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

Sukrit Ranjan,[1,2] Zoe R. Todd,[1] John D. Sutherland,[3] and Dimitar D. Sasselov[1]

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 (HS^-, HSO_3^-, SO_3^{2-}) available in surficial aquatic reservoirs on early Earth due to outgassing of SO_2 and H_2S and their dissolution into small shallow surface water reservoirs like lakes. We find that this mechanism could have supplied prebiotically relevant levels of SO_2-derived anions, but not H_2S-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; Mulkidjanian *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

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[1]Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA.
[2]MIT Department of Earth, Atmospheric, and Planetary Sciences, Cambridge, Massachusetts, USA.
[3]Medical Research Council Laboratory of Molecular Biology, Cambridge, UK.

aqueous anions (*e.g.*, hydrosulfide, HS^-; bisulfite, HSO_3^-; sulfite, SO_3^{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, Mulkidjanian *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_2S 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_2S 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_2S, 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; Mulkidjanian *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 cyano-sulfidic 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 was 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 sulfidic reductant (and feedstock) on a global basis, it would reduce the requirements for parts (or all) of this reaction 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 anion-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 H₂S and SO₂

The abundances of H_2S 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 abiotic SO_2 outgassing rates of $1-3\times10^9$ 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 $1.7-2.4\times10^9$ cm^{-2} s^{-1} (Halmer *et al.*, 2002). H_2S emission rates are indirectly estimated and much less certain; they range from 3.1×10^8 to 7.7×10^9 cm^{-2} s^{-1}. A common assumption in atmospheric modeling is that SO_2 and H_2S 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 $\sim3\times$ 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 (Self *et al.*, 2006).

No firm constraints exist for SO_2 and H_2S 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× 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 $\phi_S=3\times10^9$ 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_2S outgassing ratio of 10:1, for $\phi_S=1\times10^8$ to 1×10^{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_2S emission ratio of 2, for $\phi_S=3\times10^9$ to 1×10^{13} cm^{-2} s^{-1}. The SO_2 and H_2S 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

TABLE 1. MIXING RATIOS OF H_2S AND SO_2 FOR DIFFERENT EARLY EARTH MODELS
IN THE LITERATURE AND DIFFERENT ϕ_S

Model	r_{H_2S}	r_{SO_2}
Kasting *et al.* (1989)[a], $\phi_S = 3 \times 10^9$ cm^{-2} s^{-1}	2×10^{-10}	2×10^{-9}
Claire *et al.* (2014)[a], $\phi_S = 3 \times 10^9$ cm^{-2} s^{-1}	1×10^{-11}	5×10^{-11}
Hu *et al.* (2013)[b], $\phi_S = 3 \times 10^9$ cm^{-2} s^{-1}	4×10^{-10}	3×10^{-10}
Claire *et al.* (2014)[a], $\phi_S = 1 \times 10^{10}$ cm^{-2} s^{-1}	3×10^{-11}	1×10^{-10}
Hu *et al.* (2013)[b], $\phi_S = 1 \times 10^{10}$ cm^{-2} s^{-1}	1×10^{-9}	9×10^{-10}

[a]Surface mixing ratio.
[b]Column-integrated mixing ratio.

column-integrated mixing ratios. Since H_2S and 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 SO_2 and H_2S levels were low and increase with sulfur emission rate, but their estimates for r_{SO_2} and r_{H_2S} 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 SO_2 and H_2S 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 SO_2 and H_2S, with oceans not saturated in 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 H_2SO_4 and 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 H_2S and 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 ($\lesssim 1$ 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, $[Z]$, in aqueous solution at the air/water interface is proportional to the partial pressure of
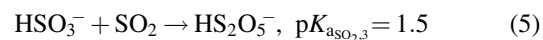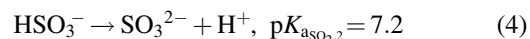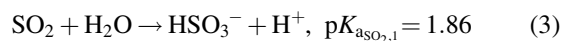
the gas at that interface. We assume the aqueous reservoir to be well mixed and equilibrated throughout, so that the concentration of $[Z]$ is uniform throughout the reservoir at the surficial value. If the reservoir is not well mixed, then the dissolved gas concentration will vary deeper into the reservoir. 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, H_2S undergoes the dissociation reactions

$$H_2S \rightarrow HS^- + H^+, \ pK_{a_{H_2S,1}} = 7.05 \tag{1}$$

$$HS^- \rightarrow S^{2-} + H^+, \ pK_{a_{H_2S,2}} = 19 \tag{2}$$

where the pK_a values are taken from Lide (2009) and can be related to the corresponding equilibrium constants by $K_{a_X} = 10^{-pK_{a_X}}$. Similarly, SO_2 undergoes the reactions

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+, \ pK_{a_{SO_2,1}} = 1.86 \tag{3}$$

$$HSO_3^- \rightarrow SO_3^{2-} + H^+, \ pK_{a_{SO_2,2}} = 7.2 \tag{4}$$

$$HSO_3^- + SO_2 \rightarrow HS_2O_5^-, \ pK_{a_{SO_2,3}} = 1.5 \tag{5}$$

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

interactions toward a certain pH[1], 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,

$$[Z] = H_Z f_Z \tag{6}$$

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_G, 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 $0 \leq [NaCl] \leq 1$ 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

$$\frac{a_{HS^-} a_{H^+}}{a_{H_2S}} = K_{a_{H_2S,1}} \tag{7}$$

$$\frac{a_{S^{2-}} a_{H^+}}{a_{HS^-}} = K_{a_{H_2S,2}} \tag{8}$$

and

$$\frac{a_{HSO_3^-} a_{H^+}}{a_{SO_2}} = K_{a_{SO_2,1}} \tag{9}$$

$$\frac{a_{SO_3^{2-}} a_{H^+}}{a_{HSO_3^-}} = K_{a_{SO_2,2}} \tag{10}$$

$$\frac{a_{HS_2O_5^-}}{a_{SO_2} a_{HSO_3^-}} = K_{a_{SO_2,3}} \tag{11}$$

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 γ_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-Huckel theory (Debye and Huckel, 1923). The activity coefficients in this formalism are calculated by

$$\log(\gamma_C) = -A z_C^2 \frac{I^{0.5}}{1 + B \alpha_C I^{0.5}} \tag{12}$$

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 $B = 0.3281$ $M^{-1/2}\mathring{A}^{-1}$, 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. α_C is an ion-specific parameter with values related to the hydration radius of the aqueous species; we took our α_C values from Misra (2012). We were unable to locate a value of α_C for $HS_2O_5^-$ and consequently take $\gamma_{HS_2O_5^-} = 1$ throughout. I is the ionic strength of the solution, defined as

$$I = 0.5 \left(\Sigma_C [C] z_C^2 \right) \tag{13}$$

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

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

$$(a_{H^+})(a_{OH^-}) = K_w \tag{15}$$

and the requirement for charge conservation:

$$\Sigma_C z_C [C] = 0 \tag{16}$$

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 1×10^{-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 [3].

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[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 McCollom, 2009; Halevy 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; Löhr *et al.*, 2005) and pH > 11 (*e.g.*, Lake Natron; Grant and Jones, 2000).

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[2]http://www.aqion.de/site/69, 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.
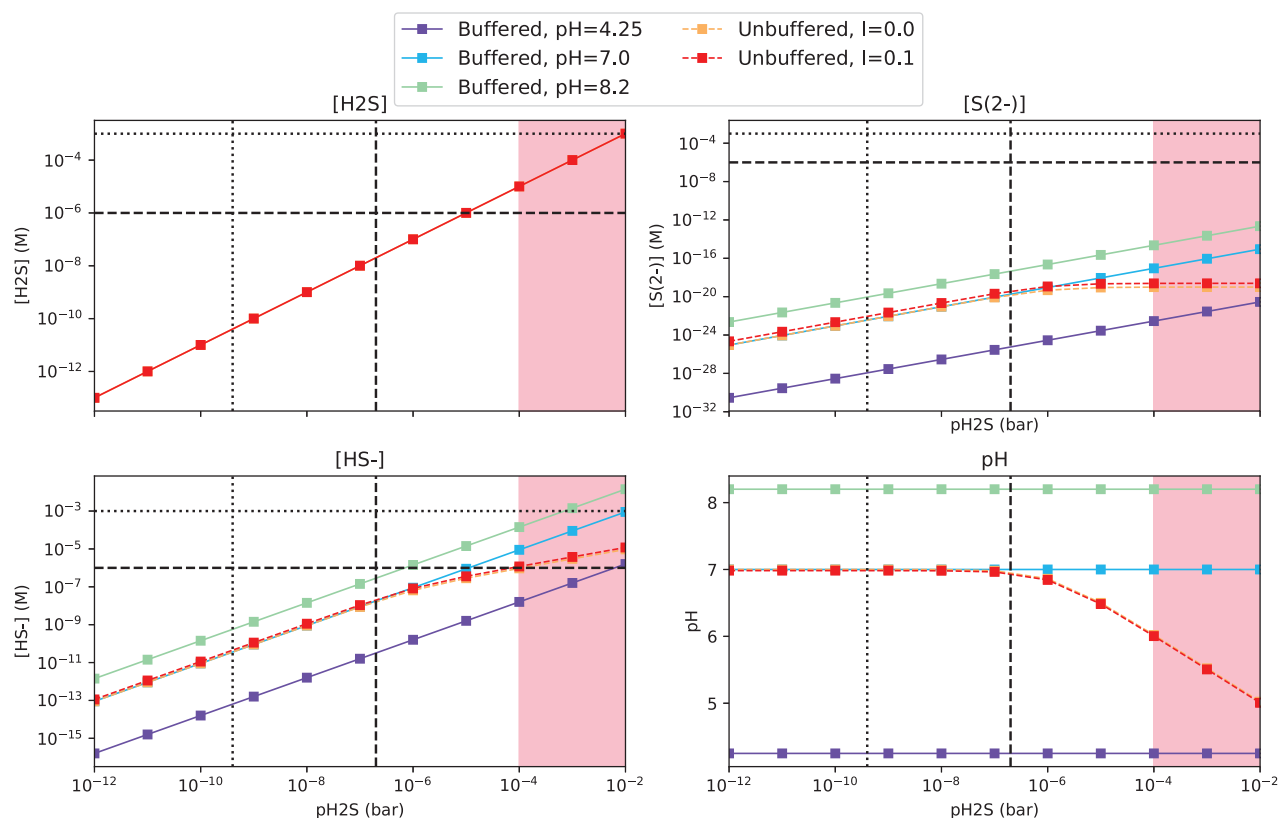
FIG. 1. Concentrations of sulfur-bearing compounds and pH as a function of pH_2S for a well-mixed aqueous reservoir. [H_2S] is calculated from Henry's law; the concentrations of HS^- and S^{2-} are calculated from equilibrium chemistry for (1) solutions buffered to various pH values and (2) unbuffered solutions with varying ionic strengths. The vertical dotted line demarcates the expected pH_2S for an abiotic Earth with a weakly reducing CO_2-N_2 atmosphere with modern levels of sulfur outgassing, from Hu *et al.* (2013). The vertical dashed line demarcates the expected pH_2S for the same model but with outgassing levels of sulfur corresponding to the upper limit of the estimate for the emplacement of the terrestrial flood basalts. In the red shaded area, pH_2S is so high it blocks UV light from the planet surface, meaning UV-dependent prebiotic pathways, *e.g.*, those of Patel *et al.* (2015), cannot function (Ranjan and Sasselov, 2017). The red curve largely overplots the orange, demonstrating the minimal impact of ionic strength on the calculation for $I \leq 0.1$. The horizontal dashed and dotted lines demarcate micromolar and millimolar concentrations, respectively. The cyanosulfidic chemistry of Patel *et al.* (2015) has been demonstrated at millimolar S-bearing photoreductant concentrations, and at least high micromolar levels of these compounds are thought to be required for high-yield prebiotic chemistry.

We calculate the speciation of sulfur-bearing species from dissolved H_2S 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_2S 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_2S or pSO_2 and pH. The results of this calculation are presented in Figs. 1 and 2 for three representative pH values. We selected pH = 8.2, corresponding to modern ocean; pH = 7, corresponding to the near-neutral phosphate-buffered conditions in which Patel *et al.* (2015) conducted their experiments; and pH = 4.25, corresponding to raindrops in a $pCO_2 \sim 0.1$ bar atmosphere (Halevy *et al.*, 2007). Such high CO_2 levels are hypothesized for young Earth in order to power a greenhouse effect large enough to maintain clement surface conditions (Kasting, 1993).

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_2S versus SO_2

Figure 1 shows the speciation of sulfur-bearing compounds from dissolved H_2S for an unbuffered reservoir, and reservoirs buffered to various pH values. Over the range of ionic strengths considered, HS^- is the dominant anion, and S^{2-}
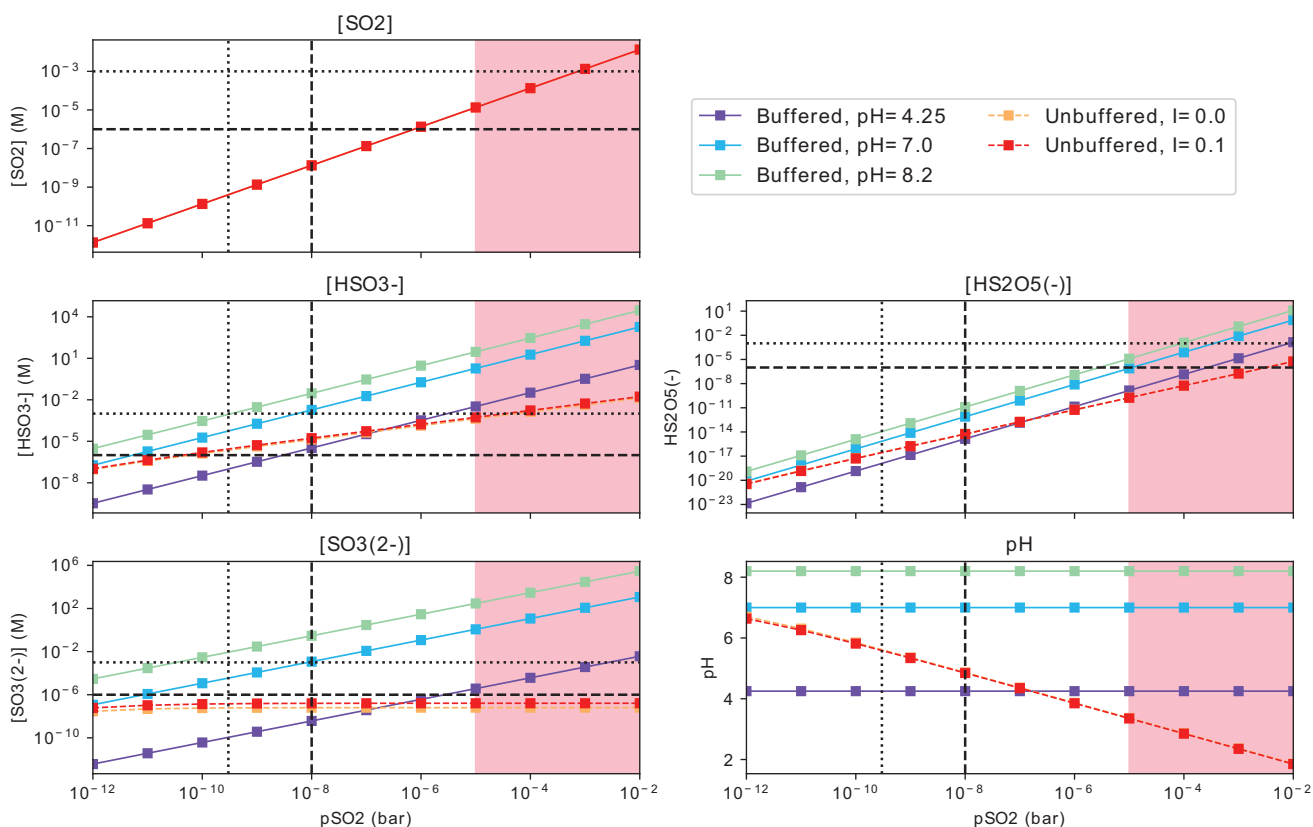
FIG. 2. Concentrations of sulfur-bearing compounds and pH as a function of pSO_2 for a well-mixed aqueous reservoir. $[SO_2]$ is calculated from Henry's law; the concentrations of HSO_3^-, SO_3^{2-}, and $HS_2O_5^-$ are calculated from equilibrium chemistry for (1) solutions buffered to various pH values and (2) unbuffered solutions with varying ionic strengths. The vertical dotted line demarcates the expected pSO_2 for an abiotic Earth with a weakly reducing CO_2-N_2 atmosphere with modern levels of sulfur outgassing, from Hu *et al.* (2013). The vertical dashed line demarcates the expected pSO_2 for the same model, but with outgassing levels of sulfur corresponding to the upper limit of the estimate for the emplacement of the terrestrial flood basalts. In the red shaded area, pSO_2 is so high it blocks UV light from the planet surface, meaning UV-dependent prebiotic pathways, *e.g.*, those of Patel *et al.* (2015), cannot function (Ranjan and Sasselov, 2017). The red curve largely overplots the orange, demonstrating the minimal impact of ionic strength on the calculation for $I \lesssim 0.1$. The horizontal dashed and dotted lines demarcate micromolar and millimolar concentrations, respectively. The cyanosulfidic chemistry of Patel *et al.* (2015) has been demonstrated at millimolar S-bearing photoreductant concentrations, and at least high micromolar levels of these compounds are thought to be required for high-yield prebiotic chemistry.

is present at negligible concentrations. As pH_2S increases, the pH of the unbuffered reservoir drops, but slowly. This is expected, since H_2S is a weak acid.

Figure 2 shows the speciation of sulfur-bearing compounds from dissolved SO_2 for an unbuffered reservoir, and reservoirs buffered to various pH values. Because of the lack of O_2 in this anoxic era, the first dissociation of SO_2 forms sulfite, rather than sulfate. HSO_3^- and SO_3^{2-} are present at comparable levels; $HS_2O_5^-$ is negligible. As pSO_2 increases, the pH of the unbuffered reservoir falls off rapidly; this is expected since hydrated SO_2 is a strong acid.

SO_2 is an order of magnitude more soluble than H_2S, and its first dissociation is much more strongly favored ($pK_{a_{SO_2,1}} = 1.86$ vs. $pK_{a_{H_2S,1}} = 7.05$). Consequently, far higher concentrations of sulfidic anions can be sustained for a given pSO_2 than for the same pH_2S (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

($pK_{a_{H_2S,2}} = 19$). 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 SO_2 gives rise to comparatively high concentrations of sulfidic anions due to higher solubility and a more favorable first ionization. Micromolar concentrations of HSO_3^- are possible for $pSO_2 > 1 \times 10^{-11}$ bar for all but very acidic solutions; micromolar concentrations of SO_3^{2-} are possible for solutions buffered to pH ≥ 7 over the same range. *Millimolar* levels of HSO_3^- and SO_3^{2-} are possible for solutions buffered to pH ≥ 8.2 for $pSO_2 \gtrsim 10^{-10}$ bar, and for pH ≥ 7 solutions for $pSO_2 \gtrsim 10^{-8}$ bar. $pSO_2 \geq 3 \times 10^{-10}$ 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 $pSO_2 = 1 \times 10^{-8}$ bar. We note

Speciation of Sulfur-Bearing Molecules
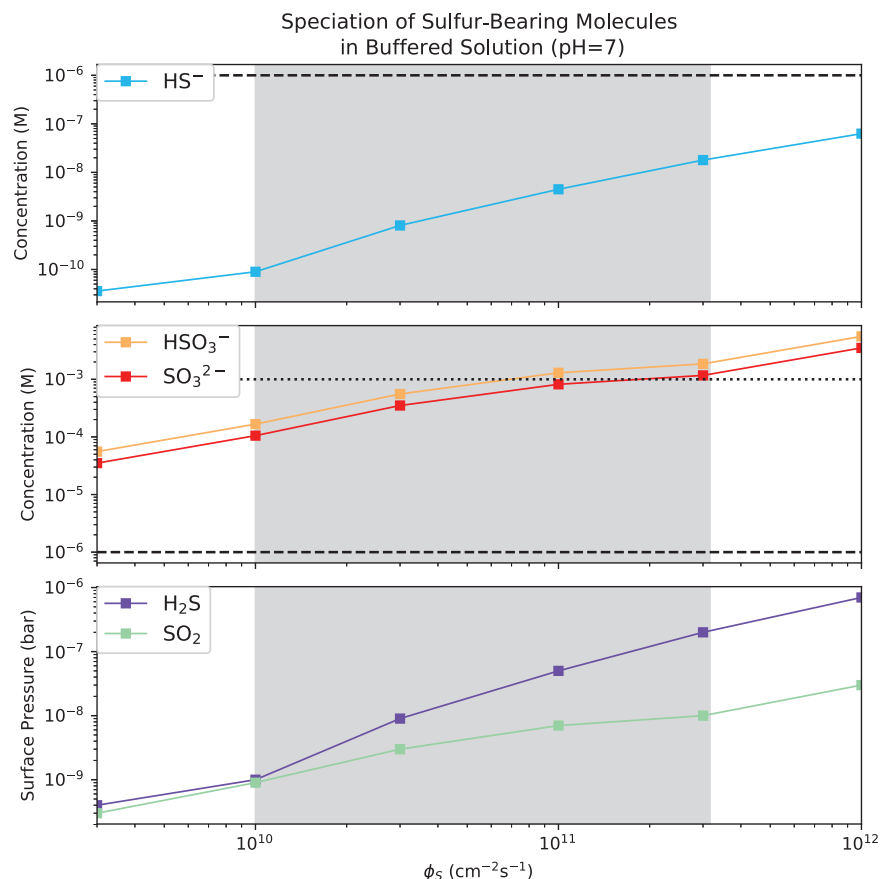in Buffered Solution (pH=7)

FIG. 3. Speciation of sulfur-bearing molecules in an aqueous reservoir buffered to pH = 7 as a function of total sulfur emission flux ϕ_S. The range of ϕ_S highlighted by Halevy and Head (2014) for emplacement of basaltic plains on Earth is shaded in gray. Horizontal dashed and dotted lines demarcate micromolar and millimolar concentrations, respectively.

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 SO_2-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 H_2S and SO_2 in isolation. However, H_2S and SO_2 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 H_2S and SO_2 in a solution buffered to pH = 7 as a function of total sulfur outgassing rate, ϕ_S. This pH corresponds approximately to the phosphate-buffered conditions in which the chemistry of Patel *et al.* (2015) proceeded[4]. 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 H_2S and SO_2 abundances to ϕ_S by the high-CO_2 model calculations of Hu *et al.* (2013).

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[4]It is thought that these chemistries should proceed over a broad range of pH. However, they will proceed best for pH $\lesssim 9.2$ (so that HCN tends to remain protonated) and pH $\gtrsim 7$ (so that the sulfidic anions tend to remain deprotonated)

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. $\phi_S = 1-3 \times 10^9$ cm^{-2} s^{-1} for modern Earth and $\phi_S = 10^{10}$ to $10^{11.5}$ cm^{-2} 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, SO_2-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 H_2S-derived anions cannot, absent highly alkaline conditions.

4.3. Coupling to the UV surface environment

H_2S, SO_2, and their photochemical aerosol by-products (S_8, H_2SO_4) 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 SO_2 and H_2S 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
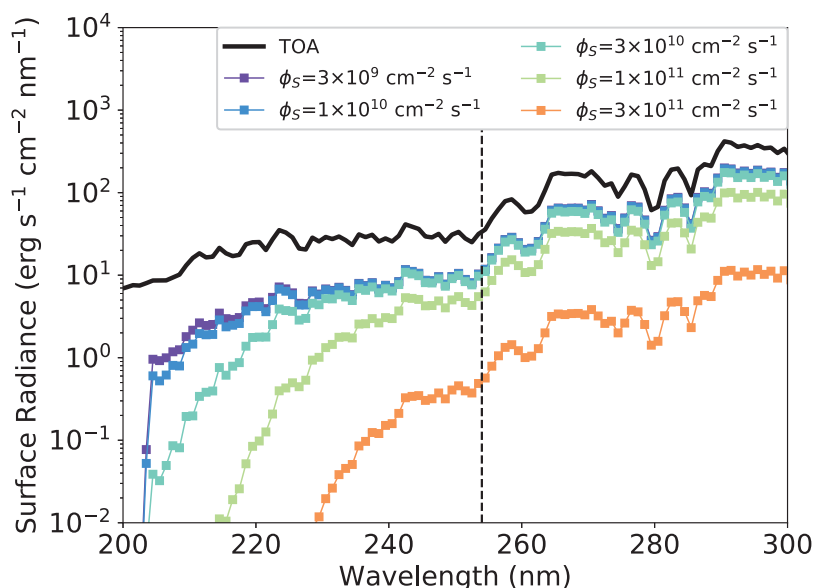
FIG. 4. UV surface radiance for early Earth as a function of ϕ_S, using the models of Hu *et al.* (2013). The black solid line indicates the top-of-atmosphere (TOA) flux, *i.e.*, the irradiation incident at the top of the atmosphere from the young Sun. The vertical dashed line demarcates 254 nm, the wavelength at which the low-pressure mercury lamps commonly used in prebiotic chemistry experiments emit.

of Claire *et al.,* 2012) by a CO_2-N_2-SO_2-H_2S 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 modeling[5] (Segura *et al.,* 2003; Rugheimer *et al.,* 2015). We once again used the work of Hu *et al.* (2013) to connect H_2S and SO_2 abundances to ϕ_S, and for consistency we assumed inventories of CO_2 and N_2 matching those assumed by Hu *et al.* (2013) (their high-CO_2 case). Our radiative transfer calculations are insensitive to the atmospheric *T/P* profile, because atmospheric emission is negligible at UV wavelengths and our UV cross-sections vary minimally as a function of temperature (Ranjan *et al.,* 2017); consequently, we assume a simple exponential profile to the vertical number density of the atmosphere. We also used the work of Hu *et al.* (2013) to estimate the total S_8 and H_2SO_4 aerosol loading in the atmosphere for each ϕ_S, and calculated aerosol optical parameters using the same size distributions and complex indices of refraction as they did. Lacking detailed atmospheric profiles of the aerosol abundance as a function of altitude, we assumed the aerosols were distributed exponentially, with a scale height equal to the bulk atmospheric scale height (*i.e.*, well mixed). In practice, sulfur aerosols tend to form photolytically at higher altitudes, meaning our approach places more aerosol at low altitude and less aerosol at high altitude. Since the radiative impact of aerosol absorption is amplified lower in the atmosphere due to enhanced scattering, this means our treatment should slightly overestimate UV attenuation due to aerosols. Similarly, Hu *et al.* (2013) assume an aerosol size distribution with surface area mean diameter $D_S = 0.1\,\mu m$, at the lower end of the plausible $D_S = 0.1$–$1\,\mu m$ range, which maximizes the possible radiative impact of the sulfur aerosols. Consequently, our results should be interpreted as a lower bound on the true UV fluence.

Figure 4 presents the UV fluence available on the surface of the prebiotic Earth as a function of ϕ_S under these assumptions. For $\phi_S \leq 1 \times 10^{11}$ cm^{-2} s^{-1}, UV radiation remains abundant on the planet surface. Millimolar levels of SO_3^{2-} and HSO_3^- are available in aqueous reservoirs buffered to pH ≥ 7 for $\phi_S = 1 \times 10^{11}$ cm^{-2} s^{-1}. Consequently, volcanism could supply prebiotically relevant levels of SO_3^{2-} and HSO_3^- without blocking off the UV radiation required by UV-dependent prebiotic pathways for sulfur emission fluxes up to $\phi_S \leq 1 \times 10^{11}$ cm^{-2} s^{-1} (near the upper edge of what is considered plausible for major terrestrial volcanic episodes). On the other hand, for $\phi_S \geq 3 \times 10^{11}$ cm^{-2} s^{-1}, atmospheric sulfur-bearing gases and aerosols, especially the UV-absorbing S_8, 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 $\phi_S \leq 1 \times 10^{11}$ 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 SO_3^{2-} and HSO_3^-, derived from the dissolution of SO_2 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 ($\phi_S \approx 1 \times 10^{11}$ 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 H_2S

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

can only be supplied at low concentrations (sub-micromolar) across the plausible range of pH$_2$S and pH[6]. 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 H$_2$S-derived anion concentrations are not significantly affected by temperature variations in this range, SO$_2$-derived anion concentrations are. This is because H_{SO_2} decreases with temperature and p$K_{aSO_2,1}$ increases with temperature[7]; both effects favor decreased concentrations of HSO$_3^-$ 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 SO$_2$-derived anions HSO$_3^-$ and SO$_3^{2-}$ are an order of magnitude higher for $T \approx 0°C$ relative to $T = 25°C$, and an order of magnitude lower for $T \approx 50°C$, assuming a near-neutral reservoir. Consequently, cooler waters are more favorable environments for prebiotic chemistry which invokes HSO$_3^-$ or SO$_3^{2-}$.

Sulfur-bearing gases and aerosols, in particular S$_8$, are strong UV absorbers, and if present at high enough levels could suppress UV-sensitive prebiotic chemistry. For $\phi_S \leq 1 \times 10^{11}$ 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 ($\phi_S = 3 \times 10^{11}$ 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[8] might create an especially clement surficial environment for UV-independent prebiotic chemistry.

These results were derived using the high-CO$_2$ model of Hu et al. (2013), which, while plausible, assumes more CO$_2$ and less N$_2$ 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 N$_2$-rich model of Hu et al. (2013). This model assumes 1 bar of N$_2$ and negligible CO$_2$ and is hence an unrealistic

approximation to early Earth, because an appreciable CO$_2$ inventory is expected due to climate constraints (Kasting, 1993; Wordsworth and Pierrehumbert, 2013) and due to volcanic outgassing of CO$_2$. Hence, this model serves as an extreme bounding case. Assuming this model, we find that H$_2$S and SO$_2$ levels are lower than for the high-CO$_2$ case. SO$_2$-derived anions remain available at micromolar levels over the plausible range of ϕ_S 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 CO$_2$-rich case. UV fluences are lower than in the CO$_2$-rich case, due to elevated levels of S$_8$ formation in this more reducing atmosphere; surface UV fluence (200–300 nm) is suppressed by an order of magnitude or more for $\phi_S \geq 1 \times 10^{11}$ cm^{-2} s^{-1}. Overall, this boundary case suggests that our finding that the atmosphere can supply prebiotically relevant levels of SO$_2$-derived anions but not H$_2$S-derived anions in conjunction with UV light remains true across a broad range of CO$_2$ and N$_2$ abundances, though both sulfidic anion abundances and UV are lower for more reducing, N$_2$-rich atmospheres. However, a detailed exploration of the pCO$_2$-pN$_2$ 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 H$_2$S and SO$_2$. 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, Fe^{2+} and Cu^{2+} react with H$_2$S(aq) to generate insoluble precipitates, like CuS and FeS$_2$ (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.

Ca^{2+}, produced by mineral weathering, reacts with sulfite to produce insoluble CaSO$_3$. Studying the Ca^{2+}-SO^{2-} system
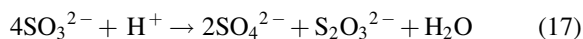
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[6]Our results are relevant to shallow, aqueous bodies of water, like lakes. By contrast, in the ocean, volcanoes vent directly into the water, and the turnover time can be long. Consequently, one could envision significant buildup of H$_2$S near deep-ocean volcanoes. This scenario is beyond the scope of this work but may be worthy of consideration for HS$^-$-dependent chemistry.

[7]The exothermic first dissociation of SO$_2$ is disfavored at higher temperatures.

[8]However, even in this case there may be a window in which prebiotic chemistry experiences both elevated SO$_2$ levels and plenty of UV light, since aerosol formation is not instantaneous. Detailed photochemical modeling is required to determine the timescale of aerosol formation after a large volcanic eruption on early Earth; absent such modeling, we note that on modern Earth, formation of sulfate aerosols from volcanic eruptions occurs on a timescale of weeks (Robock, 2000); we may speculate a similar timescale for aerosol formation on early Earth.

requires considering the effects of carbonate (CO_3^{2-}) as well, because 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 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 Ca^{2+}, as follows. Assuming parameters from Hu *et al.* (2013), the flux of carbonates into solution due to deposition and speciation of atmospheric CO_2 is $r_{CO_2} n_{atm} v_{dep, CO_2} = 2 \times 10^{15}$ cm^{-2} s^{-1} on the CO_2-rich early Earth, which exceeds the mean flux of Ca due to mineral weathering ($1–5 \times 10^{10}$ cm^{-2} s^{-1}; Watmough and Aherne, 2008; Taylor *et al.*, 2012) by 5 orders of magnitude; thus, it is reasonable to assume the solution is saturated in CO_2 with abundance dictated by Henry's law of $(3.3 \times 10^{-2}$ $M/$ bar)(0.9 bar) = 0.03 M (Sander, 2015). Then, $[CO_3^{2-}] = (0.03$ $M)(10^{7-6.35})(10^{7-10.33}) = 6 \times 10^{-5}$ M at neutral pH (dissociation constants $K_{a_{CO_2,1}} = 6.35$ and $K_{a_{CO_2,1}} = 10.33$ from Rumble [2017][9]). Since $CaCO_3$ ($K_{sp} = 3.36 \times 10^{-9}$ M^2, Rumble, 2017) is 2 orders of magnitude less soluble than $CaSO_3$ ($K_{sp} = 3.1 \times 10^{-7}$ M^2, Rumble, 2017) and the sulfite flux is much less than the carbonate flux, we can assume that $[Ca^{2+}]$ is dictated to first order by equilibrium with carbonate mineral, that is, $[Ca^{2+}] = 3.36 \times 10^{-9}$ $M^2/6 \times 10^{-5}$ $M = 6 \times 10^{-5}$ M. At this $[Ca^{2+}]$, $CaSO_3^{2-}$(s) will begin to form at $[SO_3^{2-}] = 3.1 \times 10^{-7}$ $M^2/$ 6×10^{-5} $M = 5 \times 10^{-3}$ M. The $[SO_3^{2-}]$ 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 $CaSO_3$ and precipitate does not form. Were pCO_2 lower, for example, $pCO_2 = 0.2$ bar[10], $CaSO_3$ precipitate formation begins at $[SO_3^{2-}] = 1 \times 10^{-3}$ M. However, if pH were low, the carbonate solubility would exceed sulfite solubility, and sulfite precipitates would form (Halevy *et al.*, 2007); hence, at low pH, sulfite and bisulfite concentrations will be below the values we calculate. Overall, our results are unaffected by $CaSO_3$ precipitation across most of parameter space, but $CaSO_3$ precipitation might be a significant sink on aqueous sulfite levels for acid solutions and/or for very low atmospheric 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; Halevy, 2013):

$$4SO_3^{2-} + H^+ \rightarrow 2SO_4^{2-} + S_2O_3^{2-} + H_2O \quad (17)$$

$$2HS^- + 4HSO_3^- \rightarrow 3S_2O_3^{2-} + 3H_2O \quad (18)$$

The kinetics of Reaction 17 are not well characterized near standard temperature and are an active topic of research (Mirzoyan and Halevy, 2014; Amshoff *et al.*, 2016). Meyer *et al.* (1982) report sulfite and bisulfite are stable on timescales ≥ 1 year in anoxic conditions, while Guekezian *et al.* (1997) report decay of sulfite in days at pH≥ 12.8. Halevy (2013) propose that rate coefficients in the range $k_{17} = \exp\left(\dfrac{-50\ kJ\ mol^{-1}}{RT}\right) - \exp\left(\dfrac{-40\ kJ\ mol^{-1}}{RT}\right)$ s^{-1} are plausible; at 293 K, this corresponds to 1×10^{-9} to 7×10^{-8} s^{-1}, which correspond to timescales of 0.5–30 years. The kinetics of Reaction 18 have been determined as a function of temperature at pH $= 9$ and $I = 0.2$ M by Siu and Jia (1999). At 293 K, the rate coefficient is $k_{18} = 4 \times 10^3$ M^{-2} s^{-1}. At the S-anion concentrations relevant to our work[11], the timescale of this reaction is $\gtrsim 1$ 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 pH $= 7$, with source the atmosphere and sink these redox reactions. Following the treatment of Halevy (2013), the equilibrium equations can be written:

$$r_{H_2S} n_{atm} v_{dep, H_2S} A_{catch} = \left(\frac{2}{3} k_{18}[HS^-][HSO_3^-]^2\right) A_{lake} d_{lake} \quad (19)$$

$$r_{SO_2} n_{atm} v_{dep, SO_2} A_{catch} = \left(\frac{4}{3} k_{18}[HS^-][HSO_3^-]^2 + k_{17}[S(IV)]\right) A_{lake} d_{lake} \quad (20)$$

For consistency with Hu *et al.* (2013), we adopt $v_{dep, H_2S} = 0.015$ cm s^{-1}, $v_{dep, SO_2} = 1$ cm s^{-1}, $T = 288$ K, and $n_{atm} = \frac{1\ bar}{kT} = 2.4 \times 10^{19}$ cm^{-3}. Since we are concerned with shallow, well-mixed lakes, we take the lake depth $d_{lake} = 10^2$ cm. A_{catch} is the catchment area of the lake, and A_{lake} is the surface area of the lake; we conservatively adopt $A_{catch} = A_{lake}$, which likely underestimates sulfur supply since the catchment area is often larger than the lake area. $[S(IV)]$ refers to the total concentration of S(IV) atoms in solution, and is calculated as $[S(IV)] = [SO_2] + [HSO_3^-] + [SO_3^{2-}] + 2[HS_2O_5^-] \approx [SO_2(aq)] + [HSO_3^-] + [SO_3^{2-}]$[12]. Since we have specified pH $= 7$ and know the relevant pK_a values, we can calculate $[HSO_3^-]$ from $[S(IV)]$ and vice versa. With r_{H_2S} and r_{SO_2} 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 ϕ_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

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[9]Using pK_a values for CO_2 dissociation from modern seawater, *e.g.*, Zeebe and Wolf-Gladrow (2009), results in much higher carbonate levels, much lower Ca levels, and a much higher threshold for $CaSO_3$ saturation, so this treatment is conservative.

[10]Corresponding to the lower limit suggested by Kasting (1987) from climate considerations.

[11]$[HS^-] \lesssim 10^{-8}$ M, $[HSO_3^-] \lesssim 10^{-3}$ M.

[12]$[HS_2O_5^-]$ is negligible for dilute $[SO_2]$.

FIG. 5. Speciation of sulfur-bearing molecules in a shallow lake buffered to pH = 7 as a function of total sulfur emission flux ϕ_S, using a dynamic calculation with source atmospheric deposition and sink redox reactions. The range of ϕ_S highlighted by Halevy and Head (2014) for emplacement of basaltic plains on Earth is shaded in gray. Horizontal dashed and dotted lines demarcate micromolar and millimolar concentrations, respectively. [HS⁻] would not be able to achieve the high concentrations calculated here for the slow disproportionation (low k_{17}) case due to solubility constraints.
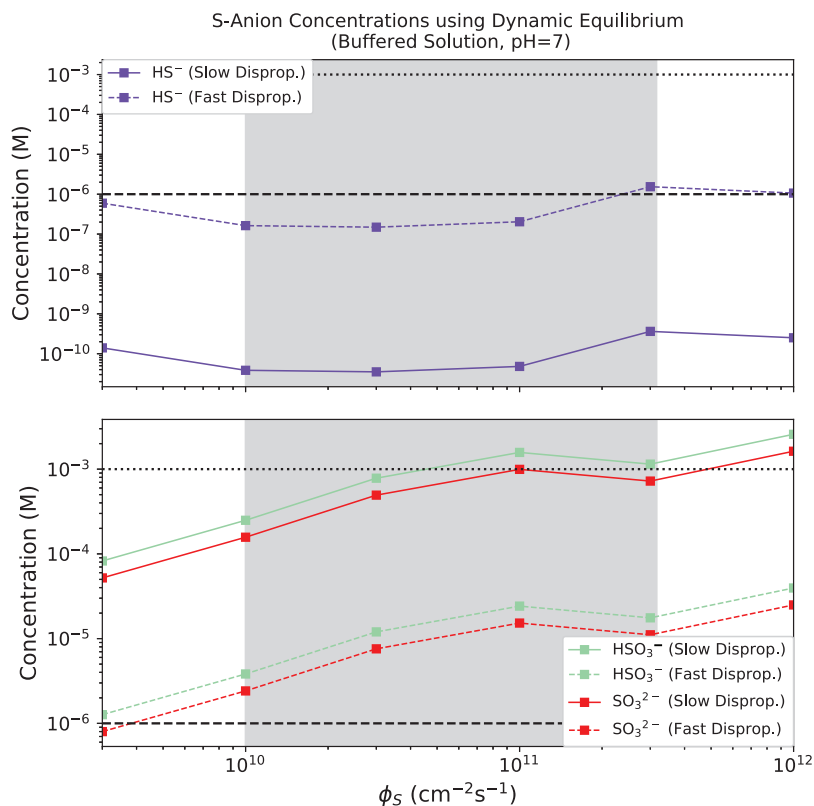
varying by 4 across the range of k_{17} suggested by Halevy (2013). However, even with this uncertainty it is clear that prebiotically relevant levels (≥1 μM) of SO_2-derived anions are available across the range of plausible sulfur outgassing fluxes, with concentrations ~1–10 μM if sulfite disproportionation is fast and ~100–1000 μM 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_2S 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_{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 ($\phi_S \geq 3 \times 10^{11}$ cm⁻² s⁻¹). Hence, epochs of moderately high volcanism 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_3^- or SO_3^{2-} instead of HS^-.

We considered alternate planetary sources for HS^- for the Patel *et al.* (2015) chemistry. We explored whether shallow hydrothermal systems, such as hot springs, might provide prebiotically relevant levels of HS^-. 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^- (Xu *et al.*, 1998; Vick *et al.*, 2010; Kaasalainen and Stefánsson, 2011). However, high concentrations of HS^- appear to only be achieved in hot systems[14] ($T > 60°C$, and typically higher). Similarly, studies of geothermal waters in Yellowstone National Park suggest sulfite availability at the 0.4–$5 \mu M$ 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_2 are available at $\geq 1 \mu M$ levels in non-acidic reservoirs for SO_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_2-derived anions may be available at $\geq 1 mM$ 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 $\sim 10 \mu M$ 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 $\geq 1 mM$ 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_2S would not have been available at micromolar levels across the plausible range of volcanic outgassing due to low solubility of H_2S 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 $\phi_S \leq 1 \times 10^{11} cm^{-2} s^{-1}$ but will be suppressed for $\phi_S \geq 3 \times 10^{11} cm^{-2} s^{-1}$; 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_2-derived anions like HSO_3^- or SO_3^{2-} instead of HS^-, 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 ($\phi_S \approx 1 \times 10^{11} cm^{-2} s^{-1}$) might have been especially clement for cyanosulfidic prebiotic chemistry which exploits SO_2-derived anions (*e.g.*, HSO_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_2 and H_2S on early Earth.

A. Atmospheric Sulfur Speciation

We use the work of Hu *et al.* (2013) to connect the sulfur emission flux ϕ_S to the speciation of atmospheric sulfur. Table A1 presents H_2S and SO_2 mixing ratios as a function of ϕ_S from Hu *et al.* (2013) (their Fig. 5, CO_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_2 and H_2S.

We use the Extended Debye-Huckel theory to calculate activity coefficients (γ_i) for the ions in our study. Extended Debye-Huckel 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_2S AND SO_2 AS A FUNCTION OF ϕ_S FROM HU *ET AL.* (2013) (THEIR FIG. 5, CO_2-DOMINATED CASE)

ϕ_S ($cm^{-2} s^{-1}$)	r_{H_2S}	r_{SO_2}
3×10^9	4×10^{-10}	3×10^{-10}
1×10^{10}	1×10^{-9}	9×10^{-10}
3×10^{10}	9×10^{-9}	3×10^{-9}
1×10^{11}	5×10^{-8}	7×10^{-9}
3×10^{11}	2×10^{-7}	1×10^{-8}
1×10^{12}	7×10^{-7}	3×10^{-8}
3×10^{12}	2×10^{-6}	8×10^{-8}
1×10^{13}	9×10^{-6}	3×10^{-7}

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[14]We speculate that HS⁻-rich shallow hydrothermal systems tend to be hot because the same volcanism that supplies elevated levels of HS⁻ also supplies elevated levels of heat.

TABLE B1. VALUES FOR THE ION-SPECIFIC PARAMETER α
(RELATED TO THE HYDRATION SPHERE OF THE ION)
USED TO CALCULATE ACTIVITY COEFFICIENTS

Ion	$\alpha_i(\mathring{A})$
HSO_3^-	4.0
SO_3^{2-}	4.5
HS^-	3.5
S^{2-}	5.0
OH^-	3.5
H^+	9.0

Extended Debye Huckel theory states that

$$\log \gamma_i = -A z_i^2 \frac{I^{0.5}}{1 + B\alpha_i I^{0.5}} \tag{B1}$$

where A and B depend on the temperature, density, and dielectric constant of the solvent (in our case water), and α_i is an ion-specific parameter. We took $A = 0.5085\ M^{-1/2}$ and $B = 0.3281\ M^{-1/2}\mathring{A}^{-1}$, corresponding to $T = 25°C$; Appendix D describes the sensitivity of our analysis to this assumption. Table B1 summarizes the α_i used in our study, taken from Misra (2012). We were unable to locate a value of α_C for $HS_2O_5^-$ and consequently take $\gamma_{HS_2O_5^-} = 1$ 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), $pK_{a_{SO_2,3}}$ 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 coefficients 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):

$$\log H_0/H = \Sigma_i(h_i + h_G) * c_i \tag{C1}$$

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

TABLE B2. PER-ION ACTIVITY COEFFICIENTS
FOR DIFFERENT IONIC STRENGTHS

Ion	I=0 M	I=0.1 M
HSO_3^-	1.0	0.770
SO_3^{2-}	1.0	0.364
HS^-	1.0	0.762
S^{2-}	1.0	0.377
OH^-	1.0	0.762
H^+	1.0	0.826

TABLE C1. PARAMETERS USED TO ESTIMATE
THE DEPENDENCE OF HENRY'S LAW
CONSTANTS ON [NaCl]

Parameter	H_2S	SO_2	Na^+	Cl^-
H_0 (*M*/bar)	0.101	1.34	—	—
h_0 (M^{-1})	−0.0333	−0.0607	—	—
h_T (M^{-1})	0[a]	0.000275	—	—
h_i (M^{-1})	—	—	0.1143	0.0318

[a]Value not found in literature search; assumed to be 0.

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] ≤ 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
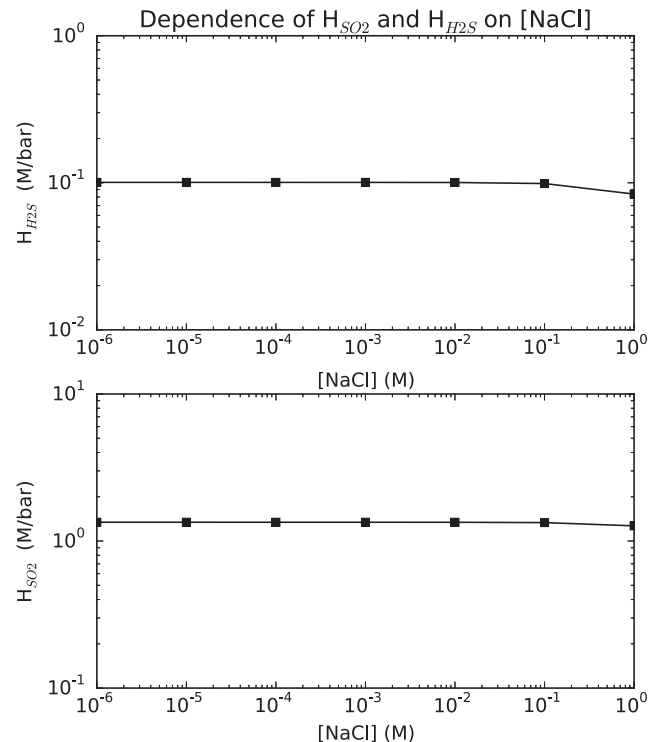

FIG. C1. Dependence of Henry's law constants for H_2S and SO_2 on [NaCl], calculated using the formalism from Burkholder *et al.* (2015). H_{H_2S} and H_{SO_2} are insensitive to [NaCl] for [NaCl] <1 M.

TABLE D1. PARAMETERS USED TO ESTIMATE DEPENDENCE OF HENRY'S LAW CONSTANT ON TEMPERATURE

Parameter	H_2S	SO_2
A	−145.2	−39.72
B	8120	4250
C	20.296	4.525

et al. (2015), that is, $\ln(H) = A + B/T + C\ln(T)$, where H is in units of M/atm and A, B, and C are gas-specific coefficients of an empirical fit. The values of these coefficients for H_2S and SO_2 were taken from Burkholder *et al.* (2015) and are summarized in Table D1. $H(T)$ for H_2S and 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:

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

where K_0 is the equilibrium constant, T is temperature, ΔH_0 is the change in enthalpy, and $R = 8.314 \times 10^{-3}$ kJ/mol/K. Solving this differential equation, assuming temperature-invariant enthalpy of solution[15], gives

$$\ln(K_2) = \ln(K_1) + \frac{-\Delta H_0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{(D2)}$$

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. ΔH is the change in enthalpy of the reaction, given by

$$\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \quad \text{(D3)}$$

The enthalpies of formation for the products and reactants of the first two acid dissociation reactions for H_2S and SO_2 are taken from Lide (2009) and are shown in Table D2. Note that $\Delta H_f^\circ = 0$ for H^+, by definition. We were unable to locate an enthalpy of formation for $H_2SO_5^-$ and consequently are unable to calculate the temperature dependence of $pK_{a_{SO_2,3}}$. Since in our analysis the supply of SO_2 is not limited (the atmosphere is treated as an infinite reservoir), $pK_{a_{SO_2,3}}$ affects only the abundance of $H_2SO_5^-$, which is a trace compound in our analysis (see Fig. 2).

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[15] We expect this assumption to be reasonable because of the limited range of temperatures that are plausible for our surface aqueous reservoir scenario.
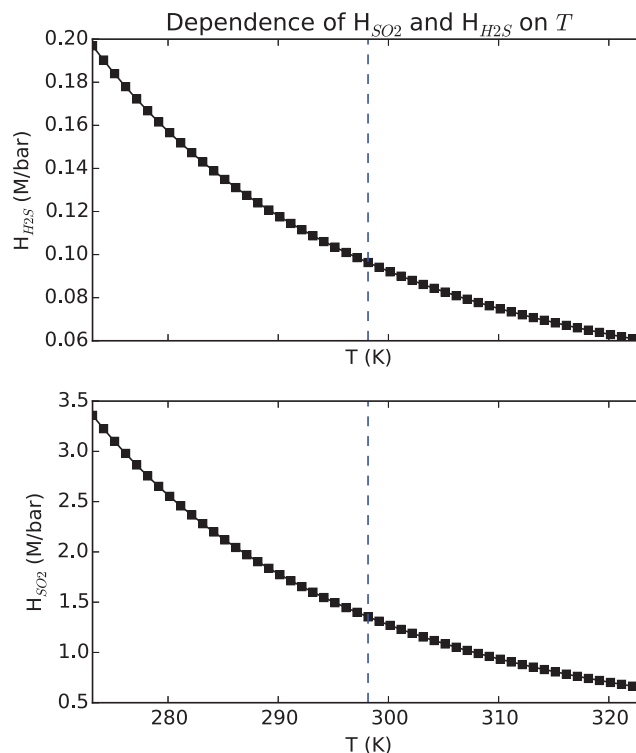

FIG. D1. Temperature dependence of Henry's law constants for H_2S and SO_2, calculated using the formalism from Burkholder *et al.* (2015). Varying the temperature by 25 K relative to the reference temperature of 298.15 K (blue line) affects the value of H_{H_2S} and H_{SO_2} by less than a factor of 2.5.

Using these values and the van't Hoff equation, we calculated the temperature dependence of the first two acid dissociation constants for aqueous H_2S and SO_2. Table D3 shows these pK_a values for SO_2 and H_2S at 0°C, 25°C, and 50°C.

The variation in pK_a is negligible for all reactions except the first dissociation of SO_2; $pK_{a_{SO_2,1}}$ increases significantly with temperature. This implies that in non-acidic solutions, the concentrations of 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, $A = 0.4883$ $M^{-1/2}$ and $B = 0.3241$ $M^{-1/2}\text{Å}^{-1}$; at $T = 25$°C, $A = 0.5085$ $M^{-1/2}$

TABLE D2. ENTHALPIES OF FORMATION USED IN THE VAN'T HOFF EQUATION CALCULATION

Molecule	ΔH_f° (kJ/mol)
HSO_3^-	−626.2
SO_3^{2-}	−635.5
SO_2	−296.8
HS^-	−17.6
S^{2-}	33.1
H_2S	−20.6
H_2O	−285.8

TABLE D3. pK_a AT TEMPERATURES OF 0°C, 25°C,
AND 50°C AND REACTION ENTHALPIES

	T = 0°C	T = 25°C	T = 50°C	ΔH_{rxn}° (kJ/mol)
H$_2$S, pK_{a1}	7.098	7.05	7.009	3.0
H$_2$S, pK_{a2}	19.81	19.0	18.31	50.7
SO$_2$, pK_{a1}	1.160	1.86	2.452	−43.6
SO$_2$, pK_{a2}	7.051	7.2	7.326	−9.3

and $B = 0.3281\ M^{-1/2}\mathring{A}^{-1}$; and at $T = 50°C$, $A = 0.5319\ M^{-1/2}$ and $B = 0.3321\ M^{-1/2}\mathring{A}^{-1}$ (Misra, 2012). From $T = 0$–50°C, the activity coefficients varied by <8% for $I \leq 0.1\ M$.

D.4. Overall sensitivity of analysis to temperature

We evaluated the overall sensitivity of our analysis to our assumption of $T = 25°C$ by repeating our analysis at $T = 0°C$ and $T = 50°C$, 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 H$_2$S-derived anions but a significant impact on the abundances of the SO$_2$-derived anions. H_{SO_2} decreases with temperature, and p$K_{a_{SO_2,1}}$ increases with temperature; both effects serve to increase the concentration of HSO$_3^-$ and its derivatives in non-acidic (pH > 2.5) waters. At $T = 0°C$, HSO$_3^-$ and SO$_3^{2-}$ concentrations are an order of magnitude higher than at $T = 25°C$. Similarly, at $T = 50°C$, HSO$_3^-$ and SO$_3^{2-}$ concentrations are an order of magnitude lower than at $T = 25°C$. Our overall conclusions are robust to these variations. However, this study does imply that significantly higher concentrations of SO$_2$-derived anions are available to prebiotic chemistry in cooler waters, and inversely that hotter waters would have access to lower levels of SO$_2$-derived anions.

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Author Disclosure Statement

The authors declare no competing financial interests.

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Address correspondence to:
Sukrit Ranjan
77 Massachusetts Avenue
Room 54-1719
Cambridge, MA 02139

E-mail: sukrit@mit.edu