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Diverse geochemical conditions for prebiotic chemistry in shallow-sea alkaline hydrothermal vents

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Hydrothermal systems, where geothermally heated water discharges through a planet's crust, occur on land or underwater. Hydrothermal systems have been proposed as environments that could support the emergence of life, with particular attention given to deep-sea vents and on-land hot springs. We propose that alkaline hydrothermal vents in shallow waters (<200 m depth), high-energy environments that display diverse and variable geochemistry, should also be considered in origin-of-life scenarios for the early Earth. Two active alkaline shallow vents—the Strytan Hydrothermal Field in Iceland and the Prony Hydrothermal Field in New Caledonia—provide examples of the conditions found in shallow-sea vents that may be relevant for facilitating prebiotic chemical reactions. These conditions include wet–dry cycling, temperature variations, and influxes of both saltwater and freshwater. We argue that the spatial and temporal geochemical variability in shallow-vent hydrothermal systems can support a range of prebiotic chemical reactions required for the emergence of life.

Predicting which geological environments can support prebiotic chemical reactions is a challenge because geological environments such as hydrothermal vents can host a range of physical and chemical conditions. To support planetary missions that are looking for signs of past life or past prebiotic environments, a broader understanding of the possible conditions that can support prebiotic chemistry in different geological settings is required. One type of environment that has been important for origin-of-life studies is hydrothermal settings. Hydrothermal prebiotic analogue environments have usually been proposed from deep-sea vent examples. For example, one theory for the origin of life—the alkaline hydrothermal vent theory[1]—proposes that prebiotic reactions could have taken place in an environment similar to the Lost City Hydrothermal Field[2,3]; prebiotically relevant aspects of Lost City that have been emphasized in the alkaline hydrothermal vent theory include pH/redox gradients between seawater and alkaline H_2- and CH_4-containing hydrothermal fluid[1,2,4], and precipitation of reactive iron-bearing minerals that could drive CO_2 reduction and/or organic/phosphorus chemistry[1,5]. On-land hydrothermal prebiotic analogue environments have also been proposed, for example, the volcanic hot springs in Yellowstone, Kamchatka, and other places[6,7], which have pools of widely variable geochemical conditions that, upon intermingling, could generate chemical gradients and potentially wet–dry cycling. Because different prebiotic reactions are optimized under different conditions, environments with variable geochemistry (such as hydrothermal systems) are particularly relevant for the origin of life. The plethora of geochemical conditions found in hydrothermal settings has sparked debate about which parameters, for example, the temperatures and fluid chemistries in different types of vents or hot spring pools, are a crucial part of necessary prebiotic reactions[6,8,9].

However, a prebiotically relevant but often overlooked category of hydrothermal system is shallow-sea vents—that is, those underwater vents that occur from intertidal to ~200 m water depth[10]. Shallow-sea vents offer an interesting hybrid environment between terrestrial hydrothermal springs and deep-sea hydrothermal vents, and they incorporate aspects of both that might be relevant to prebiotic chemistry, including temperature cycling, freshwater and saltwater influxes,

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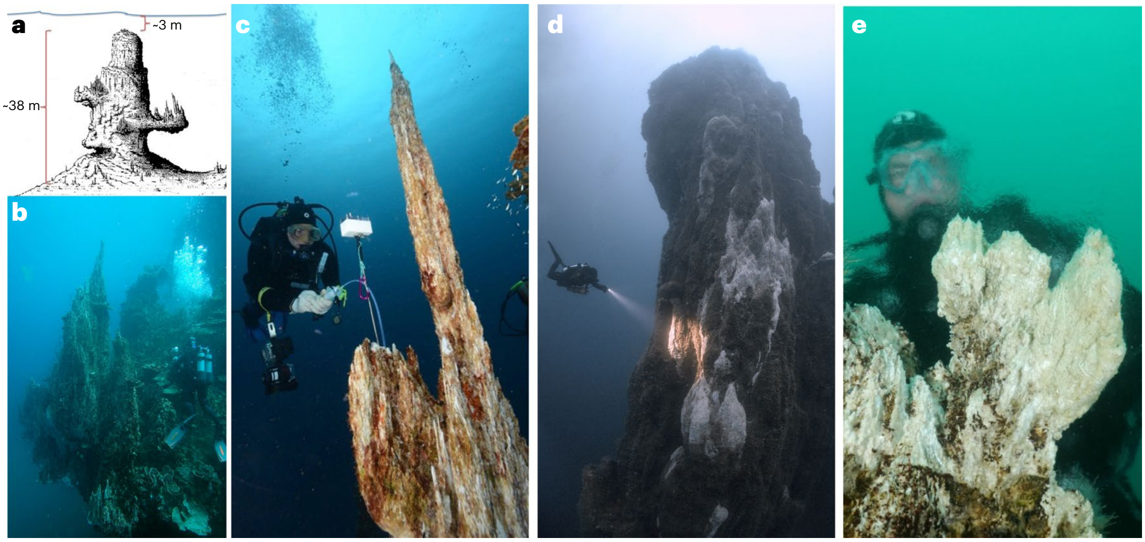

Fig. 1 | The Prony and Strytan Hydrothermal Fields provide examples of alkaline shallow-sea vents that might be analogous to prebiotically relevant early Earth environments. **a**, Schematic of the Prony Needle, a 38-m-high carbonate tower precipitated as alkaline Ca^{2+}-rich vent fluids mixed with seawater[49]. **b**, SCUBA diver on the large flange of the Prony tower shown in **a**. **c**, Diver collecting hydrothermal fluids from an active portion of the Prony Needle. **d**, Big Strytan tower at the Strytan Hydrothermal Field. **e**, The most active area at the top of Big Strytan shown in **d**. Credits: **b**, Roy Price; **c**, Eric Folcher, IRD; **d**, Steve Jones, millionfish.com; **e**, Erlendur Bogason, strytan.is.

and wet–dry cycling. These shallow-sea vents are a type of environment that might have existed on early Earth and perhaps other worlds such as early Mars, and warrants further consideration in origin-of-life scenarios.

Shallow-sea hydrothermal vents

To date, just under 80 shallow-sea vents have been reported[11]; most (~45) are associated with island arc volcanoes. The geochemical diversity of shallow-sea vents is on par with that of deep-sea vents, from focused high-temperature vent smokers to low-temperature diffuse venting through sediments. Their shallow depth and proximity to near-shore coastal environments lead to several important differences when comparing shallow-sea vents to either deep-sea vents or terrestrial hot springs. While many of the deeper subsurface processes—for example, low- to high-temperature water–rock reactions, magmatic volatile inputs, and phase separation—are analogous to those taking place at deep-sea or on-land vents, shallow-sea vents also have: (1) abundant free gas (that is, bubbles) due to ebullition of dissolved volatile gases; (2) terrigenous input of labile organic matter and phytodetritus; (3) wave action and storms; (4) light penetration; and (5) tidal ranges. The presence of light together with geothermally reduced compounds makes shallow-sea hydrothermal systems high-energy environments where photosynthesis and chemosynthesis can co-occur[10]. Another distinction of shallow-sea vents is that tides, storms and wave action can influence the temporal variability of temperature, oxygen and fluid venting rates, resulting in abrupt changes in the geochemistry of discharging fluids[12]. Furthermore, many known shallow-sea vents have hydrothermal fluids sourced from meteoric water—not seawater—even though submarine discharge can occur several kilometres offshore.

Most shallow-sea vents today are associated with mafic (basalt) to intermediate (andesite) rock types and are adjacent to volcanic islands with magmatic inputs, resulting in acidic fluids with sulfur and/or iron enrichments[13]. However, in the context of the alkaline vent theory for the origin of life[1], we will discuss the only two known alkaline shallow-sea hydrothermal vents: the basalt-hosted Strytan Hydrothermal Field in northern Iceland and the peridotite-hosted Prony Hydrothermal Field in southern New Caledonia. These two sites may represent analogues of alkaline shallow-sea vent sites on the early Earth that may have provided conditions conducive for prebiotic chemistry[4].

The Strytan Hydrothermal Field in northern Iceland

The Strytan Hydrothermal Field ('Strytan') is located in Eyjafjord, northern Iceland, at water depths ranging from 16 to 70 m (ref. [14]). The vent fluids are freshwater, alkaline (pH ~10.2) and heated (<78 °C), and the hydrothermal chimneys are magnesium silicate (saponite) towers reaching up to 55 m in height (Fig. 1d,e). Normally, hydrothermal vents associated with basalt produce acidic vent fluids; however, the Strytan alkaline vent fluid conditions are thought to result from CO_2 removal during water–rock reactions along the flow path of the meteoric water, which results in a loss of buffering capacity and increase in pH. Recent investigations[4] indicate that H_2 and CH_4 are present in the Strytan hydrothermal fluids, it is unclear if this CH_4 has an abiotic or biotic origin.

The Prony Hydrothermal Field in southern New Caledonia

The Prony Hydrothermal Field ('Prony') in southern New Caledonia is the only known ultramafic (peridotite) hosted shallow-sea vent. It discharges serpentinization-produced hydrothermal fluids that are warm (<41 °C), alkaline (up to pH ~11.2), and contain H_2 (up to 8 mM) and CH_4 (up to 6.4 mM); the origin of the CH_4 is likely microbial, based on recent clumped CH_4 isotope results. The resulting hydrothermal chimneys are carbonate towers up to 38 m high[4] (Fig. 1a–c). Prony has similarities to some terrestrial ophiolite springs, for example, Oman or Cedars, because fluids are sourced in meteoric water and discharge occurs within the photic zone; as well as to deep-sea vents such as Lost City, which also has discharge of alkaline fluids rich in H_2 and CH_4 (ref. [3]). However, because Prony is sourced in meteoric water but occurs in the photic zone of a marine environment, it is intriguing as a new type of serpentinite-hosted hydrothermal system, with similarities to both systems such as Lost City and on-land springs in Oman[15].

One intriguing aspect of Prony is that it is alternatingly submerged and exposed by tides. Several Prony vent sites are located above sea level, in the near-shore area, as well as intertidal and submarine as much as 50 m and perhaps deeper[16] (Fig. 2). In several areas, the vents and associated small cones are completely underwater at high tide, but exposed to the air at low tide. One site known as Kaori occurs within

Fig. 2 | Hydrothermal chimneys at the Kaori site, Prony Hydrothermal Field, are exposed to the air during low tide. a, Hydrothermal chimneys during low tide. The entire area is submerged by fresh river water during high tide. This contrasts with similar chimneys present at the Japonais site, where cones can be submerged in either fresh or seawater, and from the Prony Needle, which is always submerged in seawater. **b**, The white calcium carbonate tips of the chimneys where vent fluids continuously discharge. The surrounding mound structures are inactive and covered with algae and Fe-rich sediments (for map of sites see ref. [17]). Credit: Roy Price.

a freshwater river setting, and tides cause hydrothermal precipitates to be alternately submerged in fresh river water or exposed to the atmosphere. Another site, Japonais, is located in a river/estuary system, where either seawater or freshwater can submerge the cones, which can also be exposed to the atmosphere at low tide. Finally, the other sites—including the famous Needle of Prony—are entirely submerged by seawater all the time, but vent fluids are nonetheless discharging groundwater and therefore are entirely fresh. This wet–dry cycling to our knowledge has been taking place at the Prony Hydrothermal Field for at least 120 years[17].

Implications for early Earth

Seafloor rocks on the early Earth would have contained komatiite and/or basalt as evidenced by studies of Archaean volcanic rocks[18]; an olivine-rich early Earth crust has also been proposed, which could support serpentinization-driven hydrothermal systems[19]. Modern shallow-sea vents exist due to proximity to land masses, but prior to plate tectonics, the primary land masses (if any existed) in the Archaean may have been exposed volcanic islands or resurfaced seamounts or seafloor plateaus[20]. Some shallow vents are found today adjacent to intraplate volcanoes away from the plate margins, which demonstrates that these vents can form due to magmatic activity unrelated to plate tectonics; therefore, if volcanic islands or uplifted seamounts were present on the early Earth, shallow-sea vents could have formed there as well. In the Archaean, volcanic islands would have a greater tendency to remain exposed, due to seafloor shallowing induced by higher internal heating[20].

The specific rock type and amount of magmatic volatiles of an early Earth shallow-sea vent would be a main factor for determining the hydrothermal fluid chemistry and the pH/redox gradients that would be generated. If the host rock was basalt, but received no magmatic inputs, the hydrothermal fluids might have been more Strytan-like, that is, alkaline and containing silica, assuming a meteoric water source and not seawater. The elevated concentrations of CO_2 in early Earth's atmosphere might mean that the system never loses its buffering capacity, and thus fluids would potentially only reach pH values of around 8.3, a value controlled by the calcite mineral buffer[21,22]. If the host rock was komatiite, experimental studies have shown that aqueous alteration could produce H_2 (ref. [23]); however, it has also been proposed that komatiite serpentinization/carbonation would generate acidic to neutral fluids at low temperature[23]. If the host rock was olivine-rich[19], then the fluids produced by serpentinization could be similar to those at Prony, that is, alkaline and reducing.

There are several observations from modern-day alkaline vents that create unique conditions for early Earth origin-of-life scenarios. One example is alternating exposure due to tidal activity, as seen at Prony, which could allow the same vent system to experience both freshwater and seawater, wet–dry cycles, and effects of radiation (Fig. 3). One major difference between modern and early Earth shallow-vent systems would be the seawater chemistry. Early Earth had an anoxic, Fe^{2+}- and silica-containing ocean rich in dissolved HCO_3^-/CO_2 (ref. [22]). In shallow waters, photo-oxidation could also have generated some Fe^{3+} (ref. [24]), or precipitation of iron mineral precursors such as greenalite could have dominated[25]. The amount of Fe^{2+} present in the waters adjacent to a shallow vent would also be dependent on the timescales of tidal cycling relative to Fe^{2+} oxidation/precipitation processes. In any case, the influx of an alkaline hydrothermal fluid would have resulted in precipitation of any remaining $Fe^{2+/3+}$ to form iron minerals, for example, fougerite and greenalite[5,26], supplementing and/or replacing the magnesium minerals (brucite and saponite) that precipitate in alkaline shallow vents today[4,5]. It is possible that these types of mineral could form porous precipitate towers, structurally similar to those observed at Strytan or Prony. Carbonates would also probably precipitate as they do at Prony, Strytan (in trace amounts)

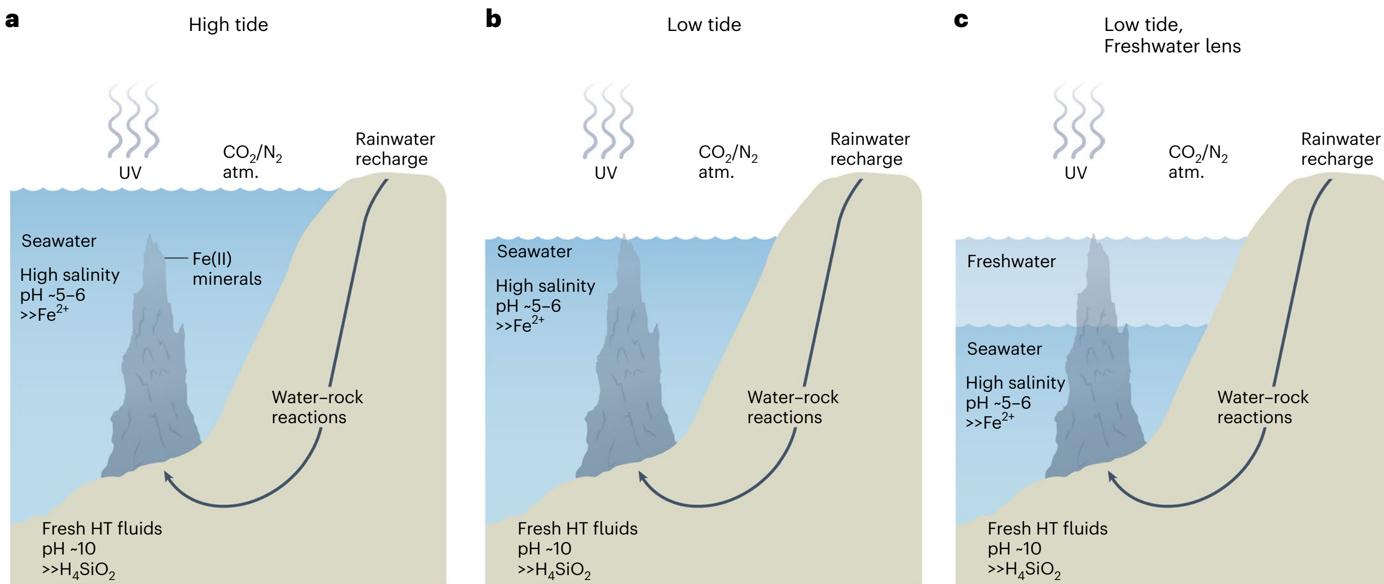

Fig. 3 | A shallow vent on the early Earth could have provided various different environments for prebiotic chemistry. a, Schematic of a hydrothermal chimney composed of mixed-valence iron minerals, including fougerite and greenalite, entirely and continuously submerged in early Earth seawater. Vent fluids are fresh as they are derived from rainwater recharge. **b**, The same chimney is exposed to atmospheric gases, wet–dry cycles and UV radiation at low tide. **c**, The same chimney can encounter a variety of different geochemical conditions, as tidal fluctuations expose it to the atmosphere and UV radiation, fresh river water and/or seawater. HT, hydrothermal; atm, atmosphere.

and Lost City; in phases of seawater influx, these could include iron carbonate (from seawater Fe^{2+}), and in phases of freshwater influx (containing Ca^{2+}) these could include calcium carbonate. The possibility of komatiite-derived hydrothermal fluids on early Earth and/or a groundwater-fed shallow-sea vent with magmatic inputs might lead to hydrothermal precipitates also containing some sulfide minerals. Another aspect of shallow-sea vents on the early Earth would be ion gradients as discharge of fresh (that is, low Na^+), alkaline, reducing, H_2- and CH_4-enriched vent fluids can interface with seawater, generating steep pH and Na^+ gradients[4].

Implications for prebiotic chemistry

Given the variable conditions of modern shallow-sea vent systems, it is worth considering how an alkaline, shallow-sea, basalt-hosted hydrothermal vent on the early Earth would have had aspects of both the Strytan and Prony systems as well as early Earth-specific aspects. For example, a prebiotic shallow hydrothermal vent could have had several dominant types of reaction conditions: (1) exposure to atmosphere and radiation during low tide; (2) exposure to shallow, freshwater environments; and (3) exposure to shallow, seawater environments, among others; this could theoretically have facilitated various kinds of prebiotic chemical reactions (some described below).

In phases where the chimney is submerged in saltwater or freshwater, various prebiotically relevant reactions and geochemical conditions could be possible. Particularly, the presence of oceanic Fe^{2+} in seawater and its absence in freshwater would provide a difference between the fresh and saltwater cases that could affect certain chemical reactions. For example, nitrate (NO_3^-) and nitrite (NO_2^-)—produced via atmospheric photochemistry[27]—can react with Fe^{2+} or Fe(II) minerals to produce reduced N species[28,29]. In a shallow-vent scenario, perhaps influx of seawater containing Fe^{2+} could precipitate Fe(II) minerals such as fougerite in the hydrothermal chimney; and then, the influx of fresh (Fe^{2+}-poor) water could provide an opportunity for nitrate/nitrite concentrations to build up and react with the hydrothermal minerals, producing reduced N species such as NH_3/NH_4^+ which could participate in organic reactions[30]. The alternating co-existing fresh and saltwater scenarios might have implications for prebiotic formation of membranes as well as RNA polymerization[8,31–33]. The varying micro-environments within the vent chimney precipitates might be able to promote proto-metabolic reactions and/or carbon reduction driven by mineral surfaces or catalysts (for example, refs. [34–37]).

When the hydrothermal precipitate is exposed to air at low tide, it would dry out and be exposed to increased ultraviolet (UV) radiation. This condition might facilitate prebiotic reactions that require or are enhanced by photochemistry (for example, refs. [38–40]). The drying out of the hydrothermal chimney precipitate and any associated organics on/in the minerals might increase the likelihood of dehydration reactions and/or polymerization (for example, refs. [41,42]). However, even when exposed to the air, the shallow-sea vent environment would still be partly aqueous because the hydrothermal fluid would continue to feed in and percolate through the chimney structure and pores. Thus, it is possible that within this chimney environment there could be a great variety of prebiotic reaction conditions that might each favour specific products, ranging from the UV-exposed, periodically dried out chimney top/exterior to the lower chimney interior, which would function as a more constant flow-through chemical reactor.

There are also key differences between modern and early Earth that present challenges for prebiotic chemistry at a shallow-sea vent. One of these is the increased intensity and frequency of tides on the early Earth[43,44]. It is possible that an extreme tide amplitude could quickly erode a fragile hydrothermal tower. However, how destructive a tide would be to a hydrothermal cone would also be a function of the surrounding geological setting and the age of the system. Over time, tides work to flatten the landscape such that the repeated influx of the tide, even of high amplitude, is not very destructive to mineral precipitate formations; chimney towers would probably become wide mounds, but hydrothermal discharges would continue. In Strytan, for example, the depth of Eyjafjord is 70–80 m, and the biggest hydrothermal chimney tower is 55 m; a very large early Earth tide of even 20 m amplitude (as suggested in ref. [9]) would only expose the top part of this chimney and would probably preserve the underlying structure. Another modern example is the Japonais site at Prony. At this site, the several-metre-diameter towers grow only 1.5–3 m high but essentially stop growing at the high tide line. Thus, in an early Earth shallow-vent scenario, it is possible that chimney towers could be exposed to air (protruding above sea level); or, that chimneys would grow to the high tide mark, and alternating cycles of erosion and new tower growth could occur, depending on the hydrogeology of the area.

UV radiation, although capable of driving some prebiotic organic syntheses, could also present another challenge to this scenario because radiation can degrade organic molecules. However, in a shallow-sea vent environment, prebiotic organics could have been protected from destructive UV radiation by environmental processes such as continued precipitation of minerals and encapsulation of organics within the chimneys, the presence of UV-attenuating Fe species in seawater[45], and frequent changes in water depth due to tides. Some organic molecules can also protect against radiation, and if present in prebiotic organic/mineral mixtures could act as shields; this interplay between prebiotic photochemistry and formation of molecules resistant to photochemical degradation may have been a selection pressure in prebiotic reaction networks[46].

Looking forward

To plausibly test whether shallow-sea hydrothermal environments could have facilitated prebiotic chemistry or the origin of life, more studies are needed. For example, continued investigations of Archaean geologic records could help clarify the extent of exposed land masses such as volcanic islands that could support shallow-sea vent environments. In addition, it would be informative to test whether origin-of-life reactions that have been previously studied in other environmental contexts can also occur under shallow-sea vent conditions. For example, organic synthesis experiments from a deep-sea vent context could also explore alternating fresh and saltwater conditions and/or effects of UV radiation; or, experiments from an on-land context could also explore organic reactions that can occur in freshwater shallow-vent hydrothermal fluids, during cyclic wetting and drying out of a reactive hydrothermal mineral precipitate.

For both cases, it would be interesting to consider how the varying environmental parameters in shallow-sea vent micro-environments might affect otherwise well-understood reactions—and, in particular, to understand if or how different prebiotic reactions might be able to co-exist in this geochemical parameter space. The modern alkaline shallow vent analogue sites described here demonstrate some of the variety of origin-of-life reaction conditions that might exist in shallow alkaline hydrothermal environments; this may also be relevant for predicting what kinds of environments should be investigated on other planets for signs of prebiotic chemistry or life. On Mars, for example, there are various lines of evidence of ancient hydrothermal activity; relevant examples include the Eridiania basin, which hosts massive saponite-containing seafloor hydrothermal deposits[47], and it is possible that hydrothermal alteration could have taken place in Jezero crater (the Perseverance landing site)[48]. Current and future missions can shed light on hydrothermal mineral formation processes on Mars and relevant prebiotic conditions that could have existed.

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Author contributions

R.E.P. conducted field work at hydrothermal sites. L.M.B. and R.E.P wrote the paper.

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