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Prebiotic materials from on and off the early Earth

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One of the greatest puzzles of all time is how did life arise? It has been universally presumed that life arose in a soup rich in carbon compounds, but from where did these organic molecules come? In this article, I will review proposed terrestrial sources of prebiotic organic molecules, such as Miller–Urey synthesis (including how they would depend on the oxidation state of the atmosphere) and hydrothermal vents and also input from space. While the former is perhaps better known and more commonly taught in school, we now know that comet and asteroid dust deliver tons of organics to the Earth every day, therefore this flux of reduced carbon from space probably also played a role in making the Earth habitable. We will compare and contrast the types and abundances of organics from on and off the Earth given standard assumptions. Perhaps each process provided specific compounds (amino acids, sugars, amphiphiles) that were directly related to the origin or early evolution of life. In any case, whether planetary, nebular or interstellar, we will consider how one might attempt to distinguish between abiotic organic molecules from actual signs of life as part of a robotic search for life in the Solar System.

Keywords: prebiotic chemistry; exogenous delivery; endogenous synthesis; impact; hydrothermal vents; IDP (interplanetary dust particle)

1. INTRODUCTION

Following Professor Thaddeus's gas-phase interstellar molecules and preceding Professor Grady's planetary carbon cycle means that, in a way, I stand between the Earth and the sky. It may sound rather mythic to say it that way, but given that the question of how life emerged on Earth is a subject that has inspired a great deal of myth, both scientific and otherwise, it is difficult to resist the temptation to be just a bit fabulous. In fact, I am going to start with a creation story from the Kojiki—Japan's eighth century chronicle that starts with the formation of the world, deities, and Japan. I will leave the specifics of the island of Japan to the geologists and the deities to subsequent speakers who are even more outrageous than I, and restrict myself in this talk to the world.

> Before the heavens and the Earth came into existence, all was a chaos, unimaginably limitless and without definite shape or form…out of this boundless, shapeless mass something light and transparent rose up and formed the heaven…(and a god emerges here)… In the meantime what was heavy and opaque in the void gradually precipitated and became the Earth, but it had taken an immeasurably long time before it condensed sufficiently to form solid ground….
>
> (Brains *et al.* 1999)

All things considered, this excerpt from the Isobe translation of the Kojiki is remarkably similar to how we currently describe the formation of the Earth within the Solar nebula that came from the collapse of a vast, dense interstellar cloud. Stars like the Sun and the clouds that precede them are composed primarily of the 'light and transparent' elements, hydrogen and helium, which escape (at least from the forming terrestrial planets) leaving behind the heavier elements that comprise the rocky planets of the inner Solar System. However, exactly how and when the 'something light and transparent rose up'—which I interpret to mean 'when did the hydrogen escape if it ever was there to begin with?' or 'What was the oxidation state of the early Earth's atmosphere?'—has important consequences for how complex and profuse one expects organic compounds to be on the early Earth.[1] The abundance of organic molecules on the early Earth is the first crucial matter we must address this week in our discussions of conditions for emergence of life on the early Earth because, as we shall see, all non-magical notions of how life emerges are predicated on the basis of the presence of organic compounds, as well as some other substances that we know make up living things today.

My apologies to the impatient chemists for not just jumping right into the organic chemistry here, but I can hardly discuss the conditions necessary for the emergence of life on the early Earth (in my case, chemical conditions) without at least briefly presenting some of the ideas about how life emerged on Earth, which will set the requirements. Incidentally, it seems to me that the conditions under which life first developed might well be more restricted than those under which life can survive or thrive thereafter; hence, I am going to assume that terrestrial life did, in fact, first begin here on the Earth and was not transported (or deliberately set down) here. Presumably, if any of you favour some kind of panspermia, at least you will find my conditions hospitable, if a bit provincial.

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One contribution of 19 to a Discussion Meeting Issue 'Conditions for the emergence of life on the early Earth'.

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So, let us briefly consider the first of these non-mythological conceptions of how life emerged as an example, and then proceed to experimental tests of that concept. The prototypical example comes from a private letter written by Charles Darwin in 1871 in which he speculated about how

> …we could conceive in some warm little pond with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc. present, that a protein compound was chemically formed, ready to undergo still more complex changes. At the present day, such matter would be instantly devoured or absorbed which would not have been the case before living creatures were formed.
>
> (Darwin 1898)

It need not be a protein of course, but it was a logical choice since Strecker had shown in the 1850s that one could make amino acids by heating an aqueous solution of simple starting materials (Strecker 1854). It is easy to forget that they did not know about nucleic acids, and besides, the kind of molecule does not matter here in Session 1 on Monday. The important part is that one goes from a random mix of essential but disordered components to the first self-replicating molecule, and from there to the last common ancestor is a simple matter of natural selection. From the 1920s onward, A. Oparin and J. B. S. Haldane publicly presented and more fully developed similar ideas of a primordial soup (Oparin 1938) but the kernel of the idea was there back in that private letter of Darwin's in 1871. In other words, scientific origins of life scenarios tend to put the pieces of life in proximity to one another, add some kind of energy and figure that eventually something or some process that can reproduce itself will arise. In Session 3, I think, Profs. Szathmáry and Ferris will speak about how a self-replicating molecule may have arisen, and Profs. Wächtershäuser and Deamer on alternatives to focusing on such a molecule; indeed I am keenly looking forward to all of those lectures. My job, thankfully, is much easier than theirs. What I want to consider in my talk is from where those pieces might have come.

2. SPARK DISCHARGE—LIGHTNING IN A REDUCING ATMOSPHERE

It is presumed that the early Earth would have had an atmosphere of simple gases of the type seen in space, or other planetary atmospheres, and/or predicted to be present based on models of how the Earth formed. Then, with these simple gases, you see if you can make biotic or prebiotic monomers by adding energy. Miller's spark discharge experiments (Miller 1953) were probably the first and certainly the most famous modern experimental attempt of that kind to make the primordial soup about which Darwin, Oparin and Haldane had written. The landmark Miller–Urey experiments showed how those first components of the first self-replicating molecule could easily be made by cooking up a little early Earth in a flask. The experiment consisted of running sparks (lightning) into a glass sphere (see figure 1) containing a reduced[1] gas mixture of simple molecules, such as hydrogen, ammonia and methane (the atmosphere), connected by a tube to a reservoir of warm liquid water (the ocean).

The results were breathtaking. When Miller analysed the organic matter that was made in that and subsequent experiments, he found certain amino acids, just the kind of thing that would have delighted Darwin. Starting with some simple common gases, a fairly minimal apparatus and a little energy, the fundamental components of proteins had formed rapidly. Although he was among the first to tackle the problem experimentally, and had only just begun, Miller had already made tremendous progress. Given that it was also the year that the structure of DNA was published, I am told that it seemed as if the secrets of life were being revealed and that very soon scientists would understand how life had come about. It turns out, of course, that the situation is not as straightforward as it may have appeared at that time. For one reason, the assumption that a mixture of reduced gases accurately represents the atmosphere of the early Earth has since been called into question.

At that time, scientists believed that Jupiter was a good model for how planets began and that the early Earth formed warm and wet and had a thick atmosphere composed of reduced gases like hydrogen, methane and ammonia left over from the formation of the Solar System. They figured that Earth's atmosphere, and that of all the planets, essentially started with solar abundances of gases, which gradually escaped, as described in the Kojiki, leaving behind the N_2 that makes up most of our atmosphere today. Our oxygen came later, of course, as a waste product of life. Apparently, part of the appeal of this reduced atmosphere for the early Earth was that it would have been a greenhouse mixture, keeping the Earth from freezing over during a period when the Sun was dimmer than it is today (Sagan & Chyba 1997).

Jupiter retained its original gases because it is so massive that the molecules could never escape. However, size is not the only difference between Jupiter and Earth; the Earth is much closer to the Sun. The notion that, from the time of formation, the Earth started with a thick Jupiter-like atmosphere was seriously undermined by models showing that the temperature in the Solar nebula here at 1 AU exceeded 1000 K (Bell *et al.* 2000). If true then the Earth formed hot and relatively devoid of atmosphere as a result, and subsequent impacts did not help any either (Sleep *et al.* 2001). Instead of being a kind of gaseous placenta, our atmosphere is thought to have accumulated about the planet thereafter by outgassing (Allegre *et al.* 1987; Turner 1989; Farley & Neroda 1998) from the Earth. When a Mars-sized object collided with the Earth leading to the formation of the Moon (Palme 2004), that must have blown away any atmosphere or ocean that the Earth had built up during those tens of millions of years after planet formation (Sleep *et al.* 2001). Continued outgassing punctuated by the occasional giant impact led to an atmosphere, but very different from that of Jupiter in both the manner of formation and the composition.

Geologic data suggested that the Earth has been at or near its current oxidation state for over 3 and probably close to 4 billion years (Delano 2001), implying an atmosphere composed of neutral or perhaps even oxidized gases, such as H_2O, CO_2 and SO_2. Such an oxidizing mixture on the early Earth would make it more difficult to make organic compounds like amino acids, by spark discharge (Stribling & Miller 1987). My understanding is that while most agree that the atmosphere was not reducing (Abelson 1966; Walker 1977; Kasting & Eggler 2002; Chyba 2005), on the other hand, there is no consensus that it was oxidizing either. Last year, there was a report asserting that even if the early atmosphere were dominated by CO_2, the rate of escape of hydrogen from the Earth had been overestimated; therefore, more molecular hydrogen would have accumulated in the Earth's atmosphere than was previously thought (Tian *et al.* 2005). This hydrogen in turn would have allowed for some terrestrial synthesis of organic compounds (as simulated by spark discharge) albeit less efficiently than with the original Miller gas mixture (Stribling & Miller 1987).

3. HYDROTHERMAL VENTS

In any case, if the spark discharge method of making organic molecules is not as important as it was originally thought to be, there are many other ways in which organic molecules may have formed on the early Earth. One very logical approach is to follow the hydrogen. After all, even if it turns out that the early atmosphere was not Jupiter-like, one might still find a place where the conditions are fairly reducing and therefore organic synthesis should be possible. Perhaps the most popular sites for potential organic synthesis in this vein are hydrothermal vents (figure 2), and with good reason. Reducing gases emerge there, at least today, and presumably the early Earth was even more tectonically active than today, so, there would have been a great many of them early on.

Personally, I think that hydrothermal synthesis enjoys a certain psychological advantage over gas-phase syntheses since humans are used to thinking about reactions in hot liquid, and hence the notion of the primordial 'soup' is so popular. Be that as it may, the laboratory experiments simulating the conditions in hydrothermal vents have been highly promising, yielding lipids and related compounds (McCollom *et al.* 1999; Rushdi & Simoneit 2001), amino acid formation (Hennet *et al.* 1992) and oligomerization (Islam *et al.* 2003; Yokoyama *et al.* 2003; Imai *et al.* 1999), nucleotide oligomerization (Ogasawara *et al.* 2000) and pyruvate (Cody *et al.* 2000, 2001, 2004). A caveat on this subject: Smirnov & Schoonen (2003) warn that stainless steel, which has sometimes been part of these laboratory equipment, can act as a catalyst for certain reactions under hydrothermal conditions; hence, one has to pay attention to experimental details. This is obviously only a cursory glance at this subject, please see Holm & Andersson 2005 for a recent review.

In addition to being a potential locally reducing environment, hydrothermal vents are also good sites for prebiotic organics owing to the way that they are perched upon gradients. I suspect that subsequent speakers may touch on this and probably could explain this far better than I but, briefly, a gradient is a wonderful place to make or maintain things that are not really stable in the thermodynamic big-long-run-picture, like us or anything else alive. By all thermodynamic rights we should all really be CO_2 and H_2O, rather than what we are, and it is under such temporary kinetic conditions that organic molecules and life survive. Like a scalding kiln against the far wall of a pottery studio where things can be heated until set, but then are removed and put aside to cool, the hot interior of the vent is an enclosed hot place where molecules are presumably made and then flow out into the surrounding water to cool. Avoiding an extended stay in the hot water that would surely hydrolyse our putative newly formed protein (or whatever) is important to the success of the laboratory experiments that demonstrate the potential of hydrothermal vents for prebiotic chemical synthesis. In practice, building up oligomers in the laboratory involves cycling the solution round and round through the heated synthetic chamber and the cooled quench, and presumably this is representative of the cycle of water around hydrothermal vent systems (figure 2).

The cycling of synthesized organics into a cooler environment where they are more stable deals nicely with one of the objections that has been raised to a static warm pond: that while one might be able to build up a biopolymer like a protein there, the abundant water that is all around this protein will, eventually and inevitably, add to the peptide bonds and break it down, and the warmer the faster (Cronin & Chang 1993). Putting proteins in warm water is, after all, what we do to cook them, and keeping them cool in the fridge is what we do to preserve them.

Taking this to the logical extreme, we should consider organic synthesis at very low temperatures, since our prebiotic organics will survive there. As water freezes it concentrates solutes just like an evaporating pond, but avoiding the break down of potential biopolymers that automatically comes with elevated temperature. The problem, of course, is that while the molecules that you have made do last longer, the reactions that synthesize these molecules go slower at low temperature too, hence, one must be patient. The chemist's rule of thumb is a factor of 2 or 3 for every 10°C, so, between boiling and freezing pure water the difference in rate should be in the range 2^{10}–3^{10} (approx. 10^3–10^5). In what must hold the record for the longest experiment ever performed, Stanley Miller and co-workers published a report on the prebiotic synthesis of purine and pyrimidine bases from a dilute solution of ammonium cyanide solution frozen at -78°C for 27 years! (Levy *et al.* 2000; Miyakawa *et al.* 2002). Similarly, however, less dramatically, it had been shown previously that hydroxy, amino and carboxylic acids can be formed in aqueous solutions at -10°C (Lerner 1995). Not only can starting materials be made under these conditions, but template-directed RNA oligomerization was recently shown to be remarkably effective in frozen seawater with temperature variation, yielding chain lengths of up to 400! (Trinks *et al.* 2005).

Regardless of whether it is spark discharge experiments intended to simulate lightning in the atmosphere, evaporating ponds, hydrothermal vents or freezing solutions, there are various ways to make

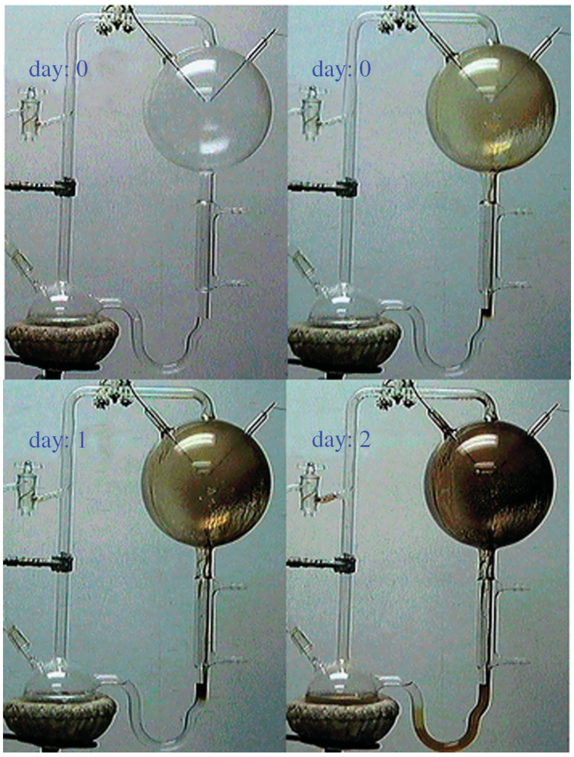

Figure 1. The kind of experimental apparatus used by Stanley Miller to perform his landmark early Earth simulation experiments involving the spark discharge of a reducing gas mixture. Reproduced with permission of Prof. S. Miller of UCSC (Miller 1953).

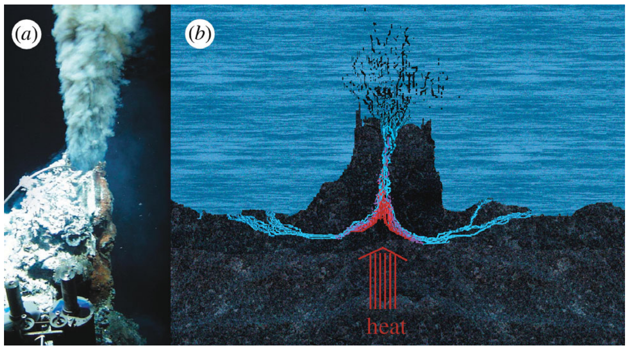

Figure 2. (*a*) An image of a smoker from the Lost City hydrothermal vent field from the University of Washington (www.washington.edu/newsroom/news/images/lostcity/). (*b*) Schematic of circulation of seawater through a hydrothermal vent. Image from Yvonne Ibarra (NASA Ames).

prebiotic organic molecules, and they all seem to be reasonable, to various extents, depending on what one believes of the early Earth. Depending on the oxidation state of the atmosphere, the prevalence of hydrothermal vents, or whether or not the Earth had enough greenhouse gases to avoid freezing over, either one or another of the processes mentioned will allow for the synthesis of some organic molecules. In addition to all these terrestrial sources of organics, there is another one too; we know that tons of organic molecules from space are swept up by the Earth every day (Love & Brownlee 1995), and perhaps these molecules played a role in making the planet habitable (Oró *et al.* 1991).

4. EXTRATERRESTRIAL INPUT

In Hollywood and among dinosaur-obsessed children, the best known way that extraterrestrial matter comes to Earth is in the form of a large comet or asteroid that has to be deflected by Bruce Willis else it will release a tremendous amount of energy leaving mayhem and thermal decomposition of organic molecules in its wake. One's intuition might suggest that such events are only destructive, but that is not the case. Not only can compounds survive such impacts (Pierazzo & Chyba 1999), but such cataclysms too are an opportunity for organic synthesis. Calculations suggest that, locally, an impactor can create an environment conducive to the synthesis of reduced carbon compounds by Fischer–Tropsch (F–T)-type reactions (Chyba & Sagan 1992; Kress & McKay 2004). In addition, experiments have shown that hypervelocity impacts will oligomerize amino acid monomers (Blank *et al.* 2001) and make other organic molecules (Mimura 1995; Gerasimov *et al.* 2000; Managadze *et al.* 2003).

Despite the drama of the aforementioned big bolide impacts, most matter from space that comes to the surface of the Earth is in the form of micrometre-sized comet and asteroidal dust (also known as interplanetary dust particles, IDPs; figure 3). Since there was a lot more debris floating around the early Solar System, there was, perhaps, a million times more matter falling onto the early Earth than there is today (Chyba & Sagan 1992). This would imply a prebiotic source of organic compounds that would rival or exceed that produced by a Miller-type synthesis using a CO_2–H_2 atmosphere (Stribling & Miller 1987; Tian *et al.* 2005), but it depends on how much dust one thinks there was 4 billion years ago, and this is rather unconstrained. In any case, this suggests a different scenario for making the Earth habitable where important inputs came from off the Earth. Since the primordial soup was such a memorable image, I have come up with a gustatory metaphor for this exogenous delivery; please think of it as the cake mix theory (figure 4). The idea is that unlike a soup from a can that comes containing everything and needs only to be warmed up, a cake mix has most of what you need but usually requires that something be added, such as some milk or butter. Similarly, our forming Earth too has most of what it needs, but perhaps not all of the moisture and organic matter that would be helpful to make the planet habitable. It is probable that much of the organic matter delivered to the early Earth was destroyed, and hence it may not matter what molecules arrived, only that it included organic carbon. On the other hand, perhaps there is more to it than just reduced carbon; maybe the compounds that are delivered actually matter, since as we shall see, the list of extraterrestrial organics includes nearly everything a prebiotic chemist could want.

Some infrared (Flynn *et al.* 2004) and mass spectra (Clemett *et al.* 1993) of IDPs exist, and new techniques are being developed for the analysis of comet dust from the Stardust mission, but our knowledge of the organics in IDPs is limited by their microscopic size. Far more is known about the carbon compounds in meteorites, and they are also thought to derive from comets and asteroids; hence, it is assumed that the organic

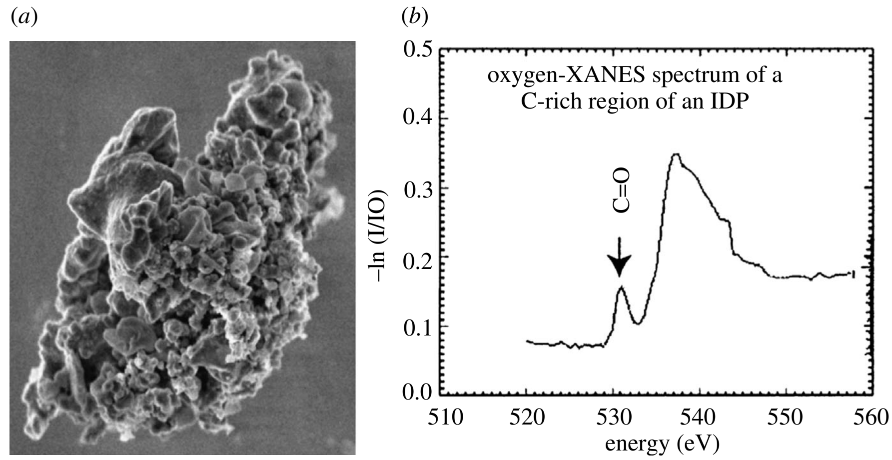

Figure 3. (*a*) A Scanning electron microscope image of L2021C5, an *ca* 10 μm IDP, and (*b*) an oxygen Xanes spectrum showing the presence of carbonyl functional groups estimated at the per cent level. These particles can contain over 90 vol% of carbon. Reprinted from Flynn *et al.* 2004, with permission from Elsevier and the author.

molecules in IDPs resemble those in meteorites. Thus, when people talk about the organic matter delivered to the early Earth, they inevitably quote lists of molecules from meteorites rather than in IDPs, even though this may not be quite correct.

Let us do a quick comparison of some of the similarities and differences in the organic matter in meteorites and IDPs. In both IDPs and meteorites, most of the carbon is in the form of a complex, insoluble, coal-like macromolecular network of reduced carbon, sometimes called ‘kerogen’ in analogy with terrestrial biotic detritus for which this name is generally reserved. This macromolecular matter is dominated by hydrocarbons, both aromatic and aliphatic, but not composed solely of carbon and hydrogen. Oxygen is common, nitrogen is present, and there are often deuterium enrichments and other isotopic anomalies.

There are some known differences between the organics in IDPs and meteorites, however. For one thing, carbon-rich meteorites have just a few per cent organic carbon, a factor of 10 less than IDPs, which can be up to 50% organic carbon by mass. For another, the distribution of functional groups in meteoritic kerogen seems to be different than that in IDPs. I base this on solid-state NMR data (figure 5) indicating that roughly one in 10 carbon atoms in meteoritic kerogen has a double bond to oxygen (C=O) such as a ketone or acid (Cody & Alexander 2005), whereas IR spectra of IDPs (figure 3) are consistent with only one or two per cent C=O (Oró *et al.* 1991). Perhaps the measurements of IDPs and meteorites, which rely on different methods, are not really comparable, i.e. there is no real difference. I had presumed that this greater abundance of C=O in meteorites was real and representative of the C/O ratio in general, that the carbon in meteorites was more oxidized than in IDPs.

Rumours of results from the analysis of Stardust samples of cometary dust suggest that I have probably oversimplified in extrapolating in this manner. In any case, it is probable that although the suite of organics in IDPs and meteorites is somewhat different they do share a common source. It would not be surprising if something in formation preferentially depleted meteorites of hydrocarbons, or subsequent processing acted

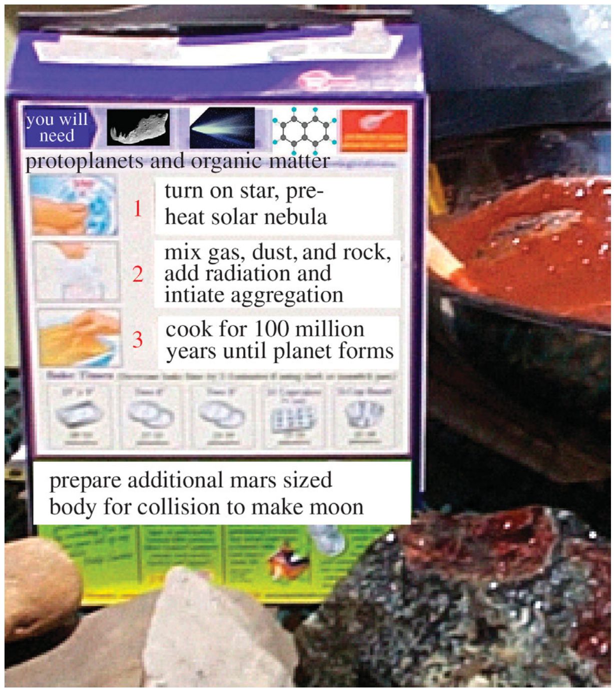

Figure 4. A cake mix as the new gustatory metaphor to replace the primordial soup as a way to think of what was needed for life to arise. Unlike a can of soup that has everything already inside, the early Earth may have been more like a boxed cake mix that requires the addition of some moisture and fat. The forming Earth acquired moisture and organic matter from asteroids and comets and it is thought this helped to make life possible. Image credit: (NASA Ames) and Karen Harpp (Colgate).

very differently on IDPs versus meteorites given the difference in size (centimetres versus micrometres). Regardless of whether these differences between them are significant or not in terms of the inventory of prebiotic organic compounds, I will now blithely treat meteoritic molecules as representative of what was available on the early Earth.

Extractions have shown that carbon-rich meteorites contain abundant individual soluble molecules of prebiotic interest, including hydroxy-, imino-, keto- and amino acids (Pizzarello & Cooper 2001; Kminek *et al.* 2002), nucleobases and other *N*-heterocycles

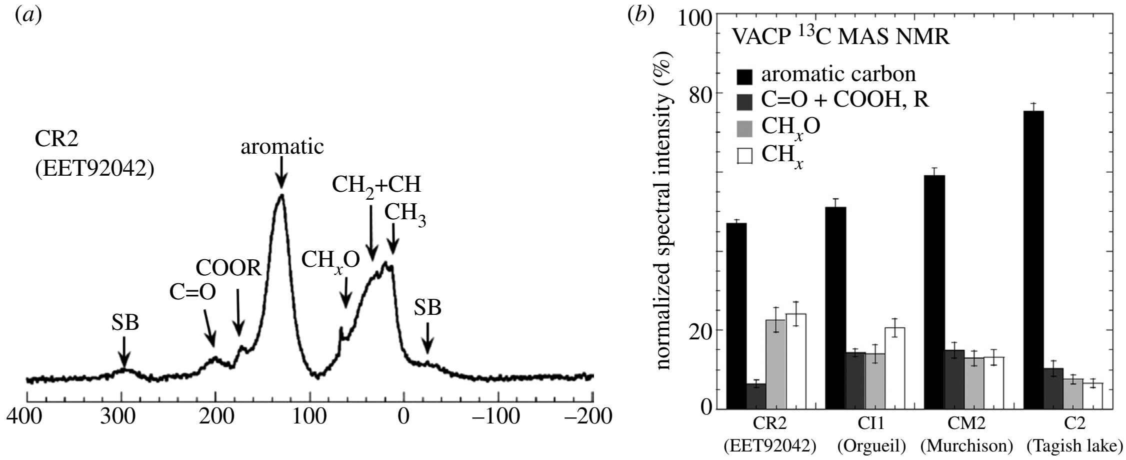

Figure 5. (*a*) NMR spectrum and (*b*) bar graph indicating a substantial amount (i.e. approx. 8% of the total) of the insoluble carbon in meteorites is in the form of a carbonyl (C=O). Reprinted from reference Cody & Alexander 2005, with permission from Elsevier and the author.

(Stoks & Schwartz 1982; Basile *et al.* 1984; Pizzarello 2001), simple sugar-like polyols (Cooper *et al.* 2001) and fatty acids (Deamer 1985; Deamer *et al.* 2002), as well as many other classes of compounds (Cronin & Chang 1993; Pizzarello *et al.* 2001; Sephton 2002). These are exactly the kinds of species that Darwin, Oparin and Haldane would have been happy to use to flavour the primordial soup, and they come ready made to the Earth from space. It is possible that all these extraterrestrial molecules are subducted, torn apart or otherwise recast by terrestrial processes, and this organic matter from space is simply a source of reduced carbon. However, it is equally possible that the delivery of a particularly rich meteorite to a small pond, or a heavy shower of IDPs at an opportune time provided a compound that survived and was useful in some way. For example, the fact that more than one (non-biological) amino acid in more than one meteorite shows a bias towards the left-handed form (Cronin & Pizzarello 1997; Pizzarello *et al.* 2004) inevitably makes me wonder whether there might have been some direct connection between the meteoritic tendency for left and the fact that left-handed amino acids dominate in living things. Or, perhaps, the fatty acids from Murchison that self-assemble into bi-layer vesicles (Deamer 1985; Deamer *et al.* 2002) provided the first self-replicating molecule with the sequestration that it needed to avoid being taken advantage of by cheaters (Szabo *et al.* 2002).

5. EXTRATERRESTRIAL SYNTHESIS

Regardless of the role they played, a rich suite of organic molecules was and is brought to the Earth from space by bits of asteroids and comets, large and small. Where do these compounds come from? A meteorite is a complex object with materials and modifications overlaid from a series of different eras (figure 6). Proceeding in reverse chronological order, first of all many extraterrestrial materials show evidence of having seen liquid water before they arrived at Earth (Robert & Epstein 1982). This is consistent with models that show that if the parent asteroid or comet from which the meteorite comes was large enough, the heating from decay of radionuclides could lead to long periods

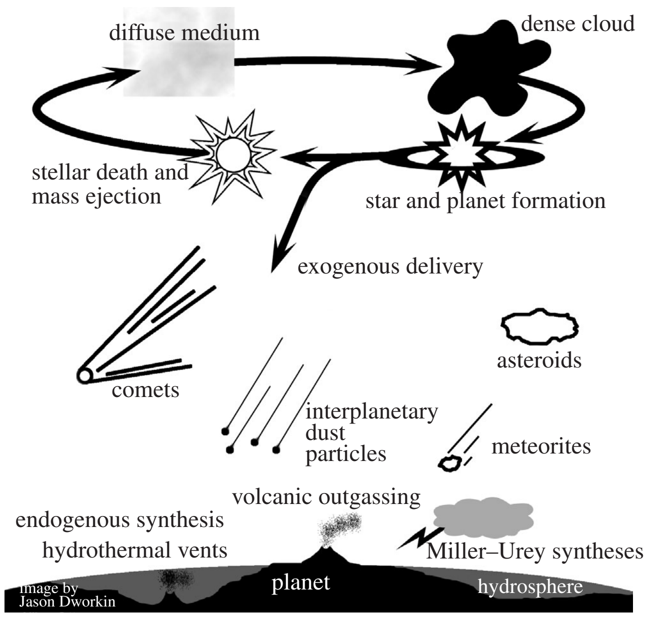

Figure 6. From the outflows of dying stars, reactions and radiation in the interstellar medium, through nebular and Solar System chemistry, to impacts and planetary processes like lightning and hydrothermal vents, there are myriad ways to make and modify carbon compounds as long as conditions are not terminally oxidizing. This image is reproduced with perimission from the creator Dr Jason Dworkin of NASA GSFC.

where liquid water is stable, which could have important implications for organic chemistry (Cohen & Coker 2000). Indeed, it is thought that most of the amino acids found in meteorites are derived from reactions in liquid water on the parent body (Peltzer *et al.* 1984; Ehrenfreund *et al.* 2001).

However, one cannot explain all the compounds in meteorites in this way; some do not look like the kind of thing that forms in liquid water—hydrocarbons for instance. The abundance of surfaces, high temperatures and the abundance of hydrogen in the solar nebula should drive F–T-type chemistry that would reduce CO or CO_2 to CH_4 and N_2 to NH_3 (Prinn 1993; Kress & Tielens 2001). CH_4 and NH_3 are great starting materials for making more complex organics,

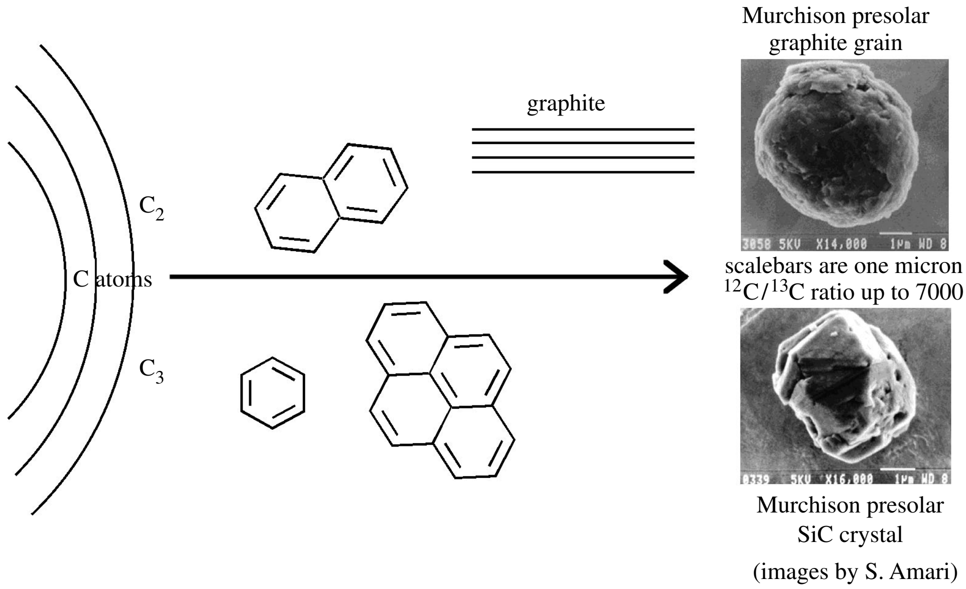

Figure 7. Carbon molecules first form around dying carbon rich stars, and some of this material survives incorporation into carbonaceous meteorites as indicated by the presence of isotopic anomalies. The Murchison grains are reproduced with permission from Dr Sachiko Amari.

but the highly branched structures that are common among meteoritic carbon compounds seem to be inconsistent with F–T being the dominant source of higher molecular weight organic matter. These meteorites contain inorganic and graphitic inclusions that are accepted as pre-solar (Ott 1993) and as Dr Thaddeus has told us, rotational spectroscopy has revealed a plethora of interstellar molecules, some fairly large; so, why not assume there is an interstellar contribution to the organic material as well? Figure 6 represents the complex history of the matter arriving on the early Earth, having components contributed from not only our Solar nebula but also from the interstellar medium and previous generations of stars as well.

Perhaps, the most convincing molecular evidence for the interstellar heritage of meteoritic molecules is their high deuterium (D) enrichment (Cronin & Chang 1993, Kerridge 1999). At low temperatures in dense molecular clouds, deuterium fractionation is expected to be efficient and elevated D/H ratios have been seen in grain mantles (Teixeira *et al.* 1999) and several gas-phase interstellar molecules, including amino acid precursors, such as formaldehyde and ammonia (Turner 2001). A reported observation of interstellar glycine in the interstellar medium (ISM) (Kuan *et al.* 2003) and experiments showing the viability of a condensed-phase interstellar synthesis (Bernstein *et al.* 2002*a*,*b*; Munoz-Caro *et al.* 2002) suggest that some meteoritic amino acids formed before the Solar System, or perhaps a precursor amino-nitrile was converted to the amino acid in liquid water (Bernstein *et al.* 2004). In addition, the vesicle forming (Deamer 1985; Deamer *et al.* 2002) meteoritic fatty acids (Huang *et al.* 2005) may also be of interstellar origin (Dworkin *et al.* 2001).

There are too many small interstellar molecules and too much work, both theoretical and experimental, on processes that lead to them (such as ion molecule reactions) for me to possibly review them here. This is a very limited and personal view, I make no claims at completeness but instead am just mentioning a few of the paths leading to prebiotically more interesting molecules here. For those who are interested in knowing more, I offer to lend you any of the books on my shelves that give greater detail (Hollenbach & Thronson 1987; Bakes 1997; Minh & van Dishoeck 2000).

However, even with all these options, some problem structures still remain. While our laboratory experiments suggest that interstellar chemistry can explain why so many of the meteoritic aromatics bear oxygen atoms (Bernstein *et al.* 1999, 2002*a*,*b*, 2003), and thus why the polar hydrocarbon fractions that contain them are deuterium-enriched (Sandford *et al.* 2001), the basic carbon skeleton is probably older. It seems that the initial carbon–carbon bonds, molecules and carbonaceous dust formed around dying carbon-rich stars (Frenklach & Feigelson 1997; Jones 1997) where the carbon atoms had been made in the first place (figure 7). Thus, the oldest chemical structures in meteorites date back, with interstellar or nebular modifications, to the previous generation of stars. Others formed in the interstellar medium, or in the solar nebula, or subsequently in the Solar System in an asteroid, an impact, etc.

The relative contributions of organic matter to the prebiotic environment from on and off the early Earth are hard to assess because each of the processes we have mentioned are rather unconstrained. Terrestrial, Miller-type synthesis (represented by yellow lightning bolts in figure 8) depends on the oxidation state of the atmosphere, but, depending on how much hydrogen was present (Stribling & Miller 1987), the predicted quantities of organic matter would be roughly in the same very wide range as what might have come from comets (Chyba & Sagan 1992), i.e. the equivalent of 10^7–10^9 kg yr^{-1}.

The amount of organic carbon on the early Earth was contributed by hydrothermal vents (represented by the smoker in figure 8) is unclear to me both owing to uncertainties in flux and because the only molecule

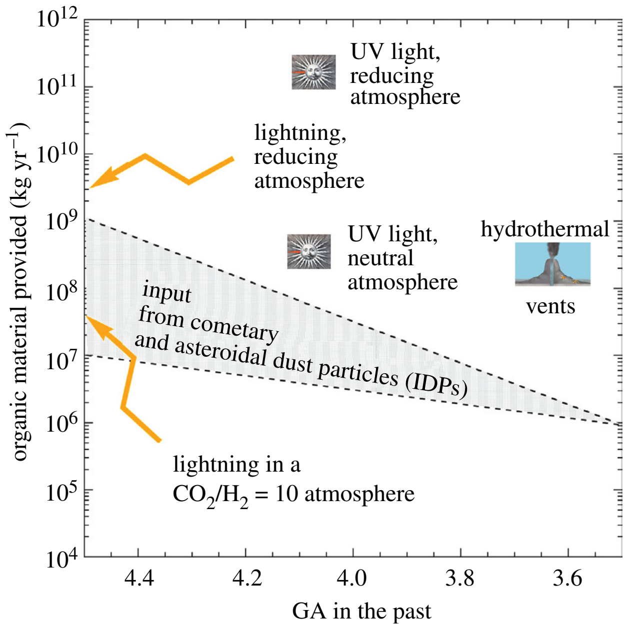

Figure 8. A visual representation summarizing the relative contributions of some major sources of organic molecules, both domestic and imported. The numbers are from citations 30 and 60, and the basic layout from a figure by S. L. Miller. Placing these on the same graph has required some significant assumptions, and especially in the case of hydrothermal vents the comparison is questionable (see text).

that we can use as a proxy is methane. Let us consider the flux first. The position on the figure corresponds to an estimate of *ca* 1–3×10^8 kg yr^{-1} (value from Elderfield & Schultz 1996, Table 14) of methane that is probably out of date largely owing to the relatively recent discovery of off-axis sites such as Lost City (an old, large, Atlantic hydrothermal vent depicted in figure 2). If such off-axis sites were very common, then the above CH_4 estimate might be too low (K. Hand 2006, personal communication). On the other hand, it assumes that this extra CH_4 is not biological in origin, which it may be. Therefore, in the end, I opted for the more conservative approach and used the lower older number. Presumably, this value too would also vary greatly depending on the oxidation state of the early ocean and how active one thinks the Earth's surface and the hydrothermal flux was at that time.

The second problem (alluded to just a moment ago) with putting vents where they are in figure 8 is that the form of carbon is methane, an assumed starting material for the other processes, such as lightning, UV, etc. In other words, in a way, vents are built into the graph inherently since the quantity of complex organics from the other processes depend on methane, at least indirectly via the oxidation state of the atmosphere. The vertical position of the vent in this diagram really should be determined by the quantity of higher molecular weight organics, such as fatty acids or amino acids, but I do not know what that is.

Chyba & Sagan (1992) suggest that synthesis of organics by UV photolysis (represented in figure 9 by Sun symbols) should actually be the largest source, but these numbers also seem to be very uncertain. They are based on estimates of absorption cross-sections of

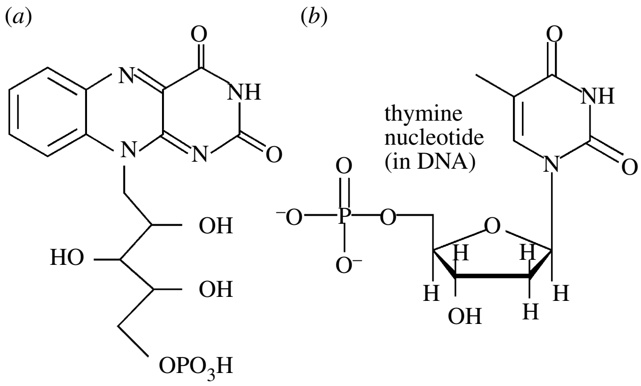

Figure 9. (*a*) The chemical structure of a base-like molecule (a flavin) and a sugar covalently bonded together in analogy to that of the bases and sugars in our DNA such as that seen in the nucleotide of thymine (*b*). The sugar and base at (*a*) are different than those on the right, but the basic classes are the same, as are the arrangement of the ketones in the upper right and the way the sugar is connected, so, would it be a biomarker?

different molecules at different wavelengths and vary by four orders of magnitude.

As summarized in figure 8, there were a number of different sources of complex organics on the early Earth making all kinds of interesting organic molecules. Clearly, these different organic syntheses contributed different kinds of compounds depending on the conditions. However, it does seem inevitable that certain kinds of molecules, such as simple amino acids and fatty acids, must have been present because we see them arise repeatedly from divergent settings like meteorites, spark discharges and hydrothermal vents. Having made these molecules, I am now looking forward to seeing what the following speakers will be able to do with them. But before that I would like to take you on a brief exobiology interlude.

6. CODA: THE SEARCH FOR LIFE IN THE SOLAR SYSTEM

While I know that this is a side path off the main route that we are to take this week, it is hard for a NASA scientist to resist trying to use some of what has been learned from studies of the origin of life for the search for life in the Solar System. Many current approaches to the robotic search for life seem to be instrument driven, with proposals to employ ever more sophisticated but off the shelf biotechnology on landers and rovers to detect proteins and nucleic acids. However, the structures of terrestrial biomolecules were almost certainly different in the past, e.g. DNA seems to be modern (Gilbert 1986; Joyce *et al.* 2002; Dworkin *et al.* 2003), hence there is no reason to think that alien biomolecules will be so similar to our own that devices designed for earthly life will work at all. The alternative bases (Horlacher *et al.* 1995; Liu *et al.* 2003), sugars (Eschenmoser 1999) and backbones (Schwartz 1986; Nielsen 1993; Orgel 1998) that have come out of this community suggest how different life may have been on Earth and can help us keep an open mind when thinking about the most difficult cases we may face in the search for alien life.

What I mean by this is while we may get lucky and see a whale breaching on Europa we have to ask ourselves about what we shall consider to be biomarkers in the event that we end up being removed, either by millions of years or by kilometres of crust, from alien life. If only molecular fragments remain, and they do not look familiar, how will we be sure that we are looking at something that was once alive, as opposed to a prebiotic mixture of amino acids, nucleobases and sugars? Obviously, an oligomer of D-amino acids would be a convincing indication of alien life, such chirality and connectivity combined would be hard to imagine forming any other way. But how narrow would the spread in chain lengths of fatty acids have to be for you to believe that it was a biomarker? I have been wondering lately whether there is some molecular assemblage that was familiar in the classes of compounds but not the particular molecular components that could be a kind of generalized biomarker. Would any base attached to any sugar be convincing? What do you think of the flavin attached to the sugar in figure 9*a*, does that seem a viable alternative to our arrangement in figure 9*b*? If the molecule in figure 9*a* with 'XX' = phosphate were detected on the surface of another planet, would you be convinced that there must have been a biological source? In fact, if XX = phosphate then the molecule (figure 9*a*) is flavin mononucleotide, which is part of biology as a component of Complex I of the electron transport chain. See for example Anderson & Mecozzi 2005. Do you think that I am being too specific in adding phosphate, that it should be seriously considered as a biomarker if the leaving group at the end were a vanadate, or if there were none at all? I will leave you with such questions to ponder. Thank you.

I would like to thank Yvonne Ibarra for making figure 3*b* and Jason Dworkin, Kevin Hand and Koichiro Matsuno for help with the 'new' version of figure 8. The original was made by Dr Dworkin with numbers from and under the direction of Prof. Stanley Miller, who presented it as part of a talk at the 1993 ISSOL meeting. I would also like to acknowledge financial support from NASA's Exobiology and Astrobiology programs, which allowed me to spend time thinking about and performing experiments on prebiotic chemistry and biomarkers. This manuscript was improved by comments from Sydney Leach and an anonymous reviewer.

ENDNOTE

[1]Defining 'organic' and 'reduced': when I refer to organic compounds, I mean those composed primarily of carbon, but may also contain nitrogen, oxygen and other elements. These are the kinds of molecules from which we and all living things are made, as opposed to carbon in the form of carbonate rocks, which is considered 'inorganic'. Technically 'reduced' carbon is that bearing hydrogen atoms, such as in methane (CH_4). Oxidized carbon is that such as in carbon dioxide (CO_2) or carbonate rock, where all of the bonding is satisfied by oxygen atoms. For the purposes of being good prebiotic molecules partially oxidized carbon species (e.g. ketones $>C=O$) will be of use in making bigger, more complicated, and biologically important compounds. A 'reduced' gas is rich in hydrogen, or compounds that bear hydrogen, such as methane (CH_4) and ammonia (NH_3). Reduced gas mixtures produce more complex organic molecules than do oxidizing ones which is why the oxidation state of the early Earth's atmosphere is so important.

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Discussion

Sydney Leach (*Départment Atomes et Molécules en Astrophysique, UMR CNRS, Observatoire de Paris-Meudon, France*). I am much struck by the amazing similarity, not only in substance, but also in the very words, between the paragraph you cited from the Kojiki and the cosmogenical statements of Ovid in book I of his 'Metamorphoses'. A sample of the Latin text is as follows:

> Ante mare et terras et, quod tegit omnia, caelum,
> unus erat toto naturae vultus in orbe,
> quem dixere Chaos, rudis indigestaque moles
> nec quicquam nisi pondus iners congestaque eodem
> Non bene iunctarum discordia semina rerum.

The translation of this sample by Mary Innes in the Penguin Classics version of 'Metamorphoses' is:

Before there was any Earth or sea, before the canopy of heaven stretched overhead, Nature presented the same aspect the world over, that to which men have given the name of Chaos. This was a shapeless uncoordinated mass, nothing but a weight of lifeless matter, whose ill-assorted elements were indiscriminately heaped together in one place.

The Latin is actually closer to the Kojiki text. It also goes on to talk about the separation of Earth and heaven (by a god) and the separation out of light and heavy elements…

This has made me wonder whether the Japanese of the eighth century had cognisance of Ovid's first century poem. Certainly, the Romans were in touch with China, via the Silk Road and Nestorian Christians were very early in China. The Japanese of course had much contact with China. Who knows…A good subject for a Ph.D. student?

Max Bernstein. You are right, the similarity is indeed striking, Ovid does also talk about some material rising and other settling down and it's impressive that Ovid knew the Earth was a 'ball.' I wondered at how familiar the Kojiki creation story seemed as I read it the first time and whether the original really had this sense, or if the translator had been influenced by western science or myths in producing the English version. My brother-in-law, Ken, who is a native speaker of Japanese, assures me that this translation of the Kojiki is representative of the original text, so, the agreement does seem to be real. It could be, as you suggest, that there was some exchange of mythology between the Greco-Roman culture and Far East. I do not know if this is the case, but others have noted some similarities between Greek myths and the Kojiki. See, for example, Matsumura Kazuo's essay on Amaterasu versus Athena at http://www2.kokugakuin.ac.jp/ijcc/wp/cpjr/kami/matsumura.html.

F. Westall (*Centre de Biophysique Moleculaire, CNRS, Orleans, France*). Regarding the formation of prebiotic molecules in hydrothermal vent environments, what is the speaker's opinion on the possibility of suitable chemical reactions occurring in structures such as beehive structures, which are highly porous and have strong gradients in temperature and chemistry?

Max Bernstein. I think that it makes sense to look to such structures since some such solids are known to be good catalysts, and depending on the temperature of precipitation might well sit at a temperature interface that is advantageous, as I advocated above. From my reading of Holm & Andersson (2005), it seems that it's very important to include minerals in the simulations. I think that we will probably hear more about this kind of situation later this week during the talk by Professor Wächtershäuser.

J. I. Lunine (*Lunar and Planetary Sciences Department, University of Arizona, USA*). You have outlined a large number of possible states for the early Earth's atmosphere and a large number of possible chemical states in which organic molecules might have been synthesized and evolved. However, a key issue is whether we can distinguish among these various physical and chemical states, to better constrain the conditions present on the early Earth—and how we might do so. In the absence of this advance, I am concerned that we cannot make much progress on the question of the origin of life. So, how do we decide what portion of your kitchen is really relevant to life's origin?

Max Bernstein. Yes, I am sorry to have been so vague as to which one was the most important; I was so, not by choice, but out of ignorance. It seems that we are in the uncomfortable position—to continue with your metaphor—of having a number of cooks proceed in different parts of the kitchen and then decide what tastes best afterwards, with little say in advance as to which recipes should be used. Personally, I feel that it is always safest to be pessimistic. So, lets presume that the early atmosphere was at most neutral, not reducing; there will still be Miller discharge synthesis and photochemistry, but limited in scope. Similarly, lets take the lower estimates of the flux of IDPs, so, we have something to work with but will not be seduced by stories of metres thick layers of organic goo raining down on the surface from these sources.

M. Wallis (*Cardiff Centre for Astrobiology, Cardiff University, UK*). There's a longstanding mystery with IDPs—how their hydrated minerals could form, when liquid water is not stable on surfaces of small atmosphere-less bodies. Their temperature is generally too low for mobile H_2O monolayers on crystalline surfaces. Intermediate size bodies must be the processing site for classes of IDPs. Comets are one obvious candidate—composed of weakly coherent, weakly gravitating material that readily disintegrates under Jupiter perturbations and under solar heating when in the inner Solar System. Planetary bodies are also a source of meteorites and IDPs via major stochastic collisions, as even for the Earth in the Chioxutub impact. Material processing in comets and planets surely generates complex organic and even biological material that are very different and potentially important components of the interstellar cloud.

Max Bernstein. Your points about the composition of IDPs and the parent bodies from which they come as important sites for chemical synthesis are very good. IDPs are rather complex, with high temperature components mixed with very fragile organics that cannot possibly have formed in the same environment, so I am sure there is a complex history there that involves lots of mixing and collisions in the nebula.

Regarding planets as a source of meteorites and IDPs, well, I am sure that you are correct that some dust comes from the collision of larger bodies, and in the early Solar System there certainly were more of these kinds of collisions going on. However, I think that today most meteorites and IDPs are from asteroids and comets or bodies smaller than planets anyway. There are certainly examples of meteorites known to be from Mars, based on trapped gasses, and Lunar meteorites that are basically basalts, but my understanding is that few meteorites or IDPs have compositions and structures consistent with being fragments of planets. Of course, we will know more about comet dust very soon after the stardust samples have been analysed, so it is to be hoped that we will know how to distinguish comet dust from other sources.

As to evidence of hydration, that is very strong, but I am not convinced that this requires a planetary precursor where liquid water was stable at the surface. A comet or asteroid, if it were large enough, could have liquid water in the interior, from the heat provided by the decay of radionuclides, or so, I have read. See, for example, Cohen & Coker (2000). Thus, it has been suggested that the organic chemistry of carbonaceous meteorites is partly a result of this kind of parent body aqueous alteration chemistry. Certainly, many of the water-soluble species in meteorites are consistent with the hydrolysis of known interstellar molecules (e.g. meteoritic carboxylic acids having derived from interstellar nitriles) or the combination of simple interstellar species into more complex compounds (e.g. formaldehyde, ammonia and HCN into glycine). I believe that this aqueous alteration happened, and perhaps this is the origin of the hydrous minerals in IDPs. I am no expert and I would guess that there are other explanations. The hydrated minerals rimming chondrules in CM chondrites have been attributed to a nebular shock (Ciesla *et al.* 2003) and perhaps given enough time hydrated minerals could even form under more gentle conditions.

C. N. Matthews (*Department of Chemistry, University of Illinois at Chicago, USA*). What do you think of the Stardust Mission which has just brought to Earth samples of cometary dust for analysis? Will these results tell us about the original organics on Earth?

Max Bernstein. I am incredibly excited about the stardust mission (stardust.jpl.nasa.gov/) which, this past Jan. 15, returned to Earth samples from comet Wild 2. It is still quite early in the sample analysis, the preliminary teams are still examining the aerogel tiles, but it's clear that there are specific compounds. At this point, there is little information on the organic material both because the organic matter does not retain its integrity on impact into the aerogel as well as the minerals grains and because they are still trying to distinguish between cometary organics and contamination. The preliminary examination team for organics intends to submit a number of manuscripts to science in the fall of 2006.

C. N. Matthews. Your discussion of the Miller–Urey experiment and the detection of α-amino acids in space need amplification. We have shown that such reactions give rise to hydrogen cyanide polymers which can then be hydrolysed/pyrolysed to yield α-amino acids, peptides and nitrogen heterocycles such as adenine. All detections of α-amino acids need to be reinterpreted. They are formed from methane, ammonia mixtures, etc., via hydrogen cyanide, which polymerizes readily and gives rise to polypeptides when treated with water. Further hydrolysis yields α-amino acids.

Essentially this answers a key question in prebiotic chemistry: how do polymers such as proteins form? They form directly from HCN polymers and water, without the need for the prior synthesis of α-amino acids by the Strecker mechanism or any other procedure.

Max Bernstein. Certainly, one can form amino acids and nitrogen heterocycles such as adenine from HCN and it seems reasonable that some of the molecules observed by Miller could have been derived from such a pathway given that they did see HCN formation in reduced gas discharge experiments. See, for example, Stribling & Miller (1987), pp. 48–52, where they assess the efficiency of HCN formation in H_2, CH_4 and NH_3 gas mixtures such as are found in the atmospheres of giant planets and were originally presumed to have been present on the early Earth.

As for meteoritic amino acids, I cannot be so sanguine. Allow me to first confess that I am a fan of alternative mechanisms for formation of amino acids and have published one of my own involving ice photolysis (Bernstein *et al.* 2002*a*,*b*; Munoz-Caro *et al.* 2002). However, a big limitation of your HCN polymer and my ice photolysis mechanism is that while we mostly make glycine, we do not form many of the other amino acids that are seen in meteorites. For example, aminoisobutyric acid in CM chondrites is taken as an indicator of a Strecker synthesis, and the β-alanine in Orgueil has been suggested to have formed via a Michael addition (see Botta (2002)).

I see that Professor Ferris has a comment…

J. P. Ferris. (*Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, New York, USA*). It is not reasonable to propose that HCN polymers are the source of all prebiotic molecules from comets, asteroids and the Miller–Urey process since there are many other compounds for the HCN to react with besides HCN.

Max Bernstein. Dr Ferris makes a very good point. The production rate ratio of HCN relative to H_2O in comets has been reported as *ca* 10^{-3}–10^{-4} (e.g. Friedel *et al.* 2005), implying a low concentration of HCN relative to H_2O in the solid phase. A reaction like $HCN+HCN \rightarrow (HCN)_2$ would depend on the square of the HCN concentration; cutting the concentration of the starting material in half would diminish the rate of formation of the dimer by a factor of four. Thus, even though HCN polymerization is facile at high concentrations, bringing together many HCN molecules would become unlikely if the concentration of HCN is low. Instead, the HCN might react with one of those other many compounds that Dr Ferris mentioned.

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