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Communication

Impact of greenhouse gas CO_2 on the heterogeneous reaction of SO_2 on alpha-Al_2O_3

Yangyang Liu[a], Tao Wang[a], Xiaozhong Fang[a], Yue Deng[a], Hanyun Cheng[a], Hongbo Fu[a], Liwu Zhang[a,b,*]

[a] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433 China
[b] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092 China

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ABSTRACT

The heterogeneous reaction of SO_2 on mineral dust surfaces is generally considered as an important chemical pathway for secondary sulfate formation in the troposphere. To this day, there are no reported studies that assess the impact of atmospheric CO_2 in sulfate production on mineral dust surfaces. In this work, we investigate the impact of CO_2 on SO_2 uptake on dust proxy aluminum oxide particles using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). CO_2 is demonstrated to suppress the heterogeneous oxidation of SO_2 on alpha-Al_2O_3. Compared to that measured in the CO_2-free case, the uptake coefficient is decreased by nearly 57% when Al_2O_3 particles are exposed to the gas flow with atmospheric CO_2 at a relative humidity (RH) of 25%. It is also found that there is a balance between the yield of active moiety −OH provided by $Al(OH)_3(CO)(OH)_2$ clusters and the loss of basic hydroxyl group on aluminum oxide surfaces blocked by CO_2-derived (bi)carbonate species. This work, for the first time, reveals a negative effect of atmospheric CO_2 on the sulfate formation, which potentially decreases solar-radiation scattering and further exacerbates global warming.

Sulfate aerosol, one of the major constituents in fine particle matter, exerts its significant impact on Earth's radiation budget by scattering solar short-wave radiation and absorbing long-wave radiation from the land surface [1,2]. They are also known to contribute to public health issues and environmental problems through acid deposition [3–5]. Currently, the emission rate of mineral dust was estimated to be 1000–3000 Tg per year and those dust aerosol emitted from the soils have been suggested to provide abundant sites for SO_2 sink [6]. Therefore, it has been highlighted that heterogeneous oxidation of SO_2 on particle surfaces is an important chemical channel to account for rapid sulfate production in the atmosphere [7,8].

At present, knowledge for the SO_2 oxidation mechanism remains insufficient to bridge the gap between ground observations and modeling [9]. This indicates that some heterogeneous channels of great oxidation potential have not been explored yet. It is noted that alumina oxide possesses a considerable mass fraction of the Earth's crust [10]. The contents of aluminum oxide could comprise up to 15% of mineral dust aerosol [11], and this metal oxide prefers to present in the form of the alpha phase [12]. Under dry conditions, sulfite species is the dominant product on Al_2O_3 surfaces through quick rearrangement of SO_2 with oxygen atoms in metal oxide lattice [13]. An increase of relative humidity alters the physicochemical properties of Al_2O_3 surfaces, and water molecules would efficiently reduce the energy barrier for SO_2 adsorption. At the same time, dissociation of H_2O into a proton (H^+) and hydroxyl group (−OH) pair on Al_2O_3 particles favors the subsequent sulfur dioxide adsorption and oxidation, well supported by both experimental results and density functional theory (DFT) studies [14–16]. The synergistic effect between NO_2 and SO_2 in their reaction on Al_2O_3 particles was also reported [17], and H_2O_2 diffusing downward from the lower stratosphere leads to the acceleration of SO_2 uptake on aluminum oxide particles [18]. Despite systematic studies [13,18–21] of SO_2 uptake kinetics on Al_2O_3 particles, SO_2 oxidation mediated by these particles in a more practical condition where atmospheric CO_2 is involved should be characterized.

Compared to those atmospheric trace gases H_2O_2 and O_3 in the concentration level of several to dozens of ppb, CO_2 of nearly 400 ppm, approximate to 4–5 orders of magnitude higher than

* Corresponding author at: Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China.
E-mail address: zhanglw@fudan.edu.cn (L. Zhang).

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trace gases, should be taken into accounts in the comprehensive study of SO_2 uptake kinetics on aluminum oxide surfaces [22–24]. For a long time, CO_2 is considered to be an inert gas under atmospheric conditions and demonstrated to show negligible significance in atmospheric chemistry [25]. To our best knowledge, studies concerning the impact of greenhouse CO_2 on SO_2 oxidation on mineral dust surfaces have never been reported.

Motivated by the above studies, we set out to investigate the impact of CO_2 on SO_2 oxidation on mineral dust proxy aluminum oxide. Several control experiments were conducted, taking both relative humidity (RH) and the molar ratio of CO_2 to SO_2 into account. More importantly, our field observations with regard to the relationship between sulfate and (bi)carbonate ions match well with the results demonstrated in the present laboratory study, which verify the significance of CO_2 in tropospheric chemistry.

In this work, we utilized sensitive diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to explore the effect of CO_2 on sulfate formation on Al_2O_3 particles. In addition, authentic aerosol was collected by Anderson 8-stage sampler to verify our findings. SO_2 uptake coefficients were measured and corrected to improve present atmospheric chemical models and global climate predictions. A more detailed description of these methods could be found in Figs. S1–S4 and Text S1 (Supporting information).

DRIFTS spectra results for SO_2 oxidation on alpha-Al_2O_3 particles in the absence and presence of CO_2 as a function of RH (5%–95%) are shown in Figs. S5a–d (Supporting information). Two spectra features at 1165 and 979 cm^{-1}, corresponding to the sulfate and sulfite species bonding to the Al_2O_3 surface, could be readily observed after the introduction of $SO_2/N_2 + O_2$, which are in good accordance with previous studies [13,20,26,27]. When $SO_2/N_2 + O_2$ was introduced in the system together with CO_2 (panel b), slight changes of sulfate and sulfite features (1300−800 cm^{-1}) could be seen within a wide RH range (5%–95%).

Water molecules adsorbed on the particle surfaces are thought to strongly determine the rate for SO_2 adsorption and subsequent oxidation. Considering the absorbance overlapping of water and (bi)carbonate species in the range of 1700−1600 cm^{-1}, a broad band with maxima at 3587 cm^{-1}, attributed to surface absorbed water at higher frequency region, was monitored as a function of RH in two cases (Figs. S5c and d) [28]. Our results clearly show a positive dependence of water adsorption on alpha-Al_2O_3 surfaces across the investigated RH range, regardless of the presence of CO_2. The negative bands between 3800 and 3700 cm^{-1} with features at 3755 cm^{-1}, assigned to the basic hydroxyl group [29], consumed drastically in intensity as RH increase. Prior works have also demonstrated that the basic hydroxyl group serves as highly active sites to facilitate SO_2 uptake on aluminum oxide surfaces [18,29].

Fig. 1 shows the integrated absorbance of sulfite and sulfate species as a function of RH in both CO_2-free (left columns) and CO_2-presence cases (right columns). Compared to the integrated areas for bands corresponding to sulfur-containing products formed upon exposure to $SO_2/N_2 + O_2$ (SO_2 with carrier gas synthetic air) on the Al_2O_3 particles, those areas decrease when CO_2 participates in the reactions under all concerned RH conditions. This result suggests that CO_2 exhibits a negative effect on the uptake of SO_2 on fresh Al_2O_3 particles, which could be explained by competitive adsorption of reactants on surface sites [30,31]. As we expect, a positive RH dependence of integrated areas for surface water was observed due to the increasing amount of partial water pressure in the gas flow (Fig. S6 in Supporting information). Interestingly, the addition of CO_2 to the system contributes to the increase of adsorbed water amount on particles in the RH range of 25%–75%. However, we found that sulfate yield is still decreased when CO_2 is introduced into the DRIFTS chamber together with $SO_2/N_2 + O_2$ despite the increased amount of adsorbed water upon exposure to the gas flow of the same RH, *e.g.*, SO_2 uptake under RH of 25% in the absence and presence of CO_2. This result further confirms the negative effect of CO_2 on SO_2 oxidation on Al_2O_3 particle surfaces.

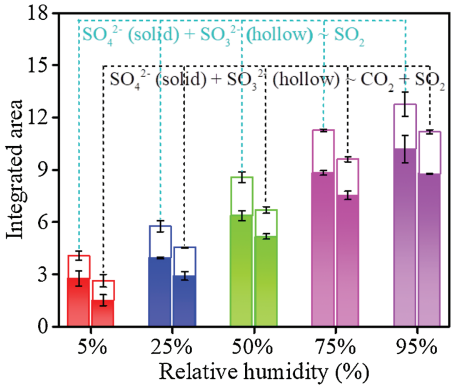

Fig. 1. Comparison of the integrated areas for sulfur-containing products obtained from DRIFTS spectra over α-Al_2O_3 (SO_3^{2-}, 1050–800 cm^{-1}; SO_4^{2-}, 1300–1050 cm^{-1}). Noting that the CO_2-presence case refers to the heterogeneous reaction of (CO_2 + SO_2)/(N_2 + O_2) (mixing ratio = 12000:2) on Al_2O_3 particles.

The concentration of SO_2 in the troposphere varies with geographical location, season, and time of the day, ranging from several to dozens of $\mu g/m^3$ in the atmosphere [22,24]. Taking both atmospheric CO_2 concentration and instrument sensitivity on the formed sulfur-related species into account, we thus investigated SO_2 uptake on alpha-Al_2O_3 surfaces in mixing ratios of CO_2 to SO_2 ranged from 0 to 12000:1. Fig. S7a (Supporting information) represents the DRIFTS spectra of sulfur-containing products on the Al_2O_3 particles after exposure to (CO_2) + SO_2/N_2 + O_2 (SO_2 with carrier gas synthetic air in the absence and presence of CO_2) at low RH (25%). Except for the increase in intensity for sulfite and sulfate bands during the 60 min reaction, only small changes in the spectra features (1300−800 cm^{-1}) are observed as the ratio of CO_2 to SO_2 increases from 0 to 12000:1. The effect of ratio on absorbed water and hydroxyl groups was also explored, as shown in Fig. S7b (Supporting information). Additionally, the difference also lies in the consumption of the basic hydroxyl group (3755 cm^{-1}) among four different experiments. Integrated absorbances of the concerned species were presented in Figs. S7c and d (Supporting information). The variation trend of sulfur-related products follows a typical profile of an initial evident decrease and subsequent slow recovery. This means that increasing the mixing ratio can compensate for the partial loss of uptake activity. Water uptake has a similar trend as the sulfur-species formation. However, the variation trend of the integrated absorbance of the basic hydroxyl group presents in an 'N' shape with increasing the ratio.

Previously, it has been suggested by Baltrusaitis and Grassian in their previous work using the quantum chemical approach that co-adsorption of H_2O and CO_2 on the $Al(OH)_3$ cluster would eventually give rise to the formation of $Al(OH)_3(CO)(OH)_2$ structure [32]. Two extra hydroxyl groups can generate through the structure rearrangement and thus provide new sites for SO_2 oxidation. $Al(OH)_3(CO)(OH)_2$ structures were formed, evidenced by the band showing at 3620 cm^{-1}, for which intensity increases as the mixing ratio enhances. In addition to the increased active sites, dust hygroscopicity seems to be promoted after exposure to gas at a higher ratio (12000:2). As demonstrated in Fig. 1 and Fig. S6, SO_2 uptake on the Al_2O_3 is positively correlated with the amount of water adsorbed on its surfaces. In most cases, absorbed water and formed hydroxyl group are known to favor the conversion of SO_2

into stable sulfur–related species *via* the following reactions (R1–R4):

$$SO_2(g) + H_2O(ad) \rightarrow S(IV)(ad) \quad (R1)$$

$$CO_2(g) + H_2O(ad) \leftrightarrow H_2CO_3 \leftrightarrow H^+ + \nu1(OH)-CO_2^- \quad (R2)$$

$$SO_2(g) + \nu1(OH) \rightarrow S(IV)(ad) \quad (R3)$$

$$S(IV)(ad) + O_2 \rightarrow S(VI)(ad) \quad (R4)$$

Overall, CO_2 shows a negative effect on SO_2 uptake at lower RH (25%) due to the following reasons: (i) Competitive adsorption between CO_2 and SO_2 on Al_2O_3 surfaces, and (ii) the block of the active surface group. Generally, sites for adsorbing reactants on the dust particles under the same environmental conditions stay constant, and one may imagine that an overwhelming dosage of CO_2 can cause a reduction in sites for SO_2 adsorption. In the presence of CO_2, consumption for the basic hydroxyl group is reduced probably due to the blocking effect of formed bi (carbonate) clusters on this site.

To understand how CO_2 affects the heterogeneous reactivity of SO_2 on Al_2O_3 surfaces at higher RH, we as well investigated the heterogeneous reaction of SO_2 on aluminum oxide upon exposure of gas flow with different mixing ratios at higher RH (95%), as shown in Fig. S8a and b (Supporting information). Except for band centered at 3620 cm^{-1}, little difference in spectra features associated with sulfur-related species, basic hydroxyl groups, and surface water could be observed. However, the trends for sulfite and sulfate formation as a function of the CO_2/SO_2 ratio at higher RH (95%) are different from those observed at lower RH (25%). When CO_2 was introduced together with the SO_2/N_2 + O_2 into the DRIFTS cell at the ratio of 12000:8, a negligible decrease of sulfite and sulfate yield could be seen on Al_2O_3 particle surfaces. A further increase in the mixing ratio from 12000:8 to 12000:1 makes CO_2 significant in the reduction of SO_2 uptake. At the same time, the consumption of the basic hydroxyl group is unexpectedly enhanced when Al_2O_3 is exposed to gas flow at the ratio of 12000:1 and reduced as the mixing ratio further increases.

Similar to the scenario observed at lower RH (25%), there is competitive adsorption between CO_2 and SO_2 on the Al_2O_3 particle surfaces at a higher one (95%). Blocking effect of formed (bi)carbonate species is dominant, forcefully suppressing surface reactivity toward SO_2. Nevertheless, there is an increased consumption in the integrated absorbance of the spectral bands assigned to the basic hydroxyl group with the ratio increasing from 0 to 12000:8.

In Fig. S9a (Supporting information), a 60 min heterogeneous process was separately analyzed in two stages with three timings, denoted as t_1, t_2, and t_3, to give an insight into the effect of CO_2 and formed (bi)carbonate species on sulfate formation. At the first stage ($t_1 - t_2$), we found that Al_2O_3 upon exposure to the gas flow at the mixing ratio of 12000:8 under lower RH (25%) shows much less activity toward to sulfate yield compared to those particles exposed to CO_2-free gas flow. Meanwhile, due to the increased hygroscopicity of dust particles after the introduction of an excessive amount of CO_2, the slight difference could be observed for sulfate production at the ratio of 0:1 and that at 12000:1 in this stage. At the subsequent stage ($t_2 - t_3$), the sulfate formation rate of Al_2O_3 particles upon exposure of gas with a mixing ratio of 12000:1 is sharply decreased as compared to the rate observed in the first stage due to the blocking effect resulted from formed (bi)carbonate species.

In Figs. S9b–g (Supporting information), several band features ranging from 3800 cm^{-1} to 3200 cm^{-1} could be mainly assigned to hydroxyl groups, surface water, and natural boehmite AlO(OH), with the detailed assignment of spectra features presented in Table S1 (Supporting information) [20,33–35]. It is shown that enhancing the ratio from 0 to 12000:8 contributes to the negligible increase of surface water and active hydroxyl groups, whereas there is an evident enhancement of those active species formed on Al_2O_3 particles upon exposure to gas flow with the ratio of 12000:1. Meanwhile, DRITFS features centered at 1556, 1450, and 1375 cm^{-1} are readily identified as carbonate and bicarbonate species according to the previous literature [32], with detailed assignment outlined in Table S2 (Supporting information). Those bands decrease in intensity as the reaction proceeds ($t_1 - t_3$) due to the substitution scheme (R5) [36]:

$$MCO_3 + SO_2(g) + H_2O(ad) \rightarrow MSO_3(ad) + CO_2(g) \quad (R5)$$

where M refers to the divalent cations. SO_2 would attack the adsorbed bi(carbonate) specie on metal oxide surfaces to form stable SO_3^{2-}, leading to the release of CO_2 into the atmosphere.

It is apparent that rather fewer amount of bi(carbonate) ions remains on the particles upon the lower ratio exposure (12000:8) as compared to that upon the higher ratio exposure (12000:1) after 60 min reaction. The mixing ratio of the gas flow can strongly affect the number of surface species on Al_2O_3 and thus lead to various heterogeneous activities toward SO_2 uptake. Particles exposed to the higher mixing ratio of gas flow (12000:1) make (bi)carbonate ion species stable, keeping a large amount of $Al(OH)_3(CO)(OH)_2$ structures on the particle surfaces in the first stage. Therefore, they increase the hygroscopicity of dust particles and provide extra −OH sites for stabilizing SO_2. On the other hand, a blocking effect would also suppress the heterogeneous oxidation of SO_2 due to the presence of formed bi(carbonate) species. The positive force compensates for the loss of uptake activity due to the negative force. Over time ($t_2 - t_3$), a further replacement of bi(carbonate) products by formed sulfur-containing species leads to the decrease of hygroscopicity and extra sites. In stark contrast, bi(carbonate) species are no longer stable and considerable when Al_2O_3 particles exposed to the gas flow of a lower ratio (12000:8). In this case, negative force becomes dominant, and the sulfate formation rate is thus reduced.

Similar to the above analyses, the whole reaction at higher RH (95%) are classified into two stages with three fragments as well (Fig. S10 in Supporting information). Different from the observations at lower RH (25%), there is no evident enhancement of surface water and hydroxyl group when Al_2O_3 particles are exposed to CO_2 + SO_2/N_2 + O_2 regardless of mixing ratio. For bi(carbonate) species formed on the particles at higher RH, we found that they tend to be sulfur-resistant and would not be easily replaced by sulfur-containing products in the entire course of heterogeneous reactions. Since formed bi(carbonate) species become more stable under the conditions where Al_2O_3 particles are exposed at higher RH (95%) and ratio (12000:1), surfaces are severely blocked by the bi(carbonate) coating and consequently show lower activity to SO_2 uptake.

Provided by the above observations, we propose that the amount of (bi)carbonate species residual absorbing on Al_2O_3 surfaces is a key factor in determining their heterogeneous reactivity to SO_2 uptake. As we pointed out, (bi)carbonate species show both positive and negative effects on the physicochemical properties of aluminum surfaces. When an excess amount of (bi)carbonate species formed on their surfaces, CO_2 would show a negative effect on SO_2 uptake on alpha aluminum oxide and *vice versa*.

We further explore the correlations between (bi)carbonate and sulfate species through both laboratory studies and field

observations. In Fig. 2a, the result demonstrates that there is a positive relationship between bi(carbonate) and sulfate species observed at the initial stage except for the case (12000:8, RH = 25%). This is because (bi)carbonate species produced on the aluminum oxide would be stable if a considerable amount of free sites remain on the particle surfaces at the early stage of SO_2 uptake. Besides, higher RH and mixing ratio make bi(carbonate) showing strong tolerance to sulfur and thus lead to the simultaneous increase in both bi(carbonate) and sulfate in the early stage of the reaction. However, those sites, including the hydroxyl groups and surface water, are almost consumed by CO_2 and SO_2 as reaction proceeds. As a result, active centers for the heterogeneous reaction of SO_2 on Al_2O_3 particles may shift from the basic hydroxyl groups to OH moieties in $Al(OH)_3(CO)(OH)_2$ clusters, triggering the consumption of bi(carbonate) and giving rise to a negative correlation between bi(carbonate) and sulfate (Fig. 2b).

Among these four plots, alpha-Al_2O_3 after exposure to gas flow of higher RH (95%) with mixing ratio at 12000:8 shows the most negative slope value (−1.12) while that exposed to the flow of lower RH (25%) at the ratio of 12000:8 has the least negative slope value (−0.192). Based on this result, we may deduce that sulfate and (bi)carbonate ions on mineral dust aerosol that goes through a long-distance transport in the atmosphere tend to show a negative correlation, evidently observed in the air parcel with higher SO_2 concentration.

In our sampling, we mainly focus on the particulate matter with their size over 3.3 μm because a rather large mass fraction of mineral dust would embed the particulate matter with larger particle diameter [37,38]. In Fig. 2c, we observed a negative relationship between (bi)carbonate and sulfate ions. In most cases, collected aerosol particles are those removed by dry and wet depositions from the troposphere, with a lifetime of 4 days to 1 week [39]. Therefore, they may experience long-term transport before entering into the ground layer. As we could expect, sulfate product accumulating on particulate matter surfaces would largely consume (bi)carbonate, matching well with the second scenario presented in our lab simulations (Fig. 2b). Overall, we demonstrate (bi)carbonate aerosol would likely to suppress sulfate formation on the particulate matter in practical atmospheric conditions where we have explored.

Lower limit (γ_{BET}) for SO_2 uptake represents effective reactive surfaces of particulate matter under authentic atmospheric conditions. Taking the gas diffusion in particle pores into account, we corrected the BET uptake of SO_2 on Al_2O_3, with a detailed description in the experimental section. In line with the above finding (Table S3 in Supporting information), we clearly observed a positive RH dependence of SO_2 uptake on Al_2O_3 particle surfaces regardless of the presence of CO_2 over a wide RH range (5%–95%). The competing effects of particle–liquid water on SO_2 uptake over Al_2O_3 particles are negligible. Once CO_2 was introduced into the reaction system, it decreases the SO_2 uptake coefficients under all investigated RHs.

We as well explored the influence of CO_2:SO_2 ratios on SO_2 uptake on Al_2O_3 particle surfaces. In the absence of CO_2, we estimated that the SO_2 uptake on Al_2O_3 particles is nearly 3.59×10^{-10} at RH of 25% (Table S4 in Supporting information). In stark contrast, its uptake on Al_2O_3 particles is sharply decreased, with its reduction up to 57.9% after CO_2 injection (mixing ratio = 12000:8). At higher RH condition (95%), the introduction of CO_2 results in the decrease of SO_2 uptake, with more evident reduction by increasing the ratio from 12000:8 to 12000:1. As we mentioned earlier, formed bi(carbonate) species can block the active basic hydroxyl group on Al_2O_3 particle surfaces. Overall, CO_2 shows a negative effect on SO_2 uptake on Al_2O_3 particles in the present experimental conditions. Coefficients measured in this work enable an improved simulation of the tropospheric sulfur source and sink in a global climate model.

Sulfate aerosol is known to have a net cooling effect in the global climate through scattering solar radiation, whereas CO_2 is a greenhouse gas that directly results in global warming. Through both laboratory studies and field observations, we, for the first time, demonstrate (bi)carbonate ions derived from atmospheric CO_2 would suppress sulfate formation on the major component of mineral dust Al_2O_3 aerosol, suggesting a negative effect of atmospheric CO_2 on global sulfate budget under some circumstances. This potentially decreases solar-radiation scattering and thus further exacerbates global warming. To be important, this work fills the gap for laboratory studies of heterogeneous chemistry of SO_2 in the presence of CO_2 and opens new perspectives for studying the mechanism of heterogeneous reaction on mineral dust aerosol surfaces. Studies need to be performed to further explore how CO_2 influences the overall atmospheric heterogeneous chemistry. Nevertheless, this work provides clear evidence that CO_2 not only acts as an inert greenhouse gas but a precursor that can affect chemical reactions taking place in the troposphere. Besides, trace gas like NH_3 and VOC_s have been demonstrated to alter the acidity and hygroscopicity of the particulate matter, and they show a great impact on heterogeneous reactivity to SO_2 in the atmosphere. Future works would investigate the interplay between CO_2 and NH_3/VOCs on sulfate formation on mineral dust particles and provide a more comprehensive understanding of the role of CO_2 in atmospheric chemistry.

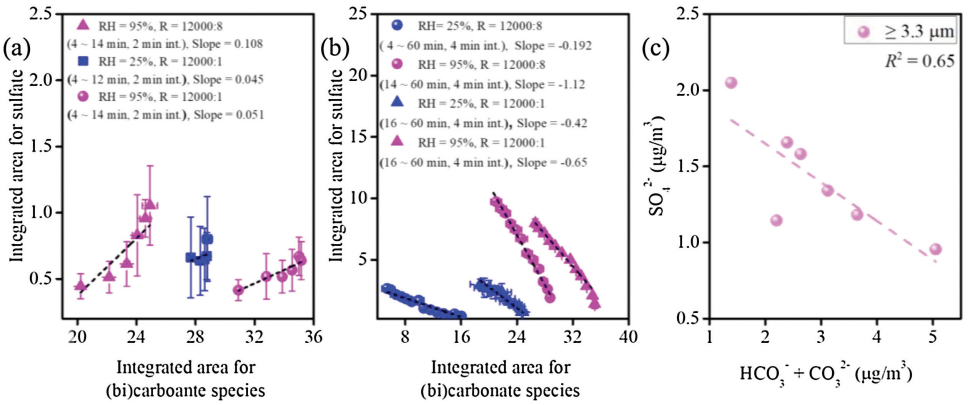

Fig. 2. Linear relationship analyses for measured sulfate ions and estimated carbonic species in the initial stage and stable stage under varied RH conditions (a, b). Correlation analyses for measured sulfate ions and estimated (bi)carbonates in the authentic particulate matter with their size larger than 3.3 μm (c).

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.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.04.037.

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