



Alkaline lake settings for concentrated prebiotic cyanide and the origin of life

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Abstract

Cyanide plays a critical role in origin of life hypotheses that have received strong experimental support from cyanide-driven synthesis of amino acids, nucleotides, and lipid precursors. However, relatively high cyanide concentrations are needed. Such cyanide could have been supplied by reaction networks in which hydrogen cyanide in early Earth's atmosphere reacted with iron to form ferrocyanide salts, followed by thermal decomposition of ferrocyanide salts to cyanide. Using an aqueous model supported by new experimental data, we show that sodium ferrocyanide salts precipitate in closed-basin, alkaline lakes over a wide range of plausible early Earth conditions. Such lakes were likely common on the early Earth because of chemical weathering of mafic or ultramafic rocks and evaporative concentration. Subsequent thermal decomposition of sedimentary sodium ferrocyanide yields sodium cyanide (NaCN), which dissolves in water to form NaCN-rich solutions. Thus, geochemical considerations newly identify a particular geological setting and NaCN feedstock nucleophile for prebiotic chemistry. © 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Keywords: Prebiotic chemistry; early Earth; Origin of life; Cyanide; Alkaline lakes

1. INTRODUCTION

Cyanide is a key ingredient in organic synthesis experiments seeking to understand prebiotic chemistry because it is a strong nucleophile (i.e. a compound that donates electron pairs to build carbon-carbon chains and C-N groups) that forms polymers, nitriles, and cyanohydrins (Sanchez et al., 1967; Miller and Orgel, 1974; Ferris and Hagan, 1984). Recent origin of life research shows that many prebiotic organic compounds can be produced simultaneously from cyanide in reaction networks involving copper, sulfur, phosphorus, and UV light (Patel et al., 2015; Ritson et al., 2018). Cyanide needed for these reactions was likely present on the early Earth due to production of hydrogen cyanide (HCN) from photochemistry (including in expected CO₂-rich atmospheres) (Zahnle, 1986; Tian et al., 2011),

high temperature reactions during asteroid impacts (Fegley et al., 1986; Ferus et al., 2017; Parkos et al., 2018; Shtyrlin et al., 2019), electrical discharges (Stribling and Miller, 1987; Cleaves et al., 2008; Ferus et al., 2017), and cometary inputs (Matthews and Minard, 2006). HCN gas in the atmosphere dissolves in rainwater and so would have been deposited onto the early Earth's surface.

A major problem for cyanide origin of life hypotheses is that relatively high cyanide concentrations are needed. At least ~10 mM HCN is required for polymerization (Sanchez et al., 1967) and published prebiotic schemes commonly use 1 M HCN (Patel et al., 2015), which is much higher than oceanic concentrations estimated from atmospheric deposition rates (Stribling and Miller, 1987; Miyakawa et al., 2002). Low oceanic cyanide is caused by dilution of HCN inputs, followed by slow decay with water to form formamide (Miyakawa et al., 2002) and reaction with formaldehyde to form glyconitrile (Schlesinger and Miller, 1973) (Supplementary Material, Appendix A).

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Hence, prebiotic cyanide chemistry requires an environmental mechanism for concentrating and protecting cyanides from decay.

Some studies have qualitatively hypothesized that cyanides could have concentrated in surface environments on the early Earth as aqueous and crystalline ferrocyanides (Keefe and Miller, 1996; Patel et al., 2015). Aqueous ferrocyanide forms via the following reaction: $\text{Fe}^{2+} + 6\text{CN}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$, $\log K^0 = 35.35$ at 25 °C (Watt et al., 1965), where the large equilibrium constant indicates a strong affinity to form the complex. At sufficiently high concentrations, ferrocyanides precipitate from solution as a variety of insoluble and highly soluble salts (Williams, 1915). Ferrocyanides may release free cyanide needed for prebiotic chemistry via UV light, thermal decomposition, or reactions with hydrogen sulfide (Arrhenius et al., 1994; Keefe and Miller, 1996; Patel et al., 2015). In particular, highly soluble Na/K ferrocyanide salts thermally decompose to form copious Na/K cyanide (Patel et al., 2015).

Keefe and Miller (1996) investigated ferrocyanide formation on the early Earth; however, their model is limited to dilute solutions and low ferrocyanide concentrations, and did not include solid phases or environmental factors, such as carbonate chemistry, that would have influenced ferrocyanide formation. Consequently, it is unknown if soluble ferrocyanides (e.g., Na/K/Ca/Mg ferrocyanides) could have formed, and if so, in what specific depositional environments. To address these issues, we develop a novel geochemical model for ferrocyanide-rich brines using new experimental data that includes environmental factors such as atmospheric CO_2 and solution alkalinity, and accounts for solid phase carbonate, chloride, and ferrocyanide salts (Supplementary Material, Appendix B). We then use this model to explore ferrocyanide formation on the early Earth and the implications for prebiotic cyanide chemistry (Sections 3 and 4).

2. METHODS

2.1. Geochemical model

We use the Pitzer model (Pitzer, 1991) to explore how cyanides speciate and accumulate in plausible early Earth environments and which salts should precipitate. The Pitzer model accounts for ionic interactions and salt formation in concentrated brines, and has proven useful for predicting evaporating solution chemistry and salt precipitation sequences. As the basis for our Pitzer model, we use FREZCHEM (Marion and Kargel, 2008), which we implement using the *frezchem.dat* database in the geochemical program PHREEQC. PHREEQC is a freeware, user-friendly model archived by the US Geological Survey that includes aqueous equilibria (specifically, the Pitzer equations), as well as gas-phase and mineral precipitation reactions (Appelo and Postma, 2005). The *frezchem.dat* database in PHREEQC includes FREZCHEM parameters up to version 7.2, but does not contain Fe^{2+} parameters. As a result, we have supplemented *frezchem.dat* by adding Pitzer parameters and solubility products for Fe^{2+} salts from version 8.3 of FREZCHEM (Marion et al., 2003).

We also supplement *frezchem.dat* with parameters for ferrocyanide salts and ferrocyanide mixtures determined using experimental data we have gathered and literature data (Supplementary Material, Appendix B). At a minimum, parameterizing a Pitzer model requires measurements of ion activity coefficients for the pure salt phases present. Because data were not available even at 25 °C for $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{Mg}_2\text{Fe}(\text{CN})_6$, and $\text{Ca}_2\text{Fe}(\text{CN})_6$ salts, we measured water activities in these solutions using the isopiestic method to near saturation (Platford, 1979). Ferrocyanide solid phases in the model include $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 11\text{H}_2\text{O}$, $\text{Fe}_2[\text{Fe}(\text{CN})_6]$, $\text{CaK}_2\text{Fe}(\text{CN})_6$, and $\text{MgK}_2\text{Fe}(\text{CN})_6$. The resulting PHREEQC program used in this study is given in Supplementary Material, Appendix C.

2.2. Modeled environmental conditions

To constrain environmental conditions in our model, we need estimates of atmospheric HCN and CO_2 concentrations on the early Earth, as well as surface water temperatures. For atmospheric CO_2 levels on the early Earth, we use a range of values from 0.01 to 1 bar CO_2 from Krissansen-Totton et al. (2018), who simulated CO_2 by systematically varying data-constrained parameters for continental and seafloor weathering, internal heat flow and outgassing history, and greenhouse gas levels. Similarly, we use a temperature range of 0 to 25 °C, which spans the lower end of plausible surface temperatures from Krissansen-Totton et al. (2018) (0–40 °C with land and 0–50 °C without any land). We did not model temperatures above 25 °C because ferrocyanide accumulation preferentially occurs at lower temperatures (Keefe and Miller, 1996).

For the HCN gas concentrations, estimates from high-temperature models of asteroid impacts range from 10^{-3} to 10^{-5} bar pHCN formed locally near impact sites, to 10^{-5} to 10^{-12} bar pHCN distributed globally (Fegley et al., 1986). HCN deposition rates following asteroid impacts are several orders of magnitude larger than photochemical production rates (Parkos et al., 2018). Predictions of photochemical models have a similarly wide range, from $\sim 10^{-4}$ bar pHCN in the case of high CH_4 concentrations, to $\sim 10^{-8}$ in the case of low CH_4 concentrations (Zahnle, 1986; Tian et al., 2011). We use a pHCN range of 10^{-8} to 10^{-5} bar in our model. We note that the photochemical and asteroid impact studies referenced above show that HCN production occurs in weakly reducing $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ -rich atmospheres, and does not require a highly reduced atmosphere.

3. RESULTS

3.1. Ferrocyanide formation on the early Earth

Cyanide inputs to surface environments on the early Earth would have been in the form of HCN gas, which dissociates to free CN^- in aqueous solutions ($\text{p}K_a = 9.2$ at 25 °C). This CN^- then combines with Fe^{2+} to form ferrocyanide; consequently, ferrocyanide formation depends

on aqueous Fe^{2+} , CN^- , and HCN^0 speciation. To see how these species vary as a function of pH, we model Fe^{2+} -rich solutions in equilibrium with HCN gas (Fig. 1). We find that insufficient cyanide is present as CN^- at low pH to drive ferrocyanide formation forward. As the pH increases, ferrocyanide rapidly forms over a narrow pH range as HCN^0 dissociates to CN^- . In particular, we find that the pH at which $\text{Fe}(\text{CN})_6^{4-} = \text{Fe}^{2+}$ (the equivalence point) is a useful threshold pH for evaluating the potential for ferrocyanide brines to form. Below this pH, ferrocyanide is minor, whereas above this pH, high ferrocyanide concentrations are possible.

Fig. 1 is merely an example with a specific pHCN and fixed total iron without considering Fe-containing minerals that might precipitate, so we need to investigate a broader range of plausible conditions to find the pH range in natural waters at which considerable ferrocyanide exists. To determine how the pH of the $\text{Fe}(\text{CN})_6^{4-} = \text{Fe}^{2+}$ equivalence point changes as a function of pCO_2 , pHCN, and temperature, we start with an initial solution of 0.1 mM Fe^{2+} based on modeled Archean surface waters (Hao et al., 2017), and then titrate with Na_2CO_3 alkalinity until the pH of the $\text{Fe}(\text{CN})_6^{4-} = \text{Fe}^{2+}$ equivalence point is reached (Fig. 2). The resulting pH values at the $\text{Fe}(\text{CN})_6^{4-} = \text{Fe}^{2+}$ equivalence point are 6.9–9.3 (Fig. 2A and B), much higher than the pH of unbuffered solutions (3.8–4.9 pH), and alkalinities are 10^{-3} – 2.4 mol kg^{-1} in the form of bicarbonate (Fig. 2C and D).

In general, our results indicate that $\text{Fe}(\text{CN})_6^{4-}$ is more stable at lower pCO_2 and temperature, and higher pHCN. In all modeled cases, the initial aqueous Fe^{2+} precipitates as sparingly soluble siderite (FeCO_3) or $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (at low temperatures only), which limits the concentration of Fe^{2+} to 10^{-9} – $10^{-5} \text{ mol kg}^{-1}$. For some solutions with high pCO_2 and low pHCN (the blank areas in Fig. 2), it is not possible to reach the $\text{Fe}(\text{CN})_6^{4-} = \text{Fe}^{2+}$ equivalence point because nahcolite (NaHCO_3) precipitates from solution, which limits the maximum possible alkalinity. As a result, such environments cannot form concentrated ferrocyanide solutions.

The previous model results indicate the minimum pH/alkalinity needed to form significant ferrocyanide in solu-

tion. Even higher ferrocyanide concentrations occur at higher pH/alkalinity, and the highest ferrocyanide concentrations occur in saturated carbonate or bicarbonate brines. Consequently, we model the highest possible ferrocyanide concentrations on the early Earth by saturating solutions with respect to Na_2CO_3 alkalinity in the presence of excess FeCO_3 (which supplies Fe^{2+} to solution) at variable pHCN, pCO_2 , and temperature (Fig. 3). Our model results indicate that high ferrocyanide concentrations and ferrocyanide salts occur over a wide range of early Earth conditions in carbonate brines. At relatively low pCO_2 and high pHCN, ferrocyanide concentrations up to 0.7 mol kg^{-1} are possible at 25°C ; in contrast, at relatively high pCO_2 and low pHCN, cyanide is present in μM concentrations due to the relatively low pH and limited availability of HCN (Fig. 3E and F). The alkalinity in all cases is dominated by bicarbonate ions because the pH is buffered by acidity from CO_2 and HCN gas (Fig. 3C and D).

High ferrocyanide concentrations cause $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (Prussian White) to preferentially form at low temperatures, low pCO_2 , and high pHCN, shown as “Na-Cy” and “Fe-Cy”, respectively, in Fig. 3. Solutions in the upper left regions of Fig. 3A–F are saturated with respect to nahcolite (NaHCO_3) and siderite (FeCO_3), but as pCO_2 decreases and pHCN increases, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ precipitates instead of nahcolite. At the lowest pCO_2 and highest pHCN conditions at 0°C , sparingly soluble $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ precipitates in addition to $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and siderite (Fig. 3B, D, and F). The formation of $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ is caused by high HCN gas concentrations, which leads to higher CN^- concentrations and increased iron concentrations from siderite dissolution. We note that although the solubility of $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ is poorly characterized experimentally (Supplementary Material, Appendix B), the geochemical rationale for its formation is reasonable.

3.2. Ferrocyanide evaporites in closed-basin lakes

Our results in the previous section show that ferrocyanide salts could have concentrated and precipitated on the early Earth in NaHCO_3 -rich alkaline brines, which points to closed-basin lakes as plausible environments for

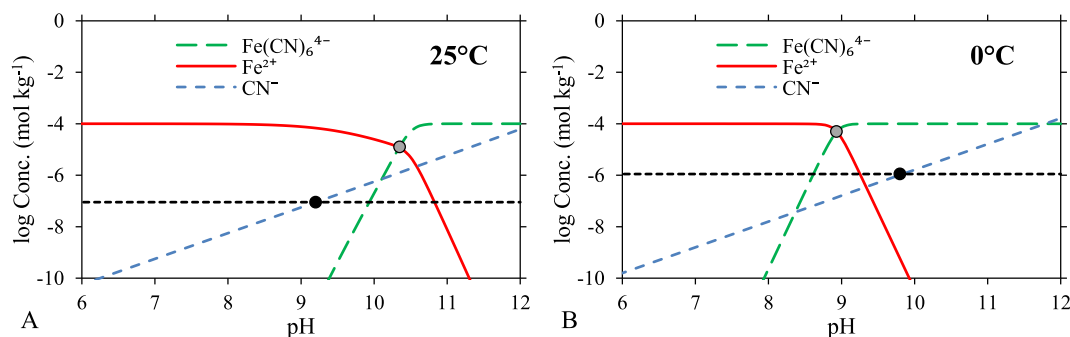


Fig. 1. Speciation in ferrocyanide solutions. Modeled solutions contain 0.1 mM total Fe in equilibrium with $\text{pHCN} = 10^{-8} \text{ bar}$ at 25°C (A) and 0°C (B) at variable pH. The $\text{CN}^- = \text{HCN}^0$ equivalence point is indicated by black circles, and the $\text{Fe}(\text{CN})_6^{4-} = \text{Fe}^{2+}$ equivalence point by grey circles. These equivalence points indicate a turning point in the predominance of CN^- vs. HCN^0 and $\text{Fe}(\text{CN})_6^{4-}$ vs. Fe^{2+} .

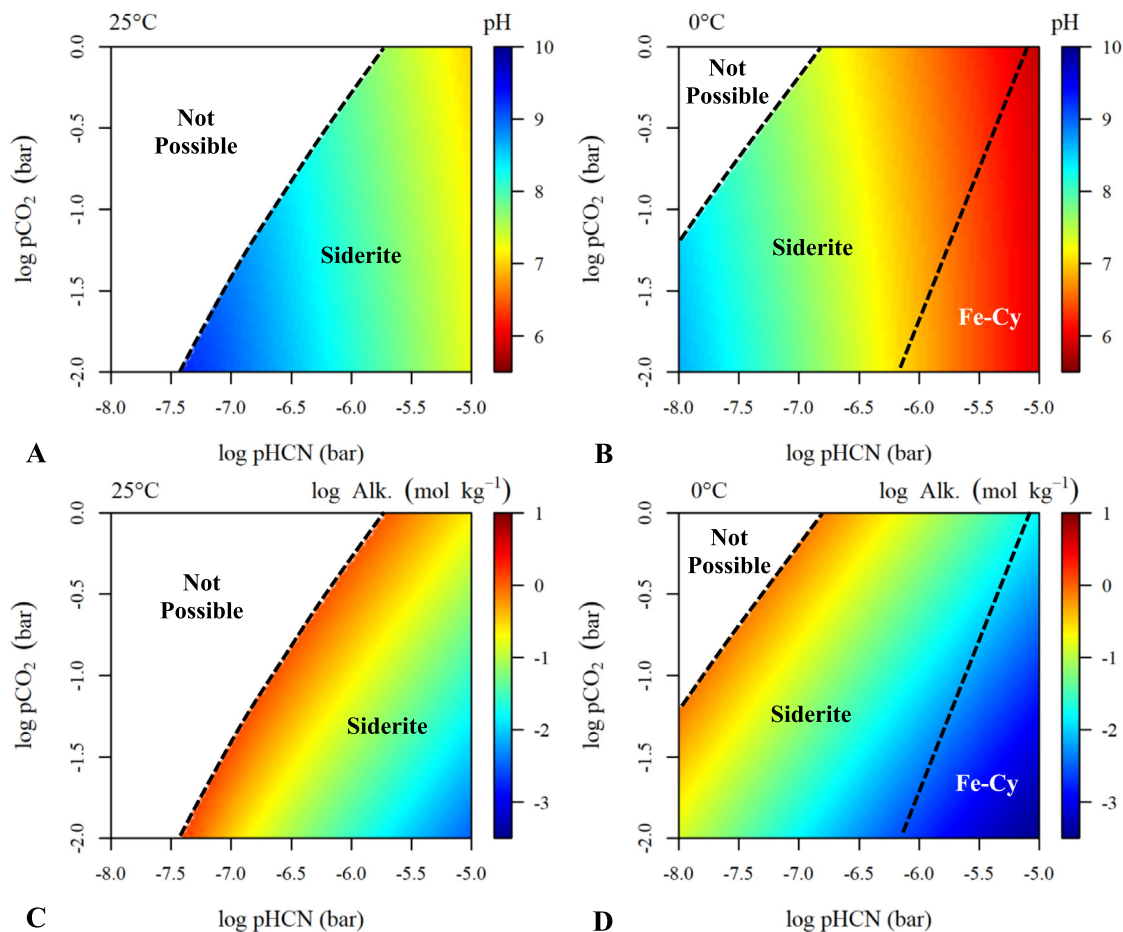


Fig. 2. The pH (A, B) and alkalinity (Alk.) (C, D) needed to form solutions in which $\text{Fe}^{2+} = \text{Fe}(\text{CN})_6^{4-}$ at 0 and 25 °C. Solutions in the white regions are not possible (i.e., $\text{Fe}(\text{CN})_6^{4-} \ll \text{Fe}^{2+}$) because nahcolite (NaHCO_3) precipitates, which limits the carbonate alkalinity and pH to lower values than needed to reach the $\text{Fe}^{2+} = \text{Fe}(\text{CN})_6^{4-}$ equivalence point. Regions where siderite and $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (designated as “(Fe-Cy)”) precipitate are delineated by dashed lines. The color scale is pH in A and B, and log alkalinity in C and D. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ferrocyanide accumulation. Closed-basin lakes accumulate dissolved ions from inflowing water, but have no outflow except for water loss by evaporation. Consequently, evaporation concentrates ions in lake waters to saturation, resulting in salt precipitation (Eugster and Jones, 1979). Closed-basin lakes with elevated salt concentrations are common in arid regions, and in many cases attain saturation with respect to $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ salts (Kempe and Kazmierczak, 2011; Pecoraino et al., 2015).

To determine if closed-basin evaporation of early Earth surface water inputs could precipitate ferrocyanide salts, we model surface water evaporation at 25 °C in equilibrium with 10^{-5} bar pHCN and 0.1 bar pCO₂ (Fig. 4). For the surface water input to the closed-basin lake, we use the Archean modeled composition from Hao et al. (2017), and achieve charge balance by adjusting $\text{Cl}^- : \text{Na}^+ = 0.187$, $\text{K}^+ = 0.0331$, $\text{Ca}^{2+} = 0.226$, $\text{Mg}^{2+} = 0.191$, $\text{Fe}^{2+} = 0.112$, $\text{Cl}^- = 0.169$, and Alk. = 1.109 mM. This surface water composition does not include SO_4^{2-} , but sulfate salts

will not significantly affect the evaporative concentration of ferrocyanide because they accumulate at lower concentrations relative to more soluble chloride salts and do not form salts with ferrocyanide.

As evaporation of this surface water input proceeds, the alkalinity increases, raising the pH and causing the precipitation of carbonate salts in the order siderite, calcite (CaCO_3), and MgCO_3 . At the lowest residual water contents, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ precipitates, followed by halite (NaCl) and sylvite (KCl) as the final salt. The final brine contains $0.07 \text{ mol kg}^{-1} \text{ Fe}(\text{CN})_6^{4-}$, which can be compared to ferrocyanide concentrations of 0.68 mol kg^{-1} in pure $\text{Na}_4\text{Fe}(\text{CN})_6$ solutions. The low solubility of $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ in brine mixtures indicates a strong tendency to precipitate ferrocyanide salts in saline lakes. Although we present results for only one set of environmental conditions here, the wider set of temperature, pHCN, and pCO₂ conditions favorable for ferrocyanide salts in Fig. 3 also yield ferrocyanide salts in evaporative models.

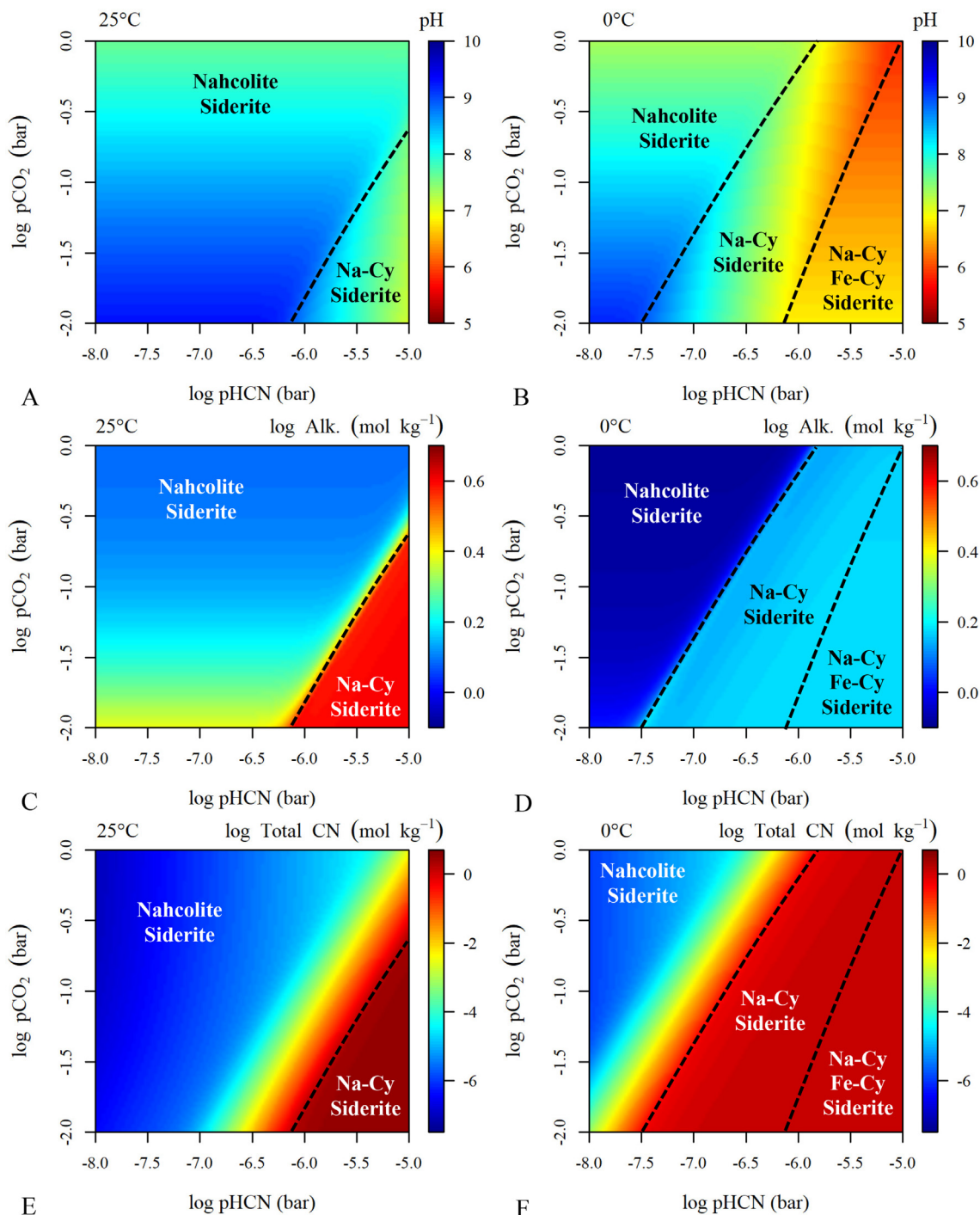


Fig. 3. Ferrocyanide concentrations in NaHCO_3 brines. The modeled pH (A, B), alkalinity (C, D), and total cyanide (E, F) in solutions saturated with Na_2CO_3 alkalinity at 0 and 25 °C. Regions where nahcolite, siderite, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ (Na-Cy), and $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (Fe-Cy) precipitate are delineated by dashed lines. Color scales are pH in A and B, $\log(\text{Alk.})$ in C and D, and $\log(\text{total CN})$ in E and F. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. DISCUSSION

4.1. Implications for the early Earth

Our model results point to a specific environment for concentrating cyanide needed for prebiotic chemistry: relatively

low-temperature, NaHCO_3 -rich, closed-basin lakes. Closed-basin lakes provide a mechanism for accumulating cyanides across hydrologic basins via inflowing waters and evaporation. Furthermore, NaHCO_3 -rich lake waters would counteract acidity from early Earth's CO_2 -rich atmosphere, stabilizing aqueous cyanide as ferrocyanide in alkaline

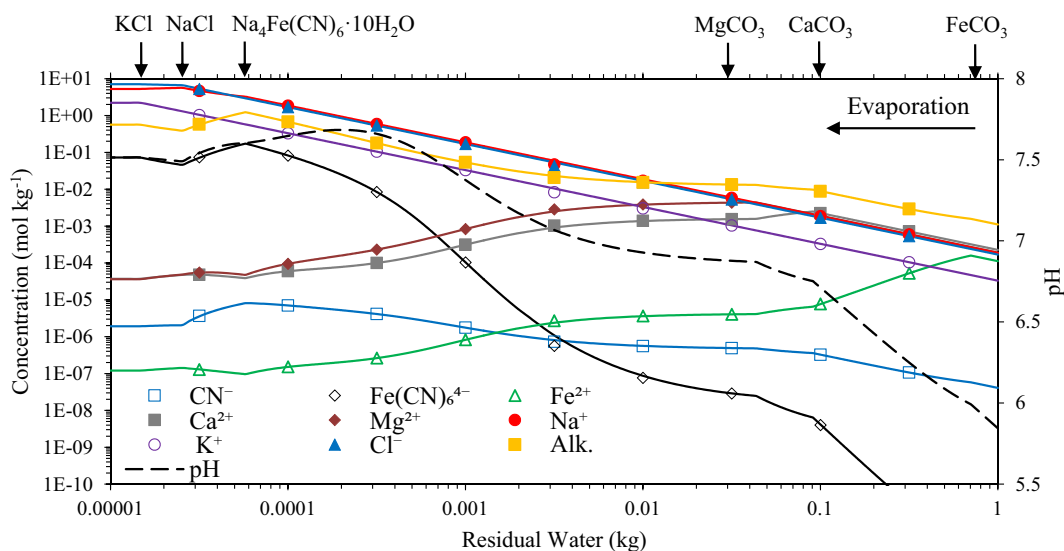


Fig. 4. Evaporative concentration of ferrocyanides. Modeled ion concentrations (mol kg^{-1}) (solid lines) and pH (dashed line) from closed basin evaporation of Archean river water compositions in Hao et al. (2017). The initial water content of the solution is 1 kg, and the residual water is the amount of water remaining as evaporation proceeds. The initial precipitation of salt phases is indicated by arrows at the top of the graph. Evaporation proceeds from right to left, where a residual water content of 1 kg is an unevaporated solution.

solutions. Closed-basin lakes would also concentrate other potential prebiotic reagents, such as abundant carbon in the form of carbonate alkalinity, sulfur compounds, phosphates or phosphites, and trace metals (Jones et al., 1998).

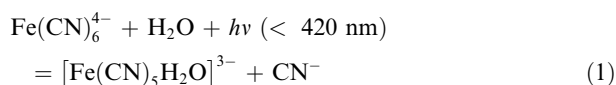
Alkaline lakes typically form in volcanic closed-basins due to chemical weathering by volcanogenic and atmospheric CO_2 , which generates carbonate-rich solutions (Garrels and Mackenzie, 1967; Kempe and Kazmierczak, 2011; Pecoraino et al., 2015; Lowenstein et al., 2017). The chemistry of such lakes is determined by chemical divides (Hardie and Eugster, 1970; Eugster and Jones, 1979) and primarily depends on the relative concentrations of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+}$ and carbonate alkalinity in the inflowing waters. Studies of present-day closed-basin lake evolution do not typically include Fe^{2+} , but in anoxic early Earth waters, Fe^{2+} would have been stable. When $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+}$ is greater than carbonate alkalinity, most of the alkalinity precipitates as insoluble carbonates, resulting in relatively low alkalinity waters (Hardie and Eugster, 1970; Eugster and Jones, 1979). In contrast, when $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+}$ is less than carbonate alkalinity, these cations are removed from evaporating waters as their carbonates and the residual lake water becomes enriched in NaHCO_3 .

Closed-basin alkaline lakes are commonly found in mafic (e.g., basaltic) terrains. Experimental studies of anoxic chemical weathering of basalts (Fabre et al., 2011) in the presence of CO_2 indicate that H^+ is consumed (increasing the pH), carbonate alkalinity increases, and Na^+ preferentially migrates into the aqueous phase relative to Ca^{2+} , Mg^{2+} , and especially Fe^{2+} . Precipitation of secondary silicate minerals also consumes Mg^{2+} , Fe^{2+} , and K^+ ions, leading to an overall condition of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} < \text{carbonate alkalinity}$. In addition, chemical weathering of mafic minerals such as olivine and pyroxene, as

well as glass abundant in mafic rocks, is relatively rapid (Gislason and Hans, 1987; Gudbrandsson et al., 2011), leading to high fluxes of carbonate alkalinity to closed-basin lakes. Upon evaporation, such inflow waters evolve to NaHCO_3 -rich brines.

On the early Earth, mafic and ultramafic rocks were common and fresh volcanic material would have been abundant due to active early volcanism (Taylor and McLennan, 1995). Furthermore, landmasses may have been present as early as the Hadean based on evidence from zircons (Harrison, 2009), possibly associated with hotspot volcanism (Bada and Korenaga, 2018), and there is strong evidence for landmasses in the early Archean based on ~ 3.8 Ga sediments in Greenland (Nutman et al., 1997; Viehmann, 2018). Chemical weathering of such landmasses in Earth's relatively high CO_2 environment (Zahnle et al., 2010) would have released alkali cations and formed alkaline waters, which upon evaporation in closed-basin settings would have formed NaHCO_3 -rich lakes. Such alkaline lake environments are inferred to have been preserved in the Archean geologic record in the Ventersdorp and Tumbiana formations (Karpeta, 1989; Stüeken et al., 2015), and may have been abundant in the early Archean and Hadean also.

A potential complication is that ultraviolet light (UV) may decompose ferrocyanide in the lake through aqueous photochemical dissociation (Broderius and Smith, 1980). Ferrocyanide absorbs UV wavelengths less than 420 nm, resulting in the rapid formation of an unstable $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ complex and free CN^- :



If ferrocyanide solutions were exposed on Earth's surface, this reaction would likely have been important because of a greater flux of near-UV radiation caused by the absence of a stratospheric ozone layer on the early Earth (Catling and Kasting, 2017; p. 291).

Although photodecomposition of ferrocyanide via reaction (13) is expected to produce free cyanide as HCN or CN^- , it can only form extremely low concentrations of free cyanide because of a rapid back reaction. For example, Åspærgær (1952) found that exposing 75 mM ferrocyanide solutions (the concentration at which ferrocyanide precipitates in our evaporative model in Fig. 4) to UV light from a mercury lamp only decomposes $\sim 0.005\%$ of the ferrocyanide after several hours of irradiation, and that decomposition completely reverses in the dark. Furthermore, reaction (13) increases the solution pH, which inhibits the formation of HCN, resulting in negligible HCN losses to the atmosphere (Åspærgær, 1952). Even if HCN were released during the daytime, it would redissolve in aqueous environments during the nighttime (Keefe and Miller, 1996).

Alkaline closed-basin lakes could have concentrated atmospheric HCN as aqueous and solid phase ferrocyanides, but prebiotic synthesis schemes require free cyanide in the form of HCN^0 or CN^- . Patel et al. (2015) qualitatively hypothesized that free cyanide could have been released in quantity by thermal decomposition of ferrocyanide salt evaporites, possibly via magmatic activity or thermal shock from asteroid impact events. The cationic form of the ferrocyanide salt is important because the thermal decomposition products differ depending on the cation (Patel et al., 2015). Na and K-ferrocyanides decompose to NaCN and KCN respectively, and the iron is sequestered as insoluble iron carbide, which does not recombine to form ferrocyanide if water is added. $\text{Mg}_2\text{Fe}(\text{CN})_6$ decomposes to magnesium nitride (Mg_3N_2), and $\text{Ca}_2\text{Fe}(\text{CN})_6$ decomposes to calcium cyanamide (CaNCN) and calcium carbide (CaC_2). Such thermal decomposition products can act as key reagents in prebiotic organic synthesis schemes (Patel et al., 2015; Ritson et al., 2018). The thermal decomposition of $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ has not been studied, but the likely solid phase decomposition products are iron carbide and carbon, which have no special significance for organic synthesis.

Our model predicts the new finding that only $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ would have formed in early Earth environments, which suggests that thermal decomposition would have yielded only NaCN for prebiotic synthesis. Ca and Mg-ferrocyanides would not form because concentrated ferrocyanides only accumulate in highly alkaline brines, which precipitate Ca^{2+} and Mg^{2+} ions as carbonates. $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ is also unlikely because it is more soluble than $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, and granitoid continental rocks on the early Earth have low K/Na ratios compared to modern granites (Condie, 1993), so the source rocks for weathering fluids and river input should be relatively K-poor. Finally, our model does not predict the formation of sparingly soluble ferrocyanide compounds such as $\text{CaK}_2\text{Fe}(\text{CN})_6$ and $\text{MgK}_2\text{Fe}(\text{CN})_6$.

Thermal decomposition would have acted on the other phases in evaporite sequences, along with sedimentary $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$. Based on our closed-basin model

(Fig. 4), the other phases should be Ca/Mg/Fe carbonates, nahcolite, halite, and sylvite, as well as possibly sulfates (not modeled here). CaCO_3 decomposes to CaO at $\sim 800^\circ\text{C}$, whereas Mg and Fe carbonates decompose to their oxides at $400\text{--}500^\circ\text{C}$ (Stern and Weise, 1969). In contrast, Na/K chlorides and Na_2CO_3 (the dehydration product of NaHCO_3) are stable to very high temperatures. Although we consider decomposition of single phases here, we note that decomposition may have occurred in salt mixtures, which could alter the decomposition temperatures and products. The addition of water to likely thermal decomposition compounds, via surface or groundwater flows, would hydrate the oxides to hydroxides, and form alkaline solutions due to Ca/Mg/Fe hydroxide and Na_2CO_3 dissolution. These decomposition products, although not necessary for the formation of aqueous NaCN, are compatible with alkaline NaCN solutions.

An alkaline NaCN-rich flow can also provide other essential chemical species needed for prebiotic chemistry (Patel et al., 2015). Reactions with pyrite, a common crustal mineral, would release thiocyanate (SCN^-) and bisulfide (HS^-), which can act as a reducing agent to build organic molecules from cyanide derivatives in photoredox reactions. Vivianite ($\text{Fe}_2(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$) derived from weathered meteoric material could dissolve to form ferrocyanide and release phosphate, a key component of nucleotides (Patel et al., 2015). Phosphate could also concentrate by evaporation, driving its reactions. Copper (II) sulfides would react to form bisulfide, as well as copper (I) cyanide (CuCN), a potential catalyst for prebiotic chemistry, and cyanogen gas (C_2N_2), a compound implicated in the formation of cytosine (Shapiro, 1999). Hence, a variety of prebiotic ingredients are possible via the interaction of aqueous NaCN with crustal minerals.

Our model does not predict the formation of $\text{Ca}_2\text{Fe}(\text{CN})_6$, which thermally decomposes to CaNCN, a component in the formation of pyrimidines in prebiotic synthesis schemes (Ritson et al., 2018). In the evaporite model (Fig. 4), calcium is removed from alkaline solutions by calcite precipitation. Consequently, cyanamide would need to form via a different geochemical pathway. Another possible route for calcium cyanamide synthesis is by the reaction of CaO (derived from thermal decomposition of CaCO_3) with nitrogen compounds under reducing conditions (Güthner and Mertschenk, 2006). For example, CaNCN could form by post-impact heating of CaCO_3 if the atmosphere were temporarily enriched in HCN, or in CO and NH_3 .

5. CONCLUSIONS

The results presented here show that high ferrocyanide concentrations and $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and/or $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ salts were possible on the early Earth over a wide and plausible range of temperature, $p\text{CO}_2$, and $p\text{HCN}$. Ferrocyanide salts could have formed in closed-basin NaHCO_3 -rich lakes, which would have been common on the early Earth due to high atmospheric CO_2 and active mafic volcanism. Evaporite salt assemblages containing ferrocyanides could have thermally decomposed to NaCN, as well as Ca/Mg/Fe oxides and Na_2CO_3 , which dissolve in aqueous

solution to form NaCN-rich solutions. This free cyanide could then have participated in prebiotic reactions. These results provide a rigorous geochemical pathway for the formation of concentrated, free cyanide, and suggest a specific environment in alkaline, closed-basin lakes. The results also indicate a specific nucleophile, NaCN, for prebiotic synthesis. Such a prebiotic lake environment may also be important for consideration of life originating on other planets, such as Mars.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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