Chapter 2
The Origin of Life Was Brought to You in Part by Silicate Rocks

Beginning at the beginning sounds like a good call. Or, if not at *the* beginning, at least at a big beginning. Will the origin of life on Earth do? Silica was more than there. Together silicate minerals, seawater, and hydrothermal heat set in motion a surprisingly simple sequence of chemical reactions that resulted in Earth's first metabolism, the first major hurdle overcome in the development of life.

Metabolism is a word that can make you think of the need to exercise and of those people, damn them, who can eat whatever they want to without piling on the pounds. But metabolism means much more than the rate at which calories are burned. Yes, the catabolic biochemical reactions of metabolism generate energy by oxidizing organic matter (made up of carbohydrates, lipids, and proteins). But metabolism also consists of anabolic biochemical reactions that consume energy during their construction of organic matter (namely the organic compounds that make up living organisms).

The initial invention of a metabolism capable of building things up as well as burning things down was a pretty big deal. Not only did it tick the first box of the instruction sheet *Basic Requirements for Life*, metabolic pathways tend to be long, convoluted chains of chemical reactions that start from a specific point and end at specific point, along the way producing specific products from specific ingredients.

Many metabolic pathways are complex enough to be the chemical equivalent of circular assembly lines. They take up a small compound and incorporate it into a larger molecule. They then either produce or consume energy while rearranging the larger molecule multiple times, as if solving a Rubik's cube. Eventually they break up the now rather rearranged larger molecule, eject the desired product, and rearrange the remaining materials to resurrect the enzymes and/or other molecules they started with. Then the cycle repeats.

As an example, take Fig. 2.1. That revolving wheel of chemical reactions, which is spinning continuously inside pretty much each and every one of your living cells, is the sort of thing a typical metabolic cycle entails. It is a complex masterpiece that managed to get itself invented out of chaos and disorder.

It would seem to be a miracle. But when you sit down and ponder the simple chemical reactions that would have been going on between water and silicate rocks

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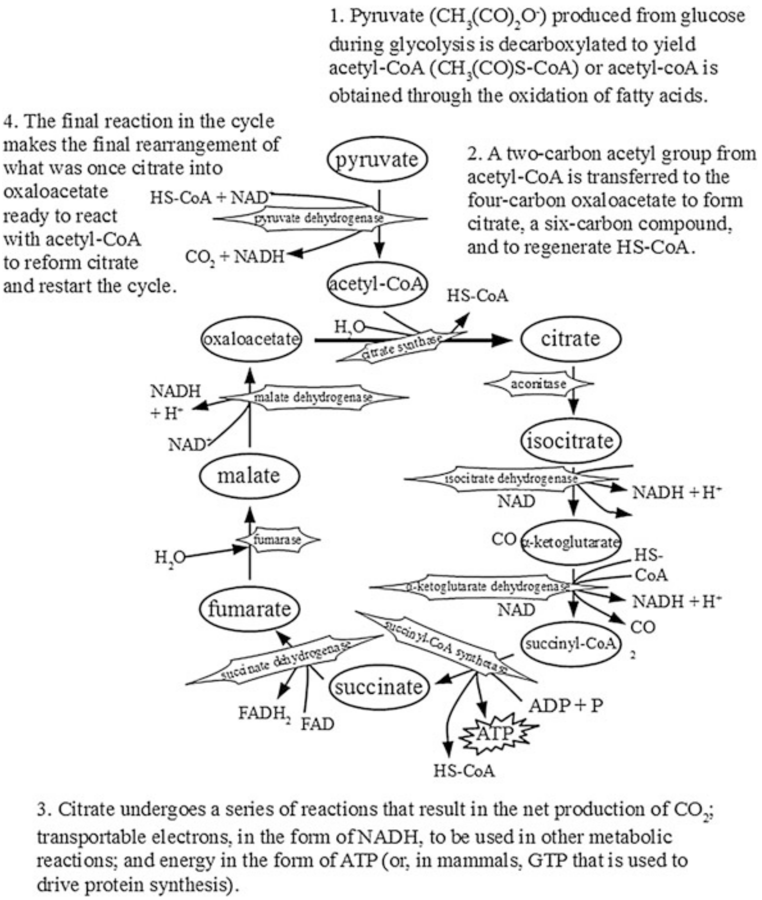

1. Pyruvate ($CH_3(CO)_2O^-$) produced from glucose during glycolysis is decarboxylated to yield acetyl-CoA ($CH_3(CO)S$-CoA) or acetyl-coA is obtained through the oxidation of fatty acids.

2. A two-carbon acetyl group from acetyl-CoA is transferred to the four-carbon oxaloacetate to form citrate, a six-carbon compound, and to regenerate HS-CoA.

3. Citrate undergoes a series of reactions that result in the net production of CO_2; transportable electrons, in the form of NADH, to be used in other metabolic reactions; and energy in the form of ATP (or, in mammals, GTP that is used to drive protein synthesis).

4. The final reaction in the cycle makes the final rearrangement of what was once citrate into oxaloacetate ready to react with acetyl-CoA to reform citrate and restart the cycle.

Fig. 2.1 All aerobic life on earth uses the citric acid cycle to generate energy by oxidizing acetate

on the flanks of undersea mountains approximately four billion years ago, the invention of metabolism starts to seem unavoidable.

And so we shall begin with this big beginning, or rather, a little bit before it because metabolism didn't invent itself in a vacuum. Metabolism came about on Earth shortly after the Earth's formation. The conditions that prevailed at that time set both requirements and constraints upon how life could have initially unfolded.

2.1 Setting the Stage

In the early days of our Solar System, there was no Earth nor any other planets, just a large, thin disk of matter rotating about the developing Sun. That disk consisted of gases and dust bumping, crashing, and crunching into each other. Sometimes when things collided, they, or at least bits of them, got stuck together. Because bigger bodies are harder to smash to pieces than smaller ones, bigger bodies began to accumulate until the inner Solar System came to be a mess of smash-ups of perhaps half a thousand planetesimals on conflicting paths. Ka-blam! Ka-blam! Ka-blam!

Most meetings resulted in the larger subsuming the smaller. Each crash added to a to-be-planet's mass and continued to reduce the overall number of objects in the inner Solar System (sometimes 1 + 1 = 1). Eventually, by this process, the crowded chaos of tiny bodies within the inner Solar System tidied itself up into the four terrestrial planets that are still there today (Mercury, Venus, Earth, and Mars) plus an asteroid belt.

The final smash for the almost-but-not-quite-Earth was with Theia. Theia, a proto-planet the size of Mars, was the smaller of the two. They may have been otherwise kindred, as surmised from the similarity in the composition of the present-day Earth and present-day Moon, which may be mostly made of Theia. If this is the case, it is likely that for millions of years, the proto-planet siblings had shared an orbit around the Sun. Accreting from the material that had accumulated at this same distance from the Sun would have meant the two protoplanets were made from materials of similar elemental and isotopic composition.

Locked in by the opposing pulls of the gravity of the Sun and the gravity of the proto-Earth, Theia either led or followed the proto-Earth by 60° as they orbited about the Sun.[1] The geometric side effect of this was that Theia circled the Earth (and vice versa) exactly one time for each full run around the Sun. So stable was this co-orbitation, Theia should still be there today, more than four and a half billion years down the line. (That would make for a very different story, one of life emerged on two similarly habitable planets and by now either learning to get along or fighting each other to death.)

But Theia is no longer there, just ahead of or just behind the Earth in orbit about the Sun. Thank the gravity of some passing planet, probably Jupiter, whose massive, wandering mass wreaked havoc in the Solar System in its early days. Tugged out of whack, Theia's orbit relative to the proto-Earth went from loopy but sustainable to simply dangerous. On one wobbly turn around the proto-Earth, Theia struck.

It's safe to say that none of us can really, fully grasp it, not even the modelers who study it using computer models and the laws of physics. It was no game of billiards. When one planetesimal struck the other, they didn't just briefly deform and ricochet. They demolished, shattered, melted, vaporized, fused, and ejected. These were the repercussions for the materials that made up Theia and the proto-Earth.

One long-standing theory for what then happened goes like this: The iron-rich core of Theia, too heavy to escape the gravity of the proto-Earth after impact, was trapped and sank to merge with the iron-rich core of the proto-Earth. To this day,

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[1] If the Earth was at 6 o'clock on an almost perfectly circular orbit whose center was the Sun, Theia would have been at either 4 o'clock or 8 o'clock.

the hearts of the alien and the non-alien sibling remain intermingled deep below our feet. Meanwhile, the energy of the impact melted what wasn't already molten on the proto-Earth. Not just melted, in fact. An impressive portion of the planet vaporized and filled the atmosphere. At the same time, a substantial mass of material (mostly from Theia's mantle) flew off. Trapped in orbit about the Earth, it coalesced and became the Moon.

Despite the mass lost to the nascent Moon, overall the planet had grown by 10% as a result of the collision, which had, by the way, taken only hours. What remained when the crash was over had, at least for the first thousand postimpact years, a super-hot, silicate rock vapor atmosphere, but it was recognizable now as Earth with no front qualifier.

Sights upon the silver screen aside,[2] the crash with Theia was the last major collision that Earth has been involved in.[3] It is therefore the last incident in the accretion of Earth. You might call it the final moment of Earth's birth, or perhaps the last of Earth's many collisional, surface-melting, mass-adding rebirths. As such it marks the earliest moment that the clock could have started ticking on the aqueous geochemical reactions that resulted in life, for as soon as there was a permanently solid surface and some liquid water, conditions approached mild enough to host the precursors to life (and then life itself). More critically, conditions were finally stable enough for progress not to be necessarily totally wiped out in a subsequent, Earth-shattering catastrophe.

To know when this happened requires pinning the first point afterward that was cool enough for the rock vapor to have rained out of the sky and a crust to have formed over the magma ocean. In principle, one must just find and date a piece of this first crust. In reality, on Earth, there's none of this first crust left. It did not sufficiently survive its first few hundred million years of shattering by asteroid attack, much less the following billions of years of physical erosion, chemical dissolution, and, finally, tectonic subduction that recycles crust through the mantle to create new crust.

But all is not lost. This first crust that formed on the Moon fared comparatively well, for the Moon lacks wet weather, life, and plate tectonics. If we could figure out when this ancient lunar crust solidified, we'd have our answer.

Happily, aside from hundreds of thousands of asteroids, the most exciting things to have hit the Moon so far have been Apollo astronauts. In the true spirit of what it means to be human, they did not take only pictures and leave only footprints, they brought back almost half a ton of lunar rocks.[4] Much of what we know of the Moon and how and when it formed is based on the geochemical analysis of these rocks.

The dating of the formation of the Moon's crust using the oldest lunar rocks is a convoluted story, but here's the gist of it: A radioactive isotope of the element hafnium (hafnium-182), which was produced during the formation of the Solar

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[2] We're thinking of Melancholia.

[3] The bolide that wiped out the dinosaurs? A fly upon the windshield.

[4] To be fair, we should point out that unmanned Soviet landers have also brought back lunar soil.

System, decays to a stable isotope of tungsten (tungsten-182). We know that there should be an excess of the daughter isotope (tungsten-182) in rocks from the Moon's surface because when the Moon solidified, the hafnium that was present would have concentrated itself in the Moon's silicate-rich mantle rather than distributing itself equally between the mantle and the Moon's metal-rich core. But some of the expected excess of tungsten in the lunar crust should be missing because the Moon formed millions of years after the formation of the Solar System, giving some of the radioactive hafnium time to decay away before the differentiation of the Moon into mantle and core.

Because we know that the half-life of the radioactive hafnium is nine million years, measurements of exactly how much tungsten is missing reveal that the Moon's crust formed 30 to 50 million years after the formation of the Solar System.

In other words, the Moon became cool enough to have a crust 4.53 billion years ago (give or take 10 million years, the error on the estimate).

Because the impact that formed the Moon is also the last event in the accretion of the Earth, 4.53 giga years ago must have been the end of the birth of the Earth and, again, now that the surface of Earth was not merely magma (or vaporized rock), the start of the clock for the geological chemical reactions that led to the bags of biochemistry called life.

2.2 A Flight of Fancy

Of course, life could have just flown in from outer space: microbes in meteorites from Mars (or Venus).

Although the surface and atmosphere of Mars currently lack vital signs, perhaps in the past, when the planet was young and pleasant, microbes teemed, lurking in the nooks and crannies of rocks and regolith. If so, what if, before Mars' internal heat expired and most of its atmosphere leaked to space, some of its life jumped ship?

For this possibility you might thank Jupiter, Saturn, Uranus, and/or Neptune. Their migration to their current orbits tossed 300 million years' worth of asteroids from the asteroid belt between Mars and Jupiter (or perhaps from the Kuiper belt just beyond Neptune) into the inner Solar System. What resulted was the Late Heavy Bombardment, which lasted from 4.1 to 3.8 billion years ago, and bombardment indeed it was. The scars can still be seen upon the helpfully non-regenerating surface of the Moon. Earth and Mars also took a beating. If there had been life on Mars at the time of the Late Heavy Bombardment, asteroid impacts would have launched microbe-infested rocks into space.

Some Martian meteoroids from that time are still out there, any hitchhikers within them long expired. (Billions of years is a long time to be cold, dry, and under vacuum.) But others made it to Earth, some only years after launch. Perhaps at least one deeply hibernating, safely rock-encapsulated microbe out of a Saganesque billions upon billions survived the trip and successfully colonized the Earth.

There are certainly meteorites that have been found on Earth that originated on Mars during the right time frame. Some of these meteorites contain microscopic structures and textures that look life-like. There are even scientists so sold on the idea, they grow bacteria in rocks that they then put under vacuum, freeze, and bombard with UV light before shooting them out of a cannon, across the lab, and into a wall to see if any bacteria survive. (Some do.) And let's face it, intrepid interplanetary bacteria have an undeniable charm. But this, as an explanation for how life began, passes the buck. Space traveling bacteria may indeed exist, and, although it dangles on a chain of ifs, this theory of interplanetary panspermia might explain how life initially arrived on Earth. But such a theory fails to explain how life initially came to be.

For the love of parsimony and of tackling questions directly, let us assume that life on Earth began on Earth. Perhaps, through experiment, observation, and consideration of thermodynamic and other constraints on chemical reactions, not to mention inspection of what scraps remain of Earth's most ancient geologic record, we can reason out a set of plausible steps.

Here is one thing we definitely know. By 3.8 billion years ago, photosynthesis, at least the more primitive anoxygenic kind, was widespread on Earth. Stable isotopes tell us so. The world's most important enzyme, Rubisco, captures carbon dioxide (CO_2) during photosynthesis so it can be used to make carbohydrate. Rubisco is better at capturing CO_2 containing the lighter stable isotope of carbon (carbon-12) than it is at capturing CO_2 containing the slightly heavier stable isotope of carbon (carbon-13). As a result, materials that include carbon that was fixed into organic matter during photosynthesis have a notably lower ratio of carbon-13 to carbon-12 than materials made from carbon that wasn't.[5] Such fingerprints of photosynthesis are all over the carbon in many of our oldest known rocks, such as the metamorphosed sedimentary rocks and the banded iron formations of the 3.6–3.7-billion-year-old Isua Greenstone Belt in southwestern Greenland and the 3.8-billion-year-old rocks of Akilia (also a part of Greenland).

These carbon isotope ratios screaming photosynthetic carbon fixation mean that by 3.8 billion years ago the process of life emerging from the chemicals of a lifeless landscape was long over. In addition, as neither the first life on Earth nor the last universal common ancestor of all life on Earth today (sweetly, LUCA, to those in the know) were photosynthetic, it also means that by 3.8 billion years ago we were already well past not just the first life form, but also well past the one form of life that gave rise to all the forms of life that exist today. Thus by 3.8 billion years ago, life had a firm foothold on Earth and was well into the (unintentional) task of improving itself through natural selection and, through the innovations that emerged, was busy increasing the capacity of the biosphere to capture energy, do

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[5] The difference in the ratios is about 0.3%, something which is easy to measure using an isotope ratio mass spectrometer.

work, sustain biomass, and create ecosystems increasingly greater in size, complexity, and activity.

So that's the window we have to squeeze the origin of life on Earth into. Earth had a crust by 4.53 billion years ago and widespread and sophisticated photosynthesizers by 3.8 billion years ago. This window is less than seven hundred million years, especially as 3.8 billion years ago must considerably postdate the origin of life.

To some seven hundred million years is too short a span of time for this sort of thing. Life's kind of a big deal to invent and we don't mean that philosophically. There is no small number of disparate parts and processes, many of them bewilderingly complex, that have to come about, come together, and synergize before you can shout, "IT'S ALIVE!" There is an impulse to think that it took eons to pass this threshold.

But you can also ask why shouldn't life come about quickly when the circumstances are such that it would come about at all and you can say that seven hundred years is anyway hardly quickly. As a chunk of time, seven hundred million years is longer than the span for which metazoans (animals) have walked the Earth (or swum, or just sat there at the sediment–water interface). If seven hundred million years was more than enough time to get from brainless filter feeders to human consciousness, why shouldn't it have been more than enough time to get from geochemistry to biochemistry?

2.3 The Early Earth Was Not Hellacious

If life was widespread and way past LUCA by 3.8 billion years ago, it most likely originated soon after the formation of the Earth. Is that possible? Were those first few hundred million years following the crash with Theia not too violent and hot?

Researchers down through the decades have made many suggestions concerning conditions at the surface of the early Earth. Aside from being continuously attacked by asteroids, the Earth at that time might have been hot and dotted with lava for a long, long time and therefore not survivable by life until close to the 3.8 billion year mark. Or, in between the bolide blasts at least, the surface of Earth could have been colder than ice, with life (or the precursors of life) huddled around some deep maternal geothermal spring. And then there is the classic view of shallow seas of warm umami broth. Fire, ice, primordial soup. The possibilities span the gamut.

This first idea, that early Earth was hellish for quite some time after the violence of its formation, has fallen out of favor. For this you can blame a handful of crystals of zirconium silicate found in the Jack Hills of Western Australia. These zircons are up to 4.4 billion years old, which makes them the oldest objects of terrestrial origin we have found so far.

It is unlikely we will ever find anything much older. To look at, these zircons may not be impressive (none approach a millimeter in size), but they are durable. Wind, rain, oxygen, the temperatures and pressures of the geologic cooking process known as metamorphism,[6] no problems there. Zirconium silicate will outlast the other minerals in the rocks that formed through the cooling of the magma from which it crystallized. And outlast they have.

Once the Jack Hills zircons were liberated by the weathering away of the other minerals in their original rock, they were washed down slopes to form sediments with the remains of rocks also ancient but less so by several hundred million years. As time went by, these sediments became buried by further geological debris. More and more material accumulated on top of them. Eventually they were deep enough in the ground to experience the temperatures and pressures of metamorphism. This altered the sediments as a whole, deforming them on the macroscale like warm plastic. On the microscale, many minerals shifted their crystal structures due to the stress, while other minerals were driven to react with still yet others to form entirely different ones. But the zircon crystals remained relatively intact.

Over further eons, the material above the now metamorphosed sediments weathered away, finally exposing them and their zircons again to the light of day and, now that life has long overrun the Earth, the curiosity and destructive effects of geologists.

That these 4.4-billion-year-old zircons exist at all is an explosive fact. First, they require Earth surface temperatures cool enough for the creation of solid rock. Second, zircons form from the sorts of acidic magmas that yield not the basaltic rocks of the ocean floor, but the granitic rocks of the continents. Together that means that a mere one hundred and fifty million years after Theia blundered in, the Earth not only had a solid crust (which we had surmised already from the dating of the ancient moon rocks), it had produced a significant mass of the differentiated material that is continental crust.

Let’s step back a bit and tell you that Earth has two types of crust, continental and oceanic. They both consist of silicate minerals, but that still leaves room for the two types of crust to significantly differ. Oceanic crust is similar in composition to the molten mantle that is its source—it is a magnesium- and iron-rich silicate comprising the sorts of rocks you see on Iceland or Hawaii. The silicate rocks of continental crust lean more toward aluminum, potassium, and sodium and are thus less dense. And so just as the mantle rides above the even more metal-rich (and therefore denser) core, continental crust floats higher above the mantle than oceanic crust and opens up the possibility for widespread areas of dry land surrounded by the sweeping expanse of deep, blue sea.

And that’s the final explosive fact. The existence of these old zircons as components of a *sedimentary* rock means that the surface of the Earth those billions of years ago was not just cool enough for rocks and evolved enough to have two types

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[6] Metamorphism refers to a change in the mineralogy of rocks at pressures and temperatures, generally around 150 °C (300 °F) to 850 °C (1560 °F), that are not high enough to melt the rocks into magma. Metamorphic effects include change in the crystal structure of the minerals or change in assemblages of minerals present in a rock, in both case towards those that are more stable at the temperatures and pressures involved.

of crust, it was cool enough for liquid water to exist and to weather rocks and wash the remnants down a slope to accumulate as sediment.

This means that from surprisingly early on, the Earth had a hydrologic cycle. And that means rain and runoff such as rivers across the continental landscape, even if the continental landscape back then was but a tiny fraction of the total of today's.

By the way, where there's liquid water, there is a possibility for life, and so we know that by at least 4.4 billion years ago, conditions on Earth were not hellacious, but for sure cool and wet enough to be survivable.

2.4 A Fly in the Soup

The idea that life assembled itself out of a so-called primordial soup, which can be traced back at least as far as Charles Darwin, inspired the classic experiment of Stanley Miller and Harold Urey, the one you probably heard about in your high school biology class. As experiments go, it must have been fun and not just because it was like playing god.

Miller and Urey set two big reservoir bulbs, Atmosphere and Ocean, into a circuit of glass tubing. Within this closed system they established what they believed to be the atmosphere on the early Earth: methane (CH_4), ammonia (NH_4), hydrogen (H_2), and water vapor (H_2O).[7] The heat source under the Ocean evaporated some of the water in that reservoir and a cooling jacket around a section of the tubing condensed the vapor to form rain that fell through the Atmosphere. But the best part of the experiment was the lightning; electrodes on either side of the apparatus discharged sparks through the Atmosphere. Their hypothesis was that this would spur the gases in the Atmosphere to react to form organic compounds[8] which would be collected by the falling rain and carried to the Ocean where they would accumulate. The idea behind this idea was that once you had organic compounds in your soup, they would react with each other, growing in variety and complexity until, voilà, life!

After merely a week, Miller and Urey sampled their Ocean and found they had succeeded, at least with the synthesis of organic compounds. There were lots in their Ocean and, most thrillingly, there was a broad suite of amino acids. (Amino acids, informally known as the building blocks of life, are not only what you need

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[7] Today's atmosphere is 78% nitrogen (N_2), 21% oxygen (O_2), 0.9% argon (Ar), and 0.04% carbon dioxide (CO_2), and contains traces of neon (Ne), helium (He), methane (CH_4), krypton (Kr), and hydrogen (H_2).

[8] Organic compounds are molecules that contain carbon–hydrogen bonds and/or carbon–carbon bonds. Thus carbon dioxide (CO_2) which has only carbon–oxygen bonds is an inorganic compound despite containing carbon, while methane (CH_4), which has carbon–hydrogen bonds, and glucose ($C_6H_{12}O_6$), which has carbon–hydrogen and carbon–carbon bonds in addition to its carbon–oxygen bonds, are organic compounds.

to make proteins, they are used in the building of the building blocks of RNA and DNA.)

This was exciting and a major accomplishment. Miller and Urey had demonstrated both *that* and *how* organic molecules could be brought about by abiotic means. Even better, they'd shown that organic macromolecules (like amino acids) that are necessary for life and which were considered only producible by life, could in fact be abiotically generated under the conditions they thought representative of the early Earth. (Although, we'd like to point out, they had cheated by adding methane, an organic molecule, at the beginning of the experiment.) To many, this was one major chicken and egg problem solved.

Unfortunately, this primordial soup hypothesis still begs the question, *how did life begin?* You can make all the organic building blocks you want, but all the right ones still have to find each other in the dilute, crazy jumble that is the entire ocean and then order themselves into a fully functioning form before you have life.

One thing that life requires to do the things that make it life is enclosed spaces. These allow disequilibria to exist. Without disequilibria, life can't work (as introductory biology teachers are wont to shout: *Equilibrium is death!*). If a living cell were to find itself equilibrated with its environment or even fully equilibrated within itself, it would be unable to run any of its chemical reactions, pumps, or engines and that would be *game over*. For cells to do the things they need to do takes concentrations of solutes such as ions (and the charges associated with them) that differ between the inside of the cell and the outside, and between the inside of membrane-bound organelles inside the cell and the cytoplasm that fills the cell. In short, life requires chemical and/or electrical gradients in order to run.

Imbalances in charge or solute concentrations on either side of some barrier (such as a membrane) act as potential energy that is harnessed and used to accomplish various tasks. When ions move from an area of higher concentration to an area of lower concentration, they generate energy that the molecular machinery of the cell gathers and then releases in a controlled manner to drive work.

For example, if on one side of a membrane you have a lot of protons (those positively charged hydrogen ions, H^+), the protons will spontaneously slide through a membrane-spanning tunnel known as an ATP synthase. At the far end of this molecular tunnel of extremely specific construction, a molecule of adenosine diphosphate (ADP) and an atom of phosphorus tend to loosely attach themselves. When the proton, driven by the concentration gradient, passes through the ATP synthase, it drives a change its shape. The loosely attached ADP and phosphorus are pushed together, causing them to bind to form adenosine triphosphate (ATP).

This molecule ATP is super energetic and unstable. It exists solely to find somebody to take the third phosphorus off its hands. When it does, the energy that is released gets work done. If ATP hands the third phosphorus to a flagella, the flagella will beat. If ATP gives the energized phosphorus to a muscle cell, that cell will contract, helping to move the muscle. If ATP gives the phosphorus to a chemical reaction that needs a little kick, the reaction will go forward.

This work that must be done by cells in order to stay alive and fulfill their functions is all but endless—take up nutrients; break down molecules to release energy and raw materials; build new enzymes, carbohydrates, amino acids, DNA, etc.; pump out waste; grow and then divide in half; etc.,—and it is carried out by complex cellular structures or sets of structures that are specific, elaborate, and multitudinous. If one little detail about their size, placement, connectedness, or constitution is incorrect, they might not function at all and the cell will die. Because of this, it is unlikely that even the most minimally fully functional kit and kaboodle of life randomly assembled itself out of even a generous supply of lightning-generated liquid aminos even given eons. It's like that monkey typing Shakespeare. It could happen, but it won't.

Any reasonable theory for the origin of life needs to be less vague than "a lot of organic matter got made then somehow assembled itself into life." A reasonable theory for the origin of life needs to outline a set of feasible processes by which working mechanisms for catabolism (the gathering and controlled release of energy), carbon fixation (the production of organic molecules out of inorganic ones), biosynthesis (the construction of complex macromolecules from smaller organic components), and replication (cell division) came about and came to be incorporated together within a semi-permeable compartment (the lipid bilayer that is the cell membrane that all of Earth's truly living creatures possess).

Those are tall orders. But, we are happy to report, in recent years, serious progress has been made in the outlining plausible steps for the invention of catabolism, carbon fixation, and the basics of biosynthesis. This is where the silicate rocks finally come into the story (aside from them comprising most of the mass of the Earth).

2.5 The Lost City

It wasn't overall hellish hot, but at the time when life was somehow coming about in a non-monkey-typing-Shakespeare fashion, the Earth was still a rough place to be. The Late Heavy Bombardment of 4.1 to 3.8 billion years ago had to either bracket or postdate the emergence of life on Earth. Somehow early life got through it. It wouldn't have been easy. Just as small Solar System bodies in kamikaze mode were launching Martian rocks into space, ones large enough to vaporize the ocean and roast the surface of the planet were hitting the Earth with alarming frequency.

Thus there is another requirement for any theory of the origin of life on Earth. Life not only needed to make the series of leaps from inorganic matter to organic compounds to organized, enclosed, self-replicating, energy-controlling entities thriving by exploiting chemical disequilibria, it needed to be doing this in a place that wasn't being sterilized every century or so by the shock wave and blistering heat of an asteroid impact.

Geothermal springs have sprung to many a researchers mind. Like geysers and fumaroles (and volcanoes), they are places where energy from the super-hot interior of the Earth escapes in a concentrated way. On land you might know them as quiet hot springs under starry skies, in the gemstone hues of the Grand Prismatic Pool in

Yellowstone National Park and its rust-colored framing by microbial mats, or from the surreal blue pools of the travertine terraces of Pamukkale. In the ocean, hydrothermal vents and springs occur along mid-ocean ridges and are famous for sprouting ecosystems based not so much on the gutless and blind as on their chemosynthetic bacterial symbionts.[9]

Geothermal springs tick some serious boxes for kick-starting life. Sunk into the Earth as cracks and fissures, they provide protection from unpredictable extremes above (such as the oceans boiling off following an asteroid impact then recondensing). As water circulates through the Earth's crust near hot pockets of magma blurped up from below, it warms and it extracts some elements from the crust and loses some others that it has been carrying. When the now heavily solute-laden fluids exit the crust to mix with colder, more dilute groundwater, river water, or ocean water, they create environments whose main feature is disequilibrium. Cooling rapidly and mixing with waters more strongly oxygenated or of considerably differing acidity (or alkalinity), the geothermal waters find themselves unable to hold all of their solutes in solution. Minerals precipitate, producing chimneys that grow around the outflow. Pocked, fissured, and continuously generating, they are surfaces upon which reactions are catalyzed and, post-origin of life, microbes sequester themselves in highly productive biofilms.

In particular, it is the warm alkaline springs which exist on the peripheries of mid-ocean ridges that have captured the imaginations of those who work on the origin of life. Unlike their more famous cousins, the black smokers that belch billowing plumes of metal sulfides at 450 °C (840 °F), the warm alkaline springs, seeping fluids of roughly 100 °C (212 °F), are not too hot for life. In addition, their solute composition differs significantly from that of seawater (both most ancient and modern). When the warm alkaline waters mixed with seawater on the early Earth, they would have served as a factory for the sorts of engines life needs to carry out work.

Although such warm alkaline springs were probably common on the early Earth, their prime modern-day examples, the ones within the Lost City hydrothermal field, were not known to humanity until the year 2000. These Lost City seeps and springs are located at 30° 7′N, 42° 7′W, more or less midway between Jacksonville, Florida and the Canary Islands and just to the west of the rift zone running down the center of the Mid-Atlantic Ridge. They've sat there on the side of the Atlantis Massif for at least the last 120,000 years, which means that as geothermal systems go, they are long-lived.

The 4250-meter (14,000-foot) Atlantis Massif is itself a roughly two-million-year-old submarine mountain. Underneath its cover of sediment and scum, it must be beautiful. It is made of peridotite, a coarse-grained rock green with olivine and peppered with the black of pyroxene. This great lunk of silicate stone crystallized

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[9] Chemosynthetic bacteria are like photosynthetic bacteria, except that instead of using solar energy to fuel the production of organic matter, chemosynthetic bacteria harness the power of chemical reactions.

from molten mantle below the oceanic crust. Later it was displaced and unearthed by the Mid-Atlantic Ridge during its continuing wedging apart of the eastern and western shores of the Atlantic Ocean.

When they were found, the Lost City springs, which terminate in tall towers of calcium carbonate, reminded us of something we'd known for a good long while: hydrothermal fluids flow through and react with silicate rocks like peridotite within the ocean floor in a process known as serpentinization. The Lost City springs also demonstrated that the resulting fluids can mix directly into seawater. And when you pay attention to the chemical reactions associated with the serpentinization of silicate rocks, you see a path that could lead to the carbon-fixing, biosynthesizing, and catabolic bases of cellular life.

2.6 Generating Organic Compounds

During serpentinization, seawater entrained into the crust and warmed reacts with peridotite. The olivine in the peridotite is converted into a mixture of two minerals, serpentine and ferrobrucite.[10] Because these warm fluids also contain abundant silica dissolved from the crust, the ferrobrucite reacts further to produce more serpentine, the mineral magnetite, and hydrogen in the form of H_2.[11]

Not to be unprofessional, but, *yow!* The early Earth didn't need to have Miller and Urey's conveniently (and probably incorrectly) hydrogen-filled atmosphere in order to make organic molecules. Hydrogen almost literally bubbles out of serpentinization. The right kind of silicate minerals, dissolved silica, and warm water (plus carbon dioxide) are all you need to start making organic matter and that is an incredibly big deal.

In other words, what happens once you have H_2? Organic compounds. To be more specific, the H_2 produced by serpentinization would have quickly reacted with carbon dioxide present in seawater to produce two organic compounds, formate ($HCOO^-$) and methane (CH_4),[12] no lightning, no life, and no cheating by having a magically already somehow H_2-rich atmosphere and an initial supply of methane.

The most brilliant thing about this proposed process for the abiotic generation of organic compounds? We don't have to do a lab experiment as a proof-of-concept. We know for a fact that these reactions happen out there in the ocean. Even today. The outflows from the Lost City warm springs contain ample abiogenic formate and

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[10] $2(Mg_{1.8}Fe_{0.2}SiO_4) + 3(H_2O) \rightarrow Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4 + Mg_{0.75}Fe_{0.25}(OH)_2$

i.e., olivine + water → serpentine + ferrobrucite.

[11] $14.25(Mg_{0.75}Fe_{0.25}(OH)_2) + 7.5(Si(OH)_4) \rightarrow 3.75(Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4) + 20.75(H_2O) + Fe_3O_4 + H_2$

i.e., ferrobrucite + dissolved silica → serpentine + water + magnetite + hydrogen.

[12] $HCO_3^- + H_2 \rightarrow HCOO^- + H_2O$

i.e., bicarbonate + hydrogen → formate ion + water.

abiogenic methane as well as other, larger, more complex organic compounds abiogenic in origin.

If you're reading this and wondering what the big deal is about generating organic compounds from inorganic materials without the involvement of life, here's what it is. As anyone who has suffered the slings and arrows of an organic chemistry laboratory course could tell you, organic compounds don't usually just come together. They're awfully hard to make. If you want to create an organic molecule from scratch, or even build a bigger organic molecule from smaller components, you have to know how much energy to put into drive the reaction, what chemical building blocks to begin with so that the right reaction occurs, and what catalysts to use so that you don't have to sit around and wait forever. Life is so darned good at this because it has immense arsenals of tools (ATP, NADPH, ion pumps, highly specific enzymes (i.e., catalysts), and scaffolding such as membranes) honed through billions of years of evolution for causing specific organic reactions to occur in a precise and controlled fashion.

Catalysts undoubtedly also prompted the abiogenic synthesis of formate on the early Earth (and still do today). The likely candidate is the nickel–iron mineral awaruite (Ni_3Fe). This mineral briefly binds dissolved carbon dioxide (in the form of bicarbonate ion, HCO_3^-) and hydrogen present in the water around or flowing past it. This brings the two molecules into close enough proximity to react with each other and become formate and water. It's a fairly run of the mill mechanism; by similar metal-catalyzed means are acetate (H_3CCOO^-)[13] and methane (CH_4)[14] formed via the addition of hydrogen atoms to dissolved carbon dioxide.

The biotic synthesis of formate, which goes on inside living organisms, also relies on a nickel–iron catalyst. This is likely no coincidence. Why would life invent a process from scratch when it could co-opt one already going on in the environment around it? Hydrothermal mounds, made of minerals precipitated from cooling hydrothermal fluids, abound with awaruite and other metallic minerals that catalyze such reactions. Even more interestingly, such metallic minerals often line the surfaces of exactly the sorts of microcavities that are shielded from the faster flow of fluids and therefore play host to chemical gradients that could be harnessed to get work done.

This is key. Catalytic mineral clusters dotting ragged surfaces within a flow of water can experience, establish, and maintain far-from-equilibrium conditions even without the aid of an organic membrane. In principle, if enough different catalysts were packed together in close proximity within the microcavities of growing geothermal surfaces, a suite of interacting reactions sufficient to be called *metabolism* could have developed prior to the invention of the cell membrane, a means of replication, or, indeed, any of the rest of the package of life. And that's the most

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[13] $2(HCO_3^-) + 4(H_2) \rightarrow (H_3C)COO^- + OH^- + 3(H_2O)$

i.e., biocarbonate + hydrogen → acetate + hydroxyl + water.

[14] $HCO_3^- + 4(H_2) \rightarrow CH_4 + OH^- + 2(H_2O)$

i.e., biocarbonate ion + hydrogen → methane + hydroxyl ion + water.

plausible scenario to be hit upon so far for the first step by which life began to be brought into existence on Earth.

It's also worth noting that the rough surfaces of hydrothermal mounds and chimneys become easily coated with abiogenic organic scum, making them not just good places to establish metal-catalyzed reactions, but also good places to invent organic membranes and easily jumble them up together with the catalysts, their chemical substrates, and their chains or cycles of reactions.

2.7 Inventing Metabolism

But we're getting ahead of ourselves. We've only gotten as far as methane, formate, acetate, and molecular hydrogen (H_2), and while that's within a hair's breadth of metabolism, it isn't quite there yet. Bear with us now as we start to really throw the letters around: not just C for carbon, H for hydrogen, and O for oxygen, but also S for sulfur, N for nitrogen, P for phosphorus, and a few other letters for a few other elements (mainly metals).

The methane, formate, acetate, and hydrogen being produced hydrothermally 4.4 billion years ago would have reacted, at times with the help of hydrothermal metal mineral catalysts, with the carbon dioxide, nitrate (NO_3^-), nitrite (NO_2^-), sulfite (SO_3^{2-}), sulfur (S), iron (Fe^{3+}), manganese (Mn^{4+}), and phosphate (e.g., HPO_4^{2-}) that existed in the early, not yet oxic ocean in series of steps to form some very key organic compounds. For instance, the green rust mineral fougèrite would have catalyzed the partial oxidation of methane by nitrate to form methanol[15] (that type of alcohol you shouldn't drink unless you would like to go blind or maybe die). Oxidation of this methanol by nitrite would result in formaldehyde.[16] Subsequent reduction, thiolation,[17] and condensation of the formaldehyde would easily yield thioacetic acid ($H_3C–CO–SH$). So far so simple and occurring over the sorts of spans of time that occur in a common chemistry laboratory even when it's filled with first year university students who are bumbling around.

The next step toward metabolism would be thioesters (which are any organic compound containing a C–CO–S–C functional group). There are numerous plausible ways they could have been produced under mild conditions. For instance, when prompted by catalysts of iron sulfide or nickel sulfide, warm water containing carbon dioxide, carbon monoxide, and hydrogen sulfide form methylsulfide (H_3CSH) which further reacts to form methylthioacetate ($H_3C–CO–S–CH_3$). As these organosulfur compounds reacted further in the alkaline springs, the thiol

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[15] $CH_4 + NO_3^- \rightarrow (H_3C)OH + NO_2^-$

i.e., methane + nitrate → methanol + nitrite

This reaction couples the partial oxidation of methane with nitrate reduction.

[16] $(H_3C)OH + NO_2^- \rightarrow (H_2C)(OH)_2 + NO^-$

i.e., methanol + nitrite → formaldehyde + nitric oxide.

[17] Addition of a sulfur that is bound to a hydrogen, i.e., a sulfhydryl group (SH).

known famously to biology as coenzyme A (of overall formula $C_{21}H_{36}N_7O_{16}P_3S$) would have started to accumulate. From there, further reaction with carbon dioxide and hydrogen to form acetyl-CoA ($C_{23}H_{38}N_7O_{17}P_3S$), which is just coenzyme A with an acetyl group (CH_3CO) joined to it at one end, would have been energetically inevitable.

What the world had now was the basis for cyclic metabolism. Not only is coenzyme A good at picking up an acetyl group to become acetyl-CoA, acetyl-CoA is very good at passing the acetyl group on to another molecule in a reaction that releases energy (the basis for catabolism) or builds up another organic molecule (the basis for anabolism). Further, in the process of losing the acetyl group, acetyl-CoA recycles itself back to being a molecule of coenzyme A capable of doing it all over again. That's the cyclic part.

So fancy that. Warmly weather the right silicate rocks at the bottom of the ancient ocean and within a short span of time and without any instructions encoded in DNA or provided by RNA, you'll end up with an abundance of two of the most important molecules of Terran metabolism.

Today we're billions of years down the line from the origin of life, but acetyl-CoA and coenzyme A still reside at the heart of how every single aerobic organism turns organic matter into energy in order to function and stay alive. There isn't, for example, a fully functional aerobic cell on Earth or inside of you that doesn't use acetyl-CoA to deliver carbon to the biochemical cycle known as the citric acid cycle (the one diagrammed in Fig. 2.1) and coenzyme A in a number of the steps subsequently needed to produce that mobile packet of energy known as ATP (without whose constant production you would quickly die because, proximately, it is the fuel that your body burns to do the work that it must do).

This thought is well worth repeating and so we will. Without any prompting, fundamental pieces of a functioning cyclical metabolism could have been derived from the byproducts of silicate weathering in a period of time too short to register even as a blip on a blip in Earth history.

2.8 The World's Earliest Biological Carbon Fixation

Conveniently and most interestingly for our hypothesis that ultimately serpentinization-derived coenzyme A is where it all began, coenzyme A and acetyl-CoA can also be used to fix carbon. To fix carbon means to take an inorganic form of carbon, such as carbon dioxide, and turn it into an organic form, perhaps, for example, a sugar or other carbohydrate. Photosynthesis is a type (but not the only type) of carbon fixation and there would be no big beautiful biosphere like the one we have today if bountiful amounts of biological carbon fixation did not occur.

The two most ancestral forms of life that still exist on Earth, the methane-producing methanogens (which are archaea) and the acetate-producing acetogens (which are bacteria),[18] both fix inorganic carbon into organic matter using the metabolic pathway known as the reductive acetyl-CoA pathway (which is also known as the Wood–Ljungdahl pathway). This is a noncyclic pathway based on the formation of acetyl-CoA from coenzyme A much as described occurring in the warm, alkaline springs. Archaea and bacteria, however, speed up the reaction using enzymes.

During this reductive acetyl-CoA carbon fixation pathway as practiced by some modern day, if metabolically antiquated microbes, carbon monoxide (CO) is produced from carbon dioxide (CO_2) by throwing the extra oxygen atoms to hydrogen atoms to form water. This reaction is catalyzed by the enzyme carbon monoxide dehydrogenase (which uses our geothermally originated friend, a Ni–Fe reaction center, to bind the CO_2). With the help of another enzyme, the carbon monoxide reacts with a methyl cation (CH_3^+) to form acetate which then binds to coenzyme A to form acetyl-CoA. This acetyl-CoA, thus containing some carbon that was just fixed into it from an inorganic source, is then shunted into cellular biochemical pathways and consumed (instead of being regenerated) in the synthesis of other organic molecules. Alternatively, acetyl-CoA may be cleaved to yield acetyl phosphate which may easily phosphorylate ADP to yield ATP, the energetic molecule that is the proximate source of energy for all work, physical and chemical, done within living organisms (including you).

This is as simple as biological carbon fixation gets. It is also the reductive acetyl-CoA pathway that is the catabolic pathway that LUCA, that last universal common ancestor of ours, and its forbears would have used to create organic matter for themselves and their energetic needs. Essentially, once the self-sustaining generation of coenzyme A occurred abiotically, it was there to be co-opted into biosynthetic reactions and more complex metabolic pathways.

The evidence that this pathway, or some rudiment thereof, was the pathway all subsequent carbon fixation pathways evolved from is the fact that acetyl-CoA is a product of all currently known carbon fixation pathways, no matter how complex. Equally importantly, there are no contradictions. There is nothing about the proposed sequence that could not have occurred given what we know about the early Earth at the time when life needed to be coming about.

2.9 Replication

Summed up, it is highly plausible that in but a few fairly simple steps the hydrothermal weathering of silicate rocks in the deep sea of the early Earth gave rise to a carbon-fixing, energy-generating metabolism based on acetyl-CoA. For a

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[18] Phylogenetically, the tree of life branches into three main domains, those of the Archaea, the Bacteria, and the Eukaryotes. We are Eukaryotes.

while, this metabolism occurred within the catalyst-lined microcavities at the outflows of warm and alkaline geothermal springs at the bottom of the ocean. As such, it was like life, but not quite yet life. There were still a few hurdles to overcome, mainly those of reproduction and of liberation.

Liberation is easier to imagine. Those microcavities, which tended to accumulate organic scum, just needed to become covered with polar lipids of the type that assemble into the lipid bilayer that encapsulates living cells. Then the metal catalysts and acetyl-CoA reactions could have become incorporated into a proto-cell. Proto-cells would have then sloughed off the walls like mad once enough acetyl-CoA, coenzyme A, polar lipids, and metal catalysts were being produced at a high rate. But this was still not quite life. No matter how numerous, nor how fast their rate of *production*, before such proto-cells could be pronounced life, they needed to possess a means of *reproduction*. They needed to be able to make new copies of themselves.

But we may have just gotten the order wrong. It could be that the problem of replication was solved before metabolism enclosed itself within sets of organic membranes. If this is correct, LUCA, the last common ancestor of all of Earth's currently living things, was not enclosed within an organic membrane. It would have still been living upon the surface of a microcavity when it developed the capability to reproduce itself.

A plausible, precise, and detailed hypothesis for the invention of reproduction remains the toughest nut to crack to finish the puzzle of the origin of life on Earth. To make a fully functioning copy of yourself, even if all you are is a simple cell with a cyclic metabolism, requires coding the instructions for building and operating yourself in a form that can be read and acted upon by molecules. Otherwise you're stuck on the wall of the warm spring and when its heat source dies out, no more of you will be produced. For most of life's tenure on Earth the instructions necessary to create and run a cell (or a multicellular organism) have been based on DNA, RNA, and tons of genes and lots of enzymes and messengers acting together. It is far beyond our current grasp the exact steps by which such an exquisitely functional tangle of complexity first came to be.

But we do at least have some vague ideas. The reactions in the warm, alkaline springs that led to acetyl-CoA and its friends would have fairly feasibly led further to the nucleic acid building blocks of RNA plus the ribose needed to hold its backbone together. Eventually the RNA led to DNA and with it came the possibility to set, read, and copy a set of instructions for the molecular machinery and engines needed to carry out the chemical reactions of a basic, functioning cell. That's more than likely the part of the origin of life that took the longest time by orders and orders of magnitude. You can almost laugh at cyclic metabolism and carbon fixation. What cakewalks. They're pathetically simple by comparison.

It was once there was DNA and the means of using and copying it that there was LUCA, again probably still in its hydrothermal mound microcavity and not yet enclosed by an organic membrane. Then things went *two* ways. The descendants of LUCA that coupled the acetyl-CoA pathway to the production of methane broke away from their geothermal chimney cloaked in the type of cell membranes we find around archaea. Meanwhile, the descendants of LUCA who coupled the acetyl-CoA pathway to the production of acetate broke away and wrapped themselves in the type of cell membranes that we find around bacteria. Both of these types of membranes are lipid bilayers, but they are of such significantly different composition that it is more plausible to conclude that they had independent origins than to conclude that one type of membrane evolved out of the other. And that's some pretty cool food for thought. The last common ancestor of all currently living creatures on Earth lived glommed onto the surface of a hydrothermal mound or chimney rather than floating about the ancient ocean as a free-living, membrane-bound living cell.

At any rate, now freed from the surfaces of a deep sea hydrothermal mound, those two new forms of life whose basic metabolisms and organic compositions owed themselves to the warm water weathering of silicate rocks were off to conquer the world.

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