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Evaluating the abiotic synthesis potential and the stability of building blocks of life beneath an impact-induced steam atmosphere

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A prerequisite for prebiotic chemistry is the accumulation of critical building blocks of life. Some studies argue that more frequent impact events on the primitive Earth could have induced a more reducing steam atmosphere and thus favor widespread and more efficient synthesis of life building blocks. However, elevated temperature is also proposed to threaten the stability of organics and whether life building blocks could accumulate to appreciable levels in the reducing yet hot surface seawater beneath the steam atmosphere is still poorly examined. Here, we used a thermodynamic tool to examine the synthesis affinity of various life building blocks using inorganic gasses as reactants at elevated temperatures and corresponding steam pressures relevant with the steam-seawater interface. Our calculations show that although the synthesis affinity of all life building blocks decreases when temperature increases, many organics, including methane, methanol, and carboxylic acids, have positive synthesis affinity over a wide range of temperatures, implying that these species were favorable to form ($>10^{-6}$ molal) in the surface seawater. However, cyanide and formaldehyde have overall negative affinities, suggesting that these critical compounds would tend to undergo hydrolysis in the surface seawaters. Most of the 18 investigated amino acids have positive affinities at temperature $<220°C$ and their synthesis affinity increases under more alkaline conditions. Sugars, ribose, and nucleobases have overall negative synthesis affinities at the investigated range of temperatures. Synthesis affinities are shown to be sensitive to the hydrogen fugacity. Higher hydrogen fugacity (in equilibrium with FQI or IW) favors the synthesis and accumulation of nearly all the investigated compounds, except for HCN and its derivate products. In summary, our results suggest that reducing conditions induced by primitive impacts could indeed favor the synthesis/accumulation of some life building blocks, but some critical species, particularly HCN and nucleosides, were still unfavorable to accumulate to appreciable levels. Our

results can provide helpful guidance for future efforts to search for or understand the stability of biomolecules on other planets like Mars and icy moons. We advocate examining craters formed by more reducing impactors to look for the preservation of prebiotic materials.

1. Introduction

How life originated on the Earth (or beyond) has been a long-lasting puzzle for decades (Haldane, 1929; Oparin and Morgulis, 1938). The origin of life relies on several environmental factors, including the availability of various molecular building blocks, such as amino acids, sugars, and nucleotides. Apart from this, chemical emergence of life is also believed to require high levels of key reactive compounds, including cyanide (HCN and CN^-), urea [$CO(NH_2)_2$], and formaldehyde (HCHO). Cyanide is thought to be one essential base to form nucleobases and other N-bearing biomolecules in the primitive ocean (Sanchez et al., 1967; Yadav et al., 2020; Pérez-Fernández et al., 2022), thus constituting a critical starting point for the "RNA World" hypothesis; urea is suggested to be a useful reagent for prebiotic phosphorylation reactions (Lohrmann and Orgel, 1971; Powner et al., 2009), whereas formaldehyde – a major hydrolysis product of cyanide – is believed to be a critical starting material for the synthesis of sugars on primitive Earth (Orgel, 1998).

There are two major sources commonly put forward for the molecules aforementioned on the primitive Earth: endogenous synthesis and extraterrestrial delivery (Chyba and Sagan, 1992). The former mainly includes synthesis processes in various high-energy environments, including the hydrothermal alteration of ultramafic rocks (e.g., McCollom and Seewald, 2007; Cardace et al., 2015; McDermott et al., 2015; Ménez et al., 2018), the heating or radiation of the primitive atmosphere and surface waters (Stribling and Miller, 1987; Kobayashi et al., 1998; Parkos et al., 2018; Li et al., 2022; Zang et al., 2022), and the lightning [e.g., the widely known Urey-Miller experiment; (Miller, 1953)]. The latter source, extraterrestrial delivery, is primarily *via* the impact of extraterrestrial materials (meteorites, comets, and interplanetary dust particles) on the early Earth, which was much more frequent than today (Ryder, 2002). These extraterrestrial materials, particularly carbonaceous chondrites and comets, can contain substantial levels of various organic compounds (Kvenvolden et al., 1970; Cronin and Chang, 1993; Furukawa et al., 2019). Additionally, people suggested that shock-induced synthesis of various organics molecules could happen during large impact events (Bar-Nun et al., 1970; Furukawa et al., 2009; Goldman et al., 2010; Martins et al., 2013; Sugahara and Mimura, 2015; Takeuchi et al., 2020).

Although life relies on liquid water, polymerization reactions that lead to functional biomolecules (e.g., polynucleotides, polypeptides) are largely dehydration processes. That is one major challenge for the origin of life studies as one usually needs very high reactant concentrations for chemical evolution to happen

in simulative experiments–for example, molar level of HCN used in synthesis reactions (Orgel, 1998; Yadav et al., 2020) vs. the $<10^{-6}$ molar concentrations that have been estimated for the primitive ocean (Miyakawa et al., 2002). Earlier simulation studies had assumed a reducing primitive atmosphere where synthesis and accumulation of organic compounds would be more favored (Miller, 1953). For example, photochemical synthesis of HCN is shown to have appreciable yields in a relatively reducing atmosphere rich in CH_4, C_2H_2, or CO (Schlesinger and Miller, 1983; Rimmer and Rugheimer, 2019). However, chemical analyses of ancient zircons implied that redox state of the early mantle was similar to the modern (Trail et al., 2011) and thus the early volcanic gas should be less reducing or weakly oxic, similar to the modern. Photochemical models further suggested that hydrogen escape to the space would only allow a weakly to moderately reducing atmosphere on the early Earth, with a partial pressure of $H_{2,g}$ inferior to 10^{-2} bar (Kuramoto et al., 2013; Hao et al., 2019). These results contradict the proposed view of highly reducing atmosphere enabling pervasive abiotic synthesis on the primitive Earth.

Recently, several studies pointed out that a reducing atmosphere could rather be periodically induced by impacts on the primitive Earth (Hashimoto et al., 2007; Genda et al., 2017a,b; Schaefer and Fegley, 2017; Parkos et al., 2018; Zahnle et al., 2020). In the proposed scenario, reducing impactors would tend to equilibrate with the induced steam atmosphere and release high levels of reducing gasses, such as H_2, CH_4, and NH_3 (Zahnle et al., 2020; Pearce et al., 2022). It was further estimated that photochemistry in this reducing atmosphere would generate high levels of reactive species critical to prebiotic chemistry, such as HCN (Benner et al., 2020; Pearce et al., 2022). However, the impact events led to not only a more reducing atmosphere but also a hot surface environment. For instance, impact simulations suggested that a large impactor (corresponding from 100 to 250 km in diameter) would generate a steam atmosphere ($>100°C$) lasting for 1 to 100 years (Segura et al., 2002; Zahnle et al., 2020; Pearce et al., 2022). Under these circumstances, surface waters presumably in equilibrium with the steam atmosphere would also be hot. Whether or not photochemically synthesized life building blocks could accumulate to high concentrations in the reducing yet hot surface waters has not been carefully examined in the previous models.

Generally, increasing temperature would imply a much faster hydrolysis rate of the building blocks of life. For example, under neutral pH conditions, the half-life time of HCN decreases from several years at ambient temperatures to mere hours at 100°C (Miyakawa et al., 2002). However, the net reaction of synthesis and hydrolysis processes would be governed by the thermodynamic

driving force. Indeed, previous studies already suggested that some small organics could reach thermodynamic equilibrium with geologically abundant gaseous species under elevated temperatures (Shock, 1988, 1990; Lazcano and Miller, 1994; Franiatte et al., 2008). In this study, we applied thermodynamic calculations to assess the chemical affinities for synthesis/degradation of the building blocks of life under the simulative post-impact conditions. We focused on the surface seawater where photochemically synthesized organics and the relevant reactive compounds from the atmosphere would precipitate and dissolve. Thus, the surface seawater might steadily reach equilibrium with the impact-induced reducing and hot atmosphere.

The organics studied here were selected so as to represent the main groups of biomolecules (amino acids, sugars, nucleobases, and nucleosides) and also include some of the major organics found in meteorites, comets, and interplanetary particles (Hayes, 1967; Pizzarello et al., 2006; Goesmann et al., 2015; Aponte et al., 2020; Glavin et al., 2020; Oba et al., 2022) (summarized in **Supplementary Table 1**). We have also considered some critical compounds used in prebiotic synthesis [cyanide (Yadav et al., 2020), formaldehyde, and urea], as well as common metabolic materials [methanol (Russell and Nitschke, 2017), glycolic acid, and pyruvic acid]. Methane is also considered here since it was thought to be a critical greenhouse gas keeping the early Earth warm under the faint young Sun (Feulner, 2012).

2. Materials and methods

2.1. Post-impact surface conditions

As mentioned above, large impact events could induce a reducing steam atmosphere lasting for years or longer. Thus, in this study, we focused on simulating post-impact surface waters beneath the steam atmosphere (**Table 1**). Specifically, we chose to model a wide range of temperatures (100–340°C, allowing a steam atmosphere above the hot surface seawater) and, correspondingly, the atmospheric pressure as the saturation pressure of water vapor. The atmospheric composition (except for H_2O) was adopted from Zahnle et al. (2020); the H_2O vapor pressure is assumed to be in equilibrium with liquid water. The surface water's redox state was assumed to be dominated by the diffusion of $H_{2,g}$ from the atmosphere, i.e., by $H_{2,g}$ partial pressure and solubility in the water. The surface seawater pH would be largely controlled by equilibration with the atmospheric CO_2 (and other acidic gasses, such as HCl) as well as alteration of the impactor (Kadoya et al., 2020). The partial pressure of acidic gases and the extent of the water-rock interaction, which are key parameters to estimate the pH, are poorly constrained and might evolve in time and space. Given these uncertainties, we decided to study a wide range of pH (2–12) in the models, thus encompassing various potential scenarios.

2.2. Abiotic synthesis reaction affinities

Gibbs free energy (G_r) of a reaction:

$$aA + bB \rightleftharpoons cC + dD \qquad (1)$$

is defined as

$$\triangle G_r = \triangle G_r^\circ + 2.303RTlog_{10}Q, \qquad (2)$$

where R is ideal gas constant (8.314 J/(mole·K), T is temperature in Kelvin (=273.15+ °C), and Q is reaction quotient $\frac{\{A\}^a \times \{B\}^b}{\{C\}^c \times \{D\}^d}$ ($\{X\}$ refers to the activity/fugacity of species X). When the reaction reaches equilibrium, it turns into a special case:

$$\triangle G_r^\circ = -2.303RTlog_{10}K, \qquad (3)$$

where K is the reaction constant at a given temperature and pressure. The reaction affinity is defined as:

$$A_r = -2.303RTlog_{10}\frac{Q}{K}. \qquad (4)$$

The actual value of A_r represents the maximum amount of energy released ($A_r > 0$) or required ($A_r < 0$) for the reaction to reach thermodynamic equilibrium ($A_r = 0$). Therefore, if $Q > K$, A_r is negative and the overall reaction tends to move backward; if $Q < K$, A_r is positive and the overall reaction tends to move forward; if $Q = K$, A_r is zero and the reaction is at equilibrium.

Here, we calculated the reaction affinities of abiotic synthesis reactions (**Supplementary Table 2**). We first calculated the reaction quotient by using the partial pressures of gaseous bases from Zahnle et al. (2020) and assuming the activity of the product as 10^{-6}. The selection of the product activity is arbitrary here for better comparison between different organics and also reflects the fact that chemical evolution reactions usually requires appreciable levels ($>10^{-6}$ molal) of dissolved bases. Reaction constants for the abiotic synthesis reactions under both ambient and hydrothermal conditions were calculated using the Deep Earth Water (DEW) model [(Sverjensky et al., 2014); free access online],[1] which was built on the revised Helgeson-Kirkham-Flowers (HKF) equation of state for aqueous species (Shock et al., 1997). We then used the calculated affinity to evaluate whether the synthesis/stability of 10^{-6} molal

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1 http://www.dewcommunity.org/

TABLE 1 Model settings for the impact calculations.

Environmental parameter	Settings	Consideration and references
Temperature	100–340°C	Temperature allowing the condensation of steam atmosphere to liquid water ocean
Total pressure (predominantly as $H_2O_{,g}$)	Saturation pressure of water	A global water ocean in equilibrium with steam atmosphere
$pCO_{2,g}$	1 bar	Zahnle et al., 2020
$pCO_{,g}$	10^{-3} bar	Zahnle et al., 2020
$pH_{2,g}$	$10^{0.9}$ bar	Zahnle et al., 2020
$pNH_{3,g}$	$10^{-2.5}$ bar	Zahnle et al., 2020
$pN_{2,g}$	1 bar	Zahnle et al., 2020
pH	2–12	A wide range representing different hydrothermal settings (Gulmann et al., 2015; Seewald et al., 2015)

product is thermodynamically favorable (positive affinity) or not (negative affinity) in hot surface seawater after impact events. For protonated organics (e.g., HCOOH and HCOO⁻), we firstly calculated the pKa(s) of the protonation reaction(s) and then used Henderson-Hasselbalch Equation to calculate speciation for a given pH (**Supplementary Figure 1**). The reported affinity for protonated species will be the sum of percentage of different protonated species multiplied by their corresponding affinities, e.g., $A_{total} = A^*_{HCOOH} \frac{[HCOOH]}{[HCOOH] + [HCOO^-]} + A^*_{HCOO^-} \frac{[HCOO^-]}{[HCOOH] + [HCOO^-]}$. Its Internally consistent thermodynamic properties (G, H, S, C_p, and HKF parameters) of the organics come from a compilation of previous studies (Shock and Helgeson, 1990; Shock et al., 1992; Schulte and Shock, 1993; Plyasunov and Shock, 2001) and are summarized here in **Supplementary Table 3**.

It is notable that we considered separately two C sources in all synthesis reactions: CO and CO_2. In the primitive atmosphere, CO could come from volcanic outgassing and photo-dissociation of CO_2; the latter might reach photochemical equilibrium in a steady state (Kasting, 2014). However, such gaseous equilibrium does not translate to the thermodynamic equilibrium of their aqueous species in surface waters due to the kinetic barrier of CO_2 reduction under ambient conditions. A similar example is the co-existence of H_2 and O_2 in modern and early atmospheres (Kasting, 1993), which certainly did not reach thermodynamic equilibrium with liquid H_2O under ambient conditions (Hao et al., 2019). Here, we also calculated the thermodynamic equilibrium constant for the reaction: $CO_{2,g} + H_{2,g}CO_g + H_2O$ and compared with the reaction quotient calculated by the reference composition in **Table 1** (**Supplementary Figure 2**). The comparison clearly shows that CO_2 and CO are not in aqueous equilibrium, and there is a reduction tendency of CO_2 to generate CO by H_2. Therefore, using CO and CO_2 separately as C source in abiotic synthesis reactions does not necessarily result in same affinity values, and in this study, the synthesis affinity value with CO would be generally lower than CO_2 due to the addition of positive affinity for the above-mentioned reaction.

3. Results

3.1. C1 species

According to our calculations, the affinity of cyanide synthesis to reach 10^{-6} molal level from either CO or CO_2 as carbon source is overall negative under a wide range of temperature and pH conditions investigated in this study (**Figure 1**). Synthesis affinity using CO as carbon base (**Figure 1A**) is generally lower than using CO_2 (**Figure 1B**). It is notable that the affinity decreases with increasing temperatures but increases at elevated pHs.

Unlike cyanide, our calculations suggest that synthesis affinities of methane and methanol are positive under the explored temperature conditions (**Figures 2A, B**). However, the synthesis affinity of formaldehyde is overall negative (**Figure 2C**), like cyanide. Comparing the three C1 organics, there is a steadily decreasing trend of synthesis affinities along with increasing oxidation state of C, i.e., synthesis affinity: $CH_4 > CH_3OH > HCHO$. However, the synthesis affinity of

formic acid + formate, which has the most oxidized C, is overall positive (**Figures 3A, B**), inconsistent with the observed trend. Like cyanide, synthesis affinity of C1 organics decreases at high temperatures but increases at elevated pHs (for formic acid). Moreover, abiotic synthesis of these C1 organics using CO as the carbon source has an overall lower affinity than using CO_2.

3.2. C2–C3 species

Similar to formic acid, acetic acid and propanoic acid have positive synthesis affinities (to reach 10^{-6} molal) at almost the whole range of temperature and pH (**Figures 3C–F**). Moreover, synthesis affinities are overall lower using CO (**Figures 3C, E**) as the carbon source than CO_2 (**Figures 3D, F**). Furthermore, the elevation of pH results in increasing reaction affinity. However, comparing the absolute affinity values of these carboxylic acids, the elongation of alkane chain seems to result in increasing affinities at relatively low temperatures (< 260°C) but decreasing affinities at high temperatures (>260°C). At T > 300°C and pH < 8, the synthesis affinity of propanoic acid even turns negative.

Synthesis affinities of glycolic and pyruvic acids show a similar trend to the above-mentioned carboxylic acids, i.e., decrease at high temperatures and low pHs (**Figure 4**). However, the affinities are overall smaller than those of acetic and propanoic acids, respectively, and become negative at relatively lower temperatures (>140°C for glycolic acid and >220°C for pyruvic acid compared with >330°C for acetic acid and >310°C for propanoic acid, at pH = 7). Moreover, pH seems to have a more pronounced effect on the synthesis affinities of glycolic and pyruvic acids than acetic and propanoic acids.

3.3. Amino acids

Here, synthesis affinities of five selected amino acids (to reach 10^{-6} molal) were plotted as functions of temperature and pH (**Figure 5**), with the rest displayed in the **Supplementary Figures 3–6**. Among them, glycine, alanine, aspartic acid, and serine are major amino acids found in meteorites (Aponte et al., 2020; Glavin et al., 2020), and lysine, despite trace or no detection in meteorites, represents another type of amino acid with two amine groups. These five amino acids have overall negative synthesis affinities at elevated temperatures and the affinity increases at lower temperatures. Among them, the affinity of serine turns positive at temperature close to 100°C and pH > 7, whereas other four at temperature <180°C. For these five amino acids, the effect of pH on their affinities varies slightly: for glycine, alanine, and serine, their affinity increases at alkaline pHs but remains constant at acidic pHs; for aspartic acid, its affinity increases steadily from acidic pHs to alkaline pHs; for lysine, the affinity increases when pH increases or decreases with the minimal value at pH ∼7, possibly reflecting joint effects of –NH_2 and –COOH groups.

For better comparison and presentation purposes, we have calculated and compared the synthesis affinities of 18 proteinogenic amino acids excluding S-containing species at neutral pH (temperature dependent, calculated by DEW model as well; **Supplementary Figure 1**). The result shows that
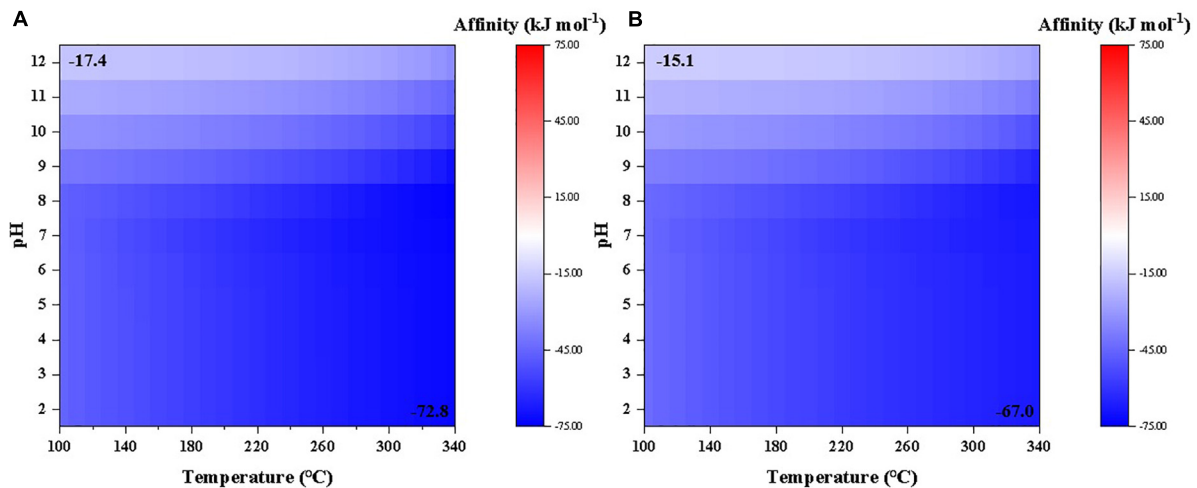
FIGURE 1
Synthesis affinity of cyanide ($HCN_{,aq}$ + CN^-) using **(A)** $CO_{,g}$ and **(B)** $CO_{2,g}$ as the carbon source.
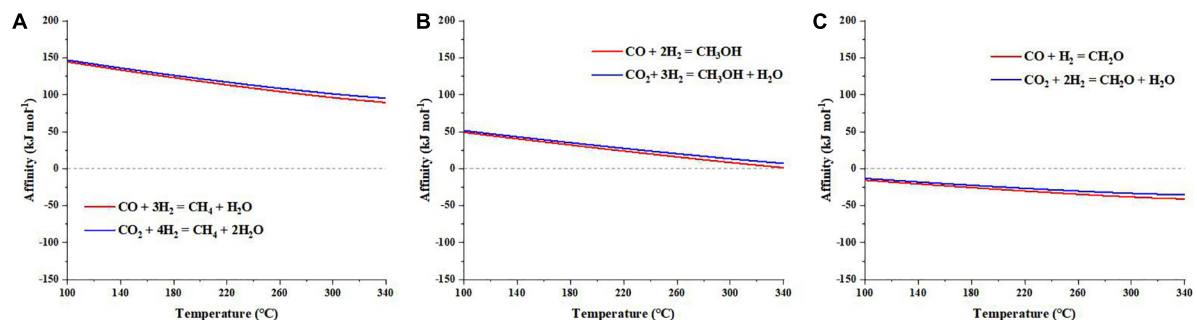
FIGURE 2
Synthesis affinity of **(A)** methane ($CH_{4,aq}$), **(B)** methanol ($CH_3OH_{,aq}$), and **(C)** formaldehyde ($HCHO_{,aq}$) using $CO_{,g}$ (in red) and $CO_{2,g}$ (in blue) as the carbon source. Given that these species are not protonated/deprotonated at the range of pH investigated here, pH has no effects on the results.

the synthesis affinities decrease with increasing temperature and nearly all amino acids have negative synthesis affinities at T > 220°C (**Figure 6**). At T < 220°C, however, most of the amino acids have positive synthesis affinities with the order: phenylalanine > leucine~isoleucine~glutamine > valine~tyrosine > tryptophan~lysine > ~proline~glutamic acid~alanine ~asparagine > aspartic acid~glycine~threonine. In contrast, serine, histidine, and arginine have negative synthesis affinities across a large range of temperatures. Like other organics mentioned above, synthesis affinities values using CO as the carbon source are slightly lower than CO_2.

3.4. Sugar, nucleobases, and nucleosides

Nearly all the investigated sugar, nucleobases, and nucleosides have negative synthesis affinities (to reach 10^{-6} molal) at a wide range of temperature and the affinities increase with lower temperatures (**Figure 7**). Among them, deoxythymidine, deoxyribose, and thymine have positive affinities at relatively low temperatures, i.e., <140°C. Generally, nucleobases and sugars have similar synthesis affinity values, which are higher overall than the

affinities of nucleosides. Like other organics, the affinities have slightly lower values using CO than CO_2 as the C source.

4. Discussion and implications

4.1. Sensitivity of organic synthesis affinity to environment settings

Given that the abiotic synthesis reactions are essentially reduction of inorganic carbon (either CO_2 or CO) by hydrogen, the hydrogen fugacity in the steam atmosphere would be expected to significantly affect the synthesis affinities. The above affinities were calculated by assuming the redox state constrained by a fixed partial pressure of $H_{2,g}$ modeled by Zahnle et al. (2020) (**Supplementary Figure 7**). However, as also discussed in previous studies, the hydrogen pressure in the steam atmosphere might vary significantly depending on the composition of the impactor as well as the size of the impactor relatively to the ocean volume (i.e., reductant/oxidant flux ratio). More reducing impactor objects, like iron meteorites, would generate (at least locally) a
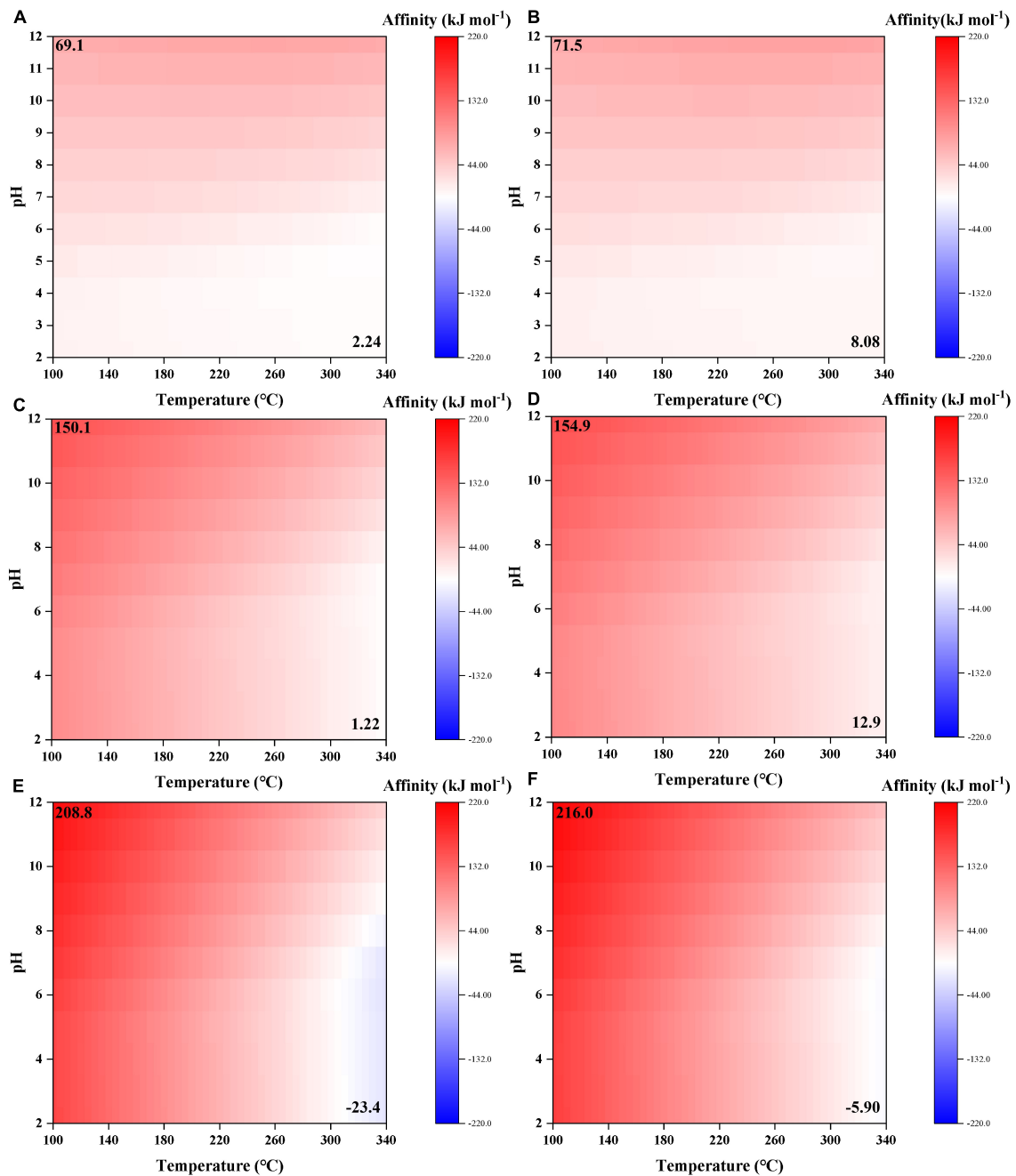
FIGURE 3
Synthesis affinity of formic [$HCOOH_{,aq} + HCOO^-$; **(A,B)**], acetic [$CH_3COOH_{,aq} + CH_3COO^-$; **(C,D)**], and propanoic [$C_2H_5COOH_{,aq} + C_2H_5COO^-$; **(E,F)**] acids using **(A,C,E)** $CO_{,g}$ and **(B,D,F)** $CO_{2,g}$ as the carbon source.

more reducing atmosphere with higher hydrogen levels (Parkos et al., 2018; Zahnle et al., 2020; Pearce et al., 2022). Moreover, big impactors would consume more oxidants in the surface environments and induce larger-scale and longer-term reducing atmosphere (Segura et al., 2002; Parkos et al., 2018; Zahnle et al., 2020). In extreme cases, if pretty big impactors deplete the oxidants in the surface environments, the hydrogen level in the post-impact atmosphere might be predominantly buffered by the reducing mineral assemblages in the impactor, e.g., Fayalite (Fe_2SiO_4)-Quartz (SiO_2)-Iron (Fe) (FQI) or Iron (Fe)-Wüstite (FeO) (IW) or else (Zahnle et al., 2020).

Here, we calculated the partial pressure of $H_{2,g}$ constrained by the equilibria of FQI and IW (**Supplementary Figure 7**) and then, examined the abiotic synthesis affinities of the selected organics using CO_2 as the C source under various hydrogen fugacities (**Figures 8, 9**). We also compared the results with Fayalite (Fe_2SiO_4)-Magnetite (Fe_3O_4)-Quartz (SiO_2) (FMQ) buffer, a more oxidizing mineral assemblage relevant with Earth's differentiated mantle (Trail et al., 2011) and hydrothermal vent systems (Trail and McCollom, 2023). Our results suggest that the affinities are indeed highly sensitive to the hydrogen fugacity in the atmosphere, and higher hydrogen fugacity greatly favors synthesis
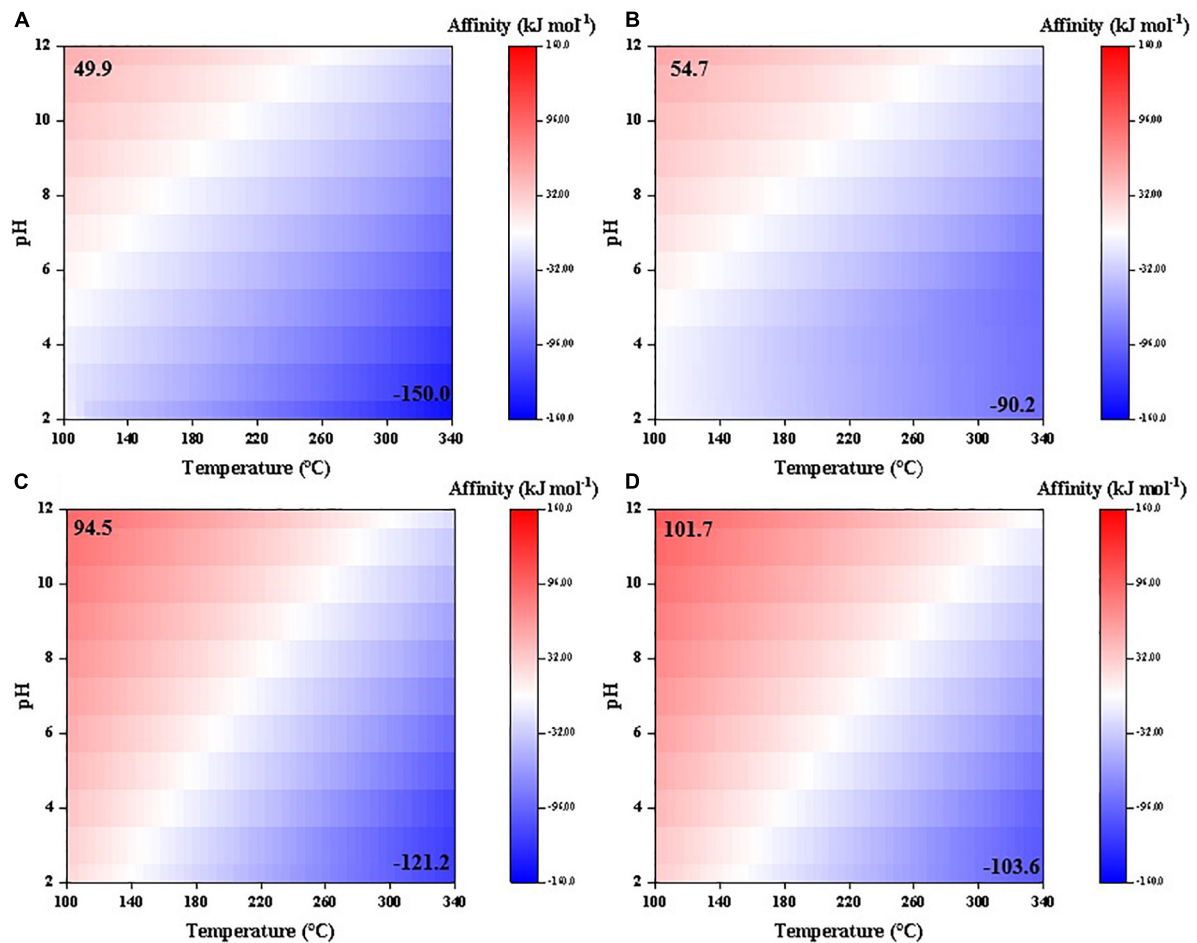
FIGURE 4
Synthesis affinity of glycolic acid [$CH_2OHCOOH_{,aq}$ + CH_2OHCOO^-; **(A,B)**] and pyruvic acid [$CH_3COCOOH_{,aq}$ + CH_3COCOO^-; **(C,D)**] using **(A,C)** $CO_{,g}$ and **(B,D)** $CO_{2,g}$ as the carbon source.
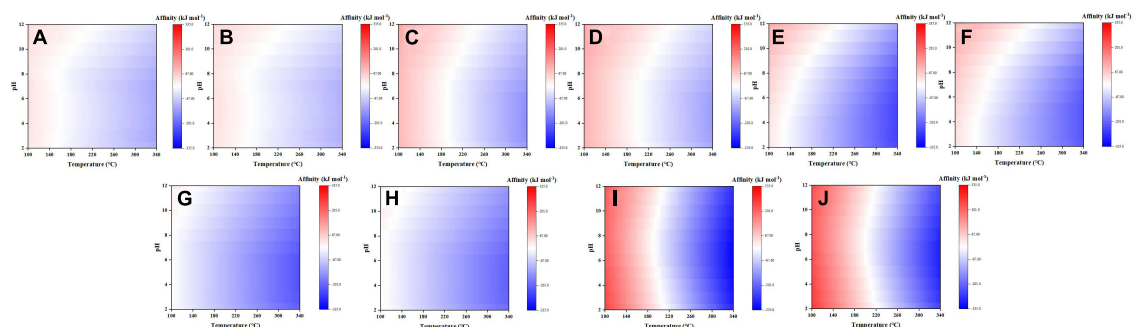
FIGURE 5
Synthesis affinity of glycine **(A,B)**, alanine **(C,D)**, aspartic acid **(E,F)**, serine **(G,H)**, and lysine **(I,J)** using $CO_{,g}$ **(A,C,E,G,I)** and $CO_{2,g}$ **(B,D,F,H,J)** as the carbon source.

of the studied compounds. For example, formaldehyde, which has negative synthesis affinities in a wide range of temperatures under the referenced redox condition (**Figure 2C**), becomes thermodynamically favored to form and accumulate (to $>10^{-6}$ molal) at high hydrogen fugacities constrained by FQI and IW (**Figure 8A**). Similarly, abiotic synthesis of 10^{-6} molal cyanide becomes favorable at high hydrogen fugacities (FQI and IW) and

high pH (>11) (**Figures 8B, C**). Glycine—which has the lowest synthesis affinity among amino acids studied under reference redox condition (**Figure 6**)–becomes strongly favored to form and accumulate to $>10^{-6}$ molal under a wide range of temperatures and pHs at high hydrogen fugacities (FQI and IW; **Figures 9A, B**); all amino acids can therefore be expected to have strongly positive synthesis affinities at high hydrogen fugacities. Similarly, abiotic
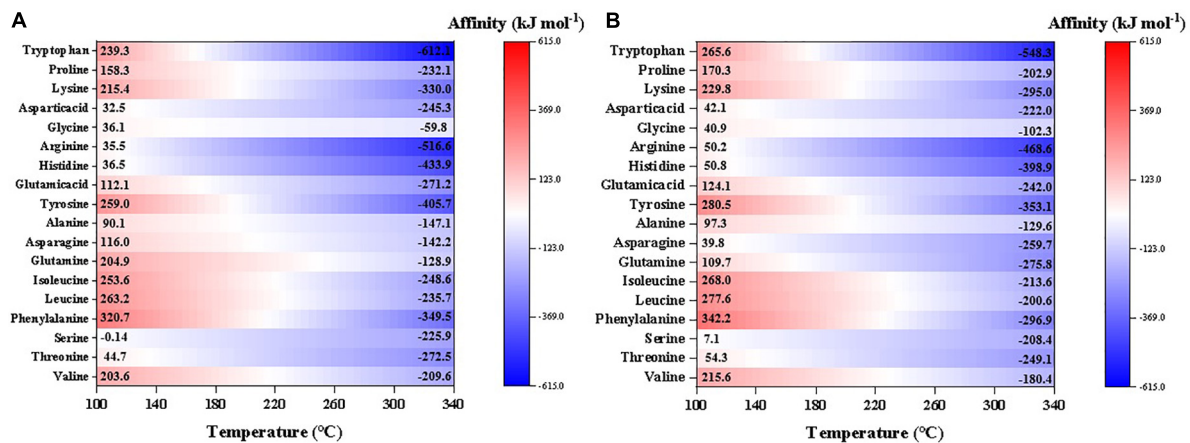
FIGURE 6
Synthesis affinity of proteinogenic amino acids excluding S-containing species using (A) CO_g and (B) $CO_{2,g}$ as the carbon source. In the calculations, pH was set neutral, which is also temperature-dependent.
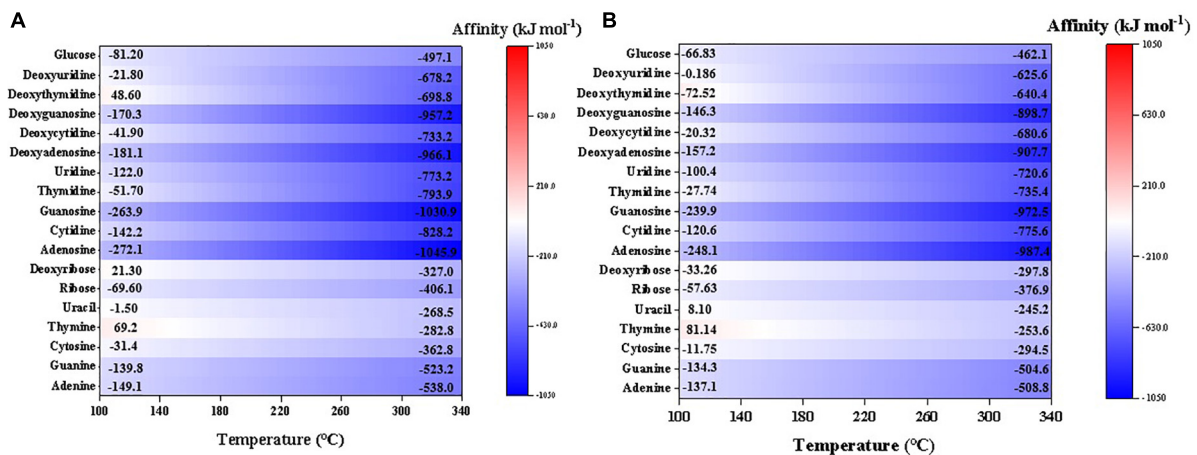

FIGURE 7
Synthesis affinity of sugar, nucleobases and nucleosides using (A) CO_g and (B) $CO_{2,g}$ as carbon source.

synthesis of most nucleosides, sugars and nucleobases (to 10^{-6} molal) becomes thermodynamically favorable at high hydrogen fugacities constrained by FQI and IW, except for adenine, guanine, adenosine and guanosine (**Figures 9D, E**).

However, at relatively low hydrogen fugacity constrained by FMQ, all the life building blocks considered in **Figures 8**, **9** have lower synthesis affinities compared with reference hydrogen fugacity, and are thus less favorable to form/accumulate. This redox state is close to the one in some hydrothermal systems on the Hadean Earth (Trail and McCollom, 2023), which was proposed to be one candidate environment for the emergence of life. Although we have not fully considered possibly different water chemistry in the hydrothermal systems, our results agree roughly with the early proposal that amino acids are not thermodynamically favorable to accumulate to levels higher than 10^{-8} molal in natural hydrothermal fluids (Amend and Shock, 1998). Thus, if the organics were synthesized locally around the crater(s) in the primitive ocean and diffused along the concentration gradient to the open ocean, they might tend to be degraded in the more

oxidizing hydrothermal vents, which is the major sink for organic matter in the modern ocean (Lang et al., 2006). Previous studies once proposed that the mixing between hydrothermal fluid and seawater would favor the abiotic synthesis of some biomolecules (e.g., Shock and Schulte, 1998; Shock and Canovas, 2010; Amend et al., 2013). A re-evaluation of this hypothesis under primitive settings is complicated given the unknown fluid chemistries and beyond the scope of our study here. Above all, reducing capacity (i.e., hydrogen) of the post-impact atmosphere has a significant effect on the synthesis affinities of organics in the primitive Earth, and beneath a more reducing steam atmosphere (at FQI or IW buffer), nearly all of life building blocks are favorable to form.

The post-impact water-rock interaction would not only induce a reducing atmosphere, but also elevate the water pH (Kadoya et al., 2020) and generate secondary minerals (Schoonen and Smirnov, 2016) inside and around the craters. Our calculations suggest a positive effect of pH on the synthesis affinity from neutral to alkaline pHs. Abiotic synthesis of cyanide even becomes thermodynamically favorable at pH > 11 under more reducing
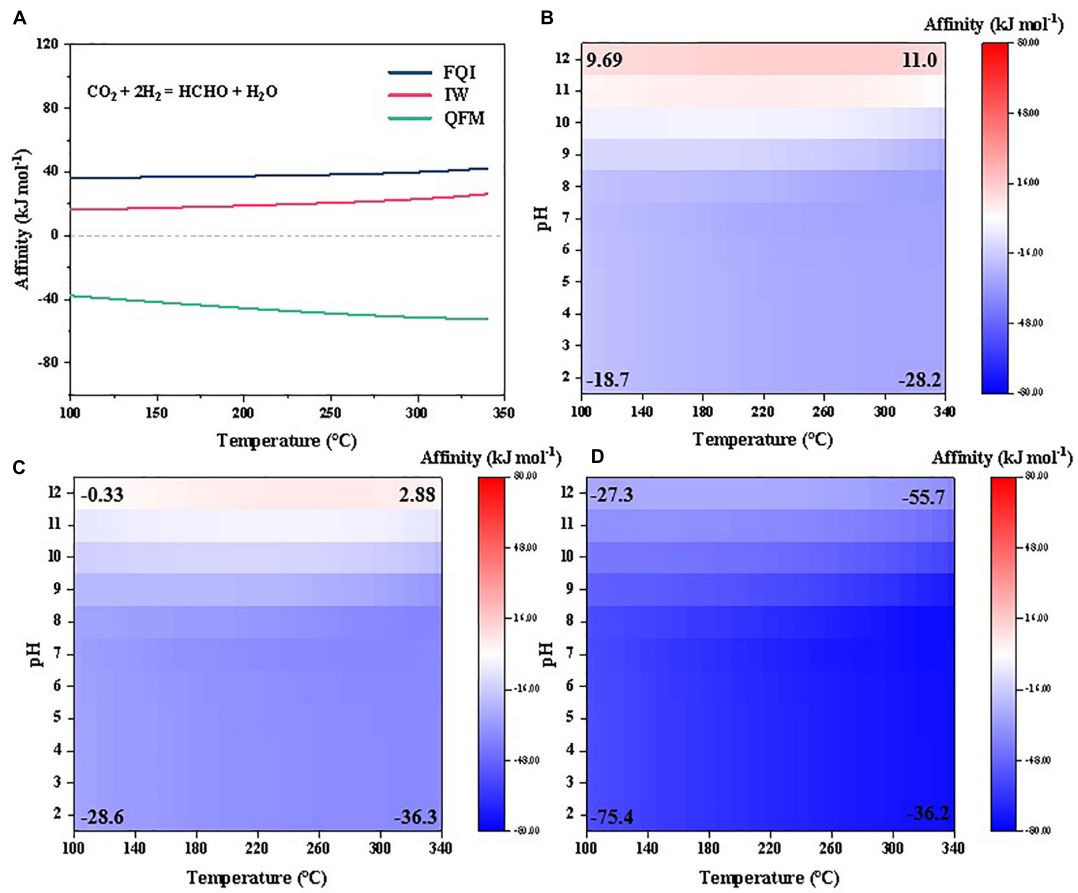
FIGURE 8
Synthesis affinity of **(A)** formaldehyde, **(B−D)** cyanide at different redox states [**(B)**, FQI; **(C)**, IW; **(D)**, FMQ] using CO_2 as the carbon source.
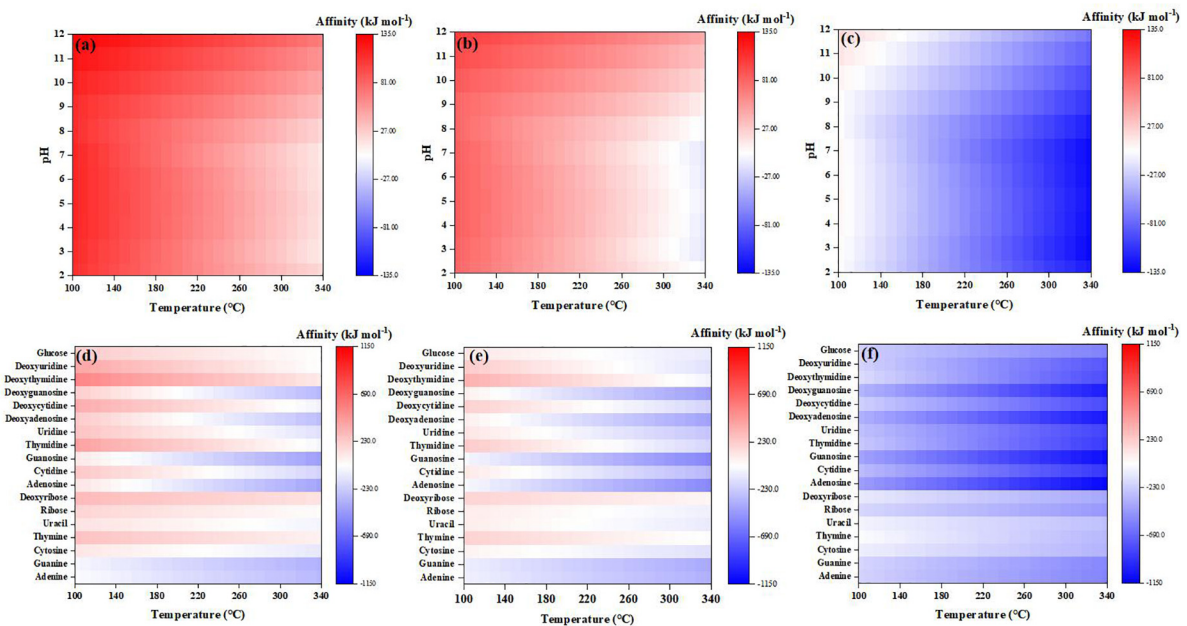

FIGURE 9
Synthesis affinity of **(a−c)** glycine, **(d−f)** sugars, nucleobases, and nucleosides at different redox states [**(a,d)**, FQI; **(b,e)** IW; **(c,f)** FMQ] using CO_2 as the carbon source.

atmospheres (**Figures 8B–D**). Such alkaline and reducing settings might be achieved in the surface waters around the craters. Our findings are also consistent with the previous proposals suggesting that alkaline waters were favorable for the accumulation of cyanide on primitive Earth (Toner and Catling, 2019). Moreover, previous studies also suggested that mineral adsorption could enhance the stability of life building blocks against potential threats like heating or UV radiation on the primitive Earth (Mignon et al., 2009; Hazen and Sverjensky, 2010; Grégoire et al., 2016). Such minerals are common product of the aqueous alteration of impactors (Rubin and Ma, 2017) and might enhance the stability of the abiotically synthesized building blocks of life against UV radiation in the shallow areas.

4.2. Stability of critical building blocks of life beneath the impact-induced steam atmosphere

Origin of life requires the accumulation of various inorganic and organic species as building blocks for chemical evolution. For example, HCN and HCHO were proposed to be the critical starting materials for the synthesis of nucleobases and sugar (Orgel, 1998; Yadav et al., 2020) and many origin-of-life experiments/hypotheses rely on high concentrations of these two compounds (Sanchez et al., 1967; Patel et al., 2015; Pérez-Fernández et al., 2022). Previous studies have proposed various pathways to form HCN and HCHO (Cleaves, 2008; Toner and Catling, 2019). Among them, the largest source was evaluated to be gaseous photochemistry in primitive atmosphere (Cleaves, 2008; Ferus et al., 2017; Pearce et al., 2022), especially after impact events (Parkos et al., 2018; Benner et al., 2020; Zahnle et al., 2020), when a more reducing atmosphere greatly improves synthesis efficiency (Tian et al., 2011; Pearce et al., 2022). Then, those photochemically generated building blocks of life would precipitate out of the steam atmosphere and accumulate in the ocean(s) for polymerization reactions (Benner et al., 2020).

However, according to our calculations, it is thermodynamically unfavorable to synthesize/accumulate appreciable levels ($>10^{-6}$ molal) of HCN and HCHO, beneath a steam atmosphere after the impacts in the reference atmospheric composition. HCN is favored to form at higher hydrogen fugacities, which is also true for HCHO if the water is highly alkaline. Rainout fluxes of HCN and HCHO synthesized by photochemistry or lightning in the atmosphere would also compete with hydrolysis in surface waters; the steady-state level of HCN and HCHO would depend on the relative rates of rainout and hydrolysis. Previous experiments demonstrated rapid hydrolysis of HCN (Miyakawa et al., 2002) and HCHO (Kopetzki and Antonietti, 2011), with half-life times that are less than a day temperatures above 100°C. Previous studies have reported rainout flux of HCN in the post-impact steam atmosphere as 10^{12}–10^{14} molecules/m^2/s (Stribling and Miller, 1987; Parkos et al., 2018; Zahnle et al., 2020). Given the hydrolysis kinetics data of HCN from Miyakawa et al. (2002), the steady-state level of HCN in the surface water would be $<10^{-9}$ molal at 100°C and pH = 6 ($<10^{-13}$ molal at 200°C and pH = 6; higher temperatures would imply faster hydrolysis and thus lower steady-state concentrations of HCN). These levels of HCN are several orders of magnitude lower than the concentrations used

in prebiotic synthesis experiments, e.g., concentrations of 10^{-2} molal and above used previously (Sanchez et al., 1967; Yadav et al., 2020; Pérez-Fernández et al., 2022). These results echo the previous suggestion that abiotic synthesis of biomolecules (amino and hydroxy acids or nucleosides) would be primarily constrained by the availability of starting bases including HCN and aldehydes in hot fluids (Schulte and Shock, 1995), even beneath a reducing steam-atmosphere after impacts. Meanwhile, strongly reducing atmospheres induced by large and more reducing impactors might favor the accumulation of critical bases for the synthesis reactions. Water bodies with high evaporation rates on land could also favor molecular condensation (Pérez-Fernández et al., 2022), but would be confronted with photodegradation processes (Cleaves, 2008; Todd et al., 2022).

4.3. Implications for life-searching efforts on other planetary bodies

In the solar system, Mars and some icy moons are believed to have (or have had) liquid water bodies and thus, represent the most promising places when looking for signs of extant or past alien life. An important target for life-searching efforts on these planetary bodies is organics, especially biomolecules. Mars, due to its proximity to the asteroid belts and its thin atmosphere, has been bombarded more heavily than Earth during its history (Hartmann and Neukum, 2001; Cox et al., 2022), and impactors might have delivered considerable fluxes of organics to its surface (Frantseva et al., 2018). Many craters are well preserved on Mars and have been selected in various landing missions as targets for *in situ* exploration. Our results suggest that some key building blocks of life, including HCN, HCHO, some amino acids, and nearly all nucleosides and sugars, could not be thermodynamically favorable to accumulate to a considerable level ($>10^{-6}$ molal) for chemical evolution under relatively oxidizing conditions, but more reducing impactors together with alkaline conditions would favor abiotic synthesis and accumulation of most building blocks of life. These results may not be directly applicable to early Mars where crustal and atmospheric compositions were possibly different from early Earth, however, the general trend observed here should hold true. Direct observations of impactor material on the surface of planetary bodies through remote sensing methods are scarce since impactors cannot be well preserved in high-velocity impacts that create impact craters and basins. However, searching for reduced impactor material is possible *via in situ* imaging and measurements of the elemental or isotopic signatures. Here, we propose that during current and future Martian missions, the mission team should consider using the rover payload to (1) investigate impacted materials with likely more reducing impactor and (2) search for alkaline mineral assemblages that could be inducive of the accumulation and preservation of organics or biosignatures.

There are several icy moons in the solar system that show strong signs of the presence of subsurface ocean, such as Enceladus, Europa, Ganymede, and Titan (National Academies of Sciences, Engineering, and Medicine, 2022). Even more excitingly, the flyby analyses of the Enceladus plume revealed signals of various organics (Waite et al., 2009), including some complex O- and N-bearing species (Magee and Waite, 2017; Postberg et al., 2018).

These observations place Enceladus among the most probably planetary bodies to find extraterrestrial life. There are also studies suggesting ongoing hydrothermal activity in the subsurface ocean of Enceladus (Hsu et al., 2015) and the hydrothermal heat flux might have been stronger in the past considering the progressive cooling of its core. However, the redox state of the hydrothermal systems on early Enceladus was suggested to be close to the FMQ buffer (Glein et al., 2008), and our current results suggest that formaldehyde, HCN, some amino acids, and nucleobases are not thermodynamically favorable to accumulate ($>10^{-6}$ molal) under these conditions, even at the high pHs proposed for Enceladus' ocean (Glein et al., 2018). Considering that Enceladus ocean water contains lower levels of other reactants involved in the synthesis reactions (i.e., CO_2 and N_2) (Waite et al., 2009; Glein et al., 2018), our results for the early Earth should be applicable to the Enceladus ocean as well. Given that Enceladus lacks an atmospheric source for these molecular compounds, they would tend to be completely degraded given the 100 s Ma to four Ga proposed history of Enceladus ocean (Ćuk et al., 2016; Neveu and Rhoden, 2019), as recently shown in a kinetic study about amino acids (Truong et al., 2019). Therefore, *in situ* origin of life in the subsurface ocean of icy moons might be threatened by the continuous hydrolysis of critical building blocks for the synthesis of biomolecules like sugar and nucleotide, in the hydrothermal systems.

5. Conclusion

In this study, we conducted thermodynamic calculations to evaluate the potential of abiotic synthesis of various building blocks of life beneath a simulative post-impact steam atmosphere. Our results show that the abiotic synthesis affinities generally decrease at elevated temperatures, and using CO as the C source would result in slightly higher synthesis affinities. Among the investigated compounds, many species, including cyanide, formaldehyde, several amino acids (e.g., aspartic acid, serine, and histidine), sugars, nucleosides, and nucleobases are not thermodynamically favored to form/accumulate to appreciable levels ($>10^{-6}$ molal) in a wide range of temperatures. However, other organics would have positive affinities, especially in temperatures lower than 220°C and/or alkaline pHs. Our sensitivity tests also suggested that the reducing capacity of the atmosphere would have a significant effect on the abiotic synthesis: at higher hydrogen fugacity in equilibrium with FQI or IW buffers, abiotic synthesis of nearly all building blocks of life (except HCN, adenine, guanine, adenosine and guanosine) becomes thermodynamically favorable, but at lower hydrogen fugacity in equilibrium with FMQ, the abiotic synthesis becomes less favorable than under the reference redox conditions. Thus, although impact events could induce a hydrogen-rich atmosphere, accumulation of some critical building blocks of life, e.g., HCN, formaldehyde, and their derivates, and might still be hard to achieve, unless in an atmosphere induced by a very large and reducing impactor. Finally, we suggest that craters generated by more reducing impactors could potentially be ideal sites in the search for biomolecules and biosignatures on other planets like Mars.

Data availability statement

The original contributions presented in this study are included in the article/Supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

JH designed the research. ZZ, HJ, PJ, LP, and JH conducted the research. GZ involved in the writing and revision of the manuscript. All authors discussed the results and wrote the manuscript and approved the submitted version.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmicb.2023.1032073/full#supplementary-material

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