Sulfidic Anion Concentrations on Early Earth for Surficial Origins-of-Life Chemistry

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Abstract

A key challenge in origin-of-life studies is understanding the environmental conditions on early Earth under which abiogenesis occurred. While some constraints do exist (e.g., zircon evidence for surface liquid water), relatively few constraints exist on the abundances of trace chemical species, which are relevant to assessing the plausibility and guiding the development of postulated prebiotic chemical pathways which depend on these species. In this work, we combine literature photochemistry models with simple equilibrium chemistry calculations to place constraints on the plausible range of concentrations of sulfidic anions ($\text{HS}^-$, $\text{HSO}_3^-$, $\text{SO}_3^{2-}$) available in surficial aquatic reservoirs on early Earth due to outgassing of $\text{SO}_2$ and $\text{H}_2\text{S}$ and their dissolution into small shallow surface water reservoirs like lakes. We find that this mechanism could have supplied prebiotically relevant levels of $\text{SO}_2$-derived anions, but not $\text{H}_2\text{S}$-derived anions. Radiative transfer modeling suggests UV light would have remained abundant on the planet surface for all but the largest volcanic explosions. We apply our results to the case study of the proposed prebiotic reaction network of Patel et al. (2015) and discuss the implications for improving its prebiotic plausibility. In general, epochs of moderately high volcanism could have been especially conducive to cyanosulfidic prebiotic chemistry. Our work can be similarly applied to assess and improve the prebiotic plausibility of other postulated surficial prebiotic chemistries that are sensitive to sulfidic anions, and our methods adapted to study other atmospherically derived trace species. Key Words: Early Earth—Origin of life—Prebiotic chemistry—Volcanism—UV radiation—Planetary environments. Astrobiology 18, 1023–1040.

1. Introduction

A key challenge for origins-of-life studies is determining the environmental conditions on early Earth. Environmental conditions (e.g., pH, temperature, pressure, chemical feedstock abundance) play a major role in determining the kinds of prebiotic chemistry that are possible or probable, and hence can help constrain the plausibility of proposed origin-of-life scenarios (e.g., Urey, 1952; Corliss et al., 1981; McCollom, 2013; Ruiz-Mirazo et al., 2014). Consequently, it is critical to understand the range of environmental conditions available on early Earth for abiogenesis to proceed. Work over the past few decades has begun to constrain the environmental conditions that may have been available for abiogenesis, including but not limited to the past presence of liquid water, the availability of UV light at the surface, the mix of gases being outgassed to the atmosphere, the bulk pH of the ocean, and the conditions available at deep-sea hydrothermal vents (Bada et al., 1994; Farquhar et al., 2000; Delano, 2001; Holm and Charlou, 2001; Mojzsis et al., 2001; McCollom and Seewald, 2007; Trail et al., 2011; Mulikidjanian et al., 2012; Beckstead et al., 2016; Sojo et al., 2016; Halevy and Bachan, 2017; Novoselov et al., 2017; Ranjan and Sasselov, 2017).

One challenging environmental factor to constrain is the abundance of trace chemical species on early Earth. These species can be important to proposed prebiotic chemical pathways as feedstocks or catalysts, but their abundances on early Earth can be difficult to determine due to their rarity and hence limited impact on an already scarce rock record. In this paper, we explore the plausible abundances of one such family of molecules: sulfidic anions, that is, sulfur-bearing...
aqueous anions (e.g., hydrosulfide, HS\(^-\); bisulfite, HSO\(_3^-\); sulfite, SO\(_2^-\)\(^2\)). Our initial interest in these molecules was stimulated by the role they play in the prebiotic chemistry proposed by Patel et al. (2015), but our calculations are applicable to studies of surficial prebiotic chemistry in general. For discussion of the relevance of the surface environment and its attendant processes to prebiotic chemistry, see, for example, Mulikidjanian et al. (2012), Walker et al. (2012), Forsythe et al. (2015), Mutschler et al. (2015), Rapf and Vaida (2016), Deamer and Damer (2017), He et al. (2017). Our results are not relevant to deep-sea origin-of-life scenarios, such as McCollom and Seewald (2007), Larowe and Regnier (2008), Martin et al. (2008), and Sojo et al. (2016).

We specifically explore the atmosphere as a planetary source for sulfidic anions through dissolution of volcanically outgassed SO\(_2\) and H\(_2\)S in small, shallow aqueous reservoirs like lakes. Prebiotic Earth’s atmosphere is thought to have been anoxic and more reducing than modern Earth (Kasting, 2014), and volcanism levels have been hypothesized to have been higher (Richter, 1985). Then the abundance of atmospheric H\(_2\)S and especially SO\(_2\) should have been higher compared to modern-day levels, and aqueous reservoirs in equilibrium with the atmosphere would have dissolved some of these gases in accordance with Henry’s law, forming sulfidic anions through subsequent dissociation reactions. We use simple equilibrium chemistry combined with literature photochemical modeling to estimate the concentrations of these sulfidic anions as a function of pSO\(_2\) and pH\(_2\)S, and as a function of total sulfur outgassing flux. Elevated levels of atmospheric sulfur can lead to the formation of UV-shielding gases and aerosols; consequently, we use radiative transfer calculations to constrain the surface UV radiation environment as a function of total sulfur outgassing flux. UV light is of interest to prebiotic chemists both as a potential stressor for abiogenesis (Sagan, 1973; Cockell, 2000), as a potential eustressor for abiogenesis (Sagan and Khare, 1971; Mulikidjanian et al., 2003; Pascal, 2012; Sarker et al., 2013; Rapf and Vaida, 2016; Xu et al., 2016), and because of evidence that the nucleobases evolved in a UV-rich environment (Rios and Tor, 2013; Beckstead et al., 2016).

We apply our calculations to the case study of the cyanosulfidic prebiotic systems chemistry of Patel et al. (2015). Building on the work of Powner et al. (2009) and Ritson and Sutherland (2012), Patel et al. (2015) proposed a prebiotic reaction network for the synthesis of activated ribonucleotides, short sugars, amino acids and lipid precursors from a limited set of feedstock molecules in aqueous solution under UV irradiation (at 254 nm). This reaction network is of interest because of the progress it makes toward the longstanding problem of nucleotide synthesis, because it offers the promise of a common origin for many biomolecules, and because it imposes specific geochemical requirements on its environment, which can be compared against what is available on early Earth to constrain and improve the chemistry’s prebiotic plausibility (Higgs and Lehman, 2015; Springsteen, 2015; Šponer et al., 2016). Relevant to our work, the Patel et al. (2015) chemistry requires sulfidic anions to proceed, as both a photoreductant and as a feedstock for a subset of the network’s reactions. Patel et al. (2015) proposed impactors as a source for the sulfidic anions; while possible, this scenario imposes an additional, local requirement for this chemistry to function. On the other hand, if the atmosphere could supply adequate redox reductant (and feedstock) on a global basis, it would reduce the requirements for transport network to function, and would make it more compelling as an origins-of-life scenario. We evaluate this scenario. While our paper focuses on the chemistry of Patel et al. (2015) as a case study, our work can be used to evaluate and improve the plausibility of any proposed sulfidic ion-sensitive surficial prebiotic chemistry. Our methods can be adapted to study the prebiotic surficial concentrations of other atmospherically sourced aqueous species.

### 2. Background

#### 2.1. Plausible prebiotic levels of H\(_2\)S and SO\(_2\)

The abundances of H\(_2\)S and SO\(_2\) in Earth’s atmosphere are set by photochemistry and are sensitive to a variety of factors. One of the most important of these factors is the outgassing rate of these compounds from volcanoes into the atmosphere. Absent biogenic sources, atmospheric photochemistry models typically assume abiogenic SO\(_2\) outgassing rates of 1–3 \(\times 10^{9}\) cm\(^{-2}\) s\(^{-1}\) (Kasting et al., 1989; Zahnle et al., 2006; Hu et al., 2013; Claire et al., 2014), consistent with the measured modern mean volcanogenic SO\(_2\) outgassing rate of 1.7–2.4 \(\times 10^{10}\) cm\(^{-2}\) s\(^{-1}\) (Halmer et al., 2002). H\(_2\)S emission rates are indirectly estimated and much less certain; they range from 3.1 \(\times 10^{10}\) to 7.7 \(\times 10^{9}\) cm\(^{-2}\) s\(^{-1}\). A common assumption in atmospheric modeling is that SO\(_2\) and H\(_2\)S are outgassed in a 10:1 ratio (e.g., Zahnle et al., 2006; Claire et al., 2014).

Early Earth is often hypothesized to have been characterized by higher levels of volcanic outgassing compared to modern Earth due to presumed higher levels of internal heat and tectonic activity. Models often assume that Archean SO\(_2\) outgassing rates were \(~3\times\) modern (Richter, 1985; Kasting et al., 1989; Zahnle et al., 2006). However, Halevy and Head (2014) point out that during the emplacement of major volcanogenic features such as the terrestrial basaltic plains, sulfur outgassing rates as high as 10\(^{10}\) to 10\(^{11.5}\) cm\(^{-2}\) s\(^{-1}\) are possible, with the upper limit on outgassing rate coming from estimates of sulfur flux during emplacement of the Deccan Traps on Earth (Selt et al., 2006).

No firm constraints exist for SO\(_2\) and H\(_2\)S levels on prebiotic Earth. Kasting et al. (1989) modeled a plausible prebiotic atmosphere of 2 bar CO\(_2\), 0.8 bar N\(_2\) under 0.75\(\times\) present-day solar irradiation to account for the effects of the faint young Sun at 3.9 Ga. Kasting et al. (1989) assumed that sulfur was outgassed entirely as SO\(_2\) at a total sulfur outgassing flux of \(\phi_{B}=3 \times 10^{9}\) cm\(^{-2}\) s\(^{-1}\) into an atmosphere overlying an ocean saturated in SO\(_2\); this last condition favors accumulation of SO\(_2\) in the atmosphere. Claire et al. (2014) modeled an atmosphere of 0.99 bar N\(_2\) and 0.01 bar CO\(_2\), under irradiation by the 2.5 Ga Sun, with an SO\(_2\):H\(_2\)S outgassing ratio of 10:1, for \(\phi_{B}=1 \times 10^{5}\) to 1 \(\times 10^{10}\) cm\(^{-2}\) s\(^{-1}\). Hu et al. (2013) modeled an atmosphere consisting of 0.9 bar CO\(_2\) and 0.1 bar N\(_2\) under irradiation by the modern Sun, with an SO\(_2\):H\(_2\)S emission ratio of 2, for \(\phi_{B}=3 \times 10^{7}\) to 1 \(\times 10^{10}\) cm\(^{-2}\) s\(^{-1}\). The SO\(_2\) and H\(_2\)S mixing ratios calculated by these models are shown in Table 1; these mixing ratios may be trivially converted to partial pressures by multiplying against the bulk atmospheric pressure. Note that the Claire et al. (2014) and Kasting et al. (1989) values are surface mixing ratios, while the Hu et al. (2013) values are
column-integrated mixing ratios. Since $\text{H}_2\text{S}$ and $\text{SO}_2$ abundances tend to decrease with altitude due to losses from photochemistry, column-integrated mixing ratios should be somewhat less than the surface mixing ratio. However, since density also decreases with altitude, mixing ratios at lower altitudes are more strongly weighted in the calculation of column-integrated mixing ratios, so the column-integrated mixing ratio tends to be close to the surface mixing ratio.

These models broadly agree that $\text{SO}_2$ and $\text{H}_2\text{S}$ levels were low and increase with sulfur emission rate, but their estimates for $r_{\text{SO}_2}$ and $r_{\text{H}_2\text{S}}$ disagree with each other by up to a factor of 400. The Hu et al. (2013) estimates are typically higher than the other estimates considered. The variation in these abundances demonstrates the sensitivity of $\text{SO}_2$ and $\text{H}_2\text{S}$ levels to atmospheric parameters such as composition and deposition velocities. Of these models, we find Hu et al. (2013) best matches the current fiducial understanding of conditions on early Earth: an atmosphere dominated by CO$_2$ and N$_2$, with volcanic outgassing of both $\text{SO}_2$ and $\text{H}_2\text{S}$, with oceans not saturated in $\text{SO}_2$ (as compared to possibilities for early Mars; see Halevy et al., 2007). Hu et al. (2013) also has the advantage of calculating atmospheric composition at higher values of sulfur outgassing flux than Kasting et al. (1989) and Claire et al. (2014), encompassing the $1 \times 10^{11.5}$ cm$^{-2}$ s$^{-1}$ flux which is the upper limit of what Halevy and Head (2014) suggest possible for the emplacement of terrestrial basaltic plains. Hu et al. (2013) model processes including wet and dry deposition, formation of $\text{H}_2\text{SO}_4$ and $\text{S}_8$ aerosol, and photochemistry and thermochemistry, with $>1000$ reactions included in their reaction network. We therefore use Hu et al. (2013) as a guide when estimating $\text{H}_2\text{S}$ and $\text{SO}_2$ levels as a function of sulfur outgassing flux (see Appendix A), with the understanding that further, prebiotic-Earth-specific modeling is required to constrain this relation with certainty.

3. Methods

We consider a gas $Z$ dissolving into a surficial aqueous reservoir ($\leq 1$ m deep), through which the UV light required for prebiotic biomolecule synthesis can penetrate (Ranjan and Sasselov, 2016); our archetypal such environment is a shallow lake. To isolate the effects of atmospheric supply of $Z$, we assume no other source of $Z$ to be present (e.g., no geothermal source at the lake bottom). Henry’s law states that the concentration of $Z$ in aqueous solution at the air/water interface is proportional to the partial pressure of the gas at that interface. We assume the aqueous reservoir to be well mixed and equilibrated throughout, so that the concentration of $[Z]$ is uniform throughout the reservoir at the surficial value. If the reservoir is not well mixed, then the dissolved gas concentration will vary deeper into the reservoir. Under our assumption of no non-atmospheric source of $Z$, $[Z]$ would decrease with depth for a poorly mixed aqueous reservoir.

This method of calculating $[Z]$ is predicated on the assumption that the aqueous body is in equilibrium with the atmosphere, that is, that the solution is saturated in $Z$ and the sink and source of $Z$ is outgassing and deposition from the atmosphere. This assumption is valid when there are no other sinks to drive the system away from equilibrium. We discuss the veracity of this assumption in Section 5.2. In brief, this assumption is valid for shallow, well-mixed lakes that are not very acidic or hot, but not valid for deep, acidic, or hot waters. For these scenarios, our calculations provide upper bounds on $[Z]$. In aqueous solution, $\text{H}_2\text{S}$ undergoes the dissociation reactions

\[
\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+ , \ pK_{\text{H}_2\text{S},1} = 7.05 \tag{1}
\]
\[
\text{HS}^- \rightarrow \text{S}^{2-} + \text{H}^+ , \ pK_{\text{H}_2\text{S},2} = 19 \tag{2}
\]

where the $pK_a$ values are taken from Lide (2009) and can be related to the corresponding equilibrium constants by $K_{\text{eq}} = 10^{-pK_a}$. Similarly, $\text{SO}_2$ undergoes the reactions

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{HSO}_3^- + \text{H}^+ , \ pK_{\text{HSO}_3,1} = 1.86 \tag{3}
\]
\[
\text{HSO}_3^- \rightarrow \text{SO}_3^{2-} + \text{H}^+ , \ pK_{\text{HSO}_3,2} = 7.2 \tag{4}
\]
\[
\text{HSO}_3^- + \text{SO}_2 \rightarrow \text{HS}_2\text{O}_5^- , \ pK_{\text{HSO}_3,3} = 1.5 \tag{5}
\]

where the $pK_a$ values are from Neta and Huie (1985).

To compute the abundances of these different sulfur-bearing compounds as a function of $[Z]$, we must make assumptions as to the background chemistry of the aqueous reservoir they are dissolved in, especially its pH. If the reservoir is completely unbuffered (e.g., pure water), its pH (and hence the speciation of S-bearing compounds) will be completely determined by $[Z]$. At the other extreme, if the reservoir is completely buffered, its pH will be independent of $[Z]$. Natural waters typically lie in between these two extremes; they are often buffered by mineral or atmospheric

| Model | $r_{\text{H}_2\text{S}}$ | $r_{\text{SO}_2}$ |
|-------|-----------------|-----------------|
| Kasting et al. (1989)$^a$, \(\phi_S = 3 \times 10^9\) cm$^{-2}$ s$^{-1}$ | $2 \times 10^{-10}$ | $2 \times 10^{-9}$ |
| Claire et al. (2014)$^b$, \(\phi_S = 3 \times 10^9\) cm$^{-2}$ s$^{-1}$ | $1 \times 10^{-11}$ | $5 \times 10^{-11}$ |
| Hu et al. (2013)$^b$, \(\phi_S = 3 \times 10^9\) cm$^{-2}$ s$^{-1}$ | $4 \times 10^{-10}$ | $3 \times 10^{-10}$ |
| Claire et al. (2014)$^b$, \(\phi_S = 1 \times 10^{10}\) cm$^{-2}$ s$^{-1}$ | $3 \times 10^{-11}$ | $1 \times 10^{-10}$ |
| Hu et al. (2013)$^b$, \(\phi_S = 1 \times 10^{10}\) cm$^{-2}$ s$^{-1}$ | $1 \times 10^{-9}$ | $9 \times 10^{-10}$ |

$^a$Surface mixing ratio.
$^b$Column-integrated mixing ratio.
interactions toward a certain pH, but with enough atmospheric supply their buffers can be overwhelmed. We explore these bracketing cases below, with the understanding that the true speciation behavior in nature was most likely somewhere in between.

3.1. Calculating dissolved gas concentration

We use Henry’s law, coupled with the well-mixed reservoir assumption, to calculate the concentration of molecules dissolved from the atmosphere. Henry’s law states that for a species $Z$,

$$[Z] = H_Z f_Z$$

where $H_Z$ is the gas-specific Henry’s law constant and $f_Z$ is the fugacity of the gas. Over the range of temperatures and pressures relevant to surficial prebiotic chemistry, the gases in our study are ideal, and consequently $f_Z = p_Z$, the partial pressure of $Z$. We make this simplifying assumption throughout our study.

At $T_0 = 298.15$ K, the Henry’s law constants for $H_2S$ and $SO_2$ dissolving in pure water are $H_{H_2S} = 0.101$ M/bar and $H_{SO_2} = 1.34$ M/bar, respectively. Increasing salinity tends to decrease $H_C$, a process known as salting out. Similarly, increasing temperature also tends to decrease $H_C$. Our overall results are insensitive to variations in temperature of 25 K from $T_0$ and $0 \leq \left[\text{NaCl}\right] \leq 1$ M; see Appendix C and Appendix D.1. For simplicity, we therefore neglect the temperature- and salinity-dependence of Henry’s law.

3.2. Unbuffered solution

Consider an unbuffered solution with dissolved $Z$, whose properties are determined entirely by the reactions $Z$ and its products undergo. From the definition of equilibrium constant, we can use the $H_2S$ and $SO_2$ speciation reactions to write

$$a_{H_2S} - a_{H^+} = K_{aH_2S}$$

$$a_{SO_2} - a_{H^+} = K_{aSO_2}$$

and

$$a_{HSO_3^-} - a_{H^+} = K_{aHSO_3^-}$$

where $a_c$ is the activity of species $C$. $a_c$ is related to the concentration of $C$, $[C]$, by $a_c = \gamma_C [C]$, where $\gamma_C$ is the activity coefficient (Misra, 2012). The use of activities instead of concentrations accounts for ion-ion and ion-$H_2O$ interactions. $\gamma=1$ for a solution with an ionic strength of $I=0$. For ionic strengths of $0-0.1$ M, we calculate the activity coefficients for each species as a function of solution ionic strength using Extended Debye-Hückel theory (Debye and Huckel, 1923). The activity coefficients in this formalism are calculated by

$$\log(\gamma_C) = -A_C^2 \frac{I^{0.5}}{1 + B_C I^{0.5}}$$

Here, $A$ and $B$ are constants that depend on the temperature, density, and dielectric constant of the solvent; we use $A = 0.5085 M^{-1/2}$ and $B = 0.3281 M^{-1/2} A^{-1}$, corresponding to 25°C water (Misra, 2012) (our results are robust to this assumption; see Appendix D). $z_C$ is the charge of species $C$. $z_C$ is an ion-specific parameter with values related to the hydration radius of the aqueous species; we took our $z_C$ values from Misra (2012). We were unable to locate a value of $z_C$ for $HSO_3^-$ and consequently take $\gamma_{HSO_3^=} = 1$ throughout. $I$ is the ionic strength of the solution, defined as

$$I = 0.5(\Sigma_C|z_C|^2)$$

We can combine these equations with the equation for water dissociation:

$$H_2O \rightarrow OH^- + H^+, \ pK_w = 14$$

and the requirement for charge conservation:

$$\Sigma_C z_C C = 0$$

With $[Z]$ specified by Henry’s law and our assumption of a well-mixed reservoir, this system is fully determined, and we can numerically solve it to determine the concentration of each of the species above as a function of $p_Z$ and $I$. A wide range of ionic strengths are possible for natural waters; modern freshwater systems like rivers have typical ionic strengths of order $1 \times 10^{-3}$ M (Lerman et al., 1995), whereas modern terrestrial oceans have an ionic strength of 0.7 M$^2$. The concentrations of divalent cations, especially Mg$^{2+}$ and Ca$^{2+}$, in early oceans have been suggested to be near 10 mM (Deamer and Dworkin, 2005). A more fundamental constraint comes from vesicle formation, which is known to be inhibited at high salt concentrations and hence ionic strengths: Maurer and Nguyen (2016) report that lipid vesicle formation is impeded in solutions with $I > 0.1$ M. These considerations motivate our focus on low-ionic-strength waters, with $I \leq 0.1$ M$^2$.

$^1$For example, the oceans on modern Earth are buffered to a pH of 8.1–8.2 due primarily to carbonate buffering (Hall–Spencer et al., 2008; Zeebe and Wolf-Gladrow, 2009); estimates of ancient ocean pH vary but often invoke slightly lower pH due to posited higher CO$_2$ levels early in Earth’s history (see, e.g., Morse and Mackenzie, 1998; Amend and McCallom, 2009; Haley and Bachan, 2017, and sources therein). Smaller bodies, like lakes, can have an even wider range of pH values due to local conditions; lakes on modern Earth can have pH < 1 (e.g., Kawah Ijen crater lake; Löhrl et al., 2005) and pH > 11 (e.g., Lake Natron; Grant and Jones, 2000).

$^2$Accessed 29 November 2016.

$^3$A further practical challenge with extending our calculations to higher ionic strengths is that the parameters required to compute the activity coefficients at high ionic strengths (e.g., via the Truesdell and Jones, 1974 formalism) are not available for many of the species we consider.
We calculate the speciation of sulfur-bearing species from dissolved H$_2$S and SO$_2$ for $I=0$ and $I=0.1$ M; the results are shown in Figs. 1 and 2. $I=0$ is the lowest possible ionic strength, and $I=0.1$ M corresponds to the limit from lipid vesicle formation.

3.3. Buffered solution

Consider now an aqueous reservoir that is buffered to a given pH. For example, the pH of the modern oceans is buffered by calcium carbonate to a global mean value of 8.1–8.2 (Hall-Spencer et al., 2008). Then, we know [H$^+$], and can hence calculate the speciation of dissolved H$_2$S and SO$_2$ from the equilibrium constant Eqs. 7–8 and 9–11 individually. Our results are insensitive to ionic strength for $I \leq 0.1$ M (see Figs. 1 and 2, and Appendix B), and $I \leq 0.1$ M is required for vesicle formation and other prebiotic chemistry (Maurer and Nguyen, 2016; Deamer and Damer, 2017), motivating us to take $I=0$ for simplicity.

With Henry’s law and our assumption of a well-mixed reservoir, we can readily calculate the concentration of the above species as a function of pH$_2$S for an unbuffered reservoir. The code used to implement these calculations is available for validation and extension at https://github.com/sukritranjan/RanjanToddSutherlandSasselov2017.git.

4. Results

4.1. H$_2$S versus SO$_2$

Figure 1 shows the speciation of sulfur-bearing compounds from dissolved H$_2$S for an unbuffered reservoir, and reservoirs buffered to various pH values. Over the range of ionic strengths considered, HS$^-$ is the dominant anion, and SO$_2^-$ is the dominant radical.
Figure 2 shows the speciation of sulfur-bearing compounds from dissolved SO2 for an unbuffered reservoir, and reservoirs buffered to various pH values. Because of the lack of O2 in this anoxic era, the first dissociation of SO2 forms sulfite, rather than sulfate. HSO3- and SO3^{2-} are present at comparable levels; HS2O5(-) is negligible. As pSO2 increases, the pH of the unbuffered reservoir falls off rapidly; this is expected since hydrated SO2 is a strong acid.

SO2 is an order of magnitude more soluble than H2S, and its first dissociation is much more strongly favored (pK_{SO2,1} = 1.86 vs. pK_{H2S,1} = 7.05). Consequently, far higher concentrations of sulfidic anions can be sustained for a given pSO2 than for the same pH2S (see Figs. 1 and 2). Maintaining micromolar concentrations of HS^{-} requires pH_{2S} \geq 1 \times 10^{-6} bar at pH = 8.2 (modern ocean), and pH_{2S} \geq 1 \times 10^{-5} bar for more neutral pH values. Maintaining micromolar concentrations of S^{2-} is impossible over plausible ranges of pH and sulfur outgassing flux (pK_{S^{2-},1,2} = 19). The concentration of sulfidic anions could be increased by going to higher pH and salinity. However, the reactions of, for example, Patel et al. (2015) have not been demonstrated to proceed under such conditions.

By contrast, dissolved SO2 gives rise to comparatively high concentrations of sulfidic anions due to higher solubility and a more favorable first ionization. Micromolar concentrations of HSO3^{-} are possible for pSO2 \geq 1 \times 10^{-11} bar for all but very acidic solutions; micromolar concentrations of SO3^{2-} are possible for solutions buffered to pH \geq 7 over the same range. Millimolar levels of HSO3^{-} and SO3^{2-} are possible for solutions buffered to pH \geq 8.2 for pSO2 \geq 1 \times 10^{-10} bar, and for pH \geq 7 solutions for pSO2 \geq 1 \times 10^{-8} bar. pSO2 \geq 3 \times 10^{-10} bar is expected for outgassing rates corresponding to the steady state on early Earth according to the model of Hu et al. (2013) (\phi_{S} = 3 \times 10^{9} cm^{-2} s^{-1}). During transient epochs of intense volcanism such as the emplacement of basaltic plains, emission rates might have risen as high as \phi_{S} = 10^{11.5} cm^{-2} s^{-1} (Self et al., 2006; Halevy and Head, 2014), corresponding to pSO2 = 1 \times 10^{-8} bar. We note
that estimates based on Hu et al. (2013) are for column-integrated abundances, and the surface abundances were likely modestly larger. Hence, it seems likely that the atmosphere could have supplied micromolar levels of SO2-derived anions for prebiotic chemistry, and perhaps even millimolar concentrations if the solution were buffered to slightly alkaline pH (e.g., pH comparable to the modern ocean).

4.2. H2S and SO2

In Section 4.1 we evaluated the prospects for buildup of sulfur-bearing anions from dissolved atmospheric H2S and SO2 in isolation. However, H2S and SO2 are injected simultaneously into the atmosphere by volcanism and would have been present at the same time. Figure 3 presents the speciation of sulfur-bearing molecules from dissolved atmospheric H2S and SO2 in a solution buffered to pH = 7 as a function of total sulfur outgassing rate, $\phi_S$. This pH corresponds approximately to the phosphate-buffered conditions in which the chemistry of Patel et al. (2015) proceeded. If the solution were buffered to higher pH, sulfidic anion concentrations would be higher due to a more favorable first dissociation, and vice versa.

As before, we connected the H2S and SO2 abundances to $\phi_S$ by the high-CO2 model calculations of Hu et al. (2013).

We took the surface mixing ratio of these gases to equal the column-integrated mixing ratio, which may slightly underestimate the surface mixing ratio of these gases. $\phi_S = 1 - 3 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ for modern Earth and $\phi_S = 10^{10}$ to $10^{11.5} \text{ cm}^{-2} \text{ s}^{-1}$ have been suggested on a transient (1–10 year) basis for major volcanic episodes like the emplacement of basaltic plains on Earth (Self et al., 2006; Halevy and Head, 2014). As discussed in Section 4.1, SO2-derived anions can build to micromolar levels at modern outgassing rates and can build to millimolar levels during volcanic episodes like the emplacement of basaltic plains, while H2S-derived anions cannot, absent highly alkaline conditions.

4.3. Coupling to the UV surface environment

H2S, SO2, and their photochemical aerosol by-products (S8, H2SO4) are robust UV shields, and at elevated levels their presence can dramatically reduce surface UV radiation (Hu et al., 2013; Ranjan and Sasselov, 2017). This effect could be good for origin-of-life scenarios which do not require UV light, since UV light can photolytically destroy newly formed biomolecules (e.g., Sagan, 1973). On the other hand, it could be bad for UV-dependent prebiotic chemistry, which depends on UV light to power their syntheses (e.g., Ritson and Sutherland, 2012; Patel et al., 2015; Xu et al., 2016). In the latter case, it begs the question whether the elevated levels of SO2 and H2S that could supply the sulfidic anions required for cyanosulfidic chemistry might also quench the UV radiation also required by these pathways.

To explore this question, we calculated the attenuation of incoming 3.9 Ga solar radiation (calculated from the models

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4It is thought that these chemistries should proceed over a broad range of pH. However, they will proceed best for $\text{pH} \leq 9.2$ (so that HCN tends to remain protonated) and $\text{pH} \geq 7$ (so that the sulfidic anions tend to remain deprotonated).
of Claire et al., 2012) by a CO2-N2-SO2-H2S atmosphere, using a two-stream radiative transfer model (Ranjan and Sasselov, 2017; Ranjan et al., 2017). We set the solar zenith angle to 48.2°, corresponding to the insolation-weighted mean value (Cronin, 2014), and the albedo to 0.2, a representative value for rocky planets consistent with past modeling5 (Cronin, 2014), and the albedo to 0.2, a representative bound on the true UV fluence. Consequently, our results should be interpreted as a lower bound on the possible radiative impact of the sulfur aerosols. Similarly, Hu et al. (2013) assume an aerosol size distribution of CO2 and N2 matching those assumed by Hu et al., 2013; Beckstead et al., 2016; Pollum et al., 2016), this suggests the biogenic nucleobases evolved in an epoch with less UV radiation than we consider plausible for major terrestrial volcanic episodes. On the other hand, for φS ≥ 3 × 10^{11} cm^{-2} s^{-1}, atmospheric sulfur-bearing gases and aerosols, especially the UV-absorbing S8, suppress surface UV radiation by an order of magnitude or more; this paucity of UV radiation may pose a challenge for UV-dependent prebiotic chemistry but could create a more clement surface environment for UV-independent prebiotic chemistries. If one accepts the idea that the nucleobases show evidence of UV selection pressure (Crespo-Hernández et al., 2004; Serrano-Andres and Merchan, 2009; Rios and Tor, 2013; Beckstead et al., 2016; Pollum et al., 2016), this suggests the biogenic nucleobases evolved in an epoch with φS ≤ 1 × 10^{11} cm^{-2} s^{-1}.

5Our results are insensitive to the precise choice of albedo or solar zenith angle.

Figure 4 presents the UV fluence available on the surface of the prebiotic Earth as a function of φS under these assumptions. For φS ≤ 1 × 10^{11} cm^{-2} s^{-1}, UV radiation remains abundant on the planet surface. Millimolar levels of SO2^{-2} and HSO3^{-} are available in aqueous reservoirs buffered to pH ≥ 7 for φS = 1 × 10^{11} cm^{-2} s^{-1}. Consequently, volcanism could supply prebiotically relevant levels of SO2^{-2} and HSO3^{-} without blocking off the UV radiation required by UV-dependent prebiotic pathways for sulfur emission fluxes up to φS ≤ 1 × 10^{11} cm^{-2} s^{-1} (near the upper edge of what is considered plausible for major terrestrial volcanic episodes). On the other hand, for φS ≥ 3 × 10^{11} cm^{-2} s^{-1}, atmospheric sulfur-bearing gases and aerosols, especially the UV-absorbing S8, suppress surface UV radiation by an order of magnitude or more; this paucity of UV radiation may pose a challenge for UV-dependent prebiotic chemistry but could create a very clement surface environment for UV-independent prebiotic chemistries. If one accepts the idea that the nucleobases show evidence of UV selection pressure (Crespo-Hernández et al., 2004; Serrano-Andres and Merchan, 2009; Rios and Tor, 2013; Beckstead et al., 2016; Pollum et al., 2016), this suggests the biogenic nucleobases evolved in an epoch with φS ≤ 1 × 10^{11} cm^{-2} s^{-1}.

5. Discussion

5.1. Sulfidic anion concentrations in surficial waters on early Earth

We have shown that terrestrial volcanism could have globally supplied the sulfidic anions SO2^{-2} and HSO3^{-}, derived from the dissolution of SO2 into aqueous solution, to shallow surficial aqueous reservoirs on early Earth. These compounds would have been available at micromolar levels for volcanic outgassing rates comparable to the modern day. During episodes of high volcanism, such as those responsible for emplacement of basaltic plains (φS ≈ 1 × 10^{11} cm^{-2} s^{-1}), these compounds could have built up to the millimolar levels in shallow aqueous reservoirs buffered to pH ≥ 7. On the other hand, due to its lower solubility and unfavorable first dissociation, sulfidic anions derived from dissolving atmospheric H2S...
can only be supplied at low concentrations (sub-micromolar) across the plausible range of pHS and pH₂. Therefore, other mechanisms must be invoked for supply of such anions, if required by a proposed prebiotic chemical pathway.

We conducted our calculations assuming a temperature of T=25°C. We investigate the sensitivity of our results to temperatures ranging from T=0°C to 50°C in Appendix D, including temperature effects on both the reaction rate and the Henry’s law coefficient. While H₂S-derived anion concentrations are not significantly affected by temperature variations in this range, SO₂-derived anion concentrations are. This is because HSO₃⁻ decreases with temperature and pK₆so₃⁻ increases with temperature; both effects favor decreased concentrations of HSO₄⁻ and its derivatives with increasing temperature, assuming a not highly acidic (pH > 2.5) solution.

We find that while our overall conclusions are unchanged, concentrations of the SO₂-derived anions HSO₃⁻ and SO₃²⁻ are an order of magnitude higher for T ≈ 0°C relative to T=25°C, and an order of magnitude lower for T ≈ 50°C, assuming a near-neutral reservoir. Consequently, cooler waters are more favorable environments for prebiotic chemistry which invokes HSO₃⁻ or SO₃²⁻.

Sulfur-bearing gases and aerosols, in particular S₈, are strong UV absorbers, and if present at high enough levels could suppress UV-sensitive prebiotic chemistry. For φₛ ≥ 1 × 10¹¹ cm⁻² s⁻¹, corresponding to most of the plausible range of sulfur emission fluxes on early Earth, surface UV fluxes (200–300 nm) are not significantly attenuated by atmospheric absorbers, meaning that in the steady state and for most volcanic eruptions, abundant UV light should have reached Earth’s surface to power UV-dependent prebiotic chemistry. However, for the very largest volcanic eruptions, corresponding to the uppermost end of the plausible range of sulfur outgassing fluxes during terrestrial basaltic flood plain emplacement (φₛ = 3 × 10¹¹ cm⁻² s⁻¹), surface UV fluence (200–300 nm) may be reduced by an order of magnitude or more. Hence, the very largest volcanic events might create an especially clement surficial environment for UV-independent prebiotic chemistry.

These results were derived using the high-CO₂ model of Hu et al. (2013), which, while plausible, assumes more CO₂ and less N₂ than other models of prebiotic Earth (e.g., Rugheimer et al., 2015) and is hence comparatively oxidizing. We explored the sensitivity of our results to this assumption via the N₂-rich model of Hu et al. (2013). This model assumes 1 bar of N₂ and negligible CO₂ and is hence an unrealistic approximation to early Earth, because an appreciable CO₂ inventory is expected due to climate constraints (Kasting, 1993; Wordsworth and Pierrehumbert, 2013) and due to volcanic outgassing of CO₂. Hence, this model serves as an extreme bounding case. Assuming this model, we find that H₂S and SO₂ levels are lower than for the high-CO₂ case. SO₂-derived anions remain available at micromolar levels over the plausible range of φₛ but in order to build to millimolar levels require the assumption of reservoirs buffered to slightly alkaline pH (e.g., pH ≈ 8.2, modern ocean). HS⁻ levels are even lower than in the CO₂-rich case. UV fluences are lower than in the CO₂-rich case, due to elevated levels of S₈ formation in this more reducing atmosphere; surface UV fluence (200–300 nm) is suppressed by an order of magnitude or more for φₛ ≥ 1 × 10¹¹ cm⁻² s⁻¹. Overall, this boundary case suggests that our finding that the atmosphere can supply prebiotically relevant levels of SO₂-derived anions but not H₂S-derived anions in conjunction with UV light remains true across a broad range of CO₂ and N₂ abundances, though both sulfidic anion abundances and UV are lower for more reducing, N₂-rich atmospheres. However, a detailed exploration of the pCO₂-pN₂ parameter space with photochemical models is required to be certain of these findings.

5.2. Impact of other sinks

Our analysis is predicated on the assumption that [Z] is set by Henry equilibrium, that is, that the aqueous reservoir is saturated in H₂S and SO₂. This assumes no major sinks other than outgassing to the atmosphere. In this section, we examine the sensitivity of our results to this assumption. Microbial sinks (e.g., Halevy, 2013) are not relevant since we are concerned with prebiotic Earth; neither are oxic sinks, since the surface of early Earth was anoxic (Kasting and Walker, 1981; Kasting, 1987; Farquhar et al., 2001; Pavlov and Kasting, 2002; Li et al., 2013). However, reactions with metal cations to produce insoluble precipitates and redox reactions could have been relevant; we explore these sinks.

5.2.1. Precipitation reactions with metal cations. We explored the possibility that reactions of S anions with metal cations might lead to formation of insoluble precipitates, which would act as a sink on S-anion concentrations. Such cations might have been delivered to aqueous reservoirs via weathering of rocks and minerals.

Under standard conditions, Fe²⁺ and Cu²⁺ react with H₂S(aq) to generate insoluble precipitates, like CuS and FeS₂ (Rickard and Luther, 2007; Rumble, 2017). Interaction of copper sulfides with cyanide solution can liberate HS⁻ (Coderre and Dixon, 1999), as invoked by Patel et al. (2015). In general, high-Cu/Fe waters (e.g., due to interaction with ores) will be even more HS⁻-poor than we have modeled, with the caveat that specific local environmental factors (like the presence of aqueous cyanide) can prevent sulfide depletion due to precipitation. This reinforces our conclusion that HS⁻ concentrations are unlikely to have reached prebiotically relevant levels on early Earth, absent unique local factors. For example, the aqueous cyanide required as a feedstock in the pathways of Patel et al. (2015) would also permit elevated HS⁻ levels.

Ca²⁺, produced by mineral weathering, reacts with sulfite to produce insoluble CaSO₄. Studying the Ca²⁺-SO₄⁻ system
requires considering the effects of carbonate \((\text{CO}_3^{2-})\) as well, because \(\text{Ca}^{2+}\) forms precipitate with this anion as well, and because high levels of carbonate are expected in natural waters on early Earth due to elevated levels of atmospheric \(\text{CO}_2\) required to solve the faint young Sun paradox (Kasting, 1987). While precisely modeling this geochemical system requires use of a geochemical model capable of accounting for all reactions involving sulfites and carbonates and their kinetics, we can get a first-order estimate of the impact of \(\text{Ca}^{2+}\), as follows.

Assuming parameters from Hu et al. (2013), the flux of carbonates into solution due to deposition and speciation of atmospheric \(\text{CO}_2\) is \(r_{\text{CO}_2}\text{Prim}^{\text{dep}} \text{CO}_2 = 2 \times 10^{15} \text{cm}^2 \text{s}^{-1}\) on the \(\text{CO}_2\)-rich early Earth, which exceeds the mean flux of \(\text{Ca}\) due to mineral weathering \((1-5 \times 10^{10} \text{cm}^2 \text{s}^{-1})\); Watmough and Ahern, 2008; Taylor et al., 2012) by 5 orders of magnitude; thus, it is reasonable to assume the solution is saturated in \(\text{CO}_2\) with abundance dictated by Henry’s law of \((3.3 \times 10^{-5} \text{M} \text{bar} / 0.9 \text{bar}) = 0.03 \text{M}\) (Sander, 2015). Then, \([\text{CO}_3^{2-}] = 0.03 M / (10^{-6.35 \cdot 0.35}) / \text{M} = 6 \times 10^{-5} \text{M} \) at neutral pH (dissociation constants \(K_{\text{aCO}_2} = 6.35 \text{M} + K_{\text{aCO}_2} = 10.33 \text{from Rumble [2017]}\)). Since \(\text{CaCO}_3 (K_{\text{sp}} = 3.36 \times 10^{-9} \text{M}^2, \text{Rumble, 2017})\) is 2 orders of magnitude less soluble than \(\text{CaSO}_3 (K_{\text{sp}} = 3.1 \times 10^{-7} \text{M}^2, \text{Rumble, 2017})\) and the sulfate flux is much less than the carbonate flux, we can assume that \([\text{Ca}^{2+}]\) is dictated to first order by equilibrium with carbonate mineral, that is, \([\text{Ca}^{2+}] = 3.36 \times 10^{-9} \text{M}^2 / 6 \times 10^{-5} \text{M} = 6 \times 10^{-5} \text{M}\). At \([\text{Ca}^{2+}]\), \(\text{CaSO}_3^{2-}\) will begin to form at \([\text{SO}_3^{2-}] = 3.1 \times 10^{-7} \text{M}^2 / 6 \times 10^{-5} \text{M} = 5 \times 10^{-3} \text{M}\). The \([\text{SO}_3^{2-}]\) we calculate does not exceed this threshold value across the plausible range of sulfur outgassing fluxes in our calculation, meaning the solution is unsaturated in \(\text{CaSO}_3\) and precipitate does not form. Were \(\text{pCO}_2\) lower, for example, \(\text{pCO}_2 = 0.2 \text{bar}\), \(\text{CaSO}_3\) precipitate formation begins at \([\text{SO}_3^{2-}] = 1 \times 10^{-3} \text{M}\). However, if pH were low, the carbonate solubility would exceed sulfate solubility, and sulfate precipitates would form (Haley et al., 2007); hence, at low pH, sulfate and bisulfite concentrations will be below the values we calculate. Overall, our results are unaffected by \(\text{CaSO}_3\) precipitation across most of parameter space, but \(\text{CaSO}_3\) precipitation might be a significant sink on aqueous sulfate levels for acid solutions and/or for very low atmospheric \(\text{CO}_2\)-levels; calculations with a more thorough geochemical model (e.g., PHREEQC, Parkhurst and Appelo, 2013) are required to constrain S-anion concentrations in this regime.

5.2.2. Redox reactions. We explored the possibility that redox reactions (disproportionation, comproportionation) might have acted as sinks to S-anion concentrations in shallow aqueous reservoirs on prebiotic Earth, or might otherwise affect the distribution of sulfidic anions. We identified the following reactions that are spontaneous near standard conditions (Siu and Jia, 1999; Haley, 2013):

\[
\text{4SO}_3^{2-} + \text{H}^+ \rightarrow 2\text{SO}_2^{2-} + \text{S}_2\text{O}_7^{2-} + \text{H}_2\text{O} \tag{17}
\]

\[
2\text{HS}^- + 4\text{HSO}_3^- \rightarrow 3\text{S}_2\text{O}_7^{2-} + 3\text{H}_2\text{O} \tag{18}
\]

The kinetics of Reaction 17 are not well characterized near standard temperature and are an active topic of research (Mizrooian and Halevy, 2014; Amshoff et al., 2016). Meyer et al. (1982) report sulfite and bisulfite are stable on timescales \(\geq 1\text{ year}\) in anoxic conditions, while Guexezian et al. (1997) report decay of sulfite in days at \(\text{pH} \geq 12.8\). Haley (2013) propose that rate coefficients in the range \(k_{17} = 0.03 \text{M} \text{s}^{-1}\) are plausible; at \(293 \text{ K}\), this corresponds to \(10^{-9} \text{ to } 7 \times 10^{-8} \text{ s}^{-1}\), which correspond to timescales of \(0.5-30\text{ years}\). The kinetics of Reaction 18 have been determined as a function of temperature at \(\text{pH} = 9\) and \(l = 0.2 \text{M}\) by Siu and Jia (1999). At \(293 \text{ K}\), the rate coefficient is \(k_{18} = 4 \times 10^{3} \text{ M}^{-2} \text{s}^{-1}\). At the S-anion concentrations relevant to our work, the timescale of this reaction is \(\geq 1\text{ year}\). For comparison, putative prebiotic chemistry in laboratory studies often occurs on timescales of hours to days (Patel et al., 2015; Xu et al., in press, e.g.).

We test the effects of redox reactions on S-anion concentrations by carrying out a dynamical equilibrium calculation for a shallow lake buffered to \(\text{pH} = 7\), with source the atmosphere and sink these redox reactions. Following the treatment of Haley (2013), the equilibrium equations can be written:

\[
\text{r}_{\text{HS}_2\text{S}^{\text{atm}}}^{\text{dep}} \text{H}_2\text{S}^{\text{catch}} + \left( \frac{2}{3} k_{18} [\text{HS}^-][\text{HSO}_3^-]^2 \right) \text{A}_{\text{lake}} \text{d}_{\text{lake}} = 0 \tag{19}
\]

\[
\text{r}_{\text{SO}_2\text{H}_{2\text{O}}}^{\text{dep}} \text{SO}_2\text{H}^{\text{catch}} = \left( \frac{4}{3} k^{\text{catch}} [\text{HS}^-][\text{HSO}_3^-] + k_{17} [\text{S(IV)}] \right) \text{A}_{\text{lake}} \text{d}_{\text{lake}} \tag{20}
\]

For consistency with Hu et al. (2013), we adopt \(v_{\text{dep}}^{\text{H}_2\text{S}} = 0.015 \text{ cm s}^{-1}\), \(v_{\text{dep}}^{\text{SO}_2\text{H}} = 1 \text{ cm s}^{-1}\), \(T = 288 \text{ K}\), and \(n_{\text{atm}} = 1 \text{ bar} = 2.4 \times 10^{19} \text{ cm}^3\). Since we are concerned with shallow, well-mixed lakes, we take the lake depth \(d_{\text{lake}} = 10^2\) cm. \(A_{\text{catch}}\) is the catchment area of the lake, and \(A_{\text{lake}}\) is the surface area of the lake; we conservatively adopt \(A_{\text{catch}} = A_{\text{lake}}\), which likely underestimates sulfur supply since the catchment area is often larger than the lake area. \([\text{S(IV)}]\) refers to the total concentration of S(IV) atoms in solution, and is calculated as \([\text{S(IV)}] = [\text{SO}_2\text{H}^+] + [\text{HSO}_3^-] + [\text{HS}_2\text{O}_7^{2-} + [\text{SO}_3^{2-}] + [\text{SO}_2\text{aq}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]\). Since we have specified \(\text{pH} = 7\) and know the relevant \(K_a\) values, we can calculate \([\text{HSO}_3^-]\) from \([\text{S(IV)}]\) and vice versa. With \(n_{\text{HS}_2\text{S}}, \text{r}_{\text{SO}_2\text{H}}\) specified from Hu et al. (2013), we have a system of two equations in two variables that we can solve. Figure 5 shows the resultant S-anion concentrations as a function of \(\phi_S\).

The dynamic calculation is very sensitive to the uncertainty in \(k_{17}\), with sulfite and bisulfite concentrations varying by 2 orders of magnitude and hydrosulfide concentrations...
varying by 4 across the range of $k_{17}$ suggested by Halevy (2013). However, even with this uncertainty it is clear that prebiotically relevant levels ($\lesssim 1\text{ M}$) of SO$_2$-derived anions are available across the range of plausible sulfur outgassing fluxes, with concentrations $\sim 1$–10 M if sulfite disproportionation is fast and $\sim 100$–1000 M if sulfite disproportionation is slow. Note depending on $k_{17}$, it is possible for [HS$^-$] in the dynamic calculation to exceed the value calculated from solubility constraints; in reality, in well-mixed solution H$_2$S would de-gas when it reached the solubility limit, voiding Eq. 19. In these cases, [HS$^-$] is lower than the value calculated from the dynamic method, modestly increasing sulfite and bisulfite concentrations since Reaction 18 is slower. S-anion concentrations increase as $d_{\text{lake}}$ and $T$ decrease, and are ultimately limited by gas solubility. Overall, our finding that prebiotically relevant levels of SO$_2$-derived anions were available in shallow well-mixed lakes on early Earth is robust to the effect of redox reactions, but it is possible for the precise concentrations to be lower than from our equilibrium calculation depending on the depth and temperature of the lake, and especially on the rate of sulfite disproportionation $k_{17}$. Constraining $k_{17}$ is key to improved modeling of abiotic sulfur chemistry.

5.3. Case study: Implications for cyanosulfidic systems chemistry of Patel et al. (2015)

The cyanosulfidic prebiotic chemistry of Patel et al. (2015) requires cyanide and sulfur-bearing anions, both as feedstocks and as sources of hydrated electrons through UV-driven photoionization. Patel et al. (2015) used HS$^-$ as their sulfidic anion, and propose impact-derived sources of metal sulfides (both from the impactor and from subsequent metallogenesis) and evaporatively concentrated iron sulfides as a source for HS$^-$. This postulated mechanism requires specific, local environmental conditions to function. By contrast, simple exposure of a non-acidic lake to the atmosphere anywhere on the planet would supply HSO$_3^-$ and SO$_3^{2-}$ at prebiotically relevant levels to either supplement the photochemical reducing capacity of HS$^-$ or function as sole sources of hydrated electrons in the Patel et al. (2015) chemistry. Indeed, recent work by the same group suggests that HSO$_3^-$ and SO$_3^{2-}$ can replace HS$^-$ as the source of hydrated electrons upon UV irradiation, and thus drive those parts of the reaction network that do not rely on HS$^-$ as a feedstocks (Xu et al., in press). Reducing or eliminating the dependence of the Patel et al. (2015) chemistry on HS$^-$ in favor of HSO$_3^-$ or SO$_3^{2-}$ increases the robustness of this chemistry, because no special local circumstances need to be invoked. This illustrates how geochemistry can inform improvements of the plausibility of prebiotic pathways.

Indeed, volcanism can be a source of more than sulfidic anions. Volcanism can also be a source of phosphates through partial hydrolysis of volcanically outgassed polyphosphates (Yamagata et al., 1991), and a supplementary source of HCN through photochemical reprocessing of volcanically outgassed reducing species like CH$_4$ (Zahnle, 1986)$^{13}$. Volcanism could thereby supply or supplement many of the C-, H-, O-, N-, P-, and S-containing feedstock molecules and photoreductants required by the Patel et al. (2015) chemistry. The UV light also required by the Patel et al. (2015) chemistry would be available at Earth’s surface for all but the largest volcanic episodes ($\phi_S \lesssim 3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$). Hence, epochs of moderately high volcanic activity may have

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$^{13}$Though some concentration mechanism would be required to achieve prebiotically relevant levels of HCN via this pathway.
been uniquely conducive to cyanosulfidic prebiotic chemistry like that of Patel et al. (2015), especially if they can be adapted to work with HSO\textsubscript{3}\textsuperscript{−} or SO\textsubscript{3}\textsuperscript{2−} instead of HS\textsuperscript{−}.

We considered alternate planetary sources for HS\textsuperscript{−} for the Patel et al. (2015) chemistry. We explored whether shallow hydrothermal systems, such as hot springs, might provide prebiotically relevant levels of HS\textsuperscript{−}. These sources are high-sulfur systems on modern Earth, and, if shallow, prebiotic chemistry in them might retain access to UV light while accessing high concentrations of sulfidic anions. Surveys of modern hydrothermal systems reveal examples of surficial systems that exhibit micromolar or even millimolar concentrations of HS\textsuperscript{−} (Xu et al., 1998; Vick et al., 2010; Kaasalainen and Stefánsson, 2011). However, high concentrations of HS\textsuperscript{−} appear to only be achieved in hot systems\textsuperscript{14} (T > 60°C, and typically higher). Similarly, studies of geothermal waters in Yellowstone National Park suggest sulfite availability at the 0.4–5 μM level. However, such levels of sulfite were again accessed only in hot waters (Kamyshny et al., 2014). It is not clear how compatible such conditions are with prebiotic chemistry; for example, most of the cyanosulfidic chemistries of Patel et al. (2015) and Xu et al. (2016) were conducted at room temperature (25°C), and in general many molecules thought to be relevant to the origin of life, such as ribozymes, RNA, and their components, are more stable and function better at cooler temperatures (Levy and Miller, 1998; Attwater et al., 2010; Kua and Bada, 2011; Akoopie and Müller, 2016). However, for hot origin-of-life scenarios, e.g., those at deep-sea hydrothermal vents, hydrothermal systems may be compelling venues for cyanosulfidic reaction networks like that of Patel et al. (2015), reinforcing the utility of volcanism for prebiotic chemistry.

6. Conclusion and Next Steps

Constraining the abundances of trace chemical species on early Earth is important to understanding whether postulated prebiotic pathways which are dependent on them could have proceeded. Here, we show that prebiotically relevant levels of certain sulfidic anions are globally available in shallow, well-mixed aqueous reservoirs due to dissolution of sulfur-bearing gases that are volcanically injected into the atmosphere of early Earth. In particular, anions derived from SO\textsubscript{2} are available at ≥1 μM levels in non-acidic reservoirs for SO\textsubscript{2} outgassing rates corresponding to modern Earth and higher. During episodes of intense volcanism, like the emplacement of basaltic fields like the Deccan Traps, SO\textsubscript{2}-derived anions may be available at ≥1 mM levels for reservoirs buffered to pH ≥7 (e.g., the modern ocean at pH=8.2) and at a temperature of T=25°C, though sulfite disproportionation may have ultimately limited concentrations to the ~10μM level; better constraints on sulfite disproportionation reaction rates are required to constrain this possibility. At cooler temperatures, even higher concentrations of these anions would have been available. Formation of mineral precipitate should not inhibit sulfite concentrations until ≥1 mM concentrations so long as the reservoir is not acidic, but might suppress sulfite levels in acidic waters. On the other hand, anions derived from H\textsubscript{2}S would not have been available at micromolar levels across the plausible range of volcanic outgassing due to low solubility of H\textsubscript{2}S and an unfavorable dissociation constant, and prebiotic chemistry invoking such anions must invoke local, specialized sources. Radiative transfer calculations suggest that NUV radiation will remain abundant at the planet surface for φ\textsubscript{S} ≤ 1 × 10\textsuperscript{11} cm\textsuperscript{-2} s\textsuperscript{-1} but will be suppressed for φ\textsubscript{S} ≥ 3 × 10\textsuperscript{11} cm\textsuperscript{-2} s\textsuperscript{-1}; such epochs may be especially clement for surficial, UV-independent prebiotic chemistry. We applied our results to the case study of the proposed prebiotic reaction network of Patel et al. (2015). The prebiotic plausibility of this network can be improved if it can be adapted to use SO\textsubscript{2}-derived anions like HSO\textsubscript{3}− or SO\textsubscript{3}− instead of HS\textsuperscript{−}, since the atmosphere is capable of supplying prebiotically relevant levels of the former directly but more localized sources must be invoked for adequate supply of the latter. Coupled with the potential for volcanogenic synthesis of feedstock molecules like HCN and phosphate (Zahnle, 1986; Yamagata et al., 1991), it appears that episodes of moderately intense volcanism (φ\textsubscript{S} ≈ 1 × 10\textsuperscript{11} cm\textsuperscript{-2} s\textsuperscript{-1}) might have been especially clement for cyanosulfidic prebiotic chemistry which exploits SO\textsubscript{2}-derived anions (e.g., HSO\textsubscript{3}−). Avenues for future work include simulating these scenarios experimentally and/or with a large general-purpose aqueous geochemistry code, improving measurements of the sulfite disproportionation reaction rate constant, and further photochemical modeling to improve constraints on the expected concentrations of SO\textsubscript{2} and H\textsubscript{2}S on early Earth.

A. Atmospheric Sulfur Speciation

We use the work of Hu et al. (2013) to connect the sulfur emission flux φ\textsubscript{S} to the speciation of atmospheric sulfur. Table A1 presents H\textsubscript{2}S and SO\textsubscript{2} mixing ratios as a function of φ\textsubscript{S} from Hu et al. (2013) (their Fig. 5, CO\textsubscript{2}-dominated atmosphere case).

B. Activity Coefficient Calculation

This appendix describes the calculation of the activity coefficients of the ions involved in equilibria reactions for SO\textsubscript{2} and H\textsubscript{2}S.

We use the Extended Debye-Hückel theory to calculate activity coefficients (γ\textsubscript{i}) for the ions in our study. Extended Debye-Hückel theory is valid for ionic strengths up to 0.1 M, which is the highest ionic strength we consider, motivated by the fact that lipid vesicle formation is inhibited at ionic strengths above 0.1 M (Maurer and Nguyen, 2016).

### Table A1. Column-Integrated Mixing Ratios of H\textsubscript{2}S and SO\textsubscript{2} as a Function of φ\textsubscript{S} from Hu et al. (2013) (Their Fig. 5, CO\textsubscript{2}-dominated Case)

| φ\textsubscript{S} (cm\textsuperscript{-2} s\textsuperscript{-1}) | r\textsubscript{H\textsubscript{2}S} | r\textsubscript{SO\textsubscript{2}} |
|----------------|----------------|----------------|
| 3 × 10\textsuperscript{9} | 4 × 10\textsuperscript{-10} | 3 × 10\textsuperscript{-10} |
| 1 × 10\textsuperscript{10} | 7 × 10\textsuperscript{-9} | 5 × 10\textsuperscript{-9} |
| 3 × 10\textsuperscript{10} | 9 × 10\textsuperscript{-8} | 7 × 10\textsuperscript{-8} |
| 1 × 10\textsuperscript{11} | 2 × 10\textsuperscript{-7} | 6 × 10\textsuperscript{-7} |
| 9 × 10\textsuperscript{-6} | 3 × 10\textsuperscript{-6} | 8 × 10\textsuperscript{-6} |
| 2 × 10\textsuperscript{-6} | 1 × 10\textsuperscript{-5} | 1 × 10\textsuperscript{-5} |

\textsuperscript{14}We speculate that HS\textsuperscript{-}-rich shallow hydrothermal systems tend to be hot because the same volcanism that supplies elevated levels of HS\textsuperscript{−} also supplies elevated levels of heat.
Extended Debye Huckel theory states that

$$\log \gamma_i = -A_i \frac{c_i^{0.5}}{1 + B c_i^{0.5}}$$

(B1)

where $A$ and $B$ depend on the temperature, density, and dielectric constant of the solvent (in our case water), and $A_i$ is an ion-specific parameter. We took $A = 0.5085 M^{-1/2}$ and $B = 0.3281 M^{-1/2} A^{-1}$, corresponding to $T = 25^\circ C$; Appendix D describes the sensitivity of our analysis to this assumption.

Table B1 summarizes the $A_i$ used in our study, taken from Misra (2012). We were unable to locate a value of $aC$ for $HSO_3^-$ and consequently take $c_{HSO_3^-}/C_0 = 1$ throughout (i.e., we do not correct for its activity). Since in our analysis the supply of $SO_2$ is not limited (the atmosphere is treated as an infinite reservoir), $pK_{aSO_2}$ affects only the abundance of $H_2SO_5^-$, which is a trace compound in our analysis (see Fig. 2).

Table B2 shows the activity coefficients for the relevant ions at the two ionic strengths considered in our study.

### C. Sensitivity of Henry’s Law Constants to Salinity

This appendix describes our assessment of the sensitivity of the Henry’s law constants for $SO_2$ and $H_2S$ to salinity.

We account for the effect of salinity on $H_G$ using the Schumpe-Sechenov method, as outlined in Burkholder et al. (2015):

$$\log H_0/H = \Sigma_i (h_i + h_G) * c_i$$

(C1)

where $H_0$ is the Henry’s law constant in pure water, $H$ is the Henry’s law constant in saline solution, $c_i$ is the concentration of the ion $i$, $h_i$ is an ion-specific constant, and $h_G$ is a gas-specific constant. $h_G$ is temperature dependent, via $h_G = h_0 + h_T$ ($T$=298.15 K). NaCl is the dominant salt in Earth’s oceans; we approximate NaCl as the sole source of salinity in our calculations. Table C1 summarizes the values of these parameters used for this study, all taken from the compendium of Burkholder et al. (2015). We were unable to locate a value for $h_T$ for $H_2S$ in our literature search, and assumed $h_T=0$ for this case.

The Henry’s law constants for these gases as a function of [NaCl] at $T=298.15$ K are shown in Fig. C1. In this study, we consider ionic strengths $I \leq 0.1$ M, corresponding to [NaCl] $\leq 0.1$ M. At such levels, salinity has a negligible effect on Henry’s law solubility, and we consequently neglect it in our calculations.

### D. Sensitivity of Analysis to Temperature

This appendix describes our assessment of the sensitivity of our calculations to the temperature of the aqueous reservoir in which the equilibrium chemistry proceeds.

#### D.1. Sensitivity of Henry’s law constants to temperature

We calculated the effect of temperature on Henry’s law using the three-term empirical fit outlined in Burkholder et al. (2015):
et al. (2015), that is, \( \ln(H) = A + B/T + C \ln(T) \), where \( H \) is in units of \( M/\text{atm} \) and \( A \), \( B \), and \( C \) are gas-specific coefficients of an empirical fit. The values of these coefficients for \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) were taken from Burkholder et al. (2015) and are summarized in Table D1. \( H(T) \) for \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) is plotted in Fig. D1. For temperatures ranging from 0°C to -50°C (273.15 to 323.15 K), the Henry’s law constants vary by less than a factor of 2.5 relative to their values at 25°C (293.15 K), which is small compared to the order-of-magnitude variations in concentration we focus on in this study. We also estimated the temperature dependence using the van’t Hoff equation as outlined in Sander (2015) and obtained similar results.

D.2. Sensitivity of reaction rates to temperature

In order to assess the temperature dependence of acid dissociation \( pK_a \) values, we use the van’t Hoff equation:

\[
\frac{\partial \ln(K_0)}{\partial T} = \frac{\Delta H_0}{RT^2} \tag{D1}
\]

where \( K_0 \) is the equilibrium constant, \( T \) is temperature, \( \Delta H_0 \) is the change in enthalpy, and \( R = 8.314 \times 10^{-3} \text{ kJ/mol/K} \). Solving this differential equation, assuming temperature-invariant enthalpy of solution\(^\text{15}\), gives

\[
\ln(K_2) = \ln(K_1) + \frac{-\Delta H_0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \tag{D2}
\]

With this equation, the acid dissociation constant \( K_2 \) can be estimated at a given temperature \( T_2 \), provided its value \( K_1 \) is known at a reference temperature \( T_1 \). \( \Delta H \) is the change in enthalpy of the reaction, given by

\[
\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \tag{D3}
\]

The enthalpies of formation for the products and reactants of the first two acid dissociation reactions for \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) are taken from Lide (2009) and are shown in Table D2. Note that \( \Delta H_f^\circ = 0 \) for \( \text{H}^+ \), by definition. We were unable to locate an enthalpy of formation for \( \text{H}_2\text{SO}_5^- \) and consequently are unable to calculate the temperature dependence of \( pK_{\text{SO}_2} \). Since in our analysis the supply of \( \text{SO}_2 \) is not limited (the atmosphere is treated as an infinite reservoir), \( pK_{\text{SO}_2} \) affects only the abundance of \( \text{H}_2\text{SO}_5^- \), which is a trace compound in our analysis (see Fig. 2).

Using these values and the van’t Hoff equation, we calculated the temperature dependence of the first two acid dissociation constants for aqueous \( \text{H}_2\text{S} \) and \( \text{SO}_2 \). Table D3 shows these \( pK_a \) values for \( \text{SO}_2 \) and \( \text{H}_2\text{S} \) at 0°C, 25°C, and 50°C.

The variation in \( pK_a \) is negligible for all reactions except the first dissociation of \( \text{SO}_2 \); \( pK_{\text{SO}_2,1} \) increases significantly with temperature. This implies that in non-acidic solutions, the concentrations of \( \text{SO}_2 \)-derived anions should decrease, and conversely that as temperature decreases they should increase.

D.3. Sensitivity of activity coefficients to temperature

Temperature dependence enters the calculation of the activity coefficients through the parameters \( A \) and \( B \) (see Appendix B for details). For water, at \( T = 0°C \), \( A = 0.4883 \text{ M}^{-1/2} \) and \( B = 0.3241 \text{ M}^{-1/2} \text{Å}^{-1} \); at \( T = 25°C \), \( A = 0.5085 \text{ M}^{-1/2} \)

| Table D1. Parameters Used to Estimate Dependence of Henry’s Law Constant on Temperature |
|---------------------------------------|----------|----------|
| Parameter | \( \text{H}_2\text{S} \) | \( \text{SO}_2 \) |
|----------|----------|----------|
| \( A \)  | -145.2   | -39.72   |
| \( B \)  | 8120     | 4250     |
| \( C \)  | 20.296   | 4.525    |

\(^{15}\text{We expect this assumption to be reasonable because of the limited range of temperatures that are plausible for our surface aqueous reservoir scenario.}\)
and $B = 0.3281 \text{ M}^{-1/2} \text{ Å}^{-1}$, and at $T = 50\degree C$, $A = 0.5319 \text{ M}^{-1/2}$ and $B = 0.3321 \text{ M}^{-1/2} \text{ Å}^{-1}$ (Misra, 2012). From $T = 0\degree - 50\degree C$, the activity coefficients varied by <8% for $I \leq 0.1 \text{ M}$.

D.4. Overall sensitivity of analysis to temperature

We evaluated the overall sensitivity of our analysis to our assumption of $T = 25\degree C$ by repeating our analysis at $T = 0\degree C$ and $T = 50\degree C$, and including the effects of temperature on Henry’s law constant, the reaction $pK_a$ values, and the activity coefficients, simultaneously. Across the tested range, temperature had a negligible impact on the abundances of the $\text{H}_2\text{S}$-derived anions but a significant impact on the abundances of the $\text{SO}_2$-derived anions. $\text{HSO}_3^-$ decreases with temperature, and $pK_{\text{aSO}_2}$ increases with temperature; both effects serve to increase the concentration of $\text{HSO}_3^-$ and its derivatives in non-acidic (pH > 2.5) waters. At $T = 0\degree C$, $\text{HSO}_3^-$ and $\text{SO}_3^{2-}$ concentrations are an order of magnitude higher than at $T = 25\degree C$. Similarly, at $T = 50\degree C$, $\text{HSO}_3^-$ and $\text{SO}_3^{2-}$ concentrations are an order of magnitude lower than at $T = 25\degree C$. Our overall conclusions are robust to these variations. However, this study does imply that significantly higher concentrations of $\text{SO}_2$-derived anions are available to prebiotic chemistry in cooler waters and inversely that hotter waters would have access to lower levels of $\text{SO}_2$-derived anions.

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Author Disclosure Statement

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