

# A Novel Pathway of Atmospheric Sulfate Formation Through Carbonate Radical

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**Abstract.** Carbon dioxide is considered an inert gas that rarely participates in atmospheric chemical reactions. Nonetheless, we show here that CO<sub>2</sub> is involved in some important photo-oxidation reactions in the atmosphere through the formation of carbonate radicals (CO<sub>3</sub><sup>•-</sup>). This potentially active intermediate CO<sub>3</sub><sup>•-</sup> is routinely overlooked in atmospheric chemistry concerning its effect on sulfate formation. Present work demonstrates that SO<sub>2</sub> uptake coefficient is enhanced by 17 times on mineral dust particles driven by CO<sub>3</sub><sup>•-</sup>. Importantly, upon irradiation mineral dust particles are speculated to produce gas-phase carbonate radical ions when the atmospherically relevant concentration of CO<sub>2</sub> presents, thereby potentially promoting external sulfate aerosol formation and oxidative potential in the atmosphere. Employing a suite of laboratory investigations of sulfate formation in the presence of carbonate radical on the model and authentic dust particles, ground-based field measurements of sulfate and (bi)carbonate ions within ambient PM, together with density functional theory (DFT) calculations for single electron transfer processes in terms of CO<sub>3</sub><sup>•-</sup>-initiated S(IV) oxidation, a novel role of carbonate radical in atmospheric chemistry is elucidated.

## 1. Introduction

Atmospheric composition changes are subjected to highly reactive light-induced radicals, such as hydroxyl (·OH), hydroperoxyl (HO<sub>2</sub>·), or nitrate radicals (NO<sub>3</sub>·), which are able to alter not only compositions but also physical and chemical properties of particulate matter (Liu et al., 2022a; Mahajan et al., 2021; Stevenson et al., 2020). However, when atmospheric chemical reactions occur over humified particles at ambient conditions, which creates a locally enriched aqueous medium of unique chemical activity, other radicals might likewise gain importance. The carbonate radical (CO<sub>3</sub><sup>•-</sup>) is typically such an active radical. The lifetime of CO<sub>3</sub><sup>•-</sup> ranges from a microsecond to even a few milliseconds and its concentration can be two

orders of magnitude higher than that of hydroxyl radicals over the water surface (Chandrasekaran and Thomas, 1983; Goldstein et al., 2001; Shafirovich et al., 2001; Sulzberger et al., 1997). In addition, the one-electron reduction potential of  $E^0(\text{CO}_3^{\cdot-}/\text{CO}_3^{2-})$  couple is 1.78 V vs. NHE at neutral pH, leaving  $\text{CO}_3^{\cdot-}$  a strong oxidant in aquatic chemistry (Bisby et al., 1998; Cope et al., 1973; Merouani et al., 2010). Previous studies concerning carbonate radical in aqueous media demonstrate that it reacts rapidly with some organic compounds (Merouani et al., 2010), especially for those electron-rich compounds amines (Stenman et al., 2003; Yan et al., 2019). Also, it has been pointed out that the scavenging of hydroxyl radicals by (bi)carbonate species leads to the formation of  $\text{CO}_3^{\cdot-}$  ions (Graedel and Weschler, 1981; Xiong et al., 2016). Besides, a high second order of rate constant, lying at  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , has been reported for the reaction of  $\text{CO}_3^{\cdot-}$  with porphyrins (Ferrer-Sueta et al., 2003), indicating that this radical ion has great oxidation capability that may trigger atmospherically relevant chemical reactions, i.e. secondary inorganic species formation. However, it is only regarded as a marginal intermediate in tropospheric anion chemistry so far (Beig and Brasseur, 2000; Ge et al., 2021; Herrmann et al., 2000; Lehtipalo et al., 2016) and its underlying role as an active oxidant for heterogeneous reaction in the atmosphere is barely explored. Very recently, our group observed the promotional effect of  $\text{CO}_3^{\cdot-}$  on atmospheric nitrate formation (Fang et al., 2021). Motivated by this finding, attempts were made to further explore its role in other important atmospherically-relevant reactions.

It is well documented that sulfate ( $\text{SO}_4^{2-}$ ) is also a key constituent of aerosols in the atmosphere (Huang et al., 2015; Su et al., 2016). It is able to serve as the precursors of efficient cloud condensation nuclei, with optical properties leading to a cooling effect (Wang et al., 2011). As a consequence, the mechanism aspect of secondary sulfate formation was the focus of numerous studies over the past decades (Hung et al., 2018; Stone, 2002; Zhang et al., 2015b). There is a consensus that high-valence sulfur (VI), produced from the oxidation of anthropogenic  $\text{SO}_2$ , is the dominant source of atmospheric secondary sulfate. However, a remarkable missing sulfate budget emerges for the atmospheric modeling (Huang et al., 2019; Itahashi et al., 2018; Liu et al., 2021), which significantly underpredicts  $\text{SO}_4^{2-}$  with respect to observational results when heterogeneous aerosol chemistry is not considered (Feng et al., 2018; Wu et al., 2021; Zheng et al., 2015). This indicates that the heterogeneous sulfate production pathway is a crucial process and exploring the unrecognized heterogeneous mechanism is very likely to narrow the gap between observations in lab studies, field measurements, and numerical modelings. Due to the missing chemical mechanism that initiated fast  $\text{SO}_2$  oxidation, atmospheric models fail to capture the key feature of atmospheric observations of high sulfate production during dust storm episodes in the troposphere (Dong et al., 2016; Huang et al., 2014; Yu et al., 2020), where an evident increase of  $\text{Ca}^{2+}$  (Li et al., 2013; Wang et al., 2005), carbonate-containing particles with high alkalinity (Abou-Ghanem et al., 2020; Li et al., 2014; Tang et al., 2016) as well as photoactive mineral components (Nie et al., 2012; Ta et al., 2003) are prevalent. Air mass is usually in low relative humidity, reported being 25-35% (Al-Salihi and Mohammed, 2015) (Csavina et al., 2014; Najafpour et al., 2020) in these events, during which the photochemical process is able to alter atmospheric constituents (Liu et al., 2022b). Consequently, there are unknown heterogeneous reaction pathways and previously unconsidered promoters that have great potential to accelerate sulfate formation in the dust storm relevant conditions.

Due to the high stability of  $\text{CO}_2$  under ambient conditions (Hossain et al., 2020), there are rare studies concerning the influence of  $\text{CO}_2$  in atmospheric chemical processes (Deng et al., 2020; Liu et al., 2020c; Xia et al., 2021).  $\text{CO}_2$  is demonstrated

to form (bi)carbonate species over humidified dust particles (Baltrusaitis et al., 2011; Nanayakkara et al., 2014) and reduced to CO under solar illumination (Deng et al., 2020). Nonetheless, its impact on atmospheric heterogeneous reactions remains poorly characterized. Our early laboratory study illustrates that CO<sub>2</sub> decreases the sulfate formation on aluminum oxide particles in the dark (Liu et al., 2020c) while upon solar illumination its role in SO<sub>2</sub> oxidation over mineral dust surfaces is still an open question. In addition, carbonate salt is abundant in authentic dust particles (Cao et al., 2005) and is reported to reach over 10% wt. of Asian dust particles (McNaughton et al., 2009). It is generally accepted that CO<sub>3</sub><sup>2-</sup> affects atmospheric chemistry and aerosol characteristics mainly through its intrinsic alkalinity, which buffers aerosol acidity and increases SO<sub>2</sub> adsorption and corresponding sulfate production in the presence of oxidants (Al-Hosney and Grassian, 2005; Bao et al., 2010; Kerminen et al., 2001; Li et al., 2007; Yu et al., 2018). In fact, either CO<sub>2</sub> or carbonate salt is able to produce the active CO<sub>3</sub><sup>-</sup> under the ambient circumstance (Ervens et al., 2003; Graedel and Weschler, 1981) and prone to increase the oxidative capacity in the atmosphere. Our early study shows that carbonate radicals serve as an active oxidant to accelerate NO<sub>2</sub> oxidation over mineral dust particles (Fang et al., 2021), allowing us to consider the possibility that fast heterogeneous SO<sub>2</sub> oxidation can be triggered by this active intermediate as well. Nevertheless, to the best of our knowledge, no work has ever considered how and to what extent the carbonate radical influences SO<sub>2</sub> heterogeneous oxidation in the atmosphere.

In the current study, through laboratory studies, we present that carbon dioxide and calcium carbonate, working as the precursor of carbonate radicals, have the ability to accelerate sulfate formation over authentic particles in the atmosphere. Together with quantum chemistry calculations, a detailed molecular mechanism regarding a single electron transfer (SET) process between carbonate radical and sulfite ions is elucidated. Furthermore, ground-based observations validate some findings from the laboratory-based simulations.

## 2. Experimental methods

### 2.1 Laboratory Studies

**Methodology for uptake coefficient estimation.** The reaction uptake coefficient was estimated by the following Eqs. 1-3, as suggested by the previous work (Kong et al., 2014):

$$\gamma = \frac{d[\text{SO}_4^{2-}]/dt}{Z} \quad [1]$$

$$Z = \frac{1}{4} \times A_s \times [\text{SO}_2] \times v \quad [2]$$

$$v = \sqrt{8RT/\pi M_{\text{SO}_2}} \quad [3]$$

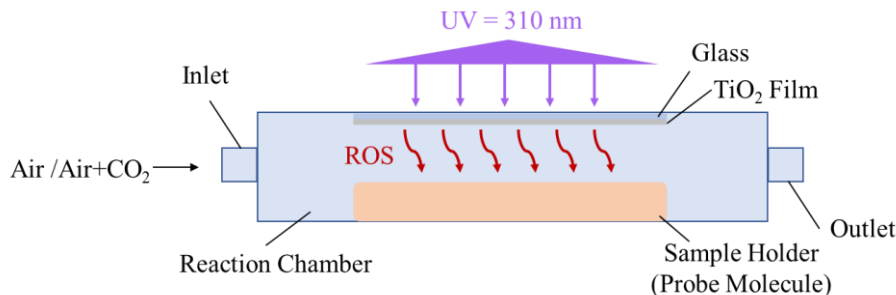
where  $v$  is the mean molecular velocity of SO<sub>2</sub>,  $A_s$  the effective sample surface,  $R$  the gas constant,  $T$  the temperature,  $M_{\text{SO}_2}$  the molecular weight of SO<sub>2</sub>, and a total number of surface collisions per unit time ( $Z$ ). To be precise, the formation rates

( $d[\text{SO}_4^{2-}]/dt$ ) in the equation were determined by ion chromatography (IC) measurements, followed by a conversion factor calculation through linear regression analysis for the integrated absorbance of sulfate bands and corresponding sulfate concentrations. By employing this method, a conversion factor of  $f = 6.34 \times 10^{15}$  ions integrated absorption units<sup>-1</sup> was obtained and corresponding SO<sub>2</sub> uptake coefficients in the “TiO<sub>2</sub>+(CO<sub>2</sub>)+SO<sub>2</sub>” system were thus estimated using seven timepoints during the heterogeneous reaction. For SO<sub>2</sub> uptake in the “TiO<sub>2</sub>+(CaCO<sub>3</sub>)+SO<sub>2</sub>” system, we estimated SO<sub>2</sub> uptake coefficients using three conversion curves established for various types of dust particles. For this purpose, we mixed the known proportion of K<sub>2</sub>SO<sub>4</sub> and dust particles of concern, and thus obtained relationship curves between the integrated absorbance of DRIFTS (i.e. diffuse reflectance Fourier transformed infrared spectroscopy) sulfate bands and corresponding theoretical sulfate content through linear fitting (Fig. S4). Ten timepoints during the heterogeneous reaction were applied for these kinetics calculations.

**Preparation for clay and dust membranes and investigation of sulfate formation on those authentic particles during the daytime and nighttime.** Each particle suspension ATD (2.5 mg~0.5 mL), IMt-2 (10 mg~ 0.5 mL) and K-GA (10 mg~ 0.5 mL) were first dispersed into water through ultrasonic bath for 5 min. After that, sample suspensions were transformed onto the cleansed round quartz films (d = 2 cm) using a pipette and subsequently sent to the infrared drying oven for 10 min to prepare dust membranes. Once taken out from the oven, samples were quickly sealed into a desiccator and cooled down to room temperature before starting experiments. A membrane sample was then mounted at the center of the reaction chamber (the top half made of quartz and the bottom half made of teflon). Before each set of experiments, a gas flow (dry air) of 300 mL min<sup>-1</sup> was introduced to the chamber for 5 min where a prepared membrane sample was installed. Afterward, samples were exposed to  $4.91 \times 10^{14}$  molecule cm<sup>-3</sup> SO<sub>2</sub> ( $+2.46 \times 10^{18}$  CO<sub>2</sub> when necessary) /N<sub>2</sub>+O<sub>2</sub> mixture in the absence and presence of irradiation (Light intensity (I) = 30 mW cm<sup>-2</sup>) for 15 min before the sample were transferred to a beaker (scale = 10 mL) with 2 mL of 2% vol. isopropanol leaching solution, extracting ions in the ultrasonic tank for 5 min using 0.22 μm PTFE membrane filter, followed by sending the sample into IC. Noting that dust and clay particles possess a considerable amount of sulfate ion background, we thus measured the background ions for each batch of synthesized dust particle membranes following the procedures described above. All data demonstrated in Fig. 6 were obtained after subtraction of background ions.

**Determination of gas-phase reactive oxygen species (ROS) production in the flow-cell reactor.** To measure the concentration of ROS released from TiO<sub>2</sub> particles in various reaction systems, an experimental approach using the probe molecule aniline was applied in this study. This is because compound aniline is reported to react rapidly with ·OH radicals and CO<sub>3</sub><sup>-</sup> radicals, which are also evidenced to be two major active ROS species that are responsible for the SO<sub>2</sub> oxidation over mineral dust particles. The method applied in this study was almost implemented as the same to that of the previous study (Behrman, 2018), with slight modification. Briefly, the degradation rate of aniline in various reaction systems were monitored through High-Performance Liquid Chromatography (HPLC, LC-10AD, SHIMADZU, Japan). A Zorbax SB C18 (4.6 mm × 150 mm, 5 μm) reverse phase column at 25 °C was used with a UV detector at 236 nm to measure the aniline concentration. The mobile phase consisted of acetonitrile/water = 55:45 (V/V) with a flow rate of 1 mL/min.

TiO<sub>2</sub> suspension (5 mg TiO<sub>2</sub> per 100 uL deionized water) was deposited onto the glass substrate (0.13 - 0.17 mm in thickness) using a pipette and then dried in an oven for 10 min to obtain a TiO<sub>2</sub>-coated film. Dilute aniline solution, using 67 mM phosphate buffer solution (pH = 7.0), was prepared and placed below the TiO<sub>2</sub>-coated film, with an intervening gap between TiO<sub>2</sub> film and solution surface around 2 mm (Fig. 1). This short distance essentially guarantees gaseous ROS (e.g. ·OH radicals or CO<sub>3</sub><sup>·-</sup> radicals) to diffuse and react with aniline molecule (Rodriguez et al., 2013).



**Figure 1.** The schematic of the flow-cell reaction chamber for gaseous ROS determination.

In the reaction system containing TiO<sub>2</sub> film upon irradiation (the UV wavelength = 310 nm) in the presence of humidified air (RH = 30%), when operated in a continuous mode, the overall degradation rate of probe molecules in the presence of TiO<sub>2</sub> film can be described by Eq. 4 (Wang et al., 2004):

$$k_{\text{obs}} = \frac{d[\text{An}]}{dt} = r_A + r_U + r_{\text{ROS}} = r_A + r_U + k_{\text{ROS, An}}[\text{ROS}][\text{An}] \quad [4]$$

Where  $k_{\text{obs}}$  is the observed degradation rate of aniline,  $[\text{An}]$  is the concentration of aniline, denoted as  $[\text{An}]$  hereafter, and  $r_A$ ,  $r_U$ ,  $r_{\text{ROS}}$  stand for aniline removal rates resulting from air stripping, UV photolysis, ROS oxidation.  $k_{\text{ROS, An}}$  are the overall second-order reaction rate constants for An with ROS.

Reference experiments without the introduction of ROS were also conducted to measure  $r_A + r_U$  in each reaction system. Upon irradiation, the dust proxy TiO<sub>2</sub> produces hole-electron pairs, further forming ·OH radicals and superoxide radicals (O<sub>2</sub><sup>·-</sup>) in the presence of absorbed water and oxygen molecules. Thus, an experiment using N<sub>2</sub> was adopted to investigate the role of O<sub>2</sub><sup>·-</sup> in consuming aniline. As illustrated in Fig. 7c, a slight change in the degradation rate of aniline after stripping oxygen from the air, indicating that O<sub>2</sub><sup>·-</sup> shows quite a smaller contribution than ·OH. This result agrees well with the finding reported by Durán et al. (Duran et al., 2019), where the removal of O<sub>2</sub><sup>·-</sup> by adding benzoquinone (BQ) into TiO<sub>2</sub> suspension results in the negligible change of An degradation rate.

Taken above, ·OH radicals are assumed to be the only active ROS that accounts for the An degradation. Hence, the maximum steady concentration of ·OH radicals can be given by the following equation:

$$-\frac{d[\text{An}]}{dt} = k_{\text{exp}}[\text{An}] = k_{\cdot\text{OH, An}}[\cdot\text{OH}]_{\text{ss-max}}[\text{An}] \quad [5]$$

Integration of Eq. 5 yields

$$-\ln \frac{[\text{An}]_t}{[\text{An}]_0} = k_{\text{exp}} t \quad [6]$$

$$k_{\text{exp}} = k_{\cdot\text{OH}, \text{An}} [\cdot\text{OH}]_{\text{ss-max}} \quad [7]$$

Together with the reported second-order rate constant ( $k_{\cdot\text{OH}, \text{An}} = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Samuni et al., 2002), the steady-state OH radical concentration  $[\cdot\text{OH}]_{\text{ss-max}}$  in buffered An solution can be calculated from Eq. 7. The observed degradation rate constant of  $k_{\text{exp}}$  can be obtained from the slope of the semi-log plot of An degradation as illustrated in Eq. 6. The maximum steady-state aqueous concentration of  $\cdot\text{OH}$  supplied by the partitioning process from gas-phase  $\cdot\text{OH}$  was thus estimated to be  $2.15 \times 10^{-15} \text{ M}$  for the “TiO<sub>2</sub>+Air” system.

When CO<sub>2</sub> (400 ppm, atmospheric relevant concentration) is introduced into a flow-cell chamber, an increased degradation rate of An is seen, which is very likely to be the generation of active carbonate radical ions (Fig. 9). Similar to the method we adopted for the estimation of  $[\cdot\text{OH}]_{\text{ss-max}}$ , reference experiments were conducted to determine the rates for air stripping and UV photolysis processes in the “TiO<sub>2</sub>+Air+CO<sub>2</sub>” system. In the next step, we quenched the hydroxyl radicals by adding tertiary butanol (TBA). This is because it reacts rapidly with hydroxyl radicals (Li et al., 2020)  $k_{\cdot\text{OH}, \text{TBA}} = (6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$  while shows a rather low reaction rate with carbonate radicals (Liu et al., 2015) ( $k_{\text{CO}_3^{\cdot-}, \text{TBA}} < 1.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ). Subsequently, we determined  $[\text{CO}_3^{\cdot-}]_{\text{ss}}$  using the previous protocol (Huang and Mabury, 2000) with known  $k_{\text{CO}_3^{\cdot-}, \text{AN}}$  ( $5.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) (Wojnarovits et al., 2020). In the extreme case, assuming that all hydroxyl radical ions were fully trapped by absorbed and dissolved HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, the maximum steady-state CO<sub>3</sub><sup>-</sup> concentration was determined to be  $1.39 \times 10^{-13} \text{ M}$  for “TiO<sub>2</sub>+Air+CO<sub>2</sub>” system, matching well with the early study where the concentration of CO<sub>3</sub><sup>-</sup> is reported to be two orders of magnitudes than  $\cdot\text{OH}$  over the water surface (Sulzberger et al., 1997).

## 2.2 Quantum Chemical Calculation

We employed density functional theory (DFT) calculations in the term of the single electron transfer (SET) process using Gaussian 09 package to investigate this novel route, detailed in Supplementary text 11 and 20.

## 2.3 Field Observations

**Sampling.** Our sampling for atmospheric particle matter was launched on the roof of the environmental science and engineering department, Fudan University (Jiangwan Campus, 31.340661°N, 121.506747°E, 16 km away from the city downtown. More geographical information for sampling has been described in detail elsewhere (Liu et al., 2020c). Observations for water-soluble ionic components of particulate matter were performed using an 8-stage non-viable-cascade-impactor type sampler (TISCH TE Inc., USA), size gradient of which are in the sequence of < 0.43, 0.43- 0.65, 0.65-1.1, 1.1- 2.1, 2.1- 3.3, 3.3- 4.7, 4.7- 5.8 5.8- 9.0 and 9.0~ μm. These sizes represent the effective cutoff diameter at each level for unit density spherical particles. In our sampling, the estimations for (bi)carbonate ions in atmospheric particulate matter is conducted for the initial four stages (3.3~ μm). Atmospheric airflow from the head was maintained at the constant rate of 28.3

L min<sup>-1</sup> to meet the operation criterion required for the Anderson-type sampler. Quartz filters (81 mm in diameter, Whatman, GE Healthcare, UK) were applied for samplings, and membranes were rinsed with ultrapure water (electrical resistivity= 18.2 MΩ) no less than three times; that is kept in the ultrasonic cleaning tank for 40 min and then rinsed with ultrapure water for twice, before being sent into the infrared drying oven, followed by packing them in aluminum foils prior to field sampling. We carried out this procedure to eliminate the water-soluble background ions as much as possible and to ensure the balance calculation for (bi)carbonate ions. Additionally, following the same aforementioned pretreatments, we measured the background concentrations of ions in blank membranes. We separated our daily samplings into two periods, 11 hours for each, to give an insight into the influence of potential photo-induced reactions on secondary sulfate formation in the atmosphere.

**(Bi)carbonate estimation.** The concentration of bi(carbonate) ions were estimated following the protocol reported in the early works (Fang et al., 2021; Liu et al., 2020c; Palmer and Cherry, 1984; Zhang et al., 2011). Two assumptions were made to simplify the estimation for bi(carbonate) concentrations within the system: a. dominating cations in each system are H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> whereas those transition and heavy metal ions were out of consideration considering their limited contents of dissolve cations in the atmospheric particulate matter; b. three typical organic acid ions (CH<sub>3</sub>COO<sup>-</sup>, COOH<sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, major soluble organic acid ions in the atmosphere) were taken into account for ionization balance and the rest of the charge gap in each system was assumed to originate from (bi)carbonate ions. Then we established balance equations (Eqs. 8-11) for each sample on the basis of charge conservation and ionization equilibrium constant of carbonic acid ( $K_1= 4.47\times 10^{-7}$  and  $K_2= 4.69\times 10^{-11}$  at 273 K).

$$[\text{H}^+] + [\text{Li}^+] + [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + [\text{F}^-] + [\text{CH}_3\text{COO}^-] + [\text{COOH}^-] + [\text{NO}_2^-] + [\text{Cl}^-] + [\text{NO}_3^-] + 3[\text{PO}_4^{3-}] + 2[\text{SO}_4^{2-}] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad [8]$$

$$[\text{HCO}_3^-] = \frac{K_1[\text{H}_2\text{CO}_3]}{[\text{H}^+]} \quad [9]$$

$$[\text{CO}_3^{2-}] = \frac{K_1 K_2 [\text{H}_2\text{CO}_3]}{[\text{H}^+]^2} \quad [10]$$

It is worth mentioning that [X] is referred to charge concentration for ions (Coulomb·M). Additionally, the temperature factor was also considered to correct the equilibrium constant for (bi)carbonate ions using the following equation:

$$\ln \frac{K_{x'}}{K_x} = -\frac{\Delta H}{R} \left( \frac{1}{T_{x'}} - \frac{1}{T_x} \right) \quad [11]$$

where ΔH is the temperature variation (K), R the ideal gas constant (8.31451 J·mol<sup>-1</sup>·K<sup>-1</sup>), and T the temperature (K) during

pH measurements. We then solved those equations to obtain a series of  $[\text{HCO}_3^-]$ , which were eventually corrected by subtracting blank values.

## 2.4 Other measurements and analysis

210 In addition to the above descriptions of measurements and calculation methodologies, more information including heterogenous reaction setup, kinetics reaction order determination, pretreatment of mineral dust, DRIFTS, IC, Raman measurements and analysis, etc. are available in the supplementary text 1-13.

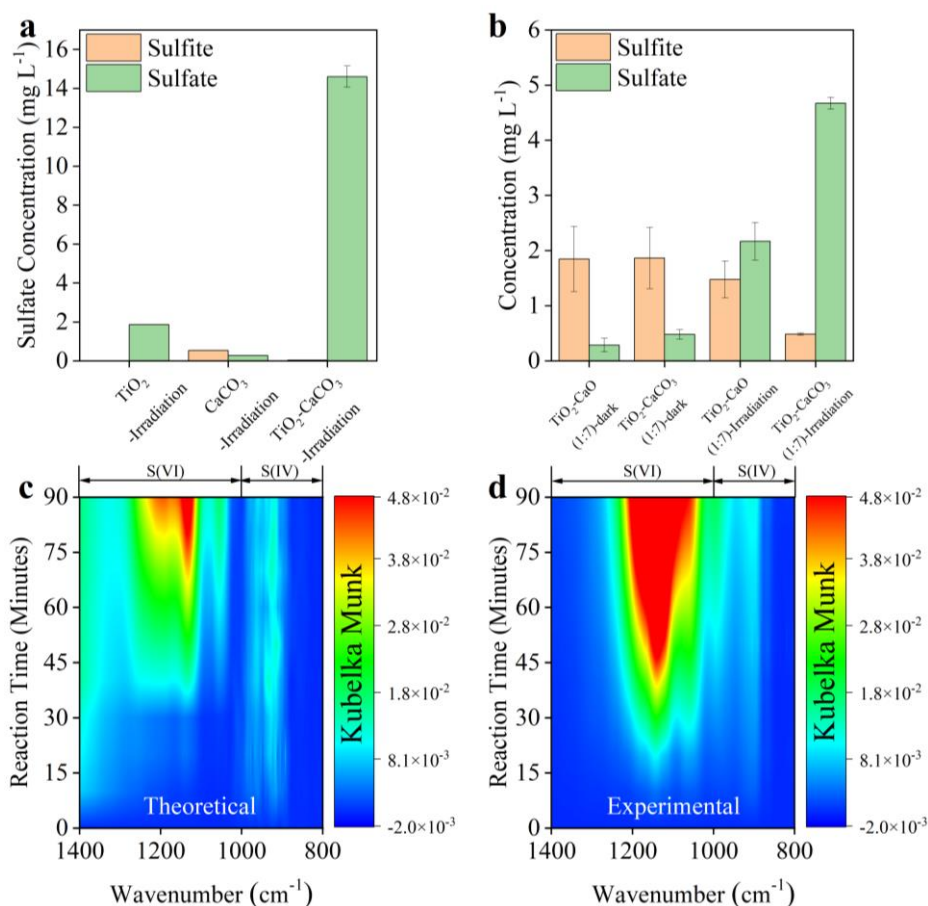
## 3. Results and discussion

### 3.2.1 Accelerated sulfate production in the presence of carbonate.

215 The physico-chemical properties of employed mineral dust proxies including BET surface area, crystal phase, and structure were first characterized (Fig. S1), consistent with early studies (Balachandran and Eror, 1982; Shang et al., 2010; Su et al., 2008), with additional discussion in supplementary text 14. The spectral irradiance of the solar simulator applied in the present study is well covered by natural sunlight (Fig. S2), as much as possible having experimental results from the lab simulate the real atmosphere. Upon solar irradiation under RH of 30%  $\text{SO}_2/\text{N}_2+\text{O}_2$  flow ( $[\text{SO}_2] = 2.21 \times 10^{14}$  molecules  $\text{cm}^{-3}$ ), the sulfate production on  $\text{TiO}_2+\text{CaCO}_3$  mixture particles (50 wt.%  $\text{TiO}_2$  and 50 wt.%  $\text{CaCO}_3$ ), measured by IC, is significantly enhanced  
220 by 7 times and 23 times compared to that of pristine  $\text{TiO}_2$  and  $\text{CaCO}_3$  (Fig. 2a), respectively. In stark contrast, there is a negligible increase in sulfate production detected in the  $\text{TiO}_2+\text{CaCO}_3$  mixture relative to that of pristine  $\text{CaCO}_3$  and  $\text{TiO}_2$  in dark experiments (Fig. S3). Great discrepancies in sulfate production over  $\text{TiO}_2+\text{CaCO}_3$  particles between dark and light experiments suggest that carbonate salt may play a different role in these two scenarios. However, the alkalinity of carbonate salt favors  $\text{SO}_2$  adsorption (Al-Hosney and Grassian, 2005; Yu et al., 2018) and the photo-oxidation process assisted by  $\text{TiO}_2$   
225 particles is able to strengthen the oxidation efficiency of adsorbed  $\text{SO}_2$  (Chen et al., 2012; Shang et al., 2010), which is a plausible explanation for increased sulfate production over  $\text{TiO}_2+\text{CaCO}_3$  particles. Following this speculation, two types of mixtures  $\text{TiO}_2+\text{CaCO}_3$  and  $\text{TiO}_2+\text{CaO}$  were employed. In the dark experiments (Fig. 2b), both  $\text{TiO}_2+\text{CaO}$  and  $\text{TiO}_2+\text{CaCO}_3$  almost yield an identical concentration of sulfite and sulfate. On the contrary,  $\text{TiO}_2+\text{CaCO}_3$  particles produce nearly two times of sulfate than  $\text{TiO}_2+\text{CaO}$  particles once irradiated, along with a sharp decrease of S(IV) species on the surface of  $\text{TiO}_2+\text{CaCO}_3$   
230 surfaces. Besides,  $\text{CaCO}_3$  tends to show relatively humble physical properties including BET surface area, surface pH, as well as solubility, etc. relative to  $\text{CaO}$  (see detailed discussion in supplementary text 15). The above results allow us to assert that the carbonate-containing system contains an alternative important mechanism for sulfate formation beyond the production of an alkaline environment (additional discussion available in supplementary text 16). Fig. 2c and 2d illustrate that the DRIFTS features of S(IV) and S(VI) species (Nanayakkara et al., 2014; Wu et al., 2011) increase over time on theoretical and  
235 experimental  $\text{TiO}_2+\text{CaCO}_3$  mixtures (wt./wt. = 50/50) upon irradiation. The “theoretical” is calculated based on the DRIFTS



experiments of pristine  $\text{TiO}_2$  and  $\text{CaCO}_3$  particles through a simple linear superposition whereas the “experimental” is directly derived from the DRIFTS experiment of  $\text{TiO}_2+\text{CaCO}_3$  (wt./wt. = 50/50) particles. These results suggest a synergistic effect presented in this mixture for sulfate formation under solar irradiation.

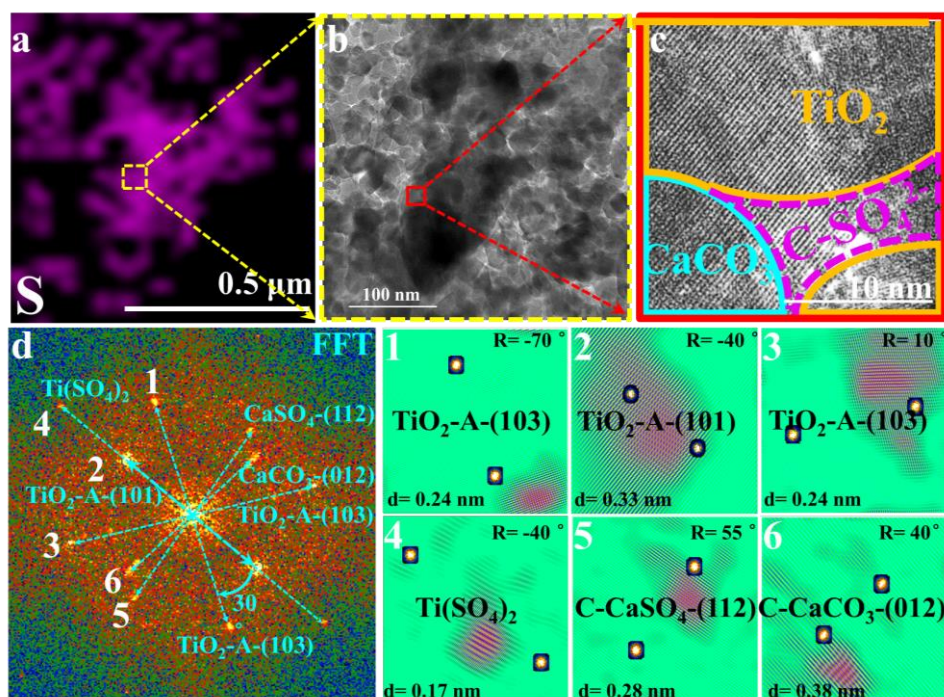


240 **Figure 2.** (a) Sulfate or sulfite concentration quantified by IC on  $\text{TiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{TiO}_2+\text{CaCO}_3$  particles (wt./wt. = 50/50) after exposure to gaseous  $\text{SO}_2$  under irradiation for 60 min. (b) Sulfate and sulfite concentration quantified by IC on mineral dust particles of concern after exposure to  $\text{SO}_2$  under dark or irradiation for 20 min. *In situ* DRIFTS of S(IV) and S(VI) production on theoretical (c) and (d) experimental  $\text{TiO}_2+\text{CaCO}_3$  mixtures (wt./wt. = 50/50) upon irradiation for 90 min. All spectra were processed by the Kubelka-Munk (K-M) algorithm. Noting that the production of sulfur species in theoretical  $\text{TiO}_2+\text{CaCO}_3$  mixtures refers to  $0.5 \times$  K-M bands of sulfur species of  $\text{TiO}_2 + 0.5 \times$  K-M bands of sulfur species of  $\text{CaCO}_3$  while that for experimental  $\text{TiO}_2+\text{CaCO}_3$  mixtures refers to  $1 \times$  K-M bands of sulfur species of  $\text{TiO}_2+\text{CaCO}_3$  mixtures (wt./wt. = 50/50). Reaction conditions: RH = 30%, Light intensity (I) =  $30 \text{ mW cm}^{-2}$ , Total flow rate =  $52.5 \text{ mL min}^{-1}$  and  $\text{SO}_2 = 2.21 \times 10^{14} \text{ molecules cm}^{-3}$ .

Combining DRIFTS experiments with the obtained calibration curve (Fig. S4), we estimated that the uptake coefficient of  $\text{TiO}_2+\text{CaCO}_3$  mixture (50wt. %  $\text{CaCO}_3$ ) is increased by about a factor of 17 as compared to that of pure  $\text{CaCO}_3$  or  $\text{TiO}_2$  (Table S1). More importantly, upon irradiation,  $\text{SO}_2$  uptake coefficients for these dust mixtures lie at the order of magnitudes of  $10^{-4}$ , which is proven to gain importance in overall sulfate production by numerical modeling investigations (Wang et al., 2014; Zhang and Carmichael, 1999). Hence, the photochemical pathway associated with carbonate species is likely a potential

driving force to increase sulfate production in the atmosphere. Meanwhile, the reaction order of  $\text{SO}_2$  in “ $\text{TiO}_2+\text{CaCO}_3+\text{SO}_2$ ” reaction system in the range of 400-20000 ppb is determined to be 0.80 (Fig. S5), indicating that the uptake coefficients obtained at the ppm level of  $\text{SO}_2$  would somewhat overestimate the real one obtained at atmosphere relevant  $\text{SO}_2$  concentration level (several or a few tens ppb). While we note that the difference between the lab and atmospheric conditions regarding  $\text{SO}_2$  concentration remains even after considering the 400 ppb case, employing hundreds of ppb  $\text{SO}_2$  in the laboratory simulation to obtain the kinetic parameter of sulfate formation is acceptable (Liu and Abbatt, 2021; Liu et al., 2020b). Therefore, we tentatively believe that uptake coefficients estimated in this work would be valid after being calibrated.

High-resolution transmission electron microscopy (HRTEM) analysis of  $\text{TiO}_2$  (50 wt.%) +  $\text{CaCO}_3$  (50 wt.%) particles after reaction, in combination with energy dispersive spectrometer mapping measurements of sulfur component, was conducted to investigate the synergistic effect between  $\text{TiO}_2$  and carbonate ions (Fig. 3 a-d and Fig. S6). A region with a relatively high density of sulfur species was selected for further observation (Fig. 3a and 3b) and the distribution of each component was determined by fast Fourier transformation (FFT) and inverse FFT analyses (panel d) of the selected HRTEM image in high resolution with lattice fringes shown in Fig. 3c. Observation of crystalline  $\text{Ti}(\text{SO}_4)_2$  and  $\text{CaSO}_4$  on the interface of  $\text{TiO}_2$  and  $\text{CaCO}_3$  components imply that the synergistic effect on sulfate production likely originates from interplays of those two types of components under solar illumination.



**Figure 3.** (a) Energy Dispersive Spectroscopy (EDS) mapping of sulfur. (b) Selected HRTEM region containing a high density of sulfur for further observation and the red rectangle refers to the region shown in panel c. (c) The HRTEM image in high resolution with lattice fringes and (d) corresponding FFT power spectra, lattice indexing, and (1-6) inverse FFT analysis of lattice signal shown in panel d. In panel c, the term C- $\text{SO}_4^{2-}$  stands for crystalline  $\text{SO}_4^{2-}$ , i.e.  $\text{CaSO}_4$  and  $\text{Ti}(\text{SO}_4)_2$ . Particles employed for the HRTEM measurement refer to  $\text{TiO}_2$  (50 wt.%) +  $\text{CaCO}_3$  (50 wt.%) mixture particles upon exposure to the  $4.42 \times 10^{14}$  molecules  $\text{cm}^{-3}$   $\text{SO}_2/\text{N}_2+\text{O}_2$  for 60 min while other reaction conditions

275 are as same as that of above sulfate quantification experiments in Fig.1. Reaction conditions: RH = 30%, Light intensity (I) = 30 mW cm<sup>-2</sup>, Total flow rate = 52.5 mL min<sup>-1</sup>.

We further assessed the importance of interfacial contact between TiO<sub>2</sub> and CaCO<sub>3</sub> in sulfate production by two synthesis approaches in which the interface abundance is modulated for comparison. Typically, a “grinding” method was used to make TiO<sub>2</sub>+CaCO<sub>3</sub> mixture with compact contact between those two components, thus leading to abundant interfaces. Meanwhile, the “shaking” method is designed to create a TiO<sub>2</sub>+CaCO<sub>3</sub> mixture of loose contact, leaving relatively fewer amounts of interfaces within the mixtures. The resulting mixing statuses of the two samples meet our expectations, evidenced by the scanning electron microscope (SEM) technique (Fig. S7). IC quantification analysis suggests that particles with considerable junctions exhibit a more pronounced promotion for sulfate production than those having relatively few junctions (Fig. S8). These results emphasize the importance of an indispensable interface contact between TiO<sub>2</sub> and CaCO<sub>3</sub> in fast production upon irradiation.

285 **Table1.** Chemical compositions of mineral dust simulants.

	SiO <sub>2</sub> (wt. %) †	Al <sub>2</sub> O <sub>3</sub> (wt. %) †	CaCO <sub>3</sub> (wt. %) *,†	TiO <sub>2</sub> (wt. %) †	‡Ca:Al (Fe:Al)
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub>	89.46	10.54	-	-	-
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +CaCO <sub>3</sub>	82.47	9.72	7.81	-	0.73 (-)
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +TiO <sub>2</sub>	88.42	10.42	-	1.15	-
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +TiO <sub>2</sub> +CaCO <sub>3</sub>	81.59	9.62	7.73	1.06	0.73 (-)
ATD	71.27	8.4	-	0.93	0.73 (0.17)

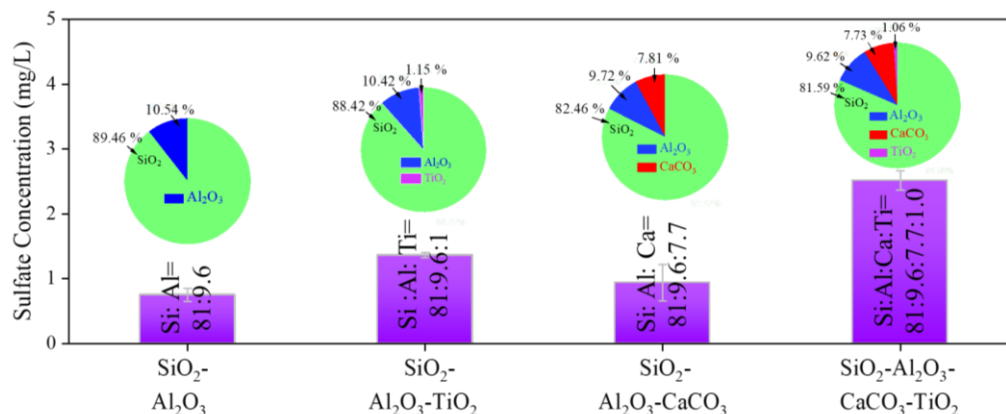
\*In the present study, CaCO<sub>3</sub> was taken as representative of alkaline-earth metal oxide in our proxies for the authentic dust.

†The mass ratio of 4 components (if any) in the simulants were controlled in the ratio of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:CaCO<sub>3</sub>: TiO<sub>2</sub>= 81.59: 9.62:7.73:1.06. For instance, the mass ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> is 81.59: 9.62 in the SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> simulant whereas is 81.59: 9.62:7.73 in the SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+CaCO<sub>3</sub> mixture. The ratios of each component are derived from the EDS mapping analysis of ATD dust particles.

290 ‡This column refers to the molar ratio.

The increased sulfate production was further probed by employing mineral dust simulants where two dominant crust constituents SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were introduced into TiO<sub>2</sub>+CaCO<sub>3</sub> particles to mimic the authentic mineral dust particles in the atmosphere, with specific component and corresponding ratio information shown in Table 1. It is worth mentioning that the determination of the ratio of each component in the simulants relies upon the EDS mapping results of ATD particles. In Fig. 4, the introduction of TiO<sub>2</sub> components (1% wt.) into SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> leads to 81.6% enhancement of sulfate production because of photolabile ROS. On the other hand, merely 24.8% wt. increase of sulfate yield was observed once ~8% wt. of CaCO<sub>3</sub> was incorporated into SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> dust particles. This can be attributed to the alkaline environment created by CaCO<sub>3</sub>, which is

thought to increase SO<sub>2</sub> adsorption (Al-Hosney and Grassian, 2005) and sulfate production accordingly. Surprisingly, mixing of ~1% mass fraction of TiO<sub>2</sub> and ~8% wt. of CaCO<sub>3</sub> into SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> gives rise to a 235% increase in sulfate formation relative to that of SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>. It represents nearly an extra 100% enhancement of sulfate production due to the presence of TiO<sub>2</sub> and CaCO<sub>3</sub> of an atmospherically relevant mass fraction. These results lead to the hypothesis that the observed synergistic effect on heterogeneous oxidation of SO<sub>2</sub> is likely to take effect in the atmosphere.



**Figure 4.** Sulfate concentration quantified by IC. Sulfate concentration was measured by IC on mineral dust simulants after exposure to gaseous SO<sub>2</sub> ( $2.46 \times 10^{14}$  molecule cm<sup>-3</sup>) under irradiation. Noting that SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub>: CaCO<sub>3</sub>: TiO<sub>2</sub> refers to the mass fraction ratios of the components in simulants. Experiments were all conducted at RH of 30% and Light intensity (I) of 30 mW cm<sup>-2</sup>.

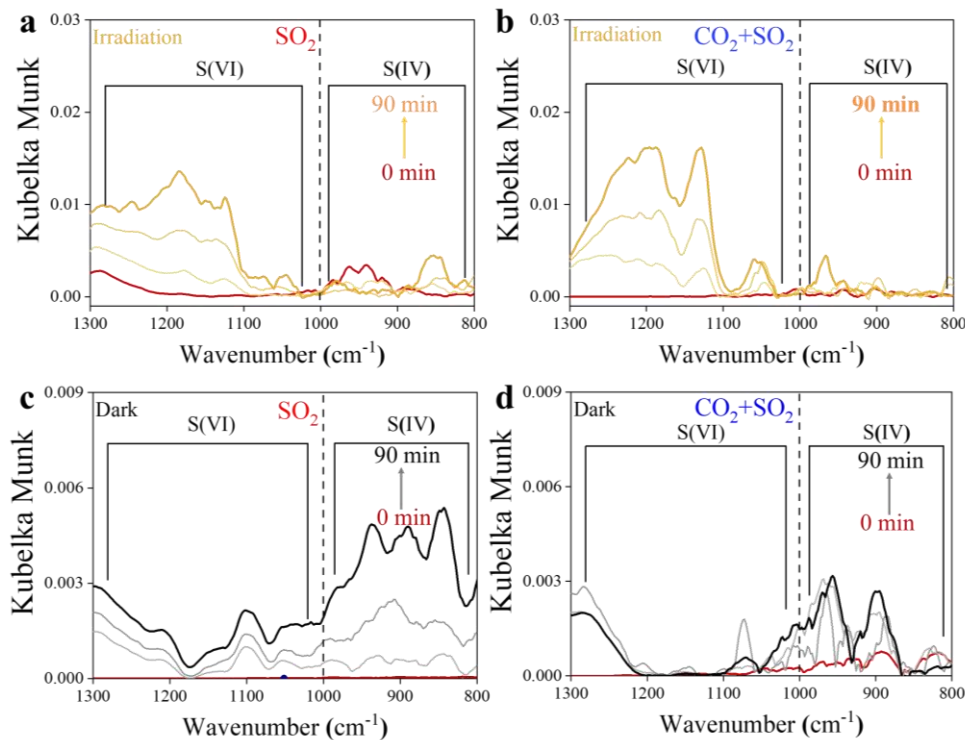
Fe<sub>2</sub>O<sub>3</sub> is also one of the crucial components found in authentic mineral dust (El Zein et al., 2013), and it has been reported to produce electron-hole pairs under solar irradiation (Li et al., 2019), thus likely involving the reaction channel considered in this work (see detailed discussion in the later section). Similar to the protocol applied for synthesizing the TiO<sub>2</sub>+CaCO<sub>3</sub> mixture, αFe<sub>2</sub>O<sub>3</sub>+CaCO<sub>3</sub> are accordingly prepared. In Fig. S9a, our results show that αFe<sub>2</sub>O<sub>3</sub> can not trigger fast SO<sub>2</sub> oxidation in the presence of carbonate ions upon irradiation, which is distinguished from the results we derived from TiO<sub>2</sub>+CaCO<sub>3</sub> mixture. This can be explained by the fact that Fe<sub>2</sub>O<sub>3</sub> shows a lower redox activity relative to TiO<sub>2</sub> (Fig. S9b), where its strong redox capability essentially enables photo-induced electrons and holes to produce O<sub>2</sub><sup>-</sup> and ·OH radical ions. In stark contrast, the valence band and conduct band of Fe<sub>2</sub>O<sub>3</sub> lie at -0.18 and at 1.68 V vs. NHE (pH = 7), lower than the redox potential required for generating O<sub>2</sub><sup>-</sup>, ·OH as well as carbonate-containing ROS (Li et al., 2016). Hence, no promoted sulfate production is seen for αFe<sub>2</sub>O<sub>3</sub>+CaCO<sub>3</sub> particles under irradiation. We also note the inconsistency between our study and the previous literature with regard to the response of SO<sub>2</sub> oxidation to solar irradiation over αFe<sub>2</sub>O<sub>3</sub> particles, which has been interpreted in supplementary text 17.

Overall, we show that upon irradiation atmospherically relevant content of TiO<sub>2</sub> (nearly 1%) in mineral dust simulants is able to interact with carbonate ions to launch an increased sulfate production, which is beyond the conventional regime of

alkaline neutralization of  $\text{H}_2\text{SO}_4$ . Unlike  $\text{TiO}_2$ ,  $\alpha\text{Fe}_2\text{O}_3$  lacks the ability to initiate fast  $\text{SO}_2$  oxidation by generating carbonate-containing ROS due to its limited photo-chemical activity although ferric chemistry is important in secondary sulfate formation in the atmosphere (Sullivan et al., 2007; Yermakov and Purnal, 2003).

### 325 3.2.2 Accelerated sulfate production in the presence of $\text{CO}_2$ .

Atmospheric  $\text{CO}_2$  is also an important source of (bi)carbonate. Its influence on photochemical  $\text{SO}_2$  uptake on mineral dust was thus studied. Distinguishing S(VI) from S(IV) species over  $\text{TiO}_2$  particles relies upon the position of the IR bands according to the assignment of previous literature (Nanayakkara et al., 2014), and S(VI) and S(IV) build up as heterogeneous reactions proceed in all cases (Fig. 5). In the presence of atmospherically relevant  $\text{CO}_2$  ( $9.83 \times 10^{15}$  molecules  $\text{cm}^{-3}$ ), sulfate yield was increased under irradiation as compared to the  $\text{CO}_2$ -free case (Fig. 5a and b). We cautiously examined the net effect of formed (bi)carbonate on sulfate production by time-resolved DRIFTS spectra (Fig. 5c and d) using dark experiments.  $\text{CO}_2$  suppresses both S(IV) and S(VI) products in the dark probably because of the competitive adsorption effect, as we observed over  $\text{Al}_2\text{O}_3$  particles (Liu et al., 2020c).



335 **Figure 5.** Time-resolved DRIFTS of S(IV) and S(VI) products over  $\text{TiO}_2$  particles after exposure to  $\text{SO}_2/\text{N}_2 + \text{O}_2$  in the absence and presence of  $\text{CO}_2$  upon irradiation (a and b) and those reactions under dark (c and d). Reaction conditions: RH = 30%, Light intensity (I) =  $30 \text{ mW cm}^{-2}$ , total flow rate =  $52.5 \text{ mL min}^{-1}$  and  $\text{SO}_2 = 7.37 \times 10^{13}$  molecules  $\text{cm}^{-3}$ .

Above observation leads us to speculate that the active intermediate derived from (bi)carbonate species upon irradiation is a plausible force to drive rapid sulfate formation. Besides, a nearly 50% increase in  $\text{SO}_2$  uptake coefficient is observed for the

340 mineral dust proxy  $\text{TiO}_2$  after being exposed to  $9.83 \times 10^{15}$  molecules  $\text{cm}^{-3}$  (400 ppm)  $\text{CO}_2 + \text{SO}_2 / \text{N}_2 + \text{O}_2$  mixture (Table S1). The pseudo-first reaction order (1.13) was also determined in the selected concentration range of 400-20000 ppb (Fig. S5b), which satisfies the prerequisite for uptake coefficients derived from laboratory chambers potentially being generalized to the atmosphere condition, as we expounded in the early context.

**Table 2.** Chemical Compositions of the ATD Dust and Standard Clays.

Minerals	ATD (%)*	IMt-2 (%)*	KGa-2 (%)*
$\text{SiO}_2$	78.11	59.57	56.93
$\text{Al}_2\text{O}_3$	7.19	19.47	37.49
$\text{Fe}_2\text{O}_3$	2.57	7.95	1.81
FeO	n.d. †	0.05	0.15
MgO	1.22	2.42	0.03
CaO	3.03	0.37	0.01
$\text{Na}_2\text{O}$	1.39	0.08	n.d. †
$\text{K}_2\text{O}$	2.06	8.72	0.06
$\text{TiO}_2$	0.46	0.99	3.43
$\text{P}_2\text{O}_5$	0.10	0.07	0.05
MnO	0.04	0.03	n.d. †
S	n.d. †	0.03	0.02
Total	99.21	99.75	99.98
Total A.E. ‡	7.70	11.59	0.10

345 \*Chemical compositions of the dust and clays were determined by XRF results.

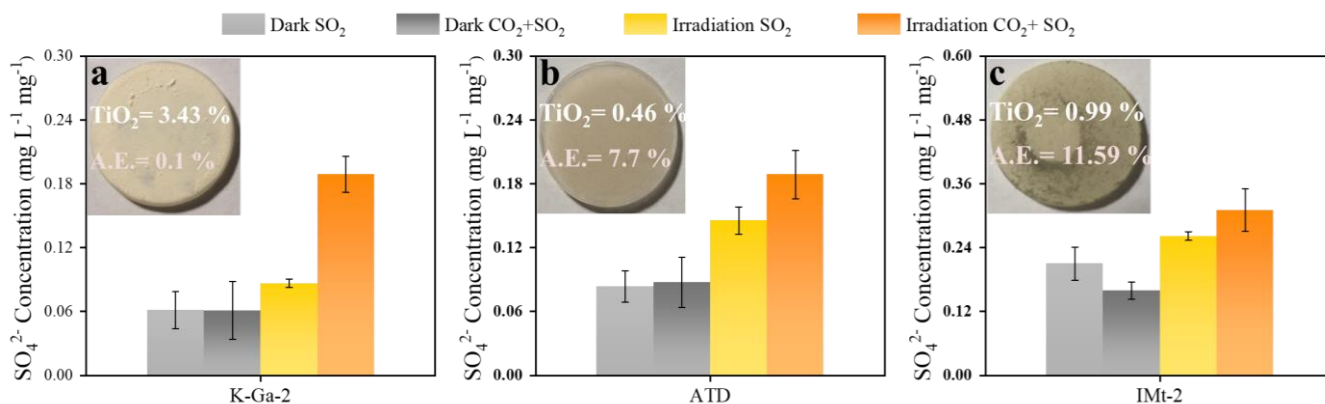
†n.d. refers to not detected.

‡A.E. refers to alkaline earth metal oxide.

As another step toward a real scenario in the atmosphere, experimental trials employing authentic mineral dust particles, i.e. K-Ga-2 (Kaolin, Georgia, USA), Arizona test dust (ATD), and clays IMt-2 (Illite, Mont., USA) were implemented, with component analysis results shown in Table 2. In Fig. 6, the pronounced increase in sulfate yield (by nearly 100% increased sulfate production in the  $\text{CO}_2$ -involved case under irradiation) is best seen in K-Ga-2 clay (panel a). The promotional effect of  $\text{CO}_2$  on sulfate formation under irradiation, nonetheless, is less evident for IMt-2 (the content of  $\text{TiO}_2 \approx 0.99\%$ ) and ATD (the content of  $\text{TiO}_2 \approx 0.46\%$ ) as compared to K-Ga-2 particles. This may correlate to their higher mass fraction of alkaline earth metal oxide (denoted as A.E.), which enables dust particles to possess a substantial number of (bi)carbonate species within the natural environment where they have experienced long-term exposure to atmospheric  $\text{CO}_2$  during the regional transport. Therefore, the aforementioned synergetic effect takes effect over IMt-2 and ATD particles even without exposure to  $\text{CO}_2$

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presumably due to the presence of abundant alkaline carbonate formed, and a relatively moderate increase in sulfate production was thus observed. On the other hand, TiO<sub>2</sub> content is not necessarily an accurate predictor of photoreactivity, the content and proportion of the active phase of TiO<sub>2</sub> in K-Ga-2 altogether contribute to a more pronounced increase in sulfate production relative to the other two clays (see detailed discussion in supplementary text 18).



**Figure 6.** Laboratory studies of sulfate production on authentic dust and clay membranes (a) K-Ga-2 (b) ATD as well as (c) IMt-2 under the dark and irradiation (30 mW cm<sup>-2</sup>) upon exposure to 4.91×10<sup>14</sup> molecules cm<sup>-3</sup> SO<sub>2</sub>/N<sub>2</sub>+O<sub>2</sub> and 2.46×10<sup>18</sup> molecules cm<sup>-3</sup> CO<sub>2</sub>+ 4.91×10<sup>14</sup> molecules cm<sup>-3</sup> SO<sub>2</sub>/N<sub>2</sub>+O<sub>2</sub> at RH of 30%. Noting that sulfate yield in three cases was normalized by the mass of dust particles employed for heterogeneous reaction.

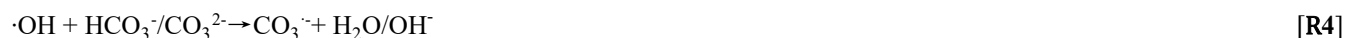
### 3.2.3 Reaction Mechanism.

The heterogeneous reaction of SO<sub>2</sub> on dust particles in the atmosphere is a complicated process, covering a series of reactions taking place in both homogeneous and heterogeneous ways. At a sufficiently low RH condition (normally below 10% RH), water readily dissociates on the surface of metal oxide under ambient atmospheric conditions, where the metal oxide surface is terminated by hydroxyl groups that hydrogen bond to adsorbed water molecules (Cwiertyny et al., 2008). In this case, SO<sub>2</sub> oxidation over dust particles is dominated by the reaction regime where the resulting hydroxyl groups react with gaseous SO<sub>2</sub> to form adsorbed S(IV)<sub>ad</sub> species. Afterward, S(IV)<sub>ad</sub> will be oxidized by oxidants in the atmosphere or photo-induced active intermediates produced from the dust surface upon irradiation. As the RH increases beyond 10%-15%, multilayer water coverage occurs, reaching approximately two monolayers at RH of 30 % (Mogili et al., 2006). Under these circumstances, the amount of water adsorbed onto the surface of the dust particles is believed to be sufficiently large that it is liquid-like in corresponding physical and chemical properties (Cwiertyny et al., 2008) (Peters and Ewing, 1997). In this work, heterogenous SO<sub>2</sub> oxidation over mineral dust proxies proceeds at the RH of 30%, and two water layers are likely to attach to dust particles. Thus, radical ions are anticipated to play a key role in fast SO<sub>2</sub> oxidation over humidified mineral dust and mechanism studies performed in the aqueous phase are persuasive to some extent.

380 Our preliminary sulfate quantification results (Fig. 2a and b) suggest that the presence of (bi)carbonate ions under solar light contributes to increased sulfate yield. In this carbonate-containing reaction system, a plausible intermediate is the active  $\text{CO}_3^{\cdot-}$ . It is readily produced via the following two pathways. First of all, carbonate anion can be directly oxidized by produced photo-induced holes from typical mineral dust upon solar irradiation (**R1** and **R2**), as the redox potential of  $\text{CO}_3^{\cdot-}/\text{CO}_3^{2-}$  is 1.78 V (vs NHE, at pH = 7), which is lower than the  $\text{TiO}_2$  valence band (VB) potential of 2.67 V (vs NHE, at pH = 7) (Li et al., 2016; Xiong et al., 2016):

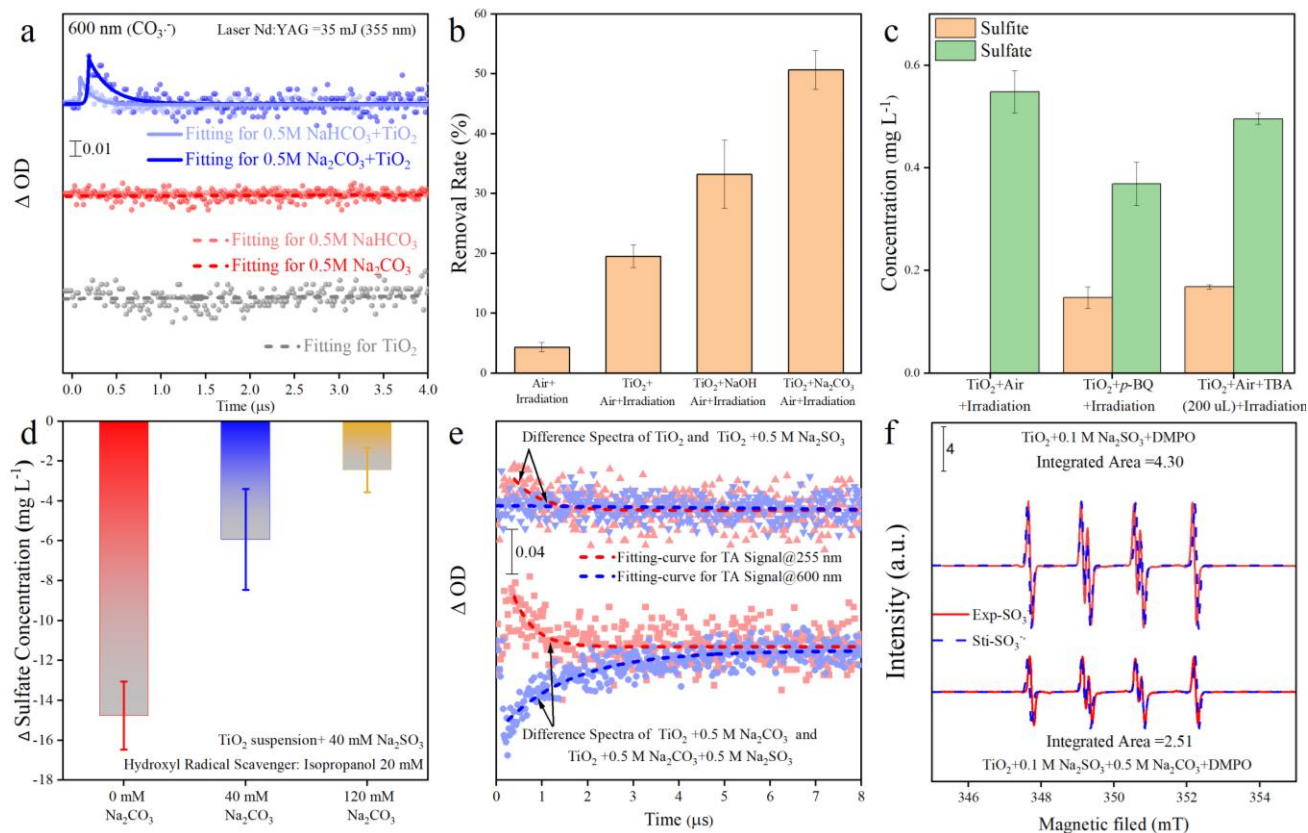


In the second pathway, carbonate radicals evolve through the reaction of (bi)carbonate anion with formed hydroxyl radicals  $\cdot\text{OH}$  over mineral dust surfaces (Zhang et al., 2015a) (**R3** and **R4**).



The above assumptions are supported by nanosecond transient absorption spectra (NTAS), in which signal ( $\Delta\text{OD}$ ) of carbonate radical  $\text{CO}_3^{\cdot-}$  at 600 nm (Bhattacharya et al., 1998) only emerges for dust suspension containing (bi)carbonate species (Fig. 7a). An increased degradation rate of aniline observed in  $\text{TiO}_2$  suspension due to the presence of carbonate ions produces additional evidence of the formation of active  $\text{CO}_3^{\cdot-}$  ions and strengthened oxidation capability of  $\text{TiO}_2$  (Fig. 7b, see additional discussion in supplementary text 19). The  $\text{CO}_3^{\cdot-}$ -induced chemistry was further evidenced by  $\cdot\text{OH}$  scavenging experiments using tertiary Butyl Alcohol (TBA) and isopropanol (i-PrOH) as they show lower reaction rates with  $\text{CO}_3^{\cdot-}$  ( $k_{\text{CO}_3^{\cdot-}, \text{i-PrOH}} < 4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{CO}_3^{\cdot-}, \text{TBA}} < 1.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ) relative to that with  $\cdot\text{OH}$  ( $k_{\text{i-PrOH}, \cdot\text{OH}} < 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{OH}, \text{TBA}} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al., 2009; Liu et al., 2015) (Liu et al., 2015) (Li et al., 2020). TBA dramatically decreases the yield of sulfate on  $\text{TiO}_2$  surface by nearly 70%, with sulfite ions being the dominant sulfur species (Fig. 7c). Meanwhile, a great loss of sulfate yield when  $\text{TiO}_2$  suspension was added with i-PrOH (Fig. 7d). This is in strong contrast to the result of a carbonate-involved system where the reactivity is sustained as carbonate radicals offer an alternative reaction pathway for  $\text{SO}_2$  oxidation. This is plausible since the carbonate ions are excellent  $\cdot\text{OH}$  scavenger, and  $\text{CO}_3^{\cdot-}$  becomes the predominant species in a relatively strong alkaline aqueous-like environment in the presence of carbonate salt. This is supported by the previous work (Sun et al., 2016), in which adding 0.1 M of bicarbonate salt into the UV/ $\text{H}_2\text{O}_2$  system ( $\text{H}_2\text{O}_2 = 0.3 \text{ mM}$ ) was sufficient to suppress  $\cdot\text{OH}$  concentration to around  $10^{-15} \text{ M}$ , creating a carbonate radical dominated regime ( $[\text{CO}_3^{\cdot-}] = 8.64 \times 10^{-12} \text{ M}$ ). In our experiments (Fig. 7b), 0.2 M of carbonate salt was employed, and the reaction rate of  $\text{CO}_3^{2-}$  with  $\cdot\text{OH}$  is nearly two orders of magnitude higher than that of  $\text{HCO}_3^-$ , thus giving rise to carbonate radical being the substitute for hydroxyl radical in the reaction. The above results suggest that  $\cdot\text{OH}$  is a major contributor to sulfate yield on  $\text{TiO}_2$  particles in the absence of carbonate ions while  $\text{CO}_3^{\cdot-}$  ions dominate  $\text{SO}_2$  oxidation over humidified carbonate-containing  $\text{TiO}_2$  particles upon irradiation. In addition to experimental investigations, the carbonate radical formation process is proved to be thermodynamically favorable, supported by density functional theory (DFT) calculations (Fig. S10 and supplementary text 20).





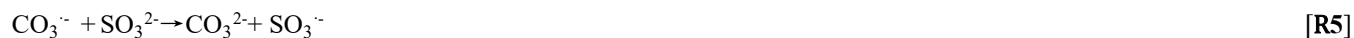
**Figure 7.** (a) Single-wavelength transient absorption spectra of various aqueous solutions. (b) The removal rate of aniline after exposure to  
 415 airflow under irradiation in the absence and presence of mineral dust particles for 300 seconds. Reaction conditions: RH = 30%, Light  
 intensity ( $I$ ) = 30 mW cm<sup>-2</sup>, Total flow rate = 52.5 mL min<sup>-1</sup>. Noting that an adequate amount of NaOH was introduced into the TiO<sub>2</sub>  
 suspension system to achieve a pH environment condition identical to that of the TiO<sub>2</sub>+Na<sub>2</sub>CO<sub>3</sub> suspension system. (c) Determination of  
 sulfite and sulfate concentration after exposure to air flow under irradiation in the absence and presence of mineral dust particles for 20 min.  
 Reaction conditions: RH = 30%, Light intensity ( $I$ ) = 30 mW cm<sup>-2</sup>, Total flow rate = 52.5 mL min<sup>-1</sup>. (d) Sulfate formation change  $\Delta(\text{SO}_4^{2-})$   
 420 is determined by different sulfate concentrations with and without the addition of isopropanol as hydroxyl radical scavenger. (e) The  
 difference in transient absorption kinetics of sulfite radical and carbonate radical at the various aqueous solutions and their corresponding  
 growth-decay fit curves.  $\Delta A$ -signal was recorded at 255 and 600 nm after pulsed 355 nm laser excitation. (f) ESR spectrometry of [DMPO-  
 SO<sub>3</sub><sup>-</sup>] intermediate formed in a solution of d TiO<sub>2</sub> (3 mg~4 mL) + 0.1 M Na<sub>2</sub>SO<sub>3</sub> and TiO<sub>2</sub> (3 mg~4 mL) + 0.5 M Na<sub>2</sub>CO<sub>3</sub> + 0.1 M Na<sub>2</sub>SO<sub>3</sub>.  
 For clarity, the integrated areas of ESR profiles were also presented for direct comparison. Exp. and Sti. stand for experimental results and  
 425 corresponding fitting results using software Isotropic Radicals.

On the other hand, early studies (Chameides and Davis, 1982; Das, 2001; Neta and Huie, 1985) agree with the key role of sulfite radical (SO<sub>3</sub><sup>-</sup>) in rapid sulfate production in an aqueous medium, and the present reaction system creates a localized environment where SO<sub>3</sub><sup>-</sup> can be readily produced from the TiO<sub>2</sub> and S(IV) species upon solar illumination (Salama et al., 1995). Consequently, probe light of NTAS at wavelength 255 nm (ascribed to sulfite radical) and 600 nm (ascribed to carbonate

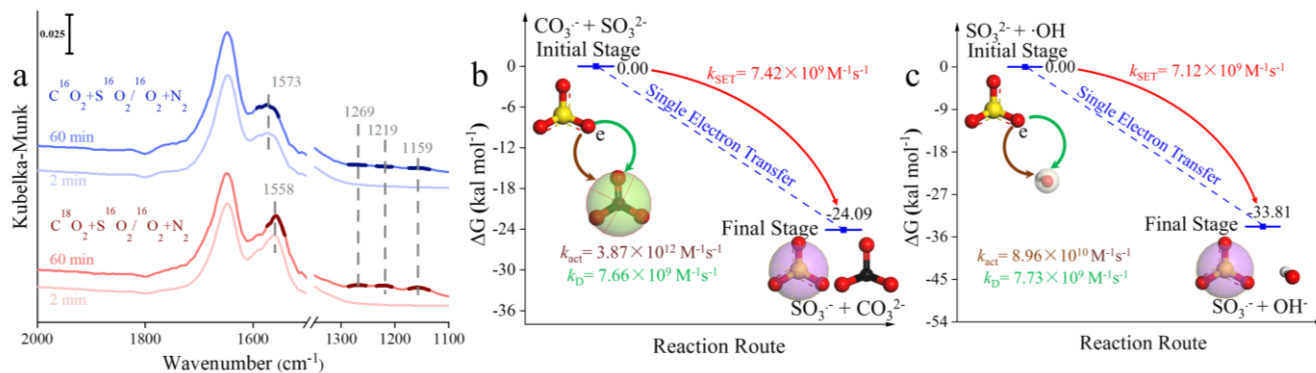
430 radical) were simultaneously monitored (Ghalei et al., 2016; Goldstein et al., 2001; Hayon et al., 1972). A weak signal of sulfite radical was observed in the system of TiO<sub>2</sub>+Na<sub>2</sub>SO<sub>3</sub> suspension under irradiation (Fig. 7e). On the contrary, the sulfite radical signal is strengthened after the introduction of carbonate ions into the TiO<sub>2</sub>+Na<sub>2</sub>SO<sub>3</sub> suspension, along with a significant decrease in the signal for carbonate radical. Electron spin resonance (ESR) data (Fig. 7f) further confirms the increase of SO<sub>3</sub><sup>•-</sup> after 2 min UV irradiation in the presence of carbonate ion. Based on the above results, one may deduce that the interplay  
 435 between carbonate radical and sulfite ions is a crucial step giving rise to the increased SO<sub>3</sub><sup>•-</sup>, which is reported to account for rapid atmospheric sulfate formation through chain propagation reactions that involve SO<sub>4</sub><sup>•-</sup> and SO<sub>5</sub><sup>•-</sup> intermediates (Hung and Hoffmann, 2015; Hung et al., 2018). Additionally, this sulfite radical ion chemistry is believed to drive fast sulfate formation over mineral dust particles as well (Gankanda et al., 2016; Rubasinghege et al., 2010). Nevertheless, there are two possibilities that might explain the aforementioned interaction. One way is the oxygen transfer and the other route is electron transfer,  
 440 which needs further clarification.

We first examined the oxygen transfer path through <sup>18</sup>O isotope labeling experiments. TiO<sub>2</sub> particles were initially exposed to C<sup>16</sup>O<sub>2</sub>/N<sub>2</sub> and C<sup>18</sup>O<sub>2</sub>/N<sub>2</sub>, followed by the exposure of SO<sub>2</sub>/N<sub>2</sub>+O<sub>2</sub> under irradiation (Fig. 8a). Bidentate carbonate band centered at 1573 cm<sup>-1</sup> appears after the introduction of C<sup>16</sup>O<sub>2</sub>/N<sub>2</sub>, while this band shifts to 1558 cm<sup>-1</sup> when C<sup>18</sup>O<sub>2</sub>/N<sub>2</sub> is introduced, indicating the incorporation of <sup>18</sup>O into bidentate carbonate species, in accord with the previous report (Liao et al.,  
 445 2002). However, no shift of IR features at 1269, 1219, and 1159 cm<sup>-1</sup>, assigned to (bi)sulfate species on TiO<sub>2</sub> particles, were observed throughout the reaction. This implies that the oxygen transfer path does not account for the rapid SO<sub>2</sub> oxidation on particles of concern.

In light of the above analysis, the electron transfer might be a plausible pathway to explain the fast oxidation within the reaction system. DFT calculations provide an accessible approach to study the electron transfer pathway. The result in Fig. 8b  
 450 illustrates SO<sub>3</sub><sup>•-</sup> formation is a SET process of CO<sub>3</sub><sup>•-</sup> and SO<sub>3</sub><sup>2-</sup>, where O atom in SO<sub>3</sub><sup>2-</sup> transfers an electron to O atom in CO<sub>3</sub><sup>•-</sup> to form SO<sub>3</sub><sup>•-</sup> and CO<sub>3</sub><sup>2-</sup>. This SET reaction is a thermodynamically favorable process, with the difference of Gibbs free energy between reactant and product lying at -24.09 kcal mol<sup>-1</sup>. We note that the insufficient O<sub>2</sub> supply in aqueous media may be an underlying constraint to the proposed CO<sub>3</sub><sup>•-</sup>-initiated SO<sub>2</sub> oxidation pathway. Therefore, careful estimation of both oxygen consumption and supply rates were conducted, revealing that oxygen supply flux can be sufficiently larger than corresponding  
 455 consumption (see additional details in the supplementary text 21). This enables us to deduce that considered chain reactions can continually proceed. Taken above results and discussions altogether, the following reactions are proposed accordingly  
**(R5-R8):**



Another important pathway needs to be considered as well; that is  $\text{SO}_3^{\cdot-}$  can also be formed via the conventional reaction of  $\cdot\text{OH}$  and  $\text{SO}_3^{2-}$  (**R9**).



465

**Figure 8.** (a) *In situ* DRIFTS of heterogeneous reaction of  $\text{SO}_2$  on the  $\text{TiO}_2$  particles for 2 and 60 min after being exposed to  $\text{C}^{16(18)}\text{O}_2/\text{N}_2$  for 20 min under irradiation. (b) Reaction pathway of interaction between carbonate radical ( $\text{CO}_3^{\cdot-}$ ) and sulfite ( $\text{SO}_3^{2-}$ ) and (c) Interaction between hydroxyl radical ( $\cdot\text{OH}$ ) and sulfite ( $\text{SO}_3^{2-}$ ) through the SET process at the CCSD (T)-F12/cc-PVDZ-F12//M06-2X/6-311++G (3df, 3pd) level and  $\Delta G_0^{\text{SET}}$  represents the difference in Gibbs free energy between reactant and product. The white, black, yellow, and red spheres represent H, C, S, and O atoms, respectively. In order to visualize the variation of surface products in oxygen isotope experiments (panel a), DRIFTS features of these concerned species were highlighted in dark colors. For interpretation of the references to color in the legends of panels b and c, the reader is referred to the Web version of this article.

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In this SET process, electron donor  $\text{SO}_3^{2-}$  reacts spontaneously with electron acceptor  $\cdot\text{OH}$  (Fig. 8c) and the calculated activation free energy barrier  $\Delta G_{\text{SET}}^\ddagger$  for this SET reaction is 2.50 kcal mol⁻¹. Hence, the reaction process of  $\cdot\text{OH}$  with  $\text{SO}_3^{2-}$  is diffusion-controlled, and the total rate constant  $k_{\text{SET-2}}$  was calculated to be  $7.12 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ . In comparison, the rate constant  $k_{\text{SET-1}}$  of the diffusion-controlled SET process for  $\text{CO}_3^{\cdot-}$  and  $\text{SO}_3^{2-}$  was estimated to be  $7.42 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ . Despite a slight net increase of the rate, the distinguishable concentration of  $\text{CO}_3^{\cdot-}$  and  $\cdot\text{OH}$  should also be taken into account for the rate comparison in varied reaction paths. To visualize the difference, relative rates were calculated according to Eq. 12:

$$r = \frac{v_{\text{CO}_3^{\cdot-} + \text{SO}_3^{2-}}}{v_{\cdot\text{OH} + \text{SO}_3^{2-}}} = \frac{k_{\text{SET-1}}[\text{CO}_3^{\cdot-}][\text{SO}_3^{2-}]}{k_{\text{SET-2}}[\cdot\text{OH}][\text{SO}_3^{2-}]} \quad [12]$$

480

Where  $r$  is the ratio of two reaction rates,  $[\text{CO}_3^{\cdot-}]$ ,  $[\text{SO}_3^{2-}]$ , and  $[\cdot\text{OH}]$  refer to the concentration of corresponding reactants. Previous literature suggests the concentration of carbonate radicals is able to show two orders of magnitude higher than that of hydroxyl radicals at the surface of the water under solar irradiation (Chandrasekaran and Thomas, 1983; Goldstein et al., 2001; Sulzberger et al., 1997), consistent with concentration gap between carbonate radicals and hydroxyl radicals through partitioning process from gas-phase determined in our reaction system (Fig.9). While the net concentrations of carbonate and hydroxyl radicals in the water layers of humified particles are very likely to be different from that found in the bulk aqueous

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media, concentration inputs of two radicals with the gap of two orders somehow could reflect the relative contribution of carbonate radicals and hydroxyl radicals to sulfate production based on literature results and our experimental trails. The concentrations of  $\text{CO}_3^{\cdot-}$  and  $\cdot\text{OH}$  were set in the range from  $1.0 \times 10^{-10}$  to  $1 \times 10^{-12}$  mol  $\text{L}^{-1}$  and from  $1.0 \times 10^{-12}$  to  $1 \times 10^{-14}$  mol  $\text{L}^{-1}$  (Sulzberger et al., 1997) and  $r$  value could thus reach to  $1.04 \times 10^4$  at most (Fig. S11). As a result, we speculate that the formation pathway of  $\text{SO}_3^{\cdot-}$  via interaction between  $\text{CO}_3^{\cdot-}$  and  $\text{SO}_3^{2-}$  is a more efficient route, corresponding well with our experimental results.

In addition to the pathway launched by photo-generated holes, the sink of photo-generated electrons is as well considered. In our reaction system,  $\text{O}_2$  is thought to be an electron trap and produce the superoxide radical ions ( $\text{O}_2^{\cdot-}$ ), which is reported to play a non-negligible role in sulfate formation (Shang et al., 2010) and should be taken into account to give a whole picture of reaction scheme in triggering sulfate formation on the surface of  $\text{TiO}_2$ -containing mineral dust particles. *p*-benzoquinone is a commonly-used  $\text{O}_2^{\cdot-}$  scavenger for trapping the  $\text{O}_2^{\cdot-}$  radical ions (Yan et al., 2018). Our data shows that adding an excess amount of *p*-benzoquinone into  $\text{TiO}_2$  particles reduces the sulfate yield by 32% along with the appearance of sulfite ions over  $\text{TiO}_2$  particles upon exposure to  $\text{SO}_2$  (Fig.7c). Notably, the decrease in sulfate yield by around 30% in the presence of  $\text{O}_2^{\cdot-}$  scavenger *p*-benzoquinone is almost complementary to that added with  $\cdot\text{OH}$  scavenger using TBA (70%), pointing toward a minor sulfate formation pathway contributed by  $\text{O}_2^{\cdot-}$  relative to the major pathway by  $\text{CO}_3^{\cdot-}$  when carbonate ions are presented to efficiently capture  $\cdot\text{OH}$  ions. Following Shang's work (Shang et al., 2010),  $\text{O}_2^{\cdot-}$  involved  $\text{SO}_2$  oxidation can be given as

**R10:**

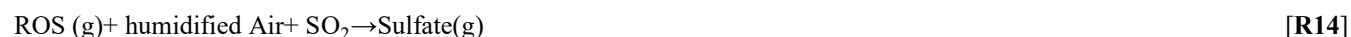


Where intermediates  $\text{SO}_3$  formed via the interaction between  $\text{SO}_2$  and  $\text{O}_2^{\cdot-}$ , subsequently couple with water molecules to produce sulfate species as a final product. pH is an important factor within aqueous chemical reaction processes and is in preference to alter the dominated regime for sulfate production. Yet so far adjusting the pH of particle surfaces is quite tough, and exploring the role of dust surface pH in the reactivity of  $\text{CO}_3^{\cdot-}$  is not easily achieved. Notwithstanding, the increase of pH in  $\text{TiO}_2$  suspension was observed to promote the production of  $\text{CO}_3^{\cdot-}$ , further strengthening the oxidation capability of dust particles (Fig. 7b). In contrast, decreasing pH is expected to reduce the yield of  $\text{CO}_3^{\cdot-}$  since the reaction rate of  $\text{CO}_3^{2-}$  with  $\cdot\text{OH}$  is nearly two orders of magnitude higher than that with  $\text{HCO}_3^-$ . On this basis, a question arises whether the surface pH of mineral dust can be sustained to maintain fast  $\text{SO}_2$  oxidation triggered by  $\text{CO}_3^{\cdot-}$  in the typical lifespan of mineral dust.

Considering that  $\text{SO}_2$  concentration employed in this work is higher than that in the real atmosphere, the concept of "equivalent exposure time" is introduced to evaluate the influence of pH on the  $\text{SO}_2$  oxidation pathway initiated by  $\text{CO}_3^{\cdot-}$  (see a more detailed discussion on determining equivalent exposure time in supplementary text 22). The heterogeneous sulfate production over  $\text{TiO}_2$  and  $\text{TiO}_2 + \text{CaCO}_3$  particles versus equivalent exposure time were plotted (Fig. S12). Clearly, the sulfate yield builds up steadily during the two-week equivalent exposure time, suggesting that the regime of  $\text{CO}_3^{\cdot-}$  initiated  $\text{SO}_2$

oxidation over  $\text{TiO}_2$  and  $\text{TiO}_2+\text{CaCO}_3$  particles is slightly affected by the possible decrease of surface pH because of the  
520 accumulation of sulfate production over entire reaction course. In the atmosphere, the lifetime of mineral dust particles ranges  
from several days to weeks (Bauer and Koch, 2005), and the equivalent exposure time considered in this study (nearly 2 weeks)  
falls right within the characteristic lifespan range of mineral dust particles. Besides, 20 ppb is assumed to be an atmospherically  
relevant concentration to calculate “equivalent exposure time” in this study whereas even low  $\text{SO}_2$  concentrations (several or  
a few tens ppb of  $\text{SO}_2$ ) were monitored in the field observation (He et al., 2014; Watanabe et al., 2020). Therefore, the reduction  
525 of dust surfaces pH would be more moderate than we now considering and even little influence of surface pH on our proposed  
reaction scheme would have. Therefore, persistent growth of sulfate shows a negligible effect on  $\text{CO}_3^-$  initiated  $\text{SO}_2$  oxidation  
scheme proposed in this work.

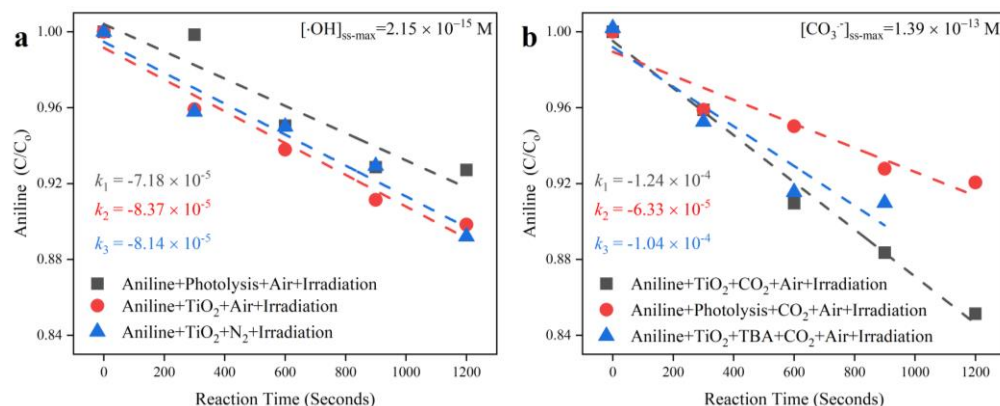
Additionally, dust particles are reported to eject the radical ions from the surface under solar light irradiation, severing as  
an underlying pathway for sulfate aerosol formation in the atmosphere (Chen et al., 2021; Dupart et al., 2012), as described as:



Where ROS (g) stands for the active intermediates in the gas phase. Over 400 ppm of  $\text{CO}_2$  is universal in the atmosphere, and  
it is expected to form (bi)carbonate ions once enters the quasi-liquid layer of humified particles. Bi(carbonate) ions are then  
prone to react with hydroxyl radical ions to form carbonate radicals. Following this line of reasoning, we attempt to monitor  
535 the plausible gas ROS species that are formed in the presence of  $\text{CO}_2$  (see detailed discussion in the experimental section).

When  $\text{CO}_2$  (atmospheric relevant concentration) is introduced into the homemade flow-cell chamber, with the intervening  
gap between  $\text{TiO}_2$ -coated film and probe molecule solution fixing at nearly 2 mm, the short distance of which guarantees  
gaseous ROS to diffuse and react with aniline (None, 2013). An increased degradation rate of this probe molecule was seen,  
which can be speculated to be the generation of active carbonate radical ions (Fig. 9). Aqueous  $\text{CO}_3^-$  is believed to be supplied  
540 by partitioning processes from  $\text{CO}_3^-(\text{g})$  that comes from humified dust particles, and its maximum steady-state concentration  
was determined to be  $1.39 \times 10^{-13}$  M for “ $\text{TiO}_2+\text{Air}+\text{CO}_2$ ” system, which is over 1.8 orders of magnitudes higher than that of  
 $\cdot\text{OH}$  for “ $\text{TiO}_2+\text{Air}$ ” system ( $2.15 \times 10^{-15}$  M). This observation matches with the early study where the concentration of  
carbonate radical can be nearly two orders of magnitudes than  $\cdot\text{OH}$  over the water surface (Sulzberger et al., 1997).

Overall, the above results suggest that the photochemistry that involves carbonate ions, more precisely  $\text{CO}_3^-$  radicals,  
545 increases sulfate production. This finding broadens the prevailing view that acceleration of  $\text{SO}_2$  oxidation over the carbonate  
salt is merely due to the favorable neutralization of  $\text{H}_2\text{SO}_4$  over an alkaline surface. To be important, upon irradiation active  
component  $\text{TiO}_2$  in mineral dust produce carbonate radicals in the gas phase when  $\text{CO}_2$  presents, therefore potentially  
promoting sulfate aerosol formation in the atmosphere. Overall, it could be speculated that (bi)carbonate species strengthen  
the oxidative capacity of  $\text{TiO}_2$ -containing dust particles with regard to  $\text{SO}_2$  oxidation.



550

**Figure 9.** The degradation rate of aniline after exposure to air flow under irradiation in the absence (a) and presence (b) of CO<sub>2</sub> over mineral dust proxy particles TiO<sub>2</sub> as function of the reaction time. Reaction conditions: RH = 30%, Light intensity (I) = 30 mW cm<sup>-2</sup>, Total flow rate = 52.5 mL min<sup>-1</sup>.

### 555 3.2.4 Field Measurements of Sulfate and (Bi)carbonate Ions.

Complement field sampling and analysis were further conducted to examine our hypothesis that intermediates CO<sub>3</sub><sup>2-</sup> may play role in secondary sulfate formation in the atmosphere. We first considered the meteorological condition wind speed, which is an important parameter determining whether the local chemical process gains importance in affecting secondary sulfate formation. Meteorological information was collected from the open-access database (<https://www.aqistudy.cn/>). During the sampling period, the wind scale mainly varies from 0 to 1, corresponding to the wind speed ranging from 0 to 1.5 m s<sup>-1</sup> (Fig. S13). All plots shown in Fig. S13 give rise to a statistical wind speed of 0.76 ± 0.73, which represents the weak dispersion of pollutants at low wind speed (not exceeding 2.5 m s<sup>-1</sup>) (Liu et al., 2020a; Witkowska et al., 2016), indicating that local source is a dominant contributor to the air pollution.

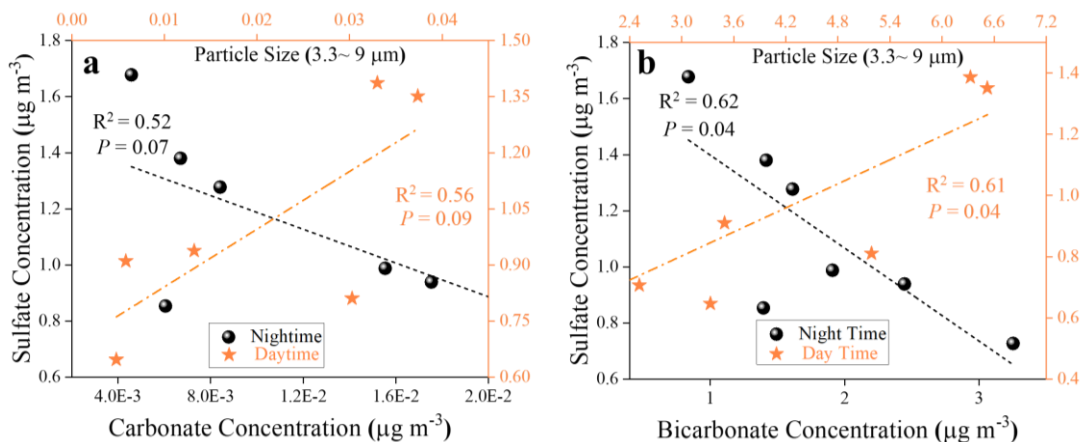
Under stagnant meteorological conditions (wind speed < 1.5 m s<sup>-1</sup>), for the coarse-mode (2.5 μm ~ 10 μm) of sulfate, the heterogeneous reaction of SO<sub>2</sub> on the dust surfaces is thought to be a major contributor (Liu et al., 2017). This correlates to the fact that a large mass fraction of mineral dust is abundant in coarse-mode particulate matter (PM) (Fang et al., 2017; Miller-Schulze et al., 2015), in which TiO<sub>2</sub> was found at mass mixing ratios ranging from 0.1 to 10% depending on the exact location where particles were uplifted (Chen et al., 2012; Hanisch and Crowley, 2003). Therefore, PM with relatively larger size dimensions is expected to contribute to secondary sulfate formation via heterogeneous reactions, which is supported by the recent field study where the carbonate fraction of coarse PM is evidenced to promote secondary sulfate production (Song et al., 2018). Considering this, rather than determining the concentration of water-soluble ions in all stages, special attention is focused on PM collected in stages 1-4 (particles with their dimension ≥ 3.3 μm). As (bi)carbonate ions are known as key precursors in producing CO<sub>3</sub><sup>2-</sup> and accelerating sulfate formation, quantifications of those relevant water-soluble ions were thus conducted (see details in the experimental section and supplementary text 13).

575 We further consider the relationships between sulfate ions and (bi)carbonate ions by means of linear regression analysis. However, under the low wind speed ( $0.76 \pm 0.73$ ), correlation coefficients  $R^2$  obtained for the relationship between bi(carbonate) and sulfate ions are not promising, 0.56 (sulfate vs carbonate) and 0.61 (sulfate vs bicarbonate) for  $PM_{3.3-PM_{9.0}}$  during daytime hours (Fig. 10). A plausible explanation is that in spite of little significance, local primary emission source also brings bias and uncertainty to the correlation results. Shanghai is a coastal city, and sulfate species such as  $K_2SO_4$  and  $Na_2SO_4$  580 from the sea salt contribute to the local sulfate emission as well (Long et al., 2014). On the other hand, this novel  $SO_2$  oxidation channel is yet to be in the infant stage, and only active mineral dust components have been considered in this work whereas other components found in the coarse mode of PM such as organic matter, elemental carbon as well as sea salt (Cheung et al., 2011) are likely to involve this mechanism and alter the response of sulfate yield to  $SO_2$  heterogeneous uptake. In addition, the water-soluble ions determined in these samples may not come from the net contribution of heterogenous reaction processes 585 in absolute daytime and nighttime periods. In other words, some of the collected samples, experiencing heterogeneous reaction that occurs during day(night)-night(day) shifts periods, inevitably being assigned to the sulfate ions measured in separate sampling hours, thus reducing the correlation coefficients.

For those large particles (LP), which refer to the particles with a diameter large than  $9 \mu m$  in this work, sulfate ions show a rather weak or even no correlation to (bi)carbonate ions during the nighttime and day-time hours (Fig. S14). This is likely due 590 to the short lifetime of LP. Generally, the aerosol lifetime is on the order of less than an hour to days (Koelemeijer et al., 2006), highly depending on particle size. For example, the lifetime of  $PM_{10}$  ranges from minutes to hours, and its travel distance, in general, is less than 10 km (Agustine et al., 2018). As a consequence, secondary sulfate formation through chemical reaction over LP is not significant with respect to *in situ* emissions. When PM downsizes to  $2.5 \mu m$ ,  $PM_{2.5}$  has a lifetime prolonged to nearly one day or longer (Wu et al., 2020). Therefore,  $PM_{3.3-PM_{9.0}}$  are expected to have a relatively long lifetime, on the order 595 of several hours on average, which enables the heterogeneous reaction process to become a more important contributor to overall sulfate measured in  $PM_{3.3-PM_{9.0}}$  than that in  $PM_{\geq 9.0}$ . This is supported by our observations where during the daytime hours the correlation coefficients for  $PM_{3.3-PM_{9.0}}$ , i.e. 0.56 (sulfate vs carbonate) and 0.61 (sulfate vs bicarbonate), are higher than that of  $PM_{\geq 9.0}$ , i.e. 0.489 (sulfate vs carbonate) and 0.36 (sulfate vs bicarbonate), respectively. Likewise, higher correlation coefficients are also observed for  $PM_{3.3-PM_{9.0}}$  than  $PM_{\geq 9.0}$  in the sample collected during the nighttime periods.

600 While we note that the correlations between sulfate and (bi)carbonate are not high in this work, ground-based field measurements of sulfate and (bi)carbonate ions shed light on their distinct correlations during the daytime and nighttime hours. In Fig. 10 and Fig. S14, the negative correlations between the mass concentrations of sulfate ions and (bi)carbonate ions are observed in the nighttime hours, consistent with the suppression of sulfate formation by  $CO_2$  in the dark experiments. This is also supported by lab-based observations where  $CO_2$ -derived (bi)carbonate species are demonstrated to suppress sulfate 605 production over two dominant mineral dust components aluminum oxide (Liu et al., 2020c) and silicon dioxide (Fig. S15 and supplementary text 23). Alternatively, while  $CO_2$ -derived (bi)carbonate may slightly affect sulfate accumulation over PM with high water content in the dark scenario, fresh PM is usually dry when emitted into the atmosphere. Due to the competitive

adsorption, the occurrence of suppression of SO<sub>2</sub> adsorption and subsequent sulfate formation is possible in the early emission stage before PM becomes wet, thus contributing to the overall negative correlation.



610

**Figure 10.** Field observation for the relationship between carbonate and sulfate ions during daytime and night-time hours. Linear relationship analyses for measured sulfate ions and estimated carbonate ions (a) and for measured sulfate ions and estimated bicarbonate ions (b) during the daytime and night-time hours, with particle sizes of PM ranging from 3.3 to 9 μm.

615 Instead, positive correlations were seen for those ions within PM sampled during the daytime hours regardless of size ranges and carbonate types (HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>). This matches with the scenarios in which sulfate production upon irradiation in the presence of (bi) carbonate ions is increased over both model and authentic dust particles. Except the case (nighttime period, size larger than 9 μm), most of the significance *P* values for their correlations were smaller than 0.1, specifically with significance *P* values below 0.5 determined for bicarbonate vs sulfate, implying the plausible underlying connection between sulfate and (bi)carbonate ions. In fact, preceding ground-based observations of a highly correlated relationship between Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> water-soluble ions (Wu et al., 2020) during the carbonate-enriched dust storm episodes, together with persistent reports on the significant role of photochemical channels in elevating the sulfate concentration level during the daytime hours (Kim et al., 2017; Wei et al., 2019; Wu et al., 2017) indirectly reflects the possibility of accelerated SO<sub>2</sub> oxidation triggered by photo-generated active intermediates associated with carbonate species.

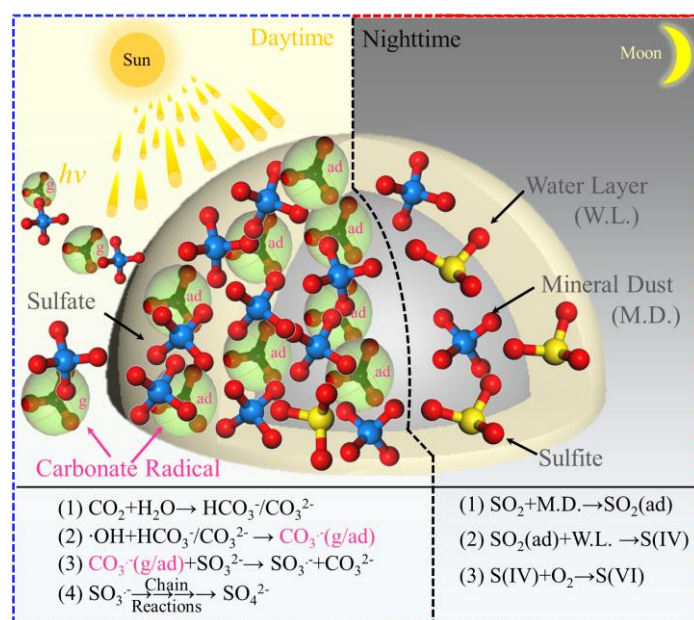
620 Overall, this is the first time that relationships between those ions are explored separately in these two periods. Taken together, carbonate radical is likely to promote sulfate production in the atmosphere during daytime hours. Detailed and systematic SO<sub>2</sub> oxidation channel triggered by CO<sub>3</sub><sup>-</sup> needs further investigations to enable a better interpretation of correlations between these inorganic ions at the given meteorological conditions of sampling and physicochemical properties of PM.

#### 4. Conclusion

630 On the basis of the experimental and theoretical results derived from this work, we for the first time propose a novel reaction channel for fast SO<sub>2</sub> oxidation over mineral dust particles due to the formation of carbonate radical ions. A schematic chart for



the sulfate formation in the presence of carbonate radicals upon solar light or bi(carbonate) ions under dark conditions is summarized and elucidated in Fig. 11. During the nighttime hours at 298 K (ambient temperature) CO<sub>2</sub>-derived (bi)carbonate species are prone to have a slightly negative effect on sulfate formation presumably due to the competitive adsorption between CO<sub>2</sub> and SO<sub>2</sub>. For alkaline carbonate salt, it favors sulfate formation through the neutralization process. On the other hand, in the daytime, both CO<sub>2</sub>-derived (bi)carbonate species and carbonate salt work as the precursor of CO<sub>3</sub><sup>•-</sup>, which promotes sulfate formation. Especially, uptake coefficients for carbonate salt containing mineral dust can be increased by 17 times, which is more pronounced than the increase due to the neutralization regime in the dark condition. Consistent with the findings reported in the early studies (Chen et al., 2021; Dupart et al., 2012), we speculate the production of gas-phase CO<sub>3</sub><sup>•-</sup> ions when mineral dust particles are irradiated in the presence of CO<sub>2</sub> (atmospherically relevant concentration 400 ppm). This observation potentially implies that the increased sulfate yield in part comes from increased external secondary sulfate aerosol triggered by CO<sub>3</sub><sup>•-</sup> (g).



**Figure 11.** Schematic of the sulfate formation in the presence and absence of carbonate radical. Noting that g and ad represent gas-phase and adsorbed carbonate radical ions, respectively.

By means of ROS scavenger experiments, direct observation of carbonate radical using NTAS analysis, oxygen isotope assay, ESR measurement as well as DFT calculations, CO<sub>3</sub><sup>•-</sup>-initiated S(IV) oxidation involving single electron transfer process are elucidated. While carbonate radical ions are mainly responsible for rapid sulfate formation, superoxide radical ions are likely to serve as a minor pathway over TiO<sub>2</sub>-containing mineral dust particles (not shown on the schematic chart to direct readers' focus on CO<sub>3</sub><sup>•-</sup>). In addition, a weak correlation between sulfate ions and (bi)carbonate ions observed for PM<sub>3.3</sub>-PM<sub>9.0</sub> in this work reasonably correlates to non-chemical primary emission and the complicated nature of CO<sub>3</sub><sup>•-</sup> regime of sulfate

production in the atmosphere. Nonetheless, complement field sampling of ambient PM and analysis of sulfate and (bi)carbonate ions in this study unfold their distinct correlations during the daytime and nighttime hours, these two tendencies of which agree with the experimental observations.

655 In this work, only atmospheric secondary sulfate formation was considered, whereas the oxidation of primary organic species yet has not been investigated. In fact, carbonate radical ions are prone to rapidly react with electron-rich organics amines (Stenman et al., 2003; Yan et al., 2019) as well as phenol (Busset et al., 2007; Xiong et al., 2016), and it may potentially serve as the key oxidants that drive the fast formation of SOA in the atmosphere. Besides, observation of strengthened photochemistry launched by carbonate radicals suggests that such chemistry may be amplified on atmospherically relevant reactions that occur in cloud droplets as well as fog water where they often contain hydroxyl radicals and water-soluble  
660 (bi)carbonate ions.

To be important, gas-phase carbonate radical ions are speculated to be formed in the atmospherically relevant CO<sub>2</sub> concentration (400 ppm) when mineral dust is irradiated. This will help the formation of external sulfate aerosol formation. Since both sulfate aerosol and CO<sub>2</sub> are well known to regulate the radiation budget and solar energy balance on the earth (Cheung et al., 2011; Möller, 1964), coupled with the CO<sub>2</sub>-initiated promoted sulfate pathway found here, their overall influence  
665 on the global climate needs further investigation. Therefore, our study highlights the necessity for a comprehensive understanding of the CO<sub>3</sub><sup>-</sup> relevant chemistry in the underlying impacts of fine PM concentration, human health, and climate. All these assumptions need to be investigated in further detail. This study provides the indication that carbonate radical not only plays a role as a marginal intermediate in tropospheric anion chemistry but also as a strong oxidant for surfacial processing of trace gas in the atmosphere.

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*Data availability.* The data that support the results are available from the corresponding author upon request.

*Author contributions.* Y.L., Y.D. and L.Z. initially proposed the idea; Y.L. and Y.D. together designed the experiments, and Y.L. performed the most of the experiments; J.L. performed DFT calculations; Y.L., X.Z. and T.W. contributed to field samplings and data analysis; K.L.,  
675 K.G., A.B., I.N., Q.G., X.Z., C.G., and L.Z. provided suggestions on the experiments and paper writing; All authors wrote the manuscript.

*Competing interests.* The authors declare that they have no conflict of interest.

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- Abou-Ghanem M, Oliynyk AO, Chen ZH, Matchett LC, McGrath DT, Katz MJ, et al.: Significant Variability in the Photocatalytic Activity of Natural Titanium-Containing Minerals: Implications for Understanding and Predicting Atmospheric Mineral Dust Photochemistry. *Environ. Sci. Technol.*, 54,13509-13516, <https://doi.org/10.1021/acs.est.0c05861>, 2020.
- 690 Augustine I, Yulinawati H, Gunawan D, Suswanto E: Potential impact of particulate matter less than 10 micron (PM<sub>10</sub>) to ambient air quality of Jakarta and Palembang. *Iop C Ser Earth Env*, 106,012057, <https://doi.org/10.1088/1755-1315/106/1/012057>, 2018.
- Al-Hosney HA, Grassian VH: Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study. *Phys. Chem. Chem. Phys.*, 7,1266-1276, <https://doi.org/10.1039/b417872f>, 2005.
- 695 Al-Salihi AM, Mohammed TH: The effect of dust storms on some meteorological elements over Baghdad , Iraq: Study Cases. *IOSR Journal of Applied Physics*, 7,Ver. II PP 01-07, <https://doi.org/10.9790/4861-07220107>, 2015.
- Balachandran U, Eror NG: Raman-Spectra Of Titanium-Dioxide. *J. Solid State Chem.*, 42,276-282, [https://doi.org/10.1016/0022-4596\(82\)90006-8](https://doi.org/10.1016/0022-4596(82)90006-8), 1982.
- Baltrusaitis J, Schuttlefield J, Zeitler E, Grassian VH: Carbon dioxide adsorption on oxide nanoparticle surfaces. *Chem. Eng. J.*, 170,471-481, <https://doi.org/10.1016/j.cej.2010.12.041>, 2011.
- Bao H, Yu S, Tong DQ: Massive volcanic SO<sub>2</sub> oxidation and sulphate aerosol deposition in Cenozoic North America. *Nature*, 465,909-912, <https://doi.org/10.1038/nature09100>, 2010.
- Bauer SE, Koch D: Impact of heterogeneous sulfate formation at mineral dust surfaces on aerosol loads and radiative forcing in the Goddard Institute for Space Studies general circulation model. *J. Geophys. Res.*, 110,D17202, <https://doi.org/10.1029/2005jd005870>, 2005.
- 705 Behrman EJ: Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation Comment. *J. Environ. Sci. China*, 64,352-352, <https://doi.org/10.1016/j.jes.2018.02.008>, 2018.
- Beig G, Brasseur GP: Model of tropospheric ion composition: A first attempt. *J. Geophys. Res.*, 105,22671-22684, <https://doi.org/10.1029/2000JD900119>, 2000.
- 710 Bhattacharya A, Amitabha D, Mandal PC: Carbonate radical induced polymerisation of pyrrole: A steady state and flash photolysis study. *J. Radioanal Nucl. Ch.*, 230,91-95, <https://doi.org/10.1007/BF02387452>, 1998.
- Bisby RH, Johnson SA, Parker AW, Tavender SM: Time-resolved resonance Raman spectroscopy of the carbonate radical. *J. Chem. Soc. Faraday Trans.*, 94,2069-2072, <https://doi.org/10.1039/A801239C>, 1998.
- Busset C, Mazellier P, Sarakha M, De Laat J: Photochemical generation of carbonate radicals and their reactivity with phenol. *J. Photoch. Photobio. A*, 185,127-132, <https://doi.org/10.1016/j.jphotochem.2006.04.045>, 2007.
- 715 Buxton GV, Greenstock CL, Helman WP, Ross AB: Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\cdot\text{OH}/\cdot\text{O}^-$  in aqueous solution. *J. Phys. Chem. Ref. Data*, 17,513-886, <https://doi.org/10.1063/1.555805>, 2009.
- Cao JJ, Lee SC, Zhang XY, Chow JC, An ZS, Ho KF, et al.: Characterization of airborne carbonate over a site near Asian dust source regions during spring 2002 and its climatic and environmental significance. *J. Geophys. Res.*, 110,1-8, <https://doi.org/10.1029/2004JD005244>, 2005.
- 720 Chameides WL, Davis DD: The Free-Radical chemistry of cloud droplets and its impact upon the composition of rain. *J. Geophys Res. Oceans*, 87,4863-4877, <https://doi.org/10.1029/JC087iC07p04863>, 1982.
- Chandrasekaran K, Thomas JK: Photochemical reduction of carbonate to formaldehyde on TiO<sub>2</sub> powder. *Chem. Phys. Lett.*, 99,7-10, [https://doi.org/10.1016/0009-2614\(83\)80259-0](https://doi.org/10.1016/0009-2614(83)80259-0), 1983.
- 725 Chen HH, Nanayakkara CE, Grassian VH: Titanium Dioxide Photocatalysis in Atmospheric Chemistry. *Chem. Rev.*, 112,5919-5948, <https://doi.org/10.1021/cr3002092>, 2012.
- Chen Y, Tong SR, Li WR, Liu YP, Tan F, Ge MF, et al.: Photocatalytic Oxidation of SO<sub>2</sub> by TiO<sub>2</sub>: Aerosol Formation and the Key Role of Gaseous Reactive Oxygen Species. *Environ. Sci. Technol.*, 55,9784-9793, <https://doi.org/10.1021/acs.est.1c01608>, 2021.
- 730 Cheung K, Daher N, Kam W, Shafer MM, Ning Z, Schauer JJ, et al.: Spatial and temporal variation of chemical composition and mass closure of ambient coarse particulate matter (PM<sub>10-2.5</sub>) in the Los Angeles area. *Atmos. Environ.*, 45,2651-2662, <https://doi.org/10.1016/j.atmosenv.2011.02.066>, 2011.

- 735 Cope VW, Chen S-N, Hoffman MZ: Intermediates in the photochemistry of carbonate-amine complexes of cobalt(III) carbonate(-) radicals and the aquocarbonate complex. *J. Am. Chem. Soc.*, 95,3116-3121, <https://doi.org/10.1021/ja00791a005>, 1973
- Csavana J, Field J, Felix O, Corral-Avitia AY, Saez AE, Betterton EA: Effect of wind speed and relative humidity on atmospheric dust concentrations in semi-arid climates. *Sci.Total. Environ.*, 487,82-90, <https://doi.org/10.1016/j.scitotenv.2014.03.138>, 2014.
- 740 Cwiertny DM, Young MA, Grassian VH: Chemistry and photochemistry of mineral dust aerosol. *Annu. Rev. Phys. Chem.*, 59,27-51, <https://doi.org/10.1146/annurev.physchem.59.032607.093630>, 2008.
- Das TN: Reactivity and role of SO<sub>5</sub>- radical in aqueous medium chain oxidation of sulfite to sulfate and atmospheric sulfuric acid generation. *J. Phys. Chem. A*, 105,9142-9155, <https://doi.org/10.1021/jp011255h>, 2001.
- 745 Deng Y, Liu Y, Wang T, Cheng H, Feng Y, Yang Y, et al.: Photochemical reaction of CO<sub>2</sub> on atmospheric mineral dusts. *Atmos. Environ.*, 223,117222.1-117222.10, <https://doi.org/10.1016/j.atmosenv.2019.117222>, 2020.
- Dong XY, Fu JS, Huang K, Tong D, Zhuang GS: Model development of dust emission and heterogeneous chemistry within the Community Multiscale Air Quality modeling system and its application over East Asia. *Atmos. Chem. Phys.*, 16,8157-8180, <https://doi.org/10.5194/acp-16-8157-2016>, 2016.
- 750 Dupart Y, King SM, Nekat B, Nowak A, Wiedensohler A, Herrmann H, et al.: Mineral dust photochemistry induces nucleation events in the presence of SO<sub>2</sub>. *Proc. Natl. Acad. Sci. USA*, 109,20842-20847, <https://doi.org/10.1073/pnas.1212297109>, 2012.
- Duran A, Monteagudo JM, Martin IS, Merino S, Chen X, Shi X: Solar photo-degradation of aniline with rGO/TiO<sub>2</sub> composites and persulfate. *Sci.Total. Environ.*, 697,134086-, <https://doi.org/10.1016/j.scitotenv.2019.134086>, 2019.
- 755 El Zein A, Romanias MN, Bedjanian Y: Kinetics and Products of Heterogeneous Reaction of HONO with Fe<sub>2</sub>O<sub>3</sub> and Arizona Test Dust. *Environ. Sci. Technol.*, 47,6325-6331, <https://doi.org/10.1021/es400794c>, 2013.
- Ervens B, George C, Williams JE, Buxton GV, Salmon GA, Bydder M, et al.: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application. *J. Geophys. Res.*, 108,4426, <https://doi.org/10.1029/2002jd002202>, 2003.
- 760 Fang T, Guo H, Zeng L, Verma V, Nenes A, Weber RJ: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity. *Environ. Sci. Technol.*, 51,2611-2620, <https://doi.org/10.1021/acs.est.6b06151>, 2017.
- Fang X, Liu Y, Kejian, Tao W, Yue D, Yiqing F, et al.: Atmospheric Nitrate Formation through Oxidation by carbonate radical. *ACS Earth Space Chem.*, 5,1801-1811, <https://doi.org/10.1021/acsearthspacechem.1c00169>, 2021.
- 765 Feng T, Bei NF, Zhao SY, Wu JR, Li X, Zhang T, et al.: Wintertime nitrate formation during haze days in the Guanzhong basin, China: A case study. *Environ. Pollut.*, 243,1057-1067, <https://doi.org/10.1016/j.envpol.2018.09.069>, 2018.
- Ferrer-Sueta G, Vitturi D, Batinić-Haberle I, Fridovich I, Goldstein S, Czapski G, et al.: Reactions of manganese porphyrins with peroxyxynitrite and carbonate radical anion. *J. Biol. Chem.*, 278,27432-27438, <https://doi.org/10.1074/jbc.M213302200>, 2003.
- 770 Gankanda A, Coddens EM, Zhang YP, Cwiertny DM, Grassian VH: Sulfate formation catalyzed by coal fly ash, mineral dust and iron(III) oxide: variable influence of temperature and light. *Environmental Science-Processes & Impacts*, 18,1484-1491, <https://doi.org/10.1039/c6em00430j>, 2016.
- Ge WD, Liu JF, Yi K, Xu JY, Zhang YZ, Hu XR, et al.: Influence of atmospheric in-cloud aqueous-phase chemistry on the global simulation of SO<sub>2</sub> in CESM2. *Atmos. Chem. Phys.*, 21,16093-16120, <https://doi.org/10.5194/acp-21-16093-2021>, 2021.
- 775 Ghalei M, Ma J, Schmidhammer U, Vandenborre J, Fattahi M, Mostafavi M: Picosecond pulse radiolysis of highly concentrated carbonate solutions. *J. Phys. Chem. B*, 120,2434-2439, <https://doi.org/10.1021/acs.jpcc.5b12405>, 2016.
- Goldstein S, Czapski G, Lind J, Merényi G: Carbonate radical ion is the only observable intermediate in the reaction of peroxyxynitrite with CO<sub>2</sub>. *Chem. Res. Toxicol.*, 14,1273-1276, <https://doi.org/10.1021/tx0100845>, 2001.
- 780 Graedel TE, Weschler CJ: Chemistry within Aqueous Atmospheric Aerosols And Raindrops. *J. Geophys. Res.*, 19,505-539, <https://doi.org/10.1029/RG019i004p00505>, 1981.
- Hanisch F, Crowley JN: Ozone decomposition on Saharan dust: an experimental investigation. *Atmos. Chem. Phys. Discuss.*, 3,119-130, <https://doi.org/10.5194/acp-3-119-2003>, 2003.

- Hayon E, Treinin A, Wilf J: Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite-bisulfite-pyrosulfite systems.  $\text{SO}_2^-$ ,  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{SO}_5^-$  radicals. *J. Am. Chem. Soc.*, 94,47-57, <https://doi.org/10.1021/ja00756a009>, 1972.
- 785 He J, Xu HH, Balasubramanian R, Chan CY, Wang CJ: Comparison of  $\text{NO}_2$  and  $\text{SO}_2$  Measurements Using Different Passive Samplers in Tropical Environment. *Aerosol Air Qual. Res.*, 14,355-363, <https://doi.org/10.4209/aaqr.2013.02.0055>, 2014.
- Herrmann H, Ervens B, Jacobi HW, Wolke R, Nowacki P, Zellner R: CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry. *J. Atmos. Chem.*, 36,231-284, <https://doi.org/10.1023/A:1006318622743>, 2000.
- 790 Hossain MD, Huang Y, Yu TH, Goddard Iii WA, Luo Z: Reaction mechanism and kinetics for  $\text{CO}_2$  reduction on nickel single atom catalysts from quantum mechanics. *Nat. Commun.*, 11,2256, <https://doi.org/10.1038/s41467-020-16119-6>, 2020.
- Huang HL, Chao W, Lin JJM: Kinetics of a Criegee intermediate that would survive high humidity and may oxidize atmospheric  $\text{SO}_2$ . *Proc. Natl. Acad. Sci. USA*, 112,10857-10862, <https://doi.org/10.1073/pnas.1513149112>, 2015.
- Huang JP, Mabury SA: Steady-state concentrations of carbonate radicals in field waters. *Environ. Toxicol. Chem.*, 19,2181-2188, <https://doi.org/10.1002/etc.5620190906>, 2000.
- 795 Huang L, An JY, Koo B, Yarwood G, Yan RS, Wang YJ, et al.: Sulfate formation during heavy winter haze events and the potential contribution from heterogeneous  $\text{SO}_2 + \text{NO}_2$  reactions in the Yangtze River Delta region, China. *Atmos. Chem. Phys.*, 19,14311-14328, <https://doi.org/10.5194/acp-19-14311-2019>, 2019.
- Huang X, Song Y, Zhao C, Li MM, Zhu T, Zhang Q, et al.: Pathways of sulfate enhancement by natural and anthropogenic mineral aerosols in China. *J. Geophys. Res.*, 119,14165-14179, <https://doi.org/10.1002/2014jd022301>, 2014.
- 800 Hung HM, Hoffmann MR: Oxidation of Gas-Phase  $\text{SO}_2$  on the Surfaces of Acidic Microdroplets: Implications for Sulfate and Sulfate Radical Anion Formation in the Atmospheric Liquid Phase. *Environ. Sci. Technol.*, 49,13768-13776, <https://doi.org/10.1021/acs.est.5b01658>, 2015.
- Hung HM, Hsu MN, Hoffmann MR: Quantification of  $\text{SO}_2$  oxidation on interfacial surfaces of acidic micro-droplets: Implication for ambient sulfate formation. *Environ. Sci. Technol.*, 52,9079-9086, <https://doi.org/10.1021/acs.est.8b01391>,
- 805 2018.
- Itahashi S, Yamaji K, Chatani S, Hayami H: Refinement of Modeled Aqueous-Phase Sulfate Production via the Fe- and Mn-Catalyzed Oxidation Pathway. *Atmosphere*, 9,132, <https://doi.org/10.3390/atmos9040132>, 2018.
- Kerminen VM, Hillamo R, Teinilä K, Pakkanen T, Allegrini I, Sparapani R: Ion balances of size-resolved tropospheric aerosol samples: implications for the acidity and atmospheric processing of aerosols. *Atmos. Environ.*, 35,5255-5265, [https://doi.org/10.1016/S1352-2310\(01\)00345-4](https://doi.org/10.1016/S1352-2310(01)00345-4), 2001.
- 810 Kim H, Zhang Q, Heo J: Influence of Intense secondary aerosol formation and long range transport on aerosol chemistry and properties in the Seoul Metropolitan Area during spring time Results from KORUS-AQ. *Atmos. Chem. Phys. Discuss.*, 18,7149-7168, <https://doi.org/10.5194/acp-2017-947>, 2017.
- Koelemeijer R, Homan CD, Matthijsen J: Comparison of spatial and temporal variations of aerosol optical thickness and particulate matter over Europe. *Atmos. Environ.*, 40,5304-5315, <https://doi.org/10.1016/j.atmosenv.2006.04.044>, 2006.
- 815 Kong LD, Zhao X, Sun ZY, Yang YW, Fu HB, Zhang SC, et al.: The effects of nitrate on the heterogeneous uptake of sulfur dioxide on hematite. *Atmos. Chem. Phys.*, 14,9451-9467, <https://doi.org/10.5194/acp-14-9451-2014>, 2014.
- Lehtipalo K, Rondo L, Kontkanen J, Schobesberger S, Jokinen T, Sarnela N, et al.: The effect of acid-base clustering and ions on the growth of atmospheric nano-particles. *Nat. Commun.*, 7,11594, <https://doi.org/10.1038/ncomms11594>, 2016.
- 820 Li BQ, Ma XY, Li QS, Chen WZ, Deng J, Li GX, et al.: Factor affecting the role of radicals contribution at different wavelengths, degradation pathways and toxicity during UV-LED/chlorine process. *Chem. Eng. J.*, 392,124552, <https://doi.org/10.1016/j.cej.2020.124552>, 2020.
- Li KJ, Kong LD, Zhanzakova A, Tong SY, Shen JD, Wang T, et al.: Heterogeneous conversion of  $\text{SO}_2$  on nano  $\alpha\text{-Fe}_2\text{O}_3$ : the effects of morphology, light illumination and relative humidity. *Environ. Sci. Nano.*, 6,1838-1851, <https://doi.org/10.1039/c9en00097f>, 2019.
- 825 Li L, Chen ZM, Zhang YH, Zhu T, Li S, Li HJ, et al.: Heterogeneous oxidation of sulfur dioxide by ozone on the surface of sodium chloride and its mixtures with other components. *J. Geophys. Res.*, 112,D18301, <https://doi.org/10.1029/2006jd008207>, 2007.
- Li WJ, Shao LY, Shi ZB, Chen JM, Yang LX, Yuan Q, et al.: Mixing state and hygroscopicity of dust and haze particles before leaving Asian continent. *J. Geophys. Res.*, 119,1044-1059, <https://doi.org/10.1002/2013jd021003>, 2014.
- 830 Li X, Yu J, Jaroniec M: Hierarchical photocatalysts. *Chem. Soc. Rev.*, 45,2603-2636, <https://doi.org/10.1039/c5cs00838g>, 2016.

- Li XR, Wang LL, Ji DS, Wen TX, Pan YP, Sun Y, et al.: Characterization of the size-segregated water-soluble inorganic ions in the Jing-Jin-Ji urban agglomeration: Spatial/temporal variability, size distribution and sources. *Atmos. Environ.*, 77,250-259, <https://doi.org/10.1016/j.atmosenv.2013.03.042>, 2013.
- 835 Liao LF, Lien CF, Shieh DL, Chen MT, Lin JL: FTIR study of adsorption and photoassisted oxygen isotopic exchange of carbon monoxide, carbon dioxide, carbonate, and formate on TiO<sub>2</sub>. *J. Phys. Chem. B*, 106,11240-11245, <https://doi.org/10.1021/jp0211988>, 2002.
- 840 Liu JR, Ning A, Liu L, Wang HX, Kurten T, Zhang XH: A pH dependent sulfate formation mechanism caused by hypochlorous acid in the marine atmosphere. *Sci.Total. Environ.*, 787,147551, <https://doi.org/10.1016/j.scitotenv.2021.147551>, 2021.
- Liu P, Ye C, Xue C, Zhang C, Sun X: Formation mechanisms of atmospheric nitrate and sulfate during the winter haze pollution periods in Beijing: gas-phase, heterogeneous and aqueous-phase chemistry. *Atmos. Chem. Phys.*, 20,4153–4165, <https://doi.org/10.5194/acp-20-4153-2020>, 2020a.
- 845 Liu TT, Hong YW, Li MR, Xu LL, Chen JS, Bian YH, et al.: Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of southeastern China: analysis of a typical photochemical episode by an observation-based model. *Atmos. Chem. Phys.*, 22,2173-2190, <https://doi.org/10.5194/acp-22-2173-2022>, 2022a.
- Liu TY, Abbatt JPD: Oxidation of sulfur dioxide by nitrogen dioxide accelerated at the interface of deliquesced aerosol particles. *Nat. Chem.*, 13,1173+, <https://doi.org/10.1038/s41557-021-00777-0>, 2021.
- 850 Liu TY, Clegg SL, Abbatt JPD: Fast oxidation of sulfur dioxide by hydrogen peroxide in deliquesced aerosol particles. *Proc. Natl. Acad. Sci. USA*, 117,1354-1359, <https://doi.org/10.1073/pnas.1916401117>, 2020b.
- Liu XC, Tang WJ, Chen HN, Guo JM, Tripathee L, Huang J: Observational Study of Ground-Level Ozone in the Desert Atmosphere. *B. Environ. Contam. Tox.*, 108,219-224, <https://doi.org/10.1007/s00128-021-03444-9>, 2022b.
- Liu Y, Wang T, Fang X, Deng Y, Cheng H, Fu H, et al.: Impact of greenhouse gas CO<sub>2</sub> on the heterogeneous reaction of SO<sub>2</sub> on Alpha-Al<sub>2</sub>O<sub>3</sub>. *Chinese Chem. Lett.*, 31,2712-2716, <https://doi.org/10.1016/j.ccllet.2020.04.037>, 2020c.
- 855 Liu YQ, He XX, Duan XD, Fu YS, Dionysiou DD: Photochemical degradation of oxytetracycline: Influence of pH and role of carbonate radical. *Chem. Eng. J.*, 276,113-121, <https://doi.org/10.1016/j.cej.2015.04.048>, 2015.
- Liu ZR, Xie YZ, Hu B, Wen TX, Xin JY, Li XR, et al.: Size-resolved aerosol water-soluble ions during the summer and winter seasons in Beijing: Formation mechanisms of secondary inorganic aerosols. *Chemosphere*, 183,119-131, <https://doi.org/10.1016/j.chemosphere.2017.05.095>, 2017.
- 860 Long SL, Zeng JR, Li Y, Bao LM, Cao LL, Liu K, et al.: Characteristics of secondary inorganic aerosol and sulfate species in size-fractionated aerosol particles in Shanghai. *J. Environ. Sci. China*, 26,1040-1051, [https://doi.org/10.1016/S1001-0742\(13\)60521-5](https://doi.org/10.1016/S1001-0742(13)60521-5), 2014.
- Mahajan AS, Li QY, Inamdar S, Ram K, Badia A, Saiz-Lopez A: Modelling the impacts of iodine chemistry on the northern Indian Ocean marine boundary layer. *Atmos. Chem. Phys.*, 21,8437-8454, <https://doi.org/10.5194/acp-21-8437-2021>, 2021.
- 865 McNaughton CS, Clarke AD, Kapustin V, Shinzuka Y, Howell SG, Anderson BE, et al.: Observations of heterogeneous reactions between Asian pollution and mineral dust over the eastern north Pacific during INTEX-B. *Atmos. Chem. Phys.*, 9,8283-8308, <https://doi.org/10.5194/acpd-9-8469-2009>, 2009.
- Merouani S, Hamdaoui O, Saoudi F, Chiha M, Petrier C: Influence of bicarbonate and carbonate ions on sonochemical degradation of Rhodamine B in aqueous phase. *J. Hazard Mater.*, 175,593-599, <https://doi.org/10.1016/j.jhazmat.2009.10.046>, 2010.
- 870 Miller-Schulze JP, Shafer M, Schauer JJ, Heo J, Solomon PA, Lantz J, et al.: Seasonal contribution of mineral dust and other major components to particulate matter at two remote sites in Central Asia. *Atmos. Environ.*, 119,11-20, <https://doi.org/10.1016/j.atmosenv.2015.07.011>, 2015.
- 875 Mogili PK, Kleiber PD, Young MA, Grassian VH: Heterogeneous uptake of ozone on reactive components of mineral dust aerosol: an environmental aerosol reaction chamber study. *J. Phys. Chem. A*, 110,13799-807, <https://doi.org/10.1021/jp063620g>, 2006.
- Möller F: On the influence of changes in the CO<sub>2</sub> concentration in air on the radiation balance of the Earth's surface and on the climate. *J. Geophys. Res.*, 68,3877-3886, <https://doi.org/10.1029/JZ068i013p03877>, 1964.
- 880 Najafpour N, Afshin H, Firoozabadi B: Dust concentration over a semi-arid region: Parametric study and establishment of new empirical models. *Atmos. Res.*, 243,104995, <https://doi.org/10.1016/j.atmosres.2020.104995>, 2020.

- Nanayakkara CE, Larish WA, Grassian VH: Titanium dioxide nanoparticle surface reactivity with atmospheric gases, CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub>: roles of surface hydroxyl groups and adsorbed water in the formation and stability of adsorbed products. *J. Phys. Chem. C*, 118,23011-23021, <https://doi.org/10.1021/jp504402z>, 2014.
- 885 Neta P, Huie RE: Free-radical chemistry of sulfite. *Environ. Health Persp.*, 64,209-217, <https://doi.org/10.1289/ehp.8564209>, 1985.
- Nie W, Wang T, Xue LK, Ding AJ, Wang XF, Gao XM, et al.: Asian dust storm observed at a rural mountain site in southern China: chemical evolution and heterogeneous photochemistry. *Atmos. Chem. Phys.*, 12,11985-11995, <https://doi.org/10.5194/acp-12-11985-2012>, 2012.
- 890 None: In-Situ Characterization of Heterogeneous Catalysts. *Focus on Catal.*, 2013,8, [https://doi.org/10.1016/S1351-4180\(13\)70477-X](https://doi.org/10.1016/S1351-4180(13)70477-X), 2013.
- Palmer CD, Cherry JA: Geochemical Evolution of Groundwater in Sequences of Sedimentary-Rocks. *J. Hydrol.*, 75,27-65, [https://doi.org/10.1016/0022-1694\(84\)90045-3](https://doi.org/10.1016/0022-1694(84)90045-3), 1984.
- Peters SJ, Ewing GE: Water on Salt: An Infrared Study of Adsorbed H<sub>2</sub>O on NaCl (100) under Ambient Conditions. *J. Phys. Chem. B*, 101,10880-10886, <https://doi.org/10.1021/jp972810b>, 1997.
- 895 Rodriguez JA, Hanson J, Chupas P: In-Situ Characterization of Heterogeneous Catalysts. *Focus on Catal.*, 2013,8, <https://doi.org/10.1002/9781118355923>, 2013.
- Rubasinghege G, Elzey S, Baltrusaitis J, Jayaweera PM, Grassian VH: Reactions on Atmospheric Dust Particles: Surface Photochemistry and Size-Dependent Nanoscale Redox Chemistry. *J. Phys. Chem. Lett.*, 1,1729-1737, <https://doi.org/10.1021/jz100371d>, 2010.
- 900 Salama SB, Natarajan C, Nogami G, Kennedy JH: The role of reducing agent in oxidation reactions of water on illuminated TiO<sub>2</sub> electrodes. *J. Electrochem. Soc.*, 142,806-810, <https://doi.org/10.1149/1.2048539>, 1995.
- Samuni A, Goldstein S, Russo A, Mitchell JB, Krishna MC, Neta P: Kinetics and mechanism of hydroxyl radical and OH-adduct radical reactions with nitroxides and with their hydroxylamines. *J. Am. Chem. Soc.*, 124,8719-8724, <https://doi.org/10.1021/ja017587h>, 2002.
- 905 Shafirovich V, Dourandin A, Huang W, Geacintov NE: The carbonate radical is a site-selective oxidizing agent of guanine in double-stranded oligonucleotides. *J. Biol. Chem.*, 276,24621-24626, <https://doi.org/10.1074/jbc.M101131200>, 2001.
- Shang J, Li J, Zhu T: Heterogeneous reaction of SO<sub>2</sub> on TiO<sub>2</sub> particles. *Sci. China Chem.*, 53,2637-2643, <https://doi.org/10.1007/s11426-010-4160-3>, 2010.
- 910 Song X, Li J, Shao L, Zheng Q, Zhang D: Inorganic ion chemistry of local particulate matter in a populated city of North China at light, medium, and severe pollution levels. *Sci.Total. Environ.*, 650,566-574, <https://doi.org/10.1016/j.scitotenv.2018.09.033>, 2018.
- Stenman D, Carlsson M, Jonsson M, Reitberger T: Reactivity of the carbonate radical anion towards carbohydrate and lignin model compounds. *J. Wood Chem. Technol.*, 23,47-69, <https://doi.org/10.1081/Wct-120018615>, 2003.
- 915 Stevenson DS, Zhao A, Naik V, O'Connor FM, Tilmes S, Zeng G, et al.: Trends in global tropospheric hydroxyl radical and methane lifetime since 1850 from AerChemMIP. *Atmos. Chem. Phys.*, 20,12905-12920, <https://doi.org/10.5194/acp-20-12905-2020>, 2020.
- Stone R: Air pollution. Counting the cost of London's killer smog. *Science*, 298,2106-2107, <https://doi.org/10.2307/3833025>, 2002.
- 920 Su H, Cheng Y, Zheng G, Wei C, Mu Q, Zheng B, et al.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Sci. Adv.*, 2,e1601530, <https://doi.org/10.1126/sciadv.1601530>, 2016.
- Su WG, Zhang J, Feng ZC, Chen T, Ying PL, Li C: Surface phases of TiO<sub>2</sub> nanoparticles studied by UV Raman spectroscopy and FT-IR spectroscopy. *J. Phys. Chem. C*, 112,7710-7716, <https://doi.org/10.1021/jp7118422>, 2008.
- Sullivan RC, Guazzotti SA, Sodeman DA, Prather KA: Direct observations of the atmospheric processing of Asian mineral dust. *Atmos. Chem. Phys.*, 7,1213-1236, <https://doi.org/10.5194/acp-7-1213-2007>, 2007.
- 925 Sulzberger B, Canonica S, Egli T, Giger W, Klausen J, Gunten Uv: Oxidative transformations of contaminants in natural and in technical systems. *Chimia*, 51,900-907, <https://doi.org/10.1051/epjconf/20101105003>, 1997.
- Sun P, Tyree C, Huang CH: Inactivation of Escherichia coli, Bacteriophage MS2, and Bacillus Spores under UV/H<sub>2</sub>O<sub>2</sub> and UV/Peroxydisulfate Advanced Disinfection Conditions. *Environ. Sci. Technol.*, 50,4448-4458, <https://doi.org/10.1021/acs.est.5b06097>, 2016.

- 930 Ta WQ, Xiao Z, Qu JJ, Yang GS, Wang T: Characteristics of dust particles from the desert/Gobi area of northwestern China during dust-storm periods. *Environmental Geology*, 43,667-679, <https://doi.org/10.1007/s00254-002-0673-1>, 2003.
- Tang MJ, Cziczo DJ, Grassian VH: Interactions of Water with Mineral Dust Aerosol: Water Adsorption, Hygroscopicity, Cloud Condensation, and Ice Nucleation. *Chem. Rev.*, 116,4205-4259, <https://doi.org/10.1021/acs.chemrev.5b00529>, 2016.
- 935 Wang XM, Huang X, Zuo CY, Hu HY: Kinetics of quinoline degradation by O<sub>3</sub>/UV in aqueous phase. *Chemosphere*, 55,733-741, <https://doi.org/10.1016/j.chemosphere.2003.11.019>, 2004.
- Wang Y, Wan Q, Meng W, Liao F: Long-term impacts of aerosols on precipitation and lightning over the Pearl River Delta megacity area in China. *Atmos. Chem. Phys.*, 11,12421-12436, <https://doi.org/10.5194/acp-11-12421-2011>, 2011.
- Wang Y, Zhuang GS, Tang AH, Yuan H, Sun YL, Chen SA, et al.: The ion chemistry and the source of PM<sub>2.5</sub> aerosol in Beijing. *Atmos. Environ.*, 39,3771-3784, <https://doi.org/10.1016/j.atmosenv.2005.03.013>, 2005.
- 940 Wang YX, Zhang QQ, Jiang JK, Zhou W, Wang BY, He KB, et al.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models. *J. Geophys. Res.*, 119,10425-10440, <https://doi.org/10.1002/2013jd021426>, 2014.
- Watanabe K, Yang L, Nakamura S, Otani T, Mori K: Volcanic Impact of Nishinoshima Eruptions in Summer 2020 on the Atmosphere over Central Japan: Results from Airborne Measurements of Aerosol and Trace Gases. *Sola*, 17,109-112, <https://doi.org/10.2151/sola.2021-017>, 2020.
- 945 Wei J, Yu H, Wang Y, Verma V: Complexation of Iron and Copper in Ambient Particulate Matter and Its Effect on the Oxidative Potential Measured in a Surrogate Lung Fluid. *Environ. Sci. Technol.*, 53,1661-1671, <https://doi.org/10.1021/acs.est.8b05731>, 2019.
- Witkowska A, Lewandowska AU, Saniewska D, Falkowska LM: Effect of agriculture and vegetation on carbonaceous aerosol concentrations (PM<sub>2.5</sub> and PM<sub>10</sub>) in Puszcza Borecka National Nature Reserve (Poland). *Air Qual Atmos Hlth*, 9,761-773, <https://doi.org/10.1007/s11869-015-0378-8>, 2016.
- 950 Wojnarovits L, Toth T, Takacs E: Rate constants of carbonate radical anion reactions with molecules of environmental interest in aqueous solution: A review. *Sci.Total. Environ.*, 717,137219, <https://doi.org/10.1016/j.scitotenv.2020.137219>, 2020.
- Wu C, Zhang S, Wang G, Lv S, Li D, Liu L, et al.: Efficient Heterogeneous Formation of Ammonium Nitrate on the Saline Mineral Particle Surface in the Atmosphere of East Asia during Dust Storm Periods. *Environ. Sci. Technol.*, 54,15622-15630, <https://doi.org/10.1021/acs.est.0c04544>, 2020.
- 955 Wu D, Fan Z, Ge X, Meng Y, Xia J, Liu G, et al.: Chemical and Light Extinction Characteristics of Atmospheric Aerosols in Suburban Nanjing, China. *Atmosphere*, 8,149, <https://doi.org/10.3390/atmos8080149>, 2017.
- Wu LY, Tong SR, Wang WG, Ge MF: Effects of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on calcium carbonate. *Atmos. Chem. Phys.*, 11,6593-6605, <https://doi.org/10.5194/acp-11-6593-2011>, 2011.
- 960 Wu Q, Tang X, Kong L, Dao X, Lu MM, Liu ZR, et al.: Evaluation and Bias Correction of the Secondary Inorganic Aerosol Modeling over North China Plain in Autumn and Winter. *Atmosphere*, 12,578, <https://doi.org/10.3390/atmos12050578>, 2021.
- Xia DM, Zhang XR, Chen JW, Tong SR, Xie HB, Wang ZY, et al.: Heterogeneous Formation of HONO Catalyzed by CO<sub>2</sub>. *Environ. Sci. Technol.*, 55,12215-12222, <https://doi.org/10.1021/acs.est.1c02706>, 2021.
- 965 Xiong XQ, Zhang X, Xu YM: Incorporative Effect of Pt and Na<sub>2</sub>CO<sub>3</sub> on TiO<sub>2</sub>-Photocatalyzed Degradation of Phenol in Water. *J. Phys. Chem. C*, 120,25689-25696, <https://doi.org/10.1021/acs.jpcc.6b07951>, 2016.
- Yan JF, Peng JL, Lai LD, Ji FZ, Zhang YH, Lai B, et al.: Activation CuFe<sub>2</sub>O<sub>4</sub> by Hydroxylamine for Oxidation of Antibiotic Sulfamethoxazole. *Environ. Sci. Technol.*, 52,14302-14310, <https://doi.org/10.1021/acs.est.8b03340>, 2018.
- 970 Yan SW, Liu YJ, Lian LS, Li R, Ma JZ, Zhou HX, et al.: Photochemical formation of carbonate radical and its reaction with dissolved organic matters. *Water Res.*, 161,288-296, <https://doi.org/10.1016/j.watres.2019.06.002>, 2019.
- Yermakov AN, Purmal AP: Iron-catalyzed oxidation of sulfite: From established results to a new understanding. *Prog. React. Kinet. Mec.*, 28,189-255, <https://doi.org/10.3184/007967403103165503>, 2003.
- 975 Yu T, Zhao D, Song X, Zhu T: NO<sub>2</sub>-initiated multiphase oxidation of SO<sub>2</sub> by O<sub>2</sub> on CaCO<sub>3</sub> particles. *Atmos. Chem. Phys.*, 18,6679-6689, <https://doi.org/10.5194/acp-18-6679-2018>, 2018.
- Yu ZC, Jang MS, Kim S, Bae C, Koo BY, Beardsley R, et al.: Simulating the Impact of Long-Range-Transported Asian Mineral Dust on the Formation of Sulfate and Nitrate during the KORUS-AQ Campaign. *ACS Earth Space Chem.*, 4,1039-1049, <https://doi.org/10.1021/acsearthspacechem.0c00074>, 2020.



- 980 Zhang GS, He XX, Nadagouda MN, O'Shea KE, Dionysiou DD: The effect of basic pH and carbonate ion on the mechanism of photocatalytic destruction of cylindrospermopsin. *Water Res.*, 73,353-361, <https://doi.org/10.1016/j.watres.2015.01.011>, 2015a.
- Zhang R, Wang G, Song G, Zamora ML, Qi Y, Yun L, et al.: Formation of urban fine particulate matter. *Chem. Rev.*, 115,3803-3855, <https://doi.org/10.1021/acs.chemrev.5b00067>, 2015b.
- 985 Zhang T, Cao JJ, Tie XX, Shen ZX, Liu SX, Ding H, et al.: Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources. *Atmos. Res.*, 102,110-119, <https://doi.org/10.1016/j.atmosres.2011.06.014>, 2011.
- Zhang Y, Carmichael GR: The role of mineral aerosol in tropospheric chemistry in East Asia - A model study. *J. Appl. Meteorol. Clim.*, 38,353-366, [https://doi.org/10.1175/1520-0450\(1999\)038<0353:Tromai>2.0.Co;2](https://doi.org/10.1175/1520-0450(1999)038<0353:Tromai>2.0.Co;2), 1999.
- 990 Zheng B, Zhang Q, Zhang Y, He KB, Wang K, Zheng GJ, et al.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in north China. *Atmos. Chem. Phys.*, 15,2031-2049, <https://doi.org/10.5194/acp-15-2031-2015>, 2015.