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Key Points:

- In haze-analog experiments with carbon dioxide (CO₂)/methane (CH₄)/N₂ precursors, addition of trace H₂S increases aerosol production by at least a factor of ~3.8
- In CO₂/CH₄/N₂ gas mixtures, high CO₂ inhibits organic aerosol formation. With trace H₂S, organic aerosol formation is independent of CO₂
- Inorganic and organic sulfate aerosol forms when trace H₂S is present, suggesting that organic sulfur is an important sulfur reservoir

Supporting Information:

Supporting Information may be found in the online version of this article.

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Trace H₂S Promotes Organic Aerosol Production and Organosulfur Compound Formation in Archean Analog Haze Photochemistry Experiments

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Abstract Organic haze and sulfur gases are ubiquitous in planetary atmospheres and were likely present in Earth's Archean atmosphere. Currently, there are few experiments investigating how H₂S influences organic haze chemistry on Archean Earth. Here, we present results from laboratory haze-analog experiments probing the role of H₂S in the composition and total mass of aerosol produced from precursor mixtures of Archean-like gas fluxes (e.g., pCO₂ ~3–50xPAL). We show that trace H₂S enhances organic aerosol production at all carbon dioxide mixing ratios studied, and we observe both organic and inorganic sulfur aerosol products. Our finding challenges predictions that H₂SO₄ and S₈ were the primary sulfur reservoirs in Earth's Archean atmosphere, and these results suggest that inorganic sulfur and organic haze chemistry are tightly coupled during the formation of organic hazes in the atmospheres of the Archean Earth and likely Archean-like exoplanets.

Plain Language Summary The Archean Eon (4.0–2.5 billion years ago) atmosphere was much different from the modern one, with very little oxygen and higher amounts of carbon dioxide (CO₂) and methane (CH₄). Light from the sun would have jump-started chemical reactions leading to a mixture of organic molecules and particles (“organic haze”). Gases in smaller amounts (trace gases) can greatly influence “haze” chemistry. One common trace gas is hydrogen sulfide (H₂S). We conducted laboratory experiments that attempted to reproduce this “haze” chemistry with gas mixtures of CO₂, CH₄, and H₂S in a nitrogen background. When H₂S was added to the gas mixture, organosulfur molecules were formed, and the mass of organic particles greatly increased. These results challenge two current assumptions about Archean organic haze and sulfur chemistry. The first is that the production of organic particles in a CO₂/CH₄ haze should decrease when CO₂ is increased; we show that organic particle mass is essentially independent of CO₂ when trace H₂S is present. The second is that sulfur particles would be composed of inorganic sulfur; we show that organosulfur accounts for a significant portion of the sulfur. Our results may affect the current understanding of the history and evolution of Earth's atmosphere.

1. Introduction

Atmospheric sulfur photochemistry is ubiquitous in planetary atmospheres within our solar system, both past and present, and is likely active in exoplanetary atmospheres (Atreya et al., 2003; Gao et al., 2017; Hu et al., 2013). Sulfur photochemistry is of particular interest to the understanding of Archean Earth (4.0–2.5 billion years ago). It is the most likely cause of the observed mass-independent fractionation of sulfur isotopes (S-MIF) in the geologic record from the Archean Eon. Mass-independent fractionation of sulfur isotopes (S-MIF) is frequently cited as evidence for an anoxic Archean atmosphere (Domagal-Goldman et al., 2008; Farquhar, Bao, et al., 2000; Farquhar & Wing, 2003; Izon et al., 2015; Kasting et al., 1989; Ono, 2017; Pavlov & Kasting, 2002; Zerkle et al., 2012). The isotopic signature of S-MIF is preserved due to sulfur funneling into at least two different reservoirs, generally believed to be H₂SO₄ and S₈ aerosol (Kasting et al., 1989; Pavlov & Kasting, 2002). Geochemical evidence also suggests the Archean atmosphere experienced an intermittent organic haze: organic aerosol particles and gases formed via methane photochemistry (Domagal-Goldman et al., 2008; Izon et al., 2015; Zerkle et al., 2012). Few studies, however, have explored how the photochemistry of sulfur in the Archean atmosphere could directly interact with the organic haze, such as by generating organosulfur compounds (Dewitt et al., 2010), which have been hypothesized as potential carriers of S-MIF (Halevy, 2013).

In Earth's modern atmosphere, organic oxidized sulfur (OOS) compounds, such as organosulfates and organosulfonates, are a significant reservoir of sulfur, comprising an estimated 5%–30% of the total organic aerosol mass

(Chen et al., 2021; Surratt et al., 2008; Tolocka & Turpin, 2012). We previously showed that organic reduced sulfur (ORS) compounds, such as thiols and sulfides, formed when trace hydrogen sulfide (H_2S) (0.5–5 ppm_v) was added to methane (CH_4)/ N_2 photochemical haze experiments (Reed et al., 2020). We estimated that organic reduced sulfur (ORS) accounted for ~20% of the total aerosol mass at 5 ppm_v hydrogen sulfide (H_2S). To our knowledge, Dewitt et al. (2010) is the only laboratory study to explore the effects of a sulfur gas on Archean-like haze chemistry, that is, with high carbon dioxide (CO_2)/methane (CH_4) mixing ratios. That work used aerosol mass spectrometry (AMS) to explore how sulfur dioxide (SO_2) affected the haze chemistry formed from methane (CH_4) mixtures with and without carbon dioxide (CO_2) and H_2 . They found evidence for the formation of organic oxidized sulfur (OOS) compounds such as methyl sulfonic acid. Taken together, these observations suggest that organic oxidized sulfur (OOS) and organic reduced sulfur (ORS) may be important sulfur reservoirs in a range of atmospheres varying from more reducing to more oxidizing.

Hydrogen sulfide (H_2S) has received little attention in laboratory studies on Archean organic haze. However, the role of H_2S in haze chemistry has been investigated in laboratory experiments of carbon dioxide (CO_2) and H_2 -rich exoplanetary atmospheres without CH_4 (He et al., 2020; Vuitton et al., 2021). Similar to SO_2 , H_2S photodissociation is capable of producing S-MIF, albeit of different magnitude and pattern (Chakraborty et al., 2013; Farquhar, Savarino, et al., 2000). Although SO_2 is presumed to be the dominant atmospheric sulfur gas, SO_2 and H_2S are co-emitted to the atmosphere with relative amounts dependent on the temperature, pressure, and redox conditions of hydrothermal or magmatic sources (Aiuppa et al., 2006). At fumarole sources and in volcanic plumes, H_2S can dominate over SO_2 , with modern measurements of volcanic SO_2 : H_2S ratios ranging from ~0.4 to 20 (Aiuppa et al., 2005). Atmospheric chemistry models suggest that H_2S can accumulate in reducing atmospheres with low levels of oxygen, such as the Archean atmosphere (Kasting et al., 1989; Kump et al., 2005). The Archean Eon likely experienced high volcanic activity and biological sulfate reduction in a reduced atmosphere, thus emission and accumulation of H_2S in the atmosphere were likely (Archer & Vance, 2006; Holland, 2002; Hu et al., 2013; Kump & Barley, 2007; Shen & Buick, 2004; Shen et al., 2001).

The goal of our study is to improve the understanding of the role of H_2S in the Archean atmosphere and, specifically, its influence on organic haze. We conducted laboratory experiments exploring how the addition of trace H_2S in CO_2 / CH_4 / N_2 gas mixtures affects photochemical haze formation as a function of the CO_2 concentration in the mixture. The composition and mass of aerosol was monitored in real time using quadrupole aerosol mass spectrometry (Q-AMS). Our general conclusions are focused on trends in aerosol mass loading and bulk composition rather than on specific values of a given experiment. We find that trace H_2S enhances organic aerosol production, even at high CO_2 mixing ratios, and forms both organic and inorganic sulfur aerosol.

2. Materials and Methods

2.1. Haze Aerosol Generation

Experiments were conducted at ambient temperature and pressure using a far ultraviolet (UV) deuterium lamp as an energy source. The flow-system and haze analog generation by UV photolysis of gas mixtures has been previously described in detail (Berry et al., 2019a; Hörst & Tolbert, 2013; Reed et al., 2020; Trainer et al., 2012) and is described in Text S1 of Supporting Information S1. Gas mixtures were made in a N_2 background gas (Airgas, ultra-high purity, 99.999%) with mixing ratios of 0.1% CH_4 (Airgas, 99.99%), CO_2 of 0.1, 0.2, 0.5, 1%, or 2% (Airgas, 99.999%), and 0 or 5 ppm_v H_2S (Airgas, 1,000 ppm_v H_2S in N_2). Rationale for these mixing ratios is given in Text S1 of Supporting Information S1 and is based on previous experiments and predicted values in the Archean atmosphere (Arney et al., 2018; Berry et al., 2019a, 2019b; Domagal-Goldman et al., 2008; Holland, 2002; Izon et al., 2015, 2017; Reed et al., 2020; Trainer et al., 2006; Zerkle et al., 2012). We confirmed the stability of H_2S against conversion to H_2SO_4 due to any residual H_2O in the system in additional experiments (Figure S1 in Supporting Information S1). All measurements reported were made after a 10-min period of the lamp being on to ensure steady state conditions of the products.

A quadrupole aerosol mass spectrometer (Q-AMS) directly samples the flow of aerosol products for real-time, quantitative measurements of total aerosol mass loading and chemical composition (Allan et al., 2002, 2003; Jayne et al., 2000; Jimenez et al., 2003). The Q-AMS has been described in detail (Allan et al., 2002). Chemically resolved aerosol composition is determined using data analysis software and a standard analysis technique developed for the AMS (Allan et al., 2002, 2004) described in Text S2 of Supporting Information S1. While the

unit mass resolution Q-AMS cannot unequivocally attribute an m/z to a given chemical species, the assignments of overall classifications are based on relationships between several ions using a fragmentation table, discussed further in Text S2 of Supporting Information S1. A discussion of detection limits and uncertainty is in Text S3 of Supporting Information S1.

2.2. Estimation of Organic Oxidized Sulfur (OOS) Aerosol

In the Q-AMS, OOS compounds fragment to produce mainly “organic” ions ($C_xH_yO_z^+$) and “sulfate” ions ($H_xSO_y^+$) as a result of decomposition during electron ionization and/or the vaporization process (Chen et al., 2019; Farmer et al., 2010; Schueneman et al., 2021). However, the relative intensity and identity of certain “sulfate” ions produced by OOS compounds differ from those produced from inorganic sulfates such as sulfate salts and H_2SO_4 . These “sulfate” ions include SO^+ (m/z 48), SO_2^+ (m/z 64), SO_3^+ (m/z 80), HSO_3^+ (m/z 81), and $H_2SO_4^+$ (m/z 98). Organosulfates do not produce the ions HSO_3^+ (m/z 81) and $H_2SO_4^+$ (m/z 98), and organosulfonates, such as methyl sulfonic acid, do not produce the $H_2SO_4^+$ ion (m/z 98) (Chen et al., 2019; Schueneman et al., 2021). Thus, the $H_2SO_4^+$ ion (m/z 98) is unique to inorganic sulfate. These differences in fragmentation have been leveraged to quantify the total amount of OOS in aerosol (Chen et al., 2019; Schueneman et al., 2021). We define the variable fH_2SO_4 (Equation 1) as the ratio of the signal from the $H_2SO_4^+$ ion (m/z 98) to the sum of the ion signals from $H_2SO_4^+$, HSO_3^+ , SO_3^+ , SO_2^+ , and SO^+ (Chen et al., 2019).

$$fH_2SO_4 = \frac{m98_{\text{sulfate}}}{m98_{\text{sulfate}} + m81_{\text{sulfate}} + m80_{\text{sulfate}} + m64_{\text{sulfate}} + m48_{\text{sulfate}}} \quad (1)$$

where $m98_{\text{sulfate}}$, $m81_{\text{sulfate}}$, $m80_{\text{sulfate}}$, $m64_{\text{sulfate}}$, and $m48_{\text{sulfate}}$ are the signals at m/z 98 ($H_2SO_4^+$), 81 (HSO_3^+), 80 (SO_3^+), 64 (SO_2^+), and 48 (SO^+) attributed to sulfate. This attribution of the signals to sulfate ions is described further in Text S2 of Supporting Information S1. We normalize the fH_2SO_4 for a given sample to fH_2SO_4 for a pure ammonium sulfate aerosol ($fH_2SO_4(\text{pure AS})$) to define the variable nfH_2SO_4 (Equation 2)

$$nfH_2SO_4 = \frac{fH_2SO_4}{fH_2SO_4(\text{pure AS})} \quad (2)$$

The mass of sulfate attributed to OOS is estimated by Equation 3

$$\text{OOS} = [\text{SO}_4] - nfH_2SO_4 \times [\text{SO}_4] \quad (3)$$

where $[\text{SO}_4]$ is the total mass loading of sulfate in the AMS spectrum (Schueneman et al., 2021). Note that the mass of OOS by this calculation is for the sulfate group only and does not include the mass of the organic backbone. In more acidic sulfur aerosol such as pure H_2SO_4 aerosol, ($\text{pH} < 0$), fH_2SO_4 is greater than the fH_2SO_4 of pure AS (Schueneman et al., 2021). Thus, finding an $nfH_2SO_4 > 1$ in the experiments conducted here would be an indicator of H_2SO_4 aerosol (Text S4 in Supporting Information S1).

3. Results and Discussion

3.1. Aerosol Mass Loading and Chemical Composition

Figure 1 shows an example of analyzed Q-AMS spectra from experiments with 0.5% CO_2 and 0.1% CH_4 with 0 (Figure 1a) or 5 ppm_v (Figure 1b) H_2S . Aerosol mass loading increased at nearly every m/z for precursor mixtures with 5 ppm_v H_2S compared to the same mixtures (CO_2 and CH_4 mixing ratios) in the absence of H_2S . Sulfate aerosol contributed to the increase in total aerosol mass (Figures 1b and 2b) and increased as a function of the CO_2 mixing ratio/O:C ratio (Figure 2b). The measurements provided no evidence of S_8 aerosol formation. Because the expected S_8 ions m/z 96, 128, 160, and 192 were absent under all conditions (example spectrum with an extended m/z range is shown in Figure S2 of Supporting Information S1), we attribute m/z 64 to SO_2^+ rather than to S_2^+ (Dewitt et al., 2010). Further, the ratio of ion intensities of m/z 48 to m/z 64 are ~ 1.1 under all conditions, consistent with the expectations of sulfate aerosol spectra (Dewitt et al., 2010). Additionally, we observed no evidence of pure H_2SO_4 and/or acidic sulfate aerosol as nfH_2SO_4 was never greater than one (Text S4 and Figure S3 in Supporting Information S1). An increase in ammonium coincident with the increase in sulfate (Figure 2b) implies the formation of inorganic salts, such as ammonium sulfate. Therefore, we attribute the sulfate fragments as originating from sulfate salts or OOS rather than S_8 or H_2SO_4 .

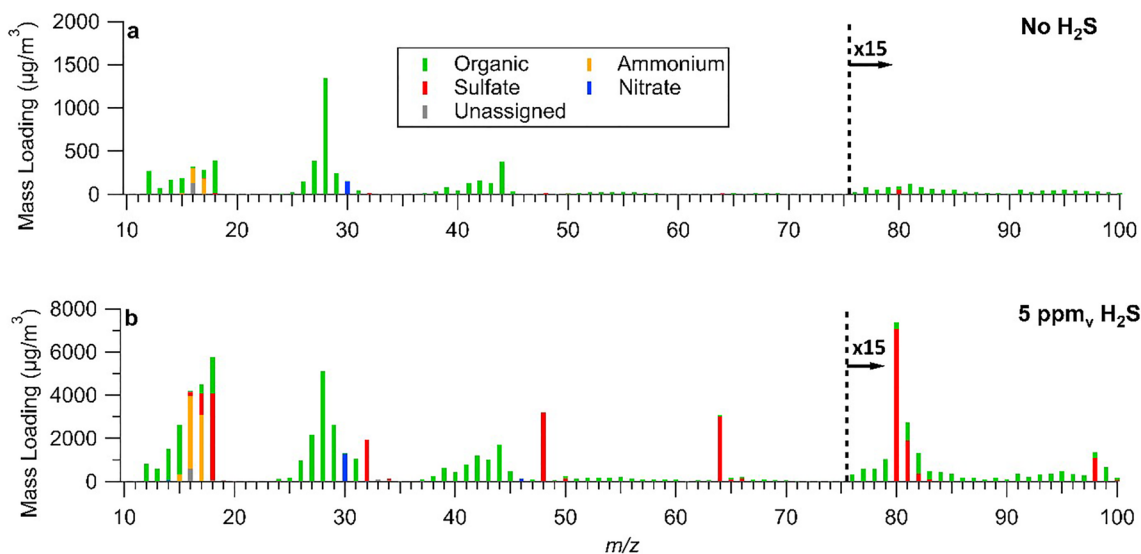


Figure 1. (a) Mass spectra of aerosol produced from 0.5% CO₂ and 0.1% CH₄ in N₂ (a) without H₂S and (b) with 5 ppm_v H₂S. Each *m/z* fragment is assigned to either organic, sulfate, ammonium, nitrate, or unassigned aerosol fragments. Note that the mass loading range for (b) is larger than (a) by a factor of 4. Ion intensities for *m/z* 75 and higher are multiplied by a factor of 15 for clarity. Colorblind-friendly figure as Figure S4 in Supporting Information S1.

The inclusion of H₂S increases the organic aerosol mass (Figures 1b and 2b) and alters the trend in organic aerosol mass as a function of O:C of the precursor mixture. The organic aerosol mass formed from precursor mixtures without H₂S decreases once O:C exceeds 4:3 (Figure 2a). This decrease in aerosol mass is consistent with past models and experiments using similar precursor mixtures showing organic aerosol decreases at high O:C ratios, typically >~1:1 (Arney et al., 2016; Trainer et al., 2006). However, in the experiments with H₂S, the organic aerosol mass exceeds the total aerosol mass of the control experiments and remains constant for O:C ratios of 1:1–40:21 (Figures 2a and 2b). The organic aerosol also increased with the addition of CO₂ compared to the H₂S/CH₄ experiment without CO₂ (Figure 2b) from our previous work, Reed et al. (2020).

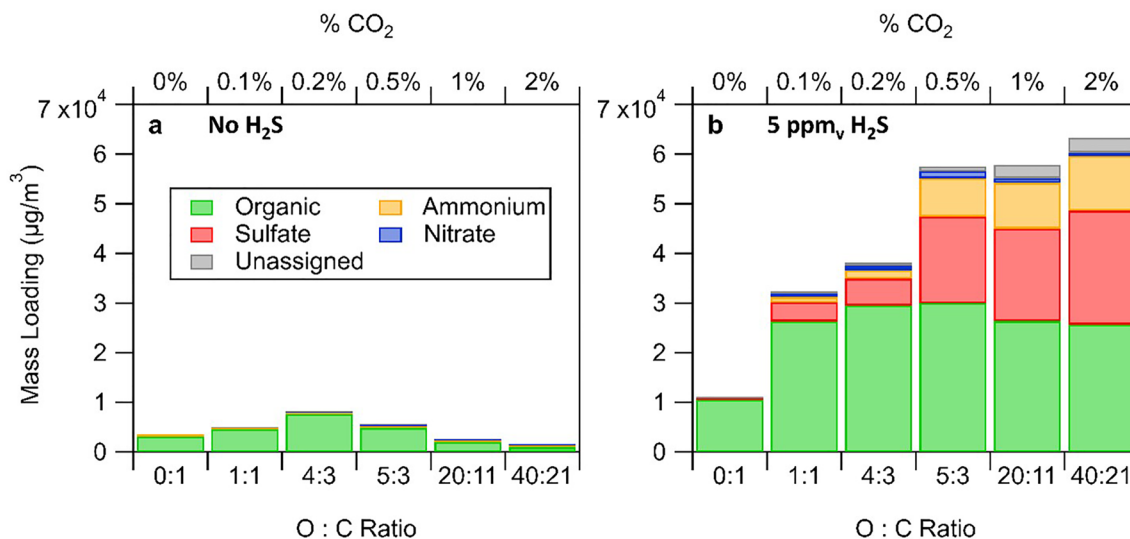


Figure 2. Aerosol mass loadings from precursor mixtures with (a) 0 ppm_v H₂S and (b) 5 ppm_v H₂S as a function of O:C ratio/% CO₂ of the precursor mixtures. Colors indicate aerosol chemical speciation. Data shown for 0:1 O:C ratio/0% CO₂ are from Reed et al. (2020). Two experiments each were conducted for 0.2% and 0.5% CO₂ with 0.1% CH₄ and 5 ppm_v H₂S to check for reproducibility; the data shown are averages. Colorblind-friendly figure as Figure S5 in Supporting Information S1.

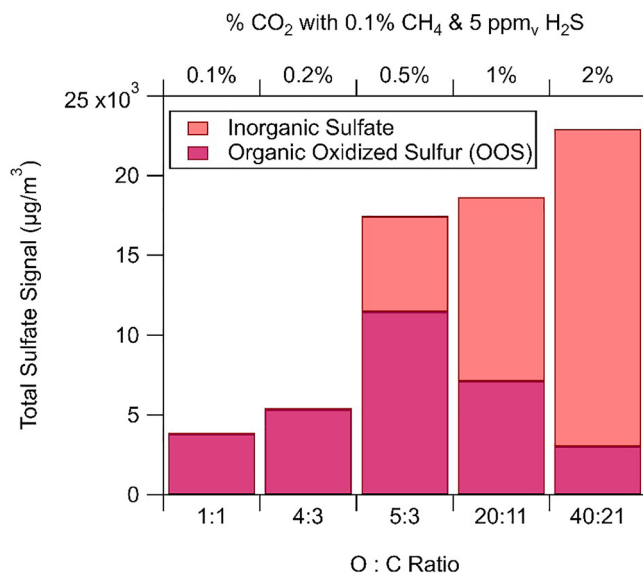


Figure 3. Total sulfate aerosol signal as a function of O:C ratio/% CO₂ showing the inorganic sulfate (salmon) and organic oxidized sulfur (OOS) (maroon) aerosol contributions. Two experiments each were conducted for 0.2% and 0.5% CO₂ with 0.1% CH₄ and 5 ppm_v H₂S to check for reproducibility; the data shown are averages. Colorblind-friendly figure as Figure S7 in Supporting Information S1.

contribution of oxygenated organic compounds to organic aerosol mass. The f45 exhibits a clear decrease as a function of O:C ratio, suggesting more of the sulfur is converted to OOS and inorganic sulfate, rather than ORS, as the initial gas mixture becomes more oxidizing. Possible mechanisms for ORS and OOS formation are discussed in Text S7 of Supporting Information S1 and are based on Reed et al. (2020) and chemistry in the modern atmosphere (e.g., Liggio & Li, 2006; Tolocka & Turpin, 2012).

3.2. Attribution of Organosulfur Aerosol

The amount of the sulfate signal originating from OOS fragments was estimated for each H₂S experiment as discussed in Section 2.2. OOS aerosol mass exhibited a maximum at 0.5% CO₂ and a minimum at 0.1% CO₂ (Figure 3). A change in oxidative capacity of the gas mixture potentially explains why OOS mass reaches a maximum and inorganic sulfate appears at 0.5% CO₂; the O:H ratio of the mixture is greater than 1 (~5:2) at 0.5% CO₂ and above. The conclusion that OOS is significant still holds even for a lower limit estimate of OOS (Text S5 and Figure S6 in Supporting Information S1).

Organic aerosol formed from the precursor mixtures with H₂S contain ions consistent with fragments of ORS compounds. These include ions (*m/z* 32–35, 45–48, and 58–62) that were identified in our past work of H₂S/CH₄ haze chemistry in the absence of CO₂ (Reed et al., 2020). These ORS masses are enhanced in signal compared to experiments without H₂S (Figure S8 in Supporting Information S1). This enhancement pattern closely matches the results of Reed et al. (2020) and is attributed to ORS formation (Text S6 in Supporting Information S1). Here we select *m/z* 45 as an ORS proxy ion because it includes the simplest ORS ion fragment, HCS⁺, and sulfate does not produce an *m/z* 45 ion. In H₂S-free experiments, the ion is attributed to oxygenated organic fragments, such as HCO₂⁺ or H₅C₂O⁺. We define the variable f45 as the fraction of the organic mass signal from *m/z* 45. Figure 4 shows f45 at each O:C ratio/CO₂ mixing ratio. The f45 is higher in experiments that included 5 ppm_v H₂S than in experiments without H₂S. We interpret this enhancement of f45 as evidence for the formation of HCS⁺ as it is unlikely that the addition of H₂S would produce an increase in the fractional

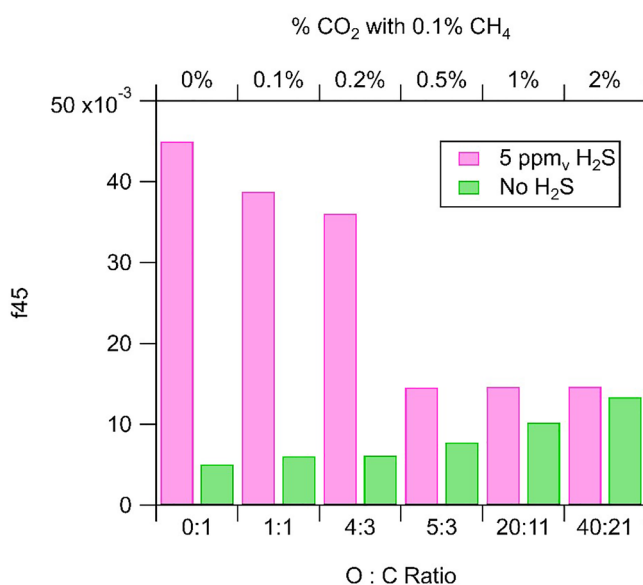


Figure 4. f45 as function of O:C ratio/% CO₂ in experiments with 5 ppm_v H₂S (pink) and without H₂S (green). The data shown at 0:1 O:C ratio/0% CO₂ are from Reed et al., 2020.

3.3. Significance for Archean Atmosphere

General thought is that little to no organic haze will form in CO₂-rich atmospheres, such as Archean Earth (Arney et al., 2016; Trainer et al., 2006). This decrease in haze production is thought to, at least in part, result from the production of O radicals from CO₂ photolysis. At higher O:C ratios (>1:1), O radicals terminate hydrocarbon chain growth chemistry, making smaller molecules with presumably higher vapor pressures that are unable to partition into the aerosol particles, decreasing the amount of organic aerosol (Trainer et al., 2006). The exact effects of this chemistry are dependent on the precursor gas mixture and metrics such as the H:O ratio. For example, He et al. (2018) showed that addition of H₂O led to an increase in organic aerosol mass (He et al., 2018). The H₂S-free experiments in this study support this general idea. In contrast, our results show that the addition of trace H₂S can enhance production of organic aerosol at O:C ratios >1. Moreover, the amount of organic aerosol formed exceeds the total aerosol produced in the H₂S-free experiments and remains constant as the O:C ratio increases, up to a ratio of 40:21. Figure 5 illustrates these overarching findings and compares our results to previous understandings of CO₂/CH₄ haze chemistry.

Our results have implications for the sulfur chemistry of the Archean atmosphere. It has generally been assumed that the dominant sulfur reservoirs in the Archean atmosphere were either S₈ and H₂SO₄ aerosol (Kasting

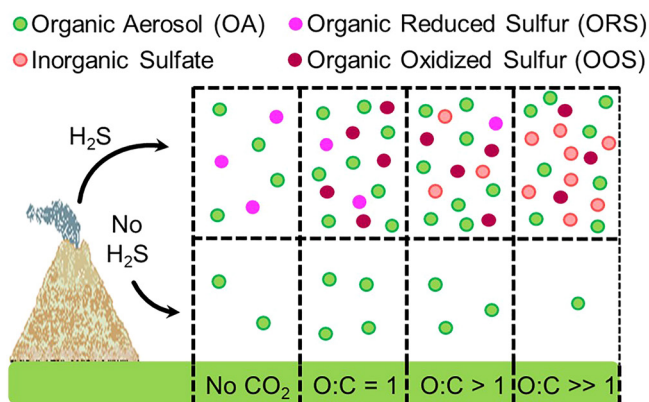


Figure 5. Illustration summarizing the results of this study. The “No CO₂” category is based on the conclusions of Reed et al. (2020). Colorblind-friendly figure as Figure S9 in Supporting Information S1.

et al., 1989; Pavlov & Kasting, 2002). However, we found no evidence in our experiments for the formation of either S₈ or H₂SO₄ aerosol although we did observe inorganic sulfate, likely present as a salt evidenced by the increased NH₄ mass loading (Figure 2b). Our study shows that OOS accounts for a significant portion (~13%–100%) of the sulfate aerosol formed. OOS aerosol was observed at all CO₂ mixing ratios studied with trace H₂S present in the precursor mixture. Our new results highlight the formation of OOS, and possibly ORS, as a potential control on the atmospheric, biological, and sedimentary expression of S-SMIF (Halevy, 2013; Lie et al., 1996; Zerkle et al., 2012). In addition to potentially revising the current paradigm surrounding S-MIF Archean atmospheric sulfur chemistry, an atmospheric sulfur cycle that is more diverse than just S₈ and pure H₂SO₄ aerosol may have implications for the early evolution of life of Earth, given the importance of organosulfur compounds in the evolution of early metabolic pathways (Lie et al., 1996; Wagner et al., 1998) and, perhaps, at the origin of life (De Duve, 2011). Recent experiments using chemical and physical conditions different from those presented here also report organosulfur formation (He et al., 2020; Vuitton et al., 2021). Further, the formation of OOS and the lack of H₂SO₄ and S₈ formation would likely depend on the H₂S/SO₂

outgassing ratio in planetary atmospheres. However, the SO₂ experiments of Dewitt et al. (2010) also reported organosulfur formation. Taken together, our results and those of past studies suggest this sulfur chemistry appears ubiquitous under a variety of atmospheric conditions.

Our results also impact the understanding of CO₂/CH₄ haze chemistry in exoplanetary atmospheres. Arney et al. (2018) proposed that an organic haze may be a potential biosignature if a significant amount of haze was present at high CO₂ mixing ratios, as this would require an additional carbon source from life (Arney et al., 2018). However, we have shown that trace H₂S enhances organic haze formation at high CO₂ mixing ratios in the absence of additional carbon sources, suggesting that an organic haze production may exhibit a large sensitivity to both biotic and abiotic trace gases.

4. Conclusions

Our results suggest that trace H₂S in Archean-like organic haze analog experiments facilitates a coupling between the carbon and sulfur haze production pathways. This coupling increases organic aerosol mass and forms organosulfur species (OOS and ORS) even at high O:C ratios. In contrast, S₈ and H₂SO₄ aerosol products were not observed under any of our experimental conditions, though inorganic sulfate aerosol was observed in the form of salts. Our work also demonstrates a potential abiotic production pathway for organosulfur compounds. Organosulfur compounds are an essential component of life, and this pathway has implications for prebiotic chemistry and nutrient production for early life. Facile production of organosulfur aerosol in the Archean atmosphere, as demonstrated here experimentally, will influence interpretations and understanding of the S-MIF record in Archean sedimentary rocks.

Data Availability Statement

All data and the fragmentation table are archived and made available through the CU Scholar data repository provided by the University Libraries at the University of Colorado, Boulder. <https://doi.org/10.25810/bnqe-wt68>.

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References

- Aiuppa, A., Federico, C., Giudice, G., Gurrieri, S., & Valenza, M. (2006). Hydrothermal buffering of the SO₂/H₂S ratio in volcanic gases: Evidence from la Fossa Crater fumarolic field, Vulcano Island. *Geophysical Research Letters*, 33, L21315. <https://doi.org/10.1029/2006GL027730>
- Aiuppa, A., Inguaggiato, S., McGonigle, A. J. S., O'Dwyer, M., Oppenheimer, C., Padgett, M. J., et al. (2005). H₂S fluxes from Mt. Etna, Stromboli, and Vulcano (Italy) and implications for the sulfur budget at volcanoes. *Geochimica et Cosmochimica Acta*, 69(7), 1861–1871. <https://doi.org/10.1016/j.gca.2004.09.018>

- Allan, J. D., Alfarra, M. R., Bower, K. N., Williams, P. I., Gallagher, M. W., Jimenez, J. L., et al. (2003). Quantitative sampling using an aerodyne aerosol mass spectrometer. 2. Measurements of fine particulate chemical composition in two U. K. cities. *Journal of Geophysical Research*, 108(D3), 4091. <https://doi.org/10.1029/2002JD002359>
- Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., et al. (2004). A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data. *Journal of Aerosol Science*, 35(7), 909–922. <https://doi.org/10.1016/j.jaerosci.2004.02.007>
- Allan, J. D., Jimenez, J. L., Williams, P. I., Rami Alfarra, M., Bower, K. N., Jayne, J. T., et al. (2002). Quantitative sampling using an Aerodyne aerosol mass spectrometer, 1, Techniques of data interpretation and error analysis. *Journal of Geophysical Research*, 108(D3), 4090. <https://doi.org/10.1029/2002JD002358>
- Archer, C., & Vance, D. (2006). Coupled Fe and S isotope evidence for Archean microbial Fe(III) and sulfate reduction. *Geology*, 34(3), 153–156. <https://doi.org/10.1130/G22067.1>
- Arney, G., Domagal-Goldman, S. D., & Meadows, V. S. (2018). Organic haze as a biosignature in anoxic Earth-like atmospheres. *Astrobiology*, 18(3), 311–329. <https://doi.org/10.1089/ast.2017.1666>
- Arney, G., Domagal-Goldman, S. D., Meadows, V. S., Wolf, E. T., Schwieterman, E., Charnay, B., et al. (2016). The pale orange dot: The spectrum and habitability of hazy Archean Earth. *Astrobiology*, 16(11), 873–899. <https://doi.org/10.1089/ast.2015.1422>
- Atreya, S. K., Mahaffy, P. R., Niemann, H. B., Wong, M. H., & Owen, T. C. (2003). Composition and origin of the atmosphere of Jupiter - an update, and implications for the extrasolar giant planets. *Planetary and Space Science*, 51(2), 105–112. [https://doi.org/10.1016/S0032-0633\(02\)00144-7](https://doi.org/10.1016/S0032-0633(02)00144-7)
- Berry, J. L., Ugelow, M. S., Tolbert, M. A., & Browne, E. C. (2019a). Chemical composition of gas-phase positive ions during laboratory simulations of titan's haze formation. *ACS Earth and Space Chemistry*, 3(2), 202–211. <https://doi.org/10.1021/acsearthspacechem.8b00139>
- Berry, J. L., Ugelow, M. S., Tolbert, M. A., & Browne, E. C. (2019b). The influence of gas-phase chemistry on organic haze formation. *The Astrophysical Journal*, 885(1), L6. <https://doi.org/10.3847/2041-8213/ab4b5b>
- Chakraborty, S., Jackson, T. L., Ahmed, M., & Thieme, M. H. (2013). Sulfur isotopic fractionation in vacuum UV photodissociation of hydrogen sulfide and its potential relevance to meteorite analysis. *Proceedings of the National Academy of Sciences of the United States of America*, 110(44), 17650–17655. <https://doi.org/10.1073/pnas.1213150110>
- Chen, Y., Dombek, T., Hand, J., Zhang, Z., Gold, A., Ault, A. P., et al. (2021). Seasonal contribution of isoprene-derived organosulfates to total water-soluble fine particulate organic sulfur in the United States. *ACS Earth and Space Chemistry*, 5(9), 2419–2432. <https://doi.org/10.1021/acsearthspacechem.1c00102>
- Chen, Y., Xu, L., Humphry, T., Hettiyadura, A. P. S., Ovadnevaite, J., Huang, S., et al. (2019). Response of the aerodyne aerosol mass spectrometer to inorganic sulfates and organosulfur compounds: Applications in field and laboratory measurements. *Environmental Science and Technology*, 53(9), 5176–5186. <https://doi.org/10.1021/acs.est.9b00884>
- De Duve, C. (2011). Life as a cosmic imperative? *Philosophical Transactions of the Royal Society A: Mathematical, Physical & Engineering Sciences*, 369, 620–623. <https://doi.org/10.1098/rsta.2010.0312>
- Dewitt, H. L., Hasenkopf, C. A., Trainer, M. G., Farmer, D. K., Jimenez, J. L., McKay, C. P., et al. (2010). The formation of sulfate and elemental sulfur aerosols under varying laboratory conditions: Implications for early Earth. *Astrobiology*, 10(8), 773–781. <https://doi.org/10.1089/ast.2009.9455>
- Domagal-Goldman, S. D., Kasting, J. F., Johnston, D. T., & Farquhar, J. (2008). Organic haze, glaciations and multiple sulfur isotopes in the Mid-Archean Era. *Earth and Planetary Science Letters*, 269(1–2), 29–40. <https://doi.org/10.1016/j.epsl.2008.01.040>
- Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., & Jimenez, J. L. (2010). Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry. *Proceedings of the National Academy of Sciences of the United States of America*, 107(15), 6670–6675. <https://doi.org/10.1073/pnas.0912340107>
- Farquhar, J., Bao, H., & Thieme, M. (2000). Atmospheric influence of Earth's earliest sulfur cycle. *Science*, 289(5480), 756–758. <https://doi.org/10.1126/science.289.5480.756>
- Farquhar, J., Savarino, J., Jackson, T. L., & Thieme, M. H. (2000). Evidence of atmospheric sulphur in the martian regolith from sulphur isotopes in meteorites. *Nature*, 404(6773), 50–52. <https://doi.org/10.1038/35003517>
- Farquhar, J., & Wing, B. A. (2003). Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters*, 213(1–2), 1–13. [https://doi.org/10.1016/S0012-821X\(03\)00296-6](https://doi.org/10.1016/S0012-821X(03)00296-6)
- Gao, P., Marley, M. S., Zahnle, K., Robinson, T. D., & Lewis, N. K. (2017). Sulfur hazes in giant exoplanet atmospheres: Impacts on reflected light spectra. *The Astronomical Journal*, 153(3), 139. <https://doi.org/10.3847/1538-3881/aa5fab>
- Halevy, I. (2013). Production, preservation, and biological processing of mass-independent sulfur isotope fractionation in the Archean surface environment. *Proceedings of the National Academy of Sciences of the United States of America*, 110(44), 17644–17649. <https://doi.org/10.1073/pnas.1213148110>
- He, C., Hörst, S. M., Lewis, N. K., Yu, X., Moses, J. I., Kempton, E. M.-R., et al. (2018). Photochemical haze formation in the atmospheres of super-Earths and mini-Neptunes. *The Astronomical Journal*, 156(1), 38. <https://doi.org/10.3847/1538-3881/aac883>
- He, C., Hörst, S. M., Lewis, N. K., Yu, X., Moses, J. I., McGuigan, P., et al. (2020). Sulfur-driven haze formation in warm CO₂-rich exoplanet atmospheres. *Nature Astronomy*, 4(10), 986–993. <https://doi.org/10.1038/s41550-020-1072-9>
- Holland, H. D. (2002). Volcanic gases, black smokers, and the great oxidation event. *Geochimica et Cosmochimica Acta*, 66(21), 3811–3826. [https://doi.org/10.1016/S0016-7037\(02\)00950-X](https://doi.org/10.1016/S0016-7037(02)00950-X)
- Hörst, S. M., & Tolbert, M. A. (2013). In situ measurements of the size and density of titan aerosol analogs. *The Astrophysical Journal Letters*, 770(1), L10. <https://doi.org/10.1088/2041-8205/770/1/L10>
- Hu, R., Seager, S., & Bains, W. (2013). Photochemistry in terrestrial exoplanet atmospheres. II. H₂S and SO₂ photochemistry in anoxic atmospheres. *The Astrophysical Journal*, 769(1), 6. <https://doi.org/10.1088/0004-637X/769/1/6>
- Izon, G., Zerkle, A. L., Williford, K. H., Farquhar, J., Poulton, S. W., & Claire, M. W. (2017). Biological regulation of atmospheric chemistry en route to planetary oxygenation. *Proceedings of the National Academy of Sciences of the United States of America*, 114(13), E2571–E2579. <https://doi.org/10.1073/pnas.1618798114>
- Izon, G., Zerkle, A. L., Zhelezinskaia, I., Farquhar, J., Newton, R. J., Poulton, S. W., et al. (2015). Multiple oscillations in Neoproterozoic atmospheric chemistry. *Earth and Planetary Science Letters*, 431, 264–273. <https://doi.org/10.1016/j.epsl.2015.09.018>
- Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., & Worsnop, D. R. (2000). Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Science and Technology*, 33(1–2), 49–70. <https://doi.org/10.1080/027868200410840>
- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., et al. (2003). Ambient aerosol sampling using the Aerodyne aerosol mass spectrometer. *Journal of Geophysical Research*, 108(D7), 8425. <https://doi.org/10.1029/2001jd001213>

- Kasting, J. F., Zahnle, K. J., Pinto, J. P., & Young, A. T. (1989). Sulfur, ultraviolet radiation, and the early evolution of life. *Origins of Life and Evolution of the Biosphere*, 19(2), 95–108. <https://doi.org/10.1007/BF01808144>
- Kump, L. R., & Barley, M. E. (2007). Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature*, 448(7157), 1033–1036. <https://doi.org/10.1038/nature06058>
- Kump, L. R., Pavlov, A., & Arthur, M. A. (2005). Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia. *Geology*, 33(5), 397–400. <https://doi.org/10.1130/G21295.1>
- Lie, T. J., Pitta, T., Leadbetter, E. R., Godchaux, W., & Leadbetter, J. R. (1996). Sulfonates: Novel electron accepters in anaerobic respiration. *Archives of Microbiology*, 166(3), 204–210. <https://doi.org/10.1007/s002030050376>
- Liggio, J., & Li, S. M. (2006). Organosulfate formation during the uptake of pinonaldehyde on acidic sulfate aerosols. *Geophysical Research Letters*, 33, L13808. <https://doi.org/10.1029/2006GL026079>
- Ono, S. (2017). Photochemistry of sulfur dioxide and the origin of mass-independent isotope fractionation in Earth's atmosphere. *Annual Review of Earth and Planetary Sciences*, 45(1), 301–329. <https://doi.org/10.1146/annurev-earth-060115-012324>
- Pavlov, A. A., & Kasting, J. F. (2002). Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic archaean atmosphere. *Astrobiology*, 2(1), 27–41. <https://doi.org/10.1089/153110702753621321>
- Reed, N. W., Browne, E. C., & Tolbert, M. A. (2020). Impact of hydrogen sulfide on photochemical haze formation in methane/nitrogen atmospheres. *ACS Earth and Space Chemistry*, 4(6), 897–904. <https://doi.org/10.1021/acsearthspacechem.0c00086>
- Schueneman, M. K., Nault, B. A., Campuzano-Jost, P., Jo, D. S., Day, D. A., Schroder, J. C., et al. (2021). Aerosol pH indicator and organosulfate detectability from aerosol mass spectrometry measurements. *Atmospheric Measurement Techniques*, 14(3), 2237–2260. <https://doi.org/10.5194/amt-14-2237-2021>
- Shen, Y., & Buick, R. (2004). The antiquity of microbial sulfate reduction. *Earth-Science Reviews*, 64(3–4), 243–272. [https://doi.org/10.1016/S0012-8252\(03\)00054-0](https://doi.org/10.1016/S0012-8252(03)00054-0)
- Shen, Y., Buick, R., & Canfield, D. E. (2001). Isotopic evidence for microbial sulphate reduction in the early Archaean era. *Nature*, 410(6824), 77–81. <https://doi.org/10.1038/35065071>
- Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., et al. (2008). Organosulfate formation in biogenic secondary organic aerosol. *Journal of Physical Chemistry A*, 112(36), 8345–8378. <https://doi.org/10.1021/jp802310p>
- Tolocka, M. P., & Turpin, B. (2012). Contribution of organosulfur compounds to organic aerosol mass. *Environmental Science and Technology*, 46(15), 7978–7983. <https://doi.org/10.1021/es300651v>
- Trainer, M. G., Jimenez, J. L., Yung, Y. L., Toon, O. B., & Tolbert, M. A. (2012). Nitrogen incorporation in CH₄-N₂ photochemical aerosol produced by far ultraviolet irradiation. *Astrobiology*, 12(4), 315–326. <https://doi.org/10.1089/ast.2011.0754>
- Trainer, M. G., Pavlov, A. A., DeWitt, H. L., Jimenez, J. L., McKay, C. P., Toon, O. B., & Tolbert, M. A. (2006). Organic haze on Titan and the early Earth. *Proceedings of the National Academy of Sciences of the United States of America*, 103(48), 18035–18042. <https://doi.org/10.1073/pnas.0608561103>
- Vuitton, V., Moran, S. E., He, C., Wolters, C., Flandinet, L., Orthous-Daunay, F.-R., et al. (2021). H₂SO₄ and organosulfur compounds in laboratory analogue aerosols of warm high-metallicity exoplanet atmospheres. *The Planetary Science Journal*, 2(1), 2. <https://doi.org/10.3847/psj/abc558>
- Wagner, M., Roger, A. J., Flax, J. L., Brusseau, G. A., & Stahl, D. A. (1998). Phylogeny of dissimilatory sulfite reductases supports an early origin of sulfate respiration. *Journal of Bacteriology*, 180(11), 2975–2982. <https://doi.org/10.1128/jb.180.11.2975-2982.1998>
- Zerle, A. L., Claire, M. W., Domagal-Goldman, S. D., Farquhar, J., & Poulton, S. W. (2012). A bistable organic-rich atmosphere on the Neoproterozoic Earth. *Nature Geoscience*, 5(5), 359–363. <https://doi.org/10.1038/ngeo1425>