Research Articles

The Formation of Sulfate and Elemental Sulfur Aerosols under Varying Laboratory Conditions: Implications for Early Earth

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Abstract

The presence of sulfur mass-independent fractionation (S-MIF) in sediments more than 2.45×10^9 years old is thought to be evidence for an early anoxic atmosphere. Photolysis of sulfur dioxide (SO_2) by UV light with $\lambda < 220$ nm has been shown in models and some initial laboratory studies to create a S-MIF; however, sulfur must leave the atmosphere in at least two chemically different forms to preserve any S-MIF signature. Two commonly cited examples of chemically different sulfur species that could have exited the atmosphere are elemental sulfur (S_8) and sulfuric acid (H_2SO_4) aerosols. Here, we use real-time aerosol mass spectrometry to directly detect the sulfur-containing aerosols formed when SO_2 either photolyzes at wavelengths from 115 to 400 nm, to simulate the UV solar spectrum, or interacts with high-energy electrons, to simulate lightning. We found that sulfur-containing aerosols form under all laboratory conditions. Further, the addition of a reducing gas, in our experiments hydrogen (H_2) or methane (CH_4), increased the formation of S_8. With UV photolysis, formation of S_8 aerosols is highly dependent on the initial SO_2 pressure; and S_8 is only formed at a 2% SO_2 mixing ratio and greater in the absence of a reductant, and at a 0.2% SO_2 mixing ratio and greater in the presence of 1000 ppmv CH_4. We also found that organosulfur compounds are formed from the photolysis of CH_4 and moderate amounts of SO_2. The implications for sulfur aerosols on early Earth are discussed. Key Words: S-MIF—Archean atmosphere—Early Earth—Sulfur aerosols. Astrobiology 10, 773–781.

1. Introduction

UNDERSTANDING THE ATMOSPHERE of early Earth during the Archean, the period of time approximately 4–2.45 billion years ago, is an important part of understanding the conditions under which life originated and developed. Not much is known with certainty about the atmosphere during the Archean. However, various pieces of geological evidence provide guidelines toward the atmospheric composition and Earth's climate at the time when life emerged on Earth.

It is thought that a major change in the oxidative state of early Earth's atmosphere occurred at the end of the Archean, approximately 2.45 Ga (Bekker *et al.,* 2004, and references therein), with perhaps the strongest evidence coming from isotopic patterns seen in S-bearing sediments through time (Farquhar *et al.,* 2000). Sulfur is emitted from volcanic ac-

tivity as either hydrogen sulfide (H_2S) or sulfur dioxide (SO_2) and readily converts between the two different starting species in a reducing atmosphere (Kasting *et al.,* 1989). Around 2 ppbv, SO_2 could have existed in the reducing atmosphere of early Earth if the volcanic outgassing rate was three times as high as it is today, assuming the ocean was saturated with SO_2 and thus rainout was not a loss process for SO_2 (Kasting *et al.,* 1989). Measurements show that sulfur mass-independent fractionation (S-MIF) occurs in sedimentary rocks older than 2.45 Ga. However, all the S-isotopes fall along a mass-dependent fractionation line in younger sediments (Farquhar *et al.,* 2000). An anoxic early Earth atmosphere could help explain these data (Pavlov and Kasting, 2002).

Laboratory experiments (Farquhar *et al.,* 2001) and model simulations (Lyons, 2007) suggest that the photolysis of SO_2

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by UV light with a wavelength <220 nm at low altitudes is one way to form the S-MIF found in the Archean sediments. For these wavelengths of UV light to reach the lower atmosphere, an anoxic early Earth atmosphere would have been necessary (Farquhar *et al.,* 2001). The formation of S-MIF below 10 km is believed to be necessary for the efficient fallout of these S-MIF–bearing species to reach the ground (Domagal-Goldman *et al.,* 2008). Ozone (O_3) and oxygen (O_2) in the current stratosphere absorb the lower-wavelength incoming solar radiation and prevent the wavelengths of light necessary to form S-MIF from reaching the lower atmosphere. The preservation of the S-MIF signals in the geological record requires the formation of at least two types of S-bearing species with different oxidative states (Kasting, 2001). The different sulfur reservoirs must be spatially and temporally separated to preserve the S-MIF signal (Pavlov and Kasting, 2002). H_2SO_4 and elemental sulfur (specifically S_8) aerosols formed from the photolysis and subsequent reactions of SO_2 are often cited as two possible reservoirs for S-MIF (Kasting *et al.,* 1989; Ono *et al.,* 2003; Zahnle *et al.,* 2006; Domagal-Goldman *et al.,* 2008). To achieve these two distinct sulfur reservoirs, it has been proposed that an extremely anoxic atmosphere is necessary, as the presence of oxygen at 10^{-5} times the present atmospheric level (PAL) would eventually cause all the sulfur in the atmosphere to become H_2SO_4 (Pavlov and Kasting, 2002).

The chemical mechanisms used in model predictions of the relative concentrations of different types of sulfur-containing aerosols often contain unknown and uncertain rate constants that may affect the results of the model (Kasting *et al.,* 1989; Pavlov and Kasting, 2002). Previous experimental work on S-MIF formation from low-wavelength photolysis by Farquhar *et al.* (2001) was performed at high levels of SO_2, approximately 1–2% SO_2 in carbon dioxide (CO_2) with, and without, added water (H_2O). At these levels of SO_2, both S_8 and H_2SO_4 aerosols were formed. However, these levels are significantly higher than those believed to have been present on early Earth (Kasting *et al.,* 1989). A model study by Ono *et al.* (2003) found that the amount of SO_2 greatly influenced the S_8/H_2SO_4 ratio, with S_8 composing about 50% of the total S-bearing aerosol mass formed at an SO_2 outgassing flux of 3.5×10^9 molecules cm^{-2} s^{-1}, while almost no S_8 was formed at an SO_2 outgassing rate an order of magnitude lower. Later models have probed the effects of other major atmospheric constituents on sulfur aerosol chemistry. Zahnle *et al.* (2006) used a 1-D model to study the formation of S_8 from photochemical reactions of O_2, methane (CH_4), and SO_2 in the atmosphere. They found that efficient S_8 production at O_2 levels of 10^{-7} PAL or lower requires the presence of reduced gases (*i.e.,* CH_4 or hydrogen, H_2). With a fixed O_2 level of 10^{-7} PAL, they found that S_8 production shuts off for $CH_4 < 8$ ppmv. Increasing the CH_4 mixing ratio allowed S_8 to form at higher O_2 levels (Zahnle *et al.,* 2006). Significant amounts of CH_4 could have come from early methanogens. Ono *et al.* (2003) found a similar positive correlation in their model with the atmospheric pressure of CH_4 and the formation of S_8. Other forms of S-bearing aerosols, such as organosulfur (a general term for species containing C and S), could also have been present under the atmospheric conditions of early Earth and may have helped preserve S-MIF signal (Lyons, 2009; Ueno *et al.,* 2009).

Here, we report the results of laboratory experiments to probe the formation of different chemical forms of sulfur-containing aerosols through UV radiation (to produce aerosols from photolysis from solar radiation) and electrical discharge (to simulate lightning). We used real-time aerosol mass spectrometry to probe the chemical composition of sulfur aerosols formed from a mixture of $CH_4/CO_2/H_2$ with SO_2. The effect of the initial partial pressure of SO_2 was also investigated.

2. Experimental

2.1. Aerosol generation

The reaction system used to perform these experiments was discussed in detail previously (Trainer *et al.,* 2004, 2006). The reactant gases were first combined in a mixing chamber where they were allowed to equilibrate for 12 hours to ensure homogeneity. The gas mixture was then flowed into a reaction chamber with a Mykrolis mass flow controller at a flow rate of 60 standard cubic centimeters per minute. As the reagent gases passed through the reaction chamber, they were exposed to either an electrical discharge (Tesla coil) to simulate lightning or a Hamamatsu broad-spectrum UV lamp with a wavelength range from 115–400 nm to simulate the UV region of the solar spectrum. Reactions within each chamber produced sulfur-containing aerosols. The gas mixtures were only exposed to the narrow line of spark discharge for a few seconds before being flowed through the reaction cell, similar to a lightning strike. The residence time for the gas inside the photochemical reaction chamber was 5 minutes. Note that particles in the real atmosphere would have far longer reaction times than those in the present work. The mechanical pump on our vacuum can theoretically pump down to 0.001 torr, which gave us a lower limit of O_2 in our system of 10^{-6} PAL. This is within O_2 levels that modelers predict should still produce S_8, especially with the addition of reducing gases (Zahnle *et al.,* 2006).

2.2. Particle characterization

Aerosol composition as a function of reagent gas was measured with a quadrupole-based aerosol mass spectrometer (Q-AMS, Aerodyne Research, Billerica, MA) (Jayne *et al.,* 2000; Canagaratna *et al.,* 2007). The reacted particle/gas mixture flowed from the reaction chamber into the Q-AMS, where submicron particles were focused into a tight beam via an aerodynamic lens. The Q-AMS can be used in either the particle time-of-flight mode or in mass spectrum mode. The particle time-of-flight mode uses the terminal velocity of the particles in vacuum to determine their aerodynamic diameter, d_{va} (DeCarlo *et al.,* 2004), while in mass spectrum mode all particles are analyzed without size selection. The chemical composition of the particles was determined by flash vaporizing the particles on a heated tungsten surface at 600°C under high vacuum, followed by electron impact ionization (70 eV) and mass analysis with a quadrupole mass spectrometer. With this technique, we were able to measure the mass spectra of the aerosol compounds in real time without the need for collection. The Q-AMS was well suited to these experiments because its inlet and differential pumping system concentrates the particles by a factor of 10^7 relative to gaseous compounds, which thus minimizes gas

phase interferences. In addition to composition and size information, the Q-AMS also supplies information on the mass concentration ($\mu g\ m^{-3}$) of the particles sampled based on a calibration of the electron impact ionization signals (Jimenez et al., 2003).

For some experiments, a high-resolution time-of-flight aerosol mass spectrometer (HR-AMS) (DeCarlo et al., 2006) was also used in conjunction with the standard unit-mass resolution Q-AMS. The HR-AMS uses the same aerosol inlet, vaporization, and ionization system as the Q-AMS but with a time-of-flight mass spectrometer detection system in place of a quadrupole detector. Two analysis modes can be used for this system: a V-mode, with an effective ion path length of 1.3 m; and a W-mode, with an effective ion path length of 2.9 m. An order of magnitude of sensitivity is gained by operating in the V-mode, but some resolution is lost (DeCarlo et al., 2006). In this study, we chose to operate the HR-AMS solely in the W-mode for maximum peak resolution. While the Q-AMS has a resolving power of $m/\Delta m \sim 2m$ at all mass-to-charge ratios (m/z), with m being the nominal m/z and Δm being full width at half maximum, the HR-AMS in W-mode has a maximum resolution of at least $m/\Delta m = 4300$ at 200 m/z, which varies slightly over other m/z (DeCarlo et al., 2006). This allows identification of peaks that have the same nominal mass but different chemical formulas. Thus, more positive identification of fragments arising from molecules with specific functional groups, such as organosulfur or oxygenated organic molecules, can be made.

2.3. Gas mixtures

Various amounts of trace gases were mixed along with a nitrogen (N_2) background overnight in a mixing chamber. SO_2 (ultra high purity), H_2 (ultra high purity), CH_4 (research grade), CO_2 (research grade), and N_2 (ultra high purity) were purchased from Airgas Intermountain. A premixed standard gas of 2000 ± 20 ppmv SO_2 in N_2 was used as the starting gas for SO_2 in some instances. Pure SO_2 was diluted with N_2 for higher mixing ratio experiments with UV photolysis. The aerosol mass spectrometer (AMS) spectra of each gas mixture was obtained before initiating reaction and then subtracted from the aerosol spectra to reduce gas interference in our results.

The HR-AMS spectrum of the background gases was used to verify the O_2 upper limit. No O_2 was detected in the mass spectrum of the background gas mixture. At our running conditions, the HR-AMS could detect O_2 gas levels of 200 ppmv and above. Thus, an upper limit of O_2 in the gas mixture less than 10^{-3} PAL was confirmed with the HR-AMS. Combining this calculation with the pumping capability of our vacuum system gives a possible range of 10^{-6} to 10^{-3} PAL O_2 in the reaction chamber.

2.3.1. Electrical discharge. To simulate a volcanic plume, 20 ± 0.2 ppmv SO_2 with, and without, 0.1% (1000 ± 20 ppmv) CO_2 and with varying amounts of H_2 were mixed together. CO_2 was used as both an additional oxidant and a potential carbon source, while H_2 was used as an additional reductant. The overall amount of H_2 was varied to change the average oxidation state of the gas mixtures. CO_2 was used in half the experiments. To simplify the aerosol spectra and their interpretation, we chose H_2 instead of CH_4

as a reductant for the electrical discharge experiments even though models have shown that both could affect SO_2 chemistry in similar ways (Zahnle et al., 2006) and both could have been present in elevated amounts in the atmosphere of early Earth (Pavlov et al., 2000; Tian et al., 2005).

2.3.2. Photolysis. We used gas mixtures with varying amounts of SO_2 and CH_4 in a N_2 background to simulate the photochemical reactions that potentially occurred in the atmosphere of Archean Earth. We varied the partial pressure of SO_2 from 2 (± 0.2) to 20,000 (± 20) ppmv in our experiments to probe the effect of the SO_2 mixing ratio on aerosol formation. SO_2 amounts from 2 to 2000 ppmv are not unreasonable for volcanic clouds in early Earth's atmosphere following a volcanic eruption. For some experiments, we added 1000 ± 20 ppmv CH_4 to our mixtures, a reasonable amount of CH_4 for the late Archean (Haqq-Misra et al., 2008). While H_2 was added to several gas mixtures, no effect was observed, likely because H_2 does not photolyze at the wavelengths used in our experiment. Thus, CH_4 was used as the main reducing gas in the photolysis studies.

3. Results

3.1. Electrical discharge

Figure 1a shows the aerosol mass spectra of 20 ppmv SO_2 exposed to an electrical discharge. At 20 ppmv SO_2, the majority of the aerosol formed was H_2SO_4, which resulted from reaction of SO_2 and hydroxyl (OH) radicals formed from trace H_2O. Although the vacuum reaction chamber was evacuated to under a torr and kept at this level, the trace amounts of water left in the vacuum chamber or brought along with the gases heavily influenced the resulting aerosol composition after the gases were exposed to electrical discharge. Farquhar et al. (2001) also saw H_2SO_4 in their experiments without added H_2O. Increasing H_2 from 0 to 10% of the total gas mixture slowly increased the relative ratio of S_8/H_2SO_4 in the aerosol formed. As an example, Fig. 1b shows the mass spectrum with 5% H_2. Here, the mass signature for elemental sulfur is clearly observed. The Q-AMS can be used to quantify the fraction of S_8 formed under varying conditions. Figure 2 shows the relative amounts of characteristic H_2SO_4 and S_8 peaks from the electrical discharge of 20 ppmv SO_2 as a function of H_2 (not including overlapping peaks). It can be seen that above 4% H_2, S_8 is the dominant S aerosol formed. The experiments were repeated with the addition of 1000 ± 20 ppmv (0.1%) CO_2 added to the $SO_2/H_2/N_2$ mixture. Figure 2 shows that again for this mixture the addition of H_2 favors the formation of S_8 over H_2SO_4. However, with the additional CO_2 oxidant added, more H_2 is needed to switch the aerosol formed from mainly H_2SO_4 to mainly S_8.

3.2. UV experiments

3.2.1. The effect of the SO_2 mixing ratio on aerosol chemistry. For the UV experiments, gas mixtures containing varying mixing ratios of SO_2 were exposed to a broad-spectrum UV light source with wavelengths that ranged from 115 to 400 nm. Varying amounts of CH_4 and H_2 were added to the gas mixtures. The empty reaction chamber was exposed to UV light for 15 minutes while under vacuum prior to each experiment to photolyze H_2O contamination on
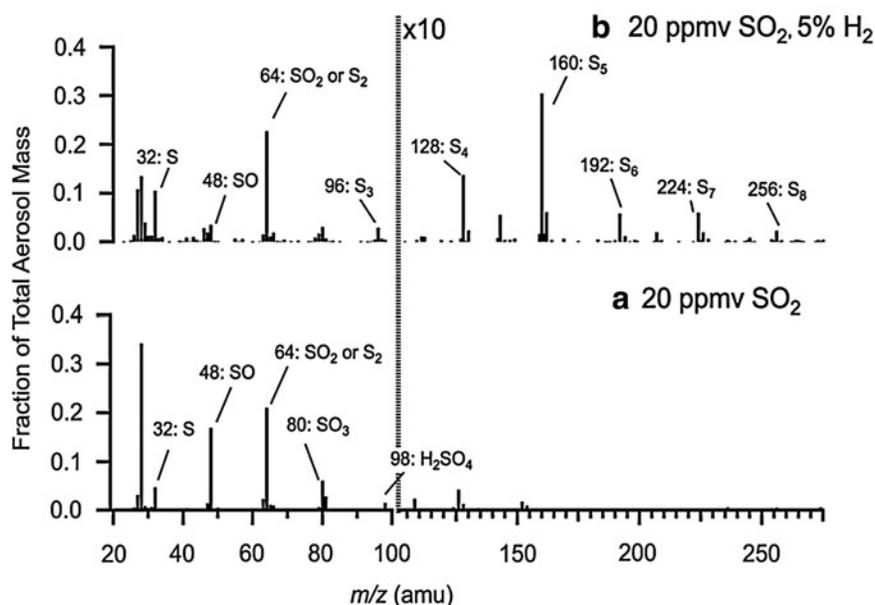
FIG. 1. Q-AMS spectra of particles formed from the electrical discharge of 20 ppmv SO_2 in N_2, without **(a)** and with **(b)** 50,000 ppmv (5%) H_2. Plotted is fraction of total aerosol mass versus m/z (amu). Likely peak identifications have been made. Spectra to the right of the dashed line have been multiplied by 10 for ease of viewing. Small signals not from S_8 or H_2SO_4 aerosols (unlabeled peaks) are around the noise level of the instrument and could be from trace contamination from the gas or flow system.

the walls of the reaction vessel. The reaction cell was also cooled both before and during reaction to 273 K with a methanol cooler in an attempt to reduce H_2O contamination. Although we achieved some reduction in H_2O, not all the H_2O contamination was removed.

The mixing ratio of SO_2 was varied to investigate the effect of initial partial pressure on the aerosol chemistry. With 2, 20, 200, and 2000 ppmv SO_2 in N_2, only the H_2SO_4 signal was observed. Figure 3a shows a representative spectrum using 2000 ppmv SO_2. When SO_2 was further increased to 2% of the total gas mixture, a complete spectral signature for elemental sulfur through S_8 was observed in addition to H_2SO_4 (Fig. 3b). Note that Farquhar *et al.* (2001) also used 2% SO_2 in N_2 and observed the formation of both S_8 and H_2SO_4 aerosols. When SO_2 was increased to 4% of the total gas mixture, a further increase in the elemental sulfur signature was observed (not shown). Two percent SO_2 photolyzed at room temperature rather than 273 K did not form S_8, possibly indicating the importance of the increased H_2O in the cell at room temperature.

3.2.2. The effect of reducing gases on SO_2 aerosol chemistry.
In addition to exploring the effects of the SO_2 mixing ratio on UV photolysis aerosol chemistry, we also probed the effect of adding reducing gases. Initially 1% H_2 was added to a 2000 ppmv SO_2 gas mixture, but no change was observed in the mass spectrum. Although H_2 does not photolyze at any of the wavelengths emitted by the UV lamp, it is possible that reactions such as $H_2 + O \rightarrow OH + H$ or $H_2 + OH \rightarrow H_2O + H$ could have occurred; thus H_2 could have affected the S-aerosol chemistry (Moses *et al.*, 2000). However, these reactions are slow, and our experimental results do not reflect them occurring. Under our experimental conditions, it is likely that the much faster reaction of $SO_2 + OH + M \rightarrow HSO_3$ outcompetes the reaction of OH with H_2.

In contrast to adding H_2 to the initial gas mixture, the combination of 1000 ppmv CH_4 with 2000 ppmv SO_2 results in a strong S_8 signal in addition to the H_2SO_4 signal (Fig. 3c), with mass signal in the aerosol mass spectrum for S_1–S_8.

Similar experiments were performed on 2% and 4% SO_2 gas mixtures, both with 1000 ppmv CH_4. In these cases, adding CH_4 to the initial gas mixture increased the amount of S_8 compared to gas mixtures with the same mixing ratio of SO_2 but without CH_4. Figure 4 shows a summary of the fraction of S_8 aerosol found as a function of SO_2 pressure, both with and without added CH_4. It can be seen that both increasing the initial SO_2 mixing ratio and adding CH_4 increase the S_8 fraction.

3.2.3. Formation of organosulfur from CH_4/SO_2 photolysis.
While Fig. 3c shows CH_4 addition helps the formation of S_8, other S-bearing peaks were observed in the AMS spectrum, especially at lower levels of SO_2. Figure 5 shows the resulting spectrum from the photolysis of 2 ppmv SO_2 and 1000 ppmv CH_4. Although the prevalent mass peaks for the 2 ppmv SO_2 mixture followed a H_2SO_4 and a separate organic ion series pattern, organosulfur species have been
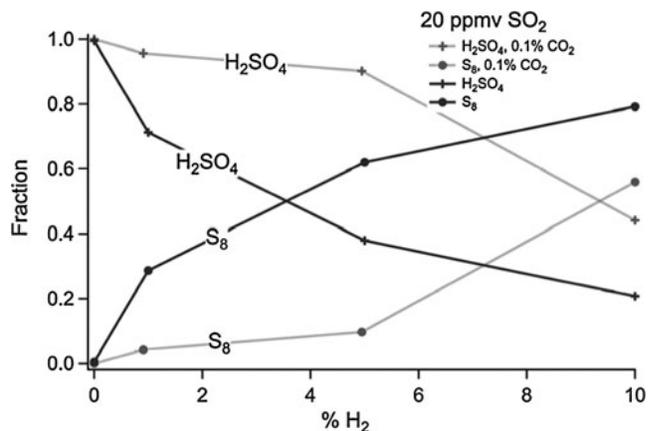
FIG. 2. Relative fraction of total S-bearing aerosol signal of characteristic H_2SO_4 peaks (crosses) and S_8 peaks (circles) versus percent H_2 calculated from Q-AMS data. Experiments with CO_2 are shown with a dashed line. Overlapping mass peaks for H_2SO_4 and S_8 (m/z 32 and 64) have not been included in these calculations.
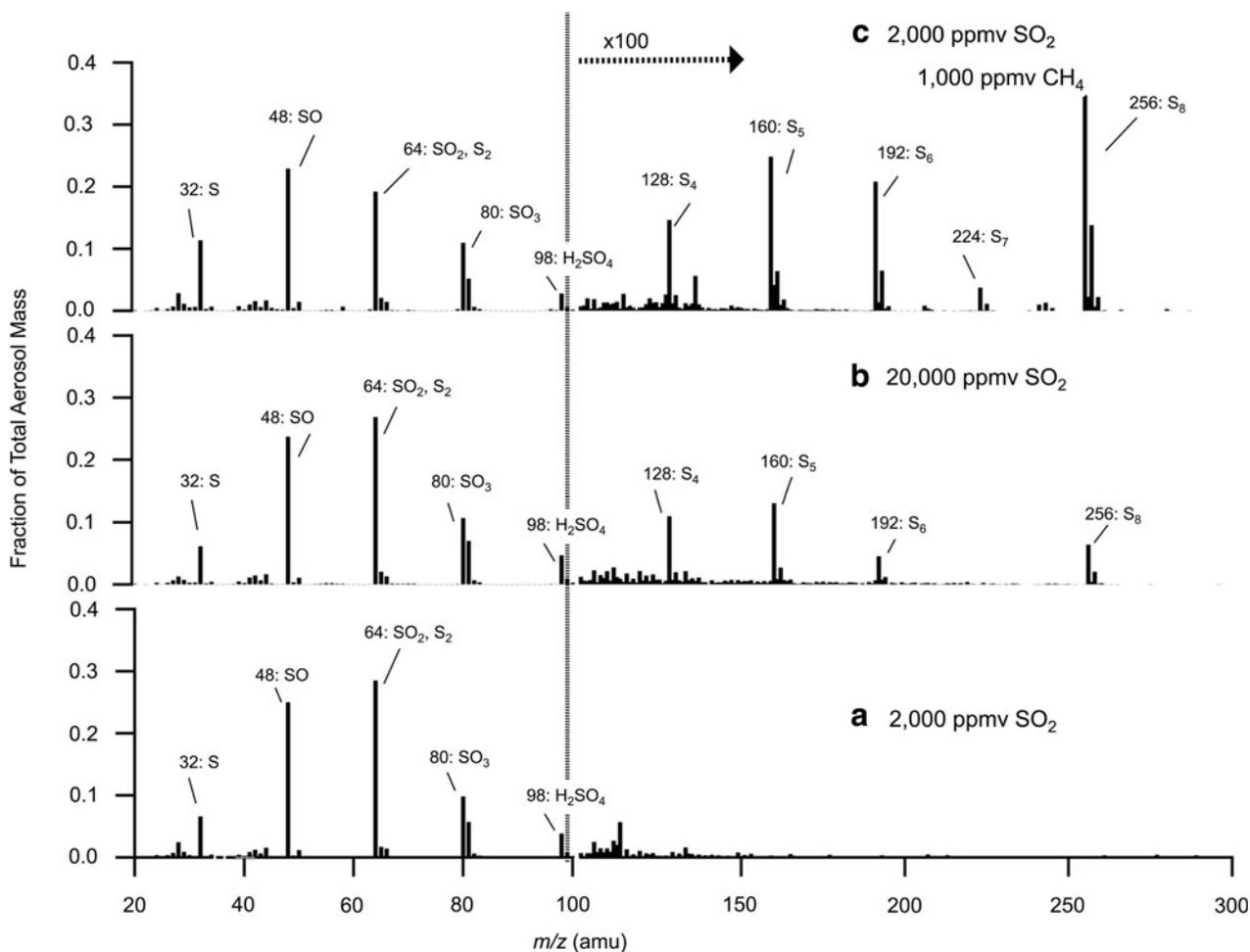
FIG. 3. Q-AMS spectra of particles formed from the photolysis of 2000 ppmv (0.2%) SO_2 in N_2 **(a)**; 20,000 ppmv SO_2 **(b)**; and 2000 ppmv SO_2 with 1000 ppmv CH_4 **(c)**. Plotted is fraction of total aerosol mass versus m/z (amu). Likely peak identification has been made. Peaks to the right of the dashed line have been multiplied by 100 for ease of viewing. Small signals not from S_8 or H_2SO_4 aerosols (unlabeled peaks) for mass spectra without CH_4 are around the noise level of the instrument and could be from trace contamination from the gas or flow system.

shown to fragment in the HR-AMS to predominately hydrocarbon and H_2SO_4 peaks. No S_8 was observed at this low level of SO_2. However, some amount of organosulfur was observed in the HR-AMS data. Specifically, $CH_3SO_2^+$ (HR-AMS spectra shown in Fig. 5 inset), CH_3SO^+, and CH_3S^+ were observed. We also observed HS^+ and H_2S^+ peaks. The $CH_3SO_2^+$ peak is prominent in the AMS spectrum of methyl sulfonic acid (MSA, CH_3SO_3H), and the fragmentation of MSA in the AMS is well characterized (Zorn *et al.,* 2008). Using MSA as a model for organosulfur species, one can determine a $CH_3SO_2^+/H_2SO_4$ ratio of 0.25 and apply this ratio to our data (Zorn *et al.,* 2008). This allows one to roughly quantify the amount of sulfate signal due to an organosulfur compound such as MSA as opposed to that from inorganic sulfate. This is illustrated in Fig. 5a. From this calculation, it can be seen that approximately 16% of the sulfate signal could be due to MSA fragmentation for 2 ppmv SO_2 with 1000 ppmv CH_4.

The spectrum was also compared to a standard organosulfate spectrum (trihydroxy sulfate ester, $C_5H_{12}O_7S$) by normalizing the organosulfate spectrum's $CH_3SO_2^+$ peak to that in the spectrum of 2 ppmv SO_2 with 1000 ppmv CH_4

(Farmer *et al.,* 2010). When comparing the resulting spectra, the normalized standard organosulfate spectrum's sulfate signal is approximately 7 times larger than that of the spectrum from these experiments. Thus, 14% of our $CH_3SO_2^+$ peak could be due to organosulfate, with the rest of the signal from other less-oxidized organosulfur species such as MSA.

Although the spectrum for the 20 ppmv SO_2 mixture looked very similar to that of the 2 ppmv SO_2 mixture, there was an approximate factor of 2 reduction in the relative prominence of organosulfur peaks as compared to H_2SO_4 peaks with increased SO_2.

Note that no S_8 was observed from the photolysis of 1000 ppmv CH_4 with 20 ppmv and below SO_2. All the UV experiments and results have been summarized in Table 1.

4. Discussion

Our studies allowed real-time analysis of nonrefractory aerosol compound produced in the flow system simulating the aerosol potentially formed from volcanic emissions in an early Earth atmosphere. In these experiments, trace amounts
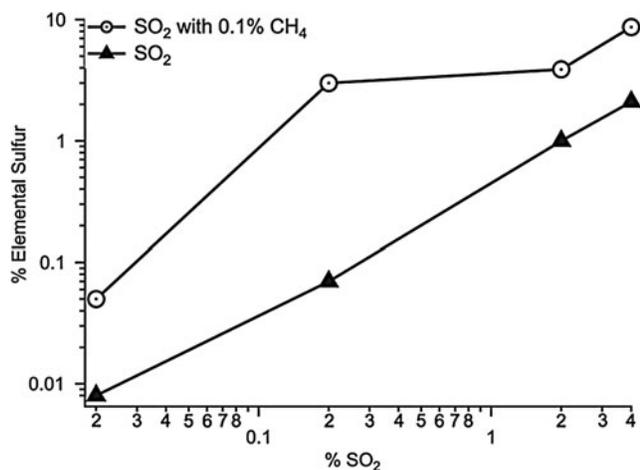
FIG. 4. Percent of S-bearing aerosol mass from S_8 as a function of the pressure of SO_2 calculated from Q-AMS data. Experiments are shown with (circles) and without (triangles) 1000 ppmv CH_4. Overlapping mass peaks for H_2SO_4 and S_8 (m/z 32 and 64) have not been included in these calculations.

of H_2O in the vacuum reaction cell were enough to oxidize most of the sulfur to H_2SO_4. We cooled our reaction vessel to 273 K. This gives us a theoretical water vapor concentration of 0.7%, or 7000 ppmv within the reaction cell as an upper limit. The HR-AMS background gas spectrum further limits the H_2O contamination to 1000 ppmv. For lower altitudes

and within volcanic plumes this would be relevant, as water would be present in at least trace amounts at low altitudes and would also be emitted along with SO_2 from volcanoes (Pavlov *et al.,* 2000; Textor *et al.,* 2003). At 2% SO_2, photolysis in a room-temperature reaction cell did not yield S_8, illustrating that the water vapor in the reaction cell was affecting the aerosol chemistry.

In our discharge experiments, we studied a simple system in which we increased the reducing gases, in this case H_2, to avoid the complication of organic chemistry from CH_4. The addition of H_2 to the gas mixture caused elemental sulfur aerosol to form in addition to H_2SO_4. Increasing the amount of H_2 increased the S_8/H_2SO_4 ratio. Zahnle *et al.* (2006) found that increasing the reduced gases in his 1-D model of early Earth's atmosphere increased the S_8/H_2SO_4 ratio, and our results appear to support this finding. One explanation for this is that H formed from the electrical dissociation of H_2 titrated the OH formed from H_2O. H_2 could also titrate the O atoms from SO_2 photolysis, facilitating the formation of more reduced sulfur compounds. Alternatively, intermediate HS_n compounds may increase S chain formation (Kasting *et al.,* 1989). Excess H_2 would contribute to the formation of HS_n compounds and partially explain our results. The same effect, albeit dampened, is observed when CO_2 is added to the gas mixture. The increased O from CO_2 photolysis most likely explains the lower amounts of S_8 formed with CO_2 than without for the same level of H_2. Our experiments do not allow us to determine the isotopic fractionation of SO_2, and in fact electrical discharge may not even produce S-MIF.
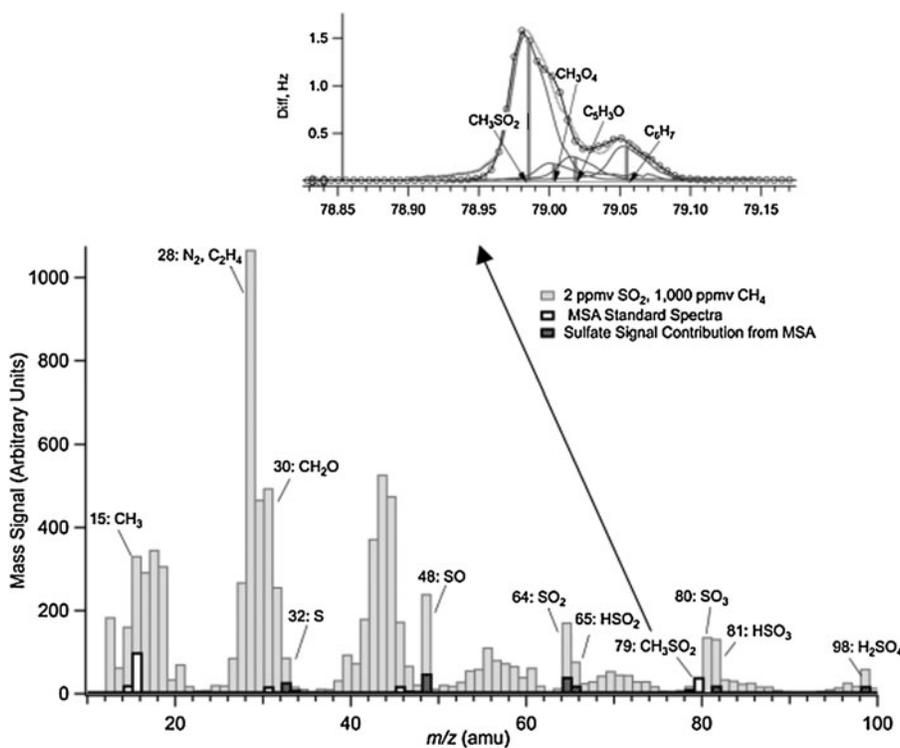
FIG. 5. AMS spectrum of particles formed from the photolysis of 2 ppmv SO_2 with 1000 ppmv CH_4 in N_2 (gray boxes) with the standard AMS spectrum of MSA (black lines). The two spectra are normalized so that the intensity of $CH_3SO_2^+ / (m/z$ 79) is equal in each spectrum. Patterned boxes are the sulfate contribution from MSA. Approximately 16% of the sulfate signal in the 2 ppmv SO_2 1000 ppmv CH_4 spectra could be from MSA. The expanded high-resolution peak from the organosulfur peak $CH_3SO_2^+$ is shown in the inset.

TABLE 1. SUMMARY OF SO$_2$ UV PHOTOLYSIS EXPERIMENTS

Experimental SO$_2$ (ppmv)	Reducing gas?	S$_8$?	Organosulfur?	H$_2$O level in experiment (upper limit)	O$_2$ level in experiment, PAL (upper limit)
2 ± 0.02	1,000 ± 20 ppmv CH$_4$	No	Yes, present and studied	Unknown	10^{-3}
20 ± 0.2	1,000 ppmv CH$_4$	No	Yes, present and studied	7,000 ppmv	10^{-3}
200 ± 2	No	No	Not studied	7,000 ppmv	10^{-3}
200 ± 2	1,000 ppmv CH$_4$	No	Not studied	7,000 ppmv	10^{-3}
2,000 ± 20	No	No	Not studied	7,000 ppmv	10^{-3}
2,000 ± 20	10,000 ± 20 ppmv H$_2$	No	Not studied	7,000 ppmv	10^{-3}
2,000 ± 20	1,000 ppmv CH$_4$	Yes	Not studied	7,000 ppmv	10^{-3}
20,000 ± 20	No	Yes	Not studied	7,000 ppmv	10^{-3}
20,000 ± 20	1,000 ppmv CH$_4$	Yes	Not studied	7,000 ppmv	10^{-3}
40,000 ± 20	No	Yes	Not studied	7,000 ppmv	10^{-3}
40,000 ± 20	1,000 ppmv CH$_4$	Yes	Not studied	7,000 ppmv	10^{-3}
Amount present on early Earth	**SO$_2$:** 10 ppbv[a] (global lower limit)	**H$_2$O:** Unknown, likely >7,000 ppmv at low altitudes[b]	**O$_2$:** modeled to be from 10^{-5} ppmv[c] to 10^{-13} ppmv[b]	**CH$_4$:** up to 1,000 ppmv[d]	

[a]Kasting *et al.* (1989).
[b]Pavlov and Kasting (2002).
[c]Farquhar *et al.* (2000).
[d]Haqq-Misra *et al.* (2008).

We observe the same effect in our photolysis experiments when we add CH$_4$ to the initial gas mixtures. With the addition of 1000 ppmv CH$_4$, S$_8$ is formed at 2000 ppmv initial SO$_2$ mixing ratio. Adding 1000 ppmv CH$_4$ to 2% and 4% SO$_2$ gas mixtures increases S$_8$ formation by a factor of 2 or more. We infer from these experiments that the relative oxidative capacity, or amount of reducing gases relative to oxidizing gases, in a volcanic plume and the ambient atmosphere can greatly change the chemical composition of the aerosols formed in and around a volcanic cloud.

The experimental paper by Farquhar *et al.* (2001) showed the formation of S$_8$ and H$_2$SO$_4$ aerosols with UV photolysis but with unrealistically high concentrations of SO$_2$ and non-continuum UV light sources. In our experiments, we exposed SO$_2$, CH$_4$, and CO$_2$ to a broad-spectrum UV light with a peak in emission at ~145 nm, under the 220 nm cutoff determined by Farquhar *et al.* (2001) to be the wavelength of UV for S-MIF formation. We probed the effect that the initial SO$_2$ pressure had on the resulting sulfur aerosol chemistry. We observed S$_8$ formation with 2% SO$_2$ but only H$_2$SO$_4$ aerosol formation with 200 ppmv and lower SO$_2$. While the lack of S$_8$ production at lower SO$_2$ values may reflect the importance of the SO$_2$ self-reaction, it may partially also reflect the relative abundance of SO$_2$ and water vapor in the system. Models predict efficient S$_8$ formation at much lower levels of SO$_2$ than we observe experimentally, at levels of 10 ppbv (Kasting *et al.*, 1989) in models versus 2000 ppmv or higher in our experiments. Our experimental photochemical reaction time of 5 minutes is significantly lower than reaction times in the atmosphere, and this could also have affected our results. The rate constants are not known well enough to determine how much of an effect reaction time would have on S$_8$ production (Kasting *et al.*, 1989). Although our theoretical lower limit for O$_2$ in our vacuum chamber was on the order of 10^{-6} PAL, we were only able to experimentally determine a 10^{-3} PAL O$_2$ upper limit after our

experiments began, giving us a wide range of possible O$_2$ levels, which could have also affected our results. Ono *et al.* (2003) also predicted a SO$_2$ pressure dependence on the S$_8$/H$_2$SO$_4$ ratio, which they attributed to the increased S atom requirement to form S$_8$ over H$_2$SO$_4$. In our system, S + +S must combine to form S$_2$, S$_2$ + S$_2$ to form S$_4$, and so on. These reactions are also sensitive to total pressure, as the combination reactions of S atoms to form S chains are three-body reactions (Kasting *et al.*, 1989). However, the possible pressure dependence of sulfur aerosol formation was not probed
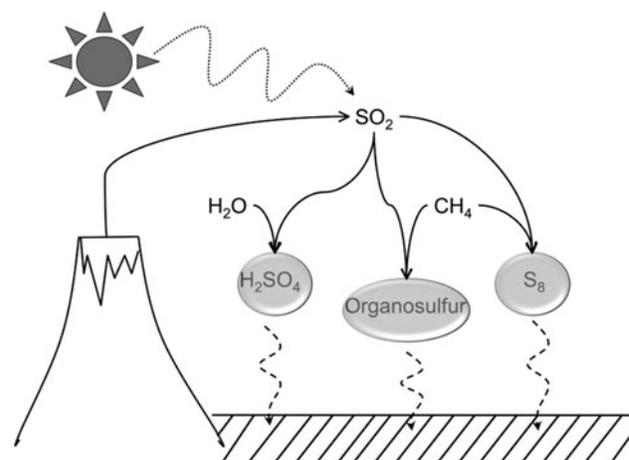
FIG. 6. A conceptual model of the formation and preservation of S-MIF in early Earth's atmosphere under different atmospheric conditions. More H$_2$O increases the formation of H$_2$SO$_4$, while moderate amounts of CH$_4$ form more organosulfur and S$_8$ aerosols. A high CH$_4$/SO$_2$ ratio increases the amount of organosulfur formed. Increasing the mixing ratio of SO$_2$ increases the amount of S$_8$ formed, as does adding CH$_4$, once the SO$_2$ pressure is at a certain threshold.

in the present work, as all our experiments were conducted at 600 torr.

Models have suggested that O_2 levels of 10^{-5} PAL or greater will shut off S-MIF formation (Pavlov and Kasting, 2002). Below this level, O_2 would not be well mixed (Pavlov and Kasting, 2002). We calculate that our mixing chamber has an upper limit of O_2 at 10^{-3} PAL. We still observe the formation of elemental sulfur aerosols under certain experimental conditions with both electrical discharge and photolysis as the driving force for these reactions. One reason for this could be that our initial SO_2 levels are significantly higher than the atmospheric levels in the models used to predict O_2 levels. For example, we observed the formation of S_8 when 2000 ppmv SO_2 was used for the photolysis experiments, a much higher amount of SO_2 than the 10 ppbv SO_2 that is predicted to have been present in early Earth's atmosphere. In addition, we added reducing gases such as H_2 or CH_4.

Organosulfur formed from the photolysis of the biologically produced gases CS_2 and OCS have been found to contain S-MIF (Lyons, 2009), and our research points to an additional abiological source of organosulfur aerosols in early Earth's atmosphere. Ueno et al. (2009) attributed the buildup of OCS in the atmosphere to the reaction $CO + S_n + M \rightarrow OCS$. In this research, we have found that it can be difficult to build up significant amounts of S_n. However, we found organosulfur to be present in aerosols formed from the photolysis of moderate amounts of SO_2 and CH_4. Although the signal from organosulfur peaks was relatively small compared to the sulfate signal in our spectra, organosulfur species have been shown to fragment in the AMS to peaks typically associated separately with organics and H_2SO_4. Using MSA as a model for organosulfur aerosols, we find that at least 16% of our sulfate aerosol signal could come from organosulfur for a gas mixture of 2 ppmv SO_2 and 1000 ppmv CH_4. Organosulfate species fractionate even more strongly into sulfate and organic peaks in the AMS, with a greater sulfate/organosulfur ratio than we observe in our laboratory spectrum. By comparing a standard organosulfate spectrum to our spectrum, we calculated an upper limit of 14% of our organosulfur signal could be from organosulfate. Additionally, we find evidence of CH_3S^+ peaks in our HR-AMS spectrum, which indicates that some of our organosulfur signal must come from species with a C–S bond, such as sulfonic acids or thiols (H–S–R). Organosulfate has only C–O–S bonds. Observing SH^+ ions in our spectrum may also suggest that we have some signal contribution from thiols. Thus, a substantial percentage of our AMS sulfate signal is likely due to the fragmentation of organosulfur compounds. Organosulfur aerosols could have acted as another reservoir for S-MIF and may require less initial SO_2 pressure, with possibly less restriction of O_2 levels in early Earth's atmosphere than the formation of S_8.

5. Conclusions

Our experiments found that the formation of S_8, H_2SO_4, and organosulfur aerosols from SO_2 is affected by several experimental factors: (1) initial partial pressure of SO_2, (2) reducing gases present during the reaction of SO_2, (3) the energy source used to initiate the reaction, and (4) the amount of water vapor present. We have summarized our conclusions in Fig. 6, modifying a figure by Ono et al. (2003) to reflect our results.

From our experiments, it appears that either high levels of SO_2 or the presence of reducing gases are necessary for the formation of S_8 in the presence of water vapor and low-wavelength UV light. The water vapor levels in our experimental chamber are most likely lower than, or close to, the levels at lower altitudes in the Archean atmosphere, and levels of OH in our chamber are probably directly related to the amount of water vapor. However, models calculate that OH levels in the Archean atmosphere would have been limited by reaction with H_2, CO, and CH_4 (Pavlov et al., 2000). The increase in S_8 with the addition of reducing gases in our experiments appears to agree with these model results. It is important to note that we did form S_8 at levels of $O_2 > 10^{-5}$ PAL with sufficiently large mixing ratios of SO_2 or sufficient amounts of reducing gases, or both. An atmosphere with more CH_4 or H_2 could potentially form more S_8 than one that is less reducing. The photolysis products of SO_2 and CH_4 can also react to form substantial amounts of organosulfur compounds. Lower mixing ratios of SO_2 are required for the formation of organosulfur aerosols than would be required for S_8 aerosols; 2 ppmv SO_2 or below are required for organosulfur formation, while 2000 ppmv SO_2 or above are needed for S_8 aerosol formation. Thus, organosulfur aerosols could provide another reservoir for S-MIF at various oxidation levels different than S_8 and H_2SO_4, and in addition can form at more reasonable levels of SO_2 in the presence of H_2O. These experiments illustrate that the atmospheric sulfur and methane cycles may have been coupled; thus important chemistry may be missing from present models of the atmosphere of early Earth. Further work should be carried out to explore the total pressure dependence and water vapor dependence of the reactions that lead to the production of S_8, H_2SO_4, and organosulfur aerosols.

Acknowledgments

Abbreviations

AMS, aerosol mass spectrometer; HR-AMS, high-resolution time-of-flight aerosol mass spectrometer; MSA, methyl sulfonic acid; m/z, mass-to-charge ratio; PAL, present atmospheric level; Q-AMS, quadrupole-based aerosol mass spectrometer; S-MIF, sulfur mass-independent fractionation.

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