

# Geochemical and Photochemical Constraints on S[IV] Concentrations in Natural Waters on Prebiotic Earth

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## Abstract

Aqueous S[IV] species ( $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ) derived from volcanogenic atmospheric  $\text{SO}_2$  are important to planetary habitability through their roles in proposed origins-of-life chemistry and influence on atmospheric sulfur haze formation, but the early cycling of S[IV] is poorly understood. Here, we combine new laboratory constraints on S[IV] disproportionation kinetics with a novel aqueous photochemistry model to estimate the concentrations of S[IV] in natural waters on prebiotic Earth. We show that S[IV] disproportionation is slow in pH[?] 7 waters, with timescale T[?] 1 year at room temperature, meaning that S[IV] was present in prebiotic natural waters. However, we also show that photolysis of S[IV] by UV light on prebiotic Earth limited  $[\text{S[IV]}] < 100\mu\text{M}$  in global-mean steady-state. Because of photolysis,  $[\text{S[IV]}]$  was much lower in natural waters compared to the concentrations generally invoked in laboratory simulations of origins-of-life chemistry ([?] 10 mM), meaning further work is needed to confirm whether laboratory S[IV]- dependent prebiotic chemistries could have functioned in nature.  $[\text{S[IV]}]$ [?] 1 $\mu\text{M}$  in terrestrial waters for: (1)  $\text{SO}_2$  outgassing [?] 20 $\times$  modern, (2) pond depths < 10 cm, or UV-attenuating agents present in early waters or the prebiotic atmosphere. Marine S[IV] was sub-saturated with respect to atmospheric  $\text{SO}_2$ , meaning that atmospheric  $\text{SO}_2$  deposition was efficient and that, within the constraints of present knowledge, UV-attenuating sulfur hazes could only have persisted on prebiotic Earth if sulfur emission rates were very high ([?] 100x modern). Our work illustrates the synergy between planetary science, geochemistry and synthetic organic chemistry towards understanding the emergence and maintenance of life on early Earth.

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## Key Points:

- We use experiments and modeling to constrain S[IV] (sulfite) concentrations in marine and terrestrial waters on prebiotic Earth (~3.9 Ga).
- We show that S[IV] was a prebiotic reagent, but its concentration were limited to  $< 100 \mu\text{M}$  by photolysis in early natural waters.
- Our work shows the need to characterize the sensitivity of proposed chemical pathways for the origin of life to S[IV] abundance.

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## Abstract

Aqueous S[IV] species ( $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ) derived from volcanogenic atmospheric  $\text{SO}_2$  are important to planetary habitability through their roles in proposed origins-of-life chemistry and influence on atmospheric sulfur haze formation, but the early cycling of S[IV] is poorly understood. Here, we combine new laboratory constraints on S[IV] disproportionation kinetics with a novel aqueous photochemistry model to estimate the concentrations of S[IV] in natural waters on prebiotic Earth. We show that S[IV] disproportionation is slow in  $\text{pH} \geq 7$  waters, with timescale  $T \geq 1$  year at room temperature, meaning that S[IV] was present in prebiotic natural waters. However, we also show that photolysis of S[IV] by UV light on prebiotic Earth limited  $[\text{S[IV]}] < 100 \mu\text{M}$  in global-mean steady-state. Because of photolysis,  $[\text{S[IV]}]$  was much lower in natural waters compared to the concentrations generally invoked in laboratory simulations of origins-of-life chemistry ( $\geq 10 \text{ mM}$ ), meaning further work is needed to confirm whether laboratory S[IV]-dependent prebiotic chemistries could have functioned in nature.  $[\text{S[IV]}] \geq 1 \mu\text{M}$  in terrestrial waters for: (1)  $\text{SO}_2$  outgassing  $\geq 20\times$  modern, (2) pond depths  $< 10 \text{ cm}$ , or (3) UV-attenuating agents present in early waters or the prebiotic atmosphere. Marine S[IV] was sub-saturated with respect to atmospheric  $\text{SO}_2$ , meaning that atmospheric  $\text{SO}_2$  deposition was efficient and that, within the constraints of present knowledge, UV-attenuating sulfur hazes could only have persisted on prebiotic Earth if sulfur emission rates were very high ( $\gtrsim 100\times$  modern). Our work illustrates the synergy between planetary science, geochemistry and synthetic organic chemistry towards understanding the emergence and maintenance of life on early Earth.

## Plain Language Summary

Sulfur cycling on early Earth is not well understood because its chemical reactions in water in the absence of biology are poorly constrained. Here, we build a new model to estimate the concentrations of a key family of sulfur molecules, S[IV] ("sulfite"), in oceans and ponds on early Earth. We use new measurements of S[IV] reactions to calibrate our model and include the effects of UV light. We show that S[IV] was present on early Earth, but that UV light limited its concentrations to  $< 100 \mu\text{M}$ . This finding has significant implications for efforts to understand the origin and maintenance of early life. First, it means that early natural environments featured S[IV], but at much lower concentrations than considered in laboratory simulations of origin-of-life chemistry. It is necessary to confirm whether proposed S[IV]-dependent origins-of-life chemistry can function at the generally lower S[IV] concentrations characteristic of early Earth environments. Second, it means that sulfur hazes could only have persisted on early Earth if volcanic sulfur emission was very high, favoring a generally UV-rich surface environment for nascent life. Our work illustrates the critical role planetary science and geochemistry play in guiding and testing chemical theories of the origin and endurance of life.

## 1 Introduction

The abundance and speciation of sulfur in natural waters on early Earth is a key question in origin-of-life studies. Sulfur is one of the main elemental components of modern biomolecules, and sulfur-bearing molecules are critically invoked in diverse proposals for origin-of-life chemistry (Wächtershäuser, 1990; Trainer, 2013; Patel et al., 2015; Bonfio et al., 2017; Goldford et al., 2019; Li et al., 2020). Further, aqueous sulfur influences planetary habitability through regulation of atmospheric sulfur (Kasting et al., 1989; Halevy et al., 2007; Tian et al., 2010; Halevy & Head, 2014). However, direct geological constraints on the composition of terrestrial prebiotic natural waters are limited due to tectonic and hydrologic processing of the rock record (Mojzsis, 2007). In the absence of direct constraints from the rock record, understanding of sulfur speciation on early Earth is guided by theoretical modeling studies (Halevy, 2013).

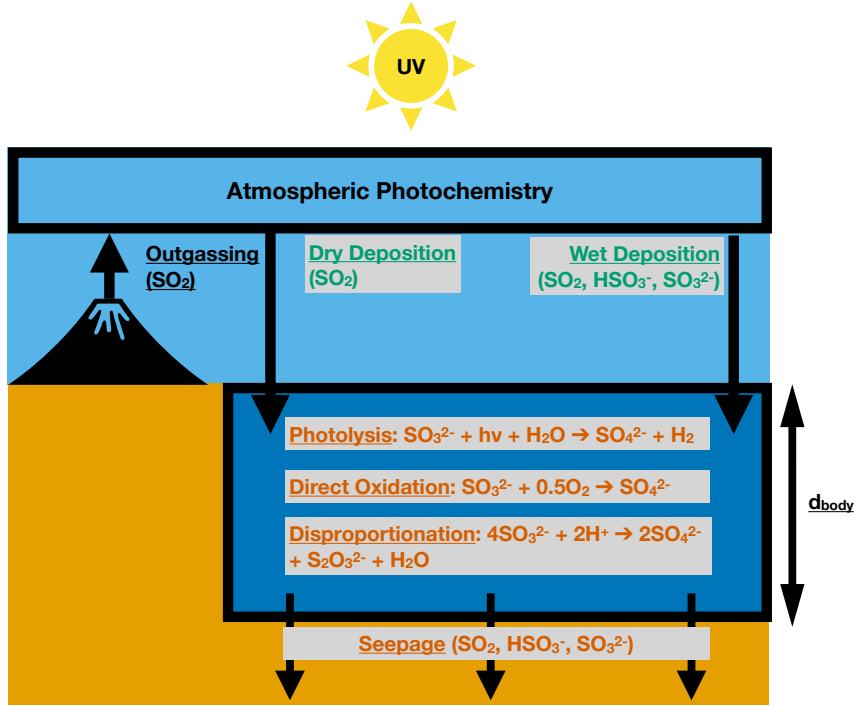
Among the sulfur species, S[IV] species ( $\text{SO}_3^{2-}$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_2$ ) have recently emerged as being of particular importance to planetary habitability. S[IV] species are often collectively referred to as “sulfite” (Halevy, 2013), though sulfite formally refers only to  $\text{SO}_3^{2-}$ . S[IV] species are derived from the dissolution of volcanogenic  $\text{SO}_2$  into liquid water, and are tightly linked by rapid acid/base equilibria (Kasting et al., 1989). S[IV] is important because of the key roles it has recently been demonstrated to play in synthetic organic chemistry experiments simulating potential prebiotic chemistry scenarios (J. Xu et al., 2018; Kawai et al., 2019; Liu et al., 2021), and in particular prebiotic ribonucleotide synthesis, a basic requirement for the RNA world model for the origin of life (Becker et al., 2019; J. Xu et al., 2020; Rimmer et al., 2021; Benner et al., 2019). S[IV] is also important because of the controlling role it plays in planetary sulfur cycling, and thereby on planetary climate and UV irradiation levels (Kasting et al., 1989; Tian et al., 2010; Hu et al., 2013; Halevy & Head, 2014).

Determining the concentration of S[IV] ([S[IV]]) in natural waters on prebiotic Earth is key to assessing the plausibility of S[IV]-dependent prebiotic chemistries and guiding the development of theories of the origin of life in general. On modern Earth, S[IV] is efficiently oxidized to sulfate (S[VI]) by ambient  $\text{O}_2$ , and S[IV] concentrations are negligible in natural waters (Hegg & Hobbs, 1978; Loftus et al., 2019). However, in the anoxic atmosphere of early Earth, direct oxidation of S[IV] would have been inhibited, raising the possibility of longer lifetimes and appreciable inventories of S[IV] in some natural waters (Kasting et al., 1989; Ranjan et al., 2018).

The main uncertainty on [S[IV]] in prebiotic natural waters are the kinetics of its loss. Particularly highlighted in the literature is uncertainty regarding the rate of disproportionation of S[IV], which is proposed as the main loss mechanism (Kasting et al., 1989; Halevy, 2013). Literature estimates of the timescale of this process span  $> 2$  orders of magnitude (Meyer et al., 1979; Guekezian et al., 1997). In addition, there are other loss mechanisms for S[IV] such as photolysis (Fischer & Warneck, 1996) that are relevant to prebiotic conditions that have not been considered in estimating prebiotic S[IV] concentrations. Finally, past modeling of S[IV] in natural waters has focused on marine waters (e.g., the ocean), neglecting the diverse terrestrial waters (e.g. lakes, ponds) that are invoked in numerous prebiotic chemistries.

In this work, we remediate these shortcomings. We conduct long-term experiments on S[IV] stability, constraining the kinetics of its disproportionation at room temperature. We incorporate these constraints into a simple box model, together with other loss processes, like photolysis, which were not previously considered for aqueous S[IV] (Figure 1). We apply our box model to both marine and terrestrial waters, consider the prospects for the accumulation of S[IV], and explore the implications for proposed prebiotic chemistry and planetary habitability. Our analysis constitutes a significant advance over past studies because (1) we experimentally measure and leverage new chemical kinetic constraints in our model, (2) we include previously-unconsidered but important loss processes for S[IV], and (3) we consider both marine and terrestrial waters. The overall structure of our work is shown in Figure 2.

While we focus on the implications of our work for prebiotic chemistry on Earth, our work has broad applications for planetary habitability and sulfur cycling on rocky planets in general. In particular, it has been long debated whether the oceans on early Earth, Mars, and analogous exoplanets saturate in S[IV] with respect to the atmosphere, in which case  $\text{SO}_2$  can accumulate in the planetary atmosphere with potential implications for planetary climate and exoplanet observables, or whether S[IV] remains sub-saturated, in which case atmospheric deposition efficiently scrubs  $\text{SO}_2$  from the atmosphere (Kasting et al., 1989; Halevy et al., 2007; Tian et al., 2010; Hu et al., 2013; Loftus et al., 2019). We address this question as well.



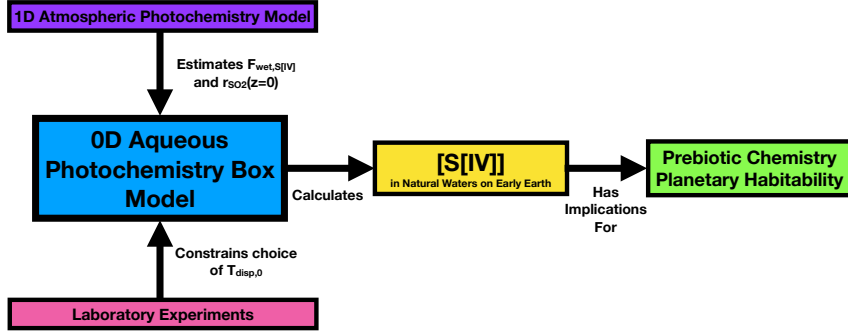
**Figure 1.** Schematic illustrating our model of S[IV] in natural waters on early Earth. Input of S[IV] from the atmosphere (ultimately derived from volcanic outgassing) into an aqueous body (dark blue box) via wet and dry deposition is balanced by loss of S[IV] in the aqueous body due to photolysis, direct oxidation, disproportionation, and seepage. Processes that are sources of aqueous S[IV] in the 0D aqueous photochemistry box model are in blue-green text, while processes that are sinks of aqueous S[IV] in the 0D aqueous phototochemistry model are in vermillion text. Specification of geochemical parameters allows simulation of both marine and terrestrial waters using this modeling approach.

## 2 Background

### 2.1 Relevance of S[IV] to Prebiotic Chemistry and Planetary Habitability

S[IV] plays diverse and critical roles in synthetic organic chemical pathways for the emergence of biomolecules, especially ribonucleotides, which are the monomers of RNA and a requirement for abiogenesis in the RNA world hypothesis (Higgs & Lehman, 2015). S[IV] can stabilize and concentrate simple sugars, providing the carbohydrate backbone for ribonucleotides (Pitsch et al., 2000; Kawai et al., 2019; Benner et al., 2019). Under irradiation, S[IV] releases solvated electrons, which enable high-yield syntheses of organics from CO<sub>2</sub> (Liu et al., 2021) as well as HCN photohomologation towards the synthesis of nucleotides, ribonucleotides and other biomolecules (J. Xu et al., 2018, 2020). Perhaps most dramatically, S[IV] underlies the only currently known pathway for the non-enzymatic synthesis of all four canonical ribonucleotides, a decades-old goal of synthetic prebiotic chemistry (Becker et al., 2019; Hud & Fialho, 2019).

S[IV] also plays an important role in planetary habitability, through regulation of atmospheric SO<sub>2</sub>. If oceanic S[IV] is sub-saturated with respect to the atmosphere, then SO<sub>2</sub> efficiently deposits into the ocean by both wet and dry deposition, and atmospheric SO<sub>2</sub> concentrations are low (Kasting et al., 1989; Hu et al., 2013). However, if S[IV] can



**Figure 2.** Schematic showing how the modeling and experimental work presented in this paper fit together. The core of the work is the novel 0D S[IV] aqueous photochemistry box model, from which our scientific conclusions are obtained. The purpose of our laboratory experiments and atmospheric photochemical modeling is to set input parameters for the aqueous photochemistry box model. The box model is then used to estimate [S[IV]] in marine and terrestrial natural waters on prebiotic Earth, and then implications for prebiotic chemistry and planetary habitability are evaluated.

ever saturate the planet surface, then the depositional sink of atmospheric SO<sub>2</sub> is suppressed, and SO<sub>2</sub> can accumulate in the atmosphere and be photochemically processed into H<sub>2</sub>SO<sub>4</sub> or S<sub>8</sub> aerosol hazes, with significant implications for planetary habitability. For example, sulfur haze layers can block UV light from reaching the surface of the planet, as on Venus. Kasting et al. (1989) show that if early Earth featured elevated temperatures and a S[IV]-saturated surface, then an S<sub>8</sub> haze would have formed, blocking UV light from reaching the planetary surface. Elevated atmospheric SO<sub>2</sub> would also influence planetary climate, but it is uncertain whether it would warm or cool the planet. While elevated SO<sub>2</sub> would power an enhanced greenhouse effect, this SO<sub>2</sub> would also generate photochemical hazes which would raise the planetary albedo and reflect more sunlight back into space. It remains debated whether enhanced SO<sub>2</sub> would result in net cooling or net heating (Tian et al., 2010; Halevy & Head, 2014).

## 2.2 Previous Modeling of S[IV] in Natural Waters

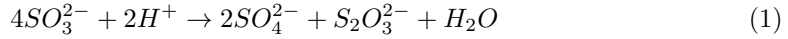
Past consideration of S[IV] in natural waters on anoxic early Earth and similar planets has focused on marine waters. Walker and Brimblecombe (1985) muse on thermodynamic grounds that the eventual fate of S[IV] would have been oxidation to sulfate, but do not attempt estimates of its concentrations. Kasting et al. (1989) explore the possibility of an early ocean saturated in S[IV] ([S[IV]] = 1.5 mM), and show that this condition might enable a UV-blocking S<sub>8</sub> haze layer on early Earth. Later works extend this possibility to early Mars, exploring implications of a S[IV]-saturated ocean on planetary climate (Halevy et al., 2007; Tian et al., 2010). These works justify S[IV]-saturated oceans by the expected suppression of S[IV] disproportionation based on reaction stoichiometry. On the other hand, Loftus et al. (2019) assume sub-saturated oceanic S[IV] for anoxic Earth-like planets, and Halevy (2013) calculate sub-nanomolar marine [S[IV]] for early Earth, based on the finding of Guekezi et al. (1997) of efficient room-temperature disproportionation of S[IV]. Assumptions regarding S[IV] disproportionation kinetics control the different [S[IV]] in these works.

Consideration of S[IV] in terrestrial waters is more limited. Recent phylogenetic evidence for ancient, exclusively sulfite-reducing metabolism in volcanic hot springs is consistent with the existence of sulfite-rich waters in volcanic environments on early Earth,

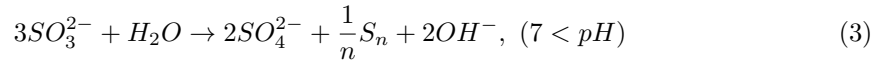
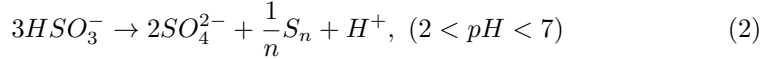
but does not constrain the presence of S[IV] in non-volcanic environments (Colman et al., 2020; Chernyh et al., 2020). Ranjan et al. (2018) find that shallow terrestrial waters on early Earth should sustain  $\geq 1 \mu\text{M}$  S[IV] concentrations, derived from dissolution of volcanogenic  $\text{SO}_2$ . However, their calculations followed previous literature in considering only thermal loss processes for S[IV], and neglected loss of S[IV] by photolysis. In this work, we remediate this omission.

### 2.3 Kinetics of S[IV] Disproportionation

Until this work, S[IV] disproportionation has been considered as the main control on aqueous S[IV] accumulation in natural waters on anoxic early Earth and similar planets, and its kinetics are proposed as the main uncertainty in model estimates of [S[IV]] (Kasting et al., 1989; Halevy et al., 2007; Halevy, 2013; Ranjan et al., 2018; Loftus et al., 2019). Aqueous S[IV] disproportionates according to the reaction (Guekezian et al., 1997):



However,  $\text{S}_2\text{O}_3^{2-}$  is itself unstable and further disproportionates. The net reaction proposed for fully equilibrated conditions (i.e. when the system has fully relaxed to its lowest-energy state) is (Meyer et al., 1982):



The kinetics of S[IV] disproportionation are extremely poorly constrained (Halevy et al., 2007; T. Xu et al., 2007). High-temperature studies find S[IV] disproportionation to be autocatalytic, with activation energies of  $E_A = 89 \text{ kJ/mol}$  ( $120 - 140^\circ\text{C}$ , initial  $\text{pH} = 0.6 - 1$ , Ryabinina and Oshman (1972)) and  $E_A = 69 \text{ kJ/mol}$  ( $110 - 180^\circ\text{C}$ ,  $\text{pH} = 2 - 5$ , Rempel et al. (1974); T. Xu et al. (2007)). The nature and accuracy of the analytical techniques employed by Ryabinina and Oshman (1972) are not detailed, nor is it clear how rigorously  $\text{O}_2$  was excluded, making it challenging to assess the reliability of these measurements. Furthermore, Halevy et al. (2007) caution against extrapolating these measurements to cooler temperatures relevant to habitable worlds because entirely different reaction mechanisms may apply at lower temperatures, and indeed Meyer et al. (1982) report the reaction rate at  $120^\circ\text{C}$  to be higher than expected compared to extrapolations from experiments conducted at  $180^\circ\text{C}$ .

If S[IV] disproportionation is poorly constrained at high temperature, it is downright contradictory at low temperatures (Table 1). Most literature studies report non-detections of S[IV] disproportionation at low temperatures, with lower limits on the room-temperature lifetime of anoxic S[IV] solutions ranging from  $> 4$  months to  $\geq 5$  years (Cohen et al., 1982; Meyer et al., 1979; Meyer et al., 1982; Petruševski et al., 2013; Halevy et al., 2007). On the other hand, Guekezian et al. (1997) reported disproportionation of room-temperature S[IV] on a timescale of 10 days. Guekezian et al. (1997) do not comment on their disagreement with prior work. A possible explanation is that Guekezian et al. (1997) worked at ultrabasic conditions ( $\text{pH} > 12.8$ ); perhaps these conditions facilitated S[IV] disproportionation. However, it is unclear whether high pH should facilitate S[IV] disproportionation, since from Equations 1-3, we would expect high pH to inhibit S[IV] disproportionation, since S[IV] disproportionation consumes  $\text{H}^+$ . Indeed,  $\text{HSO}_3^-$  is reported to be less stable than  $\text{SO}_3^{2-}$ , in accordance with stoichiometric expectation (Searcy, 1981).

The stability of S[IV] in food storage applications (e.g., wine) is not relevant to early Earth. The stability of S[IV] in food storage is due to its stabilization by a range of or-



**Table 1.** Estimates of Sulfite Disproportionation Kinetics

Study	$T_{disp,0}$	$[S[IV]]_0$ (M)
Meyer et al. (1979)	> 5 year	$\sim 0.01 - 1^a$
Meyer et al. (1982)	> 1 year	$\sim 0.01 - 1^a$
Guekezian et al. (1997)	10 days	0.09
Petruševski et al. (2013)	> 7 months	3.4

<sup>a</sup>  $[S[IV]]_0$  not stated. Lower limit based on limits of analytics (Meyer, Ospina, & Peter, 1980). Upper limit based on associated Lawrence Berkeley National Laboratory annual reports (Shirley, 1980; Searcy, 1981).

ganic molecules including alcohols and formaldehyde (Zoecklein et al., 1999; de Carvalho & Schwedt, 2000). It is not known whether such organic molecules could have abiotically accumulated in prebiotic natural waters to concentrations high enough to stabilize S[IV], and we therefore neglect this stabilization mechanism.

We conclude that the literature is highly inconsistent (> 2 orders of magnitude) regarding lifetime of S[IV] to disproportionation at temperate conditions. This conclusion motivates experiments to provide better constraints on S[IV] disproportionation rates and lifetimes under the temperate, anoxic conditions relevant to early Earth (Krissansen-Totton et al., 2018), which we have conducted in this work.

## 2.4 S[IV] Photolysis

While past work has focused on disproportionation (Kasting et al., 1989; Halevy et al., 2007; Halevy, 2013; Loftus et al., 2019), there are other loss mechanisms for aqueous S[IV] relevant to anoxic terrestrial planets. In particular,  $SO_3^{2-}$  and  $HSO_3^-$  are efficiently photolyzed by UV-C radiation, and such radiation was abundant on early Earth and Mars (Fischer & Warneck, 1996; Cockell, 2000a). UV photolysis was earlier demonstrated to limit the accumulation of abiotic  $NO_X^-$  (nitrate, nitrite) in natural waters on early Earth and Mars (Ranjan et al., 2019; Adams et al., 2021). In this paper, we consider whether photolysis could have similarly limited the accumulation of S[IV] in natural waters on early Earth.

S[IV] photolysis is studied in the environmental science literature in the context of wastewater treatment, wherein the solvated electrons produced by S[IV] photolysis are used to destroy contaminants (Yang et al., 2020; Wu et al., 2021; Cao et al., 2021). The reaction mechanism is (Fischer & Warneck, 1996):



The ultimate product of S[IV] photolysis is sulfate (S[VI]; Huang et al. (2010)).  $SO_3^{2-}$  UV absorbance has been detected to wavelengths as long as 273 nm, but  $SO_3^{2-}$  photolyzes most efficiently at shorter wavelengths ( $\leq 256$  nm). Similarly,  $HSO_3^-$  absorption has been detected out to 320 nm, but this longwave absorption is weak and its photolysis is most efficient at  $\leq 224$  nm (Fischer & Warneck, 1996; Beyad et al., 2014). UV radiation at these wavelengths is absent on modern Earth's surface due to atmospheric oxygen and ozone, but was abundant on early Earth and early Mars (Cockell et al., 2000; Cockell, 2002; Ranjan & Sasselov, 2017; Ranjan et al., 2017).



### 3 Methods

The basic goal of this paper is to calculate the steady-state global-mean concentrations of S[IV] in diverse aqueous systems on early Earth's surface. We do so by implementing a novel 0D box model, which balances the sources ( $F_{sources,S[IV]}$ ) and sinks ( $F_{sinks,S[IV]}$ ) of S[IV]:

$$F_{sources,S[IV]} = F_{sinks,S[IV]} \quad (6)$$

Such box models have been extensively used to estimate solute concentrations in aqueous systems on early Earth and Mars (Kharecha et al., 2005; Halevy, 2013; Harman et al., 2013; Wong et al., 2017; Ranjan et al., 2019; Adams et al., 2021).

We consider the atmosphere as the source of S[IV], via wet and dry deposition of SO<sub>2</sub>:

$$F_{sources,S[IV]} = F_{wet,S[IV]} + F_{dry,S[IV]} \quad (7)$$

We apply an existing atmospheric photochemical model to estimate  $F_{wet,S[IV]}$  and  $F_{dry,S[IV]}$  as inputs into the box model (Section 3.1, SI S2).

We consider both thermal (disproportionation, direct oxidation by O<sub>2</sub>, seepage into sediments) and photolytic (UV photolysis) loss processes for S[IV] (Section 3.2, SI S3):

$$F_{sinks,S[IV]} = F_{disprop,S[IV]} + F_{O_2,S[IV]} + F_{seep,S[IV]} + F_{h\nu,S[IV]} \quad (8)$$

The consideration of the photolytic sink on S[IV] is novel to this work.

Combining Equations 6-8, we calculate the steady-state [S[IV]], by numerically solving:

$$F_{wet,S[IV]} + F_{dry,S[IV]} = F_{disprop,S[IV]} + F_{O_2,S[IV]} + F_{seep,S[IV]} + F_{h\nu,S[IV]} \quad (9)$$

for various terrestrial waters on prebiotic Earth, using parameters as detailed in Section 3.3. Reports of the kinetics of room-temperature S[IV] disproportionation are contradictory in the literature; we conduct experiments to rule between the literature possibilities (Section 3.4, SI S1).

#### 3.1 Sources of S[IV]: Atmospheric Supply Mechanisms

We model the atmosphere of early Earth and its interaction with the surface to estimate the supply of S[IV] to prebiotic natural waters ( $F_{sources,S[IV]}$ ). As we focus on global-mean conditions, we consider the atmosphere as the sole source of S[IV]. We neglect the possibility of aqueous-phase production of S[IV] due to processes like S<sup>0</sup> photooxidation or polythionate disproportionation, which require substrates not known to be generally abundant on early Earth, but which may be relevant in specific terrestrial waters like hot springs (Johnston & McAmish, 1973; Li et al., 2020).

##### 3.1.1 Atmospheric Photochemical Modeling

We use the MIT Exoplanet Atmospheric Chemistry Model (MEAC; Hu et al. (2012, 2013)) to calculate the steady-state atmospheric composition of early Earth as a function of volcanic outgassing flux. MEAC has previously been used to study abiotic planets under forcing from high volcanic outgassing (Hu et al., 2013) and has recently been intercompared with two other widely-used models (Harman et al., 2015; G. Arney et al., 2016) for the case of prebiotic Earth-like planets, making it an appropriate tool for this study.

Full details of our deployment of this model, including detailed rationale of planetary scenario, parameter choices, and boundary conditions, are presented in the SI (S2,

Tables S2-S3, Figures S8-S9). Here we summarize the most important aspects: We assume a bulk atmospheric composition of 0.1 bar CO<sub>2</sub> and 0.9 bar N<sub>2</sub> and a surface temperature of 290 K, consistent with available constraints and past modeling of the prebiotic atmosphere (Rugheimer & Kaltenegger, 2018). We assume top-of-atmosphere (TOA) solar irradiation from Claire et al. (2012), and Eddy diffusion scaled from modern Earth’s by mean molecular mass. We include CO and NO fluxes at the base of the atmosphere to simulate the effects of lightning (Harman, Felton, et al., 2018). We allowed for the formation of S<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> aerosols in our model, assumed to have a mean particle diameter of 0.1 μm (Hu et al., 2013). We include volcanic outgassing in our model by scaling modern Earth volcanic emission fluxes of H<sub>2</sub>, SO<sub>2</sub>, CO, H<sub>2</sub>S and CH<sub>4</sub> by a factor  $\frac{\phi}{\phi_0}$ , where  $\phi_0$  is the volcanic outgassing flux on modern Earth and  $\phi$  is the volcanic outgassing flux in the model. We explore a broad range of volcanic outgassing levels  $\frac{\phi}{\phi_0} = 0.1 - 30$  to reflect the uncertainty on prebiotic Earth volcanism levels. Of these parameters, our modeling is most sensitive to the SO<sub>2</sub> outgassing flux  $\phi_{SO_2}$ , since over the parameter space we consider here we find that outgassed SO<sub>2</sub> is primarily removed from the atmosphere by wet and dry deposition, insensitive to the details of the photochemical scheme (Section 4.2)

### 3.1.2 Dry Deposition of S[IV]

S[IV] is transferred from the atmosphere to the surface via dry deposition of SO<sub>2</sub> (Kharecha et al., 2005). Dry deposition refers to direct transfer of a gas from the atmosphere to the surface, without the mediation of rain (wet deposition). Dry deposition occurs over surfaces of all types, including aqueous bodies (Sehmel, 1980). Dry deposition is the dominant removal mechanism for SO<sub>2</sub> for a wide range of atmospheric compositions (Hu et al., 2013; Seinfeld & Pandis, 2016). We calculate dry deposition of SO<sub>2</sub> via (Seinfeld & Pandis, 2016):

$$F_{dry,S[IV]} = v_{dep,SO_2} r_{SO_2}(z=0) n_{atm}(z=0) \quad (10)$$

where  $v_{dep,SO_2}$  is the dry deposition velocity of SO<sub>2</sub>,  $n_{atm}(z=0)$  is the atmospheric number density at the surface, and  $r_{SO_2}(z=0)$  is the volume mixing ratio of SO<sub>2</sub> at the surface.

### 3.1.3 Wet Deposition of S[IV]

SO<sub>2</sub> can be transferred from the atmosphere to the surface by precipitation (“wet deposition”). This process is an important secondary removal mechanism for SO<sub>2</sub> from the modern atmosphere (Seinfeld & Pandis, 2016). We calculate atmospheric supply of S[IV] to natural waters by wet deposition of SO<sub>2</sub> according to the equation:

$$F_{wet,S[IV]} = \phi_{SO_2,wet,model} \times \frac{P}{P_{model}} \quad (11)$$

where  $P$  is the precipitation rate (m year<sup>-1</sup>),  $P_{model}$  is the global mean precipitation rate calculated by MEAC assuming a modern Earth-like rainout frequency, and  $\phi_{SO_2,wet}$  is the global mean wet deposition rate of SO<sub>2</sub> calculated by MEAC (Giorgi & Chameides, 1985; Hu et al., 2012). For our temperature-pressure profile,  $P_{model} = 0.9$  m year<sup>-1</sup>, comparable to the modern global-mean precipitation rate of 1 m year<sup>-1</sup> (Giorgi & Chameides, 1985).  $P$  is a semi-free parameter, because terrestrial waters can integrate runoff from a catchment area, which may be many times their surface area (Davies et al., 2008). Because we are conducting steady-state modeling, we set  $P$  to balance losses due to evaporation and seepage, according to the equation:

$$P = S + E \quad (12)$$

where  $E$  is the evaporation rate and  $S$  is the seepage rate (Section 3.2.2).

## 3.2 Sinks of S[IV]: Thermal and Photolytic Loss Mechanisms

### 3.2.1 Disproportionation

The extreme uncertainties in the kinetics of S[IV] disproportionation (Section 2.3) motivate a simplistic, cautious implementation in our model. Past implementations of S[IV] disproportionation have modeled it as first order (Halevy, 2013). However, because disproportionation requires multiple S[IV] molecules, it is possible that the reaction is higher-order. Indeed, based on the stoichiometry the naive assumption would be that the reaction would be fourth-order, and thereby highly suppressed at low concentrations. We therefore implement a generalized rate law for S[IV] disproportionation. Assuming S[IV] disproportionation to be order  $n$ :

$$\frac{d[S[IV]]}{dt} = -k_{disp,n}[S[IV]]^n \quad (13)$$

where  $k_{disp,n}$  is the rate constant for S[IV] disproportionation ( $M^{1-n} s^{-1}$ ).

We build our modeling approach around  $T_{disp,0}$ , the S[IV] lifetime to disproportionation for a sample with initial S[IV] concentration  $[S[IV]]_0$ . We define  $T_{disp,0}$  as:

$$T_{disp,0} \frac{d[S[IV]]}{dt}(t=0) + [S[IV]]_0 = 0 \quad (14)$$

$$(15)$$

We build our modeling approach around  $T_{disp,0}$  because this is the parameter which is constrained by literature sources. Specifically, except for Guekezian et al. (1997), literature sources only report timescales over which S[IV] disproportionation was not detected (Meyer et al., 1979; Meyer et al., 1982; Halevy et al., 2007; Petruševski et al., 2013). We use these timescales as lower limits on  $T_{disp,0}$ . We then use  $T_{disp,0}$  to estimate  $k_{disp}$ :

$$k_{disp,n} = T_{disp,0}^{-1} [S[IV]]_0^{1-n} \quad (16)$$

We summarize literature constraints on  $T_{disp,0}$  for different  $[S[IV]]_0$  in Table 1. Values for  $T_{disp,0}$  in the literature range fall into two broad ranges:  $T_{disp,0} \gtrsim 1$  year, and  $T_{disp,0} = 10$  days. We conduct experiments to discriminate between these two possibilities, and use the results in our model (Section 4.1).

Finally, we compute the flux of S[IV] loss by disproportionation integrated through the full water column:

$$F_{disprop,S[IV]} = \int_0^{d_{body}} dy (k_{disp,n} [S[IV]]^n) = d_{body} (k_{disp,n} [S[IV]]^n) \quad (17)$$

where  $d_{body}$  is the depth of the water column (cm).

### 3.2.2 Seepage

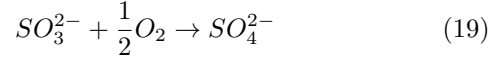
If the base of an aqueous body is not saturated with water, then water will seep out of this body, carrying with it S[IV]. Seepage can limit the concentration of solutes in lakes (Wood & Sanford, 1990; Rosen, 1994; Pearce et al., 2017). We calculate the rate of this process according to the equation (Pearce et al., 2017):

$$F_{seepage,S[IV]} = [S[IV]]S \quad (18)$$

where  $S$  is the seepage rate ( $m \text{ year}^{-1}$ ). A wide range of  $S$  is possible depending on permeability and hydraulic gradient, and we explore the range  $S = 0 - 2 \text{ m/year}$  (Toner & Catling, 2019; Steinman et al., 2010) spanning the range expected for closed-basin ponds following detailed rationale in SI S3.1.

### 3.2.3 Direct Oxidation

We follow Halevy (2013) in using the rate law of Zhang and Millero (1991) for the rate of oxidation of S[IV] by  $O_2$ :



$$\frac{d[S[IV]]}{dt} = -k[S[IV]]^2[O_2]^{0.5} = -k''[HSO_3^-][SO_3^{2-}][O_2]^{0.5} \quad (20)$$

where  $k$  ( $M^{-1.5} \text{ min}^{-1}$ ) and  $k''$  ( $M^{-1.5} \text{ min}^{-1}$ ) are rate constants. We calculate  $k''$  from the expression for  $k$  from Zhang and Millero (1991) (see SI S3.2.1 for detailed calculation). We estimate  $[O_2]$  using Henry's Law:

$$[O_2] = H_{O_2}pO_2(z = 0) \quad (21)$$

where  $H_{O_2}$  is the Henry's Law constant for  $O_2$  (Sander et al., 2011; Sander, 2015) and  $pO_2$  is the partial pressure of  $O_2$ , obtained from our atmospheric photochemistry model (SI S3.2.2).

With the rate law in hand, we compute the flux of S[IV] loss due to direct oxidation integrated through the full water column:

$$F_{O_2, S[IV]} = \int_0^{d_{body}} dy (k''[HSO_3^-][SO_3^{2-}][O_2]^{0.5}) = d_{body}(k''[HSO_3^-][SO_3^{2-}][O_2]^{0.5}) \quad (22)$$

### 3.2.4 Photolysis

Measured S[IV] photolysis rates in natural waters on modern Earth are unavailable, because S[IV] is absent from natural waters on modern Earth due to the oxic atmosphere (Loftus et al., 2019). However, S[IV] photolysis has been studied in laboratory settings, both for its fundamental photophysics, as well as for its applications to wastewater treatment (Fischer & Warneck, 1996; Sauer, Crowell, & Shkrob, 2004; Wu et al., 2021). We utilize these laboratory measurements to estimate the S[IV] photolysis rates in natural waters on prebiotic Earth.

We calculate the photolysis rate coefficient for loss of species  $X$ ,  $J_X(d)$  ( $s^{-1}$ ), at depth  $d$  according to the equation:

$$J_{SO_3^{2-}}(d) = \int d\lambda \Phi_{SO_3^{2-}}(\lambda) \sigma_{SO_3^{2-}}(\lambda) \dot{E}(\lambda, d) \quad (23)$$

$$J_{HSO_3^-}(d) = \int d\lambda \Phi_{HSO_3^-}(\lambda) \sigma_{HSO_3^-}(\lambda) \dot{E}(\lambda, d) \quad (24)$$

where  $\Phi_{SO_3^{2-}}(\lambda)$  is the quantum efficiency of net loss of  $SO_3^{2-}$  due to photolysis,  $\Phi_{HSO_3^-}(\lambda)$  is the quantum efficiency of net loss of  $HSO_3^-$  due to photolysis,  $\sigma_{SO_3^{2-}}$  ( $\text{cm}^2$ ) is the absorption cross-section of  $SO_3^{2-}$ ,  $\sigma_{HSO_3^-}$  ( $\text{cm}^2$ ) is the absorption cross-section of  $HSO_3^-$ ,  $\dot{E}(\lambda, d)$  ( $\text{cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ ) is the scalar irradiance as a function of wavelength ( $\lambda$ ) and depth ( $d$ ).

We take  $\sigma_{SO_3^{2-}}(\lambda)$  and  $\sigma_{HSO_3^-}(\lambda)$  from Fischer and Warneck (1996) and Beyad et al. (2014), as synthesized by Ranjan, Kufner, et al. (2022). We approximate  $\Phi_{SO_3^{2-}}(\lambda)$  and  $\Phi_{HSO_3^-}(\lambda)$  as piecewise-linear functions anchored by available measurements of  $\Phi_{SO_3^{2-}}$  at specific wavelengths (SI S3.3.1, Table S7, Figure S15). An important uncertainty here is  $\Phi(> 254 \text{ nm})$ , which is unconstrained; we explore limiting endmembers of  $\Phi(> 254 \text{ nm}) =$

$\Phi(254 \text{ nm})$  and  $\Phi(> 254 \text{ nm}) = 0$ , spanning the possibilities. We compute  $\dot{E}(\lambda, d)$  following the treatment of Morel (1991), which was originally developed to treat photosynthetically active radiation in the modern ocean. To do so, we use surface UV flux at the bottom of the atmosphere from Rugheimer et al. (2015), aqueous absorption due to inorganic geogenic solutes from Ranjan, Kufner, et al. (2022), and aqueous scattering due to inorganic geogenic solutes from Smith and Baker (1981). Further details of the calculation of the photolysis rate coefficient are given in SI S3.3.

We then calculate the column-integrated photolysis flux of S[IV] by integrating and adding the depth-dependent photolysis rate of bisulfite and sulfite:

$$F_{h\nu, S[IV]} = \int dy J_{SO_3^{2-}}(y) C_{SO_3^{2-}}(y) + \int dy J_{HSO_3^-}(y) C_{HSO_3^-}(y) \quad (25)$$

where  $C_X$  is the concentration of species  $X$ , assumed to be well-mixed (constant with depth) in our 0D box model.

### 3.3 Geological Scenario and Parameter Choices

The geochemical properties of prebiotic natural waters are uncertain. To reflect this uncertainty in our estimates of prebiotic S[IV], we construct S[IV] minimizing and maximizing endmember scenarios based on estimates of relevant geochemical parameters in the literature. This approach is purely parametric, and not self-consistent (i.e. we are merely choosing extreme values from the literature to get a sense of the uncertainty on S[IV], not conducting self-consistent modeling of a specific scenario). The geochemical parameters we consider are pH, for which high pH corresponds to less S[IV] because of speciation as  $SO_3^{2-}$ , which is more vulnerable to photolysis; background absorptivity, for which lower absorptivity corresponds to less S[IV], because of more efficient photolysis due to less efficient UV attenuation; and  $I$ , for which higher  $I$  corresponds to less S[IV] due to more efficient direct oxidation. The endmember scenarios for the prebiotic ocean are given in Table 2, with detailed rationale presented in SI S3.5.

In calculating terrestrial S[IV], we focus on shallow closed-basin waters, which are particularly invoked in proposed prebiotic chemistry because of their potential for wet-dry cycling, their propensity to accumulate key prebiotic reagents, and their favorable physicochemical conditions (Patel et al., 2015; Becker et al., 2018; Ranjan et al., 2019; Sahai et al., 2022; Benner, 2023). We specifically focus on freshwater (Damer & Deamer, 2020) and carbonate lakes (Toner & Catling, 2020; Sahai et al., 2022). The endmember scenarios for prebiotic closed-basin freshwater and carbonate lakes are presented in Table 3, with detailed rationale presented in SI S3.5. While we simulate only two types of prebiotic terrestrial waters in detail, our methods and open-source code can be readily adapted to other natural waters. Further, we expect our basic closed-basin results to generalize to diverse closed-basin terrestrial waters (e.g., Sahai et al. (2022)) because the same basic supply and loss processes apply.

### 3.4 Experimental Constraints on S[IV] Disproportionation Kinetics

Literature estimates of the lifetime of aqueous anoxic S[IV] near standard temperature and pressure are contradictory and fall into two time ranges:  $\sim 10$  days and  $\gtrsim 1$ –5 years (Section 2.3). We conducted experiments to discriminate between these two possibilities.

We prepared solutions of  $Na_2SO_3$  in anoxic conditions at varying concentration and pH (Table 4), and sealed them into airtight cuvettes for aging (Section 3.4.1). The reaction stoichiometry (Equations 1-3) means that S[IV] disproportionation may scale up to quartically with concentration (if the redox step is rate-limiting). Consequently, we chose a high baseline initial S[IV] concentration of 100 mM, to maximize the rate of S[IV]

**Table 2.** Extremal geochemical parameters assumed in estimating [S(IV)] in marine waters on early Earth. Parameters are categorized by whether they maximize or minimize [S(IV)], thus enabling a measure of the uncertainty. Note that this approach is purely parametric, and is not self-consistent. In simulating marine waters, we set  $S = 0 \text{ m year}^{-1}$  and  $P = P_{model}$ , and take  $d = 3.8 \times 10^5 \text{ cm}$ , corresponding to the modern ocean (Rumble, 2017).

Parameter	[S(IV)]- minimizing	[S(IV)]- maximizing	Comment
pH	9.0	6.25	(Krissansen-Totton et al., 2018; Kadoya et al., 2020)
$a(\lambda) \text{ (cm}^{-1}\text{)}$	Ocean, low- $a$ endmember	Ocean, high- $a$ end- member	(Ranjan, Kufner, et al., 2022) (S(IV) removed)
$I \text{ (M)}$	0.72	0.3	(Knauth, 2005; Marty et al., 2018)

**Table 3.** Extremal geochemical parameters assumed in estimating [S(IV)] in closed-basin terrestrial waters on early Earth. Parameters are categorized by whether they maximize or minimize [S(IV)], thus enabling a measure of the uncertainty. Note that this approach is purely parametric, and is not self-consistent. We simulate lakes with  $d = 1 \text{ m}$ .

Parameter	[S(IV)]- minimizing	[S(IV)]- maximizing	Comment
<u>Carbonate Lake</u>			
pH	9.0	6.5	(Toner & Catling, 2020)
$I \text{ (M)}$	0.72	0.1	(Toner & Catling, 2020)
$a(\lambda) \text{ (cm}^{-1}\text{)}$	Carb. Lake, low- $a$ end- member	Carb. Lake, high- $a$ end- member	(Ranjan, Kufner, et al., 2022) (S(IV) removed)
$S \text{ (m yr}^{-1}\text{)}$	0	2	
<u>Freshwater Lake</u>			
pH	6.34	6.34	(Hao et al., 2017)
$I \text{ (M)}$	0.001	0.001	(Lerman et al., 1995; Hao et al., 2017)
$a(\lambda) \text{ (cm}^{-1}\text{)}$	Fresh. Lake, low- $a$ end- member	Fresh. Lake, high- $a$ end- member	(Ranjan, Kufner, et al., 2022) (S(IV) removed)
$S \text{ (m yr}^{-1}\text{)}$	0	2	

disproportionation and facilitate analytics. We considered solutions with unadjusted pH, and pH adjusted to 7 and 13, to explore the effect of pH. We also considered an unadjusted solution at a lower S(IV) concentration of 10 mM. We did not consider S(IV) concentrations higher than 100 mM to avoid formation of disulfite (Beyad et al., 2014). We experimented with S(IV) solutions at acidic pH and in complex solutions more representative of realistic prebiotic lakes, but our analytics failed for these cases and we are unable to report robust results (SI S1.3).

After 10.5 months, we opened the cuvettes and quantified the remaining S(IV) in the aged solutions via electropotentiometry (Section 3.4.2) and the amount of sulfate (S(VI)) in the aged solutions via gravimetry (Section 3.4.3). We separately characterized both S(IV) and sulfate to check our results for consistency (e.g. mass conservation). We also monitored the solutions with non-invasive UV-Vis spectroscopy, as additional corrob-

**Table 4.** S[IV] Samples Prepared for Disproportionation Study

$[\text{Na}_2\text{SO}_3]_0^a$ (mM)	$\text{pH}_0^a$	$\lambda_m$ (nm)	$N_{\text{samp}}$	Start	Solution Analytics Date	UV-Vis Through Date
100	7	260	4	10/05/21	8/20/22	8/8/22
100	13	260	4	10/05/21	8/20/22	8/8/22
100	Unadjusted	260	3 <sup>b</sup>	10/05/21	8/20/22	8/8/22
10	Unadjusted	240	4	10/05/21	8/20/22	8/8/22

<sup>a</sup>At study start.<sup>b</sup>1 sample accidentally destroyed during study.

oration (Section 3.4.5). Our results are described in Section 4.1, and raw data under-  
lying both sets of measurements are presented in the SI and Supplemental Data Set S1.

### 3.4.1 Solution Preparation and Storage

All salts were purchased from Sigma-Aldrich (USA) at the highest available pu-  
rity grade and used without further purification. All samples were dissolved anoxically  
in LC-MS grade freshwater (LiChrosolv, Millipore Sigma, USA). The water used to dis-  
solved the salts was degassed for 30 minutes inside of a glovebox (7150000 Anaerobic Cham-  
ber, Type A, Coy Lab Products) with atmospheric O<sub>2</sub> levels ranging from 30ppm (steady-  
state) to 200ppm (after the box was opened/closed). While this glovebox is nominally  
specified to achieve 0-5 ppm O<sub>2</sub> concentrations, in practice we found that on average 30  
ppm O<sub>2</sub> were our long-term conditions inside the box. The pH was adjusted utilizing a  
1 molar NaOH solution and a 6 molar HCL solution. MQuant® pH-Indicator Strips were  
used to monitor the pH of the solution as it was being adjusted.

The dissolved samples were kept in sealable spectrosil quartz cuvettes (1-Q-10-GL14-  
C, Starna Cell's, USA) with a sample depth of 10 mm. The volume per cuvette was 4  
mL. The cuvettes were cleaned solely with LS-MS grade water; we did not clean with  
acetone as we discovered in preliminary experiments that absorptivity due to residual  
acetone contaminated UV-Vis measurements. All samples were kept at 23°C. All sam-  
ple cuvettes were kept in a covered box to minimize long-term exposure to light, inside  
the glovebox. One sample (100 mM unadjusted pH, sample #1) was accidentally dropped  
and destroyed during the course of the study, and consequently we do not report results  
for it. Another sample (10 mM unadjusted, sample #2) showed pH much smaller than  
the other samples in its experimental condition at the conclusion of the study, which we  
interpret as evidence of experimental error; we therefore do not report results for this  
sample, though we discuss it in SI 1.3.3 for completeness.

### 3.4.2 S[IV] electropotentiometry

We measured [S[IV]] via electropotentiometry, which directly measures ion concen-  
trations by measuring the electrical potential across an ion-selective membrane (Sohail  
& De Marco, 2013). We fabricated a bisulfite-potentiometric Ion-Selective Electrode (ISE)  
(Kuratli & Pretsch, 1994). We calibrated the sensor in a neutral and alkaline background  
solution of NaOH/H<sub>2</sub>O to match the pH of each sample. We have used these calibra-  
tion curves of the ISE to convert the measured emf (electromotive force) values to the  
concentrations of S[IV] in the measured samples (SI Supplemental Data).

**3.4.2.1 Materials** Tridodecylmethylammonium chloride (TDMACl), bis(ethylhexyl)  
sebacate (DOS), high molecular-weight poly(vinylchloride) (PVC), tetrahydrofuran (THF,  
inhibitor-free, for HPLC), hydrogen sulfite ionophore (Octadecyl 4-formylbenzoate), ni-



trophenyloctyl ether(NPOE, Selectophore grade) monohydrogen potassium phosphate, potassium chloride, sodium chloride, sodium hydroxide, sodium sulphate, barium chloride, sodium thiosulfate, potassium bicarbonate, barium chloride, and sodium phosphate were purchased from SigmaAldrich and used in the measurements described here and in the SI.

**3.4.2.2 Measurements and Equipment** We measured the response of the sensors using a 16-channel potentiometer (Lawson Labs) at room temperature against a free-flow double-junction AgCl/Ag reference electrode (with a movable glass sleeve junction, 1.0 M lithium acetate bridge electrolyte) purchased from Mettler Toledo. We performed the calibrations of  $\text{SO}_3^{2-}$  through performing successive dilutions of a 20 mL sample. Each 18 mL aliquot removed was replaced with the addition of 18 mL of sodium phosphate buffer (pH = 8.6), and the emf was measured for each dilution.

**3.4.2.3 Fabrication of Conventional Ion-Selective Electrodes** The membrane is composed of 660 mg of PVC, 1320 mg of NPOE, and 10 mg of TDMACl. We dissolved these components in 8 mL of THF, stirred the mixture until a homogenous solution was achieved, poured the solution into a petri dish and left it covered overnight; this procedure allowed the THF to evaporate and formed the membrane that provided the ISE. Circular pieces of the membrane with a diameter of  $\sim 1.1$  cm and thickness of  $\sim 1.2$  mm were cut and placed onto PVC tubing, which was wet with THF (causing the membrane to be fused to the PVC tubing).

**3.4.2.4 Fabrication of bisulfite-selective electrode** We prepared the ion-selective membranes following established protocols presented in the literature. The  $\text{HSO}_3^-$  sensing membrane consisted of NPOE, hydrogen sulfite ionophore (1 wt %) and TDMACl (0.20 wt. %). We dissolved these components in 8 mL THF, stirred the mixture until a homogeneous solution was achieved, poured the solution into a petri dish and left it covered overnight; this procedure allowed the THF to evaporate and formed the membrane that provided the ion selective electrode (ISE). Circular pieces of the membrane with a diameter of 1.1 cm and thickness of 1.2 mm were cut and placed onto PVC tubing, which is wet with THF (causing the membrane to be fused to the PVC tubing). The PVC S3 tube was filled with 2 mL of an inner-filling solution consisting of 10 mM  $\text{SO}_3^-$  in phosphate buffer (pH 8.6) and 15 mM NaCl. The membrane was placed into a solution of 10 mM  $\text{SO}_3^{2-}$  for 3 hours before starting the sensor calibration, following the immersion of a Ag/AgCl wire into the inner-filling solution. This procedure allows  $\text{SO}_3^{2-}$  to replace the chloride ion associated with TDMA.

**3.4.2.5 Estimation of Errors** For each sample, we measured the emf three times with three different sensors. We report the concentration corresponding to the best-conditioned sensor, sensor #2, and estimate the uncertainty as the standard deviation on the three measurements collected by the three sensors. Calibration curves were obtained by serial dilution, and Nernstian response (Sohail & De Marco, 2013) was confirmed in the concentration range where samples were measured.

### 3.4.3 Sulfate Gravimetry with $\text{BaCl}_2$ and $\text{HCl}$

Sulfate is a main product of S[IV] disproportionation and is the sole product of direct S[IV] oxidation (Meyer et al., 1982; Guekezian et al., 1997). We quantified the amount of sulfate in the sample via the barium chloride gravimetric method for sulfate detection (Ferrús & Torrades, 1985). Sulfate precipitates as  $\text{BaSO}_4$  using  $\text{BaCl}_2$  in presence of 2 M  $\text{HCl}$  (n.b.  $\text{BaSO}_3$  is soluble under these conditions).

In our study, we followed a procedure similar to Ferrús and Torrades (1985). We combined 0.8 mL of sample with 2 mL of 2 M  $\text{HCl}$  and added hot ( $\sim 60^\circ \text{C}$ ) 1 M  $\text{BaCl}_2$  until precipitation went to completion. We boiled the solution for 3 minutes. We gath-

ered the precipitate with a rubber-tipped glass rod (“policeman”) onto filter paper. The resulting precipitate was then washed with H<sub>2</sub>O, filtered, dried, ignited apart from filter paper and weighed as BaSO<sub>4</sub>. We took three measurements from each aged sample; we report the mean, and use the standard deviation to estimate the error. Because this technique was destructive of the sample, it was the final test we conducted.

#### 3.4.4 Analytics Timescale

To minimize oxidation by ambient O<sub>2</sub>, we conducted our electropotentiometry and extraction of BaSO<sub>4</sub> precipitate in  $\leq 30$  min for each sample. The drying and weighing steps of the gravimetry take a further  $\sim 1$  day to complete. Additionally, the drying and weighing steps of the gravimetry were conducted some months after the precipitate extraction, due to experimenter constraints. BaSO<sub>4</sub>(s) is stable at standard conditions, so this does not affect the accuracy of our results.

#### 3.4.5 UV-Vis Monitoring

We non-invasively tracked the evolution of the UV-Vis absorption spectra of the samples. These data are corroborative but not on their own definitive, because the potential products of S[IV] disproportionation are themselves UV absorbers (Meyer et al., 1982; Guenther et al., 2001; Islam, 2008; Beyad et al., 2014). The UV-Vis monitoring is therefore secondary to the solution-phase analytics. All absorbance spectra were recorded by a Shimadzu UV-1900 UV-Vis spectrophotometer located outside of the glovebox once a week. Before each measurement, cuvettes were blown with dry air to remove any dust from the surface. A blank water spectrum was taken with each measurement in order to correct for cuvette errors. As a control, we exposed a sample of sulfite to ambient air overnight and verified loss of UV opacity as expected due to the rapid oxidation of UV-absorbing sulfite to UV-transparent sulfate (Beyad et al., 2014; Birkmann et al., 2018).

## 4 Results

In this section, we lay out our results. We begin by presenting our experimental constraints on S[IV] disproportionation kinetics (Section 4.1) and our atmospheric modeling of S[IV] supply to the surface (Section 4.2), which provide inputs to our aqueous photochemistry box model. We then apply the aqueous photochemistry box model to marine (Section 4.3) and terrestrial (Section 4.4) waters, using the parameters in Tables 2 and 3, respectively (Figure 2).

### 4.1 S[IV] Disproportionation Experiments & Implications for Modeling

Our experimental results are consistent with a long lifetime ( $T_{disp,0} \geq 1$  year) of anoxic S[IV] solutions (Table 5). This finding is valid at  $\text{pH} \geq 7$ , near standard temperature and pressure, and in the absence of catalysts and UV light. Our electropotentiometric measurements of S[IV] and gravimetric measurements of sulfate are consistent with mass conservation in every sample, and the long lifetimes inferred from the solution-phase analytics are consistent with the slow rate of change of UV absorbance measured by the UV-Vis tracking. The largest degree of S[IV] loss is seen in the 10 mM solutions, which show loss of 60-70% of S[IV] over 10.5 months (electropotentiometry). We use these measurements to estimate  $T_{disp,0}$  by

$$T_{disp,0} = \frac{[S[IV]]_0(T_f - T_0)}{([S[IV]]_0 - [S[IV]]_f)} \quad (26)$$

**Table 5.** Analytics of Aged S[IV] Samples

$[\text{Na}_2\text{SO}_3]_0^\dagger$ (mM)	$\text{pH}_0^\dagger$	Sample	$[\text{S[IV]}]_f^{\ddagger,a}$ (mM)	$[\text{SO}_4^{2-}]_f^{\ddagger,b}$ (mM)	$\lambda_m$ nm	$\frac{A_{\lambda_m,f}}{A_{\lambda_m,0}} \star$
100	7	1	$85 \pm 4$	$8.4 \pm 0.2$	260	$0.87 \pm 0.13$
100	7	2	$83 \pm 5$	$9.1 \pm 0.1$	260	$0.91 \pm 0.14$
100	7	3	$84 \pm 3$	$9.5 \pm 0.2$	260	$0.91 \pm 0.14$
100	7	4	$83 \pm 4$	$12.1 \pm 0.1$	260	$0.89 \pm 0.13$
100	Unadjusted	2 $\blacklozenge$	$84 \pm 3$	$9.5 \pm 0.3$	260	$0.85 \pm 0.13$
100	Unadjusted	3	$86 \pm 4$	$10.5 \pm 0.5$	260	$0.90 \pm 0.13$
100	Unadjusted	4	$81 \pm 2$	$10.6 \pm 0.3$	260	$0.87 \pm 0.13$
100	13	1	$83 \pm 3$	$9.7 \pm 0.4$	260	$0.87 \pm 0.13$
100	13	2	$84 \pm 2$	$11.7 \pm 0.5$	260	$0.84 \pm 0.13$
100	13	3	$83 \pm 3$	$11.0 \pm 0.5$	260	$0.89 \pm 0.13$
100	13	4	$81 \pm 3$	$12.6 \pm 0.5$	260	$0.89 \pm 0.13$
10	Unadjusted	1	$3.7 \pm 0.3$	$4.9 \pm 0.2$	240	$0.35 \pm 0.05$
10	Unadjusted	3 $\blacktriangle$	$3.1 \pm 0.3$	$5.7 \pm 0.2$	240	$0.33 \pm 0.05$
10	Unadjusted	4	$3.8 \pm 0.3$	$4.2 \pm 0.2$	240	$0.24 \pm 0.04$

 $^\dagger$ Sample preparation (10/5/2021) $^\ddagger$ Cuvettes opened 8/20/2022 $^a$ Electropotentiometry $^b$ Gravimetry $\star$ UV-Vis last day 8/8/2022 $\blacklozenge$  Sample #1 was accidentally destroyed during course of experiment $\blacktriangle$  Sample #2 appears to reflect experimenter error and is not reported (Section 3.4.1, SI 1.3.3)

where  $T_0$  is the time at experiment start,  $T_f$  is the time at experiment end, and  $[\text{S[IV]}]_0$  and  $[\text{S[IV]}]_f$  are the  $[\text{S[IV]}]$  at experiment start and end. Our measurements correspond to a S[IV] disproportionation lifetime of  $T_{\text{disp},0} \geq 1$  year.

However, 1 year may significantly underestimate  $T_{\text{disp},0}$ . The 100 mM S[IV] solutions uniformly show lower fractional loss than the 10 mM solution, corresponding to  $T_{\text{disp},0} = 4\text{--}5$  years. We are unaware of any rationale for higher concentrations of S[IV] to show slower disproportionation rates; indeed, the opposite is naively expected given the reaction stoichiometry (Equation 1). One possible explanation is that a substantial amount of S[IV] loss in our samples was due to direct oxidation caused by slow leakage of  $\text{O}_2$  into our cuvettes over the multi-month course of the experiments. Though we took care to minimize  $\text{O}_2$  leakage by utilizing airtight cuvettes and storing the cuvettes in an anaerobic glove box, complete exclusion of  $\text{O}_2$  was not possible in our setup. Our anaerobic glove box still maintained 30–200 ppm  $\text{O}_2$ , and the frictive seals of our nominally gas-tight cuvettes may still admit some degree of gas interchange on the long timescales of our experiment. In support of this hypothesis is the observation that the absolute concentration of sulfate in the aged 10 mM and 100 mM samples are similar to within  $\leq 3\times$ . Similar sulfate concentrations are consistent with a significant contribution of direct oxidation (which should be controlled by the rate of  $\text{O}_2$  leakage and insensitive to S[IV] concentration), but not an origin from S[IV] disproportionation (which should be sensitive to S[IV] concentration). In fact, the sulfate concentrations we measure are in 13/14 cases consistent within  $5\sigma$  of the amount of S[IV] lost. This means that in most of our samples we cannot rule out the possibility that all of the S[IV] lost from our samples was stoichiometrically converted to sulfate, as expected from direct oxidation but not disproportionation (SI S5, Table S8). Furthermore, there is a tentative positive correlation between sulfate concentration and sample number. Since our samples were an-

analyzed in sample number order, later sample numbers were present in ambient (oxic) air longer, and their slightly higher sulfate concentrations are consistent with direct oxidation during this period. Our samples may therefore reflect contributions from direct oxidation in addition to disproportionation and our results must therefore be considered lower bounds on  $T_{disp,0}$ . Finally, for our gravimetric analysis, the solution was acidified, which may increase disproportionation rates. Formally, this means that disproportionation rates inferred from our gravimetry may be overestimated; in practice, this effect is negligible, because our gravimetric measurements were conducted in  $< 1$  hour, while UV-Vis tracking suggests that the timescale for disproportionation is  $\geq 10$  days even in acidic conditions (SI S1.3.1, Figure S5). Additionally, our conclusions are robust to the possibility of increased disproportionation during acidification during gravimetry, because correcting for it can only strengthen our finding that  $T_{disp,0} \geq 1$  year. In summary, it is very possible that  $T_{disp,0} \gg 1$  year.

We cannot claim a definitive constraint on S[IV] disproportionation lifetime. For one, as discussed above, it is possible that the loss of S[IV] from our samples includes substantial contributions from non-disproportionation loss processes such as direct oxidation. More significantly, we are unable to explain why Guekezian et al. (1997) find such a short lifetime for S[IV]. The experiments of Guekezian et al. (1997) were conducted at ultrabasic pH ( $\text{pH} > 12.8$ ), and we hypothesized that perhaps basic conditions somehow contributed to faster S[IV] disproportionation. However, the samples of S[IV] that we adjusted to  $\text{pH}=13$  showed *slower* decay than the unadjusted S[IV] (Table 5), contradicting this hypothesis. We also considered the hypothesis that  $n < 0$ , which would explain the shorter S[IV] lifetime of Guekezian et al. (1997) ( $[S[IV]]_0 = 0.01\text{M}$ ) compared to the results at higher  $[S[IV]]_0$  (Meyer et al., 1979; Meyer et al., 1982; Petruševski et al., 2013) and would be an alternative explanation for the higher relative [S[IV]] loss in our 10 mM samples relative to our 100 mM samples. However, negative reaction kinetics are extremely rare, and are generally associated with heterogeneous reactions (e.g., due to competition for a fixed supply of reaction sites on a catalyst); no such mechanism applies here. Further, the S[IV] timecurve reported by Guekezian et al. (1997) does not show evidence of  $n < 0$ , and in fact shows some evidence of  $n > 0$ . Specifically, the timecurve is concave up, though whether this result is statistically significant is unclear because Guekezian et al. (1997) do not report measurement uncertainties. For these reasons,  $n < 0$  is not a viable hypothesis to reconcile Guekezian et al. (1997) with the rest of the literature. S[IV] disproportionation is sensitive to a wide range of catalysts and inhibitors, including to multivalent transition metal ions (Meyer, Mulliken, & Weeks, 1980b, 1980a; Meyer, 1980; Searcy, 1981; Meyer et al., 1982; Petruševski et al., 2013), and it is possible that a catalyst for S[IV] disproportionation was unknowingly present in the Guekezian et al. (1997) measurements. Efforts to contact the authors of Guekezian et al. (1997) to explore this possibility were unsuccessful, and it therefore remains speculation. These caveats mean that our data do not fully stand on their own as definitive estimates of  $T_{disp,0}$ .

However, our data do clearly favor one family of literature reports of anoxic S[IV] lifetime over the other, contradictory literature report. Specifically, even the fastest-decaying of our S[IV] samples shows S[IV] lifetimes  $\geq 1$  year, favoring the literature reports indicating long S[IV] lifetimes (Meyer et al., 1979; Meyer et al., 1982; Petruševski et al., 2013; Cohen et al., 1982; Halevy et al., 2007) over the literature report indicating short ( $\sim 10$  days) S[IV] lifetimes (Guekezian et al., 1997). In our modeling, we therefore do not adopt the lifetime measure of Guekezian et al. (1997). We instead consider  $T_{disp,0} \geq 1 - 5$  years (Meyer et al., 1979; Meyer et al., 1982), a range consistent with our work and that of others (Cohen et al., 1982; Halevy et al., 2007; Petruševski et al., 2013). The bracketing range of key chemical parameters we consider to account for uncertainties in disproportionation kinetics and photolysis quantum yields is summarized in Table 6.

**Table 6.** Ranges of chemical parameters considered in estimating [S[IV]] in natural waters on early Earth. Parameters are categorized by whether they maximize or minimize [S[IV]], thus enabling a measure of the uncertainty on this quantity. These ranges reflect intrinsic uncertainty regarding the chemical processes controlling [S[IV]] in temperate anoxic environments.

Parameter	[S[IV]]- minimizing	[S[IV]]- maximizing	Comment
$T_{disp,0}$ (years)	1 <sup>a</sup>	5 <sup>a</sup>	(Meyer et al., 1979; Meyer et al., 1982)
$[S[IV]]_0$ (M)	1	1	(Meyer et al., 1979; Meyer et al., 1982; Searcy, 1981)
$n$	1	4	Halevy (2013); reaction stoichiometry
$\Phi(> 253.7 \text{ nm})$	$\Phi(253.7 \text{ nm})$	0	

<sup>a</sup> Lower bounds

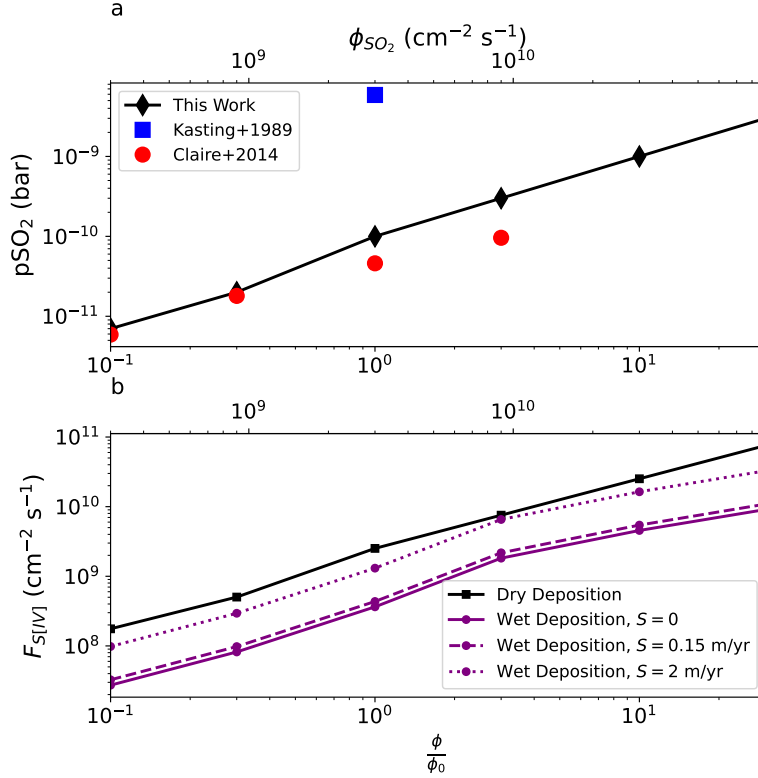
## 4.2 Atmospheric Processing and Surface Deposition of SO<sub>2</sub>

Our photochemical modeling predicts SO<sub>2</sub> surface concentrations on early Earth that are sensible in comparison to past work (Kasting et al. (1989); Claire et al. (2014); Figure 3). Our predicted pSO<sub>2</sub> is much lower than that calculated by Kasting et al. (1989) for early Earth; this is because Kasting et al. (1989) considered the limiting case of no surface deposition of SO<sub>2</sub>. We include surface deposition of SO<sub>2</sub>, which suppresses pSO<sub>2</sub>. Our predicted pSO<sub>2</sub> is slightly higher than that calculated by Claire et al. (2014) for high  $\phi_{SO_2}$ . We attribute this to the assumption of Claire et al. (2014) that SO<sub>2</sub> is substantially explosively outgassed, which injects SO<sub>2</sub> into the stratosphere where it is photochemically processed into aerosols, reducing pSO<sub>2</sub> relative to our calculation.

Our modeling predicts that most outgassed SO<sub>2</sub> is returned to the surface via wet and dry deposition. This reflects our assumption of low-altitude outgassing of SO<sub>2</sub>, where it is most vulnerable to surface deposition (Hu et al., 2013). If SO<sub>2</sub> is instead released explosively at high altitudes, then at elevated  $\phi_{SO_2} \sim 0.5$  of the SO<sub>2</sub> can be photochemically processed into sulfate and elemental sulfur aerosols (Claire et al., 2014). This means that our calculation may overestimate SO<sub>2</sub> deposition by up to  $\sim 2\times$  at elevated  $\phi_{SO_2}$ .

## 4.3 Prebiotic Marine Waters

A wide range of chemical (Table 6) and planetary (Table 2) uncertainties affect estimates of [S[IV]] in marine waters on early Earth. We explore this range. We find that chemical uncertainties dominate the uncertainty in prebiotic marine [S[IV]], with geological uncertainties playing a secondary role that is only relevant in the limit of inefficient chemical loss of S[IV] (Figure 4). The main source of chemical uncertainty is the reaction order of S[IV] disproportionation  $n$ . If  $n = 1$ , then prebiotic marine S[IV] concentrations are suppressed to sub-micromolar concentrations, and possibly sub-nanomolar concentrations, in concordance with Halevy (2013). On the other hand, if  $n = 4$ , then S[IV] disproportionation is kinetically inhibited and S[IV] is able to accumulate to higher concentrations, as recognized by Kasting et al. (1989). An upper limit on [S[IV]] is imposed by photolysis even in the limit of  $n > 1$  and even if S[IV] photolysis is inefficient ( $\Phi_{HSO_3^-}(> 254 \text{ nm}) = \Phi_{SO_3^{2-}}(> 254 \text{ nm}) = 0$ ). This upper limit keeps S[IV] sub-saturated with respect to atmospheric SO<sub>2</sub>, meaning that surface deposition of SO<sub>2</sub> was efficient on prebiotic Earth.



**Figure 3.** Photochemical processing of  $\text{SO}_2$  in the atmosphere of prebiotic Earth. (a) Top: partial pressure of  $\text{SO}_2$  as a function of surficial  $\text{SO}_2$  emission rate. Shown for comparison are similar estimates from Kasting et al. (1989) and Claire et al. (2014), Figure 6. (b) Bottom: wet and dry deposition fluxes of  $\text{S[IV]}$  species from the atmosphere to the surface. Wet deposition fluxes are given for various seepage rates, which for the steady-state modeling we conduct here dictate the implied precipitation rate.

#### 4.4 Prebiotic Terrestrial Waters

Terrestrial waters embrace hydrological and chemical diversity far exceeding marine waters (Lerman et al., 1995), and it is impractical to explore their full diversity. Nevertheless, we can gain some sense of  $[\text{S[IV]}]$  in terrestrial waters on prebiotic Earth by considering a few representative end-member scenarios, motivated by proposed origin-of-life theories. We specifically consider 1 m-deep freshwater and closed-basin carbonate lakes, with inorganic ion composition and corresponding absorbances following Ranjan, Kufner, et al. (2022) (Table 3).

We find that the choice of geological scenario dominates chemical uncertainties in controlling  $[\text{S[IV]}]$  (Figure 5). Thermal loss processes are less important than the photochemical loss processes, because they are integrated over a shallower column compared to the marine scenario. Photolysis is the main control on  $\text{S[IV]}$  in most terrestrial scenarios. In most scenarios, photolysis regulates  $\text{S[IV]}$  to sub-micromolar concentrations for  $\frac{\phi}{\phi_0} \leq 10$ .  $\text{S[IV]}$  exceeds micromolar concentrations for enhanced volcanic outgassing rates relative to modern Earth ( $\frac{\phi}{\phi_0} > 10$ ). As in the marine case, the uncertainty in disproportionation rates is dominated by the order of reaction of sulfite disproportionation, but the influence of this uncertainty on  $\text{S[IV]}$  is muted by the decreased importance of disproportionation relative to photolysis. Photolysis is minimized in non-basic waters



where less-absorptive  $\text{HSO}_3^-$  is the main form of S[IV]. Photolysis may also be reduced in UV-opaque waters, though in this case radical generation from absorption of UV by environmental reagents may yet lead to S[IV] loss (e.g., Li et al. (2020)). In this scenario, S[IV] may exceed micromolar concentrations at modern Earth-like outgassing fluxes, and disproportionation and seepage may be sinks of comparable importance to photolysis (Figure 5).

## 5 Discussion

### 5.1 [S[IV]] in Prebiotic Natural Waters

S[IV] was a prebiotic reagent, but its steady-state global-mean concentrations were modest due to photolysis. This basic conclusion was derived from our full model, but is recovered in a simple order-of-magnitude calculation, increasing our confidence in this finding (SI S4). The rate of disproportionation of S[IV] at temperate conditions, previously proposed as the main sink of prebiotic S[IV], is slow even at high concentrations, and may be even slower at prebiotically-relevant [S[IV]]. However, UV photolysis places a strong upper limit on prebiotic [S[IV]], which was neglected by previous studies (Kasting et al., 1989; Halevy, 2013; Ranjan et al., 2018; Loftus et al., 2019).  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ , the main forms of S[IV] at concentrations and pH relative to prebiotic natural waters, are strong UV chromophores. Absorption of prebiotically-abundant UV radiation by  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  ultimately leads to oxidation to sulfate. This phenomenon has been characterized in the laboratory, and is used in environmental applications to remove aqueous pollutants (Fischer & Warneck, 1996; Huang et al., 2010; Cao et al., 2021; Wu et al., 2021).

Photolysis confines S[IV] to sub-micromolar concentrations in the prebiotic ocean across most of parameter space. For S[IV] to exceed micromolar concentrations, the kinetics of chemical loss of S[IV] need to be near the inefficiency limit allowed by experiments ( $\Phi(\lambda > 254 \text{ nm}) = 0, n \geq 2$ ). Additionally, volcanic outgassing on early Earth must exceed volcanic outgassing on modern Earth by an order of magnitude or more ( $\frac{\phi}{\phi_0} \geq 10$ ), and the pH must be acidic (maximizing the amount of sulfite in less-photolytic  $\text{HSO}_3^-$ ). However, the pH likely cannot be too acidic, due to tentative indications that disproportionation is more efficient at low pH (SI 1.3.1; Searcy (1981)). We may wonder whether it is possible for enhanced concentrations of S[IV] to build up in the deep ocean, where it is protected from photolysis. If the sole source of S[IV] is the atmosphere and assuming diffusion to be the sole mechanism transporting S[IV] from the surface where it is injected down to depth, then this scenario is not possible, because it would require diffusion to create a gradient. However, local sources of  $\text{SO}_2$  at depth (e.g., hydrothermal systems; (Butterfield et al., 2011; Peters et al., 2021; Barge & Price, 2022)) could generate locally enhanced [S[IV]] at depth. Similarly, non-diffusive transport processes might be able to generate enhanced marine [S[IV]] at depth. Models incorporating 3D transport are required to probe these possibilities and resolve the degree of enhancement possible.

Higher concentrations of S[IV] are possible in atmospherically-supplied terrestrial waters relative to marine waters, because the supply rate remains the same while loss processes have a shallower column over which to operate. Even so, photolysis limits accumulation of S[IV]. Achieving higher [S[IV]] in terrestrial waters at modern Earth-like volcanic outgassing requires a geologically favorable environment, of which the most important factors are the background UV absorptivity and the depth. Shallower waters can accumulate higher [S[IV]] because fewer total UV photons are absorbed (Figure 6). In other words, as depth decreases, a larger fraction of incident photons are absorbed by the base of the water body or scattered back out of the surface, as opposed to photolyzing S[IV]. Similarly, if UV-absorbing compounds are present in the water, then these compounds can absorb UV photons that would otherwise photolyze S[IV], which may permit S[IV] accumulation (Figure 7). We say *may* because absorption of UV photons by



background absorbers may yet lead to sulfite loss. For example, absorption of UV radiation by UV-attenuating halogen salts leads to radical production (Jortner et al., 1964), and such radicals may react with and destroy S[IV] (Yu et al., 2018). On the other hand,  $\text{Fe}^{2+}$  appears to inhibit S[IV] photolysis by attenuation of UV (Li et al., 2014), as does humic acid (Yang et al., 2020). Detailed studies on a case-by-case basis of specific natural waters are required to confirm the effect of background absorbers on S[IV] accumulation (Yang et al., 2020; Cao et al., 2021).

The volcanic outgassing rate, especially of  $\text{SO}_2$ , is a key uncertainty on [S[IV]]. If steady-state volcanic outgassing were elevated relative to modern ( $\frac{\phi}{\phi_0} \geq 20$ ), then steady-state [S[IV]] should have exceeded micromolar [S[IV]] in even geologically unfavorable terrestrial waters. On the other hand, if steady-state volcanic outgassing were suppressed relative to modern ( $\frac{\phi}{\phi_0} \leq 0.1$ ), then micromolar [S[IV]] is not accessible in even geologically favorable terrestrial waters.  $\phi_{\text{SO}_2}$  is highly uncertain. Scalings based on plate tectonics suggest volcanic outgassing was enhanced on early Earth by a factor of  $4\text{--}9\times$  (Richter, 1985; Sleep & Zahnle, 2001). However, early Earth may have featured less  $\text{SO}_2$  outgassing due to lower concentrations of recycled oceanic sulfate (Harman, Pavlov, et al., 2018), or due to higher magmatic degassing pressures (Gaillard et al., 2011), though this is debated (Brounce et al., 2017; Korenaga, 2021). Measurements of sulfur mass-independent fractionation (S-MIF) may ultimately directly constrain early sulfur outgassing fluxes, and indeed attempts to match S-MIF measurements with photochemical models hint at enhanced  $\text{SO}_2$  column densities (Endo et al., 2016). However, all photochemical models ultimately fail to reproduce the S-MIF signal to the accuracy required to infer  $\phi_{\text{SO}_2}$  (Ono et al., 2003; Claire et al., 2014; Harman, Pavlov, et al., 2018; Endo et al., 2019). We advocate for detailed modeling of early Earth  $\text{SO}_2$  outgassing, as well as the improved laboratory measurements and photochemical modeling required to directly constrain  $\text{SO}_2$  emission rates from S-MIF measurements, to constrain this key uncertainty.

## 5.2 Implications for Prebiotic Chemistry and Early Habitability

S[IV] was suppressed in prebiotic terrestrial waters by photolysis. [S[IV]]  $< 100\ \mu\text{M}$  for terrestrial waters in almost all of the parameter space relevant to early Earth, and [S[IV]] could have been in the nM range for transparent global-mean 1-m deep ponds and lakes if volcanic outgassing were suppressed relative to modern ( $\frac{\phi}{\phi_0} = 0.1$ ). For comparison, [S[IV]] used in laboratory studies of prebiotic chemistry ranges from 10 mM (Kawai et al., 2019; Rimmer et al., 2021; Liu et al., 2021) to 3 M (Becker et al., 2019). That these concentrations are unrealistically high is well-understood, and justified on the grounds that reaction mechanisms discovered at elevated concentrations which render their kinetics accessible to laboratory study will still apply at lower, more prebiotically relevant concentrations. There is evidence to support this view; for example, HCN homologation via photoredox cycling of cyanocuprate was first demonstrated with 10 mM Cu[I] but also functions at  $63\ \mu\text{M}$  Cu[I] (Ritson & Sutherland, 2012; Todd et al., 2018), sugar sequestration via sulfonate formation was demonstrated at 10 mM S[IV] but should function at micromolar S[IV] as well (Kawai et al., 2019; Benner et al., 2019), and  $\text{CO}_2$  photoreduction by S[IV] improves in yield with 10 mM S[IV] compared to 100 mM S[IV] (Liu et al., 2021). However, it is also possible that there is a critical [S[IV]] below which a given S[IV]-dependent prebiotic chemistry will not function, just as there are critical UV flux levels below which UV-dependent prebiotic chemistries fail to function (Rimmer et al., 2018; Rimmer et al., 2021). To confirm that a S[IV]-dependent prebiotic chemistry demonstrated in the laboratory could have occurred in nature, it is necessary to characterize the minimum [S[IV]] required for the chemistry to function, and to compare this threshold [S[IV]] to the [S[IV]] available in the natural waters invoked by the prebiotic chemical scenario (Benner et al., 2010, 2019; Sasselov et al., 2020; Walton et al., 2022). We advocate for such studies.

While steady-state global-mean  $[S[IV]]$  was low,  $[S[IV]]$  was transiently elevated after stochastic events like large volcanic eruptions and perhaps also after large impacts which generate a UV-attenuating haze layer. During major volcanic eruptions on Earth,  $\frac{\phi}{\phi_0} = 20 - 200$  for a period of 10 – 1 years (Self et al., 2006; Halevy & Head, 2014), which would permit  $\geq 1\mu M$   $S[IV]$  in shallow closed-basin lakes during the eruption (Figure 5). Origins-of-life chemistry invoking this scenario would need to be shown to function with transient, relatively short-lived elevated  $S[IV]$ . Similarly, early Earth is proposed to have experienced epochs with very low surface UV irradiation due to formation of UV-attenuating atmospheric hazes in the aftermaths of large impacts (Benner et al., 2020; Zahnle et al., 2020; Citron & Stewart, 2022; Itcovitz et al., 2022). In the absence of UV light, the sink on  $S[IV]$  due to photolysis would have been absent, permitting accumulation of  $S[IV]$  until limited by disproportionation, seepage, or outgassing. This scenario would work for prebiotic chemistry which does not require UV light (e.g., Benner et al. (2019); Becker et al. (2019)). However, prebiotic chemistry that invokes  $S[IV]$  in conjunction with UV light would not be able to exploit this case (e.g., J. Xu et al. (2018); Liu et al. (2021); Green et al. (2021)).

Steady-state  $S[IV]$  could also have been enhanced in specific geophysical contexts. Most obviously,  $[S[IV]]$  would have been high in hydrothermal systems such as hot springs. Terrestrial hot springs have been proposed as compelling venues for origins-of-life chemistry, due to favorable ionic composition for lipid membrane assembly, presence of key reagents for prebiotic syntheses, and propensity for wet-dry cycles towards oligomerization and compartmentalization (Mulkiđjanian et al., 2012; Rimmer & Shorttle, 2019; Damer & Deamer, 2020; Omran & Pasek, 2020). Such hot springs could have featured enhanced  $[S[IV]]$  due to continuous hydrothermal supply from below; for example, hot springs in Yellowstone National Park feature  $[S[IV]] = 0.4 - 5\mu M$  (Kamyshny et al., 2014). In support of this hypothesis is phylogenetic evidence suggesting ancient sulfite-reducing metabolism in hot spring-dwelling microbes, which implies the existence of hot springs with elevated sulfite concentrations early in Earth’s history (Colman et al., 2020). Hot springs would have been a particularly favorable environment for prebiotic chemistry which also invokes sulfide (e.g., J. Xu et al. (2020)), which was not generally available beyond hydrothermal systems (Ranjan et al., 2018).

$[S[IV]]$  is also enhanced in extremely shallow waters, due to a reduced column over which loss processes can operate while the atmospheric delivery flux remains unchanged (Figure 6). Notably, waters undergoing wet-dry cycles pass through shallow phases during which  $[S[IV]]$  would have been enhanced; the timescale for a 1-cm layer of water to accumulate  $1\mu M$  of  $S[IV]$  from dry deposition under an early Earth atmosphere under exposure to modern Earth-like outgassing rates is 3 days. This means that a pond experiencing slow seasonal wet-dry cycling as invoked by some prebiotic chemistries (Deamer & Damer, 2017; Pearce et al., 2017; Becker et al., 2018; Campbell et al., 2019) would inevitably have passed through  $S[IV]$ -rich phases.

Finally, waters which contain a UV-shielding compound (one which absorbs UV light at concentrations accessible in natural waters on early Earth without generating  $S[IV]$ -destroying products) would have accumulated higher  $[S[IV]]$ .  $Fe^{2+}$  is a potential UV shield based on its broad UV absorption (Fontana et al., 2007; Ranjan, Kufner, et al., 2022), which inhibits  $S[IV]$  photolysis at  $2\text{ mg L}^{-1}$  ( $36\mu M$ ) in industrial applications (Li et al., 2014). However, the abundance of  $Fe^{2+}$  in prebiotic natural waters remains unclear, with dependence on  $pCO_2$ ,  $pH_2S$ , and assumptions regarding photoredox cycling, among other parameters (Brateman et al., 1983; Konhauser et al., 2017; Hao et al., 2017; Sahai et al., 2022). Our consideration of potential UV absorbers is by no means exhaustive; a number of further candidates remain to be evaluated, including silicate and basaltic dust and meteoritic or atmospheric organics. Lastly, prebiotic chemistry may itself generate UV-attenuating organic surface layers (Cleaves & Miller, 1998; Yang et

al., 2020; Todd et al., 2021). We encourage the experimental and modeling work required to self-consistently explore these potential UV-shielded prebiotic scenarios.

Marine S[IV] levels were even lower than terrestrial S[IV]. Global mean marine S[IV] could only have exceeded micromolar concentrations if volcanic outgassing were significantly enhanced relative to modern ( $\frac{\phi}{\phi_0} \geq 10$ ), oceanic geologic parameters (especially pH) favorable for S[IV] accumulation, and the kinetics of prebiotic S[IV] near the inefficiency limit currently allowed by measurements (subject to the caveats in Section 5.3). However, most marine abiogenesis scenarios invoke specific marine sub-environments, especially hydrothermal vents (Martin et al., 2008; Barge & Price, 2022). Submarine volcanic and hydrothermal settings can feature enhanced [S[IV]] even on modern Earth (Butterfield et al., 2011; Peters et al., 2021), and might have furnished enhanced [S[IV]] on early Earth as well. Such environments are promising venues for S[IV]-dependent chemistry in marine environments.

Our findings imply that SO<sub>2</sub> deposition into the oceans of early Earth was efficient, meaning that UV-blocking sulfur haze layers could only form if the volcanic emission flux was very high ( $\frac{\phi}{\phi_0} \gtrsim 100$ ). Previously, Kasting et al. (1989) showed that if S[IV] reached saturation in the early oceans, a UV-blocking S<sub>8</sub> haze could form at SO<sub>2</sub> emission fluxes comparable to modern-day SO<sub>2</sub> emission fluxes ( $\frac{\phi}{\phi_0} \approx 1$ ), because S[IV] saturation suppresses SO<sub>2</sub> surface deposition and instead permits the SO<sub>2</sub> to remain in the atmosphere and undergo photochemical transformations into haze. However, here we show that photochemical loss of SO<sub>2</sub> in the prebiotic oceans kept marine S[IV] sub-saturated by orders of magnitude, meaning that atmospheric SO<sub>2</sub> would have deposited into the oceans at its current, rapid rate (1 cm/s; Sehmel (1980)). Under these conditions, Kasting et al. (1989) do not predict the formation of haze at concentrations sufficient to significantly attenuate surface UV.

Kasting et al. (1989) point out that the polymerization kinetics of sulfur en route to S<sub>8</sub> are uncertain, and if much more efficient than they assumed, then sulfur haze might form even if S[IV] were sub-saturated. However, Hu et al. (2013) revisit this question with an updated sulfur reaction scheme with substantially more efficient (albeit still uncertain) sulfur polymerization kinetics. They find that uncertainties in the reaction kinetics and parameters like the H<sub>2</sub>S/SO<sub>2</sub> emission ratio and atmospheric temperature-pressure profile play secondary roles in controlling haze accumulation, although uncertainties in the reaction kinetics may merit further investigation. Instead, they find that sulfur haze formation is primarily controlled by sulfur emission rate, mean particle size, and surface deposition velocity. If surface deposition is efficient, then high sulfur emission fluxes of  $\gtrsim 3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$  ( $\frac{\phi}{\phi_0} \gtrsim 100$ ) are required to produce optically thick hazes capable of attenuating surface UV by an order of magnitude or more (Hu et al., 2013; Ranjan et al., 2018). Our modeling here is consistent with this past work. Even assuming a small mean haze particle size of 0.1  $\mu\text{m}$  favorable to haze accumulation, surface UV is suppressed by less than an order of magnitude across the  $\frac{\phi}{\phi_0} = 0.1 - 30$  ( $\phi_{\text{SO}_2} = 3 \times 10^8 - 9 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ ) in our model, if S[IV] surface deposition is efficient. This result favors a generally UV-rich environment on prebiotic Earth. However transient hazy epochs in the aftermath of large impacts or volcanic explosions may have occurred (Ranjan et al., 2018; Benner et al., 2020; Zahnle et al., 2020).

The effect on planetary climate is more difficult to predict, because planetary climate appears more sensitive to modest amounts of haze; for example, in modeling of the effect of sulfur aerosols on the climate of early Mars, Tian et al. (2010) found noticeable changes in the surface temperature relative to the no-aerosol baseline for aerosol extinction optical depths at 550 nm ( $AOD|_{550 \text{ nm}}$ ) of  $AOD|_{550 \text{ nm}} \geq 0.02$ . Our model is unable to treat the effects of sulfur haze on planetary climate because it lacks a climate module. Detailed climate modeling is required to elucidate the effects of sulfur haze on the climate of early Earth.

We may wonder about the possibility of a bistability in  $[S[IV]]$ . If early Earth experienced a UV-suppressed phase due to abundant sulfur haze, e.g. in the aftermath of a large volcanic explosion, might it be possible for  $S[IV]$  to saturate the surface due to a reduced photolytic sink, thereby stabilizing the sulfur haze layer? We argue that such a scenario is unlikely, because such an equilibrium is unstable. Volcanic emission of sulfur-bearing gases is stochastic, with emission fluxes varying with time and space around a long-term global mean. If a putative haze layer ever thinned to the point where significant UV reached any part of the planetary surface, then surficial  $S[IV]$  would have been rapidly depleted, enhancing  $SO_2$  deposition and therefore depleting atmospheric  $SO_2$  and the sulfur haze, therefore further increasing UV transmission and  $S[IV]$  depletion. This constitutes a positive feedback loop that would rapidly scrub  $S[IV]$  from the oceans. While 3D modeling which resolves the stochasticity and spatial heterogeneity of volcanic outgassing is required to confirm this qualitative argument, we argue that combined with the extraordinarily large volcanic outgassing that would be required to suppress UV enough to permit  $S[IV]$  to accumulate (Ranjan et al., 2018) and the length of time that outgassing would need to be sustained to saturate the oceans in  $S[IV]$ , the bistability scenario is unlikely.

### 5.3 Validity and Effect of Simplifying Assumptions

In this section, we review the simplifying assumptions we have employed in this work, and the sensitivity of our results to their validity. We present these assumptions in order from least to most potentially impactful on to our conclusions. While we overall find that our conclusions are robust, we highlight how future experimental, theoretical, and observational work can reduce the need for such assumptions and improve the accuracy and precision of estimates of  $[S[IV]]$  in natural waters on prebiotic Earth.

Our modeling is steady-state, and therefore does not resolve time-dependent effects relevant to terrestrial waters. In particular, our modeling ignores the fact that terrestrial waters are likely to vary in depth and therefore  $[S[IV]]$  as a function of time, e.g. due to seasonal variations in precipitation and evaporation rate. Time-dependent modeling (e.g., Pearce et al. (2017)) is required to resolve this effect. Similarly, our modeling is global-mean, and does not resolve the heterogeneity of early Earth environments. For example, photolysis rates will be lower in polar regions and higher in equatorial regions relative to the global-mean conditions we model here. Further,  $SO_2$  may not be well-mixed in early Earth's atmosphere, but should have been more abundant near volcanic  $SO_2$  source regions and less abundant far from them, proportionately affecting surface deposition rates; 3D atmospheric modeling is required to capture this affect (Warneck, 1998; Chin et al., 2000). These limitations mean that our modeling is accurate only to the order-of-magnitude level, which is relevant when interpreting its results.

We have neglected processing in the high-temperature conditions in hydrothermal vents as a loss mechanism for  $S[IV]$  in marine waters (Kusakabe et al., 2000). This is because  $S[IV]$  loss at hydrothermal vents is negligible compared to other loss mechanisms like photolysis in a global-mean sense. Even assuming enhanced cycling of the ocean through hydrothermal vents on early Earth ( $3 \times 10^6$  years, vs.  $1 \times 10^7$  years today; Laneville et al. (2018)) and unity efficiency of  $S[IV]$  loss at vents, processing at vents is subdominant to even inefficient photolysis by 3 orders of magnitude. Similar conclusions were reached for  $NO_3^-$  (Ranjan et al., 2019), and arise ultimately from the dramatically higher chemical free energy supplied by solar UV photons compared to thermal sources of energy on early Earth (Deamer & Weber, 2010).

Our approach to estimating  $T_{disp,0}$  will overestimate  $T_{disp,0}$  if  $n > 1$  and  $[S[IV]]_f \ll [S[IV]]_0$ . However, if  $n > 1$ ,  $S[IV]$  disproportionation is an insignificant loss process compared to other loss mechanisms like photolysis at  $[S[IV]]$  characteristic of natural waters (Figures 4, 5). We conducted sensitivity tests where we adjusted  $T_{disp,0} = 10$  days for

$n = 4$ , and found our conclusions to be unaffected. Similarly, our results are insensitive to the uncertainty in  $[S[IV]]_0$  (Meyer et al., 1979; Meyer et al., 1982), because this uncertainty only affects  $k_{disp,n}$  when  $n > 1$ , for which disproportionation is subdominant to other processes like photolysis. We conclude that our results are insensitive to our approach to estimating  $T_{disp,0}$ .

In calculating wet deposition with MEAC, we have implicitly assumed raindrop pH=5, as on modern Earth (Giorgi & Chameides, 1985; Hu et al., 2012). However, on early Earth with elevated  $pCO_2$ , raindrops would have been more acidic (Halevy et al., 2007; Sahai et al., 2022). More acidic pH would have reduced S[IV] concentrations in raindrops due to less favorable acid dissociation, meaning that this assumption overestimates wet deposition of  $SO_2$ . Our conclusions are insensitive to this simplification because for the closed-basin waters we model here, S[IV] supply is dominated by dry deposition, not wet deposition. Furthermore, decreased efficiency of wet deposition is partially compensated by increased efficiency of dry deposition, since less efficient wet deposition of atmospheric  $SO_2$  increases  $pSO_2$ . However, raindrop pH may have more significant implications for open basin systems, which can be modeled as weathered rainwater (Hao et al., 2017; Sahai et al., 2022).

When calculating scalar irradiance in aqueous solution, we have employed formalisms primarily derived from marine waters. These formalisms may not be accurate for terrestrial waters. In particular, for marine waters we may assume that the radiation field vanishes at depth, but the radiation field might not vanish at depth for terrestrial waters. By analogy with atmospheric UV transmission (Ranjan & Sassellov, 2017), photolysis rates may be enhanced up to  $4\times$  for the worst-case scenario of shallow, low-absorptivity waters underlain by a surface with high-UV reflectivity. However, this worst-case scenario is unlikely to be realized, because most natural surfaces, including the basalts proposed to have constituted the first land (Bada & Korenaga, 2018; Rosas & Korenaga, 2021; Korenaga, 2021), have low UV reflectivity (Dollfus et al., 1980; Turner & Parisi, 2018), meaning that the radiation field should vanish at depth.

In our calculations, we have followed our underlying sources and past work in quantifying chemical kinetics using chemical concentrations, not activities (Zhang & Millero, 1991; Halevy, 2013). That is, we have implicitly assumed activity coefficients of unity, neglecting the potentially decreased reactivity of chemical species like S[IV] in solutions with high ionic strength. Formally, this means that our calculations may underestimate S[IV] in solutions with high ionic strength. This does not directly affect our conclusions, as the upper limits on  $[S[IV]]$  are set by photolysis. However, increased ionic strength can suppress the efficacy of photolysis, with  $SO_3^{2-}$  photolysis quantum yields decreasing by 6-12% per 1M ionic strength (Sauer, Shkrob, et al., 2004). This means that our calculation may underestimate  $[S[IV]]$  by  $\leq 14\%$  in the prebiotic ocean and  $\leq 2\times$  of closed-basin carbonate lakes. Our conclusions are robust to uncertainties of this magnitude.

In modeling S[IV] disproportionation, we have neglected the effects of temperature, applying constraints derived at room temperature ( $23^\circ C = 296 K$ ) to the early Earth as a whole. Yet, the temperature of the prebiotic Earth remains uncertain, with global-mean temperature estimates spanning 273K-323K (Krissansen-Totton et al., 2018). There are no measurements of the temperature-dependence of S[IV] disproportionation rates at these temperatures. In the absence of data, we can extrapolate from the high-temperature measurements, which suggest  $E_A = 40 - 50 \text{ kJ mol}^{-1}$  (Halevy, 2013; Ranjan et al., 2018). This procedure is risky due to evidence that S[IV] disproportionation is controlled by different reaction mechanisms at the cooler temperatures relevant to our study (Section 2.3). If, nevertheless, we so extrapolate, we find that the rate of S[IV] disproportionation may be up to  $6\times$  slower at 273K and up to  $5\times$  faster at 323K compared to what we have assumed in our model. We have re-run the calculations in our paper and verified that our conclusions, which are order-of-magnitude, are not sensitive to uncertainties of this magnitude.



We have employed 3.9 Ga to represent the prebiotic era when estimating solar UV and its atmospheric transmission, because it is consistent with available theoretical and geological constraints on the era of abiogenesis (Ranjan & Sasselov, 2017; Pearce et al., 2018), and because it aligns with previous work estimating the prebiotic environment (Kaltenegger et al., 2007; Rugheimer & Kaltenegger, 2018). Our results are insensitive to this assumption, because solar emission at the  $> 200$  nm UV wavelengths transmitted to the surface through a habitable planet atmosphere varies by less than a factor of 2 from 4.4-3.8 Ga (Claire et al., 2012). Our results are also insensitive to our assumed atmospheric composition, because atmospheric transmission of prebiotic UV on early Earth is insensitive to most of the considerable uncertainty on early Earth’s atmospheric composition in steady-state (Ranjan & Sasselov, 2017). The one exception is the possibility that early Earth had a massive (7-70 bar)  $\text{CO}_2$  atmosphere (Kasting, 1987; Kasting, 1993). Such  $p\text{CO}_2$  is an extreme possibility inconsistent with coupled carbon cycle-climate models which predict  $p\text{CO}_2 \leq 1$  bar (Krissansen-Totton et al., 2018; Kadoya et al., 2020), but nevertheless is not ruled out by direct geochemical proxies. If such a massive  $\text{CO}_2$  atmosphere were present, surficial photoprocesses would have been suppressed by 1-2 orders of magnitude relative to what we model here (Ranjan & Sasselov, 2017), raising the possibility of significantly enhanced  $[\text{S[IV]}]$ . However,  $\text{SO}_2$  outgassing would also be suppressed for surface pressures  $\geq 10$  bar (Gaillard & Scaillet, 2014). Detailed modeling incorporating both effects is required to estimate  $[\text{S[IV]}]$  in the extremal possibility of a massive  $\geq 7$  bar  $\text{CO}_2$  atmosphere on prebiotic Earth.

The  $[\text{S[IV]}]$  photochemical kinetic parameters employed at this work were typically derived at  $[\text{S[IV]}]$  much higher than available in realistic prebiotic environments. It is possible that the value of some of these parameters is a function of  $[\text{S[IV]}]$ . For example, studies of photolysis of 2-aminooxazole and photodegradation of ferrocyanide suggest concentration-dependent effective loss rates, perhaps explained by more efficient geminate recombination (i.e. back-reactions which reform the photolyzate) at high photolyzate concentrations (Todd et al., 2021; Todd et al., 2022). We have attempted to control for this effect by selecting terminal quantum yields when available for our model, which account for prompt geminate recombination (Lian et al., 2006). Nevertheless, we advocate for characterization of  $[\text{S[IV]}]$  photochemical kinetics at lower, more prebiotically relevant  $[\text{S[IV]}]$  to confirm the validity of our approach.

We have modeled the transformations of  $[\text{S[IV]}]$  in isolation in this work, as is common in assessing potential prebiotic reagents on early Earth (e.g., Harman et al. (2013); Wong et al. (2017); Adams et al. (2021)). In reality,  $[\text{S[IV]}]$  would have existed in conjunction with diverse other chemical species on early Earth, and those chemical species could have interacted with  $[\text{S[IV]}]$ . For example,  $\text{NO}_3^-$  was likely also atmospherically synthesized on early Earth (Mancinelli & McKay, 1988; Summers & Khare, 2007; Ranjan et al., 2019), and may have reacted with  $[\text{S[IV]}]$ , further depleting it (Littlejohn et al., 1986). On the other hand,  $\text{CH}_2\text{O}$  was also likely atmospherically synthesized on early Earth (Pinto et al., 1980; Wen et al., 1989; Ranjan et al., 2020), and may have stabilized  $[\text{S[IV]}]$  if present at high enough concentrations (Munger et al., 1984, 1986; de Carvalho & Schwedt, 2000; Cleaves, 2008). Similarly, it is possible there exist prebiotic reagents which facilitate the backreaction of the products of  $[\text{S[IV]}]$  photolysis back to  $[\text{S[IV]}]$ , as OH accomplishes for  $\text{NO}_3^-$  (Mack & Bolton, 1999). If so, then our calculation overestimates the efficacy of  $[\text{S[IV]}]$  photolysis and underestimates  $[\text{S[IV]}]$ . The generally robust photolysis of  $[\text{S[IV]}]$  in wastewater treatment applications suggest such reagents are not common (Yang et al., 2020; Wu et al., 2021); nevertheless, this possibility is accessible to experimental test, and we support such investigations. Finally, inorganic ions that might be present in prebiotic natural waters may catalyze  $[\text{S[IV]}]$  disproportionation.  $\text{I}^-$  can catalyze  $[\text{S[IV]}]$  disproportionation at high (1 M) concentrations (Petrusevski et al., 2013), but our “carbonate lake” sulfite incubations suggest this catalysis is insignificant at natural  $[\text{I}^-]$  (SI S1.3.2). There are hints that transition metals like Fe and Mn catalyze  $[\text{S[IV]}]$  disproportionation (Searcy, 1981; Meyer et al., 1982), but further work is required to determine the significance of

catalysis at concentrations and speciation relevant to natural waters. We advocate coupled modeling/laboratory simulation of the interaction of S[IV] with other prebiotic reagents to remediate this caveat.

The quantum yield of  $\text{HSO}_3^-$  photolysis,  $\Phi_{\text{HSO}_3^-}(\lambda)$  is extremely poorly constrained, and may be overestimated in our model. We are aware of only one constraint on  $\Phi_{\text{HSO}_3^-}(\lambda)$ , at 213.9 nm, and this measurement must be interpreted as an upper bound (Fischer & Warneck, 1996; Sauer, Crowell, & Shkrob, 2004). We have implemented  $\text{HSO}_3^-$  photolysis in our model under the assumption that  $\Phi_{\text{HSO}_3^-}(213.9 \text{ nm})$  corresponds to its upper bound, and estimated its value at other wavelengths on the basis of scaling the quantum yield of  $\text{SO}_3^{2-}$  photolysis. While this scaling reproduces the observation that solutions with S[IV] primarily present as  $\text{HSO}_3^-$  photolyze less efficiently than solutions with S[IV] primarily present as  $\text{SO}_3^{2-}$  (Li et al., 2012, 2014; Wu et al., 2021), this is an easy constraint to satisfy and our estimate of  $\Phi_{\text{HSO}_3^-}(\lambda)$  remains a major assumption with minimal physical justification. In particular, our implementation leaves open the possibility that we are overestimating the efficiency of  $\Phi_{\text{HSO}_3^-}(\lambda)$ . For example, studies of the effect of pH on S[IV] photolysis-driven photodegradation are able to reproduce measurements while neglecting  $\text{HSO}_3^-$  photolysis altogether (solely considering  $\text{SO}_3^{2-}$  photolysis), even at pH regimes where  $\text{HSO}_3^-$  is dominant (Li et al., 2012, 2014). Sensitivity tests with  $\Phi_{\text{HSO}_3^-} = 0$  indicate that we may underestimate [S[IV]] by up to a factor of a few at slightly acidic pH (pH= 6.25). The underestimate may be worse at more acidic pH due to increased speciation as  $\text{HSO}_3^-$ , but our current modeling is not able to probe this regime because we lack robust constraints on  $T_{\text{disp},0}$  at acidic pH. We advocate better constraints on  $\Phi_{\text{HSO}_3^-}(\lambda)$  to remediate this caveat.

#### 5.4 Prospects for Empirical Test

The calculations in this paper constitute theoretical predictions of [S[IV]] on early Earth. Direct geological tests of these predictions are challenging because of the generally high solubility of S[IV] minerals which inhibits their preservation through geological time on Earth. However, a number of pathways are emerging which may permit empirical constraints on early [S[IV]].

First, phylogenetic studies have begun to elucidate the origin of sulfur reducing metabolism, including whether it was sulfite or sulfate that was first reduced, and in which environments (Colman et al., 2020; Chernyh et al., 2020). Since the existence of sulfite reduction implies the existence of sulfite, such studies may eventually probe [S[IV]] in early natural waters.

Second, nitrate and nitrite minerals face similar preservation challenges as S[IV] minerals, but isotopic studies of ancient kerogens have constrained differential  $\text{NO}_x^-$  abundances in marine and lacustrine waters on 3.2 Ga Earth by probing for signatures of  $\text{NO}_x^-$ -reducing metabolism (Homann et al., 2018). If similar techniques can be developed for S[IV], they may permit similar constraints on early [S[IV]] in natural waters.

Third, studies of banded iron formations (BIFs) may constrain early marine [S[IV]], by searching for evidence of the interference of S[IV] in the photochemical cycling of Fe, which is one of the hypotheses proposed to explain the BIFs (Millero et al., 1995; Nie et al., 2017; Dodd et al., 2022).

Finally, plate tectonics and hydrology on Earth render ancient rocks rare, but these processes have been inoperative on Mars for billions of years, and much of the Martian surface is ancient (Sasselov et al., 2020). Measurements from the Curiosity rover are consistent with the presence of trace Fe sulfate or Ca sulfite minerals on Mars (McAdam et al., 2014; Franz et al., 2017; Franz et al., 2019). If Martian chemical analyses can be refined to discriminate between these two progenitor possibilities, then they will enable



direct tests of models like the one developed here, though secondary alteration processes must be controlled for (Marion et al., 2013).

We note that our prediction disfavoring long-lived UV-blocking sulfur hazes on prebiotic Earth is consistent with the sulfur mass-independent fractionation (S-MIF) record, whose existence means that UV-blocking high-altitude hazes were not persistent on early Earth (Farquhar et al., 2001; Ono, 2017). However, S-MIF does not necessarily constrain the existence of low-altitude sulfur hazes. While our model predicts such hazes are unlikely except at very high sulfur emission fluxes, development of a proxy for haze formation or UV irradiation is required to directly test this aspect of our prediction.

## 6 Conclusions

S[IV] plays key roles in proposed prebiotic chemistries and in controlling planetary climate and UV irradiation. Here, we have developed a novel 0D aqueous photochemical model calibrated with new laboratory measurements of S[IV] disproportionation kinetics and 1D atmospheric photochemical modeling to estimate [S[IV]] in marine and closed-basin terrestrial waters on early Earth. We show that S[IV] disproportionation was inhibited at  $\text{pH} > 7$  ( $T_{\text{disp},0} \geq 1$  year), meaning that S[IV] was a prebiotic reagent on early Earth. Nevertheless, we also show that photolysis imposed a firm upper limit on [S[IV]] ( $< 100 \mu\text{M}$ ). Marine [S[IV]] was sub-saturated with respect to atmospheric  $\text{SO}_2$ , meaning atmospheric deposition of  $\text{SO}_2$  was efficient on early Earth. This implies that sulfur hazes capable of attenuating surface UV by an order of magnitude or more could only have persisted on early Earth if volcanic outgassing was very high ( $\frac{\phi}{\phi_0} \gtrsim 100$ ). Terrestrial [S[IV]]  $\geq 1 \mu\text{M}$  was achieved on a steady-state global-mean basis in shallow closed-basin waters if volcanic outgassing of  $\text{SO}_2$  was enhanced relative to modern ( $\frac{\phi}{\phi_0} \geq 20$ ). Terrestrial [S[IV]]  $\geq 1 \mu\text{M}$  was also possible on a transient global-mean basis after major volcanic eruptions and after large, haze-generating impacts. Terrestrial [S[IV]]  $\geq 1 \mu\text{M}$  could be obtained on a steady-state local basis in waters proximate to  $\text{SO}_2$  supply (e.g., hydrothermal systems), in shallow waters ( $d < 10$  cm), or in UV-opaque waters. Terrestrial [S[IV]]  $\geq 1 \mu\text{M}$  on a transient local basis for waters undergoing wet-dry cycling, as has been invoked by diverse prebiotic chemistries. Our predictions may eventually be empirically tested by phylogenetic studies, terrestrial geochemical measurements, or measurements from Martian rocks may directly constrain early S[IV]. We encourage such investigations.

Our work is a first step in understanding prebiotic [S[IV]]. The substantial uncertainties on our estimates of prebiotic [S[IV]] can be reduced by an improved understanding of S[IV] photochemical kinetics and the early geochemical environment. The main planetary uncertainties are the  $\text{SO}_2$  outgassing rate ( $\phi_{\text{SO}_2}$ ) and the absorptivity of prebiotic natural waters. Outgassing modeling and/or interpretation of the S-MIF record can constrain the former; self-consistent investigation of potential UV absorbers (e.g.,  $\text{Fe}^{2+}$ ) and their abundances in prebiotic natural waters can constrain the latter. For terrestrial waters, it is most important to measure  $\Phi_{\text{HSO}_3^-}(\lambda)$  ( $\lambda = 200\text{--}320$  nm),  $\Phi_{\text{SO}_3^{2-}}(\lambda)$  for  $\lambda = 254\text{--}280$  nm, the reaction order of S[IV] disproportionation  $n$  at standard conditions and at prebiotically-relevant concentrations ( $< 100 \mu\text{M}$ ), and  $T_{\text{disp},0}$  at standard conditions, in that priority sequence. For marine waters, it is most important to measure  $n$ ,  $\Phi_{\text{HSO}_3^-}(\lambda = 200\text{--}320$  nm),  $\Phi_{\text{SO}_3^{2-}}(\lambda = 254\text{--}280$  nm) and  $T_{\text{disp},0}$  at standard conditions, in that priority sequence. Finally, we advocate for experimental characterization of the sensitivity of S[IV]-dependent prebiotic chemistries to [S[IV]], to confirm whether organic synthetic chemical pathways that work under laboratory conditions ([S[IV]]  $\geq 10$  mM) could also have functioned in natural prebiotic environments ([S[IV]]  $< 100 \mu\text{M}$ ). Such work is being done for UV irradiation (Rimmer et al., 2018; Rimmer et al., 2021); we argue for similar work for S[IV] (Benner et al., 2019).

## 7 Open Research

The code implementing the S[IV] aqueous box model, the UV-Vis raw data and processing scripts, and the atmospheric photochemistry model inputs and outputs employed in this work, along with processing scripts to interpret them, are available both at Zenodo (Ranjan, 2023) and on GitHub (<https://github.com/sukritranjan/sulfite-kinetics-release>). The solution-phase analytics raw data and processing is available in Supplemental Information Data Set 1, which is also stored at the same Zenodo and GitHub repositories (Ranjan (2023), <https://github.com/sukritranjan/sulfite-kinetics-release>). MEAC (Hu et al., 2012) is not publicly available due to sharing restrictions in the user agreement; access to MEAC may be requested from R. Hu ([renyu.hu@jpl.nasa.gov](mailto:renyu.hu@jpl.nasa.gov)).

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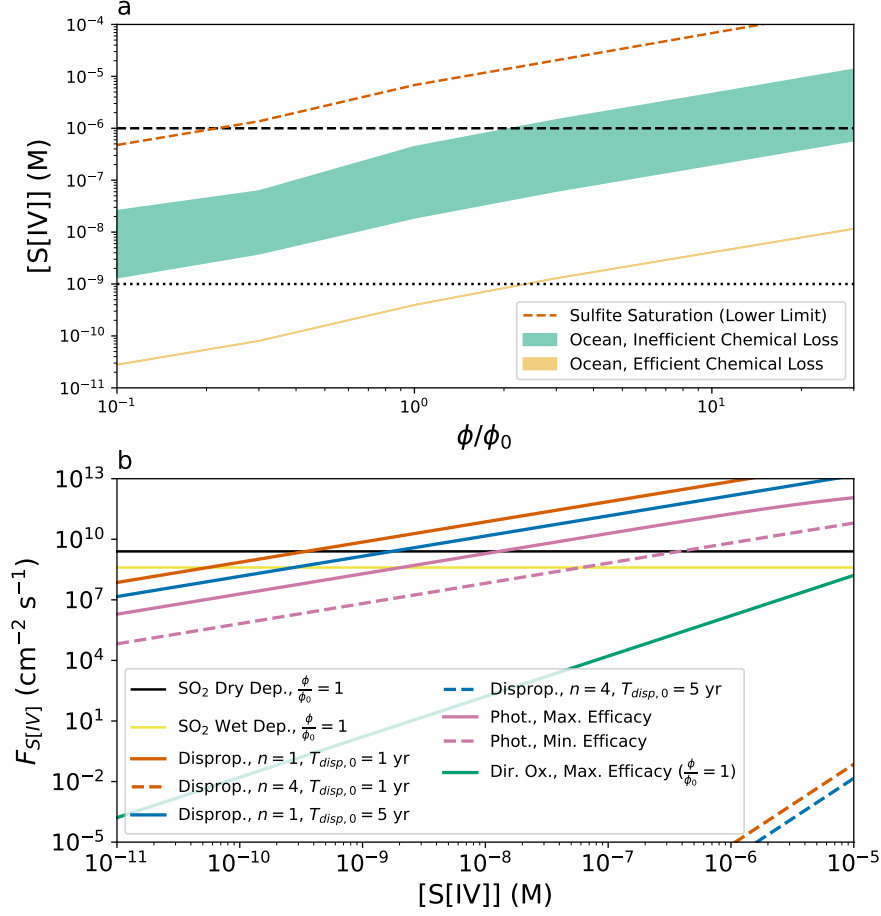
We thank Rebecca Rapf and Alec Kroll for discussions regarding sulfite in raindrops; S. Furkan Ozturk for assistance with the electropotentiometry setup; Ruiho Hu for investigations of precipitate formation in some of our failed experiments; Itay Halevy for sharing a poster (Mirzoyan & Halevy, 2014); David Catling for answers to questions (Toner & Catling, 2020); and Furkan Ozturk, Itay Halevy, Kaitlyn Loftus, Sarah Crucilla, Paul Rimmer, Steven Benner, William Bains, and John Sutherland for valuable discussions. We thank B. Pearce for many instructive discussions, including his suggestion that silicate dust, basaltic dust, meteoritic organics, and atmospheric organics may provide sources of UV attenuation to prebiotic terrestrial waters (c.f. Ranjan, Kufner, et al. (2022)). We thank the Simons Collaboration on the Origin of Life and the Harvard Origins of Life Initiative for nurturing many fruitful conversations related to this paper. We thank the editor and three anonymous reviewers for constructive feedback which substantially improved this paper. We acknowledge Wong (2011) for the colorblind-optimized color scheme used in several Figures in this paper.

## Author Contribution Statement:

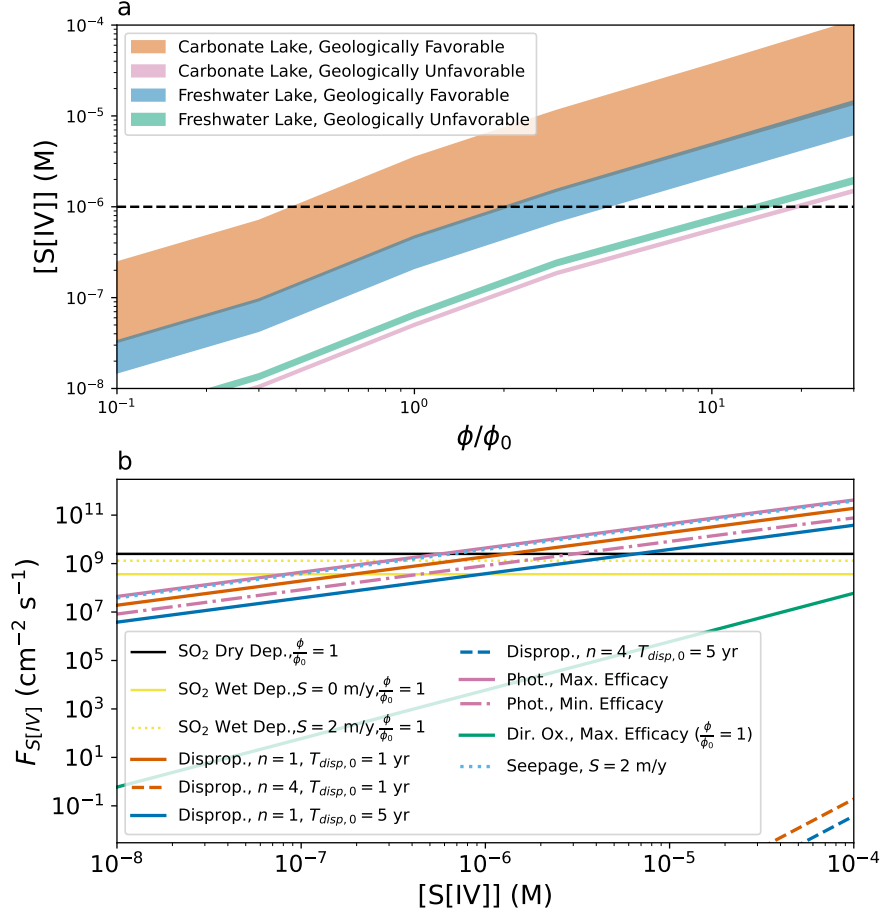
S.R. conceived research; K. A. developed solution analytics; K.A. and C.Y.Z. executed solution analytics; G. L. and C. K. developed and carried out preparation of solutions and UV-Vis spectroscopy; S. M. and S. R. carried out atmospheric photochemical modelling; S. R. developed and executed aqueous photochemistry modeling; N.S. critiqued aqueous modeling; S. R., Z. R. T., and D. D. S. explored implications for prebiotic chemistry; S. R. drafted manuscript. All authors reviewed and commented on the manuscript.

## Conflict of Interest

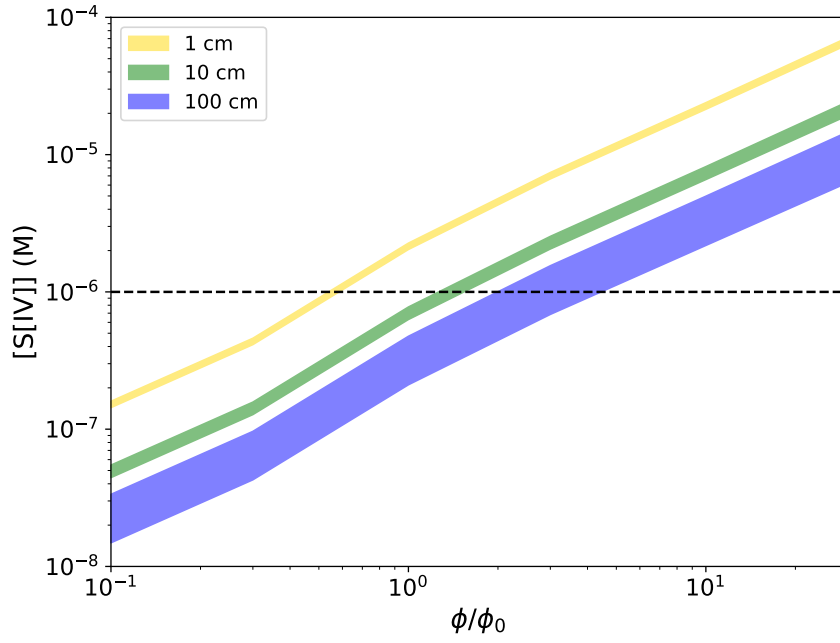
The authors declare no conflicts of interest relevant to this study.



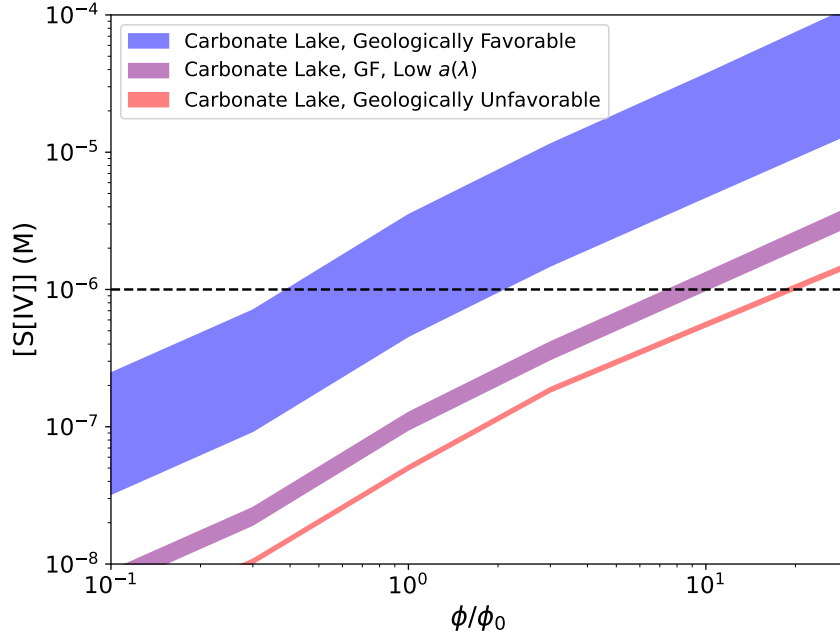
**Figure 4.** (a) Top: Range of  $S[IV]$  concentrations in the prebiotic ocean as a function of volcanic outgassing. Uncertainty in prebiotic marine  $[S[IV]]$  is dominated by uncertainties in the chemical parameters, with uncertainty in the geological parameters playing a secondary role. Regardless, the oceans do not saturate in  $S[IV]$  (vermillion dashed line).  $S[IV]$  saturation threshold calculated assuming Henry equilibrium with the atmosphere, including the first and second dissociations of  $SO_2$ , and for an acidic ocean  $pH = 6.25$  which favors saturation (Millero et al., 1989; Burkholder et al., 2015; Ranjan et al., 2018; Krissansen-Totton et al., 2018). The horizontal black dashed and dotted lines demarcate micromolar and nanomolar concentrations, respectively. (b) Bottom: Major  $S[IV]$  supply and loss processes in the prebiotic ocean, broken out to enable scrutiny of the details of our calculation. Each line represents the rate of  $S[IV]$  supply/loss as a function of  $[S[IV]]$ .  $pO_2$  adopted in estimating oxidation rate corresponds to  $\frac{\phi}{\phi_0} = 1$ ;  $pO_2$  decreases as  $\frac{\phi}{\phi_0}$  increases because of the increased reductant flux. The main chemical uncertainty is the order of the disproportionation reaction; if disproportionation is high-order, then sulfite disproportionation is kinetically inhibited (Kasting et al., 1989). Regardless, photolysis imposes an upper bound on  $[S[IV]]$  that keeps the oceans sub-saturated.



**Figure 5.** (a) Top: Range of  $[S(IV)]$  concentrations in prebiotic terrestrial waters as a function of volcanic outgassing. Range of  $[S(IV)]$  is dominated by geological scenario ( $[S(IV)]$ -minimizing vs.  $[S(IV)]$ -maximizing endmember; Table 3). The horizontal black dashed line demarcates micromolar concentrations. (b) Bottom: Major  $[S(IV)]$  supply and loss processes for the geologically-favorable ( $[S(IV)]$ -maximizing) carbonate lake scenario from (a), broken out to enable scrutiny of the details of our calculation. Each line represents the rate of  $[S(IV)]$  supply/loss as a function of  $[S(IV)]$ .  $p\text{O}_2$  adopted in estimating oxidation rate corresponds to  $\frac{\phi}{\phi_0} = 1$ ;  $p\text{O}_2$  decreases as  $\frac{\phi}{\phi_0}$  increases because of the increased reductant flux. The dotted lines show the enhanced wet deposition and seepage loss for  $S = 2 \text{ m/y}$ , corresponding to a lake with a porous bottom.



**Figure 6.**  $[S[IV]]$  in lakes as a function of volcanic outgassing, for lakes of depth 1 cm, 10, cm, and 100 cm. Shallow lakes favor S[IV] accumulation because of a shorter column for loss processes to operate over. Scenario corresponds to a prebiotic freshwater lake with geologically favorable parameters for S[IV] accumulation (Table 3). Spread for each scenario is due to uncertainties in chemical kinetics. The horizontal black dashed line demarcates micromolar concentrations.



**Figure 7.**  $[S[IV]]$  in prebiotic carbonate lakes for geologically favorable and geologically unfavorable scenarios for  $S[IV]$  accumulation (Table 3). The main difference between the favorable and unfavorable scenarios is the background absorptivity of the lake ( $a(\lambda)$ ), as illustrated by the purple curve, which corresponds to the favorable scenario with the sole modification that  $a(\lambda)$  is taken to correspond to the low-absorptivity endmember. The purple curve is closer to the red curve than the blue, illustrating the controlling role of  $a(\lambda)$  and the need to understand the UV absorptivity of prebiotic natural waters (Ranjan, Kufner, et al., 2022). Spread for each scenario is due to uncertainties in chemical kinetics. The horizontal black dashed line demarcates micromolar concentrations.

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# Supplementary Information: Geochemical and Photochemical Constraints on S[IV] Concentrations in Natural Waters on Prebiotic Earth

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**Introduction**

In this Supporting Information, we give further details on our work. These details are ancillary to the main thrust of our work, but are potentially of interest to specialists or individuals seeking to reproduce or validate our work. Specifically, in Section S1, we give further details of the experimental study of aged S[IV] solutions, including the solution-phase sulfite electropotentiometry, corroborative UV-Vis tracking, and information regarding failed experiments; in Section S2, we give further details of the atmospheric photochemical modeling, including species-by-species chemical boundary conditions; in Section S3, we present explicitly the details of our aqueous photochemical modeling, including our validation of our photolysis calculation against nitrate, and graphical presentation of key input data; in Section S4, we demonstrate that we can recover the main results of our detailed modeling with a simplistic order-of-magnitude calculation, increasing our confidence in the conclusions; in Section S5, we present a brief study of the sulfur mass balance in the experimental part of our study. In Data Set S1, we give the raw data from the solution-phase analytics, and show the processing applied to it to extract the measurements shown in Table 7 of the main text.

## S1. Further Details on S[IV] Lifetime Experiments

### S1.1. Further Details on Sulfite Electropotentiometry

#### S1.1.1. Effect of pH

The influence of pH on the potentiometric response of the ISE sensors to sulfite anion was studied by making calibration curves at pH values close to both neutral pH range (6.0–9.0), acidic pH range (3.5–4.5) and alkaline pH range (12.0–13.0) by using few drops of 6M HCl and NaOH as shown in Data Set S1. The reason behind studying the pH effect at different values is the presence of two electrically ionizable groups within the sulfite anion structure with pKa values of 1.9 and 7.2 (Beyad et al., 2014).

For this reason, the results showed that a significant differences in the corresponding calibration Nernstian slopes in acidic rather than neutral and alkaline conditions. At acidic conditions pH range (3.5–4.5), the sulfite anion is singly charged (monovalent ion,  $\text{HSO}_3^-$ ) when it was sensed by the ISE, and hence a Nernstian slope of almost  $47.2 \pm 5$  mV/concentration decade was obtained. While at neutral conditions (at pH 7.6), the sulfite anion is mostly sensed as divalent ion and the corresponding Nernstian slope of about  $30.0 \pm 3.0$  mV/concentration decade was obtained. At alkaline conditions (pH~13.0), the sulfite anion is fully doubly charged, and therefore it was sensed as divalent ion and the corresponding Nernstian slope of about  $27.0 \pm 2.0$  mV/concentration decade was obtained in the first day of measurements. However, one of the main challenges that was practically observed when considering sulfite measurements in extremely alkaline solution is the remarkable decrease in the slope in the following day of measurements, (especially upon longer exposure to an alkaline solution background as a storage solution between mea-

surements), which may possibly be attributed to interference of hydroxyl group (Hutchins et al., 1994).

### **S1.1.2. Dynamic Response Time**

Dynamic response time is an important factor for analytical applications of ISEs. In this study, practical response time was recorded by diluting the initial sulfite anion concentration (100 mM) up to 1000-fold. The required time for the sensors to reach values within  $\pm 2$  mV of the final equilibrium potential was  $\sim 40$  s for the three sensors. The time traces of the calibration curve of the sensors are presented in Data Set S1.

### **S1.1.3. Repeatability of the Measurements**

Repeatability of the potential reading for each sensor was examined by subsequent measurement in the range of 100 mM to 10  $\mu$ M of sulfite anion solution immediately after measuring the first set of samples. The electrode potential for three replicate measurements exhibit a standard deviation of 1.31, 1.42 and 1.21, respectively. While the corresponding values in samples solution of pH 13 showed a standard deviation of 1.59, 1.05 and 1.85, respectively. This indicates an acceptable repeatability of the potential response of the three proposed electrodes.

### **S1.1.4. Performance characteristics of the sulfite ISE**

The potentiometric response characteristics of the designed sensors (n=3) were checked by plotting the potential readings against the logarithmic concentrations as presented in Data Set S1. Results of performance characteristics showed that the linear dynamic range of our sulfite ISE (100 mM to 10  $\mu$ M) was comparable to that of another previously reported electrode (500 mM to 5  $\mu$ M; Hutchins et al. (1994)). The response times in samples with concentration higher than 10 mM were of the order of seconds ( $\sim 20$  s), whereas

in more diluted samples the time required to reach a stable potential was considerably longer, around 45 s for the three sensors.

The lifetime of the proposed sensors was evaluated by constructing calibration graph on different days over a period of three weeks. The prepared ISEs exhibited life span of 14 days; during this time the slope of calibration curves remained constant with no significant change in slopes of the calibration curves. After this period, a remarkable decrease in the slope was practically observed which might be attributed to the ionophore leaching from the sensing membrane as previously reported (Hutchins et al., 1994).

After 3 weeks of dry storage, the ISE is still sensitive to sulfite; it showed a close to Nernstian response ( $24.4 \pm 1$  mV/decade) in the linear range from 100 mM to 0.1 mM. The improvement in the electrode lifetime may be attributed to the leaching of the ionophore from the electrode matrix due to the lack of external storage solution and inner filling solutions. Therefore, the potentiometric sulfite-ISEs can be stored in dry conditions for relatively prolonged periods with no significant loss of performance characteristics.

### **S1.2. Further Details of UV-Vis Tracking**

Figures S1, S2, S3, and S4 present the detailed UV-Vis measurements summarized in main text Table 5.

### **S1.3. Failed Experiments**

We initially sought to explore a broader range of experimental conditions than discussed in the main text. Specifically, we sought to explore acidic solutions (pH=4), as well as solutions enriched in inorganic ions with compositions representative of carbonate lakes (Toner & Catling, 2020). We successfully prepared these solutions and tracked them with

UV-Vis spectroscopy. However, our solution-phase analytics failed for these additional solutions. We consequently do not report them in the main text, but for the sake of completeness we discuss them here. We also discuss here sample #2 of the 10 mM [S[IV]] unadjusted pH experimental condition, which we discarded because we suspected experimenter error in its preparation or storage.

### S1.3.1. Acidic S[IV] Solution

We prepared and aged solutions of 100 mM S[IV] adjusted to acidic pH=4 as the other samples. However, we were unable to measure [S[IV]] in the aged solution via electropotentiometry, because we were unable to construct stable calibration curves via serial dilution. We attribute this instability to significant speciation of S[IV] as SO<sub>2</sub> at this pH, which then exsolves, altering [S[IV]] over time. Indeed, in attempting to calibrate the ISE at pH=4 we observed strong sulfur smells from our calibration solutions, consistent with exsolution. We therefore do not report results for this regime.

However, we did conduct UV-Vis tracking of these samples (Figure S5), which reveals behaviour very different from the non-acidic samples. Specifically, the acidic samples are characterized by an absorbance *increase* with time (as opposed to decrease with the non-acidic samples), and the rate of change of absorbance is much higher than in the non-acidic samples. We hypothesize that these observations can be explained by disproportionation. This hypothesis explains the increase in absorbance with time, because the sulfite is turning into reduced forms of sulfur like thiosulfate or sulfide, which are more absorptive than sulfite. This hypothesis explains the faster rate of change in the acidic solutions relative to the non-acidic solutions, because we expect faster disproportionation at lower pH based on the overall reaction stoichiometry (main text Equations 2-3). Faster

disproportionation at low pH was mentioned in a non-peer-reviewed LBL technical report, which is consistent with this scenario (Searcy, 1981). These observations are suggestive (but not definitive) that S[IV] concentrations in very acidic waters should be lower than S[IV] concentrations in non-acidic waters due to enhanced efficiency of disproportionation.

### S1.3.2. “Carbonate Lake” Solutions

Our experimental study focuses on S[IV] in pure water, but other solutes were likely present in natural waters on prebiotic Earth which may have catalyzed or inhibited S[IV] loss (Vincent et al., 2021; Walton et al., 2022; Ranjan, Kufner, et al., 2022). For example, formaldehyde and alcohols stabilize sulfite, while ammonia and elemental sulfur catalyze sulfite disproportionation (Karchmer, 1970; de Carvalho & Schwedt, 2000; Meyer et al., 1979; Meyer et al., 1980b, 1980a). As a sensitivity test, we aged 100 mM sulfite in a background solution containing inorganic ions at concentrations motivated by closed-basin carbonate lakes (Toner & Catling, 2020). We constructed two sample waters, with compositions approximately motivated by a closed-basin carbonate lake with  $10^{-2}$  mol kg<sup>-1</sup> P. We constructed dilute (low ionic strength) and concentrated (high ionic strength) end-members to approximately bracket the range of compositions expected for such a lake, drawing primarily on Toner and Catling (2020) (especially their Figure S1), augmented by Ranjan, Kufner, et al. (2022) (their Table 2). For the dilute and concentrated end-members, we adjusted the solution to pHs of 9 and 7 respectively, reflecting the assumed [HCO<sub>3</sub>] and [CO<sub>3</sub>] (Ranjan, Kufner, et al., 2022). Given the high carbonate concentration in the concentrated scenario, we omitted Mg<sup>2+</sup> and chose a lower Ca<sup>2+</sup>, to minimize removal of carbonate by precipitation. Tables S5 and S6 summarize our preparation of these background waters.



As in the acidic case, our solution-phase analytics failed for the “carbonate lake” solutions. We were unable to confirm that the background ions present in the solution did not interfere with the ISE, and therefore were unable to robustly measure [S[IV]]. Consequently, we do not report results from this sensitivity test. However, as with the acidic case, we were able to conduct UV-Vis tracking of these samples. The UV-Vis evolution of these 100 mM sulfite-doped “carbonate lake” samples (Figure S6, S7) was very similar to the UV-Vis evolution of the 100 mM sulfite-doped non-acidic pure water samples (Figures S1-S3). This leads us to speculate that the ions in this sensitivity test did not radically accelerate or inhibit S[IV] loss.

### S1.3.3. Discarded Sample

One sample (10 mM S[IV], unadjusted pH, Sample #2) showed significantly lower pH (7.2 vs 8.3) compared to other samples in its experimental condition upon opening for solution-phase analytics. We have no explanation for why this particular sample showed lower pH than its peers, interpret this anomaly as evidence of experimenter error in the preparation or storage of this sample which somehow influenced its pH, and consequently do not report results from this sample in the main text. However, for completeness, we report its results here (Table S1). The lower UV-Vis absorptivity of this sample can be attributed to its lower pH, which would lead to greater speciation of S[IV] as less-absorptive  $\text{HSO}_3^-$  ( $\text{pK}_a = 7 - 7.2$ ; Millero, Hershey, Johnson, and Zhang (1989); Neta and Huie (1985)). The  $T_{\text{disp},0}$  inferred from this sample is  $T_{\text{disp},0} = 1.3$  years (electropotentiometry), which remains consistent with the  $T_{\text{disp},0} > 1$  year reported in the main text.

## **S2. Further Details on Atmospheric Photochemistry Simulation**

### **S2.1. Details of Atmospheric Photochemical Model**

We use the MIT Exoplanet Atmospheric Chemistry model (MEAC) to calculate the atmospheric composition as a function of volcanic outgassing flux (Hu et al., 2012). MEAC solves the 1D continuity-transport equation to calculate the steady-state composition of a planet’s atmosphere. Our version of MEAC incorporates new H<sub>2</sub>O cross-sections and correction of errors in CO<sub>2</sub> cross-sections, Henry’s Law estimation, and reaction rates (Ranjan et al., 2020; Hu, 2021; Ranjan, Seager, et al., 2022). Importantly, MEAC has recently been intercompared with two other models (Harman et al., 2015; G. Arney et al., 2016) for the case of prebiotic Earth-like planets, and produces consistent results as measured by pCO and O<sub>2</sub> false positives (Ranjan et al., 2020). MEAC encodes processes including wet and dry deposition, eddy diffusion, molecular diffusion and escape of H and H<sub>2</sub>, formation and deposition of S<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> aerosols, and photolysis. S<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> aerosols are assumed to have a mean particle diameter of 0.1 $\mu$ m in our model (Hu et al., 2013). Shortwave radiative transfer is calculated by the  $\delta$  two-stream approximation and includes gas absorption, Rayleigh scattering, and H<sub>2</sub>SO<sub>4</sub> and S<sub>8</sub> aerosol absorption and scattering. However, MEAC does not self-consistently calculate planetary climate, meaning adjustments to the temperature-pressure profile due to photochemical effects (e.g., haze formation) must be accounted for with separate calculations.

### **S2.2. Details of Planetary Scenario**

We construct our planetary scenario by modifying the abiotic CO<sub>2</sub>-dominated benchmark atmosphere of Hu et al. (2012). In Table S2, we present the simulation parameters of our photochemical model. In Table S3, we present the detailed boundary species-

by-species conditions associated with our photochemical model. We discuss the most important aspects of our planetary scenario here.

We assume bulk prebiotic atmospheric composition of 0.1 bar CO<sub>2</sub> and 0.9 bar N<sub>2</sub>, which produces clement global-mean temperatures on 3.9 Ga Earth, consistent with zircon evidence interpreted as evidence of global surface oceans in this epoch (Harrison, 2009; Rugheimer & Kaltenegger, 2018). We construct our temperature-pressure profile by assuming dry adiabatic evolution in the troposphere from a 290K surface to an isothermal 180K stratosphere (Pierrehumbert, 2010), which approximates detailed models of the prebiotic atmosphere<sup>1</sup> (Rugheimer & Kaltenegger, 2018). We assume an eddy diffusion profile scaled from modern Earth by atmospheric mean molecular mass (Hu et al., 2012). We estimate the top-of-atmosphere (TOA) irradiation from the 3.9 Ga Sun from Claire et al. (2012). We include 86 CHOSN species linked by 734 reactions, excluding the higher hydrocarbon chemistry relevant to organic haze formation (Ranjan, Seager, et al., 2022). This neglect is justified because at the very low CH<sub>4</sub> emission rates prevalent on prebiotic Earth, higher hydrocarbon formation is negligible (DeWitt et al., 2009; G. N. Arney et al., 2017; Harman, Pavlov, et al., 2018). We include CO and NO fluxes of  $3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$  at the base of the atmosphere to simulate the effects of lightning (Harman, Felton, et al., 2018; Hu & Diaz, 2019).

We set volcanic outgassing fluxes by scaling modern Earth outgassing fluxes. The choice of these modern fluxes requires comment, especially the critical modern SO<sub>2</sub> volcanic outgassing flux ( $\phi_{SO_2,0}$ ). Efforts to directly measure  $\phi_{SO_2,0}$  yield estimates of  $\phi_{SO_2,0} = 1 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ , mostly emitted non-eruptively at ground level (Halmer et al., 2002; Carn et al., 2017). However, these estimates are lower bounds, because they miss the

tail of weak  $\text{SO}_2$  sources which are numerically abundant (Carn et al., 2017; Catling & Kasting, 2017). Catling and Kasting (2017) argue that  $\phi_{\text{SO}_2,0} = 7 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ , based on scaling  $\text{CO}_2$  emission fluxes assuming equilibrium with modern magmas. We choose an intermediate value of  $\phi_{\text{SO}_2,0} = 3 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ , which has been used as a representative “Earth-like” value in the past (Hu et al., 2012). We take  $\phi_{\text{H}_2\text{S},0} = 3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ , based on the common assumption that  $\frac{\phi_{\text{H}_2\text{S},0}}{\phi_{\text{SO}_2,0}} = 0.1$  (Zahnle et al., 2006; Hu et al., 2012; Claire et al., 2014). We take  $\phi_{\text{H}_2,0} = 5 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$  and  $\phi_{\text{CO},0} = 4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$  (Catling & Kasting, 2017). We assume  $\text{CH}_4$  emission of  $3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$  due to serpentinization (Hu et al., 2012; Guzmán-Marmolejo et al., 2013). Serpentinization on early Earth may have been less efficient than on modern Earth (Tutolo et al., 2020); our calculations are robust to this uncertainty as  $\text{CH}_4$  has minimal photochemical influence on  $\text{SO}_2$ .

We scale modern earth volcanic emission fluxes by  $\frac{\phi}{\phi_0}$  to explore a broad range of volcanic outgassing levels. Volcanic outgassing rates on early Earth are highly uncertain (Catling & Kasting, 2017). A common assumption is for steady-state volcanic emission to have been enhanced up to an order of magnitude relative to the present day due to higher interior heat flux (Richter, 1985; Kasting et al., 1989; Sleep & Zahnle, 2001; Zahnle et al., 2006), but volcanic emission of sulfur species may also have been lower due to lower concentrations of recycled sulfur in melts due to low oceanic sulfate and sulfide (Harman, Pavlov, et al., 2018). Further, during major volcanic eruptions, volcanic outgassing may have been transiently enhanced by up to 2 orders of magnitude, though it is uncertain whether that  $\text{SO}_2$  was released primarily from fissures (i.e., at the surface) or from cones (i.e., into the upper atmosphere where it could be processed into aerosol instead of deposited as S[IV]) (Self et al., 2006; Halevy & Head, 2014; Claire et al., 2014;

Lamotte et al., 2021). We consequently consider a range of prebiotic volcanic gas emission rates relative to modern of  $\frac{\phi}{\phi_0} = 0.1 - 30$ , but caution that our reported pSO<sub>2</sub> for  $\frac{\phi}{\phi_0} \gtrsim 10$  represent an upper limit because of the uncertainty regarding release altitude.

### S2.3. Further Details on Simulation Outputs

In Table S4, we present the SO<sub>2</sub> mixing ratios and wet deposition rates predicted by our photochemical modeling. The SO<sub>2</sub> mixing ratios correspond to Figure 1 from the main text.

## S3. Further Details of Aqueous Photochemistry Model

### S3.1. Detailed Rationale for Range of Seepage Rates

We explore a range of seepage rates  $S = 0 - 2$  m/year for closed-basin terrestrial waters; in this section, we give the rationale for adopting this range. The lower limit for  $S$  is motivated by closed-basin lakes with impermeable bottoms. These systems are characterized by no surface outflow and water loss dominated by evaporation, resulting in concentration of solutes (Toner & Catling, 2019). Modeling of salinity and water budgets for some lakes excludes seepage altogether (Langbein, 1961; van der Kamp et al., 2008; Yapiyev et al., 2017). Estimates of seepage for Lake Titicaca range from  $\sim 0 - 10\%$  of evaporation, or  $\sim 0 - 0.15$  m year<sup>-1</sup> (Roche et al., 1992; Carmouze et al., 1992; Delclaux et al., 2007; Yapiyev et al., 2017). Modeling of oxygen isotopes in Lakes Scanlon and Castor reveals outseepage of  $0.5 \pm 0.3\%$  and  $1.5 \pm 0.3\%$  of the lake volume per month, respectively, corresponding to seepage rates of  $0.4 - 0.5$  m year<sup>-1</sup> and  $2$  m year<sup>-1</sup>, respectively (Steinman et al., 2010). A value of  $2$  m year<sup>-1</sup> also corresponds to the average seepage rate in fishponds near Auburn, Alabama; this rate is higher than the seepage seen in many

natural ponds (Boyd, 1982; Pearce et al., 2017), and we adopt it as the upper bound of the range we explore.

### S3.2. Details of Direct Oxidation Calculation

#### S3.2.1. Details of estimation of $k''$ from $k$

For modern seawater at pH=8.2, Zhang and Millero (1991) report

$$\log_{10}\left(\frac{k}{1\text{M}^{-1.5}\text{min}^{-1}}\right) = 19.54 - 5069.47T^{-1} + 14.74I^{0.5} - 2.93I - 2877.0I^{0.5}T^{-1} \quad (1)$$

where  $T$  is temperature,  $I$  is molal ionic strength, and this relation is valid for  $T = 288 - 318\text{K}$  and  $I = 0 - 0.72$  (salinity  $S_A = 0 - 35$ ). We use this expression for  $k$  to estimate  $k''$ , according to the equation (Zhang & Millero, 1991):

$$k'' = \frac{k}{\alpha_{\text{SO}_3^{2-}, \text{seawater}} \alpha_{\text{HSO}_3^-, \text{seawater}}} \quad (2)$$

where  $\alpha_{\text{SO}_3^{2-}, \text{seawater}}$  is the mol fraction of S[IV] in  $\text{SO}_3^{2-}$  and  $\alpha_{\text{HSO}_3^-, \text{seawater}}$  is the mol fraction of S[IV] in  $\text{HSO}_3^-$  in seawater at  $S_A = 35$  and  $T = 298\text{K}$ . We estimate  $\alpha_{\text{SO}_3^{2-}}$  and  $\alpha_{\text{HSO}_3^-}$  according to the equations (Millero et al., 1989; Zhang & Millero, 1991):

$$I = \frac{0.0199S_A}{1 - 10^{-3}S_A} \quad (3)$$

$$pKa_1^* = 1.87 - 0.50I^{0.5} + 0.31I (T = 298\text{K}) \quad (4)$$

$$pKa_2^* = 7.12 - 1.052I^{0.5} + 0.36I \quad (5)$$

$$\alpha_{\text{HSO}_3^-} = \left(\frac{[H^+]}{K_1^*} + \frac{K_2^*}{[H^+]} + 1\right)^{-1} \quad (6)$$

$$\alpha_{\text{SO}_3^{2-}} = \left(\frac{[H^+]^2}{K_1^*K_2^*} + \frac{[H^+]}{K_2^*} + 1\right)^{-1} \quad (7)$$

Where  $Ka_1^*$  and  $Ka_2^*$  correspond to the first and second dissociation constants for  $\text{SO}_2$ , and  $pKa = -\log_{10}(Ka)$  as usual. These expressions assume the main forms of S[IV] to



be  $\text{SO}_2$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$ . They are invalid at high  $[\text{S[IV]}]$ , where sulfite dimers form (Beyad et al., 2014). We do not deploy our models in this regime.

With this formalism, we are able to reproduce the  $k''$  measured at  $\text{pH}=8.2$  to within 0.11 log units<sup>2</sup> (Figure 7 of Zhang and Millero (1991)). Note that for solutions with relative solute concentrations corresponding to seawater, there is additional pH dependence not fully captured by this formalism; Zhang and Millero (1991) attribute this to pH-dependent complex formation in seawater. These uncertainties do not affect our conclusions because direct oxidation is not a significant loss mechanism for S[IV] in the anoxic conditions prevalent on prebiotic Earth.

### S3.2.2. Details on Estimation of $[\text{O}_2]$

We estimate  $[\text{O}_2]$  using Henry’s Law, i.e.:

$$[\text{O}_2] = H_{\text{O}_2} p\text{O}_2(z = 0) \quad (8)$$

Photochemical models predict abiotic  $\text{O}_2$  volume mixing ratios to be sub-parts per billion (ppb) (Kasting & Walker, 1981; Ranjan et al., 2020), while the upper limit on  $\text{O}_2$  mixing ratio derived from model interpretation of the sulfur mass-independent fractionation signal (S-MIF) is  $2 \times 10^{-7}$  (Zahnle et al., 2006). We adopt  $p\text{O}_2$  from our photochemical model calculations. We take  $H_{\text{O}_2} = 1.3 \times 10^{-3}$  M/bar (Sander et al., 2011; Sander, 2015), which is valid for 298 K and 0 salinity. Increased salinity would decrease  $H_{\text{O}_2}$  and hence  $[\text{O}_2]$ , suppressing direct oxidation even more than calculated here.

## S3.3. Further Details on Aqueous Photolysis Calculation

### S3.3.1. Detailed Derivation of Depth-Dependent Photolysis Rate Coefficient

We calculate the photolysis rate coefficient for loss of species  $X$ ,  $J_X(d)$  ( $\text{s}^{-1}$ ), at depth  $d$  according to the equation:

$$J_{\text{SO}_3^{2-}}(d) = \int d\lambda \Phi_{\text{SO}_3^{2-}}(\lambda) \sigma_{\text{SO}_3^{2-}}(\lambda) \dot{E}(\lambda, d) \quad (9)$$

$$J_{\text{HSO}_3^-}(d) = \int d\lambda \Phi_{\text{HSO}_3^-}(\lambda) \sigma_{\text{HSO}_3^-}(\lambda) \dot{E}(\lambda, d) \quad (10)$$

In this section, we provide a detailed walkthrough of how each parameter in this equation was estimated from the literature.

**S[IV] Absorption Cross-Sections:** We compute the absorption cross-section  $\sigma$  from the linear decadic absorption coefficient  $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ), which is more commonly reported for aqueous absorbers, according to the equation (Lakowicz, 2010):

$$\sigma = \frac{10^3 \ln(10)}{N_A} \epsilon \quad (11)$$

where  $N_A$  is Avogadro's number, and  $\sigma$  and  $\epsilon$  are in units of  $\text{cm}^2$  and  $\text{M}^{-1} \text{cm}^{-1}$  respectively. We take  $\epsilon$  for  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  from Fischer and Warneck (1996) and Beyad et al. (2014), as synthesized by Ranjan, Kufner, et al. (2022). We neglect corrections to absorptivity and quantum yield due to high ionic strength (Sauer, Shkrob, et al., 2004).

**S[IV] Photolysis Quantum Yields:** We synthesize estimates for  $\Phi_{\text{HSO}_3^-}(\lambda)$  and  $\Phi_{\text{SO}_3^{2-}}(\lambda)$  based on laboratory measurements. These laboratory measurements are summarized in Table S7 and fall into two types. Many of these studies sought to quantify the quantum yields of primary photolysis, i.e. production of  $H$  for  $\text{HSO}_3^-$  photolysis and production of  $\text{e}_{aq}^-$  for  $\text{SO}_3^{2-}$  photolysis. However, this is not necessarily the same as the quantum yield of net loss of the photolyzed molecules, because  $H$  and  $\text{e}_{aq}^-$  can subsequently undergo back-reactions to regenerate  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ , respectively (Sauer,

Crowell, & Shkrob, 2004; Lian et al., 2006; Li et al., 2012, 2014). The efficacy of the back-reaction depends on the composition of the solution: if scavengers for the photoproduct radicals are present, the back-reaction is inefficient and the net loss to photolysis is higher (Fischer & Warneck, 1996).

In this study, we assume the quantum yield of sulfite and bisulfite photolysis ( $\Phi$ ) to be equal to the quantum yield of net loss of sulfite and bisulfite due to photolysis ( $\Phi_C$ ; Fischer and Warneck (1996)). Our choice is motivated by the more abundant data available for direct photolysis, as well as by the belief that in natural waters scavengers for radicals like  $H$  and  $e_{aq}^-$  would likely have been present that would have inhibited the back-reaction. This is the case for  $NO_X^-$ , which is regenerated after photolysis in pure water but not in natural waters (Zafiriou & True, 1979b, 1979b; Mack & Bolton, 1999). In efforts to measure both  $\Phi$  and  $\Phi_C$ ,  $\Phi_C$  has been within a factor of 1.6 of  $\Phi$  (Fischer & Warneck, 1996). Our conclusions are robust to such uncertainty in  $\Phi$ .

We approximate the quantum yield of sulfite photolysis as a piecewise linear function, anchored by measured quantum yields (Figure S15). This simple approach guarantees reproduction of measured quantum yields while conforming to the theoretical expectation that quantum yields should be nonincreasing as wavelength increases (Li et al., 2012; Wu et al., 2021). Where available, we adopt the terminal quantum yields, as opposed to the prompt quantum yields; the terminal quantum yields account for geminate recombination immediately after photolysis. Our function is anchored by  $(\lambda, \Phi_{SO_3^{2-}})$  of (193 nm, 0.39) (Sauer, Crowell, & Shkrob, 2004), (200 nm, 0.23) (Lian et al., 2006), (248 nm, 0.11) (Sauer, Crowell, & Shkrob, 2004) and (253.7 nm, 0.116) (Li et al., 2012). Sauer, Crowell, and Shkrob (2004) argue that measurements based on scavenger actinometry overestimate  $\Phi$ ,

because at the high concentrations employed in such studies the scavenger itself interfered with the process of photolysis, e.g. through scavenging geminate electrons. Based on their argument, we do not utilize the quantum yield at 254 nm measured by Fischer and Warneck (1996) using scavenger actinometry, which is indeed higher ( $\sim 4\times$ ) than follow-up studies which are otherwise consistent (Li et al., 2012, 2014). We are not aware of constraints on  $\Phi_{SO_3^{2-}}$  at wavelengths  $> 253.7\text{nm}$ . To bracket the possibilities, we explore  $\Phi_{SO_3^{2-}}(> 253.7\text{nm}) = 0$  and  $\Phi_{SO_3^{2-}}(> 253.7\text{nm}) = \Phi_{SO_3^{2-}}(253.7\text{nm})$  (Figure S15).

Measurements of the quantum yield of bisulfite photolysis are extremely scarce. The sole measurement we found is that of Fischer and Warneck (1996) at 214 nm, but that measurement must be interpreted as an upper limit (Sauer, Crowell, & Shkrob, 2004). We convert the upper limit of Fischer and Warneck (1996),  $\Phi_{HSO_3^-}^{UL}$ , to an estimate of  $\Phi_{HSO_3^-}$  by assuming that  $\Phi_{HSO_3^-}^{UL}$  is enhanced proportionately to  $\Phi_{HSO_3^-}$  as their estimate of  $\Phi_{SO_3^{2-}}^{UL}$  is enhanced relative to  $\Phi_{SO_3^{2-}}$ :

$$\Phi_{HSO_3^-}(214\text{nm}) = \frac{\Phi_{SO_3^{2-}}(253.7\text{nm})}{\Phi_{SO_3^{2-}}^{UL}(253.7\text{nm})} \times \Phi_{HSO_3^-}^{UL}(213.9\text{nm}) \quad (12)$$

implying that  $\Phi_{HSO_3^-}(213.9\text{nm}) = \frac{0.116}{0.39} \times 0.19 = 0.057$ . This still leaves the question of how to treat photolysis at other wavelengths. In the absence of guiding data, we assume bisulfite photolysis quantum yields to be proportional to sulfite quantum yields, i.e.:

$$\Phi_{HSO_3^-} = \frac{\Phi_{HSO_3^-}(213.9\text{nm})}{\Phi_{SO_3^{2-}}(213.9\text{nm})} \Phi_{SO_3^{2-}} \quad (13)$$

We sensitivity-test our conclusions to the possibility that  $\Phi_{HSO_3^-} = 0$  and find our overall conclusions to be unaffected, justifying this treatment, but advocate for better constraints on this quantity to improve our calculations (Main Text Section 5.4).

**Estimation of Scalar Irradiance:** We estimate the scalar irradiance  $\dot{E}(\lambda, d)$  by adapting the treatment of Morel (1991), which was originally developed to treat photosynthetically active radiation in the modern ocean. We begin by estimating the downwelling (planar) irradiance (flux)  $E_d(\lambda, d)$  (Morel, 1991; Mobley et al., 2009):

$$E_d(\lambda, d) = E_d(\lambda, 0^-) \exp\left(-\int_0^d dx K_d(\lambda, x)\right) \quad (14)$$

Here,  $E_d(\lambda, 0^-)$  is the downwelling irradiance just below the surface and  $K_d$  is the apparent vertical Napierian downwelling attenuation coefficient.

We estimate  $E_d(\lambda, 0^-)$  from the downwelling flux just above the surface,  $E_d(\lambda, 0^+)$ , according to the equation (Morel, 1991; Sakshaug et al., 1997):

$$E_d(\lambda, 0^-) = r_{sky} E_{d,sky}(\lambda, 0^+) + r_{sun} E_{d,sun}(\lambda, 0^+) \quad (15)$$

Where  $E_{sky}(\lambda, 0^+)$  is the diffuse irradiance just above the surface,  $r_{sky}$  is the reflectance of the diffuse irradiance,  $E_{sun}(\lambda, 0^+)$  is the direct (solar) irradiance just above the surface,  $r_{sun}$  is the reflectance of the direct irradiance (altitude-dependent), and  $E_d(\lambda, 0^+) = E_{sky}(\lambda, 0^+) + E_{sun}(\lambda, 0^+)$ . We take  $E_{sun}(\lambda, 0^+)$  and  $E_{sky}(\lambda, 0^+)$  from Ranjan and Sassellov (2017), assuming a prebiotic Earth atmospheric composition from Rugheimer, Segura, Kaltenegger, and Sassellov (2015), a solar zenith angle  $\theta_{sun} = 60^\circ$ , and a surface albedo  $A = 0.2$  ( $A$  and  $\theta_{sun}$  chosen for consistency with Rugheimer et al. (2015)). We take  $r_{sky} = 0.066$  (Morel, 1991; Cockell, 2000). We compute  $r_{sun}$  as a function of solar zenith angle via the Fresnel equations assuming unpolarized light incident on a flat water surface and a ratio of aqueous and aerial indices of refraction of  $\frac{n_{aq}}{n_{air}} = 1.33$  (Kirk, 1994), following

Cockell (2000). Reflectance losses are small for  $\theta_{sun} < 70^\circ$  (Kirk, 1984), meaning that our sensitivity to these assumptions is minimal.

The heart of the aqueous radiative transfer calculation is computation of  $K_d$ . Precisely calculating  $K_d$  requires a full solution of the aqueous radiative transfer equations as a function of Napierian absorption coefficient  $a(\lambda, d)$ , Napierian scattering coefficient  $b(\lambda, d)$ , the volume scattering function for the water in question, and the radiance distribution above the surface (Kirk, 1984; Morel, 1991). Given these complexities,  $K_d$  is in practice generally empirically constrained or estimated (Thomas & Stamnes, 2002). We follow Morel (1991) in estimating  $K_d$  according to the equation (Kirk, 1984):

$$K_d = \frac{a}{\mu_0} [1 + (0.425\mu_0 - 0.19)\frac{b}{a}]^{0.5} \quad (16)$$

where  $\mu_0$  is the average cosine for downwelling radiation. This expression is valid for waters with volume scattering function corresponding to the waters of modern San Diego Harbor (Kirk, 1984). We estimate  $\mu_0$  according to the equation (Morel, 1991):

$$\mu_0(\lambda) = \frac{1}{E_d(\lambda, 0^-)} [\mu_{sun,aq} E_{d,sun}(\lambda, 0^-) + \mu_{sky,aq} E_{d,sky}(\lambda, 0^-)] \quad (17)$$

Here,  $E_{d,sun}(\lambda, 0^-)$  is the component of  $E_d(\lambda, 0^-)$  due to the direct solar irradiance,  $E_{d,sky}(\lambda, 0^-)$  is the component of  $E_d$  due to the sky (diffuse) irradiance,  $\mu_{sun,aq}$  is the cosine of the solar zenith angle after refraction, and  $\mu_{sky,aq} = 0.86$  is the cosine of the sky zenith angle after refraction.

The above formalism to estimate  $K_d$  is complex. To determine the sensitivity of our results to the estimation of  $K_d$ , we consider two simpler approximations for  $K_d$ . First, we estimate  $K_d = \frac{1.0395}{\mu_0}(a + b_b)$ , where  $b_b$  is the backscattering coefficient; this expression is known to be valid for diverse marine waters (Morel et al., 2007). Second, we estimate

$K_d = \frac{a}{\cos(\theta_{sun,aq})}$ , ignoring scattering entirely. Our conclusions were unaffected, indicating that they are robust to choice of  $K_d$  calculation technique.

We take values for  $a$  from Ranjan, Kufner, et al. (2022), converting their linear decadic absorption coefficients  $\epsilon$  to linear Napierian absorption coefficients via  $a = \epsilon \ln(10)$  (Kirk, 1994). We adopt  $b$  from the tabulation of Smith and Baker (1981) for modern freshwater and seawater. We use modern freshwater  $b$  for prebiotic freshwater lakes, and the Smith and Baker (1981) seawater  $b$  for the prebiotic ocean and prebiotic carbonate lakes. We approximate  $b_b = 0.5b$  (Smith & Baker, 1981). This approximation is valid for waters with low particulate scattering, which is reasonable for early Earth since prebiotic waters should have been less scattering than modern waters due to the absence of biogenic organics (Cockell, 2000; Morel et al., 2007).

So far, we have computed the downwelling plane irradiance  $E_d$ , which calculates the net flow of energy across a plane, but the quantity required to estimate photolysis rates is  $\dot{E}$ , the scalar irradiance. We estimate  $\dot{E}$  according to (Morel, 1991; Mobley et al., 2009):

$$\dot{E}(\lambda, d) \approx \frac{K_d(\lambda, d)}{a(\lambda, d)} E_d(\lambda, d) \quad (18)$$

This formalism is valid for waters which are absorption-dominated, as is the case for most natural waters on modern Earth (Morel, 1991; Sakshaug et al., 1997; Cockell, 2000). However, it is possible that some natural waters may be scattering-dominated on early Earth, in which case the above expression would dramatically overestimate  $\dot{E}$ . We impose an ad-hoc correction for this case by imposing a ceiling on  $\dot{E}$ ,  $\dot{E}_{max} = 2.5 \frac{E_d}{\mu_0}$ . This ad-hoc correction is based on the finding of Kirk (1994) that for extremely highly scattering waters,  $\frac{\dot{E}}{E_d} = 2.0 - 2.5$  for vertically incident light ( $\mu_0 = 1$ ), and adding a correction for  $\mu_0 \neq 1$ .

### S3.3.2. Photolysis Calculation Validation With Nitrate

We validate our photolysis calculation method by using it to estimate the photolysis of nitrate in modern ocean water and comparing it to the estimates of Zafiriou and True (1979a). We use nitrate absorption cross-sections from Ranjan, Kufner, et al. (2022), nitrate photolysis quantum yields from Mack and Bolton (1999) (their Table 2), UV surface flux from Ranjan and Sassellov (2017) (their modern Earth validation case), and oceanic attenuation coefficients from Smith and Baker (1981) (corresponding to the clearest modern ocean waters). We find that our method estimates a surface photolysis rate for nitrate which fits within the range of surface photolysis rates measured by Zafiriou and True (1979a) (our estimate:  $5 \times 10^{-8} \text{ s}^{-1}$ , Zafiriou and True (1979a):  $8 \times 10^{-9} - 7 \times 10^{-8} \text{ s}^{-1}$ , median  $2 \times 10^{-8} \text{ s}^{-1}$ ). Consistency with this measurement is an important check on our methodology.

We compare our estimate of column-integrated photolysis rate to the simplified calculation of Zafiriou and True (1979a). In estimating the column-integrated photolysis rate, we explicitly integrate over depth and include wavelength-dependent attenuation via clear ocean water (Smith & Baker, 1981), while Zafiriou and True (1979a) follow a simplified procedure, assuming step-function photolysis down to the 310 nm photic depth of ocean water. We estimate a column-integrated photolysis rate  $8\times$  that of Zafiriou and True (1979a). Of this, a factor of  $2\times$  is attributable to our higher surface photolysis rate compared to the median; a factor of  $3.0\times$  is attributable to our explicit integration over depth; and a factor of  $1.2\times$  is attributable to our consideration of wavelength-dependent attenuation. This calculation demonstrates the necessity of explicit integration over depth in calculating photolysis rates.



We conclude that the validation case of nitrate photolysis in the modern ocean suggests that our procedure is capable of estimating column-integrated photolysis rate to within an order of magnitude but may overestimate photolysis rate by a factor of a few, possibly due to neglect of back-reactions which reform the photolyzed substrate.

### S3.4. Graphical Representations of Key Inputs.

In Section 3.4 of the main text, we described key inputs into our aqueous photochemistry model. Here, we provide graphical representations of these inputs, for easy evaluation by readers. Specifically, Figure S10 presents the surface UV flux at the base of the atmosphere, from Ranjan and Sasselov (2017); it can be compared to similar<sup>3</sup> estimates (Cockell, 2002; Rugheimer et al., 2015). Figures S11, S12, and S13 present the high- and low-absorbance endmembers considered for the prebiotic oceans, freshwater lakes, and carbonate lakes, modified from Ranjan, Kufner, et al. (2022) by removing S[IV] species; the ocean case can be compared to Anbar and Holland (1992). Figure S14 presents  $\sigma_{HSO_3^-}(\lambda)$  and  $\sigma_{SO_3^{2-}}(\lambda)$ , based on underlying data from Fischer and Warneck (1996) and Beyad et al. (2014) and synthesized by Ranjan, Kufner, et al. (2022). Figure S15 presents  $\Phi_{HSO_3^-}(\lambda)$  and  $\Phi_{SO_3^{2-}}(\lambda)$ , estimated as described in Section 3.4.1.1, along with the literature measurements at specific wavelengths on which the estimate is based.

### S3.5. Detailed Rationale For Parameter Choices in Limiting Endmember Geological Scenarios

In Section 3.5 of the main text, we constructed S[IV] maximizing and minimizing end-member scenarios for the prebiotic ocean and a fiducial prebiotic closed-basin carbonate and freshwater lakes (Tables 2, 3). Here, we give the detailed rationale behind the parameter choices in constructing those endmember scenarios.

For the prebiotic ocean, we consider a pH range of 6.25-9 (Krissansen-Totton et al., 2018; Kadoya et al., 2020; Sahai et al., 2022), with higher pH corresponding to less S[IV] because of speciation as  $\text{SO}_3^{2-}$ , which is more vulnerable to photolysis. We consider background marine UV linear decadic absorption coefficients corresponding to the low-absorption and high-absorption endmember scenarios from Ranjan, Kufner, et al. (2022), with S[IV] removed. Low absorption minimizes S[IV] due to more efficient photolysis. Higher  $I$  corresponds to less S[IV] due to more efficient direct oxidation; we would like to consider an ionic strength range of  $I = 0.3 - 1.2$  (Knauth, 2005; Marty et al., 2018), but are forced to impose a ceiling of 0.72 on  $I$  because of limitations of the formalism we use to estimate direct oxidation rates of S[IV] (Zhang & Millero, 1991); this does not affect our conclusions because direct oxidation is a minor loss process for S[IV] (Section 4). This approach is purely parametric, and not self-consistent (i.e. we are merely choosing extreme values from the literature, not conducting self-consistent modeling of a specific scenario).

As with marine waters, we explore a wide range of parameter space to construct extremal endmember S[IV]-maximizing and -minimizing scenarios for closed-basin carbonate and freshwater lakes (Table 3). For carbonate lakes, we draw pH and ionic strength estimates from (Toner & Catling, 2020). We are forced to impose a ceiling of 0.72 on  $I$  because of limitations of the formalism we use to estimate direct oxidation rates of S[IV]; this does not affect our conclusions because direct oxidation is a minor loss process for S[IV] (Figure 5). For freshwater lakes, we draw pH and ionic strength estimates from (Hao et al., 2017). For both lakes, we draw estimates of background UV absorptivity from Ranjan, Kufner, et al. (2022), with S[IV] species removed. As in the marine case, the higher pH, higher

$I$ , and less absorptive waters minimize S[IV]. We consider  $S = 0 - 2 \text{ m year}^{-1}$  (Main Text Section 3.3.2). As in the marine case, our approach is purely parametric, and is not self-consistent.

#### S4. Simplified Order-of-Magnitude Calculation

The model calculation we have described in this paper is complex, raising the risk that it contains an implementation error that might invalidate its results. In this section, we carry out a simplified order-of-magnitude analytic calculation and demonstrate recovery of our main finding that sulfite was a trace prebiotic reagent, with higher concentrations in terrestrial waters compared to marine waters. The agreement of this highly simplified calculation with our full model increases our confidence in our conclusions.

We seek to solve Equation 6:

$$F_{sources,S[IV]} = F_{sinks,S[IV]}$$

The primary fate of atmospheric  $\text{SO}_2$  is deposition back to the surface. So, we can approximate  $F_{sources,S[IV]} \approx \phi_{\text{SO}_2}$ , taking a drainage ratio of 1. The main sink of aqueous S[IV] is photolysis. So we can take  $F_{sinks,S[IV]} \approx F_{h\nu,S[IV]} = [S[IV]] \int d\lambda \phi_{S[IV]}(\lambda) \sigma_{S[IV]}(\lambda) \dot{E}(\lambda, d)$ . For transparent shallow terrestrial waters, we can further simplify  $F_{h\nu,S[IV]} \approx [S[IV]] \times d \times \int d\lambda \Phi_{S[IV]}(\lambda) \sigma_{S[IV]}(\lambda) \dot{E}(\lambda, 0) \approx [S[IV]] \times d \times \Delta\lambda \times \overline{\Phi_{S[IV]} \sigma_{S[IV]} \dot{E}(\lambda, 0)}$ . Rearranging, for shallow terrestrial waters we have

$$[S[IV]] \approx \frac{\phi_{\text{SO}_2}}{d \Delta\lambda \overline{\Phi_{S[IV]} \sigma_{S[IV]} \dot{E}(\lambda, 0)}}$$

For a 1-m lake at basic pH at Earthlike outgassing, S[IV] is present as  $\text{SO}_3^{2-}$ , and we can estimate by eye from Figures S10-S15 that

$$\begin{aligned}
 [S[IV]] &\approx \frac{3 \times 10^9 \text{cm}^{-2} \text{s}^{-1}}{100 \text{cm} \times 80 \text{nm} \times 0.2 \times 10^2 \text{M}^{-1} \text{cm}^{-1} \times 10^{12} \text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}} \\
 &= \times 10^{-8} \text{M}
 \end{aligned}$$

which is the same order of magnitude as our detailed calculation (Figure 4, purple curve,  $\frac{\phi}{\phi_0} = 1$ ).

If we instead assume acidic pH, such that S[IV] is present as  $\text{HSO}_3^-$ , we instead estimate

$$\begin{aligned}
 [S[IV]] &\approx \frac{3 \times 10^9 \text{cm}^{-2} \text{s}^{-1}}{100 \text{cm} \times 100 \text{nm} \times 0.1 \times 10^1 \text{M}^{-1} \text{cm}^{-1} \times 10^{12} \text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}} \\
 &= 10^{-7} \text{M}
 \end{aligned}$$

which recovers our finding that S[IV] can accumulate to higher concentrations when present as  $\text{HSO}_3^-$  at lower pH, consistent with environmental chemistry studies (Li et al., 2012).

For the ocean, assuming efficient S[IV] chemical loss,  $n = 1$ , disproportionation dominates loss, and  $F_{\text{sinks}, S[IV]} \approx d \times [S[IV]] T_{\text{disp}, 0}^{-1}$ . Then, we estimate

$$\begin{aligned}
 [S[IV]] &\approx \frac{\phi_{\text{SO}_2}}{dT_{\text{disp}, 0}^{-1}} \\
 &\approx \frac{3 \times 10^9 \text{cm}^{-2} \text{s}^{-1}}{3 \times 10^5 \text{cm} \times (3 \times 10^7 \text{s})^{-1}} \\
 &= 3 \times 10^{11} \text{cm}^{-3} \\
 &= 10^{-9} \text{M}
 \end{aligned}$$

which is the same order of magnitude as our detailed calculation (Figure 3, yellow curve,  $\frac{\phi}{\phi_0} = 1$ ).

If on the other hand S[IV] chemical loss is inefficient, then photolysis dominates S[IV] loss, as in the lake case. However, unlike the lake case, for the ocean the optically thin assumption is not valid; at depth, every incident photon will be absorbed by either S[IV] or seawater in proportion to their spectral absorbances. We can therefore write  $\phi_{SO_2} \approx \overline{\Phi_{S[IV]}}(\Delta\lambda\dot{E}(\lambda, 0)) \frac{[S[IV]]\overline{\sigma_{S[IV]}}}{\overline{a_{ocean}} + [S[IV]]\overline{\sigma_{S[IV]}}}$

Solving for [S[IV]], we find

$$\begin{aligned} [S[IV]] &\approx \frac{\overline{a_{ocean}}}{\overline{\sigma_{S[IV]}} \left( \frac{\Delta\lambda\dot{E}(\lambda, 0)\overline{\Phi_{S[IV]}}}{\phi_{SO_2}} - 1 \right)} \\ &= \frac{10^{-3} \text{cm}^{-1}}{10^2 \text{M}^{-1} \text{cm}^{-1} \left( \frac{80 \text{nm} \times 10^{12} \text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1} \times 0.2}{3 \times 10^9 \text{cm}^{-2} \text{s}^{-1}} - 1 \right)} \\ &= 10^{-8} \text{M} \end{aligned}$$

which is the same order of magnitude as our detailed calculation (Figure 3, green curve,  $\frac{\phi}{\phi_0} = 1$ ).

The above calculations are not accurate, because they consider only a few of the relevant processes and because they neglect the spectral shapes of the relevant variables and their interplay, and one should not read too much into them. However, that the general conclusions extracted from them broadly agree with the more detailed, accurate model strengthen our confidence in the general findings from the more accurate model.

## S5. Sulfur Mass-Balance

In this section, we briefly discuss the mass balance of sulfur in our samples, and specifically whether our experimental results can be explained solely by direct oxidation from O<sub>2</sub> leakage, or whether disproportionation is required to explain them. If direct oxidation is the main loss mechanism removing S[IV] from our samples, then the S[IV] lost by our samples should be stoichiometrically converted to sulfate (S[VI]), and the amount of sulfite

lost should equal the amount of sulfate gained. On the other hand, if disproportionation is a major contributor to loss of S[IV], then more S[IV] should be lost from the samples than sulfate gained, because some of the disproportionated S[IV] will become reduced sulfur species.

We evaluate this mass balance in Table S8 (see also Data Set S1). We find that all samples are consistent with the operation of disproportionation, in that in all samples [S[IV]] decreased, [S[VI]] increased, and less S[VI] appeared than S[IV] was lost. However, most of our samples were also consistent within experimental error of stoichiometric conversion of S[IV] to S[VI], as expected from direct oxidation. We are able to rule out direct oxidation as the sole S[IV] loss mechanism to  $\geq 3\sigma$  confidence in only 3/14 of our samples, and to  $\geq 5\sigma$  confidence in just 1/14 samples. We suggest our results are best explained by a combination of direct oxidation and disproportionation of S[IV], but that improved experimental precision is required to conduct a more substantive and high-confidence mass balance analysis.

**Data Set S1.** The Excel file `sulfite_solution_phase_raw_processed_data_v5.xlsx` gives the raw data from the solution-phase analytics of the long-term S[IV] experiment, and shows the processing applied to these data to generate the information presented in Table 5 of the main text. This file is available as Supporting Information and also on Zenodo (Ranjan, 2023) and GitHub (<https://github.com/sukritranjan/sulfite-kinetics-release>).

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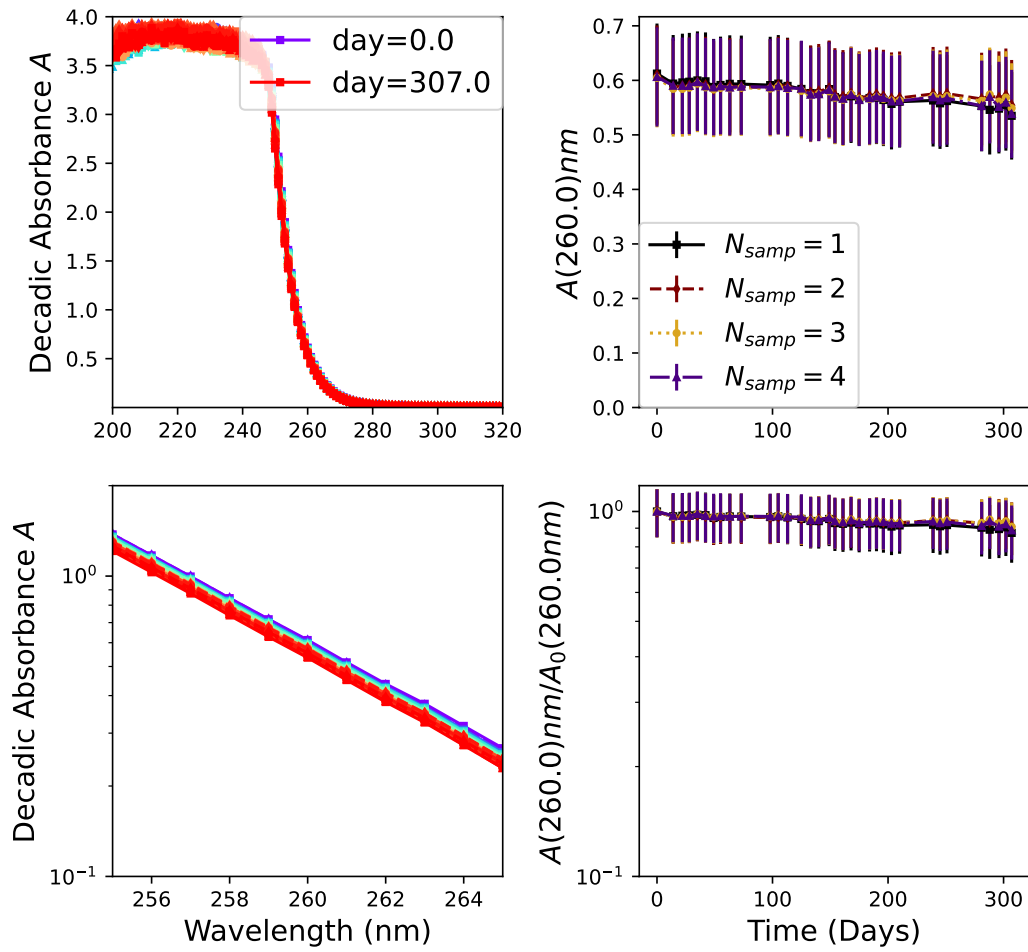
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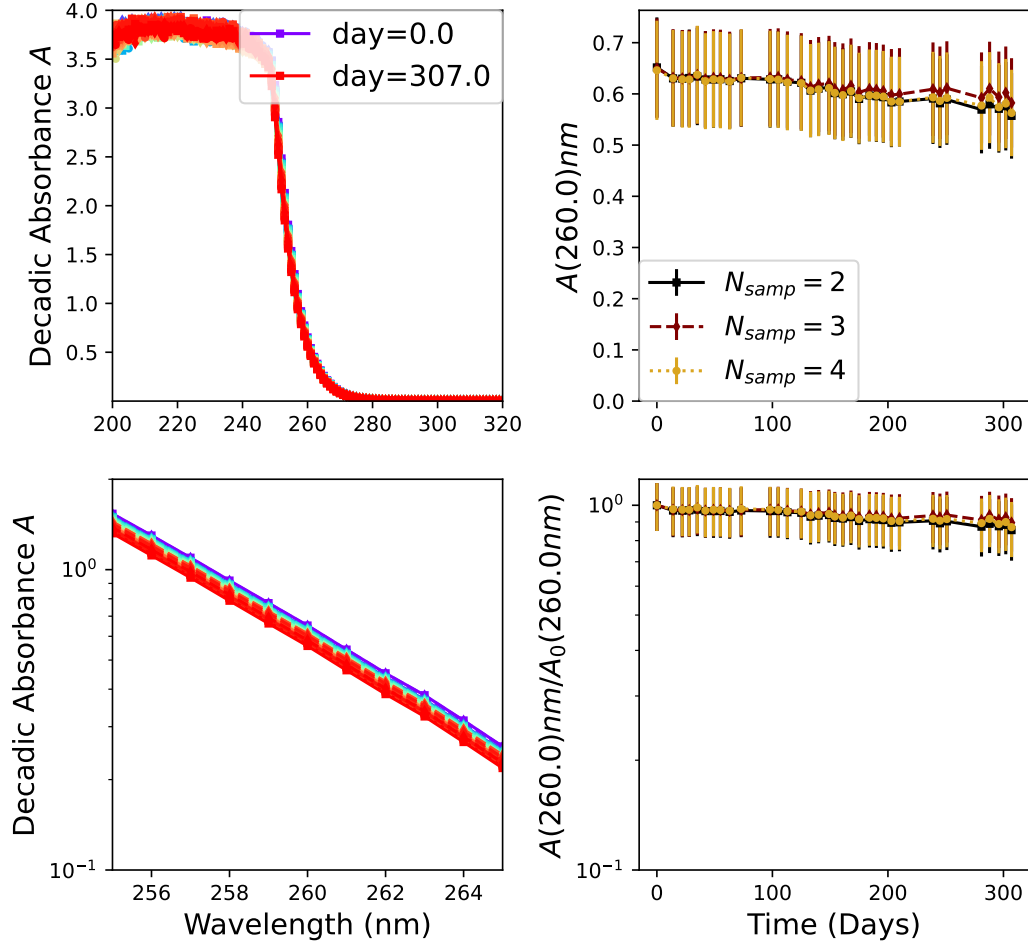
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## Notes

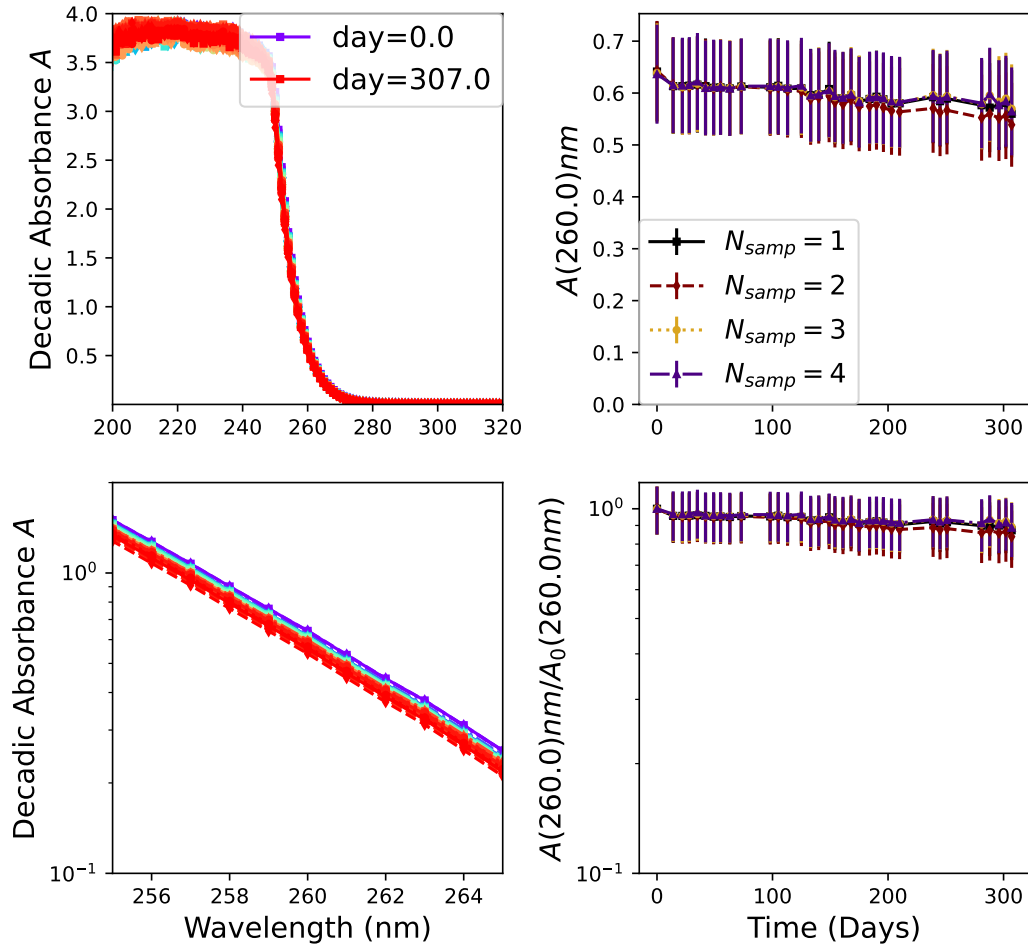
1. S. Rugheimer, personal communication, 10/17/2019.
2. Note that Zhang and Millero (1991) feature a persistent typo: the values they quote in-text for  $k''$  are really for  $\log_{10}(k'')$ .  
This can be seen by comparing the quoted values to Figure 7 of their paper, and by attempting to calculate  $k''$  directly from  $k$ .
3. But not identical; care must be taken with the specific radiative quantity compared (Ranjan & Sassellov, 2017)



**Figure S1.** UV-Vis tracking of the 100 mM S[IV],  $\text{pH}_0 = 7$  samples. Upper left: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left: same as upper left, but zoomed in to the wavelength region around 260 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 260 nm specifically as a function of time for the different samples at this experimental condition. In this plot, it is possible to distinguish the different samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition shows very little change over 10 months, consistent with the solution analytics.

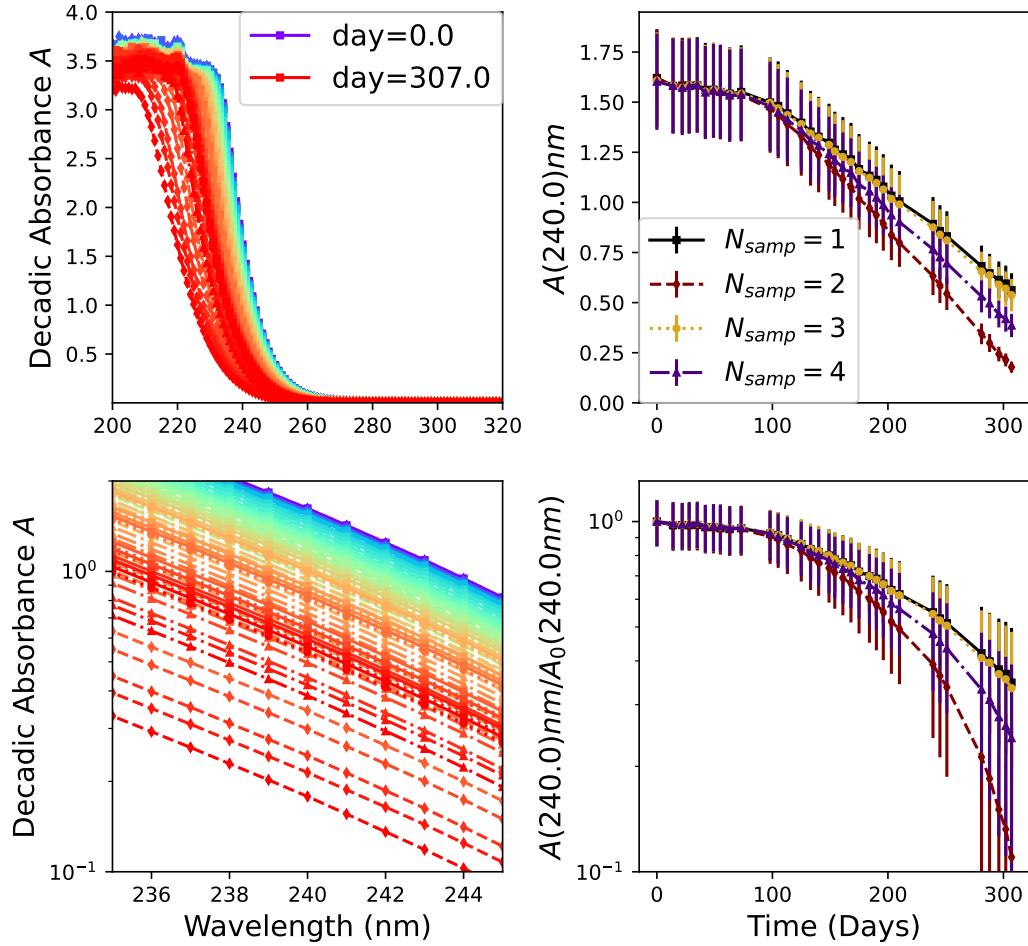


**Figure S2.** UV-Vis tracking of the 100 mM S[IV], pH-unadjusted samples. Upper left: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left: same as upper left, but zoomed in to the wavelength region around 260 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 260 nm as a function of time for the different samples at this experimental condition. In this plot, it is possible to distinguish the different samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right plot: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition shows very little change over 10 months, consistent with the solution analytics.

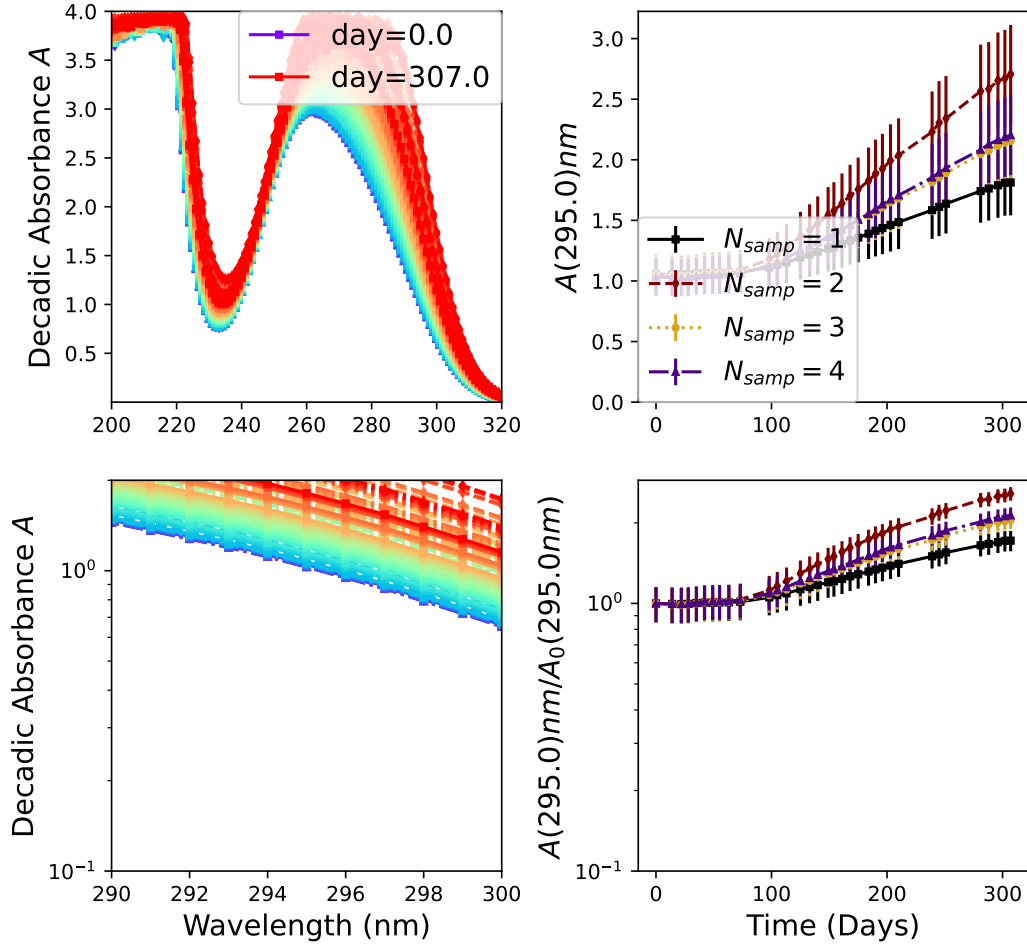


**Figure S3.** UV-Vis tracking of the 100 mM S[IV],  $\text{pH}_0 = 13$  samples. Upper left plot: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left: same as upper left, but zoomed in to the wavelength region around 260 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 260 nm as a function of time for the different samples at this experimental condition. In this plot, it is possible to distinguish the different samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition shows very little change over 10 months, consistent with the solution analytics but inconsistent with Guekezian et al. (1997).

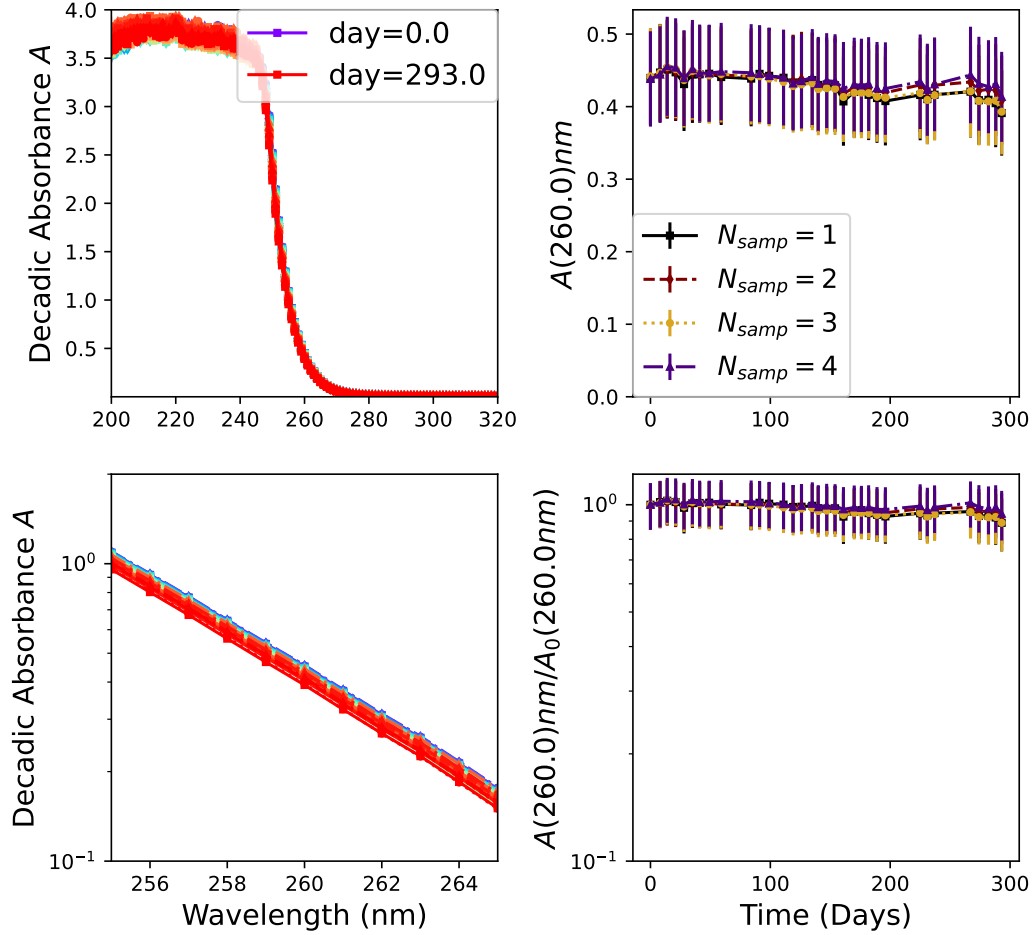




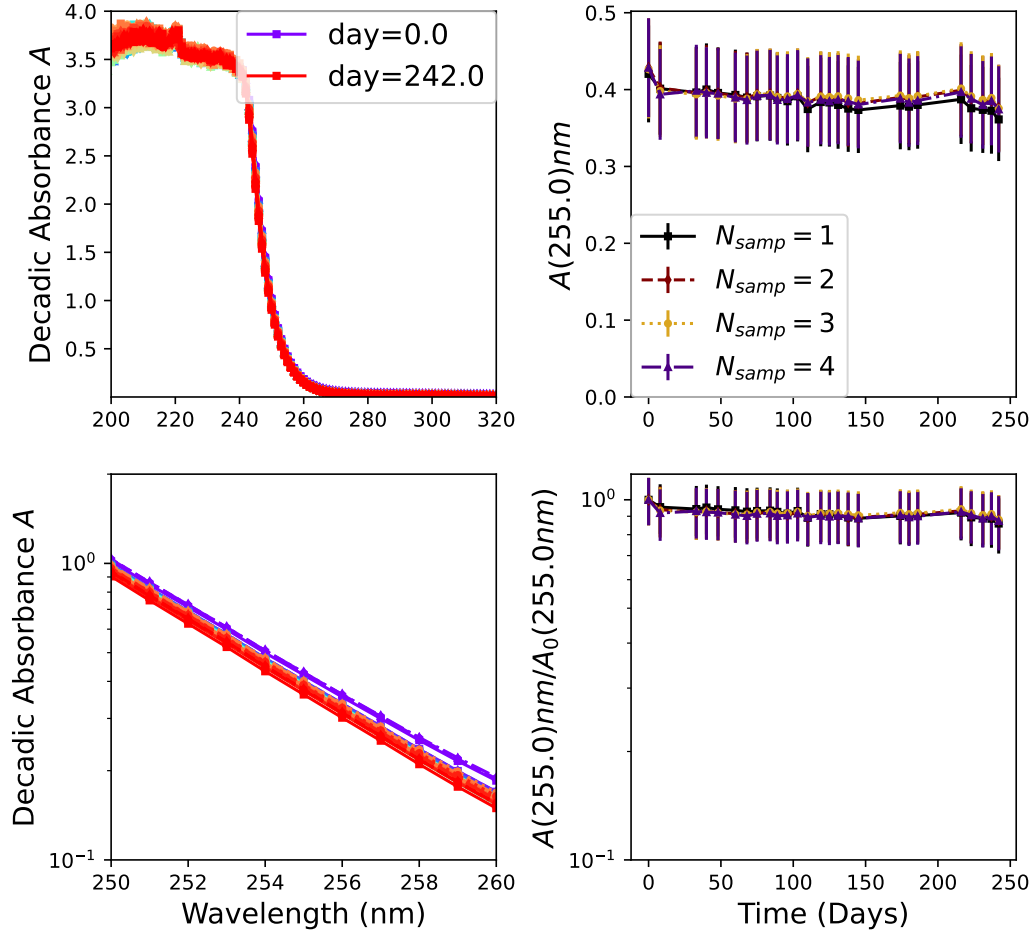
**Figure S4.** UV-Vis tracking of 10 mM S[IV], pH-unadjusted samples. Upper left: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left plot: same as upper left, but zoomed in to the wavelength region around 240 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 240 nm as a function of time for the samples at this experimental condition. In this plot, it is possible to distinguish the different samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right plot: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition shows significant change over 10 months. Samples 1, 3 and 4 are consistent with solution-phase analytics. Sample 2 indicates an absorbance that is a factor of  $\sim 3$  lower than expected based on the solution-phase analytics. Nevertheless, the rate of change is still too slow to be consistent with Guekezian et al. (1997).



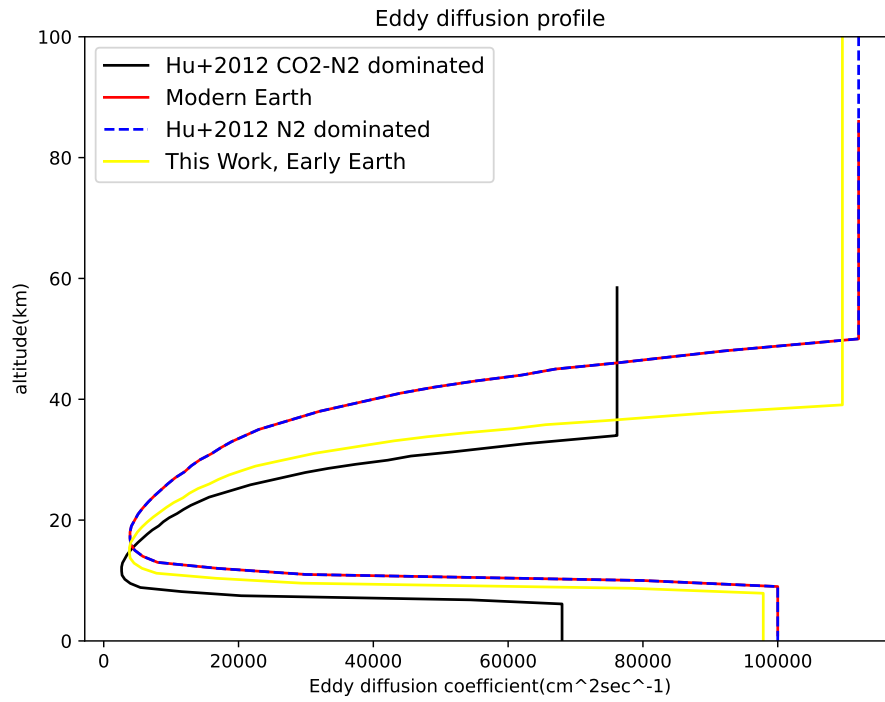
**Figure S5.** UV-Vis tracking of the 100 mM S[IV],  $\text{pH}_0 = 4$  samples. Upper left: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left: same as upper left, but zoomed in to the wavelength region around 295 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 295 nm specifically as a function of time for the different samples. In this plot, it is possible to distinguish the samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right plot: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition shows different UV-Vis evolution than the non-acidic conditions, with an increase in absorbance with time and more rapid change. This different behaviour potentially aligns with reports indicating more efficient disproportionation at low pH (Searcy, 1981).



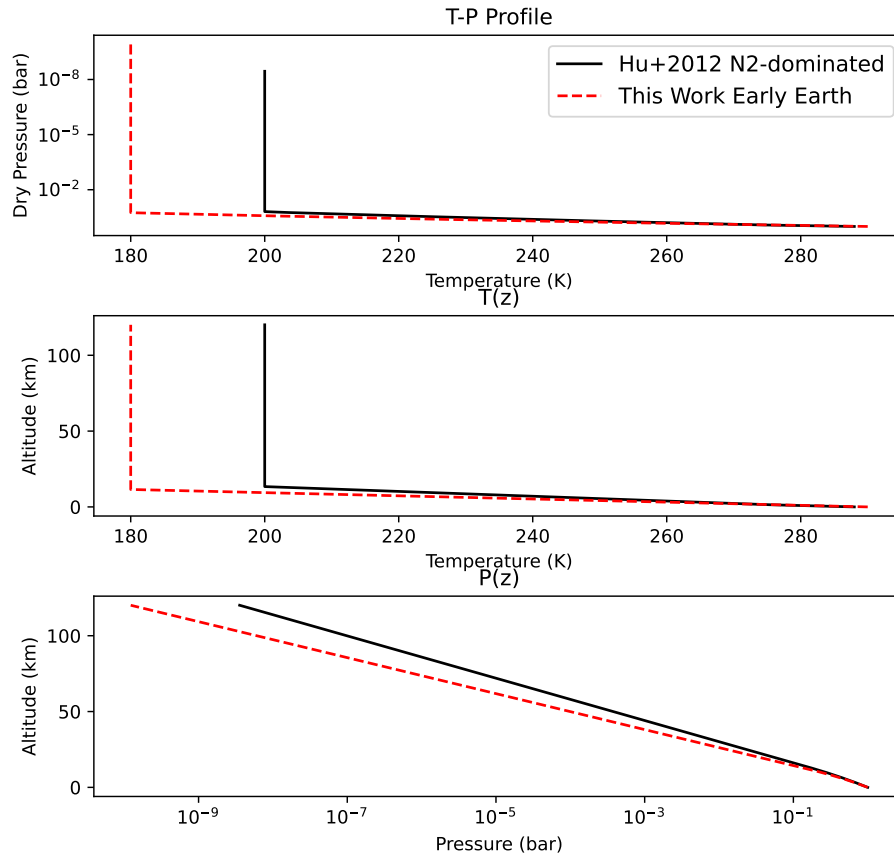
**Figure S6.** UV-Vis tracking of the 100 mM S[IV] samples in the low-concentration carbonate lake sensitivity test. Upper left: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left: same as upper left, but zoomed in to the wavelength region around 260 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 260 nm specifically as a function of time for the different samples. In this plot, it is possible to distinguish the samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right plot: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition behaves similarly to the non-acidic pH pure water experimental condition.



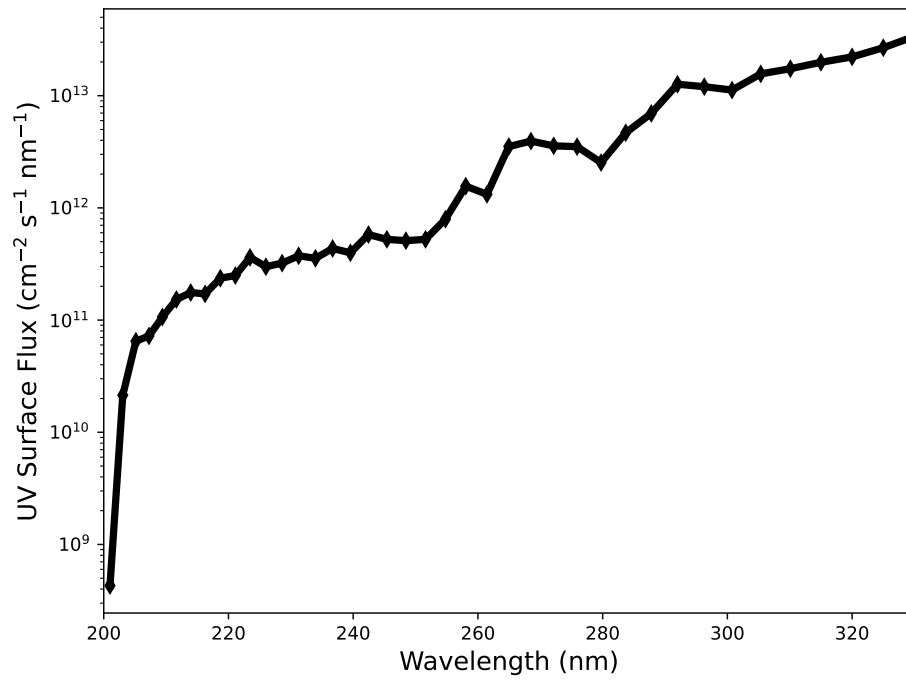
**Figure S7.** UV-Vis tracking of the 100 mM S[IV] samples in the high-concentration carbonate lake sensitivity test. Upper left: decadic absorbances ( $A$ ) measured from the samples. The colorscale is rainbow, with more purple colors corresponding to earlier times and more red colors corresponding to later times. The different samples are demarcated with different linestyles, but are challenging to distinguish by eye. Error bars are omitted for clarity. Lower left: same as upper left, but zoomed in to the wavelength region around 255 nm, where  $A$  responds linearly to changes in concentration. Upper right: absorbance at 255 nm specifically as a function of time for the different samples. In this plot, it is possible to distinguish the samples; to facilitate this differentiation, in addition to different linestyles they are assigned different colors, which do not correspond to the color scheme of the left column. Lower right plot: same as upper right, except the absorbances are normalized to the absorbance on day 0 (showing relative change). This experimental condition behaves similarly to the non-acidic pH pure water experimental condition.



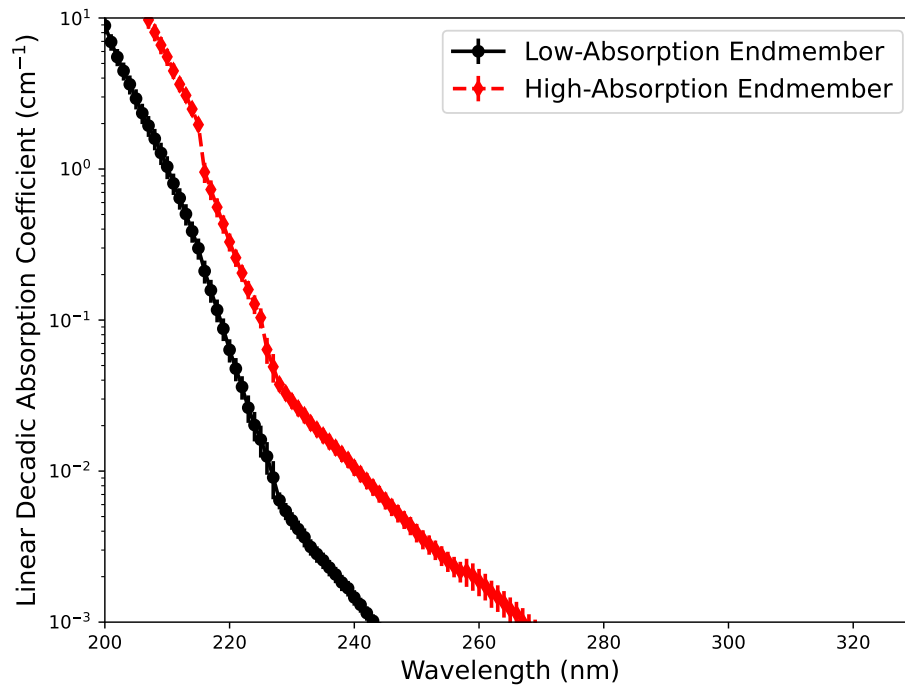
**Figure S8.** Eddy diffusion profile assumed in the photochemical calculation. Also shown for context are modern Earth eddy diffusion profile, and the eddy diffusion profiles in the Hu et al. (2012) CO<sub>2</sub>-N<sub>2</sub> and N<sub>2</sub>-dominated benchmark scenarios.



**Figure S9.** Temperature-pressure profile assumed in the photochemical calculation. Also shown for context is the temperature-pressure profile for the Hu et al. (2012) N<sub>2</sub>-dominated benchmark scenario.

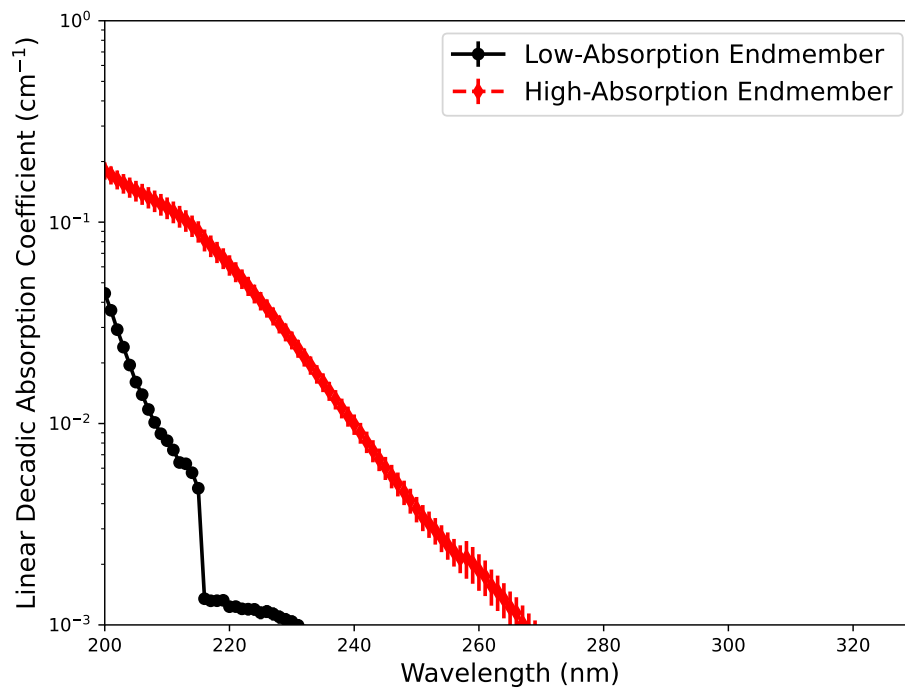


**Figure S10.** Surface UV irradiation (base of the atmosphere, but just above the water column). From (Ranjana & Sasselov, 2017), with atmospheric composition and conditions from Rugheimer et al. (2015).

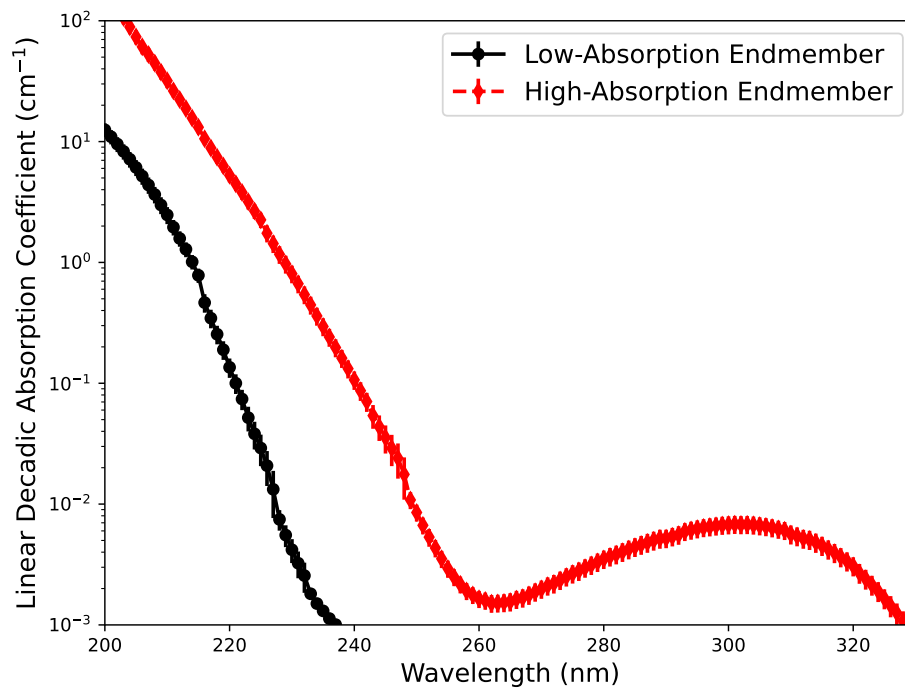


**Figure S11.** Low- and high-absorption endmember linear decadic absorption coefficients for the prebiotic ocean. Modified from Ranjan, Kufner, et al. (2022), with S[IV] species removed.

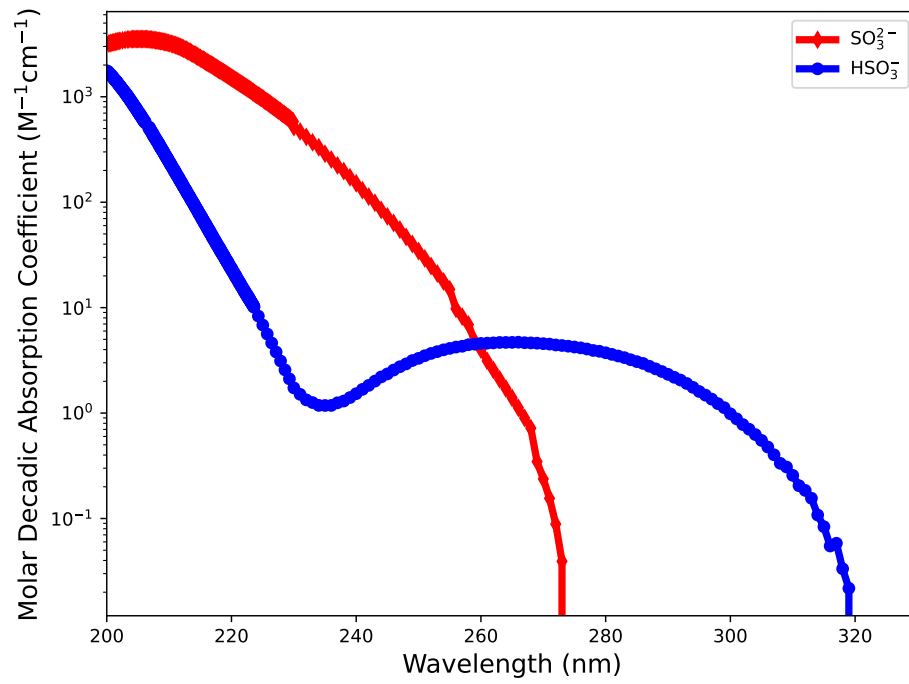




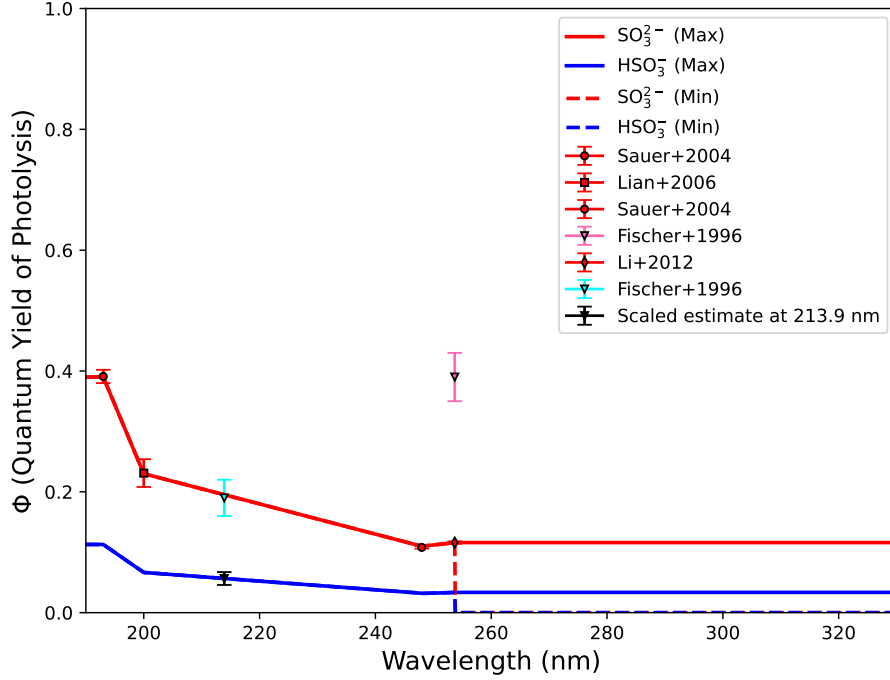
**Figure S12.** Low- and high-absorption endmember linear decadic absorption coefficients for prebiotic freshwater lakes. Modified from Ranjan, Kufner, et al. (2022), with S[IV] species removed.



**Figure S13.** Low- and high-absorption endmember linear decadic absorption coefficients for prebiotic carbonate lakes. Modified from Ranjan, Kufner, et al. (2022), with S[IV] species removed.



**Figure S14.** Absorption spectra of  $\text{SO}_3^{2-}$  and  $\text{HSO}_3^-$ , synthesized by Ranjan, Kufner, et al. (2022) from Fischer and Warneck (1996) and Beyad et al. (2014).



**Figure S15.** Prescribed S[IV] net photolysis quantum yields used in this work. The solid lines show the prescriptions assuming  $\Phi(> 254\text{nm}) = \Phi(254\text{nm})$  (Max), and the dashed lines show the prescriptions assuming  $\Phi(> 254\text{nm}) = 0$  (Min), which should span the uncertainty on  $\Phi(> 254\text{nm})$ . The red points indicate available experimental constraints on  $\Phi_{\text{SO}_3^{2-}}$ , which we extrapolate between to construct the prescription (Sauer, Crowell, & Shkrob, 2004; Lian et al., 2006; Li et al., 2012). The cyan and pink points indicate the upper bounds on  $\Phi_{\text{SO}_3^{2-}}(254\text{nm})$  and  $\Phi_{\text{HSO}_3^-}(214\text{nm})$  used to estimate  $\Phi_{\text{HSO}_3^-}(214\text{nm})$  (black point). Overall, the quantum yields of S[IV] photolysis and especially bisulfite photolysis are extremely poorly constrained and should be prioritized for future study.

**Table S1.** Analytics of Discarded Aged S[IV] Sample

$[\text{Na}_2\text{SO}_3]_0^\dagger$ (mM)	$\text{pH}_0^\dagger$	Sample	$[\text{SO}_3^{2-}]_{f,tot}^{\ddagger,a}$ (mM)	$[\text{SO}_4^{2-}]_f^{\ddagger,b}$ (mM)	$\lambda_m$ nm	$\frac{A_{\lambda_m,f}}{A_{\lambda_m,0}} \star$
10	Unadjusted	2	$3.4 \pm 0.2$	$5.5 \pm 0.2$	240	$0.11 \pm 0.02$

<sup>†</sup>Sample preparation (10/5/2021)

<sup>‡</sup>Cuvettes opened 8/20/2022

<sup>a</sup>Electropotentiometry

<sup>b</sup>Gravimetry

$\star$ UV-Vis last day 8/8/2022

**Table S2.** Simulation Parameters For Planetary Scenario.

Parameter	Value
Reaction Network	As in Ranjan, Seager, et al. (2022). Excludes $\text{C}_{>2}$ -chem
Stellar Irradiation	3.9 Ga Sun (Claire et al., 2012)
Semi-major axis	1 AU
Planet size	$1 M_\oplus, 1 R_\oplus$
Surface albedo	0.
Major atmospheric components	0.1 bar $\text{CO}_2$ , 0.9 bar $\text{N}_2$
Surface temperature	290
Surface $r_{\text{H}_2\text{O}}$ (lowest atmospheric bin)	0.01
Eddy Diffusion Profile	See Figure S8
Temperature-Pressure Profile	See Figure S9
Vertical Resolution	0-90 km, 1.8 km steps
Rainout	Earthlike; rainout turned off for $\text{H}_2$ , $\text{CO}$ , $\text{CH}_4$ , $\text{NH}_3$ , $\text{N}_2$ , $\text{C}_2\text{H}_2$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_6$ , and $\text{O}_2$ to simulate saturated ocean on abiotic planet
Atmospheric Redox Balance Checked	Yes
Global Redox Conservation Enforced	No

**Table S3.** Detailed species-by-species boundary conditions for photochemical modeling.

Species	Type <sup>1</sup>	Surface Flux <sup>2</sup> ( $\text{cm}^{-2} \text{s}^{-1}$ )	Surface Mixing Ratio <sup>2</sup> ( <i>relative to <math>\text{CO}_2 + \text{N}_2</math></i> )	$v_{dep}$ ( $\text{cm s}^{-1}$ )	TOA Flux <sup>3</sup> ( $\text{cm}^{-2} \text{s}^{-1}$ )
$\text{N}_2$	C	—	0.9	0	0
$\text{CO}_2$	X	—	0.1	0	0
$\text{H}_2\text{O}$	X	—	0.01	0	0
NO	X	3E8	—	0.02	0

<sup>1</sup>“X”: full continuity-diffusion equation is solved for the species. “A” aerosol species; “C”: chemically inert.

<sup>2</sup>For the bottom boundary condition, either a surface flux is specified, or a surface mixing ratio.

<sup>3</sup>TOA flux refers to the magnitude of outflow at the top-of-the-atmosphere (TOA). A negative number corresponds to an inflow.

Continuation of Table S3					
Species	Type <sup>1</sup>	Surface Flux <sup>2</sup> (cm <sup>-2</sup> s <sup>-1</sup> )	Surface Mixing Ratio <sup>2</sup> (relative to CO <sub>2</sub> +N <sub>2</sub> )	$v_{dep}$ (cm s <sup>-1</sup> )	TOA Flux <sup>3</sup> (cm <sup>-2</sup> s <sup>-1</sup> )
CO	X	3E8+4E8× $\frac{\phi}{\phi_0}$	—	$1 \times 10^{-8}$	0
CH <sub>4</sub>	X	3E8× $\frac{\phi}{\phi_0}$	—	0	0
SO <sub>2</sub>	X	3E9× $\frac{\phi}{\phi_0}$	—	1	0
H <sub>2</sub> S	X	3E8× $\frac{\phi}{\phi_0}$	—	0.015	0
H <sub>2</sub>	X	5E9× $\frac{\phi}{\phi_0}$	—	0	Diffusion-limited
H	X	0	—	1	Diffusion-limited
O	X	0	—	1	0
O(1D)	X	0	—	0	0
O <sub>2</sub>	X	0	—	0	0
O <sub>3</sub>	X	0	—	0.4	0
OH	X	0	—	1	0
HO <sub>2</sub>	X	0	—	1	0
H <sub>2</sub> O <sub>2</sub>	X	0	—	0.5	0
CH <sub>2</sub> O	X	0	—	0.1	0
CHO	X	0	—	0.1	0
C	X	0	—	0	0
CH	X	0	—	0	0
CH <sub>2</sub>	X	0	—	0	0
<sup>1</sup> CH <sub>2</sub>	X	0	—	0	0
<sup>3</sup> CH <sub>2</sub>	X	0	—	0	0
CH <sub>3</sub>	X	0	—	0	0
CH <sub>3</sub> O	X	0	—	0.1	0
CH <sub>4</sub> O	X	0	—	0.1	0
CHO <sub>2</sub>	X	0	—	0.1	0
CH <sub>2</sub> O <sub>2</sub>	X	0	—	0.1	0
CH <sub>3</sub> O <sub>2</sub>	X	0	—	0	0
CH <sub>4</sub> O <sub>2</sub>	X	0	—	0.1	0
C <sub>2</sub>	X	0	—	0	0
C <sub>2</sub> H	X	0	—	0	0
C <sub>2</sub> H <sub>2</sub>	X	0	—	0	0
C <sub>2</sub> H <sub>3</sub>	X	0	—	0	0
C <sub>2</sub> H <sub>4</sub>	X	0	—	0	0
C <sub>2</sub> H <sub>5</sub>	X	0	—	0	0
C <sub>2</sub> H <sub>6</sub>	X	0	—	$1 \times 10^{-5}$	0
C <sub>2</sub> HO	X	0	—	0	0
C <sub>2</sub> H <sub>2</sub> O	X	0	—	0.1	0
C <sub>2</sub> H <sub>3</sub> O	X	0	—	0.1	0
C <sub>2</sub> H <sub>4</sub> O	X	0	—	0.1	0
C <sub>2</sub> H <sub>5</sub> O	X	0	—	0.1	0
S	X	0	—	0	0
S <sub>2</sub>	X	0	—	0	0
S <sub>3</sub>	X	0	—	0	0

Continuation of Table S3					
Species	Type <sup>1</sup>	Surface Flux <sup>2</sup> (cm <sup>-2</sup> s <sup>-1</sup> )	Surface Mixing Ratio <sup>2</sup> ( <i>relative to CO<sub>2</sub>+N<sub>2</sub></i> )	$v_{dep}$ (cm s <sup>-1</sup> )	TOA Flux <sup>3</sup> (cm <sup>-2</sup> s <sup>-1</sup> )
S <sub>4</sub>	X	0	—	0	0
SO	X	0	—	0	0
<sup>1</sup> SO <sub>2</sub>	X	0	—	0	0
<sup>3</sup> SO <sub>2</sub>	X	0	—	0	0
HS	X	0	—	0	0
HSO	X	0	—	0	0
HSO <sub>2</sub>	X	0	—	0	0
HSO <sub>3</sub>	X	0	—	0.1	0
HSO <sub>4</sub>	X	0	—	1	0
H <sub>2</sub> SO <sub>4</sub> (A)	A	0	—	0.2	0
S <sub>8</sub>	X	0	—	0	0
S <sub>8</sub> (A)	A	0	—	0.2	0
OCS	X	0	—	0.01	0
CS	X	0	—	0.01	0
CH <sub>3</sub> S	-	0	—	0.01	0
CH <sub>4</sub> S	-	0	—	0.01	0

**Table S4.** Surface mixing ratio and wet deposition of SO<sub>2</sub> as a function of volcanic emission flux

$\frac{\phi}{\phi_0}$	$\phi_{SO_2}$ cm <sup>-2</sup> s <sup>-1</sup>	$r_{SO_2}(z=0)$	SO <sub>2</sub> wet deposition flux cm <sup>-2</sup> s <sup>-1</sup>
0.1	$3 \times 10^8$	$7 \times 10^{-12}$	$3 \times 10^7$
0.3	$9 \times 10^8$	$2 \times 10^{-11}$	$9 \times 10^7$
1	$3 \times 10^9$	$1 \times 10^{-10}$	$4 \times 10^8$
3	$9 \times 10^9$	$3 \times 10^{-10}$	$2 \times 10^9$
10	$3 \times 10^{10}$	$1 \times 10^{-9}$	$5 \times 10^9$
30	$9 \times 10^{10}$	$3 \times 10^{-9}$	$1 \times 10^{10}$

**Table S5.** Construction of dilute carbonate lake solution sensitivity test.

Salt	Mass <sup>a</sup> (mg)	Na <sup>+</sup> (M)	K <sup>+</sup> (M)	Ca <sup>2+</sup> (M)	Mg <sup>2+</sup> (M)	Cl <sup>-</sup> (M)	Br <sup>-</sup> (M)	I <sup>-</sup> (M)	NO <sub>3</sub> <sup>-</sup> (M)	PO <sub>4</sub> <sup>3-</sup> (M)	B (M)	SO <sub>4</sub> <sup>2-</sup> (M)	S <sup>2-</sup> +HS <sup>-</sup> (M)	CO <sub>3</sub> <sup>2-</sup> +HCO <sub>3</sub> <sup>-</sup> (M)	SO <sub>3</sub> <sup>2-</sup> +HSO <sub>3</sub> <sup>-</sup> (M)
NaCl	116.88	0.1	0	0	0	0.1	0	0	0	0	0	0	0	0	0
KCl	44.73	0	0.03	0	0	0.03	0	0	0	0	0	0	0	0	0
CaCl <sub>2</sub> · 6H <sub>2</sub> O	0.44	0	0	1 × 10 <sup>-4</sup>	0	2 × 10 <sup>-4</sup>	0	0	0	0	0	0	0	0	0
MgCl <sub>2</sub>	0.02	0	0	0	1 × 10 <sup>-5</sup>	2 × 10 <sup>-5</sup>	0	0	0	0	0	0	0	0	0
NaBr	2.06	1 × 10 <sup>-3</sup>	0	0	0	0	1 × 10 <sup>-3</sup>	0	0	0	0	0	0	0	0
NaI	1.2 × 10 <sup>-4</sup>	4 × 10 <sup>-8</sup>	0	0	0	0	0	4 × 10 <sup>-8</sup>	0	0	0	0	0	0	0
NaNO <sub>3</sub>	8.5 × 10 <sup>-6</sup>	5 × 10 <sup>-9</sup>	0	0	0	0	0	0	5 × 10 <sup>-9</sup>	0	0	0	0	0	0
Na <sub>2</sub> HPO <sub>4</sub>	28.39	2 × 10 <sup>-2</sup>	0	0	0	0	0	0	0	1 × 10 <sup>-2</sup>	0	0	0	0	0
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	4.02	2 × 10 <sup>-3</sup>	0	0	0	0	0	0	0	0	4 × 10 <sup>-3</sup>	0	0	0	0
Na <sub>2</sub> SO <sub>4</sub>	852.24	6 × 10 <sup>-1</sup>	0	0	0	0	0	0	0	0	0	3 × 10 <sup>-1</sup>	0	0	0
Na <sub>2</sub> S · 6H <sub>2</sub> O	4 × 10 <sup>-5</sup>	1.6 × 10 <sup>-8</sup>	0	0	0	0	0	0	0	0	0	0	8 × 10 <sup>-9</sup>	0	0
NaHCO <sub>3</sub>	84.01	5 × 10 <sup>-2</sup>	0	0	0	0	0	0	0	0	0	0	0	5 × 10 <sup>-2</sup>	0
Na <sub>2</sub> SO <sub>3</sub>	252.08	2 × 10 <sup>-1</sup>	0	0	0	0	0	0	0	0	0	0	0	0	1 × 10 <sup>-1</sup>
Total		9.7 × 10 <sup>-1</sup>	3 × 10 <sup>-2</sup>	1 × 10 <sup>-4</sup>	1 × 10 <sup>-5</sup>	1.3 × 10 <sup>-1</sup>	1 × 10 <sup>-3</sup>	4 × 10 <sup>-8</sup>	5 × 10 <sup>-9</sup>	1 × 10 <sup>-2</sup>	4 × 10 <sup>-3</sup>	3 × 10 <sup>-1</sup>	8 × 10 <sup>-9</sup>	5 × 10 <sup>-2</sup>	1 × 10 <sup>-1</sup>

<sup>a</sup> Salts were added to 20 mL H<sub>2</sub>O, and solution was adjusted to pH=9. No solids were observed after preparation.

October 4, 2023, 3:29pm



**Table S6.** Construction of concentrated carbonate lake solution sensitivity test.

Salt	Mass <sup>a</sup> (mg)	Na <sup>+</sup> (M)	K <sup>+</sup> (M)	Ca <sup>2+</sup> (M)	Mg <sup>2+</sup> (M)	Cl <sup>-</sup> (M)	Br <sup>-</sup> (M)	I <sup>-</sup> (M)	NO <sub>3</sub> <sup>-</sup> (M)	PO <sub>4</sub> <sup>3-</sup> (M)	B (M)	SO <sub>4</sub> <sup>2-</sup> (M)	S <sup>2-</sup> +HS <sup>-</sup> (M)	CO <sub>3</sub> <sup>2-</sup> +HCO <sub>3</sub> <sup>-</sup> (M)	SO <sub>3</sub> <sup>2-</sup> +HSO <sub>3</sub> <sup>-</sup> (M)
NaCl	2337.60	2.0	0	0	0	2.0	0	0	0	0	0	0	0	0	0
KCl	447.30	0	0.3	0	0	0.3	0	0	0	0	0	0	0	0	0
CaCl <sub>2</sub> · 6H <sub>2</sub> O	0.44	0	0	1 × 10 <sup>-4</sup>	0	2 × 10 <sup>-4</sup>	0	0	0	0	0	0	0	0	0
MgCl <sub>2</sub>	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NaBr	20.58	1 × 10 <sup>-2</sup>	0	0	0	0	1 × 10 <sup>-2</sup>	0	0	0	0	0	0	0	0
NaI	1.8 × 10 <sup>-3</sup>	6 × 10 <sup>-7</sup>	0	0	0	0	0	6 × 10 <sup>-7</sup>	0	0	0	0	0	0	0
NaN <sub>3</sub>	1.70	1 × 10 <sup>-3</sup>	0	0	0	0	0	0	1 × 10 <sup>-3</sup>	0	0	0	0	0	0
Na <sub>2</sub> HPO <sub>4</sub>	28.39	2 × 10 <sup>-2</sup>	0	0	0	0	0	0	0	1 × 10 <sup>-2</sup>	0	0	0	0	0
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> <sup>b</sup>	1207.32	0.6	0	0	0	0	0	0	0	0	1.2	0	0	0	0
Na <sub>2</sub> SO <sub>4</sub>	2840.80	2.0	0	0	0	0	0	0	0	0	0	1.0	0	0	0
Na <sub>2</sub> S · 6H <sub>2</sub> O	5 × 10 <sup>-3</sup>	2 × 10 <sup>-6</sup>	0	0	0	0	0	0	0	0	0	0	1 × 10 <sup>-6</sup>	0	0
NaHCO <sub>3</sub>	168.02	1 × 10 <sup>-1</sup>	0	0	0	0	0	0	0	0	0	0	0	1 × 10 <sup>-1</sup>	0
Na <sub>2</sub> SO <sub>3</sub>	252.08	2 × 10 <sup>-1</sup>	0	0	0	0	0	0	0	0	0	0	0	0	1 × 10 <sup>-1</sup>
Total	4.93	3 × 10 <sup>-1</sup>	1 × 10 <sup>-4</sup>	0	2.3	1 × 10 <sup>-2</sup>	6 × 10 <sup>-7</sup>	1 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	1.20	1.00	1 × 10 <sup>-6</sup>	1 × 10 <sup>-1</sup>	1 × 10 <sup>-1</sup>	

<sup>a</sup> Salts were added to 20 mL H<sub>2</sub>O, and solution was adjusted to pH=7. Solids were observed after preparation, which we attribute to Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.  
<sup>b</sup> Based on Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solubility at 20°C.

**Table S7.** Laboratory Measurements of Quantum Yields Relevant to Aqueous S[IV] Photolysis

Study	Species	$\lambda$ nm	Photoprocess	Quantum Yield
Fischer and Warneck (1996)	$\text{HSO}_3^-$	213.9	$\text{HSO}_3^{2-}$ photolysis	$\Phi_{\text{HSO}_3^-} = 0.19 \pm 0.03$
Fischer and Warneck (1996)	$\text{HSO}_3^-$	213.9	Net photolytic $\text{HSO}_3^-$ loss in anoxic $\text{H}_2\text{O}$	$\Phi_{\text{C,HSO}_3^-} = 0.12 \pm 0.03^b$
Sauer, Crowell, and Shkrob (2004)	$\text{SO}_3^{2-}$	193	$\text{SO}_3^{2-}$ Photolysis	$\Phi_{\text{SO}_3^{2-}} = 0.391 \pm 0.011$
Lian et al. (2006)	$\text{SO}_3^{2-}$	200	$\text{SO}_3^{2-}$ Photolysis	$\Phi_{\text{SO}_3^{2-}} = 0.231 \pm 0.023^a$
Sauer, Crowell, and Shkrob (2004)	$\text{SO}_3^{2-}$	248	$\text{SO}_3^{2-}$ Photolysis	$\Phi_{\text{SO}_3^{2-}} = 0.108 \pm 0.001$
Fischer and Warneck (1996)	$\text{SO}_3^{2-}$	253.7	$\text{SO}_3^{2-}$ Photolysis	$\Phi_{\text{SO}_3^{2-}} = 0.39 \pm 0.04$
Fischer and Warneck (1996)	$\text{SO}_3^{2-}$	253.7	Net photolytic $\text{SO}_3^{2-}$ loss in anoxic $\text{H}_2\text{O}$	$\Phi_{\text{C,SO}_3^{2-}} = 0.25 \pm 0.02^b$
Li et al. (2012)	$\text{SO}_3^-$	253.7	$\text{SO}_3^{2-}$ Photolysis	$\Phi_{\text{SO}_3^{2-}} = 0.116 \pm 0.002$

<sup>a</sup>Uncertainty not explicitly stated in source publication; assumed to be 10%, as for  $\text{OH}^-$  and  $\text{I}^-$ .  
<sup>b</sup> Subscript C emphasizes that this photoprocess is not the same as direct photolysis.

**Table S8.** Analytics of Aged S[IV] Samples. The calculations shown here are also performed in Data Set S1.

$[\text{Na}_2\text{SO}_3]_0$ (mM)	pH <sub>0</sub>	Sample	$ \Delta[S[IV]] $ (mM)	$\sigma_{\Delta[S[IV]]}$ (mM)	$ \Delta[S[VI]] $ (mM)	$\sigma_{\Delta[S[VI]]}$ (mM)	$\frac{ \Delta[S[IV]] - \Delta[S[VI]] }{\sqrt{\sigma_{\Delta[S[IV]]}^2 + \sigma_{\Delta[S[VI]]}^2}}$ ( $\sigma$ )
100	7	1	14.8	3.7	8.4	0.2	1.7
100	7	2	16.8	4.6	9.1	0.1	1.7
100	7	3	15.6	2.7	9.5	0.2	2.3
100	7	4	16.9	4.1	12.1	0.1	1.2
100	Unadjusted	2	15.8	3.2	9.5	0.3	2.0
100	Unadjusted	3	14.3	3.7	10.5	0.5	1.0
100	Unadjusted	4	19.4	2.0	10.6	0.3	4.3
100	13	1	16.5	3.4	9.7	0.4	2.0
100	13	2	15.8	2.5	11.7	0.5	1.6
100	13	3	16.5	2.8	11.0	0.5	2.0
100	13	4	19.4	2.6	12.6	0.5	2.5
10	Unadjusted	1	6.3	0.3	4.9	0.2	3.8
10	Unadjusted	3	6.9	0.3	5.7	0.2	2.9
10	Unadjusted	4	6.2	0.3	4.2	0.2	5.2