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Published in:
Journal of Aerosol Science

Link to article, DOI:
[10.1016/j.jaerosci.2022.105956](https://doi.org/10.1016/j.jaerosci.2022.105956)

Publication date:
2022

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Enghoff, M. B., Shaviv, N. J., & Svensmark, H. (2022). Sulphuric acid aerosols in low oxygen environments. *Journal of Aerosol Science*, 162, Article 105956. <https://doi.org/10.1016/j.jaerosci.2022.105956>

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Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

Sulphuric acid aerosols in low oxygen environments

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ARTICLE INFO

Keywords:

Archean atmosphere
Sulphuric acid
Nucleation
Low oxygen
Relative humidity
UV
Ionization

ABSTRACT

Experiments on sulphuric acid nucleation in low oxygen atmospheres were done in order to investigate the role of nucleation in the Archean atmosphere. Nucleation initiated by photolysis of SO₂ and subsequent reaction between atomic O and SO₂ was measured with a PSM and a separate CPC. The parameters were < 10 ppm O₂ with varying levels of SO₂ (4 levels from 40 to 105 ppb), RH (3 levels from 0 to 51%), UV light (254 nm, 4 levels from 55 to 100% power), and ionization (2 levels: Background (~3 cm⁻³ s⁻¹) and increased w. gamma sources (~42 cm⁻³ s⁻¹). We find that nucleation is possible under these conditions and that the measured formation rates correlate positively with all varied parameters. This suggests that the sulphuric acid nucleation system could have played a role in the Archean atmosphere.

1. Introduction

Aerosol nucleation can proceed via numerous pathways in the modern day atmosphere. The most fundamental chemical compound is sulphuric acid which can participate in both binary nucleation with water (Kulmala & Laaksonen, 1990), and a variety of ternary pathways (Kulmala et al., 2000) although path-ways involving e.g. purely organic molecules (Bianchi et al., 2016) or iodine (Hoffmann et al., 2001; Mäkelä et al., 1997) are also possible. Nucleation can be both neutral and ion-induced (Svensmark et al., 2007; Kirkby et al., 2011; Raes & Janssens, 1985; Lovejoy et al., 2004). Neutral nucleation is dominant in most parts of the atmosphere (Manninen et al., 2010) particularly when there are large quantities of nucleating compounds while ion-induced nucleation works best in clean environments (Lovejoy et al., 2004; Pedersen et al., 2012) such as the free troposphere (Kirkby et al., 2011).

The primary production pathway for sulphuric acid is via the oxidation of SO₂ by the OH radical (Reaction 1), which requires molecular oxygen for its production.



In the atmosphere of Archean Earth oxygen only existed in low quantities making this pathway largely ineffective. But aerosols are still speculated to have played a part in the ancient Earth climate system. Lower nucleation rates due to lower available gas concentrations (Rosling et al., 2010) could be (part of) the explanation of the Young Faint Sun Paradox along with other candidates such as increased concentrations of greenhouse gases (e.g. NH₃, CO₂, CH₄, and OCS) (Ueno et al., 2009) and reduced ion-induced nucleation (Shaviv, 2003; Svensmark, 2003).

To understand the role of aerosols in the Archean climate we must understand which nucleation pathways were available. Previously the N₂/CO₂/CH₄ system and its sensitivity to O₂ has been investigated (Horst et al., 2018). In this work we investigate the

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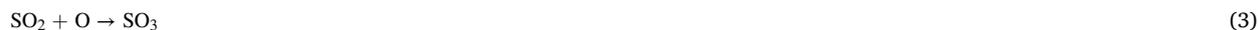
Received 23 August 2021; Received in revised form 13 January 2022; Accepted 17 January 2022

Available online 29 January 2022

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possibility of forming sulphuric acid in quantities large enough for aerosol nucleation to take place in atmospheres containing only trace amounts of oxygen. While oxidation of SO_2 via OH may not have been viable, alternatives exist. SO_2 can be photolysed by UV light with wavelengths up to 330 nm (Danielache et al., 2008). UV light between 200 and 300 nm is thought to have been higher by orders of magnitude during the Archean (Cnossen et al., 2007) and the resulting atomic oxygen can proceed to form SO_3 , which then becomes H_2SO_4 in the presence of water:



This is only relevant in atmospheres with higher SO_2 concentrations than today since O can be consumed in numerous reactions. The Archean atmosphere is not well constrained with regards to atmospheric SO_2 (Catling & Zahnle, 2020). In the modern atmosphere anthropogenic sources play a large part which are not relevant for prehistoric atmospheres, and biogenic sources that proceed via dimethyl sulfide (DMS) production and oxidation are not very relevant either due to possible lack of DMS producing microorganisms and certainly due to lack of oxidation mechanisms. On the other hand volcanic activity may have been higher, particularly towards the end of the Archean (Marty et al., 2019). Sinks for SO_2 were lower since e.g. Reaction 2 was not relevant. Previously, models of the Archean atmosphere have included SO_2 concentrations up to 10 ppm to simulate large input from volcanoes (Ueno et al., 2009). Therefore we assume an SO_2 concentration higher than today.

2. Materials and methods

2.1. Experimental setup

Experiments were performed in a 1 m^3 double shell cylindrical stainless steel reactor (Fig. 1) operated at room temperature and pressure. UV light at 253.7 nm can be transmitted into the chamber by 10 external 36 W TUV mercury discharge lamps 64 quartz windows of various shapes, most of which are $77 \times 77 \text{ mm}$, located at one end of the chamber. Before entering the light is collimated by an 80 mm deep honeycomb collimator.

The chamber was supplied with a continuous flow of 5.5 L/min N_2 from a Parker Midigas 6 nitrogen generator with a O_2 content of max. 10 ppm (the generator generally showed 2 ppm during experiments). SO_2 was supplied from a bottle of 5.3 ppm SO_2 in N_2 (N60, Air Liquide) with a flow of 40–100 mL/min depending on the desired SO_2 concentration. The SO_2 was measured using a Thermo model 43 CTL. Inlet flows were filtered for small aerosols to achieve an aerosol background of $\sim 0 \text{ cm}^{-3}$. Aerosols were measured with an Airmodus A10 PSM operated with 1 L/min saturator flow for a cut-off diameter of $\sim 1.4 \text{ nm}$ for ammonium sulphate particles. The PSM was connected to a TSI CPC 3776 and a separate TSI CPC 3775 with a cut-off diameter of $\sim 4 \text{ nm}$. The two aerosol instruments were sampling from the same line and had similar pathways since they were connected with a t-split. The relative humidity (RH) could be varied by passing the N_2 through a humidifier consisting of a Goretex tube with temperature regulated water. The RH of the chamber was measured along with temperature and pressure.

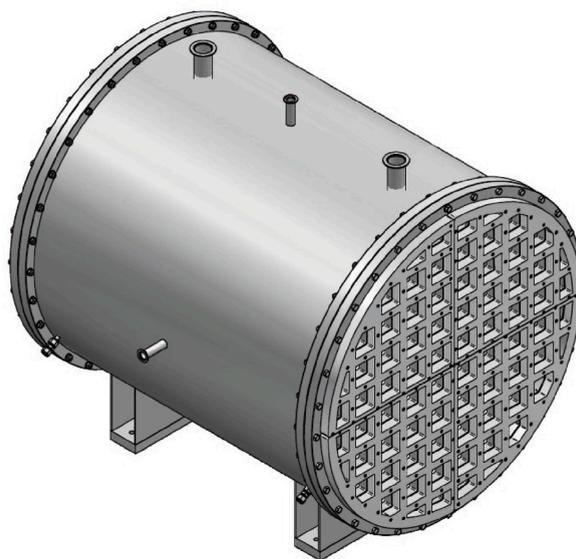


Fig. 1. The reaction chamber, made of electropolished stainless steel. The front end shows the quartz windows - the collimator and UV lamps are placed in front of those. The back end contains various inlets, in addition to those shown on the side and top of the chamber.

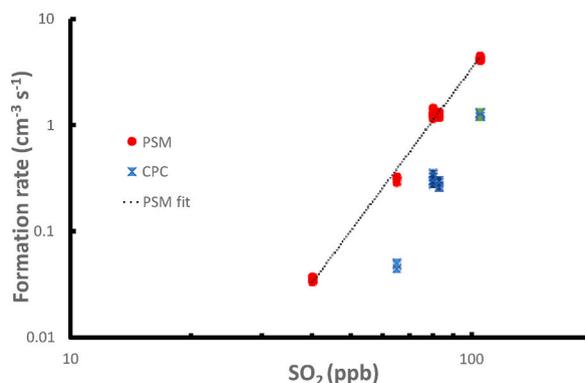


Fig. 2. Formation rates measured by the PSM (red circles) and CPC (blue crosses) as function of SO_2 concentration, in log-log format. A fit with a slope of 5.1 is also shown (see text).

Ionization in the chamber could be increased using two ^{137}Cs gamma sources of 25 MBq that were positioned about 90 cm from the side of the chamber. They were shielded by lead curtains which could be opened to irradiate the chamber. Using the G4beamline simulation code (<http://public.muonsinc.com/Projects/G4beamline.aspx>), we estimate that the background ionization levels of 3 ion-pairs $\text{cm}^{-3}\text{s}^{-1}$ increased to 42 ion-pairs $\text{cm}^{-3}\text{s}^{-1}$ with the curtains removed (averaged over the chamber).

2.2. Experimental procedure

Each series of experiments were initiated by adjusting the flows of the chamber and allowing the gas concentrations to reach a steady state. Aerosols were generated by turning on the UV light for 20 min to generate a burst of aerosol nucleation. The chamber was allowed 3 h 40 m to relax between UV bursts. Two main sets of experiments were performed. In the first set the gas composition was varied between different levels of SO_2 and RH. In the second set the ionization was varied using the external gamma sources and the influence of the ionization was tested for different levels of UV illumination. For these experiments the UV light was only on for 10 min and the relaxation time was 3 h 50 m. In addition some experiments with higher $[\text{O}_2]$ were performed.

2.3. Data analysis

Aerosol data was analyzed to find formation rates at the cut-off sizes for the PSM and CPC using the method of Tomić et al. (2018) where a linear fit is made to the rising side of each smoothed aerosol peak between 20 and 80% of the peak maximum. The slope of the fit is then the formation rate. Experiments under the same set of conditions were used to correct for drift caused by e.g. gradual changes in chamber impurities. The correction was a simple linear drift term applied to the formation rates. This is possible when experiments under the same conditions are performed at the beginning and end of a series, such as seen in Fig. 3. When corrections were applied to experiments with different conditions then the correction was scaled with the relative magnitude of formation rates between the reference condition and the one being corrected.

Loss of aerosols in the sampling system has previously been estimated to be $\sim 15\%$ for 4 nm particles and $\sim 50\%$ for 1.4 nm particles (Tomić et al., 2018). The half life of aerosols in the chamber measured by the PSM and CPC were about 13 and 15 min, but the exact

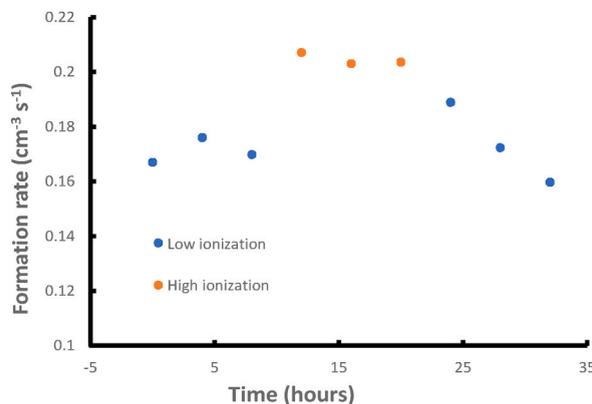


Fig. 3. Formation rates measured by the CPC at 60% UV illumination, with low ($3 \text{ cm}^{-3} \text{ s}^{-1}$) and high ($42 \text{ cm}^{-3} \text{ s}^{-1}$) ionization. $t = 0 \text{ h}$ is the time of the first experiment. The results and associated uncertainties are summarized in Table 2.

size dependent loss function is not known. The losses have not been corrected for. Since the losses are a factor that will be applied equally to all measurements with the same instrument the phenomenological conclusions in the paper would not be affected by the loss rates. The absolute values would ofcourse increase if losses were taken into account but since this paper is not trying make a parametrization of formation rates a loss correction is not necessary.

3. Results

3.1. SO₂ and RH variation

Fig. 2 shows the formation rates measured by the PSM and CPC from the set of experiments where the SO₂ concentration was varied. To be able to correct for drift measurements at 80 ppb were repeated throughout the set.

The formation rate results for all experiments where SO₂ and RH were varied are shown in Table 1. These experiments were conducted over a period of 11 days. The experiments where SO₂ was varied had a fixed RH of 51%, and when RH was varied SO₂ was kept at 80 ppb. Both series started and ended with the same set of conditions (80 ppb SO₂ for the RH variations and 35% RH for the SO₂ variations). Experiments were also done without adding any water vapour, resulting in an RH of 0.0% in which case SO₂ had to be increased to above 320 ppb before any particles were detected by the PSM.

Formation rates increased with increasing levels of both SO₂ and RH showing that both are needed for forming the nucleating molecules. Formation rates increased by two orders of magnitude in the PSM when SO₂ was increased from 40 to 105 ppb. The CPC could not detect sufficient particles at 40 ppb to calculate a formation rate. A linear fit to the natural logarithm of the PSM formation rate as a function of the natural logarithm of [SO₂] gives an r² of 0.99 and a slope of 5.1 and 5.0 when using all individual data points and the mean values from Table 1 respectively. The fit can also be seen in Fig. 2. This indicates that the formation rate depends on the [SO₂] to the power of 5. Note that SO₂ is a proxy for H₂SO₄ and that the scaling between the two is not linear since SO₂ participates both through the photolysis (Reaction 2) and further reaction with the photolysis product (Reaction 3). The actual scaling will depend on what the limiting reactions are, but the concentration of H₂SO₄ should depend on [SO₂] to the order of somewhere between 1 and 2. If H₂SO₄ depends on [SO₂]² then the actual scaling of the formation rate with sulphuric acid is [H₂SO₄]^{2.5} which is closely in line with observations (Sipila et al., 2010; Kirkby et al., 2011).

The ratio of the formation rates between the PSM and CPC was between 3.3 and 7.9. The ratio decreased with increasing concentrations of SO₂ and RH indicating that both these gases are important not only for formation but also growth of the small clusters.

3.2. O₂ variation

The presence of oxygen should decrease the sulphuric acid production in our system as O can react with O₂, producing O₃. Although O₃ can be photolysed with the lamps in the experiment it can also react with O to produce 2 O₂. Two separate measurements with an ozone analyzer (Teledyne T400) instead of the aerosol equipment were made with 20 min UV 100% power. The [O₂] was slightly higher (12–14 ppm) than during the other experiments. A small ozone production resulting in a [O₃] of no more than 0.1 ppb could not be ruled out, but this is not enough to significantly alter the interpretation of the.

Results. The effect of oxygen was tested by adding 100 mL/min of air, mixed with 5.4 L/min of N₂, which should result in an [O₂] of 3800 ppm. The air was introduced using two different sources: An external compressor with active charcoal and citric acid filtering and bottled synthetic air (Scientific synthetic air 5.5, Linde Gas). In both cases the formation rates increased by a factor of up to 6, contrary to expectations. There was a large drift in the chamber during these experiments, making adjustments unrealistic and a quantitative discussion difficult. The formation rates using air from the compressor were higher than those using synthetic air. These results indicate that the oxygen-containing air contained trace pollutants assisting in the nucleation and that the two sources contained different amounts of pollutants (see Discussion and Conclusion).

Table 1

Formation rates from the experiments with varying RH and SO₂. When RH was fixed it was 51%, when SO₂ was fixed it was 80 ppb. The uncertainties are 1 standard deviation. The number of samples varies between PSM and CPC because for some measurements there was no useful data for one of the instruments. For the lowest [SO₂] the CPC did not register enough aerosols to calculate a formation rate. Ratio refers to the formation rate measured by the PSM relative to that measured by the CPC.

	Fixed RH				Fixed SO ₂	
	SO ₂ (ppb)				RH (%)	
	40	65	80	105	35	51
PSM (cm ⁻³ s ⁻¹)	0.036 ±0.020	0.31 ±0.016	1.3 ±0.089	4.3 ±0.14	0.18 ±0.030	1.2 ±0.32
Samples (#)	3	4	7	5	11	11
CPC (cm ⁻³ s ⁻¹)	–	0.048 ±0.0025	0.30 ±0.04	1.29 ±0.025	0.023 ±0.0065	0.212 ±0.11
Samples (#)	3	4	8	5	8	12
Ratio	–	6.5	4.3	3.3	7.9	5.6

3.3. Ionization and UV variation

Fig. 3 shows the series of experiments at a fixed UV level where the ionization was increased by exposing the chamber to the gamma sources. Similar series were made at 3 other UV settings and the results are shown in Table 2. The PSM was not available for these experiments and the UV intensity could not be measured. The formation rate increased with increasing UV illumination as expected if photolysis is the driver of nucleation and the increase in formation rate due to increased ionization rate is consistent with ion-induced nucleation (Dunne et al., 2016; Enghoff et al., 2008; Kirkby et al., 2011; Svensmark et al., 2007). Furthermore the effect of ionization shows the strongest effect at the lowest levels of UV. Previously it has been shown that ion-induced nucleation is more dominant, compared to neutral nucleation, when the concentrations of the nucleating gases are low (Dunne et al., 2016; Pedersen et al., 2012).

4. Discussion and Conclusion

The scaling of formation rates with $[\text{SO}_2]$ and UV levels indicate that the photolysis of SO_2 is central for the nucleation as expected for a sulphuric acid based system. The scaling of formation rates with $[\text{SO}_2]^5$ was explored using KINTECUS (v6.8, www.kintecus.com). 113 reactions were modelled including 7 photolysis reactions along with the sulphur chemistry and O–C–H chemistry described in Ueno et al. (2009). The photolysis rates were modified to fit with UV-fluxes measured on a similar chamber and then reduced to produce more realistic sulphuric acid concentrations. Fig. 4 shows the modelled sulphuric acid as a function of SO_2 for 51% RH, runs for 35% RH were also made but provided similar results. The model output shows that the dependence of sulphuric acid on SO_2 can be described well using a 2nd degree polynomial with r^2 values of 0.997 or a power law with an exponent of 1.8 ($r^2 = 0.998$). These model runs show that the sulphuric acid depends on $[\text{SO}_2]^a$ with a being closer to 2 than 1 and thus supports the idea that formation rates at the PSM detection limit depends on $[\text{H}_2\text{SO}_4]^{-2.5}$.

The measurements also indicate a strong dependence on RH which could be an indication that Reaction 4 is important. Normally this is not a rate limiting reaction but since we have higher concentrations of SO_2 there is also more SO which can react with SO_3 to form 2 SO_2 . However water also participates directly in the nucleation with sulphuric acid and it is not easy to separate the two effects. Dunne et al. (2016) reported an increase in nucleation rate of a factor of ten when increasing RH from 40 to 80% at 298 K and in their parametrization the nucleation rate only increases by a factor of 2 when going from an RH of 35–51% at 298 K. In this study the formation rate in the PSM (similar to the instrument used by Dunne et al. (2016)) increases by a factor of ten when increasing RH from 35 to 51% indicating a higher dependence on RH for this system. However the modelling results show that sulphuric acid does not depend significantly on RH. Under other conditions, such as higher photolysis rates or even higher concentrations of SO_2 this would be different. Thus, under the right circumstances Reaction 4 would be more important than in the modern day atmosphere. Increasing RH increases the rate that SO_3 is converted to sulphuric acid and thus decreases the risk of SO_3 getting lost to other reactions, which has a higher risk of occurring in a high $[\text{SO}_2]$ scheme.

Modelling the effect of oxygen shows that increasing $[\text{O}_2]$ to 3800 ppm would decrease sulphuric acid significantly, which should lead to a decrease in nucleation rate, in contrast to what was measured. This supports that the injected air contained unknown pollutants active in the formation (and growth) of the aerosols, as has previously been suspected for the gas system used (Tomicic et al., 2018). Only trace amounts are needed to stabilize early cluster formation (Dunne et al., 2016) and growth (Troestl et al., 2016). Impurities are probably also present in the experiments without added oxygen which would lead to higher measured formation rates than expected for a pure sulphuric acid and water system by perhaps 1–2 orders of magnitude, based on the estimated impurity levels from Tomicic et al. (2018) and the parametrization of Dunne et al. (2016).

A small ($[\text{O}_3] < 0.1$ ppb) production of ozone due to atomic oxygen reacting with O_2 could not be ruled out and would lead to

Table 2

Formation rates from the experiments with varying ionization and UV levels. The first column shows the setting of the UV lamps in percentage of full power. Note that lamp output does not scale linearly with lamp power. The next two columns show the formation rate measured by the CPC for experiments without and with extra ionization from the gamma sources along with one standard deviation. The final column shows the ratio between columns 3 and 2 where the standard deviation is found using the formula for error propagation.

UV (%)	γ off ($\text{cm}^{-3} \text{s}^{-1}$)	γ on ($\text{cm}^{-3} \text{s}^{-1}$)	ratio (-)
100	2.3	2.6	1.1
	± 0.094	± 0.019	± 0.046
(Samples (#))	6	3	–
80	1.1	1.1	0.99
	± 0.086	± 0.057	± 0.093
(Samples (#))	6	3	–
60	0.17	0.20	1.2
	± 0.0098	± 0.0022	± 0.069
(Samples (#))	6	3	–
55	0.083	0.12	1.6
	± 0.0072	± 0.018	± 0.26
(Samples (#))	7	6	–

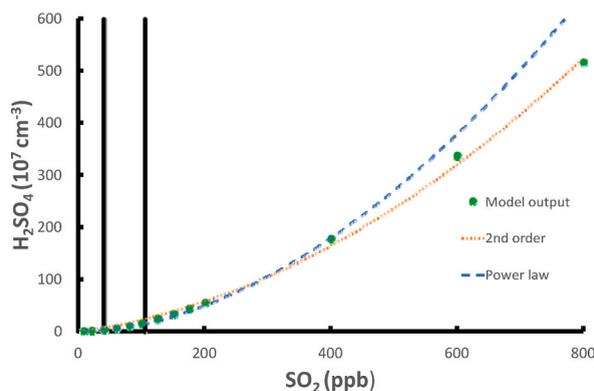


Fig. 4. Model output showing the dependence of sulphuric acid on SO_2 (green points). Also shown are a power law fit (blue dashed line) and a 2nd order polynomial ($y = ax^2 + bx$, orange dotted line). Dashed vertical lines show the interval where the experiments have been done.

additional sulphuric acid being formed via the traditional pathway of OH reacting with SO_2 , but this would not be a large contributor under the experimental conditions. Larger photolysis rates would mean that this pathway would contribute more to sulphuric acid production.

The effect of ionization on the formation rates is in line with previous measurements on the effect of ionization on sulphuric acid-water systems (Svensmark et al., 2007; Enghoff et al., 2008; Kirkby et al., 2011; Pedersen et al., 2012, pii; Dunne et al., 2016).

The Archean atmosphere still contains many mysteries. This study shows that aerosol formation with the sulphuric acid system, which is prevalent today, was also possible back then, within the current constraints on the Archean atmospheric composition. The requirements for this is higher SO_2 levels than today, combined with elevated amounts of UV radiation. The higher the UV level, the less SO_2 is required, and vice versa.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank Sebastian Danielache and Matthew S. Johnson for insightful conversations and help in understanding the sulphur chemistry. NJS thanks the generous support of the Israel Ministry of Energy. We thank the Kurt J. Lesker company for use of the drawing in Fig. 1.

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