Hydrothermal vents and the origin of life

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Abstract | Submarine hydrothermal vents are geochemically reactive habitats that harbour rich microbial communities. There are striking parallels between the chemistry of the H_2–CO_2 redox couple that is present in hydrothermal systems and the core energy metabolic reactions of some modern prokaryotic autotrophs. The biochemistry of these autotrophs might, in turn, harbour clues about the kinds of reactions that initiated the chemistry of life. Hydrothermal vents thus unite microbiology and geology to breathe new life into research into one of biology's most important questions — what is the origin of life?

The chemistry of life is the chemistry of reduced organic compounds, and therefore all theories for the origin of life must offer testable hypotheses to account for the source of these compounds. The best-known theories for the origin of organic compounds are based on the notion of an 'organic soup' that was generated either by lightning-driven reactions in the early atmosphere of the Earth or by delivery of organic compounds to the Earth from space (BOX 1). When submarine hydrothermal vents were discovered 30 years ago, hypotheses on the source of life's reduced carbon started to change. Hydrothermal vents revealed a vast and previously unknown domain of chemistry on the Earth. These vents harbour rich ecosystems, the energy source of which stems mainly from mid-ocean-ridge volcanism[1,2]. The 360°C sulphide chimneys of the vent systems are primordial environments that are reminiscent of early Earth, with reactive gases, dissolved elements, and thermal and chemical gradients that operate over spatial scales of centimetres to metres. This discovery had an immediate impact on hypotheses about the origin of life, because it was recognized that the vent systems were chemically reactive environments that constituted suitable conditions for sustained prebiotic syntheses[3].

In 2000, a completely new type of vent system was discovered that is characterized by carbonate chimneys that rise 60 metres above the ultramafic sea-floor[4,5]. This vent system was named the Lost City hydrothermal field (LCHF), and might be particularly relevant to our understanding of the origins of life. The ultramafic underpinnings of the Lost City system have a similar chemical composition to lavas that erupted into the primordial oceans on early Earth[5,6]. Consequently, the LCHF provides insights into past mantle geochemistry and presents a better understanding of the chemical constraints that existed during the evolutionary transition from geochemical to biochemical processes.

Hydrothermal vents occur at sea-floor spreading zones and have a global distribution (FIG. 1): vent systems have been discovered at almost all sea-floor locations that have been studied in detail[7]. At spreading zones, magma chambers that contain molten rock (800–1,200°C) discharge lavas onto the ocean floor over time periods that range from <10 years between eruptions to >50,000 years between eruptions[8]. These eruptions produce black smokers and associated diffuse flow systems that host dense and diverse biological communities[9,10]. By contrast, the mountains of the Lost City-like systems are tens of kilometres off-axis, rarely contain volcanic rocks and are formed by sustained fault activity that has lasted for millions of years[4,5,11]. Lost City systems are profoundly different from black smokers, so it is important to contrast the two (for an in-depth comparison of Lost City systems and black smokers, see REF. 12).

Black smokers

Examples of black smokers, such as the Faulty Towers complex (FIG. 2a), are located directly above magma chambers that are found 1–3 kilometres beneath the sea-floor[12]. Black smoker chimneys emit hot (up to 405°C), chemically modified sea-water[13]. Beneath the fissured sea-floor, downwelling sea-water comes into close contact with the magma chamber during its circulation from the ocean floor, before moving through the crust to re-emerge at the vents. Effluent at black smokers is typically acidic (pH 2–3) and rich in dissolved transition metals[14], such as Fe(II) and Mn(II). Because the black smoker systems are fuelled by volcanoes, black smoker fluids commonly contain high concentrations of

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Box 1 | **Prebiotic soup theory**

The concept that life arose from a prebiotic soup or primeval broth that covered the Earth is generally attributed to Oparin[84] and Haldane[85]. The theory received support from Miller's[86] demonstration that organic molecules could be obtained by the action of simulated lightning on a mixture of the gases CH_4, NH_3 and H_2, which were thought at that time to represent Earth's earliest atmosphere. The organic compounds that were measured included hydrogen cyanide (HCN), aldehydes, amino acids, oil and tar. Additional amino acids were produced by Strecker synthesis through the hydrolysis of the reaction products of HCN, ammonium chloride and aldehydes, and in later experiments polymerization of HCN produced the nucleic acid bases adenine and guanine[87]. However, further condensation and polymerization of these organic precursor molecules requires some mechanism to promote their concentration. Suggestions for this mechanism have included evaporation of tidal pools, adsorption to clays, concentration in ice through eutectic melts and giant oil slicks. Temperature cycling might also have been a factor in peptide production, although cold to freezing conditions are now considered to be more favourable for prebiotic soup[87].

In their original models, Oparin[84] and Haldane[85] assumed that protein was the source of genetic information, which would have been transferred directly from protein to protein as colloidal organic droplets (coacervates) that subsequently multiplied through the assimilation of further organic molecules. Oparin[84] favoured abiotic synthesis, in which an information-containing protein was the first step to life. By contrast, Haldane[85] proposed that some form of metabolism was the first step.

This issue of an 'information first' (or RNA world) versus a 'metabolism first' (or autotrophic origins) mechanism is still debated in the origin-of-life community today. Current formulations of the information-first view posit that an evolutionary transition occurred from peptide nucleic acids to tetrose nucleic acids, and eventually to RNA[87,88], during which tetrose was derived from formaldehyde condensations and bases were derived from HCN condensations. A large repertoire of RNAs then took over as self-replicating entities in a prelude to the advent of DNA and proteins. According to this view, the various stages that are involved in the origin and evolution of life from the prebiotic epoch culminated in exhaustion of the initial prebiotic supply of preformed organic molecules, prompting the evolutionary-origin genetically encoded biosynthetic pathways as compensation. Variants of the prebiotic broth theory propose that the essential building blocks of life were synthesized in space and reached early Earth by comets[89]. Although there has been no debate about the occurrence of organic molecules in comets, this mechanism still produces organic soup, but without the help of lightning.

An alternative proposal to prebiotic broth involves the H_2-dependent chemistry of transition-metal sulphide catalysts in a hydrothermal-vent setting. Such chemical conversions are similar to those involved in the CO_2-reducing biochemistry of modern microorganisms that use the Wood–Ljungdahl acetyl-coenzyme A (acetyl-CoA) pathway and present a plausible starting point for biochemical evolution. However, this pathway leads not to prebiotic broth, but to acetyl-CoA, an energy-rich thioester that could be the most central carbon backbone in microbial metabolism. The synthesis of acetate and CH_4 from H_2 and CO_2 releases energy, and therefore energy need not be derived from lightning or conditions in space. Hence, the reactions typically take place readily on the Earth, both in modern acetogenesis and methanogenesis, as well as in abiogenic CH_4 or acetate production at contemporary hydrothermal vents. The favourable thermodynamics of CH_4 and acetate formation could, in principle, support synthesis of more complicated biomolecules that could become concentrated at their site of synthesis[63].

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magmatic CO_2 (4–215 mmol per kg), H_2S (3–110 mmol per kg) and dissolved H_2 (0.1–50 mmol per kg), with varying amounts of CH_4 (0.05–4.5 mmol per kg) that is formed both through biogenic and abiogenic processes[12]. A range of temperatures exist, from the hot interior of black smokers to the interface with cold (2°C), oxygenated sea-water (FIG. 2b).

The dissolved gases and metals in black smokers fuel the microbial communities that serve as the base of the food chain in these ecosystems. Some of the archaea in black smokers can replicate at temperatures up to 121°C[15], which is currently thought to be the upper temperature limit of life. There are also examples of ancient, fossilized black smokers, including one found in 90-million-year-old copper deposits in Cyprus that contained fossilized fauna[16] and another found in 3,235-million-year-old sulphide deposits in Western Australia that contained filamentous microfossils[17].

Lost City systems
The off-axis vents are radically different to black smokers. However, our current understanding of these systems is based on research into only one system: the LCHF[5,18]. Off-axis vents are located several kilometres away from the spreading zone. Their exhalate has also circulated through the crust, where it can be heated up to ~200°C[19,20], but their waters do not come into close contact with the magma chamber. Supplementary information S1 (figure) shows a schematic view of the LCHF, which is located near the summit of a 4,000-metre mountain named the Atlantis Massif that sits on 1.5–2-million-year-old crust, at a water depth of ~750 metres[4,21].

Fluid circulation within the massif is driven by convection that dissipates heat from the underlying mantle rocks, and perhaps, in part, by exothermic chemical reactions between the circulating fluids and host rocks. These rocks have different compositions compared with those of submarine volcanoes, because they are dominated by the magnesium- and iron-rich mineral olivine and because they have lower silica concentrations. This geochemical setting results in a highly alkaline (pH 9–11) effluent and a combination of extreme conditions that have not previously been observed in the marine environment, including venting of 40–91°C hydrothermal fluids with high concentrations of dissolved H_2, CH_4 and other low-molecular-mass hydrocarbons, but almost no dissolved CO_2 (REFS 5,20,22). As discussed below,
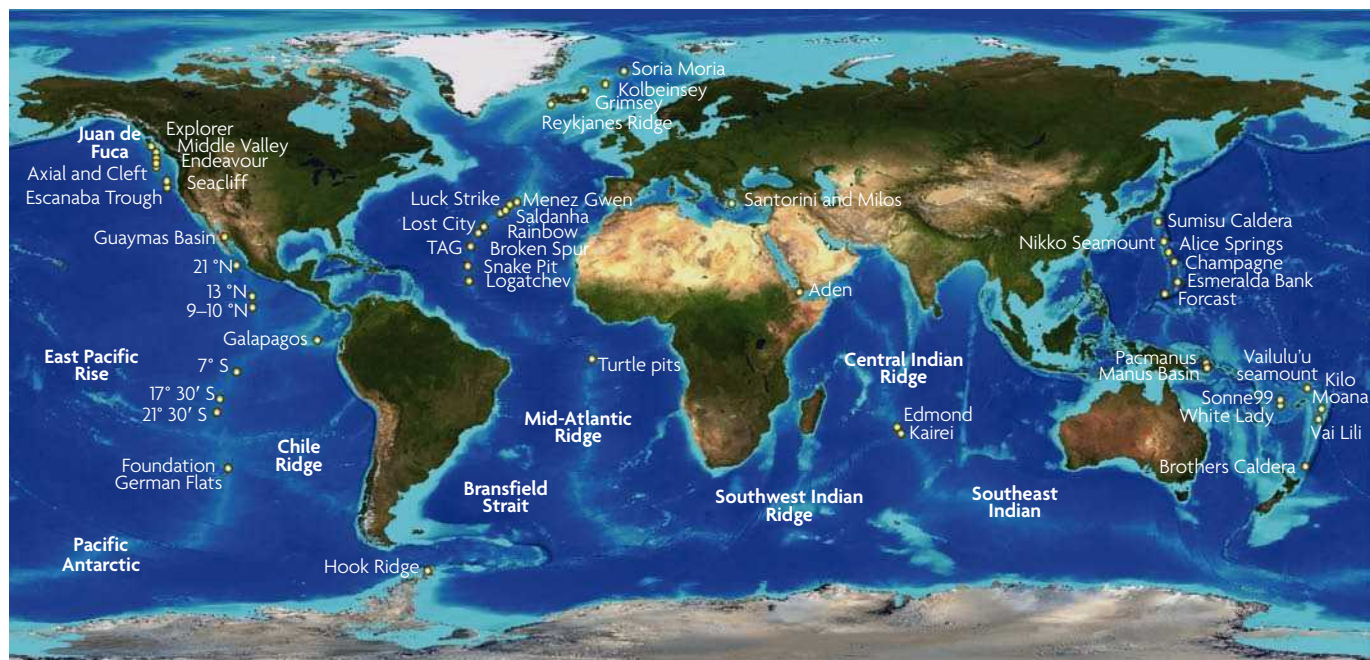
Figure 1 | **Global distribution of known hydrothermal vents.** Temperature and chemical anomalies hint that many more sites exist throughout the world's oceans. Data courtesy of D. Fornari and T. Shank, Woods Hole Oceanographic Institute, Massachusetts, USA.

alkaline pH is an important property of vents that should be considered when contemplating the biochemical origins of life.

Mixing of warm, high-pH fluids with sea-water results in carbonate precipitation and the growth of chimneys that tower up to 60 metres above the surrounding sea-floor. [14]C radioisotopic dating indicates that hydrothermal activity has been ongoing for at least 30,000 years[19], whereas recent uranium–thorium dating indicates that venting has been active for ~100,000 years[23]. A substantial proportion of the exposed sea-floor that is on, and near to, slow- and ultra-slow spreading ridges consists of ultramafic rocks that are similar to those that host the LCHF[24–26]. These rocks are sites of an important set of geochemical reactions named serpentinization (BOX 2), and have been producing geological H_2 for as long as there has been water on the Earth.

What grows at Lost City, and how?

Metagenomics and environmental sequencing of ribosomal RNA have shown that microbial communities in actively venting carbonate chimneys in the LCHF (FIG. 2c–e) are dominated by a novel phylotype of anaerobic methanogens from the Methanosarcinales order[5,27,28]. These methanogens can use several organic compounds, some of which have been implicated in anaerobic methane oxidation (AMO) in both hydrothermal sediments[29,30] and methane seeps[31,32]. In chimneys that have little or no active venting, the Lost City Methanosarcinales (LCMS) group is replaced by a single phylotype of the anaerobic methanotrophic clade ANME-1. A diverse bacterial assemblage populates the chimney exteriors, where sulphur-oxidizing and methane-oxidizing bacteria use the interface of oxygenated sea-water with H_2- and CH_4-rich

hydrothermal fluid. Sulphate-reducing Firmicutes have also been identified; these organisms might serve as a link between the high-temperature, anaerobic chimney interiors and the sea-water-bathed chimney exteriors. Some of the relevant core metabolic reactions that underlie microbial growth at the LCHF are summarized in TABLE 1. The vent effluent is devoid of oxygen and harbours only anaerobes, although aerobes occur where there is contact with ocean water.

Where the LCHF carbonate chimneys are bathed in >80°C hydrothermal fluid, the LCMS group forms dense biofilms that are tens of micrometres thick and comprise ~100% of the archaeal community[28]. Recently, methyl-coenzyme M reductase (*mcrA*) gene sequences that correspond to both LCMS and ANME-1 have also been recovered from LCHF carbonate chimneys[28]. ANME-1 has been identified in numerous environments, including CH_4 seeps in anoxic marine sediments, CH_4 hydrates, carbonate reefs in the Black Sea and mud volcanoes[31–35]. Genomic evidence indicates that anaerobic, methane-oxidizing archaea harbour nearly all of the genes necessary for methanogenesis, including *mcrA*[36,37], but it has been unclear whether LCMS and ANME-1 are sources or sinks of CH_4 within the Lost City system.

In all marine environments in which AMO is known to occur, anaerobic, methanotrophic archaebacteria co-occur with sulphate-reducing eubacteria, commonly in tightly coupled consortia[32], although cells are not always in direct physical contact with each other[29]. However, a recent report has also linked AMO with denitrification in a freshwater canal[38]. Incubation experiments show that the marine consortia represent a syntrophic metabolic relationship between CH_4-oxidizing archaea

Consortia
Two or more different microorganisms that associate during growth to form characteristically ordered structures.
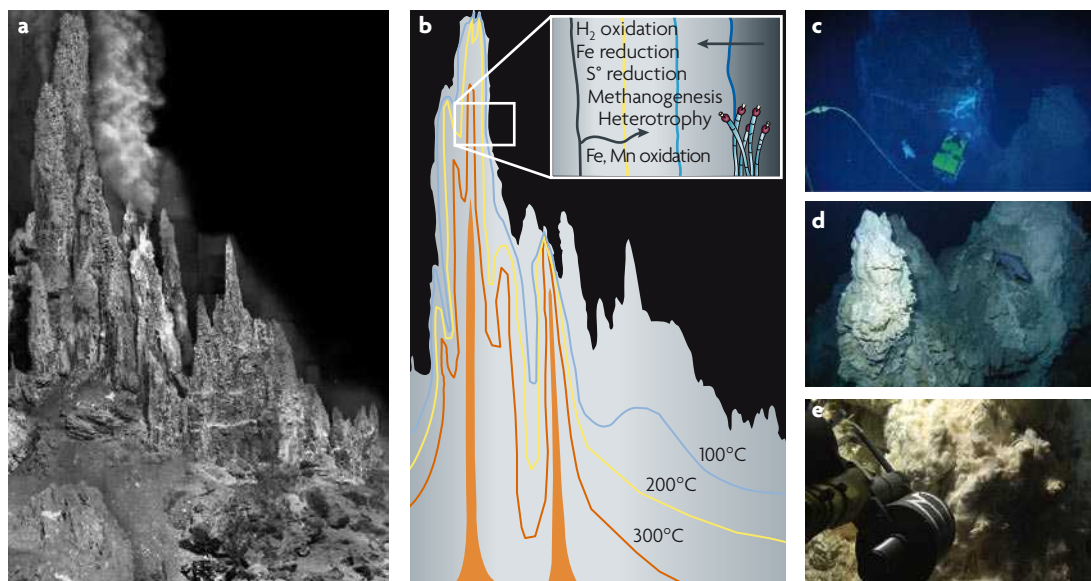
Figure 2 | **Hydrothermal vents.** There are two main types of hydrothermal vent: the black smoker type (**a,b**) and the Lost City type (**c–e**). **a** | A black smoker in the Faulty Towers complex in the Mothra hydrothermal field on the Endeavour Segment of the Juan de Fuca Ridge. The tallest chimney rises 22 metres above the sea-floor. The 'furry' appearance of the chimneys reflects the fact that the chimney walls are encrusted in dense communities of tube worms, scale worms, palm worms, sulphide worms and limpets. The two-pronged chimney in the middle with an active plume is a 300°C chimney called Finn, from which a 121°C organism was cultured that uses Fe(III) as an electron acceptor in the presence of N_2 and CO_2 (REF. 15). **b** | The outer surface of black smoker chimneys is bathed in a mixture of 2°C, oxygenated sea-water and warm vent fluid that escapes from within the structure. The inner walls that form the boundary of the central up-flow conduits commonly exceed 300°C, and temperatures are fixed by a steady supply of rapidly rising, strongly reducing vent fluid. Intermediate conditions exist as gradients between these extremes. Changes in microbial abundance, diversity and community structure have been associated with inferred environmental gradients in the chimney walls[99,100]. **c** | Microbial sampling at the Lost City hydrothermal field. The robotic vehicle Hercules is shown hovering near the summit of the 60-metres-tall Poseidon complex. White areas are active or recently active sites of venting. **d** | The top left part of the Nature Tower. Wreck-fish, which are ~1 metre in length and are commonly found at a water depth of 750 metres, routinely investigated the vehicles. The Poseidon complex has four pinnacles, two of which are shown here. Actively venting edifices are composed of aragonite ($CaCO_3$) and brucite ($Mg(OH)_2$). The grey–brown material also contains carbonate, but is richer in calcite that has recrystallized from aragonite. **e** | A close up of a 75°C, diffusely venting carbonate chimney showing a titanium water sampler. Dense colonies of filamentous bacteria thrive in the high pH, CH_4- and H_2-rich fluids. The insides of the chimneys are dominated by a single phylotype of archaea from the Methanosarcinales order that grow at 80°C. A phylotype of anaerobic methanotrophic archaea are restricted to lower-temperature chimneys. Bacterial 16S ribosomal RNA gene sequences correspond to a diverse community that includes species of *Methylobacter* (or *Methylomonas*), species of *Thiomicrospira*, members of the Firmicutes phylum and *Desulfotomaculum alkaliphilus*[28]. Parts **a,b** courtesy of D. Kelley and J. Deloney, University of Washington, USA. Images **c–e** courtesy of D. Kelley, Institute for Exploration, University of Rhode Island, USA, and the National Ocean and Atmospheric Administration Office of Ocean Exploration.

Stable isotope study
The use or analysis of stable isotopes, such as ^2H, ^{13}C or ^{15}N, that do not undergo radioactive decay. Isotope discrimination properties of an enzymatically catalysed process can produce characteristic isotope ratios, for example ^{13}C or ^{12}C, that differ from those generated by various non-enzymatic processes. This provides insights into the partitioning of elements during microbial metabolism, and in geochemistry, can provide insights into the biological and geological source of substances such as CH_4.
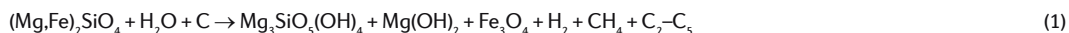
and sulphate-reducing bacteria[39–42]. AMO is not energetically feasible unless sulphate-reducing bacteria or some other metabolic group of bacteria or archaea are present to use H_2 that is generated from the anaerobic oxidation of CH_4.

Almost all marine sites where AMO has been shown to occur are cold, sediment-hosted environments that are supported by CH_4 hydrates, CH_4 seeps or mud volcanoes. The only two exceptions are the Guaymas Basin, where warm sediments overlie a hydrothermal system and AMO can occur at temperatures as high as 85°C[30,43,44], and the LCHF, where biofilms that are composed of organisms related to the ANME-3 group are in direct contact with serpentinization-derived CH_4 at temperatures in excess of 90°C[5,28]. The results from earlier phylogenetic and natural stable isotope studies[5,27,28,45]

were unable to determine whether actively venting carbonate chimneys at Lost City are sites of methanogenesis or AMO. Newer data, however, indicate that CH_4 and associated short hydrocarbons in the effluent of LCHF are not formed by biological activity, but instead are of geochemical origin[22]. This, in turn, suggests that LCMS and ANME-1 are probably oxidizing CH_4 at LCHF, and that they are doing so in the presence of abundant environmental H_2. This interpretation would be consistent with the recent intriguing results of Moran *et al.*[46], who showed that high partial pressures of H_2 did not significantly inhibit AMO in active sediments, but that methyl sulphide was inhibitory, which indicated an important role for methyl sulphide and only a peripheral role, if any, for H_2 in AMO in this sediment system.

Box 2 | **Serpentinization: the source of H_2 and CH_4 at Lost City**

Hydrothermal vents, and Lost City in particular, have sparked interest in a geochemical process known as serpentinization[90]. At off-axis vents, sea-water invades the warm (100°C) to hot (400°C) oceanic crust through cracks and crevasses where the chemical reactions of serpentinization take place. The relevant sea-water constituents for the serpentinization reaction are H_2O and CO_2 (dissolved as HCO_3^-). The relevant crustal constituents are Fe^{2+}-containing rocks[91]. At Lost City, this rock consists mainly of the mineral olivine (~$Mg_{1.6}Fe_{0.4}SiO_4$). Seismic data indicate that the fluids beneath Lost City percolate to depths of 500 metres (or deeper) beneath the sea-floor at moderately high temperatures (150–200°C) The crust beneath Lost City is 1–2 million years old based on magnetic anomaly information, and it is likely that the rocks which are ~500 metres to 1 kilometre beneath the sea-floor reach temperatures of ~300°C. Under these conditions, Fe^{2+} in the rocks reduces H_2O to produce Fe^{3+}, H_2 and hydrocarbons according roughly to Equation 1.

$$(Mg,Fe)_2SiO_4 + H_2O + C \rightarrow Mg_3SiO_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2 + CH_4 + C_2–C_5 \qquad (1)$$

Unaltered and hydrothermally altered mantle rocks contain various carbon compounds, including graphite, CH_4 and CO_2. Work by Proskurowski *et al.*[22] indicates that beneath Lost City, hydrocarbons can be generated according to Equation 2.

$$CO_{2aq} + [2 + (m/2n)]H_2 \rightarrow (1/n)C_nH_m + 2H_2O \qquad (2)$$

The resulting minerals are magnetite (Fe_3O_4), which contains Fe^{3+} as a product of Fe^{2+} oxidation, brucite ($Mg(OH)_2$) and a hydroxylated magnesium–iron silicate called serpentine ($Mg_{2.85}Fe_{0.15}Si_2O_5(OH)_4$), after which the process is named.

Serpentinization has probably been ongoing since there were oceans on the Earth[92]. One cubic metre of olivine can deliver approximately 500 moles of H_2 during serpentinization[93]. Most of the Earth's oceanic crust consists of olivine (or pyroxene, which can also participate in serpentinization reactions), and the total volume of the Earth's ocean is estimated to circulate through hydrothermal vents every ~100,000 years[93]. Thus, the vast amounts of Fe^{2+}, the Earth's electron reservoir for H_2 production via serpentinization, in the mantle is nowhere near exhaustion[92]. Serpentinization delivers, and has always delivered, a substantial amount of H_2 as a source of electrons for primary production in submarine ecosystems. At the Lost City hydrothermal field (LCHF), serpentinization produces H_2 that can reduce CO_2 to CH_4 geochemically[22]. The same geochemical process might have given rise to the energy-releasing chemical reactions at the core of carbon and energy metabolism in methanogens and acetogens, reactions that were eventually augmented by cofactors and enzymes[63].

Serpentinization occurs both beneath the hot and acidic (pH 2–3) black smokers and within the cooler and alkaline (pH 9–11) off-axis vent systems, such as Lost City[12]. Therefore, although both types of vent would have offered a pH gradient that was similar to the Hadean ocean (see the main text), the lower temperatures found at off-ridge vents would provide more favourable conditions for sustained abiotic synthesis and accumulation of reduced carbon compounds[58]. The chimneys at the LCHF are mainly composed of carbonates, rather than of iron monosulphide (FeS) minerals, which because of their catalytic properties play a central part in our thinking about biochemical origins[63–65]. However, the Hadean ocean was replete with Fe(II), and therefore FeS chimneys would have been abundant at that time. Thus, although the chemistry of the serpentinization process in the Hadean was perhaps not much different than that observed today, the specific geochemical conditions at the vent–ocean interface in the Hadean would have differed markedly from those observed in today's oxic oceans[64].

Clues from Lost City effluent CH_4

The millimolar concentrations of abiogenic CH_4 present in the Lost City effluent do not seem to originate from marine CO_2 in down-draft waters, but instead seem to originate from CO_2 that has leached from an inorganic carbon source in the mantle[22]. Provided that H_2 from serpentinization is the reductant for CH_4 synthesis at LCHF, the overall reaction that produces CH_4 in the subsea-floor hydrothermal system is the same as that used by methanogens to fuel carbon and energy metabolism (TABLE 1). This thought-provoking finding raises an important question: is the geochemical synthesis of CH_4 at Lost City a model for the simple types of core chemical reactions from which biological CH_4 production arose?

Keeping in mind that the answer might be no, the idea is worth pursuing. It should be noted that proponents of the idea that life started from prebiotic soup (BOX 1) would certainly disagree with this view[47], but we will not argue their case here. Hypotheses about the origin-of-life chemistry have long been couched in terms of chemical equilibria[48]. However, life is far from an equilibrium process. In all living systems, there is a

main chemical reaction at the core of energy metabolism — the chemical reaction that cells use to synthesize their ATP — and a few examples of core chemical reactions that generate ATP in the bacteria and archaea that inhabit the Lost City are listed in TABLE 1.

Hydrothermal vents have breathed fresh life into a century-old concept regarding the origin of life. This concept is known today as autotrophic origins and posits that life started from CO_2, that the first organisms were autotrophs and that these autotrophs obtained their reduced carbon from CO_2 and other simple C_1 compounds, using H_2 as the main electron donor[3]. Central to some versions of the autotrophic origins hypothesis is the view that the acetyl-coenzyme A (acetyl-CoA) pathway of CO_2 fixation is the most ancient among modern CO_2-fixing pathways[49,50] and that the biochemistry of this pathway might parallel a simpler abiotic chemistry at the origin of metabolism. The acetyl-CoA pathway that is found in modern acetogens and methanogens is particularly relevant to this hypothesis. This is because, in contrast to the other four pathways of CO_2-fixation that are known[51,52], the acetyl-CoA pathway not only

Table 1 | **Anaerobic and aerobic microbial metabolic reactions and potential energy yields in hydrothermal vent environments**

Metabolism	Reaction	$\Delta G^{0\prime}$ (kJ per mole)*	Examples in vent environments
Anaerobic			
Methanogenesis	$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O$ $CH_3CO_2^- + H_2O \rightarrow CH_4 + HCO_3^-$ $4\,HCOO^- + H^+ \rightarrow 3\,HCO_3^- + CH_4$	−131 −36 −106	*Methanococcus* spp. common in magma-hosted vents; Methanosarcinales at Lost City
S° reduction	$S^\circ + H_2 \rightarrow H_2S$	−45	Lithotrophic and heterotrophic; hyperthermophilic archaea
Anaerobic CH_4 oxidation	$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$	−21	*Methanosarcina* spp. and epsilonproteobacteria at mud volcanoes and methane seeps
Sulfate reduction	$SO_4^{2-} + H^+ + 4\,H_2 \rightarrow HS^- + 4\,H_2O$	−170	Deltaproteobacteria
Fe reduction	$8\,Fe^{3+} + CH_3CO_2^- + 4\,H_2O \rightarrow 2\,HCO_3^- + 8\,Fe^{2+} + 9\,H^+$	Not calculated‡	Epsilonproteobacteria, thermophilic bacteria and hyperthermophilic Crenarchaeota
Fermentation	$C_6H_{12}O_6 \rightarrow 2\,C_2H_6O + 2\,CO_2$	−300	Many genera of bacteria and archaea
Aerobic			
Sulfide oxidation§	$HS^- + 2\,O_2 \rightarrow SO_4^{2-} + H^+$	−750	Many genera of bacteria; common vent animal symbionts
CH_4 oxidation	$CH_4 + 2\,O_2 \rightarrow HCO_3^- + H^+ + H_2O$	−750	Common in hydrothermal systems; vent animal symbionts
H_2 oxidation	$H_2 + 0.5\,O_2 \rightarrow H_2O$	−230	Common in hydrothermal systems; vent animal symbionts
Fe oxidation	$Fe^{2+} + 0.5\,O_2 + H^+ \rightarrow Fe^{3+} + 0.5\,H_2O$	−65	Common in low-temperature vent fluids; rock-hosted microbial mats
Mn oxidation	$Mn^{2+} + 0.5\,O_2 + H_2O \rightarrow MnO_2 + 2\,H^+$	−50	Common in low-temperature vent fluids; rock-hosted microbial mats; hydrothermal plumes
Respiration	$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$	−2,870	Many genera of bacteria

*From REFS 73,103 and W.J. Brazelton (personal communication). ‡Some hyperthermophiles from the Archaea and Bacteria domains can couple the reduction of Fe with the oxidation of H_2 (REFS 104,105). §Some epsilonproteobacteria from subsea-floor hydrothermal vents, including newly erupted vents, can oxidize H_2S to S° (REF. 106).

Chemiosmotic coupling
The coupling of endergonic and exergonic reactions through a proton motive force. Chemiosmotic coupling results in the conservation of chemical energy. In its most familiar form, chemiosmotic coupling entails the pumping of protons from the inside of the cell to the outside of the cell as electrons are passed from a donor to an acceptor through an electron transport chain in the prokaryotic plasma membrane. This generates a pH and electrical-potential gradient across the plasma membrane known as the proton motive force. The proton motif force represents electrochemical energy that can be harnessed in various ways, but the best-known of these involves ATPases, also called coupling factors, which synthesize ATP from ADP and inorganic phosphate as protons pass through them to re-enter the cytoplasm.

provides a source of carbon, but is also the source of ATP. During the reduction of CO_2 with electrons from H_2, acetogens and methanogens use the acetyl-CoA pathway to generate an ion gradient that can be harnessed by chemiosmotic coupling[53–55]. Using CO for either methanogenesis or acetogenesis instead of H_2 and CO_2 provides more energy[56], and thus might be of interest in the context of the origins of life.

Such considerations bring C_1 metabolism into focus and have drawn attention to the thermodynamic equilibria of carbon species that result from the H_2–CO_2 couple at hydrothermal vents (FIG. 3). In the hot (>350°C) conditions of black smokers, carbon that is in equilibrium with water, even in the presence of significant levels of H_2, usually occurs as CO_2. As temperatures decrease to 150°C or lower, as at the LCHF, reduced-carbon species are favoured[57,58]. McCollom and Seewald[59,60] investigated the equilibria that are present between H_2, CO_2 and reduced C_1 species in conditions that mimicked serpentinization-driven reactions in off-axis vents. They found that, perhaps surprisingly, there are no substantial kinetic barriers in the reduction of CO_2 to formate (and CO), formaldehyde and methanol (the reactions proceed quickly), but that kinetic barriers in the reduction to CH_4 were appreciable[60]. In particular, the reaction $HCO_3^- + H_2 \rightarrow HCOO^- + H_2O$ was found to be "rapid on geologic timescales at temperatures as low as 100°C." (REF. 59)

If these experimental conditions approximate Lost City conditions in the subsurface, which seems likely, CH_4-rich Lost City effluents should contain reduced carbon species in addition to CH_4. Indeed, the Lost City fluids contain dissolved organic carbon at 95 μM, which is more than twice the concentration of local background (non-vent) water, and both formate and acetate are present in significantly higher concentrations than in deep sea-water[61,62]. The presence of acetate and formate (in addition to CH_4) fits well with the hypothesis that the types of chemical reactions which are catalysed by minerals in the mantle at Lost City are inorganic analogues, and even the possible evolutionary precursors, of the energy-releasing reactions that predated microbial metabolism[63]. If life started from CO_2, and life began in hydrothermal vents, then a better understanding of the reduction of CO_2 to CH_4, formate and acetate during serpentinization, and a better understanding of the catalysts and the chemical intermediates in that process, might allow new insights into the initial reactions that provided reduced carbon for life. Simple chemical compounds that could focus some of our current thinking on primordial biochemistry in the context of hydrothermal origins include transition metals and transition metal sulphides[64,65], methyl sulphide[63,66], thioesters[67], CO[68], acetyl phosphate[69] and carbonyl sulphide[70], as well as carbamyl phosphate, carboxy phosphate and formyl phosphate[63]. Theoretically, it would seem that CO and

Box 3 | The RNA-world concept

The discovery that RNA has catalytic activities[94], similar to proteins, but also carries heritable information, similar to DNA, had an immense impact on our thinking about early evolution. The 'RNA world' (REF. 95) was envisaged as an inventive phase of biogenesis in which RNA alone performed the vital functions of life (catalysis, heredity, recombination and evolution), together with RNA-like cofactors, such as NAD^{+} or FAD[96]. This concept is so conceptually satisfying that questions which surround the origins of DNA and protein from RNA are sometimes couched in terms of how rather than if[83]. But the RNA world does not solve conceptual problems that relate to life's origin for free; rather, it exacts an exorbitant price. As one of the most esteemed proponents of the RNA world hypothesis, the late Leslie E. Orgel[88], once pointed out: "[w]hile acceptance of an RNA World greatly simplifies the problem of the origin of life, it also has a negative aspect. If the origin of the RNA World preceded the origin of protein synthesis, little can be learned about the chemistry of the origin of life from the study of protein enzyme mechanisms. The justification of prebiotic syntheses by appealing to their similarity to enzymatic mechanisms has been routine in the literature of prebiotic chemistry. Acceptance of the RNA World hypothesis invalidates this type of argument. If the RNA World originated *de novo* on the primitive Earth, it erects an almost opaque barrier between biochemistry and prebiotic chemistry."

This quote symbolically marks the dividing line in the 'metabolism first' versus 'information first' debate (BOX 1). Did enzymes invent all biochemical reactions or did chemistry (similar to some biochemical reactions) naturally exist before the assistance of enzymes? Enzymes do not perform feats of magic, but merely allow chemical reactions that have a tendency to occur anyway to occur more rapidly. The enzymes that generate CH_4 from H_2 and CO_2, for example, are complex and highly ordered in modern methanogens, but the overall reaction that they catalyse takes place in hydrothermal vents either with (microbially) or without (geochemically) the help of proteinaceous catalysts. Indeed, the first step of biological methanogenesis, the formation of a carbamate, is spontaneous and requires no protein at all[97]. Of course, it remains within the realm of possibilities that modern microbial metabolism holds no relics of the chemistry that preceded the origin of genetic material[88]. An alternative, however, is that the evolutionary growth of organically catalysed reactions was derived from a central trail blazed by exergonic, spontaneous and/or inorganically catalysed reactions, and that this trail was, in turn, constrained by that which is thermodynamically favourable[98]. Prerequisite to this view is a sustained source of chemical energy, which hydrothermal vents provide. In this sense, the similarity between chemical conversions presented by the acetyl-coenzyme A pathway[63] and carbon reduction at hydrothermal vents[22] (FIG. 3) are deserving of closer inspection, as both release energy, some of which is harnessed by the acetyl-coenzyme A pathway to allow additional chemical work.

chemically accessible methyl groups, such as CH_3SH, would be able to support sustainable acetyl thioester and acetyl phosphate synthesis in a hydrothermal vent setting. Acetate would be the initial end product of such primordial biochemistry, which would involve substrate-level phosphorylation. It has been suggested that a simple carbon and energy metabolism of this type at an alkaline hydrothermal vent might have been capable of supporting the origin of microbial life even up to translation, genes and proteins[63]. The origin of chemiosmotic coupling, the main means of ATP synthesis among microorganisms, is more complicated. However, as discussed below, alkaline vents offer a possible solution even for this mechanism, because they provide a geochemically generated electro-chemical gradient of protons at the vent–ocean interface.

Alkaline pH and gradients are important

An exciting property of Lost City effluent is its alkalinity (pH 9–11), which produces a pH gradient at the vent–ocean interface. It is feasible that the naturally chemios-motic nature of alkaline hydrothermal vents in the Hadean eon, when chimney interiors had a pH of 9–10 and the outer walls of chimneys were bathed in ocean fluids with a pH of 5–6, were essential for the origin of free-living cells[63,64,71]. The nature and chemistry of chemiosmotic har-nessing[72] (through an ATPase) is more conserved than the myriad of mechanisms or proteins that generate proton gradients in bacteria and archaea[73,74]. Accordingly, it has been suggested that the ability to harness a continuous and naturally existing proton gradient at an alkaline hydro-thermal vent is older than the ability to generate a proton gradient with a chemistry that is specified by genes[63].

This idea might seem counter-intuitive, but what are the alternatives? At the most basic level, there are protein–cofactor complexes that generate chemios-motic potential (for example, the myriad proteins and membrane-soluble carriers that comprise electron-transport chains among prokaryotes[75,76]) and protein complexes that harness chemiosmotic potential to conserve chemical energy as ATP (ATPases)[77,78]. Regarding the question of which came first, there are two simple possibilities: either energy-consuming pumping or energy-conserving chemiosmotic harness-ing came first. It is possible that early chemical systems could have expended energy to generate ion gradients and only later developed mechanisms to harness them. However, this hypothetical scenario would require energy to burn, something that early chemical systems might not have had in abundant supply.

Alternatively, it is also possible that the ion gradi-ents were always present, being produced by alkaline hydrothermal effluents that interfaced with almost pH-neutral ocean water. In turn, this naturally existing energy source could have been tapped into by proteins that later evolved a more complicated and diversified chemistry in which ion gradients were generated across the plasma membrane[63]. This would have provided early chemical systems with energy to burn, which would have boosted biochemical evolution in a dramatic man-ner, as a large amount of chemical-free energy would have been made available in the form of phosphoan-hydride bonds. These bonds provide phosphorylating potential that allow reactions which are thermody-namically unfavourable (but perhaps are favourable for
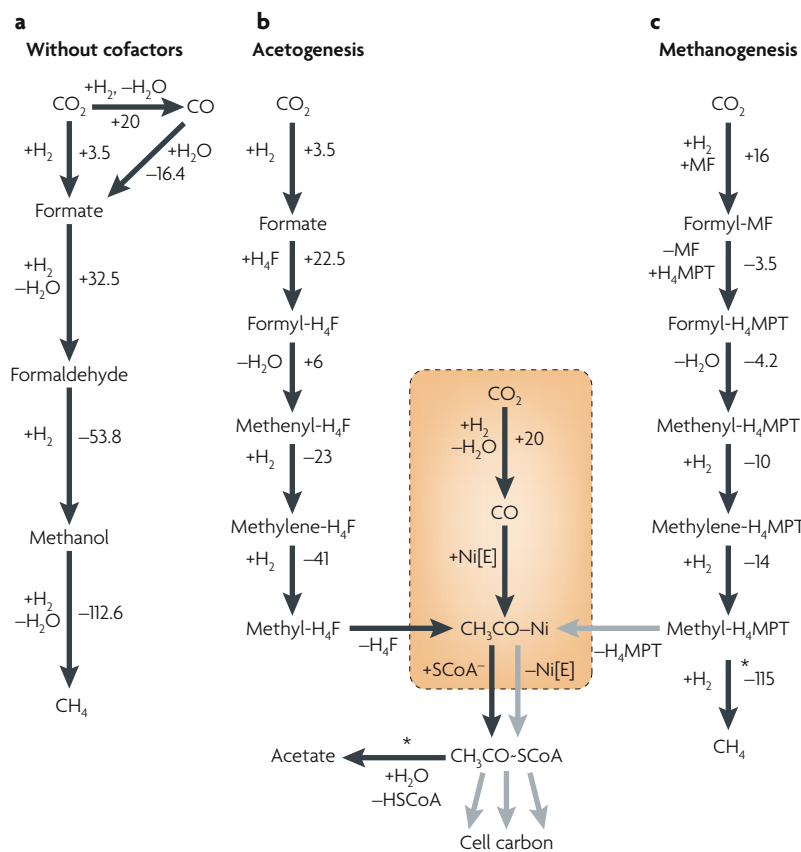
a
Without cofactors

CO_2 $\xrightarrow{+H_2, -H_2O \atop +20}$ CO

$+H_2$ $+3.5$ $+H_2O \atop -16.4$

Formate

$+H_2 \atop -H_2O$ $+32.5$

Formaldehyde

$+H_2$ -53.8

Methanol

$+H_2 \atop -H_2O$ -112.6

CH_4

b
Acetogenesis

CO_2

$+H_2$ $+3.5$

Formate

$+H_4F$ $+22.5$

Formyl-H_4F

$-H_2O$ $+6$

Methenyl-H_4F

$+H_2$ -23

Methylene-H_4F

$+H_2$ -41

Methyl-H_4F

$-H_4F$

CO_2

$+H_2 \atop -H_2O$ $+20$

CO

$+Ni[E]$

$CH_3CO–Ni$

$+SCoA^-$ $-Ni[E]$

Acetate $\longleftarrow$ * CH_3CO-SCoA

$+H_2O \atop -HSCoA$

Cell carbon

c
Methanogenesis

CO_2

$+H_2 \atop +MF$ $+16$

Formyl-MF

$-MF \atop +H_4MPT$ -3.5

Formyl-H_4MPT

$-H_2O$ -4.2

Methenyl-H_4MPT

$+H_2$ -10

Methylene-H_4MPT

$+H_2$ -14

Methyl-H_4MPT

$-H_4MPT$

$+H_2$ $*$ -115

CH_4

Figure 3 | **Chemical and biochemical reactions.** A schematic of the H_2-dependent conversions of CO_2 to CH_4 without cofactors (**a**) and with cofactors (**b,c**) in acetogens (to acetate) and methanogens growing on H_2 and CO_2. The numbers next to the arrows indicate the approximate change in free energy (ΔG^0) at 25°C and pH 7 ($\Delta G^{0'}$) in kJ per mole. The thermodynamic values are taken from REFS 55,56. For details of the biologically catalysed reactions, see the review by Maden[55]. For details of the reactions without cofactors under hydrothermal conditions, in which the thermodynamic values provided do not directly apply, see REF. 101. The dotted oval represents bifunctional CO dehydrogenase/acetyl-coenzyme A (acetyl CoA) synthase (CODH/ACS), a conserved enzyme that is common to the acetyl-CoA pathway of CO_2 reduction in both acetogens and methanogens. The enzymes that are involved in methyl synthesis in acetogens and methanogens are not evolutionary related, even though similar chemical steps are involved[55,63]. This has been interpreted to mean that the overall exergonic chemical conversions are more ancient than the enzymes that catalyse them in modern cells. Although all reactions shown are reversible, arrows are shown in only one direction for simplicity. The asterisks at the methyl-H_4MPT to CH_4 conversion and the acetyl-CoA to acetate conversion[54] indicate that several enzymes and cofactors that are not shown here are involved[55]. In both acetogens[54] and methanogens[53], net energy conservation (ATP gain) involves the generation of ion gradients using the overall reaction shown. This chemiosmotic potential is then harnessed by an ATPase. The coupling site in methanogenesis (not shown) entails the conversion of methyl-H_4MPT to CH_4 (REF. 53); the coupling site in acetogenesis (not shown) has recently been suggested to involve a ferredoxin–NAD^+ oxidoreductase[102]. The formate to formyl-H_4F conversion in acetogens involves ATP hydrolysis (not shown), which lowers $\Delta G^{0'}$ for the reaction to –10 kJ per mole[55]; the chemiosmotic potential is required for the synthesis of formyl-MF in methanogens[53]. For both acetogens and methanogens, black arrows indicate reactions that are involved in core ATP synthesis, whereas grey arrows indicate that a portion of the total carbon flux is used to satisfy the carbon needs of the cell. H_4F, tetrahydrofolate; H_4MPT, tetrahydromethanopterin; HSCoA, coenzyme A; MF, methanofuran; Ni[E], an Fe–Ni–S cluster in CODH/ACS. Part **a** adapted, with permission, from REF. 101 © (2006) National Academy of Sciences. Parts **b,c** adapted, with permission, from REF. 55 © (2000) Portland Press.

self-replication or geochemically independent reactions) to proceed more readily. For example, the conversion of formate to the formylated pterin cofactor (formyl-H_4F) shown in FIG. 3b is thermodynamically unfavourable ($\Delta G^{0'}$ equals 22 kJ per mole) without ATP hydrolysis, but is favourable ($\Delta G^{0'}$ equals –10 kJ per mole) when accompanied by ATP hydrolysis[55], whereby acetogens gain their net ATP from chemiosmotic coupling[54]. Curiously, the synthesis of formyl-H_4F in methanogenesis from formyl-H_4MPT (FIG. 3c) also requires energy input[55], but this energy does not come from ATP. Instead the enzyme that directly catalyses the reaction consumes the part of the chemiosmotic gradient that is generated by the later reactions of methane synthesis[79]. Both modern acetogenesis and methanogenesis require chemiosmotic gradients to operate, which points to the antiquity of chemiosmotic coupling mechanisms and suggests that before mechanisms evolved to harness naturally existing chemiosmotic potential at alkaline vents, geochemically provided reduced-C_1 compounds were essential to the initiation of both acetogenesis and methanogenesis[63]. Such C_1 compounds could have been methyl groups that were generated through serpentinization, which would agree with recent findings from Lost City[22].

The temperature gradients and porous structure of both modern[5] and ancient[71] hydrothermal vents could also enable the concentration[80] and perhaps even replication[81] of the products of organic synthesis to form primitive genetic material[82]. The view that life arose at a hydrothermal vent is compatible with concepts germane to the RNA world[83] (BOX 3), in that microcompartments at vents would provide a physical and chemical environment that is conducive to chemical synthesis, concentration and polymerization.

Conclusion

The discovery of hydrothermal vent systems profoundly changed how we view the geological, geochemical and ecological history of the Earth. Under-sea vents are abundant on the floor of the world's oceans and are important sources of many elements and organic compounds that are transferred into the hydrosphere. They can support life without input from photosynthesis and they harbour fascinating life with symbiotic relationships that involve lithoautotrophic microorganisms that use chemical energy to support metazoans. Moreover, a real or virtual sojourn to active deep-sea hydrothermal vent environments is also a visit to primordial Earth — active hydrothermal systems existed as soon as liquid water accumulated on the Earth more than 4.2 billion years ago. It is possible that present-day hydrothermal vent microorganisms harbour relict physiological characteristics that resemble the earliest microbial ecosystems on the Earth. It is also possible that geochemical processes of carbon reduction in hydrothermal systems represent the same kind of energy-releasing chemistry that gave rise to the first biochemical pathways. Life need not have evolved this way, but the mere prospect that it could have is reason enough to probe these environments further.

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