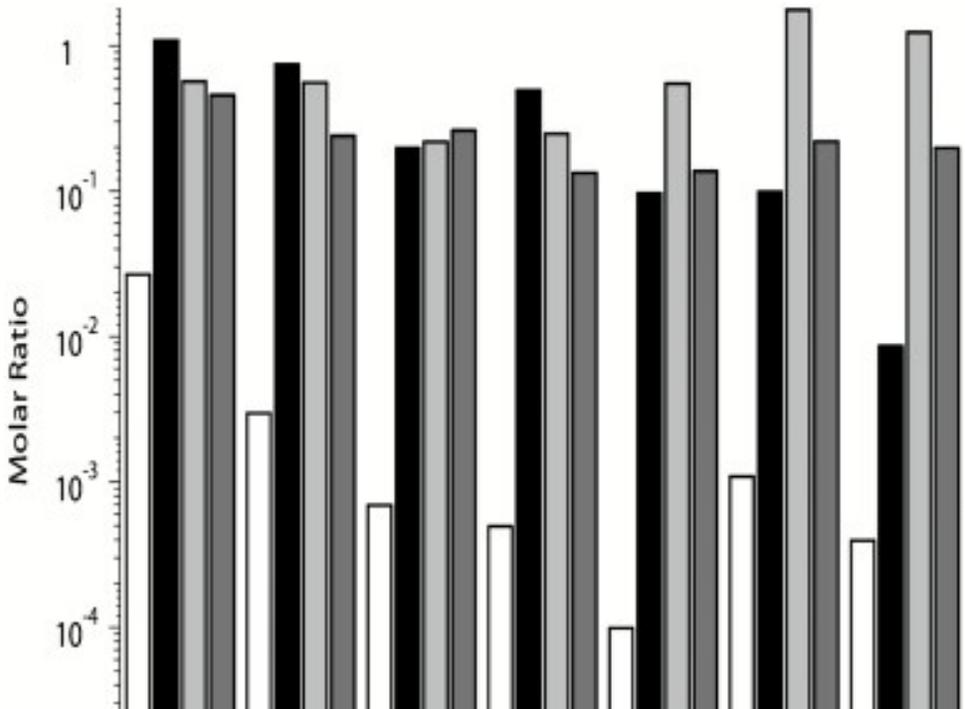

Figure 9: Image above shows that amino compounds isolated from multiple Murchison Meteorite samples and Antarctic samples are commensurate with MU results, even though these ET objects have been in existence for billions or years, undergoing varied temperature conditions as they travel through space. (Graph from the Parker et al. 2008)

But to some, this is a plausible scenario because it is so far removed from us and anything is possible "out there". Looking at Figures 9 and 10, we find on the MM, LON 94102, QUE 99177 and EET 92042 carbonaceous chondritic meteorites, that they contain much

the same amino acid compounds found in the H_2S MU experiments (Johnson, et al, 2008, supplemental material).

TABLE 2. *Relative abundances of amino acids in the Murchison meteorite and an electric-discharge synthesis*

Amino acid	Murchison meteorite	Electric discharge
Glycine	4	4
Alanine	4	4
α-Amino-*n*-butyric acid	3	4
α-Aminoisobutyric acid	4	2
Valine	3	2
Norvaline	3	3
Isovaline	2	2
Proline	3	1
Pipecolic acid	1	<1
Aspartic acid	3	3
Glutamic acid	3	2
β-Alanine	2	2
β-Amino-*n*-butyric acid	1	1
β-Aminoisobutyric acid	1	1
γ-Aminobutyric acid	1	2
Sarcosine	2	3
N-Ethylglycine	2	3
N-Methylalanine	2	2

Mole ratio to glycine (= 100): 0.05–0.5, 1; 0.5–5, 2; 5–50, 3; >50, 4. The meteorite abundances are estimated from the published gas chromatogram (2); these estimates are approximate.

Table 2 and chromatogram (2) from Wolman, 1972.

From Table 2 we see again even another study, that shows some interesting similarities exist between MU yields and MM amino acid compounds found (Wolman, et al. 1972). But in the same study, two particularly large amino acid derivatives were created in the MU and the same two found in MM. Now even though these two organic acids of MW 269 and 281 Da were seen in the gas chromatography, they were not identified, other

than knowing that they are derivatives of Valine, MW 117 Da and Pipecolic acid of MW 129 Da respectively (Wolman, et al. 1972). It is interesting to note that even on the MM, a MW increase of 152 Da is the same as the MW increase seen in MU and in the probabilistic model of being the Tmin of chemical reactions on the order of second, a common amount of time to a reaction to proceed and finish. To see that happened such an ancient object is remarkable.
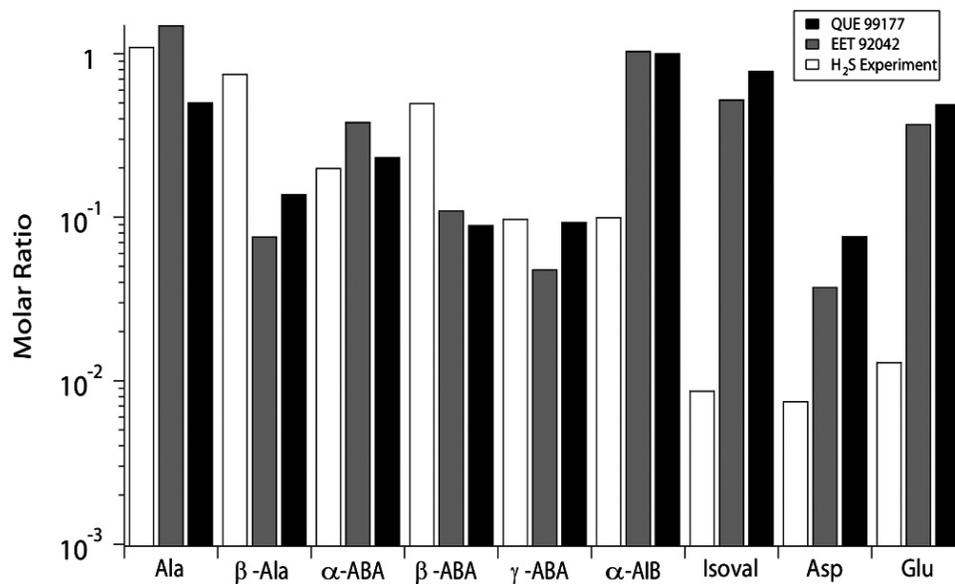

Image above shows that amino compounds isolated from multiple Antarctic samples are commensurate with MU results, even though these ET objects have been in existence for billions or years, undergoing varied temperature conditions as they travel through space. (Graph from the Parker et al. 2008 "Supplemental Information")

In another investigation of the MM, they found "insoluble organic material" (IOM) which is a huge hard "spitball" of random organics that are very hard to isolate and purify, many of which are larger than my 200 Da cutoff of the model (Schmitt-Kopplin, et al., 2010). This would be concerning at first glance because one could say that this is no longer a cutoff and a 227 Da MW nucleoside could then be formed given enough

time. But none of the precious nucleoside and nucleotides have ever been isolated from MM or any other ET object, even in the face of so many large organics being found. So, in reality, these nucleobases found in these ET objects are "chemical dead-ends", and this can be for many chemical reasons (Sarfarti, 2008). I believe another strong reason is that, as discussed earlier, with the chemical space of 10^60 possible organics with MW less than 500 Da, that 4.6 billion years is not enough time to randomly create one of a small handful of nucleosides we need for life.

Summary

We analyzed 4 different versions of the MU electric spark discharge experiment and identified a maximum cutoff MW for the targeted proteogenic products of these experiments of 180 – 183 Da. A more important result was that this cutoff represented a 146 – 149 Da MW gain over and above the largest precursor material in the experiment, in this case H_2S gas with a MW of 34 Da. This approximate maximum gain cutoff identified was seen in 3 total isolated "experiments". First, MW gain of the Volcanic experiment (148 Da), then the two large unidentified molecules found from the MM (152 Da), and third from the "one pot" experiment (143 Da) trying to synthesize nucleosides from prebiotic precursor materials. We showed that a statistical model invoking "deep time" and Planck Time, can accurately predict this MW gain cutoff by calculating a minimum time of formation (Tmin) using the targeted species' MW and the MW of the largest precursor material used in the experiment. In the cases of the MU "Volcanic and "H_2S" experiment, the cutoff of 147 – 149 Da would compute to a Tmin of 9.6 – 38 seconds. Both are long times of formation, but not in the context of an experiment that ran one week. Extrapolating with the statistical model, a detectable amount of

proteogenic material with a molecular weight of 218 Da, formed using a "one pot" method with water as the largest precursor, would have a Tmin of 4.7 Billion years. This is well below the 227 Da of Deoxycytidine, the smallest nucleoside. Also, we saw that ET carbonaceous chondrites, such as the MM, contain similar yields of proteogenic materials as the MM experiments and do not violate the cutoff MW's discussed. We saw that even on the MM, a MW increase of 152 Da is the similar to the MW increases seen in MU and in the probabilistic model of being the Tmin of chemical reactions on the order of seconds and minutes, a common amount of time to a reaction to proceed and finish. We reiterate that see that MW increase cutoff with such a short Tmin on such an ancient object is remarkable. We also discussed the large IOM molecules found in the MM and how, even though the opportunity existed for large molecules to "grow" on the MM, no nucleoside or nucleotides have been found on an ET object to date, because this small handful of "targeted" proteogenic species to be produced is vanishingly infinitesimal in the face of the virtually infinite "chemical space" that exists for organic C,N,O,H,S molecules under 500 Da. Therefore, we conclude that 4.6 Billion years is not enough to form a nucleoside abiotically, even in the most favorable random conditions.

References

Bergman, Jerry. 2000. Why Abiogenesis is Impossible. *CRSQ* 36:195–207.

DeMassa, John M, Boudreaux, Edward A. 2013. Formic Acid: A Significance but Ignored Product in the Miller-Urey Experiment. CRSQ 49:211-217.

Henahan, Sean. 2008. "Exobiology: An Interview with Stanley L. Miller". Accessexcellence.org.

Hull, D.E. 1960. Thermodynamic and Kinetics of Spontaneous Generation. Nature 186:693.

Johnson, Adam P., Cleaves, H. James, Dworkin, Jason P., Glavin, Daniel P., Lazcano, Antonio and Bada, Jeffrey L. 2008. The Miller Volcanic Spark Discharge Experiment. Science 322 (5900), 404.

Martin, F., Fabio Pietrucci, Antonino Marco Saitta, Antonín Knížek, Petr Kubelík, Ondřej Ivanek, Violetta Shestivska, and Svatopluk Civiš. 2017. Formation of nucleobases in a Miller–Urey reducing atmosphere. Proc Natl Acad Sci. 114(17): 4306–4311.

Muchowska, K.B., Varma, S.J. & Moran, J. 2019. Synthesis and breakdown of universal metabolic precursors promoted by iron. Nature 569, 104–107

Parker, Eric T., Cleaves, Henderson J., Dworkin, Jason P., Glavin, Daniel P., Michael Callahan, Andrew Aubrey, Antonio Lazcano, and Bada, Jeffrey L. 2011. Primordial synthesis of amines and amino acids in a 1958 Miller H2S rich spark discharge experiment. Proc Natl Acad Sci. 108(14): 5526–5531.

Philippe Schmitt-Kopplin, Zelimir Gabelica, Régis D. Gougeon, Agnes Fekete, Basem Kanawati, Mourad Harir, Istvan Gebefuegi, Gerhard Eckel, Norbert Hertkorn, 2010. High molecular diversity of extraterrestrial organic matter in Murchison meteorite revealed 40

years after its fall. Proceedings of the National Academy of Sciences Feb 2010, 107 (7) 2763-2768

Reymond J.L., Van Deursen R., Blum I.C., Ruddigkeit, L. 2010. Chemical Space as a Source for New Drugs. ChemComm 1: 30–38.

Saitta A.M., Saija F. 2014. Miller experiments in atomistic computer simulations. Proc Natl Acad Sci. 111:13768–13773

Sarfarti, Johnathan. 2008. *Nucleic Acid Bases in Murchison Meteorite?* http://www.creation.com.

Sharp, Doug B., 1977. Interdependence in Macromolecule Synthesis: Evidence for Design. CRSQ 14:54–61.

Stout, Timothy and Matzko, George. 2019. Creation Matters, A Natural Origin-of-Life: Every Hypothetical Step Appears Thwarted by Randomization.

Thornton, Steven T. and Rex, Andrew. 2002. Modern Physics for Scientists and Engineers, 2nd Ed., p. 535

Williams, Emmett L. 1967. The evolution of complex organic compounds from simpler chemical compounds: Is it thermodynamically and kinetically possible? *CRSQ* 4:30–35.

Wolman, Yecheskel., Havenland, William J., and Miller, Stanley L. 1972., Nonprotein Amino Acids from Spark Discharges and Their Comparison with the Murchison Meteorite Amino Acids. Proc. Nat. Acad. Sci. USA, Vol. 69, No. 4, pp. 809-811