

Viscosity and phase state of wildfire smoke particles in the stratosphere from pyrocumulonimbus events: an initial assessment

Authors:

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Abstract.

Large wildfires periodically inject massive amounts of biomass burning organic aerosol (BBOA) into the stratosphere ($\sim 15 \text{ km} \leq \text{altitude} \leq 50 \text{ km}$) via pyrocumulonimbus (pyroCb) events. These aerosols may remain aloft for many months and engage in multiphase chemistry that contributes to the destruction of stratospheric ozone. To predict this chemistry, it is essential to understand the viscosity and phase state of BBOA in the stratosphere. In this study, we use laboratory data and a thermodynamic model to evaluate these properties. Our findings indicate that unaged and aged wildfire smoke particles may be in a glassy state (viscosity $\geq 10^{12} \text{ Pa s}$) for certain conditions in the stratosphere, particularly when the H_2SO_4 -to-BBOA mass ratio in the aerosol particles is $\lesssim 0.33$. Lidar observations of wildfire smoke in the stratosphere are consistent with these findings. In such a state, bulk reactions will be inhibited, and multiphase chemistry will be limited to the particle surfaces. The glassy state may also nucleate crystalline polar stratospheric clouds, potentially exacerbating stratospheric ozone depletion. Even after prolonged aging and a H_2SO_4 -to-BBOA mass ratio of 1 (considered a likely upper limit for pyroCb smoke in the lower stratosphere with an aging time of $\lesssim 1$ year), the viscosities may reach 10^6 to 10^{11} Pa s for specific temperatures and relative humidities. These high viscosities should be considered when describing the stratospheric chemistry of wildfire smoke particles. We also identify critical areas where future research is needed to better constrain the viscosity and phase state of BBOA in the stratosphere; and thus, its impact on stratospheric ozone.

Keywords: Aerosols, biomass burning, viscosity, phase state, glass state, polar stratospheric clouds, ozone layer, oxidation, atmospheric aging

Synopsis statement: This study evaluates the viscosity and phase state of wildfire smoke aerosols in the stratosphere, crucial for understanding their impact on ozone depletion.

1. Introduction:

Smoke from wildfires consists of mostly organic aerosol particles, called biomass-burning organic aerosol (BBOA).¹ For example, smoke sampled from wildfires in the western U.S.A. comprised of $> 90\%$ BBOA by mass.^{2,3} Wildfires also emit large amounts of volatile organic compounds (VOCs). In the atmosphere, hydroxyl radicals (OH) and ozone (O_3) oxidize VOCs, and some of the products of these reactions condense onto existing particles, adding to the BBOA mass.⁴ OH and O_3 can also react directly with BBOA, forming a more oxidized aerosol. These combined processes result in aged BBOA (Fig. 1A). Meanwhile, sulfuric acid (H_2SO_4) can also condense on the BBOA to form aged BBOA- H_2SO_4 particles (Fig. 1A).

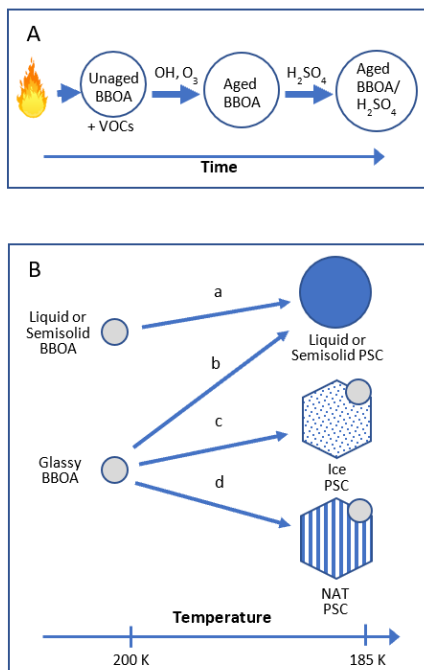


Figure 1. A) Aging of biomass burning organic aerosol (BBOA) in the stratosphere. VOCs represent volatile organic compounds. B) Possible formation pathways of polar stratospheric clouds (PSCs). NAT represents nitric acid trihydrate. PSCs form at temperatures less than $\cong 200$ K.

Large wildfires periodically inject massive amounts of BBOA into the stratosphere (~ 15 km \leq altitude ≤ 50 km) via pyrocumulonimbus (pyroCb) events and associated deep convection. Examples include the large-scale wildfires in the Pacific Northwest of North America in 2017 and the Australian "black summer" fires in 2019 — 2020.^{5, 6} Aged smoke is also ubiquitous in the upper troposphere and is mixed into the lowermost stratosphere.^{7, 8}

Once in the stratosphere, BBOA can linger for many months.^{5, 9} Recent studies suggested that multiphase reactions in the stratosphere occur on or in BBOA, leading to an unexpected depletion of the UV-blocking stratospheric ozone layer.¹⁰⁻¹² In a warming world, these multiphase reactions could delay the recovery of the ozone layer for years to come, leading to an increase in ultraviolet radiation exposure at the Earth's surface and an increase in cases of skin cancer.^{11, 12} BBOA in the stratosphere from pyroCb events can also influence the formation of polar stratospheric clouds (PSCs), possibly leading to additional depletion of the stratospheric ozone layer.¹³

Important properties of BBOA are the viscosity and phase state (i.e., liquid, semisolid, or amorphous solid). The viscosity and phase state are tightly connected: liquids have a viscosity $< 10^2$ Pa s, semisolids have a viscosity of 10^2 — 10^{12} Pa s, and amorphous solids have a viscosity $> 10^{12}$ Pa s.¹⁴ A viscosity of $> 10^{12}$ Pa s of a non-crystalline material is also referred to as a glassy solid state. The viscosity and phase state of BBOA particles can strongly impact their multiphase chemistry since viscosity is inversely related to the diffusion rates of reactants and products

within the BBOA particles.¹⁵⁻¹⁸ As a result, high viscosities and the glass state could inhibit bulk reactions and limit multiphase chemistry to the surfaces of BBOA particles.

The viscosity and phase state of BBOA may also impact the formation pathways of PSCs (Fig. 1B). If BBOA particles are in a non-glassy state, they can take up H₂O and HNO₃ at low temperatures to form non-glassy PSCs (pathway a). Ansmann et al. speculated that BBOA particles in a glassy state could heterogeneously nucleate crystalline ice or crystalline nitric acid hydrate (NAT) (pathways c and d).¹³ We also speculate that glassy BBOA may take up H₂O and HNO₃ to form non-glassy PSCs due to the plasticizing effect of small molecules like H₂O and HNO₃ (pathway b). Nevertheless, which pathways are important in the polar stratosphere is unknown.

Despite their importance, the viscosity and phase state of BBOA at stratospheric conditions have not been quantified. As a result, the effect of wildfire smoke on the stratospheric ozone layer and PSCs remains highly uncertain. In the following, we use laboratory data and a thermodynamic model to predict the viscosity and phase state of BBOA in the stratosphere from pyroCb events. We first estimate the viscosity and phase state for aging times of 0 days and 1.5 days by OH and O₃ in the stratosphere. Next, we estimate the viscosity and phase state after long-term aging (weeks to months) in the stratosphere. Finally, we considered the effect of H₂SO₄ uptake on the viscosity and phase state. The implications of the results for stratospheric chemistry and PSCs are also discussed as well as observational constraints of the viscosity and phase state of BBOA in the stratosphere. We also provide an outlook for future research on the viscosity and phase state of BBOA in the stratosphere.

2. Methods.

2.1. Scenarios

Listed in Table 1 are the scenarios considered and the proxies used to represent BBOA and BBOA-H₂SO₄ particles in the stratosphere from pyroCb events. Below we discuss each scenario in more detail and justify the proxies used to represent BBOA and BBOA-H₂SO₄ particles.

<i>Scenarios</i>	<i>BBOA Proxy</i>	<i>O/C</i>	<i>H/C</i>	H₂SO₄:BBOA mass ratio
<i>BBOA after 0 days of aging</i>	BBOA from combustion of pine wood. ¹⁹	0.55	1.83	0
<i>BBOA after 1.5 days of aging</i>	BBOA from combustion of pine wood. Aged in oxidation flow reactor for equivalent of 1.5 days. ¹⁹	0.98	1.55	0
<i>BBOA after weeks to months of aging</i>	Mixture of 5 short-chained dicarboxylic acids (equal masses of each).	1.01	1.4	0
<i>BBOA after weeks to months of aging and low H₂SO₄ uptake</i>	Mixture of 5 short-chained dicarboxylic acids (equal masses of each).	1.01	1.4	0.33
<i>BBOA after weeks to months of aging and high H₂SO₄ uptake</i>	Mixture of 5 short-chained dicarboxylic acids (equal masses of each).	1.01	1.4	1

Table 1. Scenarios considered and proxies used to determine the viscosity of wildfire smoke in the stratosphere from pyroCb events.

2.1.1 The viscosity of BBOA in the stratosphere after 0 days of aging

Xu et al. reported the glass transition temperature of unaged BBOA generated from the combustion of pine wood using flaming conditions.¹⁹ The average oxygen-to-carbon atomic ratio (O/C) and hydrogen-to-carbon atomic ratio (H/C) of the unaged pine-wood BBOA studied by Xu et al. are listed in Table 1. The average O/C ratio of the unaged BBOA is similar to those for BBOA sampled close to real fires.²⁰ Here, we use the glass transition temperature for unaged pine-wood BBOA reported by Xu et al. (275.3 K) to predict the viscosity of BBOA in the stratosphere after 0 days of aging. The method of calculating viscosities as a function of RH and temperature from glass transition temperatures is discussed in Section S1.

2.1.2 The viscosity of BBOA in the stratosphere after 1.5 days of aging

Xu et al. also reported the glass transition temperature of pine-wood BBOA aged by OH and O₃ equivalent to \cong 1.5 days in the atmosphere.¹⁹ The O/C and H/C ratios of the aged pine-wood BBOA studied by Xu et al. are listed in Table 1. We use the glass transition temperature from that study (286.5 K) to predict the viscosity and phase behavior of BBOA aged 1.5 days in the stratosphere.

2.1.3 Viscosity of BBOA in the stratosphere after weeks to months of aging

The viscosity of BBOA after long-term aging (weeks to months) has not been investigated and, hence, is highly uncertain. To represent BBOA in the stratosphere after long-term aging, we used a mixture of five different dicarboxylic acids (equal masses of malic acid, malonic acid, maleic acid, glutaric acid, and methylsuccinic acid). As done previously, we refer to this mixture as M5.²¹ To determine the viscosity of the M5 mixture, we used the AIOMFAC-VISC thermodynamic model.^{22, 23}

The M5 mixture has been used previously to represent water-soluble material, representative of the more oxidized components of organic aerosols in the atmosphere.^{21, 24} The M5 mixture is a reasonable proxy for BBOA after long-term aging for several reasons. First, the average O/C of the M5 mixture is larger than unaged BBOA (Table 1). Long-term aging of BBOA is expected to lead to higher O/C values due to oxygen addition reactions.²⁵ Second, the organic molecules in the M5 mixture have smaller carbon numbers than most organic molecules in unaged BBOA (\leq 5 carbon atoms for the M5 mixture vs. 6 to 30 carbon atoms for unaged BBOA).²⁶⁻²⁸ Long-term aging of BBOA is expected to lead to smaller carbon numbers due to fragmentation reactions.²⁵ Third, dicarboxylic acids are a significant component of aged BBOA in the troposphere, and the relative amount of dicarboxylic acids in wildfire plumes increases with age, suggesting they form by chemical reactions in the atmosphere.²⁹⁻³¹

2.1.4 Viscosity of BBOA in the stratosphere after weeks to months of aging and H₂SO₄ uptake (H₂SO₄-to-BBOA mass ratio of 0.33 and 1)

BBOA in the atmosphere can take up H₂SO₄ that is present in the background atmosphere (dilution mechanism) or H₂SO₄ that is formed in the plume by the oxidation of sulfur dioxide (SO₂) emitted from wildfires.^{7, 32, 33} The conversion of SO₂ to H₂SO₄ is a slow process in the

stratosphere, with the stratospheric lifetime of SO₂ on the order of several weeks.³⁴ Due to a very limited number of measurements, the rate and amount of H₂SO₄ uptake onto pyroCb BBOA in the stratosphere is highly uncertain. To constrain the possible effect of H₂SO₄ on the viscosity and phase state of pyroCb BBOA in the stratosphere, we consider H₂SO₄-to-BBOA (H₂SO₄:BBOA) mass ratios of 0.33 and 1 (Table 1). For these two scenarios, we use the M5 mixture to represent BBOA. To determine the viscosity of an M5 mixture combined with H₂SO₄, we used the AIOMFAC-VISC thermodynamic model with the Zdanovskii-Stokes-Robinson (ZSR) mixing rule option.^{22, 23}

One can estimate an upper limit to the H₂SO₄:BBOA mass ratio of pyroCb smoke in the stratosphere based on very limited measurements. In 2017, the NASA Atmospheric Tomography (ATom) mission sampled pyroCb smoke in the northern hemisphere and lowest part of the stratosphere from the large-scale wildfires in the Pacific Northwest of North America.^{35, 36} Single particle measurements that were part of this mission indicate that the average H₂SO₄:BBOA mass ratio was ~0.37 and ~0.79 for 2 months and 9 months, respectively, after the initial pyroCb injection into the stratosphere (Section S2 and Fig. S1).³⁵⁻³⁷ The H₂SO₄:BBOA mass ratio was even smaller for the largest particles ($\geq 0.5 \mu\text{m}$) (Fig. S2). Based on the size distributions of the typical smoke in the stratosphere and smoke from pyroCb events, the largest particles were likely mostly from pyroCb events, whereas the smaller particles were likely aged smoke that is widespread in the upper troposphere and lower stratosphere.^{8, 36} Infrared spectra of pyroCb smoke in the stratosphere from wildfires in the Pacific Northwest of North America, 2017 and Australia, 2019 — 2020 have also been recorded.^{10, 38} BBOA was clearly identified in the spectra, but no features were assignable to H₂SO₄, possibly suggesting that the H₂SO₄ content was not dominant, however, calibrations are needed to confirm this assertion.^{10, 38} Based on these limited measurements, we suggest that a H₂SO₄:BBOA mass ratio of 1 is likely an upper limit for pyroCb smoke in the lower stratosphere with an aging time of $\lesssim 1$ year.

3. Results and discussion:

3.1 Relative humidity and temperature in the stratosphere

Before discussing the viscosity of BBOA in the stratosphere, we first considered the relative humidity (RH) and temperature in the stratosphere since these parameters strongly impact viscosity. As the relative humidity (RH) increases, the water activity (and hence water content) of BBOA particles increases to maintain equilibrium with the gas phase, and the viscosity decreases due to the plasticizing effect of water.^{14, 39} In addition, the viscosity decreases as the temperature increases.⁴⁰

Typical water vapor mixing ratios in the stratosphere are 5 ppmv. However, higher mixing ratios have been observed in wildfire plumes that have reached the stratosphere via pyroCb events. Kablick et al. reported water vapor mixing ratios > 15 ppmv in plumes from Australian wildfires in 2019 — 2020 after reaching the stratosphere via pyroCb events.⁴¹ Yu et al. also reported a water vapor mixing ratio > 5 ppmv in plumes from Canadian wildfires in 2017 after reaching the stratosphere via pyroCb events.⁴² To be consistent with these observations, we considered water vapor mixing ratios of 5 and 15 ppmv.

We calculated the RH as a function of temperature in the stratosphere at altitudes of 15 and 32 km and water vapor mixing ratios of 5 and 15 ppmv (See Section S3 for details of the calculations). An altitude range of 15 — 32 km corresponds to the range of altitudes where wildfire plumes have been observed in the stratosphere.^{41, 43, 44} The results of these calculations are shown in Figure 2. The horizontal bar above Figure 2 illustrates the temperature range of 177 — 250 K, which is most relevant for the altitude range of 15 — 32 km in the stratosphere (see Fig. S3). We will focus on this temperature range for the remainder of the article.

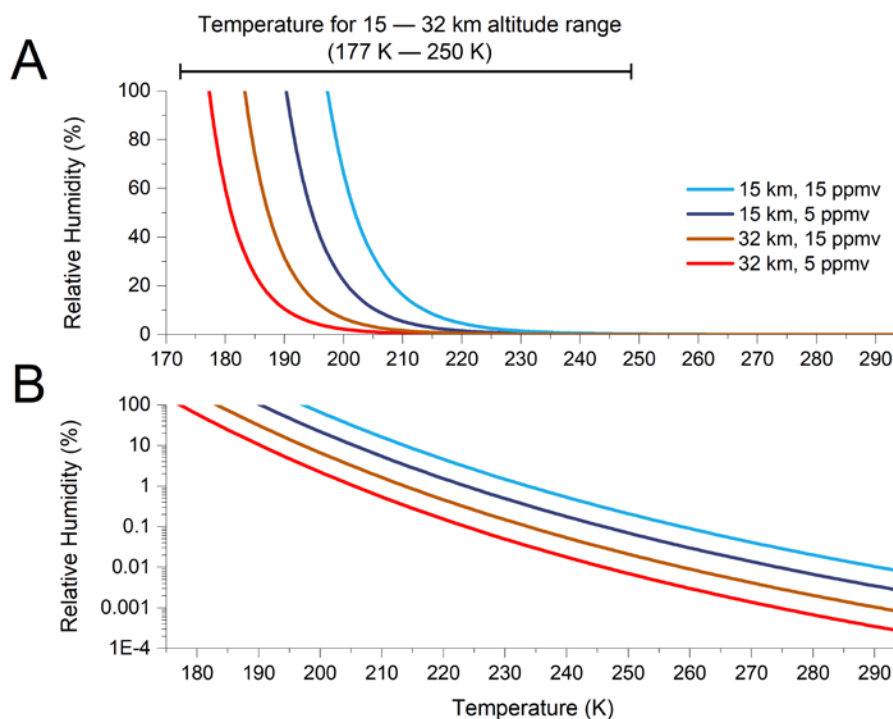


Figure 2. Relative humidity as a function of temperature in the stratosphere for altitudes of 15 and 32 km and water vapor mixing ratios of 5 and 15 ppmv. Data with the RH on a linear scale (A), and data with the RH on a logarithmic scale (B).

Based on our calculations, at temperatures of 250 — 230 K and altitudes of 15 — 32 km, the air is very dry ($\approx 1\%$ RH) (Fig. 2). At temperatures of 230 — 177 K and altitudes of 15 — 32 km, the RH can increase sharply and can reach 100% (Fig. 2). In contrast, in the troposphere, the RH is almost always $> 10\%$.⁴⁵ These results have important implications for the viscosity of BBOA in the stratosphere (see below).

3.2 The viscosity of BBOA in the stratosphere after 0 days of aging

Shown in Figure 3A is the estimated viscosity as a function of temperature and RH of unaged BBOA based on the glass transition temperatures of unaged pine-wood BBOA from Xu et al. (Table 1 and Methods). Superimposed on Figure 3A are the temperature and RH values in the stratosphere at 15 and 32 km and water vapor mixing ratios of 5 and 15 ppmv. From Figure 3A and the temperature and RH values in the stratosphere at 15 and 32 km, we estimated the viscosity of unaged BBOA in the stratosphere as a function of temperature (Figure 3B).

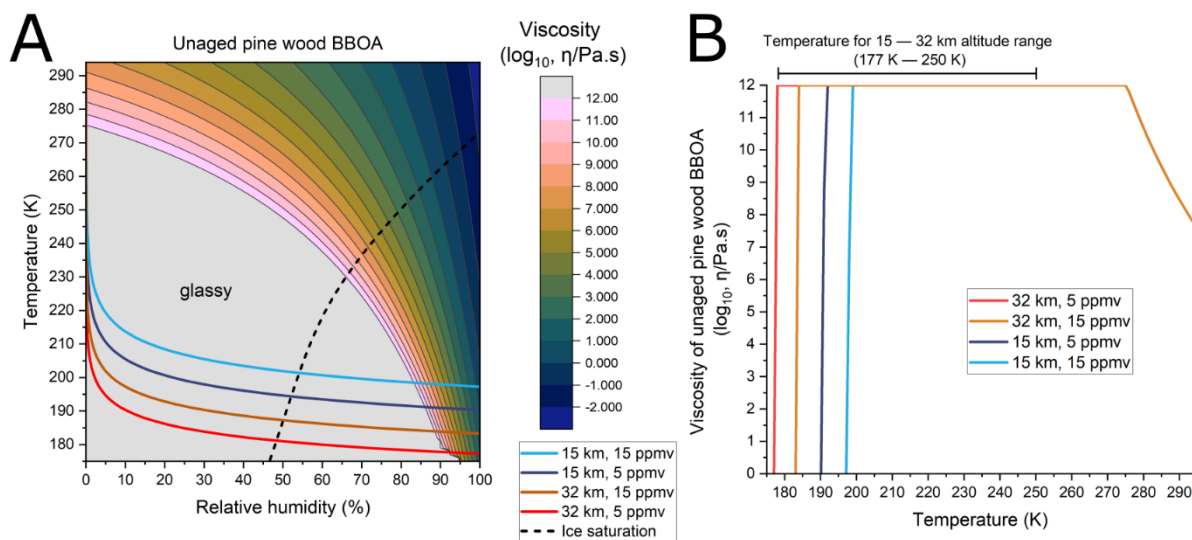


Figure 3. Estimations of the viscosity of BBOA in the stratosphere after 0 days of aging. A) Viscosity of unaged pine-wood BBOA as a function of temperature and RH based on glass transition temperatures from Xu et al.¹⁹. Superimposed are the RH and temperature for stratospheric conditions (solid lines). Also superimposed is the RH and temperature in the stratosphere when water vapor is supersaturated with respect to ice (dashed line). RH and temperature conditions to the right of this line correspond to conditions at which ice is stable and ice nucleation is possible. B) Viscosity as a function of temperature of unaged BBOA in the stratosphere based on the data from panel A.

Based on Figure 3B, between 250 — 200 K, unaged BBOA in the stratosphere will have a viscosity of $> 10^{12}$ Pa s and be in a glassy solid state. These extremely high viscosities are due to a combination of low RH values and low temperatures (Fig 3A). At temperatures < 200 K, the BBOA can switch from a glassy solid state to a semisolid or liquid state (Fig. 3B) due to the heightened RH in this low-temperature regime (Figure 2). At an altitude of 15 km, the transition from a glassy state to a semisolid/liquid state occurs at about 200 — 190 K. At an altitude of 32 km, the transition occurs at about 185 — 175 K.

To estimate the viscosity for the unaged scenario we used the glass transition temperature of unaged pine-wood BBOA from Xu et al. Xu et al. also reported the glass transition temperatures of unaged poplar-wood BBOA and unaged cedar-wood BBOA. The viscosities predicted using the glass transition temperatures of unaged poplar-wood and unaged cedar-wood BBOA from Xu et al. are similar to those for unaged pine-wood BBOA (compare Fig. 3A and Figs. S4-S5). The viscosity predictions using the glass transition temperatures of unaged pine-wood BBOA are also consistent with viscosities reported by Schnitzler et al. and Gregson et al. for BBOA generated from the smoldering of pine wood (compare Fig. 3A and Figs. S6-S8).^{15, 16}

3.3 The viscosity of BBOA in the stratosphere after 1.5 days of aging

Shown in Figure 4A is the estimated viscosity, as a function of temperature and RH, of BBOA after 1.5 days of aging based on the glass transition temperature of aged pine-wood BBOA (1.5 days of aging) from Xu et al. (Table 1 and Methods). From Figure 4A and the temperature and

RH values in the stratosphere at 15 and 32 km, we estimated the viscosity of the BBOA after 1.5 days of aging in the stratosphere as a function of temperature (Figure 4B).

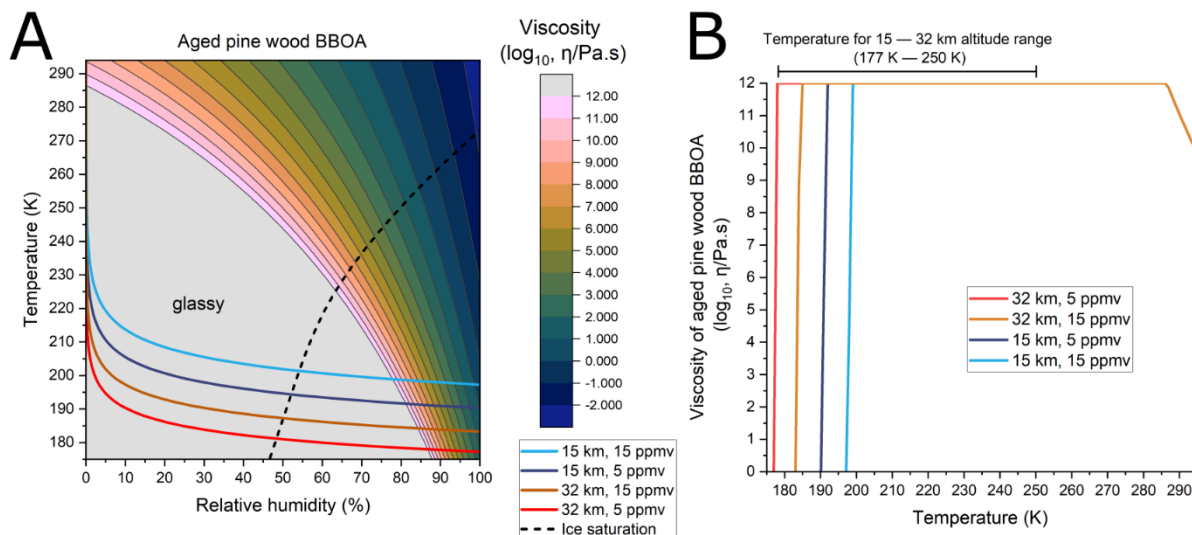


Figure 4. Estimations of the viscosity of BBOA in the stratosphere after 1.5 days of aging. A) Viscosity of pine-wood BBOA (aged 1.5 days) as a function of temperature and RH based on glass transition temperatures from Xu et al.¹⁹. Superimposed are the RH and temperature for stratospheric conditions (solid lines). Also superimposed is the RH and temperature in the stratosphere when water vapor is supersaturated with respect to ice (dashed line). RH and temperature conditions to the right of this line correspond to conditions at which ice is stable and ice nucleation is possible. B) Viscosity as a function of temperature of 1.5-day BBOA in the stratosphere based on the data in Panel A.

The trends predicted for 1.5 days of aging are similar to those predicted for unaged BBOA. Based on Figure 4B, the particles are in a glassy solid state (viscosity $> 10^{12}$ Pa s) between 250 — 200 K. At temperatures < 200 K, the BBOA transitions from a glassy solid state to a semisolid/liquid state.

We used the viscosity of aged pine-wood BBOA (1.5 days of aging by OH and O₃) from Xu et al. to estimate the viscosity for the 1.5-days of aging scenario. Xu et al. also reported glass transition temperatures of aged poplar-wood BBOA and aged cedar-wood BBOA (both 1.5 days of aging). The viscosities predicted using the glass transition temperatures of aged poplar-wood and cedar-wood are similar to those for aged pine-wood BBOA (compare Fig. 4A and Figs. S9-S10). The viscosity predictions using the glass transition temperature for aged pine-wood BBOA are also consistent with viscosities reported for secondary organic aerosol generated from the gas-phase oxidation of phenols, which are volatile organic compounds emitted from wildfires (compare Fig. 4A and Fig. S11).⁴⁶

3.4 Viscosity of BBOA in the stratosphere after weeks to months of aging

As BBOA lingers in the stratosphere, it is continuously oxidized by OH and O₃. We used a mixture of dicarboxylic acids, referred to as the M5 mixture, to represent BBOA after long-term aging (Table 1 and Methods). Shown in Figure 5A is the estimated viscosity as a function of

temperature and RH of BBOA in the stratosphere after long-term aging based on this proxy. Figure 5B shows the estimated viscosity of the BBOA in the stratosphere based on the stratospheric temperature and RH values and the viscosities shown in Figure 5A. Between 250 — 205 K, the viscosity is $> 10^{12}$ Pa s; hence, the particles are in a glassy state. At temperatures < 205 K in the stratosphere, the particles transition from a glassy state to a semisolid/liquid state. At an altitude of 15 km, the transition from a glassy state to a semisolid/liquid state occurs at about 205 — 190 K. At an altitude of 32 km, the transition occurs at about 185 — 175 K.

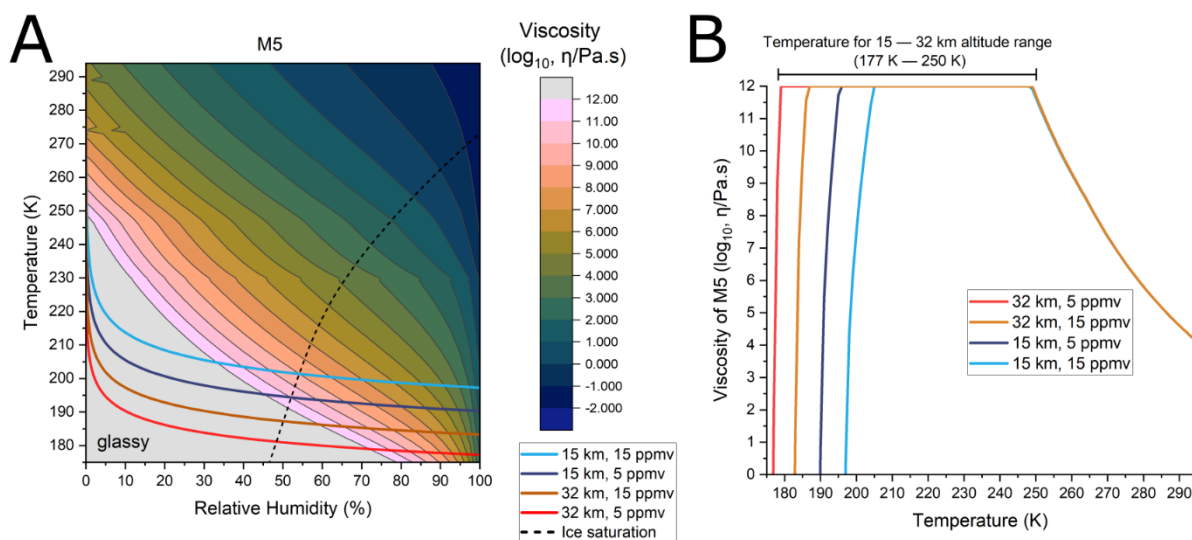


Figure 5. Estimations of the viscosity of BBOA in the stratosphere after weeks to months of aging. A) Temperature- and RH-dependent viscosity of a mixture of five different short-chained dicarboxylic acids (equal masses of malic acid, malonic acid, maleic acid, glutaric acid, and methylsuccinic acid). We refer to this mixture as M5. Superimposed are the RH and temperature for stratospheric conditions (solid lines). Also superimposed is the RH and temperature in the stratosphere when water vapor is supersaturated with respect to ice (dashed line). RH and temperature conditions to the right of this line correspond to conditions at which ice is stable and ice nucleation is possible. B) Viscosity as a function of temperature of BBOA in the stratosphere after long-term aging based on the data in Panel A.

The trends predicted for the long-term aging scenario (Fig. 5b) are similar to the 1.5-day aging scenario (Fig. 4B), except the viscosities of the long-term aging scenario are lower than for the 1.5-day aging scenario for temperatures > 250 K and < 205 K. The lower viscosities are possibly because the M5 mixture has a smaller average molecular weight than the 1.5-day aged scenario, and lower molecular weights correlate with lower viscosities.⁴⁷⁻⁴⁹ In addition, the M5 mixture is more hygroscopic, meaning a higher aerosol water content at intermediated RH levels (e.g. 50% RH) than in the 1.5-day aging scenario. Nevertheless, the viscosity for the long-term aging scenario is still high and glassy for a large range of stratospheric conditions.

3.5 Viscosity of BBOA after weeks to months of aging and uptake of H_2SO_4 in the stratosphere

For the long-term aging scenario, we also investigated the effect of H_2SO_4 uptake on viscosity. As above, the BBOA after long-term aging is represented by the M5 mixture. First, we consider the M5 proxy mixed with H_2SO_4 for a H_2SO_4 :BBOA mass ratio of 0.33. (Table 1 and Methods).

Shown in Figure 6A is the estimated viscosity as a function of temperature and RH for this system. Figure 6B shows the estimated viscosity in the stratosphere at 15 — 32 km based on the viscosities in Figure 6A. Between 250 — 210 K, the viscosity ranges from 10^8 to $> 10^{12}$ Pa s. For three out of the four trajectories (all except 15 km at 15 ppmv), the viscosity reaches $> 10^{12}$ Pa s within this temperature range; hence, the particles can be in a glassy state. At temperatures < 205 K, the particles can transition from a glassy state to a semisolid/liquid state. At an altitude of 15 km, the transition occurs at about 205 — 190K. At an altitude of 32 km, the transition occurs at about 190 — 175 K.

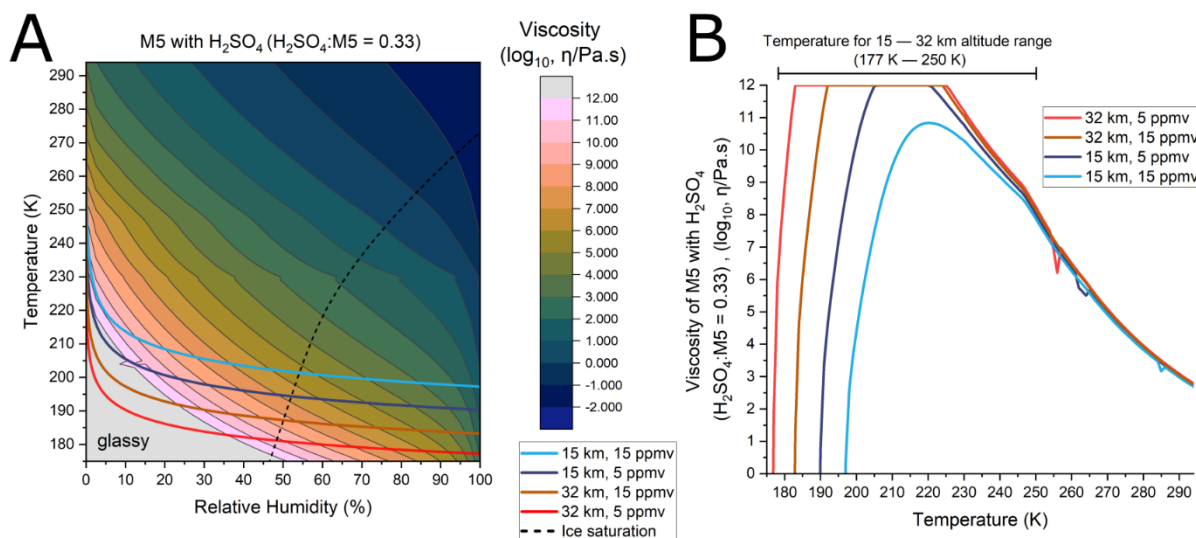


Figure 6. Estimations of the viscosity of BBOA in the stratosphere after long-term aging and mixed with H_2SO_4 (H_2SO_4 :BBOA = 0.33). A) Temperature- and RH-dependent viscosity of a mixture of five different short-chained dicarboxylic acids (equal masses of malic acid, malonic acid, maleic acid, glutaric acid, and methylsuccinic acid, M5) mixed with H_2SO_4 (H_2SO_4 :BBOA = 0.33). Superimposed are the RH and temperature for stratospheric conditions (solid lines). Also superimposed is the RH and temperature in the stratosphere when water vapor is supersaturated with respect to ice (dashed line). RH and temperature conditions to the right of this line correspond to conditions at which ice is stable and ice nucleation is possible. B) Viscosity as a function of temperature of BBOA- H_2SO_4 particles in the stratosphere based on the data in Panel A. Note, the visible spikes and steps in the curves and contours are not physically meaningful. They stem from an incomplete equilibrium solution computed by the thermodynamic model for those specific conditions.

The viscosities predicted for BBOA after long-term aging with a H_2SO_4 :BBOA mass ratio of 0.33 (Fig. 6B) are significantly lower than without H_2SO_4 (Fig. 5B), clearly illustrating that the addition of H_2SO_4 and the associated aerosol water uptake has a large effect on the viscosity of the BBOA particles. Nevertheless, the viscosity of long-term aged BBOA with a H_2SO_4 :BBOA mass ratio of 0.33 is still large and can reach a glassy state for a range of conditions in the stratosphere.

Next, we consider the M5 proxy mixed with H_2SO_4 at a H_2SO_4 :BBOA mass ratio of 1. (Table 1 and Methods). Shown in Figure 7A is the estimated viscosity as a function of temperature and RH. Figure 7B shows the estimated viscosity in the stratosphere based on the data in Figure 7A.

At 250 K, the viscosity is 10^5 Pa s (i.e. a semi-solid). At colder temperatures, the viscosity reaches 10^6 to 10^{11} Pa s, depending on altitude and water vapor mixing ratio. Although not glassy, these viscosities are still large. For comparison, the viscosity of tar pitch is $\sim 10^8$ Pa s.

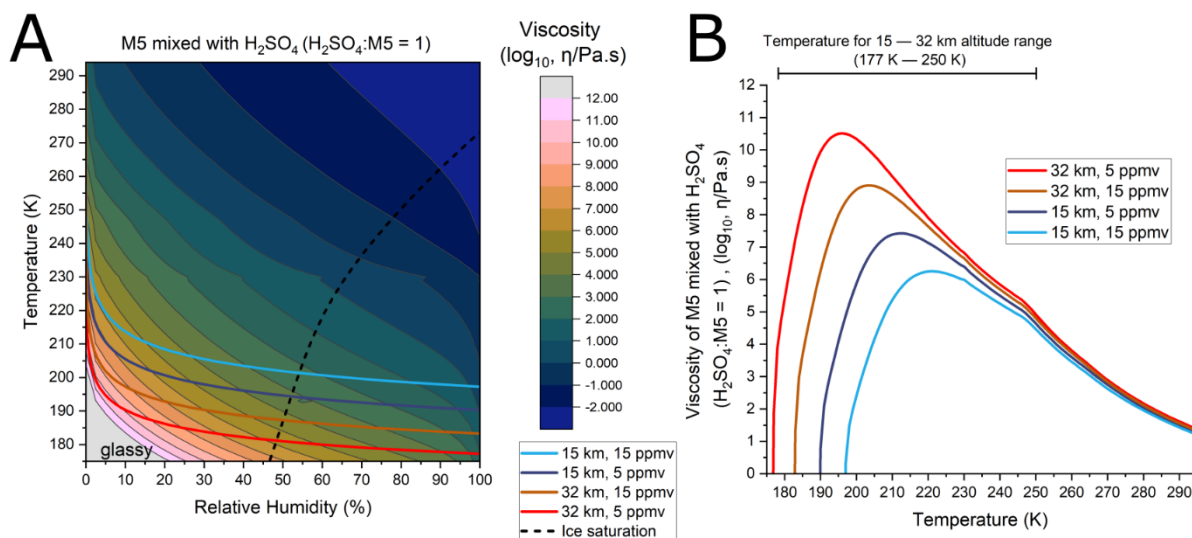


Figure 7. Estimations of the viscosity of BBOA in the stratosphere after long-term aging and mixed with H₂SO₄ (H₂SO₄:BBOA = 1). A) Temperature- and RH-dependent viscosity of a mixture of five different short-chained dicarboxylic acids (equal masses of malic acid, malonic acid, maleic acid, glutaric acid, and methylsuccinic acid, M5) mixed with H₂SO₄ (H₂SO₄:BBOA = 1). Superimposed are the RH and temperature for stratospheric conditions (solid lines). Also superimposed is the RH and temperature in the stratosphere when water vapor is supersaturated with respect to ice (dashed line). RH and temperature conditions to the right of this line correspond to conditions at which ice is stable and ice nucleation is possible. B) Viscosity as a function of temperature of BBOA-H₂SO₄ particles in the stratosphere based on the data in Panel A. Note, the visible spikes and steps in the curves and contours are not physically meaningful. They stem from an incomplete equilibrium solution computed by the thermodynamic model for those specific conditions.

4. Implications

Recent studies have suggested that reactions occur on or in BBOA in the stratosphere, leading to unexpected depletion of the UV-blocking stratospheric ozone layer.¹⁰⁻¹² In modelling studies, researchers have assumed that the BBOA-H₂SO₄ particles in the stratosphere are in a non-glassy state and that reactions occur in the bulk of the BBOA-H₂SO₄ particles.^{11, 12} These assumptions have generally aligned with model-measurement comparisons.^{11, 12} Our results suggest that wildfire smoke particles can be in a glassy state (viscosity $\geq 10^{12}$ Pa s) under certain temperatures and relative humidities in the stratosphere, particularly when the H₂SO₄:BBOA mass ratio is ≤ 0.33 . In such a state, bulk reactions will be inhibited, and multiphase chemistry may be restricted to the surface of the particles. Therefore, surface reactions may need to be considered for some conditions in the stratosphere.

Our results also suggest that even after long-term aging and a H₂SO₄:BBOA mass ratio of 1 (likely an upper limit for BBOA in the lower stratosphere from pyroCb events with aging times

of $\lesssim 1$ year), viscosities may reach 10^6 — 10^{11} Pa s for specific temperatures and relative humidities. These high viscosities will influence the characteristic reaction diffusive length scale and reactive uptake rates, and hence, these high viscosities may need to be considered to accurately describe the stratospheric chemistry and the physicochemical evolution of wildfire smoke particles.

As mentioned above, BBOA may influence the formation mechanisms of PSCs via several pathways (Fig. 1B). In the current study, we address the possibility of pathways a and c in Figure 1B. In Figures 3-7, we have included the RH and temperature when vapor is supersaturated with respect to ice (dashed lines). RH and temperature conditions to the right of this line correspond to situations when ice nucleation is possible.

For the 0-day, 1.5-days, and long-term aging scenarios without H_2SO_4 uptake, our viscosity estimations suggest that there are conditions in the stratosphere under which the particles are in a glassy state and the vapor is supersaturated with respect to ice (i.e. the glass state exists to the right of the dashed lines in Fig. 3A, 4A, and 5A). For these cases, the particles provide possible surfaces for heterogeneous ice nucleation and the formation of ice-containing PSCs (pathway c, Fig. 1B).

For the long-term aging scenario with a H_2SO_4 :BBOA mass ratio of 0.33, the glass state only exists to the left of the dashed line in Figure 6A, suggesting heterogeneous ice nucleation is not possible on glassy aerosol for these scenarios under equilibrium conditions. However, if the glassy particles formed in these scenarios are cooled rapidly, as occurs in orographic waves in the polar stratosphere, water uptake can be kinetically limited by the diffusion of water within the particles, and a glassy core can persist to lower temperatures and higher RH values than predicted by equilibrium thermodynamics.^{50, 51} Under these conditions, a glassy core may persist long enough to initiate heterogeneous ice nucleation (pathway c, Fig. 1B).

For the long-term aging scenario with a H_2SO_4 :BBOA mass ratio of 1, the aged H_2SO_4 -BBOA particles never reach the glassy state (Fig. 7A and 7B). Under these conditions, heterogeneous nucleation by solid state BBOA particles is not possible and a liquid or semisolid BBOA should form a liquid or semisolid PSC (pathway a in Fig. 1B).

5. Observational constraints of viscosity and phase state of wildfire smoke particles in the stratosphere

Lidar observations indicate that fresh smoke particles in the stratosphere exhibit a high depolarization ratio, suggesting the presence of non-spherical particles.^{5, 52-54} This elevated depolarization could signal that BBOA is in a glassy or highly viscous state in the stratosphere. In newly emitted smoke plumes, BBOA particles can coagulate into fractal aggregates.⁵⁵ If BBOA is in a glassy or highly viscous state, the material will not flow, maintaining its fractal structure after coagulation, which would contribute to a high depolarization ratio.⁵⁶⁻⁵⁸ Additionally, black carbon particles from combustion sources initially have a fractal geometry. When coated with a low-viscosity material, the fractal geometry can become more compact and spherical, with a low depolarization ratio.⁵⁹ However, if black carbon is coated with BBOA in a glassy or highly viscous state, black carbon can maintain its fractal geometry, and the

depolarization ratio can stay high.⁵⁹ Nevertheless, interpretation of lidar depolarization is complicated because depolarization depends on particle size as well as the degree of non-sphericity.⁵⁶

Lidar data also show that the depolarization ratio of smoke in the stratosphere decreases over a period of 3-4 months, eventually approaching zero (< 0.05).^{5, 60} This trend may indicate that BBOA transitions from a highly viscous state to one with lower viscosity. A decrease in viscosity would allow fractal aggregates of BBOA to transform into spherical particles, which should have a near-zero depolarization ratio. Similarly, a reduction in BBOA viscosity would enable fractal black carbon aggregates coated with BBOA to compact into a core-shell structure, with a low depolarization ratio. Baars et al. pointed out that the decrease in depolarization ratio of smoke in the stratosphere with time is consistent with the aging of smoke particles and the addition of a coating around the solid black carbon core aggregates, which would change the shape towards a spherical form.⁵ We add here that the coating would also need to be in a non-glassy and lower viscosity state,⁵⁹ which may be accomplished by aging with OH and O₃, uptake of H₂SO₄, and coagulation of smoke particles with H₂SO₄ particles present in the stratosphere.

6. Outlook

- 1) We used a mixture of five dicarboxylic acids as a proxy for BBOA after long-term aging in the stratosphere. Measurements are needed to confirm that the M5 mixture is a reasonable proxy for BBOA in the stratosphere from pyroCb events and after long-term aging.
- 2) We assumed that BBOA forms a single phase when mixed with H₂SO₄. Previous studies have shown that when secondary organic aerosol with an average O/C ratio ≥ 0.8 is mixed with ammonium sulfate aerosols, the resulting particles form a single phase.⁶¹⁻⁶³ Studies are needed to confirm if a similar threshold applies for BBOA mixed with H₂SO₄.
- 3) For predictions of viscosity in the stratosphere, we extrapolated viscosities of organic aerosol at a certain temperature to colder or warmer temperatures using the Vogel-Fulcher-Tammann equation and an assumed fragility parameter of 10 (Section S1 and the AIOMFAC-VISC thermodynamic model). Measurements are needed to confirm that a fragility of 10 is appropriate for BBOA.
- 4) Additional measurements are needed to determine the H₂SO₄ content in wildfire aerosols as a function of age in the stratosphere. These measurements could be carried out by high-altitude aircraft or by using infrared spectra of wildfire smoke in the stratosphere from satellite measurements.¹⁰
- 5) Observational constraints on the viscosity and phase state of BBOA in the stratosphere are essential. Lidar depolarization measurements of wildfire smoke in the stratosphere offer valuable insights into these properties, but additional measurements are needed. Lidar depolarization measurements indicate that wildfire smoke in the stratosphere is often non-spherical,⁶⁰ but depolarization is an indirect measurement that does not uniquely determine phase and viscosity.
- 6) Measurements should also differentiate between ordinary smoke particles slowly lofted into the stratosphere and smoke rapidly injected into the stratosphere through large pyroCb events. PyroCb smoke is by definition processed through a cloud during its ascent. This could result in a different mix of organic molecules than smoke that is not cloud-processed.

- 7) Our results suggest that aged BBOA and aged BBOA mixed with H₂SO₄ will be in a glassy state for some conditions in the stratosphere. Previous studies have shown that certain types of organic aerosols in a glassy state can nucleate ice heterogeneously.⁶⁴⁻⁶⁷ However, the ice nucleation efficiency of glassy organic aerosols is still an area of active research.⁶⁸ Studies are needed to determine whether BBOA in a glassy state can nucleate crystalline PSCs.
- 8) We considered the uptake of water and H₂SO₄ by BBOA in the stratosphere. At the coldest temperatures, BBOA particles can also take up nitric acid (HNO₃), similar to background H₂SO₄ particles in the stratosphere, which could further change the composition, and hence, the viscosity of the wildfire smoke particles.⁶⁹ Smoke particles can also take up HCl and potentially other chlorine compounds.¹² This uptake should be considered in future studies.

Author contributions:

The writing of the manuscript was led by AKB with contributions from MFZ. MFZ calculated viscosities from glass transition temperatures of BBOA and produced the figures in the manuscript with contributions from NGG. AZ calculated the viscosities of the M5 mixtures and M5 mixtures combined with sulfuric acid using the AIOMFAC-VISC thermodynamic model. DM and GS provided measurements of BBOA in the lower stratosphere. DM identified the observational constraints of viscosity and phase state in the stratosphere. All authors discussed and interpreted data and contributed to revising the original manuscript.

Supporting Information

Additional calculations, details of the ATom campaign, BBOA:H₂SO₄ mass ratio figure, simulated monthly temperature figure, and BBOA viscosity figures (DOC).

Acknowledgements:

The authors thank Yifeng Peng from Lanzhou University for providing simulated zonal mean monthly temperatures from the Whole Atmosphere Community Climate Model (WACCM).

Financial support:

This research has been supported by the Natural Sciences and Engineering Research Council of Canada (grant no. RGPIN-2023-05333 and RGPIN-2021-02688) and Environment and Climate Change Canada (grant no. GCXE20S049). We also acknowledge support from the Natural Sciences and Engineering Research Council of Canada for a postgraduate scholarship award (PGS D-579464-2023) for funding NGAG. The ATom mission as a whole was supported by NASA's Earth System Science Pathfinder Program EVS-2 funding. Participation in ATom Mission flights by DMM and GPS was supported by NOAA climate funding (no. NNH15AB12I).

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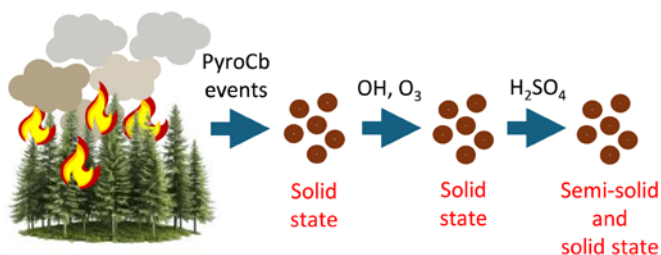
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Phase state of wildfire smoke in the stratosphere at 250 — 205 K
and 15 — 32 km.