

# Did life originate from a global chemical reactor?

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## ABSTRACT

Many decades of experimental and theoretical research on the origin of life have yielded important discoveries regarding the chemical and physical conditions under which organic compounds can be synthesized and polymerized. However, such conditions often seem mutually exclusive, because they are rarely encountered in a single environmental setting. As such, no convincing models explain how living cells formed from abiotic constituents. Here, we propose a new approach that considers the origin of life within the global context of the Hadean Earth. We review previous ideas and synthesize them in four central hypotheses: (i) Multiple microenvironments contributed to the building blocks of life, and these niches were not necessarily inhabitable by the first organisms; (ii) Mineral catalysts were the backbone of prebiotic reaction networks that led to modern metabolism; (iii) Multiple local and global transport processes were essential for linking reactions occurring in separate locations; (iv) Global diversity and local selection of reactants and products provided mechanisms for the generation of most of the diverse building blocks necessary for life. We conclude that no single environmental setting can offer enough chemical and physical diversity for life to originate. Instead, any plausible model for the origin of life must acknowledge the geological complexity and diversity of the Hadean Earth. Future research may therefore benefit from identifying further linkages between organic precursors, minerals, and fluids in various environmental contexts.

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## INTRODUCTION

The settings for the origin of life are unknown and greatly debated. Historically, these debates have revolved around what requirements for the origin of life are met – or not met – by a particular environmental setting. In particular, disagreements over which environmental factors are best suited for the synthesis of individual organic polymers have dominated origin of life research. This focus on synthesis has been wildly successful in terms of discovering properties of biochemical molecules, but it offers little insight into the conditions necessary to achieve all of the properties essential to a self-replicating entity that is capable of Darwinian evolution.

A wide chasm exists between what is known about the mechanisms involved in the synthesis of organic compounds and an understanding of the sequence of reactions leading to a proto-metabolic network or to replicating macromolecules, a situation exemplified by the RNA world hypothesis. One probable root cause of this disconnect is the notion, originally promulgated by Darwin and Haldane, that life arose in a single location – a ‘primordial soup’ – which hosted a suite of different organic compounds. Modifications to this model include periods of evaporation to facilitate organic polymerization and the periodic input of high-energy processes such as lightning discharge, bolide impacts, radioactive decay, and/or ultra-

violet radiation. Although much useful information has resulted from this approach, including a broader understanding of mechanisms leading to the abiotic synthesis and polymerization of organic compounds, most research within the primordial soup model has been limited to laboratory experiments that do not yield sufficient insight into how natural processes on the early Earth would have resulted in the emergence of life.

As a way forward, we propose that environmental complexity was a necessary requirement for the origin of biological complexity. A large number of steps must have been required to produce a living entity from organic precursors, suggesting that a wide range of environmental conditions must have been involved in the origin of life. Furthermore, life may not have been the product of a highly unlikely sequence of events, but instead the gradual outcome of a number of frequently occurring and inter-related processes. We illustrate our proposition by examining eight broad categories of possible environmental settings of the Hadean Earth (3.8–4.5 Ga) that could have contributed one or more of the ‘reaction-steps’ leading to life. Although our limited knowledge of the Hadean Earth is a clear impediment to this line of research, there are enough features of the Hadean that are known or can be inferred to provide useful constraints to the origin of life. We also take advantage of the extensive literature that delineates the range of physical and chemical conditions that can result in the synthesis of organic precursors; these include conditions outside of the bounds for life as we know it. We thus uncouple the conditions that may have led to the origin of life from life itself. Four central hypotheses, derived from a synthesis of previous ideas, permeate our argument and are developed throughout the text:

**Hypothesis 1:** The various settings that contributed to the origin of life were not necessarily coupled in time or space to the settings that supported the growth of the earliest microbial communities.

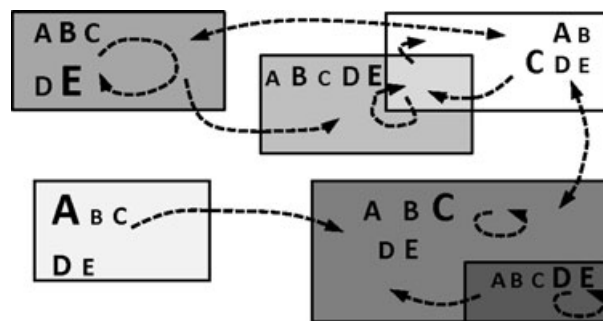
**Hypothesis 2:** Mineral catalysis provided high concentrations of organic compounds important for the synthesis of macromolecules and high-energy compounds, such as acetyl-CoA, through ‘proto-metabolic’ networks that necessitated catalysis by multiple minerals.

**Hypothesis 3:** Dynamic surface and subsurface circulation systems were necessary to transport various organic compounds synthesized under specific sets of conditions to other environments for further reactions. This resulted in a greater diversity of organic compounds and prebiotic reaction networks. Included in these different environmental settings was a narrow subset of environmental conditions that spawned and maintained early life forms.

**Hypothesis 4:** Global diversity and local scarcity of reactants and products were keys for prebiotic chemistry. Each unique environmental setting in the Hadean would have favored the production of a few important compounds, and mixing processes on large and small scales allowed the products of each setting to interact with each other (Fig. 1). Thus, on a global scale, the great variety of ingredients required for life could be generated and combined in biochemically more productive ways than it would be possible in a primordial soup at one location.

One advantage of a single setting for the origin of life may be the close spatial proximity of different reactions. However, the possibility of dilution does not make it implausible to envision the origin of life as a global phenomenon. First, under anoxic conditions and prior to the evolution of heterotrophy, organic matter would presumably have had a much longer lifetime in the ocean, allowing compounds to accumulate to high concentrations (e.g. Lasaga *et al.*, 1971; Bada, 2004). Secondly, numerous mechanisms in many environmental settings, in particular adsorption and encapsulation (Section ‘Concentration’), would have concentrated molecules from diluted fluids in a range of local environments. The characteristic sorption and diffusion properties of different molecules could have led to chemical selection (Sections ‘Particles as stabilizing agents for transport’ and ‘The benefits of gradients in prebiotic chemistry’), such that specific compounds may have become concentrated from a diverse mixture. Lastly, we argue that the origin of life was a natural outgrowth of fundamental geological processes. Instead of constructing specialized scenarios that circumvent the risk of dilution for specific important compounds, it may therefore be more fruitful to identify how such compounds could have been generated from the most important geochemical processes on the early Earth.

We are not attempting to provide an answer to the question of which environment served as the setting in which



**Fig. 1** Abstract illustration of how the abundance of compounds A to E differs between settings with different physicochemical conditions (boxes) and selective transport processes (arrows).

the first living organism formed and thrived. Rather, we propose that future research in this field should consider the larger context of individual settings by treating them as potentially linked components of a global chemical reactor. To this end, this review paper seeks to synthesize previous work on potential Hadean environments in which important prebiotic reactions may have occurred in order to place the origin of life within a global context, with the aim of presenting a fresh perspective on the origin of life and, moreover, evaluating the possibility of a second independent origin of life on another planetary body.

## PREREQUISITES FOR THE ORIGIN OF LIFE

While there is active debate regarding the precise requirements for the origin of life, it is generally agreed that they include a source of energy, a source of carbon, and a means of concentration and catalysis. What follows is a necessarily brief overview of each of these prerequisites and how they might have been provided on the Hadean Earth. For more exhaustive discussions of these topics, see De Duve (1995), Lahav (1999), Morowitz (2004), Hazen (2005), Deamer (2011), and Hazen (2012).

### Energy

We define energy as a collective term for all the drivers of physical and chemical processes that were necessary for prebiotic chemical reactions to proceed (e.g. Deamer (2007) and Deamer & Weber (2010)). Of the various forms of energy that were required for the origin of life, metabolic energy is the only *internal* energy source (Deamer (2007)); i.e. it is electrochemical energy carried within high-energy molecules like ATP that can be stored inside a cell. Modern life harnesses electrochemical energy by coupling reduced and oxidized chemicals obtained from the environment, and it may be expected that the precursors to modern metabolic cycles operated on the same principle. We therefore expect that a redox gradient would have been important in an origin of life setting to establish proto-metabolism (Section ‘The benefits of gradients in prebiotic chemistry’). Maintaining a redox gradient over geologically significant periods of time requires continuous sources of *external* energy, and the two largest and most ubiquitous sources of energy on Earth are solar radiation and geothermal heat.

Solar energy can create species useful for modern life and potentially also for prebiotic chemistry by photolysis of atmospheric constituents. For example, UV photolysis of volcanogenic SO<sub>2</sub> and H<sub>2</sub>S is thought to have produced a mixture of SO<sub>2</sub>, H<sub>2</sub>S, S<sup>0</sup> and H<sub>2</sub>SO<sub>4</sub> (Farquhar *et al.*, 2001; Ono *et al.*, 2003), which could have acted as important oxidation or reduction species for protometabolisms. Another photolytic product may have been Fe<sup>3+</sup> produced from Fe<sup>2+</sup> in the surface ocean (Anbar & Holland, 1992).

Nitrate (NO<sub>3</sub><sup>-</sup>) may have been produced during lightning events (reviewed in Ducluzeau *et al.*, 2008) and served as an electron acceptor or as a source of fixed nitrogen.

Geothermal energy, which drives mantle convection, plate tectonics, and hydrothermal circulation of water through the crust, can also be translated into electrochemical energy because the process of planetary differentiation has set up a redox gradient between water and ferrous iron contained in oceanic crust. Consequently, aqueous alteration of oceanic crust by serpentinization (Section ‘Hydrothermal systems’) results in the production of molecular hydrogen (H<sub>2</sub>) and oxidized (ferric) iron (McCammon, 2005; Hellevang, 2008). H<sub>2</sub> can in turn serve as an electron donor to volcanogenic CO<sub>2</sub> or to other oxidants produced by photolysis or lightning. The extent to which H<sub>2</sub> in the Hadean would have vented from hydrothermal chimney-like structures with highly focused flow (resulting in high local H<sub>2</sub> concentrations), vs. venting from diffuse flow systems (H<sub>2</sub> distributed over a larger area, resulting in lower local concentrations), remains poorly constrained. Massive quantities of H<sub>2</sub> (up to 50 bars) were also generated during the moon-forming impact at 4.5 Ga by oxidation of ferrous iron (Fe<sup>2+</sup>) and platinum group elements in the mantle (Sleep *et al.*, 2004). After the moon-forming impact, global atmospheric H<sub>2</sub> levels decreased due to loss to space, but the timing and rates of this process are unclear (Tian *et al.*, 2005, 2006; Catling, 2006). On the anoxic Hadean Earth, H<sub>2</sub> presumably had a significantly longer lifetime and was therefore probably ubiquitous in most environments.

Protometabolic cycles and early metabolisms would have depended upon the presence of a continuously produced redox couple. While photolysis and lightning could have produced locally high concentrations of reactive compounds that fueled important reactions in environmental niches, geothermally produced H<sub>2</sub> and volcanogenic CO<sub>2</sub> in particular may have been the drivers of many prebiotic and early biotic reactions on a global scale. One advantage of the H<sub>2</sub> + CO<sub>2</sub> redox couple as a source of electrochemical energy is that both species are volatile, sufficiently water-soluble, and can easily diffuse into organic or inorganic compartments because they are uncharged. Consequently, this source of electrochemical energy would likely have been abundant in most or all environmental settings on the Hadean Earth.

### Synthesis of organic carbon compounds

Initial stages in the origin of life likely required a continuous source of organic compounds to act as precursors to important biological polymers. Those prebiotic monomers had to be activated, *e.g.* by loss of water molecules or by addition of phosphate, for polymerization to be thermodynamically feasible (Deamer & Weber, 2010). Broadly speaking, three prebiotic sources of organic compounds are most

commonly described: electrical discharge or ultraviolet radiation; input from meteorites, particularly carbonaceous chondrites; and reactions associated with sites of active serpentinization at hydrothermal vents (Charlou *et al.*, 1998).

The basic building blocks of life as we know it consist primarily of nucleotides, peptides, lipids, and carbohydrates. Mechanisms have been found that can produce subsets of all those basic building blocks (Table 1). There is no consensus on how prevalent those mechanisms would have been on the Hadean Earth, but, as discussed below, they do not mutually exclude each other on a global scale. It is therefore plausible that many of the building blocks formed through different mechanisms and interacted with each other in prebiotic reaction networks.

One often-discussed and potential source of organic compounds is meteorites, including interplanetary dust, which may have delivered organic material (Chyba & Sagan, 1992; Pizzarello & Shock, 2010; Schmitt-Kopplin *et al.*, 2010) and phosphorus (Pasek & Lauretta, 2005) or produced HCN in the atmosphere by shock heating (Chyba & Sagan, 1992). Experimental work suggests that under UV radiation, biological co-factors (Meierhenrich *et al.*, 2005) and non-racemic amino acids (de Marcellus *et al.*, 2011) can be produced in interstellar ices, which may have been delivered to Earth through comet impacts.

Given the pervasiveness of H<sub>2</sub> and CO<sub>2</sub> on the Hadean Earth (section 'Energy'), reactions between these two compounds may have occurred in multiple environmental settings and produced myriads of organic compounds. So far, this process has mostly been studied in the context of serpentinization-driven hydrothermal systems, where H<sub>2</sub> is most abundant today (Proskurowski *et al.*, 2008). The power of H<sub>2</sub> to drive biochemical synthesis (Morita, 1999; Nealson *et al.*, 2005) is most evident in the persistence of dense biofilm communities around modern sites of active H<sub>2</sub>-production such as the Lost City vent field. However, H<sub>2</sub> also plays an important role in other modern ecosystems because H<sub>2</sub>-transfer is at the heart of almost every biochemical reduction or oxidation reaction (Nealson *et al.*, 2005). It is therefore conceivable that H<sub>2</sub> fueled

many prebiotic synthesis reactions by coupling not only with CO<sub>2</sub> but also with organic substrates.

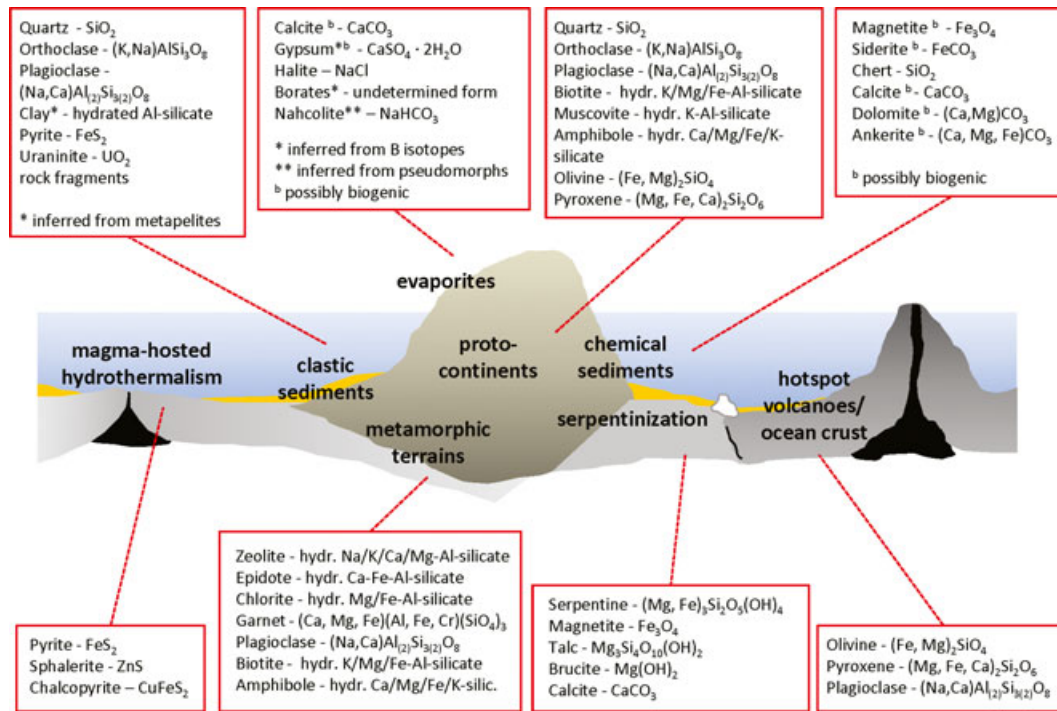
### Catalysis

Catalysts increase the rate of chemical reactions by reducing the activation energy of chemical reactions and can serve as a means of 'selecting' favored products over others (Copley *et al.*, 2007). While proteins serve as the primary catalysts in modern biochemistry (enzymes), coding for complex proteins would not have been available in prebiotic chemistry. Instead, minerals are commonly invoked as non-biological catalysts for life's origin. The abundance of specific minerals in the Hadean was controlled by geological processes and the redox state of the Earth's surface (Fig. 2; see Hazen *et al.* (2008) and Papineau (2010) for a more detailed review on this topic). A diversity of micro-environments with different physicochemical characteristics and mineral assemblages likely increased the diversity of catalyzed primordial reactions.

We can infer which minerals are the most likely to have been important catalysts in the prebiotic Earth through both top-down and bottom-up approaches. For example, the only carbon fixation pathway that is present in both archaea and anaerobic bacteria, the reductive acetyl-CoA, or Wood-Ljungdahl, pathway (Berg *et al.*, 2010) (Fig. 3), involves enzymes with catalytic centers that are remarkably similar to metal sulfide minerals (Russell & Martin, 2004). The minerals alone, without the organic components, can successfully catalyze at least some of the steps in the reductive acetyl-CoA pathway (Huber & Wächtershäuser, 1997; Cody *et al.*, 2000, 2004). This pathway has also been proposed as the most ancient carbon fixation pathway because of its simplicity (Fuchs & Stupperich, 1985; Berg *et al.*, 2010; Fuchs, 2011) and the phylogeny of its proteins (Peretó *et al.*, 1999). Most organisms that utilize this pathway today are fueled by the H<sub>2</sub> + CO<sub>2</sub> redox couple, and the exceptions almost certainly represent later evolutionary innovations (Bapteste *et al.*, 2005). Hydrogenases, which catalyze the uptake and production of

**Table 1** Summary of compounds found universally in modern life and settings that have been proposed for their prebiotic synthesis

Biological component	Setting	Energy source	Selected references
Amino acids	Atmosphere/ocean, continents, terrestrial volcanoes, extraterrestrial synthesis (meteors), hydrothermal vents	Lightning, impact shock, heat	Miller (1953); Chyba & Sagan (1992); Tingle & Hochella (1993)
Nucleotides	Evaporating pond, extraterrestrial synthesis (meteors)	Evaporation, heat, UV	Kvenvolden <i>et al.</i> (1970); Orgel (1998); Zubay & Mui (2001); Powner <i>et al.</i> (2009)
Lipids	Peridotite-hosted hydrothermal vents, extraterrestrial synthesis (meteors)	Serpentinization (Fischer-Tropsch-type reactions), heat	Deamer (2007)
Carbohydrates	Extraterrestrial synthesis (meteors), peridotite-hosted hydrothermal vents, atmosphere/ocean, alkaline streams	Serpentinization (Fischer-Tropsch-type reactions), lightning, heat	Deamer (2007); Benner <i>et al.</i> (2010)



**Fig. 2** Major and some important minor minerals present on the Archean Earth as inferred from the geologic record, listed in no particular order. While all biogenic minerals for which no non-biological mechanism can be invoked would have been absent during the Hadean prior to the origin of life, the primary mineral phases of solidifying magma and their secondary alteration products were probably similarly common. (For references see text).

$\text{H}_2$ , also contain iron and/or nickel at their catalytic sites. Both iron and nickel are commonly associated with serpentinites (Sleep *et al.*, 2004). Hence, this is consistent with the idea that early biochemical pathways were driven by  $\text{H}_2$ , and that the first biochemical pathways evolved as mimicry of already operating geochemical reactions (Cody & Scott, 2007). The distribution and availability of certain mineral catalysts within different environments (Section ‘Hadean micro-environments and their potential role in the origin of life’) may thus help constrain the extent to which different environmental settings may have contributed to certain steps in the origin of life (further discussed in Section ‘Merging bioinformatics with geochemistry’).

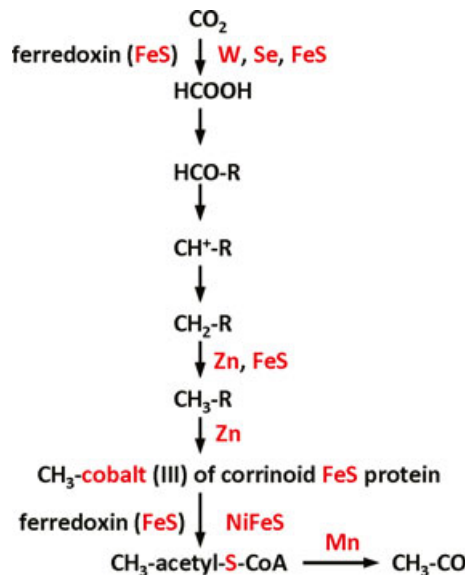
### Concentration

Mechanisms of concentration increase the overall rates of chemical reactions. Concentration mechanisms in pore spaces, on mineral surfaces, or within non-biogenic lipid membranes could also have acted as prebiotic forms of encapsulation which prevented the diffusion of biochemically useful products or even provided the grounds for genetic heredity (Maynard-Smith & Szathmary, 1997; Sowerby *et al.*, 2001, 2002).

Modern life utilizes lipid membranes as encapsulation mechanisms to prevent diffusion of cellular components, to generate concentration gradients, and to maintain a unit of

heredity. Many researchers have focused on possible mechanisms for the formation of early lipid membranes, such as micelles (Deamer *et al.*, 2002). There is dispute, however, regarding how early such encapsulating membranes would have played a role in the evolution of life; some argue that encapsulating membranes must have been an early feature of life, while others argue that it would have been a much later development. The latter point of view suggests that the earliest stages of life’s formation may have involved encapsulation through inorganic micro-compartments such as fluid inclusions, vesicles, porous sediments and hydrothermal chimneys or sea-ice brine pockets (Section ‘Hadean micro-environments and their potential role in the origin of life’). If inorganic micro-compartments served as concentration points for prebiotic molecules, then it is possible that lipid membranes only became important at later stages in the origin and evolution of biochemicals (Koonin & Martin, 2005). However, it is also conceivable that non-biological lipid membranes played a more active role by transporting prebiotic compounds between different environmental settings.

Our current state of knowledge does not allow us to constrain the prerequisites for the origin of life well enough to identify a single environmental setting as the location where life originated. This may change with further experimental research, but it may also indicate that more than one setting was necessary to provide all the



**Fig. 3** The reductive acetyl-CoA pathway of carbon fixation (as employed by methanogens), annotated to highlight steps that involve metals and sulfur, all of which are common in hydrothermal systems. Metals and sulfur found in the corresponding enzymes for each step are shown at the right, and metal-sulfur clusters in ferredoxin cofactors are shown at the left. The atomic structure of the FeNiS complex associated with the acetyl-CoA-generating step is remarkably similar to that of the mineral greigite (Russell & Martin, 2004). Other information compiled from (Ragsdale, 1991) and (Ljungdahl, 1986).

energy sources, organic precursors, catalysts and concentration mechanisms. If so, then life was only able to originate on the Hadean Earth because the unique physical, geological and chemical attributes of individual micro-environments allowed for a greater diversity of reactions to occur simultaneously (Fig. 1). Through global mixing processes, these elements were able to interact and create each of the successive stages for life's origin.

## HADEAN MICRO-ENVIRONMENTS AND THEIR POTENTIAL ROLE IN THE ORIGIN OF LIFE

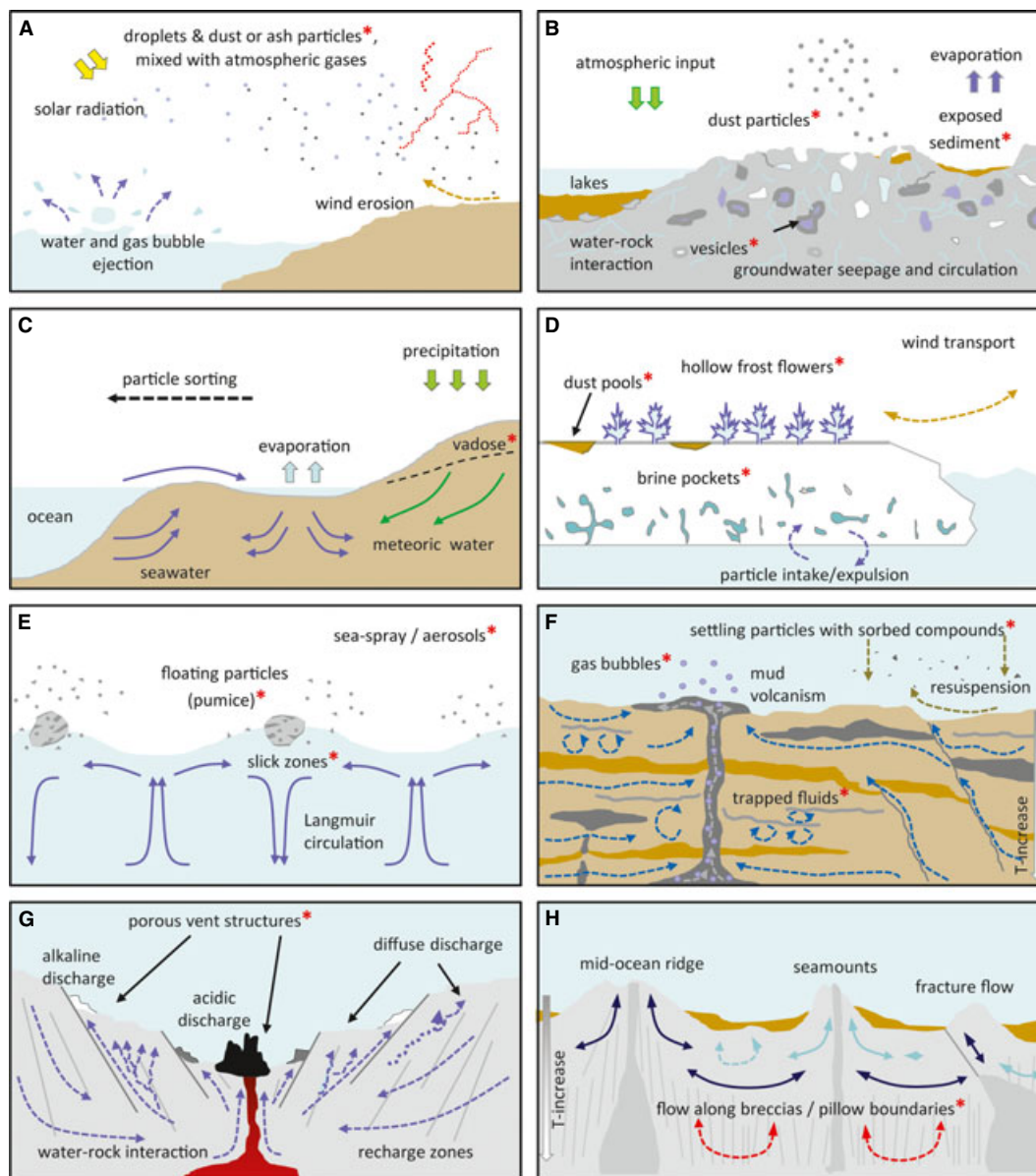
It is almost certain that a great number of inter-connected micro-environments existed on the Hadean Earth soon after the formation of oceans. The age and extent of oceans on Earth are unknown, but Hadean zircons provide geochemical evidence for liquid water near the Earth's surface since 4.4 Ga (Mojzsis *et al.*, 2001; Wilde *et al.*, 2001; Hoskin, 2005). Geological evidence for life extends back to 3.5 billion years (Ga), possibly 3.8 Ga (reviewed in Buick, 2007); hence the origin of life most likely happened in the early Archean (3.5–3.8 Ga) or Hadean (3.8–4.5 Ga) eon. Although the scarcity of direct evidence preserved in the rock record makes it challenging to draw detailed conclusions about the micro-environments present at

that time, careful extrapolations and modeling results allow us to identify eight broad categories of settings (Fig. 4) that may have existed and played a role in the origin of life. For a more detailed review of Hadean and Archean geology, refer to Rollinson (2007) and references therein.

## The atmosphere

The Earth's atmosphere (Fig. 4A) has been prescribed a pivotal role in the creation of life's building blocks since the experiments of Urey and Miller reported in 1953. The experiments demonstrated the production of biologically important organic compounds (including amino acids) by passing electric charge through a mixture of gases which were at the time considered to be the components of Earth's early, reducing atmosphere ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{NH}_3$ ) (Miller, 1953). However, the redox state of the Hadean atmosphere is not well constrained, as it depends (among other factors) on the escape rate of hydrogen, which remains uncertain. Results of more recent models of the early atmosphere range from highly reducing with as much as 30%  $\text{H}_2$  (Tian *et al.*, 2005; but see also Catling, 2006; Tian *et al.*, 2006) to nearly neutral, dominated by  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ , with lesser amounts of  $\text{H}_2$ ,  $\text{SO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  (Kasting & Catling, 2003). Under neutral conditions, the synthesis of organic compounds by electric discharge is much less efficient (Schlesinger & Miller, 1983). Nevertheless, even in a neutral atmosphere a wide array of amino acids could still have been produced by lightning in volcanic eruption clouds (Johnson *et al.*, 2008), which may have been frequent on the Hadean Earth.

The Hadean atmosphere could also have hosted particulate matter with catalytic surfaces. On the modern Earth, natural dust particles are largely derived from continental erosion. On the early Earth that fraction may have been smaller if dry land masses were less extensive. Instead, volcanic ash particles may have been more abundant relative to modern Earth. As today, wind churning the ocean surface would have created seawater aerosols. Marine aerosols, volcanic ash, and dust particles could have acted as a continually recycled population of reaction chambers and catalytic surfaces, experiencing variable degrees of radiation, temperature and water activity during vertical and horizontal atmospheric transport (Dobson *et al.*, 2000; Tuck, 2002). In particular, dehydration of amino acids during atmospheric transport has been suggested as a mechanism for activation and polymerization (Tuck, 2002). Additionally, amphiphiles (organic molecules with both hydrophilic and lipophilic properties) including stearic and oleic acids have been shown to form exterior films on marine aerosols that could have served as proto-membranes in prebiotic chemistry (Tervahattu *et al.*, 2002; Donaldson *et al.*, 2004). The source alkanes for these amphiphiles on the early Earth may have been derived from the reaction of



**Fig. 4** Examples of micro-environments on the Hadean Earth and their major physicochemical properties relevant to the origin of life. Micro-compartments that can concentrate reagents are marked with red asterisks.

water with iron carbide derived from Earth's interior or perhaps from iron-rich meteorites where such carbides exist (Marquez *et al.*, 1996). Thus, the Hadean atmosphere likely created a large number of concentration points for potential prebiotic organic synthesis reactions.

Another important role of the modern atmosphere is to protect life in surface environments from solar UV radiation. In the Hadean, the Sun's output in the extreme UV range was stronger than it is today (Cockell, 2000), while at the same time the Earth was lacking a protective ozone layer (reviewed in Catling & Kasting, 2007). It is possible that a hydrocarbon haze acted as a UV shield

transparent to visible light (Wolf & Toon, 2010), but in the absence of a UV shield, solar UV radiation could have had both positive and negative impacts on prebiotic chemical reactions in the lower atmosphere and in surface-exposed settings, through either activating or destroying prebiotic molecules.

#### Water bodies on land

Continental crust may have appeared as early as 4.35 Ga, as suggested by isotopic evidence from detrital zircons (Harrison *et al.*, 2008), but this interpretation is still

debated (e.g. Pietranik *et al.*, 2008; Kemp *et al.*, 2010). Models for the evolution of continental crust volume show a possible range from >50% of today's volume at 3.8 Ga (e.g. Brown, 1979; Armstrong, 1981) to <5% (e.g. Veizer & Jansen, 1979; McLennan & Taylor, 1982). Most authors favor the idea that continental crust was not widespread during the Hadean; however, that does not preclude the presence of land masses exposed to the atmosphere. Islands could have been created by hotspot volcanism, by crustal expansion during water-rock interaction (serpentinization, Section 'Hydrothermal systems') or by tectonic uplift. Hence, non-marine water bodies including lakes, pore waters in vesicular volcanic rocks or in sediments, and groundwater contained in subsurface aquifers (Fig. 4B) were almost certainly available to host prebiotic reactions that required salt-free conditions.

Due to the great variety of factors influencing the chemistry and hydrology of terrestrial water bodies, it is difficult to assign them a general role in the origin of life. Cyclical evaporation of fluids exposed to the atmosphere could have concentrated the water content and perhaps facilitated dehydration, activation, and polymerization of organic monomers (e.g. Rode *et al.*, 1999; Section 'Synthesis of organic carbon compounds'). Terrestrial hot springs may have created strong gradients in temperature, metal availability, and other chemical parameters (Mulkiđjanian *et al.*, 2012). Atmospheric reaction products in particular would have been concentrated in these exposed environments on land where they could have undergone further reactions. Furthermore, clay minerals produced during weathering of the crust could have provided sites for adsorption and polymerization of organic monomers (Meng *et al.*, 2004; Ferris, 2005a). Continental groundwater would have differed from fluids circulating through oceanic crust (Section 'Oceanic crust') because Hadean proto-continents likely harbored a greater variety of minerals created by felsic and mafic magmatism and metamorphic processes (Fig. 2), thus perhaps allowing a wider range of mineral-catalyzed prebiotic reactions to occur. The maximum depth of groundwater flow systems is mostly controlled by the topography of land masses, but it can also be limited by subsurface brines (Phillips & Castro, 2004). The interface between such brines and meteoric groundwater could have established strong gradients in salinity and pH with possibly important implications for prebiotic chemistry (Section 'The benefits of gradients in prebiotic chemistry'). Similarly, discharge of groundwater along continental margins would have mixed any prebiotic reactants and products contained in groundwater with those contained in coastal and marine waters.

### Beaches

The location of beaches (Fig. 4C) at the interface between land, seawater, and air may have given them a prominent

role in the origin of life, because it would have allowed them to concentrate and process a huge variety of reactants transported by rivers, the ocean, and the atmosphere. Furthermore, beaches have four characteristics advantageous for prebiotic organic synthesis: accumulation of heavy detrital minerals, evaporation-concentration cycles, a gradient in water activity, and high porosity.

In the Hadean beach, sand around volcanic islands may have been rich in mafic minerals such as olivine or pyroxene. Along the shores of proto-continents, heavy detrital minerals could have included uraninite and monazite (Rasmussen & Buick, 1999). Radioactive radiation of detrital uraninite has been proposed as a source of heat and as a catalyst of organic reactions through the formation of radicals (Parnell, 2004; Adam, 2007). It may also have liberated phosphate through bombardment of detrital monazite (Adam, 2007).

Evaporation-concentration cycles in tidal pools on beaches would have promoted dehydration reactions leading to biomolecule polymerization. Furthermore, evaporation of seawater would have led to the precipitation of evaporite minerals, especially if the salinity of the ocean was higher than it is today (Knauth, 2005). Evaporites could have included halite, carbonate or nahcolite and possibly gypsum (although prebiotic sulfate was likely rare) (Boulter & Glover, 1986; Buick & Dunlop, 1990; Lowe & Worrell, 1999; Sugitani *et al.*, 2003), and they may have offered a unique set of catalytic surfaces or concentration points within fluid inclusions. Interestingly, calcite has crystallographic features that could have led to chiral selection (Hazen *et al.*, 2001; Hazen & Sholl, 2003). Beaches may also have been a site of accumulation of evaporitic borate minerals, for which there is tentative isotopic evidence back to the Archean (Grew *et al.*, 2011). Borate is known to stabilize ribose, the backbone of RNA, but it is not clear whether the tectonic processes necessary for accumulation of boron would have been active early enough to play an important role in prebiotic chemistry (Benner *et al.*, 2010; Grew *et al.*, 2011).

The high porosity of beaches enables fluid exchange between the permanently flooded (phreatic) zone and the overlying (vadose) zone and creates a gradient in moisture, temperature and light intensity. Fluid exchange along those gradients by convection (Section 'Convection in air and water masses') and chromatographic separation of compounds (discussed by Cleaves *et al.*, 2012) could have promoted a greater variety of prebiotic reaction products.

### Sea-ice

Although the young Sun was 25–35% fainter in the early history of the Solar System (Gough, 1981), a number of mechanisms have been suggested that could have led to a globally warm climate (Kasting, 2010). Other models, however, suggest that early oceans may have been covered by thin ice, at least locally (reviewed in Zahnle *et al.*,



2010), and especially if latitudinal temperature gradients were stronger (Bada *et al.*, 1994) (Section 'Atmospheric transport'). Modern sea-ice commonly incorporates organic compounds, either sorbed to particles entrained in the ice matrix, sorbed to the ice itself, or in solution (Pfirman *et al.*, 1995; Wania *et al.*, 1998). Today, those compounds include formaldehyde (Douglas *et al.*, 2012), methane, and various biogenic sulfur species (Thomas & Dieckmann, 2002). In an abiotic Hadean ocean, sea-ice would have captured volatiles and organics produced on the seafloor or in the atmosphere and encapsulated them for reaction with other chemical species (Fig. 4D).

As ice freezes, it partitions into a solid and liquid phase with salt and other solutes being rejected from the solid into the liquid phase. The volume fraction of the liquid phase relative to the solid phase is a function of temperature and bulk salinity of the ice matrix (Cox & Weeks, 1983; Pringle *et al.*, 2009). Lowering the salinity or temperature will increase the proportion of solid ice crystals relative to liquid brine - a process called *eutectic freezing*. The effect of eutectic freezing on solutes, including organics, contained within ice brines is to increase their concentration as temperatures decrease. Because of this concentrating effect and because the low temperature of sea-ice environments slow down the degradation of reaction products, ice environments have been cited as a potentially significant site for the production of prebiotic molecules (Levy *et al.*, 2000; Kanavarioti *et al.*, 2001; Miyakawa *et al.*, 2002a,b; Price, 2007, 2009; Pierre-Alain & Hans, 2008) (Supplementary Table S1).

Furthermore, ice provides spatial and temporal gradients of pH, water activity, and temperature. As these parameters strongly affect the behavior of organic and inorganic chemical species, the presence of gradients will increase the number of potential chemical reactions, some of which could be important for the origin of life. For example, the precipitation of calcite ( $\text{CaCO}_3$ ) at  $-2.1\text{ }^\circ\text{C}$  will result in the loss of the carbon buffering system in seawater and a decrease in pH. In a similar manner, salts have an effect on water activity; salts with low eutectic points interact more strongly with water molecules and impart a stronger influence on water activity. It is difficult to model or empirically derive the precipitation of specific salts as the exact starting composition of Hadean seawater is unknown. However, temperature variations over diurnal or seasonal cycles would have led to changes in brine composition over time, thus creating a variety of chemical micro-environments within the ice. Additionally, temperature also controls horizontal and vertical gradients in pH and water activity within ice. A vertical gradient is created due to the difference in temperature between the upper (atmospheric) and lower (seawater) interfaces. Horizontal temperature gradients can be established by the presence of low albedo material such as volcanic ash or cryoconite (windblown

dust) deposited on the surface (Wharton *et al.*, 1985). Under exposure to sunlight, this detrital material emits in the infrared, warming the surrounding ice, and in extreme cases, creating melt ponds. On the contemporary Earth, cryoconite holes host distinct microbial ecosystems (Christner *et al.*, 2003); on the prebiotic Earth, they were likely to have hosted distinct chemical environments.

### Sea-surface microlayer

The sea-surface microlayer (SSML, Fig. 4E) describes the interface between the ocean and the atmosphere and is operationally defined as the upper 1000  $\mu\text{m}$  of the ocean (Liss & Duce, 1997). The SSML may have been a crucial setting for prebiotic synthesis or polymerization reactions due to an abundance of both organic material and external energy sources. Attenuation of UV light in the water column results in a comparatively high abundance of photons at the SSML, and while often associated with its destructive potential for biomolecules, a variety of biochemically useful molecules have been synthesized under UV light, including deoxyribose, ribose, amino acids, aldehydes, and uracil (Shigemasa *et al.*, 1977; Folsome *et al.*, 1983; Pestunova *et al.*, 2005; Nuevo *et al.*, 2009), perhaps creating an oil slick at the sea surface (Lasaga *et al.*, 1971; Nilson, 2002). The SSML is rich in organic and inorganic materials collected from both the atmosphere and ocean, held in place by buoyancy, electrostatic attraction, physical or chemical adsorption, and surface tension (Hunter & Liss, 1977; Sieburth, 1983; Liss & Duce, 1997). Material from the water column is transported to the sea surface via a number of processes including diffusion, turbulent mixing, bubble and particle transport, and large-scale circulation driven by wind (Langmuir circulation), tidal forces, and internal waves (Frew, 1997).

In addition to dissolved molecules, suspended particulates composed of volcanic ash or pumice could have accumulated in slick zones within the SSML (Section 'Ocean circulation') (cf. Brasier *et al.*, 2011). Volcanic ash alters to zeolite, which has hydrophobic surfaces that provide protected sorption sites for the polymerization of water-insoluble organic monomers. Pumice and volcanic ash can release phosphorus (Timperley, 1983; Frogner *et al.*, 2001), one of the cardinal elements required for life. Furthermore, the high porosity of pumice allows it to entrain and concentrate organic material, and because it floats, pumice is conducive to distribution by ocean currents. Annual contemporary production of pumice is estimated at billions of cubic meters of drift pumice (Jokiel & Cox, 2003) from a variety of locales (Timperley, 1983; Timperley & Vigor-Brown, 1985; Felitsyn & Kirianov, 2002; Jokiel & Cox, 2003).

Products and reactants from the SSML would thus have been connected on timescales of seconds to days with the

deep ocean via particle settling and with the atmosphere via ejection of bubbles and aerosols (Wallace & Duce, 1978).

### Marine sediments

Organic and inorganic material produced at the surface of the ocean, on land, or in the atmosphere eventually sinks down to the ocean floor. On the modern Earth, clay minerals with a high affinity for adsorption are responsible for 80% of organic net export from the surface ocean to the deep ocean (Kennedy *et al.*, 2002). On the prebiotic Earth, this mechanism probably provided an efficient shuttle of monomers and polymers to deep marine sediments (Fig. 4F). Modern marine pelagic sediments are largely dominated by biogenic minerals such as carbonates and silica (Li & Schoonmaker, 2003). In the absence of biogenic material and due to more volcanic activity in the Hadean, prebiotic marine sediments would have contained a larger proportion of metal-rich phases, mafic minerals, volcanic ash, pumice and their alteration products, in particular zeolites and smectite clays. A common constituent of parts of the Archean marine sedimentary rock record is banded iron formations (BIFs) composed of iron oxides and silica (chert) (Nutman *et al.*, 1997). Although biological formation processes for BIFs are thought to be more plausible (Konhauser *et al.*, 2007), abiotic oxidation of ferrous iron by photolysis (Cairns-Smith, 1978; Braterman *et al.*, 1983; François, 1986) could have occurred on a smaller scale prior to life's origin. Iron oxides can act as catalysts for the formation of nucleobases (Shanker *et al.*, 2011).

Burial and diagenesis of sediment packages would have led to progressively increasing temperatures, as well as changes in pore fluid salinity and pH. This process may have created a great variety of prebiotic reactors enclosed in pore spaces with different physicochemical characteristics. However, fluid exchange across sediment packages would have been slow during quiescent periods, as clays and abiotically precipitated silica likely formed impermeable layers (Hofmann & Bolhar, 2007). Nonetheless, flow paths could have been created during catastrophic events (Section 'Catastrophic events') or mud volcanism (Mazzini, 2009) associated with methane gas production by serpentinization in the underlying oceanic crust (Section 'Hydrothermal systems'). Evidence for such activity in the Archean was recently discovered at Isua, Greenland (Pons *et al.*, 2011). Like terrestrial beach sediments, marine sediments may have concentrated organic compounds from a variety of environments, but the fluid residence time in marine sediment packages was likely much greater. Hence, kinetically inhibited reactions that can proceed in the absence of light and in saltwater may have occurred in this setting.

### Hydrothermal systems

Marine hydrothermal systems (Fig. 4G), generally found at mid-ocean ridges and along ridge flanks, occur where seawater interacts with crustal rock, creating strong gradients in temperature and chemical composition, while the altered crust becomes enriched in chemical precipitates and metamorphic minerals. The temperature of the early Earth's mantle was higher than it is today (Turcotte, 1980; Richter, 1988), and that extra heat was probably dissipated by longer mid-ocean ridges, or faster spreading, or a combination of both (e.g. Hargraves, 1986). Thus, hydrothermally active sites almost certainly existed in the Hadean ocean and may have been a more common feature than they are today.

Today, known hydrothermal vent systems can be broadly classified into magma-driven, basalt-hosted systems and serpentinization-driven, peridotite-hosted systems. Some fields, such as Rainbow hydrothermal field on the Mid-Atlantic Ridge, which is magma-driven but peridotite-hosted, display characteristics of both (see below). Found at spreading centers or at seamounts where water is heated by rising magma, contemporary magma-driven systems have fluids reaching temperatures up to 400 °C and acidities as low as pH 2. They are enriched in transition metals, sulfide, CO<sub>2</sub>, methane, and hydrogen, but depleted in magnesium relative to seawater (von Damm, 1990). In the Hadean, magma-driven hydrothermal systems may have contained more Fe<sup>2+</sup> and H<sub>2</sub> than today due to the lack of oxidizing sulfate in anoxic seawater (Kump & Seyfried, 2005). When hydrothermal fluid rises buoyantly through porous oceanic crust and mixes with cold alkaline seawater, minerals precipitate to form chimney structures. Pyrite (FeS<sub>2</sub>), a principal component of these vent structures, has been suggested as a catalyst for the production of several organic precursors for the origin of life because it can facilitate the fixation of CO or CO<sub>2</sub> to form simple organic molecules (Wächterhäuser, 1988a, b, 1990; Cody, 2004).

In the absence of oxidative weathering on land, magma-driven hydrothermal vent systems were likely the major source of transition metals to the Hadean ocean. Transition metals, many of which are important components of enzymes (e.g. Schoepp-Cothenet *et al.*, 2012b), are easily scavenged by dissolved sulfide (Zerle *et al.*, 2005); however, their solubility can be enhanced if they become complexed with organic molecules. On the modern Earth, organically complexed Fe and Cu derived from hydrothermal vents account for 9% and 14% of the deep-ocean reservoir of total Fe and Cu, respectively (Sander & Koschinsky, 2011). Hence, dissolved metals liberated in magma-driven hydrothermal vents in the Hadean could have been distributed around the globe as organic complexes.

In serpentinization-driven hydrothermal systems, in contrast – a geochemical reaction between seawater and olivine leading to the formation of magnetite and serpentine (serpentinization) can alter fluid chemistry and provide heat for circulation even in the absence of magmatic heating. Serpentinization-driven hydrothermal systems are exemplified by the Lost City hydrothermal field (Kelley *et al.*, 2001, 2005). Hydrothermal fluids venting from Lost City chimneys do not exceed ~90 °C and can reach a pH of 11, resulting in the precipitation of carbonate minerals.

Most significantly for the origin of life, serpentinization-associated Fischer-Tropsch type reactions also generate organic compounds (Holm & Charlou, 2001; McCollom & Seewald, 2007), including high levels of formate, (Lang *et al.*, 2010), methane (Proskurowski *et al.*, 2008), hydrogen cyanide (Holm & Neubeck, 2009), and organic sulfur compounds (Heinen & Lauwers, 1996). Larger hydrocarbons containing at least four carbon atoms have been detected as well (Proskurowski *et al.*, 2008). If organic matter from other sources (Table 1) were introduced and concentrated in a serpentinizing environment, the highly reducing conditions could promote synthesis of longer carbon chains. In addition to organic carbon, hydrothermal vents may also have provided a source of fixed nitrogen (Brandes *et al.*, 2008; Holm & Neubeck, 2009) and phosphorus (Yamagata *et al.*, 1991) for the origin of life. Hennet *et al.* (1992) showed that amino acids are produced in laboratory conditions meant to simulate hydrothermally altered submarine crust, producing a similar variety to those produced in Miller's electric spark experiments, but in significantly greater quantities (Hennet *et al.*, 1992).

Perhaps more so than the presence of essential elements or polymerization, the greatest contribution of both magma-driven and serpentinization-driven hydrothermal systems to the origin of life may have been the formation of geological, physical, and chemical gradients as a result of the dynamic mixing and mineral formation associated with hydrothermal systems (Baross & Hoffman, 1985). Mixing of hydrothermal fluids with seawater both above and below the seafloor creates gradients in temperature, pH, chemical composition, and redox state which may have allowed many important prebiotic reactions to occur in tandem (Koonin & Martin, 2005; Martin & Russell, 2007; Martin *et al.*, 2008; Lane *et al.*, 2010) before interacting and integrating into a larger reaction network. Moreover, phase separation into brine and vapor phases could contribute to the number of microenvironments in which reactions can occur and perhaps allow prebiotic dehydration reactions to proceed within the brine phase.

It has been suggested that in the early Archean, hydrothermal fluids were overall more alkaline than today (Shibuya *et al.*, 2010). However, both hydrothermal sul-

fides (Vearncombe *et al.*, 1995; Huston *et al.*, 2002) and serpentinites (Blais & Auvray, 1990) have been detected in the Archean rock record, so both magma-driven and serpentinization-driven systems probably co-occurred during the Hadean. As mentioned above, the modern Rainbow hydrothermal field on the Mid-Atlantic Ridge has magmatically heated, acidic hydrothermal fluids that circulate through ultramafic rocks and are enriched in both H<sub>2</sub> and various metals (Charlou *et al.*, 2002; Douville *et al.*, 2002). These mixing systems may have been ideal for prebiotic chemistry (Russell *et al.*, 2010).

### Oceanic crust

Fluid circulation through oceanic crust is most vigorous near hydrothermal systems at mid-ocean ridge axes where the fluid residence time ranges from days to years (Johnson & Prius, 2010). Although the volume of fluid flux dissipates with distance from the ridge axis, fluids continue to be exchanged in the upper crust for many millions of years, even where typical hydrothermal vent features have long disappeared, which creates a separate unique environment for prebiotic chemical reactions (Fig. 4H). Overall, it has been estimated that at least 60% of the oceanic crust is hydrologically active (Schrenk *et al.*, 2010). Recharge seems to occur at point sources such as unsedimented seamounts, and flow velocities are on the order of tens to hundreds of meters per year (Fisher & Becker, 2000; Spinnelli & Fisher, 2004; Bekins *et al.*, 2007; Hutnak & Fisher, 2007; Hutnak *et al.*, 2008). Seamounts are abundant features on the modern Earth and may have been more prevalent in the Hadean. It therefore seems likely that this hydrological dynamism was an important feature of the ocean crust. While the Precambrian ocean was probably saturated with silica (Siever, 1992; Hofmann, 2011) and possibly carbonate, which may have lowered the porosity of the crust by precipitation, stronger tidal interaction and more vigorous tectonism could have opened up fractures and thus sustained permeability. Today, the subsurface fluid flow connects mid-plate regions over a distance of many kilometers. On a more hydrothermally active Hadean planet, these flow paths could have allowed fluids from very different chemical and mineralogical regimes to mix and exchange reactants and products of prebiotic reactions.

Intra-crustal fluids are characterized by long residence times in contact with crustal minerals and by moderately warm temperatures, which today range from 10 to 30 °C at the bottom of the marine sediment layer to 20–40 °C at the bottom of the crustal high-porosity zone (Johnson & Pruis, 2003). Hence, these fluids are much warmer than the modern deep ocean (~2 °C), allow more time for mineral-catalyzed reactions than vent systems, and are well protected from radiation compared to surface environments.

The minerals of the greatest interest for the origin of life in the ocean crust may have been the alteration products of mafic minerals and basaltic glass, particularly clays and zeolites. Fluid flux through the crust occurs preferentially through connected channels, such as around breccia zones and pillow and flow boundaries (Fisher & Becker, 2000), so these regions would have been exposed to the greatest alteration. Experiments with basalt alteration reactions under elevated CO<sub>2</sub> concentrations, as might be expected in the Hadean, produced Ca-Mg-Fe carbonates, Fe-hydroxides, and Ca-Mg-Fe clays (Gysi & Stefansson, 2012), which could have participated in prebiotic synthesis or polymerization reactions. Moreover, the region for potential catalysis and polymerization in the deep subsurface is extensive, as evidenced by the presence of cryptoendolithic microbial communities supported by serpentinization by-products at depth (Hazen *et al.*, 2012; Menez *et al.*, 2012). Thus, the potential reaction space for prebiotic chemistry within the ocean crust is vast, hydrologically dynamic, and interconnected globally.

#### Where did life originate?

Table 2 compares the different settings based on their ability to fulfill the requirements for life (Section 'Prerequisites for the origin of life'). Although some settings appear to have similar characteristics, they may differ markedly in their mineralogy and hydrology, and they have the potential to produce unique sets of organic compounds. Consequently, Table 2 does not show which single setting was best for the origin of life. On the contrary, it highlights that multiple settings were probably needed to satisfy all of the requirements. It is therefore unreasonable to favor a single setting for all steps in the origin of life.

A more parsimonious scenario is that the Hadean Earth hosted a diverse array of settings, each of which provided specific constraints for different chemical reactions (Fig. 1). Only physical interaction and exchange of reactants and products among this variety of settings would have provided all the necessary ingredients for life.

The importance of mixing processes, however, does not imply that all of the important prebiotic reactions occurred in an 'organic soup', in which the biochemically productive reactions comprised only a tiny subset of all the reactions occurring. In contrast, we argue that the diversity of settings in the Hadean would have allowed different reactions to occur in different settings, and each setting would have provided constrained parameters to nurture sparse reaction networks that could conceivably generate specific modules of modern biochemistry (Morowitz & Smith, 2007; Trefil *et al.*, 2009). Thus, life was not a highly improbable outcome of a single experiment in an organic soup, but instead a gradual emergence from successful interactions among globally distributed, simultaneously forming reaction products.

#### GLOBAL TRANSPORT AND CONCENTRATION PROCESSES ON THE HADEAN EARTH

If the origin of life was a global phenomenon that involved multiple environmental settings, then transport processes would have been critical for the exchange of prebiotic reactants and products. Here, we consider major mixing mechanisms on the Hadean Earth that may have served to connect crustal, sedimentary, marine, terrestrial, and atmospheric sites where relevant prebiotic reactions could have occurred (Fig. 5).

**Table 2** Summary of chemical and physical properties of distinct environmental settings. Intensity of parameters is rated from near absent (–) to very high (+++)

Environment	Parameter							
	Organic synthesis	Concentration		Energy and gradients			Catalytic minerals	Fluid residence time
		Encapsulation	Dehydration	Light energy	pH gradient	Temperature gradient		
Atmospheric gases and particulates	+++	++	+	+++	–	–	–	Days to weeks
Exposed lakes	+	–	+	++	–	–	++	Months to years
Continental Groundwater	+	++	–	–	++	+	++	Years to Ma
Beach settings	++	+++	+++	++	–	+	++	Hours to days
Sea-ice	+	+++	++	++	+	+	+	Months
Sea-surface microlayer	+	–	–	+++	–	–	+	Seconds
Hydrothermal vents	+++	++	++	–	+++	+++	+++	Days to weeks
Upper oceanic crust	+	+	–	–	+	++	++	Years to ka
Marine sediments	–	+	–	–	–	+	+++	Years to Ma

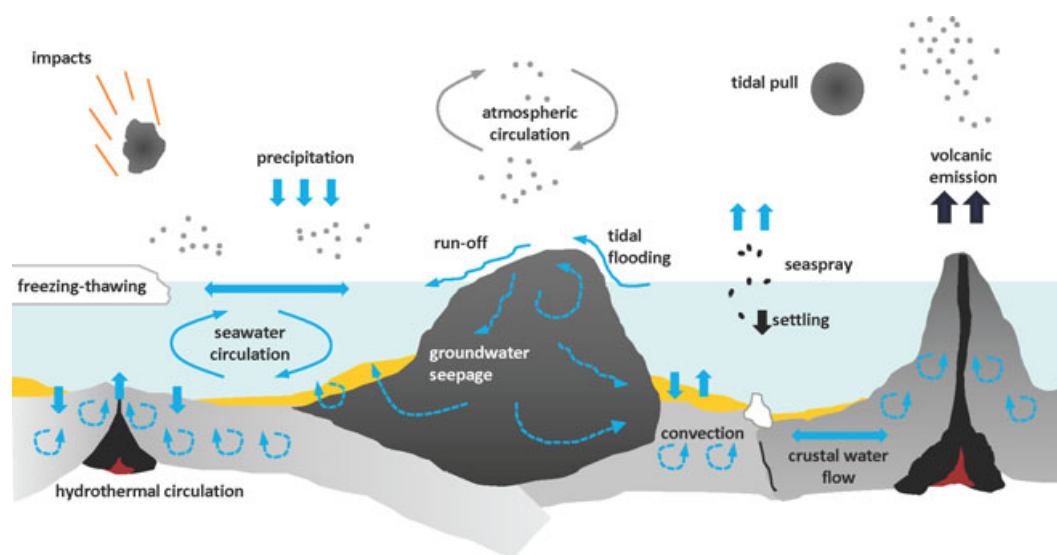


Fig. 5 Overview of mixing processes that may have linked different sites on the Hadean Earth and facilitated reactions between a greater variety of compounds.

### Local and global mixing processes

#### *Atmospheric transport*

The combination of incoming solar radiation coupled with planetary rotation governs atmospheric circulation. This results in atmospheric longitudinal bands (the Hadley, Ferrel, and polar cells) that dictate the transport of air masses and heat. Today, an air mass can circulate around the globe in 2 weeks (Jacob, 1999). Regional differences in air pressure further mix the atmosphere by causing winds and turbulence.

In the Hadean, the rotation period of the planet was most likely faster than it is today (Wahr, 1988; Williams, 2000). Extrapolating from Mid-Precambrian geological evidence (Williams, 2000) to about 4 Ga yields a Hadean rotation period of approximately 14 h. Williams & Holloway (1982) predict that a doubling of today's rotation rate reduces the latitudinal extent of the Hadley cell from 30° to approximately 18°, while at the same time increases the number of longitudinal bands from three to four. Longitudinal winds would probably become more vigorous. Hence, if the Hadean Earth was rotating at nearly twice the modern rate, then the products of Miller-Urey-type reactions (Section 'The atmosphere') and liquid or particulate aerosols would have been efficiently transported around the planet in a direction parallel to the equator. A faster rotation would also have led to a stronger Coriolis effect and thus limited the transport of air masses and material across lines of latitude. An additional consequence might have been a steeper latitudinal temperature gradient in the Hadean (Williams & Holloway, 1982), which may have led to a greater variety of environmental settings.

#### *Ocean circulation*

Atmospheric circulation cells coupled with landmass distribution are the dominant factor in surface ocean circulation. Wind, directionally controlled by the parameters of Hadley cell formation, imparts a stress on the sea surface. Coriolis forces and friction shift the direction of transport away from this stress. The speed of water transport at the sea surface is inversely proportional to the Coriolis force, and therefore to Earth's angular momentum (Ekman, 1905). On the contemporary Earth, this mechanism concentrates material floating on the sea surface within subtropical gyres, which have become infamous as 'garbage patches' (Moore *et al.*, 2001). With a stronger Coriolis force (Section 'Atmospheric transport'), this effect would probably have been even more pronounced in the Hadean ocean, thus allowing ice, pumice, organics within the SSML, and other debris floating in the Hadean surface ocean to become concentrated in small eddies. Large ocean gyres, however, were probably weaker, resulting in reduced latitudinal transport of water masses (Hunt, 1979).

The volume of continental mass present in the Hadean is still subject to debate (see Section 'Water bodies on land'), and these intervening landmasses would have had a strong influence on the nature of ocean circulation. Pope *et al.* (2012) recently estimated ocean volume in the early Archean to be up to 26% more voluminous than modern oceans. This may have effectively reduced the amount of terrestrial landmass available. If, however, continental crust was less extensive, a more voluminous ocean may not necessarily have been deeper. It is therefore likely that volcanic islands were common and led to the formation of eddies and regional water mixing. Small eddies are so efficient at

transport that the water parcels they contain maintain an identifiable heat signature weeks after formation, and marine organisms can be transported hundreds of kilometers (Olson & Backus, 1985). Furthermore, Adams *et al.* (2011) demonstrated that deep-reaching eddies can entrain material from deep-sea hydrothermal vents and transport it over several kilometers. Combined with stronger tidal pumping resulting from a much closer Moon, ocean currents may thus have efficiently transported materials along regional environmental gradients.

#### *River runoff*

Fluvial networks in the Hadean would have played the same central role as modern rivers in eroding and transporting continental material to the ocean. Rivers are also a medium for aqueous chemistry between material transported along the river bed and atmospheric constituents, brought into contact through turbulent mixing. The oxidation of soluble ferrous iron into insoluble ferric iron by entrained atmospheric oxygen is a modern example. However, a critical difference in the Hadean was the lack of vegetation, which likely led to fundamentally different river forms and dynamics compared with modern vegetated analogs. Most importantly, vegetation perturbs near-bank flow and binds sediments, which increases bank stability. Hence, it limits shear-stress and thus erosion of the bank walls (Miller, 2000). Field observations (Mackin, 1956), theoretical arguments (Miller, 2000), and flume experiments (Gran & Paola, 2001) consistently show that unvegetated channels are typically braided (exhibiting multiple channels that are separated by erodible bars), and the individual channels migrate laterally at higher rates. This leads to a higher width-to-depth ratio in unvegetated river systems. It can therefore be assumed that Hadean terrain was scoured by rivers more frequently compared with modern floodplains. Atmospheric reaction products deposited on Hadean land surfaces thus had a higher probability of being transported to the ocean.

#### *Convection in air and water masses*

Convection caused by thermal or compositional gradients between fluids can contribute to mixing on a local or regional scale. Gradients are ubiquitous within and between many environmental settings on Earth, and buoyancy-driven convection results as long as the time-scales of gradient dissipation by diffusion are comparatively longer.

In prebiotic chemistry, convective transport may have played an important role because the cyclical nature of convection implies that compounds contained in convecting fluids are repeatedly exposed to various physicochemical conditions. This could have led to chemical selection and maturation of specific reaction products. Furthermore, small, closed convection cells within thin films of fluid may have encapsulated organic compounds that were dissolved in fluids or adsorbed to suspended solids. This concentrat-

ing mechanism may have been able to speed up the rate of chemical reactions.

The Hadean Earth probably had a variety of environments where convection occurred. For example, where tides transport seawater inland, the seawater will quickly sink into fresh-water saturated sediments. Convection driven by the density gradient between salt water and fresh water makes this mixing process more efficient than diffusion alone. Dissolved constituents can thus be exchanged rapidly between sediment packages protected from radiation and exposed tide pools (Smetacek *et al.*, 1976). Environments with thermal gradients could have produced Rayleigh-Bénard convection cells (convection caused by temperature-dependent density gradients). Examples of such environments include the geothermal gradient in permeable oceanic crust and sediments, the interface between hydrothermal fluids and seawater, or diurnally heated air masses. Temperature may also facilitate convection in fluids by changing surface tension (Bénard-Marangoni convection).

Convection at the microscale can have a concentrating impact as well. Baaske *et al.* (2007) simulated molecular transport of nucleotides in elongated hydrothermal pores and found that thermal convection along the pore combined with thermodiffusion across the pore resulted in accumulation of nucleotides. Budin *et al.* (2009) experimentally tested this concept with microcapillary diffusion columns and experimentally verified accumulation of nucleotides, oligonucleotides, as well as fatty acids. Moreover, they observed that accumulation of fatty acids resulted in self-assembly of large vesicles containing encapsulated DNA, a potentially crucial first step in the origin of life.

#### *Catastrophic events*

Large-scale mixing of fluids and minerals likely occurred during catastrophic events such as asteroid and comet impacts, volcanic eruptions, or earthquakes, all of which may have resulted in slope failure (turbidites), tsunamis, and crustal deformation.

The Earth was subject to heavy meteorite bombardment in the late Hadean up to 3.8 Ga (Kring & Cohen, 2002). Large impacts may have sterilized the planet (Sleep *et al.*, 1989) or restricted habitable environments to the deep subsurface (Abramov & Mojzsis, 2009). However, it is not certain whether life originated before, during, or after the time of potentially sterilizing impacts, or whether sterilizing impacts ever even occurred on Earth (Ryder, 2003). Smaller, non-sterilizing impacts would have likely enhanced the exchange of material between sites by triggering ocean-wide tsunamis, crustal faulting, and exposure of subsurface settings (Grieve, 1987; Pickering *et al.*, 1991; Dypvik & Jansa, 2003; Glikson, 2004).

Volcanic eruptions were probably more common on the Hadean Earth due to higher geothermal heat flux (Martin

*et al.*, 2007). Subaerial explosive eruptions deliver ash particles and gases into the upper atmosphere, from where they are distributed around the globe (Section 'Atmospheric transport'). After rainout, fine ash particles and vesicular material such as pumice can remain suspended in the ocean water column for long periods of time (Section 'Particles as stabilizing agents for transport'). Hadean volcanoes therefore provided large amounts of material with catalytic surfaces to various environmental settings.

With frequently erupting volcanoes (Martin *et al.*, 2007) and with more tectonic activity (Hargraves, 1986), submarine seismic events were perhaps also more common in the Hadean than today. It has been hypothesized that seismicity could have supplied an entire subsurface ecosystem on the early Earth with enough nutrients for millions or billions of years (Sleep & Zoback, 2007). Moreover, micro-earthquakes, caused by tidal interaction between the Earth and the Moon (Tolstoy *et al.*, 2002), were probably stronger when the Moon was significantly closer than it is today (Williams, 2000). Hence, eruptions, seismicity, and tides together would have caused frequent crustal fracturing and faulting, opening up new flow paths for fluid circulation into the subsurface. Even today lunar effects on hydrothermal flow patterns are measurable (Aliani *et al.*, 2004), and on a more volcanically and hydrothermally active early Earth, the Moon could have acted as an important pump for reagents and products traveling through crust and sediment packages.

### Particles as stabilizing agents for transport

Some of the previously described settings naturally occurred in close spatial proximity such that degradation and dilution of reactants and products during transport from one setting to another would not have been significant. Other far apart settings interacted as a result of large-scale mixing processes as described above. In the anoxic Hadean ocean, oxidative degradation of organics during transport, the primary cause of organic destabilization today (Keil *et al.*, 2004), would have been negligible. Nevertheless, reactants and products were probably transported more efficiently and altered minimally between sites if they were either encapsulated in membranes, contained within porous particles, or adsorbed onto mineral surfaces. Many minerals such as smectite clays, feldspars, and iron oxides have been shown to stabilize numerous organic molecules, including organic acids, sugars, proteins, and lipids, by adsorption (Sansone *et al.*, 1987; Ding & Henrichs, 2002; Keil *et al.*, 2004). In the modern ocean, these minerals are present on scales of milligrams per kg of seawater, and transported in enormous quantities, in the range of tens of megatons per yr (MacKenzie *et al.*, 1979; Summons, 1993; Li, 2000; Syvitski *et al.*, 2003). The surface area of erodible land masses in the Hadean is uncertain, but even if the flux of land-derived

mineral grains to the ocean was smaller, it was perhaps compensated by larger quantities of volcanic ejecta. Sulfide particles produced by submarine hydrothermal processes (Trochine & Trefry, 1988) would also have been more stable in the anoxic Hadean ocean. Suspended particles that eventually settle on the seafloor or that become re-suspended during strong tidal or catastrophic events (Section 'Catastrophic events') would thus have created a vertical shuttle of adsorbed material between the atmosphere, land masses, the sea surface, and the deep ocean. Lateral transport may also have been important in connecting different environments. In the modern ocean, fine-grained particles can be transported laterally for hundreds of kilometers by ocean currents (Mollenhauer *et al.*, 2006).

Overall, the particulate load suspended in the atmosphere and ocean, in combination with mixing and transport processes, could have served as important vectors for transport of prebiotic organic molecules and mineral catalysts between environmental settings.

### The benefits of gradients in prebiotic chemistry

As discussed above, chemical and physical gradients likely stimulated fluid convection and exchange of material with important implications for prebiotic chemistry. However, gradients in temperature, pH, redox potential, light intensity, salinity, pressure, density, and chemical composition could also have played a more direct role in the production of complex biomolecules. The interaction of substrates and/or fluids far from equilibrium with each other is necessary to provide energy for organic synthesis (Shock & Schulte, 1998). Furthermore, the energy that is made available during convective mixing can be exploited by a greater diversity of reactions, including reaction networks, if gradients in multiple parameters are present. One excellent example of this multiplicity of gradients is found in mid-ocean ridge flanks (Section 'Hydrothermal systems'), where hydrothermal fluids mix with ambient seawater to create gradients of temperature, pH, redox potential, and concentrations of many inorganic and organic species (Baross & Hoffman, 1985; Shock & Schulte, 1998). Other examples include beaches, where meteoric fresh water mixes with seawater and where water activity decreases from the bottom toward the top of a sediment layer (Section 'Beaches'); or sea-ice, where seawater undergoes changes in salinity, pH, and temperature during eutectic freezing (Section 'Sea-ice'). In all cases, physical and chemical gradients can progressively impact the thermodynamics of synthesis reactions and increase the number of possible reactants and products.

Redox gradients, which are exploited for metabolism in modern organisms, were likely particularly important in establishing proto-metabolism (Section 'Energy'). It seems plausible that living cells adopted this strategy from natural

gradients that were harnessed by prebiotic chemistry (cf. Martin & Russell (2007)).

Pressure gradients are an understudied subject in prebiotic chemistry. Models suggest that at high pressure, such as in the deep ocean or within the ocean crust, the polarity of H<sub>2</sub>O molecules decreases, which lowers the stability of ionic species in solution but increases the solubility of apolar organic molecules or gases (Shock, 1992; Bassez, 2003). High-pressure environments may therefore be conducive to otherwise thermodynamically unfeasible reactions.

Gradients could also have played an important role in mineral catalysis. The charge of both mineral surfaces and organic monomers changes as a function of pH (Stumm & Morgan, 1996; Williams & Frasca, 2001; Munsch *et al.*, 2001): low pH leads to more positive overall charge, but the pH creating a zero charge is specific to each organic compound and to each crystallographic face of a mineral. Consequently, mineral grains that are exposed to variable pH conditions, such as during convective or advective transport, could potentially adsorb and desorb different amino acids (Churchill *et al.*, 2004) or nucleotides (Ferris, 2005b) over time. This process could in turn have diversified organic polymers in prebiotic chemistry.

Once complex organic polymers had formed, transport along gradients could have affected their secondary and tertiary fold structure, allowing them to undergo a greater set of further reactions. For example, RNA in modern organisms requires specific concentrations of Mg or Ca ions in order to obtain a three-dimensional structure that makes it biochemically useful (e.g. Dann *et al.*, 2007). In particular, Mg has been shown to stabilize phosphate groups of nucleotides (Holm, 2012). If ionic concentrations change, the organic polymer rearranges into a different configuration. Some proteins change their fold structure with temperature and pressure (Heremans & Smeller, 1998; Serganov & Patel, 2007). Hence, convective transport of organic polymers within or between different environments on the Hadean Earth would have caused those changes to occur repeatedly.

## MERGING BIOINFORMATICS WITH GEOCHEMISTRY

Embracing the immense diversity of niches and microenvironments is clearly important for a bottom-up approach to the origin of life. However, certain key processes are likely to have selectively produced some of the most important elements for the origin of life. One means by which we can identify those important processes is through a top-down perspective: those geochemical processes that have left an imprint in modern biochemistry must clearly have played a prominent role in prebiotic reaction networks.

Traditional top-down approaches to the origin of life often begin with the phylogenetic tree of all extant organisms. Universal phylogenetic analyses of conserved genes demonstrate that all known organisms evolved from a single ancestor or genetically continuous community (Cairns-Smith, 2003; Theobald, 2010) resulting in the ‘unity of biochemistry’ of all extant organisms (Kluyver & Donker, 1959). By identifying the root of the phylogenetic tree, such studies also suggest that this Last Universal Common Ancestor (LUCA) lived in a hot environment (Schwartzmann & Lineweaver, 2004; Gaucher *et al.*, 2008) and had an autotrophic metabolism (Pace, 1997; Berg *et al.*, 2010). LUCA is now understood to have been a complex ‘organism’ with a sophisticated genetic system (Harris *et al.*, 2003; Goldman *et al.*, 2010), perhaps composed of an RNA genome (Glansdorff *et al.*, 2008), and metabolism (Caetano-Anolles *et al.*, 2007; Srinivasan & Morowitz, 2009). However, any extrapolation from these features of LUCA to a geochemical environment will only reflect the final stages in the origin of life, because the prebiotic world and modern world are separated by extensive geological and biological evolution. As such, no direct evidence linking modern life to any single prebiotic chemistry regime or origin of life setting currently exists. The development of LUCA probably took place well after the origin of life, and thus under completely different circumstances. Some have suggested that LUCA or the bacterial and archaeal last common ancestors were survivors of hot conditions, such as an impact event (Gogarten-Boekels *et al.*, 1995; Nisbet & Sleep, 2001). Therefore, traditional genome phylogeny can only give us limited information about the origin of life itself.

Nonetheless, prebiotic chemistry is thought to have left a distinct imprint on molecular biology, particularly in the form of metalloenzymes. Metalloenzymes are proteins that bind metal or metal compounds and coordinate the metal’s regular catalysis (Karlin, 1993). The metal ion cofactors are known to greatly enhance enzyme catalytic potential and protein stability (Cvetkovic *et al.*, 2010). Of all characterized modern proteins, about a third require a metal cofactor for function (Rosenzweig, 2002). However, the evidence indicates that almost 50% of metalloproteins in *Pyrococcus furiosus* are uncharacterized and include metals not observed in characterized proteins from *P. furiosus* (Cvetkovic *et al.*, 2010). The importance of metal cofactors in modern biochemistry may thus be even greater than previously thought. A survey of metal usage in modern enzymes is summarized in Table 3. These enzymes are grouped in road categories as designated by the Enzyme Commission. Oxidoreductases catalyze the transfer of hydrogen or oxygen atoms or electrons from one substance to another; transferases transfer functional groups from one substance to another; hydrolases cleave chemical bonds through the formation of water; lyases add or remove func-



**Table 3** Metal cofactor usage, indicated by 'x' if present, in the six major categories of enzymes as defined by the Enzyme Commission (Webb, 1992). Metal usage is surveyed from the Kyoto Encyclopedia of Enzyme Genes and Genomes database (Kanehisa *et al.*, 2006)

	Cd	Ca	Co	Cu	Fe	Fe-S	Mn	Mg	Mo	Ni	K	Se	W	Zn
Oxidoreductases		x	x	x	x	x	x	x	x	x	x	x	x	x
$A^- + B \rightarrow A + B^-$														
Transferases	x	x	x		x	x	x	x			x			x
$A-X + B \rightarrow A + B-X$														
Hydrolases	x	x	x		x	x	x	x	x	x	x			x
$A-X + H_2O \rightarrow A-OH + B-H$														
Lyases		x	x	x	x	x	x	x			x			x
$A-B - X \rightarrow A=B + X$														
Isomerases			x		x		x	x						x
$A-B \rightarrow B-A$														
Ligases							x	x						x
$A-X + B \rightarrow A-B + X$														

tional groups without hydrolysis; isomerases bring about intramolecular rearrangement; and ligases use ATP to bring together new molecules. Interestingly, oxidoreductases, which catalyze key energy-generating reactions, exhibit the broadest range of metal cofactors. Although it is possible that some of these cofactors were later evolutionary innovations, perhaps triggered by the onset of oxidative weathering in the late Archean (e.g. Boyd *et al.*, 2011), the ability of metals to catalyze biochemically useful reactions suggests that they may also have played a prominent role in prebiotic chemistry (cf. Section 'Catalysis', Fig. 3). A model for the origin of life will therefore be more convincing if it includes geological processes that constantly replenish the supply of transition metals.

The results of protein evolution studies indicate that iron-, manganese-, cobalt-, nickel-, molybdenum-, and tungsten-containing proteins are ancient and probably existed at the time of LUCA (Dupont *et al.*, 2010; Schoepp-Cothenet *et al.*, 2012a,b). Members of the 'Complex-Iron-Sulfur-Molybdoenzyme' (CISM) family have received particular attention as they appear to have been involved in the harvest of energy at the earliest stages of life (Schoepp-Cothenet *et al.*, 2012b). Tungsten can substitute for molybdenum in CISM (Schoepp-Cothenet *et al.*, 2012b) and is more soluble under reducing conditions (Schoepp-Cothenet *et al.*, 2012a). But because tungsten is much rarer than molybdenum in the Earth's crust and mantle, the importance of CISM-like catalysts in prebiotic chemistry may indicate that at least some components of early metabolism evolved in geological settings that were particularly enriched in metals above crustal background, such as acidic hydrothermal systems (Section 'Hydrothermal systems').

It is thought that the earliest enzymes mimicked slow abiotic reactions that were already taking place (Lazcano & Miller, 1999). An example from laboratory experiments is the demonstration that Fe/Ni sulfides can catalyze the reduction of CO<sub>2</sub> to acetyl thioesters (Huber & Wächtershäuser, 1997). Thus, some metalloenzymes and their catalytic mechanisms may have originated during the

transition from prebiotic chemistry to genetically directed metabolism (van der Gulik *et al.*, 2009; Schoepp-Cothenet *et al.*, 2012a). As the primitive genetic system took metabolic control of its chemical context, prebiotic reactions catalyzed by metal ions or mineral surfaces may have been replaced by their enzymatic counterparts. However, the potential catalytic reactions of most transition metal minerals are unknown, particularly their reactions under different pH, temperature, and pressure conditions (Section 'Future research directions'). More information of this kind, in particular about the types of organic metal complexes that could have formed under prebiotic conditions (cf. Sander & Koschinsky, 2011), about the distribution of particulate mineral grains at the Earth's surface, and about the metal requirements of the most ancient enzyme sub-categories may thus further elucidate the relative importance of different environmental settings for certain steps in the origin of life.

If transition-metal minerals catalyzed the important reaction steps that eventually resulted in metabolic pathways, then an unavoidable conclusion is that some of the earliest steps leading to life occurred on metallic mineral surfaces. If it can be demonstrated that other minerals such as clays were essential for the formation of certain ligands or for polymerization of monomers, then this may be evidence for a physical linkage between different geological settings (e.g. metal-rich hydrothermal settings or meteorite debris linked with marine or lacustrine sediments) during the origin of life.

## FUTURE RESEARCH DIRECTIONS

One appeal of a single setting for the origin of life is the possibility to artificially recreate most relevant prebiotic processes in the laboratory. If, however, the origin of life were indeed a global or at least regional phenomenon, it will clearly make experimental research under plausible environmental conditions more challenging. Nevertheless, progress toward testing the hypothesis of a global chemical

reactor can still be made by further exploring the effects of geochemical gradients and by better constraining the catalytic potential of diverse mineral surfaces and solutes under different conditions.

### Exploring geochemical gradients

As discussed above (Section ‘The benefits of gradients in prebiotic chemistry’), the physicochemical properties of many mineral surfaces and organic compounds can change with temperature, pressure, pH, or fluid composition. The importance of collecting more data of this kind has been widely appreciated only recently by experimentalists. For example, the use of geochemically relevant buffers is relatively new to origin of life experiments (Shock, 1990; Holm & Andersson, 2005; McCollom & Seewald, 2007; Powner *et al.*, 2009), and the behavior of biochemical reactions in disequilibrium environments or in flow-through systems is completely unexplored (Shock & Schulte, 1998). The few studies that have been conducted in plausible prebiotic conditions were performed in closed systems with one potential catalyst, and only one possible reaction was assayed (McCollom & Seewald, 2007).

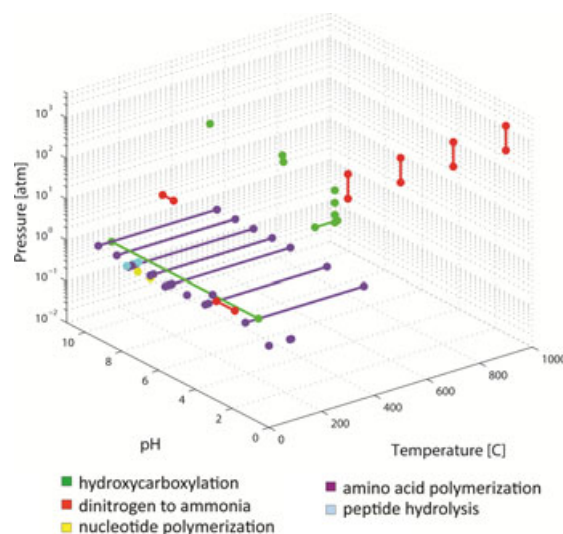
Future experiments could benefit from exploring a wider range of conditions that represent the expected diversity of settings in the Hadean (Hazen & Sverjensky, 2010). For example, it would be useful to test how the products of a Urey–Miller type reaction behave and react when exposed to evapo-concentration processes on a beach or to alkaline or acidic and metal-rich fluids in a hydrothermal vent (such as with a setup similar to that used by Mielke *et al.*, 2010). Furthermore, it is known that at the extreme ends of salinity, pH and temperature gradients, biomolecules can decompose (Demirjian *et al.*, 2001; Tenchov *et al.*, 2006), but these stability limits need to be further explored in an environmental context.

### Wider reaction space

Recent experimental studies have measured the ability of individual minerals to catalyze organic synthesis reactions (Cody *et al.*, 2004; Foustoukos & Seyfried, 2004; Schoonen *et al.*, 2004), but not all reactions require the same minerals. The Hadean Earth hosted a plethora of mineral species (Hazen *et al.*, 2008; Hazen & Ferry, 2010; Papineau, 2010) whose substrates and products were frequently exchanged by various mixing processes. Clearly, the next generation of prebiotic chemistry experiments would benefit from exploring a wider range of potential mineral catalysts. Moreover, as has been noted before (Hazen & Sverjensky, 2010), the incorporation of realistic physical and chemical conditions, in which complex combinations of compounds interacted within gradients and fluid fluxes, could move prebiotic synthesis

experiments beyond the synthesis of simple building blocks.

As for biological enzymes, mineral catalysis for any given reaction has an optimum suite of environmental conditions which will determine the efficiency of the reaction. Expanding the experimental reaction space of mineral catalysis would complement the already significant body of literature on mineral catalysis produced in recent decades (summarized in Fig. 6 and in Table S2). Because the Hadean Earth was composed of innumerable environmental micro-niches hosting chemical disequilibria capable of facilitating mineral-catalyzed prebiotic synthesis, added scientific value would result from constraining the limits of pressure (P), temperature (T), and pH for specific reactions. This knowledge could then be used to place constraints on the extent of plausible synthesis reactions taking place on the Hadean Earth, but also on asteroids and comets that delivered extraterrestrial organic precursors. Parts of the P/T/pH space (in particular very high temperatures) are precluded from interest by predicted organic chemistry. However, given the multiple parameter-space involved in these reactions, constraining this unexplored space may reveal heretofore unanticipated products under conditions potentially relevant to the origin of life. More specific suggestions regarding potential experiments in mineral surfaces research are discussed in Hazen & Sverjensky (2010).



**Fig. 6** Charted above is the chemical reaction space (temperature, pressure, pH) examined for a number of potentially relevant mineral-catalyzed prebiotic reactions. The figure does *not* include all mineral-catalyzed reaction studied so far, but a selection of the reactions most commonly discussed in the literature. The space examined does not indicate successful production, only the space which has been investigated. Values not reported are plotted as a 0 value on the respective axis. Not included in the plot are reactant suites and the time of reaction. For references see Supplementary Table S2.

### Homogeneous catalysis

The role of minerals in heterogeneous catalysis has been emphasized repeatedly above; however, metals in solution might be more accessible catalysts in aqueous environments. Recent advances in structural inorganic chemistry allow the investigation of their importance in the origin of life (Morowitz *et al.*, 2010).

Transition metals are most abundant in sulfide phases, and before the rise of oxygen, hydrothermal alteration of oceanic crust would have been their major source to the ocean (Section 'Hydrothermal systems'). In addition to water-rock interactions at the seafloor, impacts of meteorites, some of which are more metal-rich than the Earth's crust, could have led to temporary enrichments of metals on the Hadean surface. Hence, different geological processes would have established gradients of transition metals in the ocean and in crustal settings.

The involvement of dissolved metals in prebiotic chemistry is an understudied subject (Morowitz *et al.*, 2010), although the rules of chemistry and physics governing those reactions are the same as in modern life forms as they were in the Hadean. For example, the compact, divalent zinc ion with a high affinity for oxygen is commonly used in extant organisms for rapid ligand-exchange reactions (Frausto da Silva & Williams, 1991; Shriver & Atkins, 1999). The multiple possible redox states of copper and iron, on the other hand, are the basis of many electron transfer reactions (Frausto da Silva & Williams, 1991; Shriver & Atkins, 1999). Different metals have different preferences for ligands and molecular geometries, and life exploits those preferences for its own chemical machinery. Based on these data, it seems plausible that dissolved metals could have played a significant catalytic role in prebiotic chemistry, and future experiments would benefit from exploring this possibility.

### CONCLUSION

We propose that investigations into the origin of life must account for the geochemical complexity of the early Earth system. The origin of life was a complex process that resulted in a global transformation of our planet; it is only reasonable to conclude that it required complex interactions among many processes and settings on a global scale.

Envisioning the origin of life in a global context is advantageous because it makes prebiotic chemistry more plausible and because the global context is an inescapable reality. Origin of life research is often discussed in terms of a dichotomy: productive chemical reactions vs. environmental relevance. We have argued that thinking about prebiotic processes in a global context eliminates the dichotomy and opens the possibility that the relevant chemical reactions are also the most productive.

How can we use this information in our search for life elsewhere? Life as we know it could probably not have originated without active geological processes (*e.g.* rock and hydrological cycles) and the environmental conditions that result from these processes. As a corollary, any rocky planetary body with water and active geological cycles may have the potential for a *de novo* origin of Earth-like life. As such, it may be more important for astrobiologists to understand the dynamic geological properties of a planetary body than to understand how exactly life originated on Earth.

Of course, a tremendous amount of laboratory and field-based research is required to demonstrate how natural reactions involving a variety of energy sources, catalysts, and organic and inorganic compounds can lead to reaction networks and biological systems. Much insight can be gained from highly focused experiments with one kind of molecule under one set of conditions. However, if one views the origin of life as a complex network of reactions occurring in multiple sets of conditions over extended periods of time and space, then this complexity should be reflected in the design of future experimental studies. This paper has not attempted to solve the problem of the origin of life, but rather to describe an approach that may prove useful for a field that is still in its beginning stages.

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## SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

**Table S1.** Organic synthesis reactions at low temperatures

**Table S2.** Selected mineral-catalyzed organic synthesis reactions, plotted in Figure 6 with colors indicated in column 1