Response Letter

Review 3:

In this manuscript, Liu and co-authors examine SO_2 uptake by carbonate-containing mineral dust, and explore the potential role of carbonate radical-mediated processes in enhancing sulfate formation. The premise of the article is interesting and worthwhile; at the same time, the manuscript in its current form is very difficult to follow and the experimental conditions are sufficiently different from those in the ambient atmosphere that the reported conclusions require much more in the way of discussion and qualification of limitations than is currently provided. Given these concerns, I think that the manuscript requires significant (major) revisions prior to publication. I hope that the authors find my comments useful; I have aimed to be constructive throughout.

Author general reply:

We are very appreciative of your valuable suggestions, which enable us to improve the manuscript. According to your comments, we have noticed shortcomings mentioned in the comment list, especially for the aspect of atmospheric chemical relevance and the way of discussion. We improved the structure of the manuscript, and revised the original manuscript to clarify more convincing explanations to the readers, allowing them to follow the string of reasoning. We carefully consider all your comments posted to the previous version of the manuscript, and the detailed point-by-point revisions are presented as follows.

d1—Writing style

The manuscript is extremely difficult to follow, primarily because data and results text are largely in the supplemental information. As written, the supplemental reads like a point-by-point response to reviewers rather than a clear and concise summary of supporting information. As a result of this separation of information, important points in the text are quickly glossed over. For example, to me, Figure S3 seems to show that there is substantial production of sulfate at the surface of TiO_2–CaO upon illumination. Isn't it possible that the difference between $CaCO_3$/CaO is related to other factors? Specific surface area differences? Hygroscopicity? Solubility? In my opinion, the manuscript requires significant reorganizational effort to address this issue, since I (as a relative expert in the field) am finding it difficult to be sure that I am convinced by the data and the results as presented.

Response to Q: We carefully consider your suggestion regarding writing style and have placed our great efforts to change the layout of supporting information. Some supporting information of significance to support our statement has been moved to the main text. In addition, we have reorganized the data demonstration to convince readers of our results.

The CaO particles applied in our experiment are commercially available from the SINOPHARM company, and their BET surface area is determined to be 2.54 m^2 g^{-1} in the literature (Tang et al., 2016b). On the other hand, the BET surface area for $CaCO_3$ particles in this study was determined to be 1.35 m^2 g^{-1} (Quantachrome). Hence, $CaCO_3$ particles disadvantage in BET surface area compared to CaO, and it would not be the factor that promotes sulfate yield.

We compared the hygroscopicity of $CaCO_3$ and CaO by specifying RHs that allow them to form a monolayer of water. A prior study shows that a monolayer of water formed on the surface of $CaCO_3$ particles when RH is over 52 % (Li et al., 2010). On the other hand, RH of 27 % enables CaO to form a monolayer of water (Goodman et al., 2001). While those results are collected from different literature and a bias may come from different measurement systems. However, this evident gap leads us to conclude that CaO exhibits a stronger hygroscopicity than $CaCO_3$ does. Following this, we believe at least the hygroscopicity is not the force to produce more sulfate over TiO_2+$CaCO_3$ relative to TiO_2+CaO upon irradiation. Additionally, this comparison also gives an explanation for substantial sulfate production at the surface of TiO_2+CaO under illumination due to its strong hygroscopicity.

We obtained solubility information from “CRC CHEMISTRY and PHYSICS HANDBOOK (97th Edition, 2016)”, where calcium carbonate (calcite) is 6.6 mg/100 g H_2O (Section “Physical Constants of Inorganic Compounds”, page 4-53). However, the specific solubility of CaO is not available in this handbook or literature we have been searching for so far. Nevertheless, calcium oxide (CaO) is likely to have a higher solubility than calcium carbonate since it can react with H_2O to form $Ca(OH)_2$ and form a saturated solution (160 mg/100 g H_2O) (Chrzan, 1987).

Collectively, we show that $CaCO_3$ shows humble physical properties including BET surface area, hygroscopicity as well as solubility relative to CaO while TiO_2+$CaCO_3$ particles have higher sulfate production than TiO_2+CaO particles do under irradiation. Together with the observation of sulfate production over TiO_2/$CaCO_3$/TiO_2+$CaCO_3$, in combination with the analysis of sulfur species over TiO_2+CaO/TiO_2+$CaCO_3$, active intermediates derived from TiO_2+$CaCO_3$ are speculated to account for the increased sulfate production, as we stated in the main text. We have put the relevant discussion in the main text to solidify our argument.

2—General comments and concerns

Why would the authors expect that carbonate radical would promote sulfate oxidation more than hydroxyl radical produced by TiO_2? Perhaps I am missing something here, but if the idea is that carbonate is scavenging OH to produce carbonate radical, then why would the overall S(IV) to S(VI) conversion be any different?

Response to Q: Thanks for your thoughtful question. DFT calculations produce theoretical evidence that carbonate radical ions decrease the energy barrier for $SO_3^{\cdot-}$formation, and its reaction with SO_3^{2-} is thus faster than that with hydroxyl radical (Fig. 8 b and c). Considering this, CO_2 and carbonate ions severs as a precursor of $CO_3^{\cdot-}$, and thus increase sulfate production. Therefore, overall S(IV) to S(VI) conversion mediated by carbonate radicals is faster than that by hydroxyl radicals.

The experiments shown in the main experimental figure (Figure 1) were performed at almost 10 ppm SO_2. The mismatch between these experimental conditions and those relevant for the actual atmosphere warrants discussion. What challenges do the authors anticipate when using these results to make predictions about behaviour under more realistic conditions?

Response to Q: We understand your concern about the gap between the lab and realistic conditions regarding SO_2 concentration. Therefore, we conducted the SO_2 concentration dependence experiments, and the reaction order of SO_2 in “TiO_2+$CaCO_3$+SO_2” reaction system in the range of 400-20000 ppb is determined to be 0.80 (**Fig. R1.**), indicating that the uptake coefficients obtained at ppm level of SO_2 would somewhat overestimate the real one obtained at atmosphere relevant SO_2 concentration (ppb level of SO_2), and the uptake coefficients should be calibrated before being employed for model simulation for sulfate.

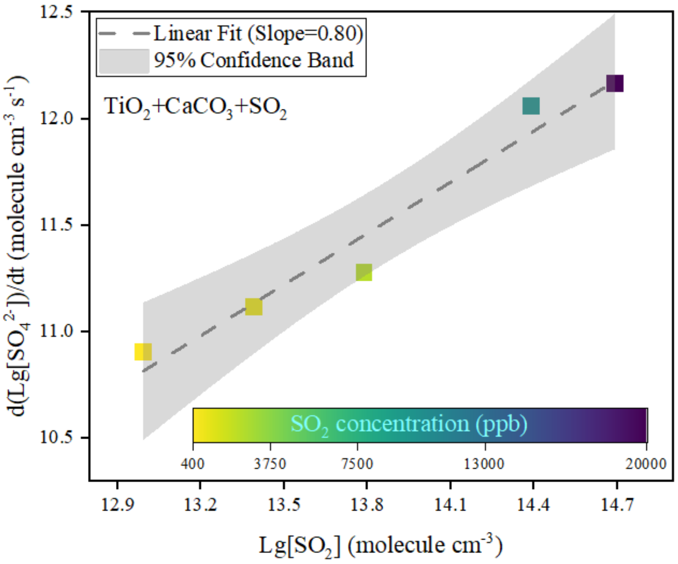

Fig. R1. Reaction order determination. The Lg-Lg curve of the sulfate production rate of TiO_2 mixed with $CaCO_3$ (50 wt. %) upon varied SO_2 concentration exposure (400-20000 ppb, RH = 30 %) under irradiation (30 mW cm^{-2}) plotted against the concentrations of SO_2 molecules exposed.

Abstract

L18—Is there direct evidence for the proposed mechanistic pathways?

Response to Q: We have removed this statement from the abstract.

L20—Is there direct evidence for production of gas-phase carbonate radical?

Response to Q: We have changed our statement in a conservative way; that is “Importantly, upon irradiation mineral dust particles are speculated to produce gas-phase carbonate radical ions when the CO_2 of atmospherically relevant concentration presents”

Introduction

L29—These references seem somewhat out of date.

Response to Q: We have updated the citations.

L31—What does “unique chemical activity” mean? Are nanometer-sized particles relevant for dust chemistry?

Response to Q: This term means that the chemical activity of water-adsorbed particles is higher than that of dry particles since radical-initiated reactions occur over humidified particles.

Strong nucleation events are initiated by the strong dust events, and a high concentration of nano-sized particles along with aerosol nucleation is observed (Dupart et al., 2012; Guo et al., 2014; Sun et al., 2014).

Nano-sized particles are important constituents found in the atmospheric aerosol, with lifetimes of up to several days and can be transported over thousands of kilometers (Tang et al., 2016a), which is a major contributor to ambient air pollution (Whiteside and Herndon, 2018) and employed for understanding heterogeneous sulfate production within dust chemistry (Ma et al., 2019; Shang et al., 2010; Wang et al., 2018).

However, we want to avoid to arise the undesired dispute due to the above argument, thus have changed to a conservative expression by replacing "nanometer-sized" with "humidified"; that is "However when atmospheric chemical reactions occur over humified particles at ambient conditions."

L33—Are these references for the aquatic environment? Or for the atmosphere? What does "over the water surface" mean?
Response to Q: While these references refer to an aquatic environment, the media of which can be also found in the atmosphere, e.g. cloud/fog drops and aerosol liquid water.

Water surface refers to the surface of aquatic/aqueous media.

L37—Higher selectivity than what? What selectivity does the carbonate radical have?
Response to Q: This term is redundant here, and we thus removed it from the current manuscript.

L40—Phenol is presumably only one organic compound that is degraded by carbonate radical—why was this one chosen to highlight here?
Response to Q: Thanks for your suggestion. We have removed specific highlight of an organic compound from the current manuscript.

L41—Are porphyrins relevant in an atmospheric context? Is this rate constant relevant? Higher than what?
Response to Q: Porphyrin is observed in the atmosphere (Hodgson and Baker, 1969) and is known as a functional pigment of biology (Kay and Gratzel, 1993).

While rate constant in the unit of M^{-1} s^{-1} is usually applied for describing the rate of reactions that occur in aqueous media, the order of 10^9 stands for a fast reaction process, somehow reflecting the great oxidative potential of $CO_3^{\cdot -}$ in the atmospherically relevant aqueous media, e.g. fog, cloud, and aerosol water.

We revised the term "higher" to "high" to fulfill the context.

L42—"great oxidation capability that may trigger atmospherically relevant chemical reactions"—this is vague/unclear.
Response to Q: We change to "great oxidation capability that may trigger atmospherically relevant chemical reactions, e.g. secondary inorganic species formation."

L44—These references seem out of date as well. Are there any tropospheric modelling-type papers (CAPRAM? GAMMA?) that provide carbonate radical rate constants?

Response to Q: Thanks for your suggestion. We have updated citations, adding recent modeling works in the current main text.

Ge and coworkers investigated the effect of in-cloud aqueous-phase chemistry on SO_2 oxidation using Community Earth System Model version 2 (CESM2), the improved run of which incorporates aqueous $CO_3^{\cdot-}$ chemistry to estimate sulfate production (Ge et al., 2021). It is noted that the most of aqueous $CO_3^{\cdot-}$ chemistry and corresponding rate constants applied in the study are derived from many early works (before the year 2000). Another work using CAPRAM modeling (Herrmann et al., 2000) also reported the production and the loss flux of the carbonate radical anion in the troposphere, and a series of sulfur chemistry have been considered.

However, some of the rate constants in the above two works are much lower than that are derived from theoretical calculations in our study. Besides, this estimation does not incorporate the role of mineral dust particles, which can significantly increase the production of $CO_3^{\cdot-}$, as suggested in this study and our early work (Fang et al., 2021).

L53—Where does this underproduction occur? Under what sorts of conditions? Also, what about other sulfate production pathways, e.g., the DMS chemistry being explored in Timothy Bertram's group?

Response to Q: In this work, sulfate underproduction during the dust storm episode is the scenario we are mainly concerned about (Dong et al., 2016; Huang et al., 2014; Yu et al., 2020). During the dust storm period, mineral dust components are abundant and the photochemical process under low RH conditions can also produce substantial sulfate. A more detailed discussion is as follows:

Long-term field studies have suggested underlying enhancements of sulfate production due to mineral aerosols and found a high consistency between sulfate and calcium in Asia dust particles (Arimoto et al., 2004; Li et al., 2013; Wang et al., 2012). Besides, it is believed that the evident increase of Ca^{2+} in Beijing and Tangshan relates to dust storm events (Li et al., 2013; Wang et al., 2005). Many early studies have shown that carbonate-containing particles with high alkalinity are prevalent in the troposphere during dust storm episodes (Abou-Ghanem et al., 2020; Li et al., 2014; Tang et al., 2016a). TiO_2 was found at mass mixing ratios ranging from 0.1 to 10 % depending on the exact location where dust particles were uplifted (Chen et al., 2012; Hanisch and Crowley, 2003).

The photochemical process that occurs during dust storm events can alter atmospheric constituents (Liu et al., 2022). By employing Atmospheric Mineral Aerosol Reaction (AMAR) model, Jang's group highlights the significant contribution of heterogenous photochemical reaction that occurs over dust particles to overall sulfate formation (Yu and Jang, 2018; Yu et al., 2017), accounting for 79-93 % of total sulfate production, while the sulfate production that comes from the gas-phase oxidation and aqueous-phase oxidation or heterogeneous reactions in the dark case accounts for the residual of overall sulfate yield (Yu et al., 2017).

Besides, during dust storm episodes, the air mass is usually in low relative humidity, reported to be 25-35 % (Al-Salihi and Mohammed, 2015) (Csavina et al., 2014; Najafpour et al., 2020).

Given above, a detailed revision of the main text presents as follows:
"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; Yu et al., 2020), where an evident increase of 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., 2016a) 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 photochemical process is able to alter atmospheric constituents (Liu et al., 2022). Consequently, there are unknown heterogeneous reaction pathways of significance and previously unconsidered promoters that have great potential to accelerate sulfate formation in the dust storm relevant conditions."

Dimethylsulfoniopropionate (DMS) chemistry is illustrated to play important role in sulfate formation over the marine atmosphere (Kilgour et al., 2022; Mayer et al., 2020). Once emitted into the marine atmosphere, DMS is oxidized by gas-phase hydroxyl radical and halogen radicals to form lower volatility products, which can contribute to new particle formation after further oxidation to sulfate (Novak and Bertram, 2020). However, herein we mainly focus on the continental sulfate production over dust particles.

L55–60—"unconsidered heterogeneous mechanism is very likely to narrow the gap …" — to me, this seems speculative, if only one aerosol study is cited (Zheng 2015). Is it certain that heterogeneous pathways will close this gap?
Response to Q: Thanks for your suggestion. We have cited more references here; that is, "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 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)."

L66—Carbonate salt is enriched over what? What does "authentic dust aerosol" mean here?
Response to Q: As carbonate salt is one of the key constituents in mineral dust particles, reported to reach over 10 % wt. of Asian dust particles. Instead of being enriched, the word "abundant" is more appropriate in the context. Besides, we attempt to express the mineral dust aerosol found in the atmosphere using authentic mineral dust. This term, however, seems to be controversial and odd to readers. Taken together, we thus correct this sentence to "Carbonate salt is abundant in mineral dust particles".

L70—How does carbonate alkalinity "favour sulfate formation"? What exactly does this mean?
Response to Q: It is believed that the increase in alkalinity leads to an increase in SO_2 adsorption and subsequent oxidation of SO_2 to sulfate in the presence of oxidants. We have noted that the expression may cause difficulties for readers to follow, and we thus have corrected this expression in the current manuscript; that is "…intrinsic alkalinity, which buffers aerosol acidity and increases SO_2 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., 2018a)."

L71—Where is this information provided in the literature (that CO_2/carbonate produces carbonate radical)?
Response to Q: Thanks for your reminder, and we have supplied the reference accordingly.
For reference (Ervens et al., 2003), the relevant information is visible on page 15, section "4.5.7. Carbonate Chemistry".
For reference (Graedel and Weschler, 1981b), the relevant information is visible on page 510, section "3. Inorganic Carbon Chemistry".

L73—What does "fast SO_2 oxidation" mean here? Why is it likely to be a driving force?
Response to Q: Acceleration of SO_2 oxidation. In our early study (Fang et al., 2021), we provide experimental evidence that carbonate radicals produced over the mineral dust surface are able to promote NO_2 oxidation to secondary nitrate formation. Therefore, we tentatively believe that this active intermediate can serve as a driving force to accelerate SO_2 oxidation as well.

Here, we note that some information is missing to bridge "acceleration of SO_2 oxidation" and "a driving force", and we thus correct the sentence as follows:
"Our early study shows that carbonate radicals serve as an active oxidant to accelerate NO_2 oxidation over mineral dust particles, allowing us to consider the possibility that fast heterogeneous SO_2 oxidation can be triggered by this active intermediate as well."

L76—What does "extend their ability" mean?
Response to Q: "have the ability", and we have revised the expression in the current manuscript.

Methods
General—As I noted at the beginning of my comments, is there a reason why all of the techniques, etc., are in the supplement? It would be very helpful to have information regarding the samples (which "authentic dust" samples and which "authentic simulants"? What does "authentic" mean here?) as well as the experimental set-up in the main text. A reference for the carbonate radical measurement strategy is needed, as well (aniline as probe molecule).
Response to Q: We understand your concern about the inconvenience of reading flow when relevant techniques and information were placed in SI.

However, it would be tedious if we put all of the technical descriptions in the main text. Maybe cover 9-10 pages in length in the main text.

Considering this, we put part of the technique characterizations, which you have emphasized in the comments, into the section of "Experimental Methods". Supporting information on authentic dust and authentic simulants as well as experiment set-up have been moved into the main text. The term "authentic" refers to the "real", i.e. what is found in the atmosphere.

We have cited relevant references in the current manuscript.

Field Observations—Where is the department? Was sulfate determined in all size fractions? More information is needed here. Citations for the "ionization balance approach" are needed. Which sulfate is expected to be non-water-soluble? Were the authors concerned about S(IV) to S(VI) conversion in the sample extracts? How was this addressed? Some of this information may be in the supplement, but as a reader, I do not want to have to shift back and forth between documents to find it.

Response to Q: More geographical information for sampling is available in our early study (Liu et al., 2020b) and we have mentioned the information and cited the reference. We have added relevant information to the main text.

We only considered the coarse mode of sulfate since the heterogeneous reaction of SO_2 on the dust surfaces is believed 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-model particulate matter (PM) (Fang et al., 2017; Miller-Schulze et al., 2015). Sulfate and (bi)carbonate in PM (3.3 μm ⩽ Size ⩽ 9 μm) were our major focus. We also determined the concentrations of sulfate and (bi)carbonate in PM (Size ⩾ 9 μm) and performed a correlation analysis for comparison.

Citations for the "ionization balance approach" are now available in the current submission.

To our humble knowledge, non-water-soluble sulfate (non-WSS) is not usually considered in field observation probably due to its low content found in the particulate matter (Canelli and Husain, 1982). Therefore, we do not pay much attention to these species.

The content of S(IV) species is low relative to S(VI) species. In the early study, Dixon and Aasen determined both S(IV) including sulfite and HMS as well as S(VI) species in collected PM (Dixon and Aasen, 1999). They extracted the sample using methanol mixed with a preserving solution to prevent the unexpected conversion of S(IV) to S(VI). In all their considered sample, nearly 1/3 of samples are beyond detection limit or not detected. For others, S(IV) species are on the order of ng m^{-3} whereas S(VI) species are on the order of μg m^{-3}, thus giving rise to more than two orders of magnitudes gap between S(IV) species and S(VI) species. This is consistent with observation where S(IV) is not detectable in the rain water due to a rather low sulfite concentration, which is beyond the detection limit of ion chromatography (Jin et al., 2020). The above results suggest the content of S(IV) is much lower than that of S(VI).

Hence, while we did not employ preservation procedures to prohibit the conversion of S(IV) to S(VI), we believe the unexpected S(IV) oxidation during the sampling/extraction steps gives a slight influence on determining S(VI) species.

Results

L102—At this point, no information about the mineral dust proxies has been presented. How are their properties "consistent with earlier studies"?

Response to Q: While we note that straightforward data shown in the main text would help readers to follow the conclusion we draw, it may distract readers from focusing on the main discussion flow instead. After all, they are just supplementary data to support our statement and the limited information we attempt to expand to discuss. For the characterization of mineral dust proxies, kindly you may understand our concern, allowing us to reserve the original arrangement. We have also updated relevant information in the supporting information to support our argument in the main text.

In the supporting information, BET surface area, crystal phase, and structure have been characterized by using N_2 adsorption-desorption isotherm, XRD as well as Raman spectra. Our results match well with the early works.

L105—What is the experiment being discussed here? What kind of experimental conditions were employed? “Upon irradiation” of what? What were the SO_2 concentrations here? What was the humidity?

Response to Q: We have clarified the experimental conditions in the main text; that is “Upon solar irradiation under RH of 30 % SO_2/N_2+O_2 flow ($[SO_2] = 2.21\times10^{14}$ molecules cm^{-3}), the sulfate production on TiO_2+CaCO_3 mixture particles (50 wt. % TiO_2 and 50 wt. % $CaCO_3$), measured by IC, is significantly enhanced by 7 times and 23 times compared to that of TiO_2 and $CaCO_3$ (Fig. 2a), respectively.”.

L106—How are the authors distinguishing between S(VI) and S(IV) in these experiments? What quality assurance/quality control-type experiments were performed? How did the authors prevent S(IV) to S(VI) oxidation during extraction/prior to analysis? Was S(IV) quantified in these experiments? I would assume that it would have been present in all extracts … why are these data not shown in Figure 1?

Response to Q: For *in situ* DRIFTs technique, distinguishing S(VI) from S(IV) species over TiO_2 particles relies upon the position of the IR bands according to the assignment of previous literature (Nanayakkara et al., 2014; Wu et al., 2011).

For the IC technique, distinguishing S(VI) from S(IV) species relies on the retention time of the sulfur species. These two species can be distinguished by employing the optimized measurement method.

Our group accumulates a lot of measurement experience for *in situ* DRIFTs and IC techniques, especially for determining the concentration of S(IV) and S(VI) species. We have already benchmarked the measurement methodologies for each technique that has been applied for heterogeneous reaction studies (Liu et al., 2020b; Liu et al., 2020c; Wang et al., 2020a; Wang et al., 2020b; Wang et al., 2018).

In the experiments where we conducted heterogeneous reactions of SO_2 over TiO_2, $CaCO_3$, and TiO_2+CaCO_3 (50 wt. % TiO_2 and 50 wt. % $CaCO_3$) particles, we applied isopropanol to avoid unexpected conversion of S(IV) to S(VI).

We have put the quantified S(IV) results in the current submission. Sulfite species is only observable in $CaCO_3$ particles because it has no photoactivity while sulfite species is negligible in TiO_2 and TiO_2+CaCO_3 particles.

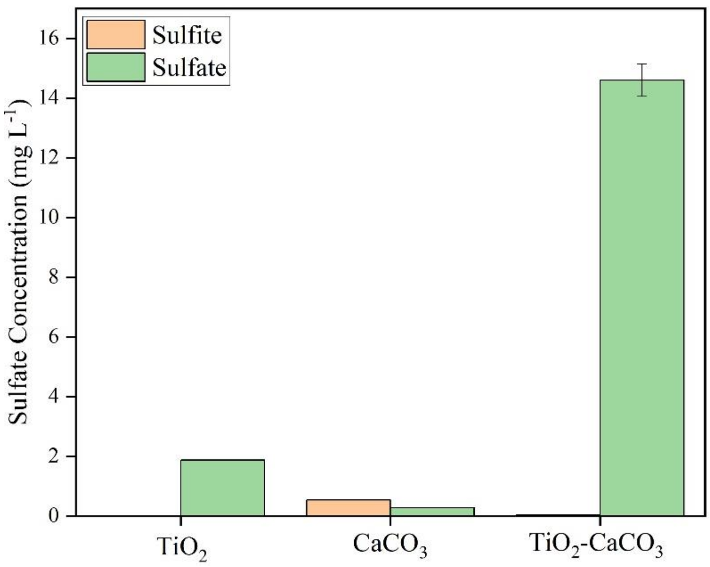

Fig. R2. Sulfate or sulfite concentrations quantified by IC on mineral dust particles after exposure to gaseous SO_2 under irradiation for 60 min. Reaction conditions: RH = 30 %, Light intensity (I) = 30 mW cm^{-2}, Total flow rate = 52.5 mL min^{-1} and SO_2 = 2.21×10^{14} molecules cm^{-3}.

L109—What does "it remains unclear for the role of carbonate salt …" mean?

Response to Q: Thanks for your kinder reminder. Our point is that a great discrepancy regarding sulfate production is observed between dark and irradiation experiments in which we conducted heterogeneous reactions of SO_2 over TiO_2+$CaCO_3$ particles. Therefore, $CaCO_3$ may play a different role in the dark and irradiation cases. However, this set of experiments is not solid enough to justify our speculation that carbonate salt plays a distinct role in these two scenarios.

We note that suddenly jumping into the argument "unclear for the role of carbonate salt" would be hard for readers to follow. We have corrected the original sentence to "Great discrepancies in sulfate production over TiO_2+$CaCO_3$ particles between dark and irradiation experiments suggest that carbonate salt may play a different role in these two scenarios."

L110—"There is a prevailing view" — reference? What does this statement mean?

Response to Q: In the current manuscript, we have revised this sentence to "The alkalinity of carbonate salt favors SO_2 adsorption (Al-Hosney and Grassian, 2005; Yu et al., 2018b) and photo-oxidation process assisted by TiO_2 particles can strengthen the oxidation efficiency of adsorbed SO_2 (Chen et al., 2012; Shang et al., 2010), which is a plausible explanation for rapid SO_2 oxidation over TiO_2+$CaCO_3$ particles."

L113—These data (CaO/$CaCO_3$ comparison) need to be presented clearly in the main text, since they are part of the authors' overall argument. "as they are likely to present similar physical and chemical properties" — what surface pH do they present? Are they comparable? Do they have similar hygroscopicities?

Response to Q: Thanks for your suggestion, and we have moved this data to the main text.

Our early study measured the pH of leaching solution of 0.625 mg $CaCO_3$ + 0.625 mg TiO_2 and

0.625 mg CaO + 0.625 mg TiO_2, and they are 9.27 and 11.26, respectively (Fang et al., 2021). On this basis, we could deduce that the surface pH of CaO is higher than $CaCO_3$.

You have raised the hygroscopicity issue in the early comment. For your convenience, we copy the answer, as follows:
"We compared the hygroscopicity of $CaCO_3$ and CaO by the specifying RHs that allow them to form a monolayer of water. A prior study shows that a monolayer of water formed on the surface of $CaCO_3$ particles when RH is over 52 % (Li et al., 2010). In contrast, RH of 27 % enables CaO to form a monolayer of water (Goodman et al., 2001). While those results are collected from different literature and the bias may come from different measurement systems. However, this evident gap leads us to conclude that CaO exhibits a stronger hygroscopicity than $CaCO_3$ does."

L118—I find this use of "theoretical" and "experimental" confusing.
Response to Q: While they are not commonly-used expression in the publications, we have defined them in the legend of Figure 2; that is "the production of sulfur species in theoretical TiO_2+$CaCO_3$ mixtures refers to 0.5 × K-M bands of sulfur species of TiO_2 + 0.5 × K-M bands of sulfur species of $CaCO_3$ while that for experimental TiO_2+$CaCO_3$ mixtures refers to 1 × K-M bands of sulfur species of TiO_2+$CaCO_3$ mixtures (wt./wt. = 50/50).

To clarify these terms, allowing readers to follow, we have revised the original sentence in the main text to "The "theoretical" is calculated based on the DRIFTS experiments of pristine TiO_2 and $CaCO_3$ particles through a simple linear superposition whereas the "experimental" is directly derived from DRIFTS experiment of TiO_2+$CaCO_3$ (wt./wt. = 50/50) particles."

L125—Again, these data need to be presented in the text. The need to flip back and forth between the main text and the supplementary information is very frustrating for the reader.
How were these uptake coefficients determined? Are they surface-area scaled? How does this pathway compare to other heterogeneous SO_2 oxidation mechanisms? This statement (that this is "likely a potential driving force to trigger fast SO_2 oxidation …"seems like an overreach to me in the absence of supporting calculations.
Response to Q: Thanks for your suggestion and we have put relevant data in the main text. Detailed methodology for uptake coefficient calculation is available in the experimental section.

These uptake coefficients are derived from dividing the observed sulfate production rate by a total number of surface collisions per unit time (Z), and Z is scaled by surface area.

Since we do not do the calculation of the relative contribution of this pathway to overall sulfate production or make a comparison with other pathways, we employed quite a mild tone to express that "the photochemical pathway associated with carbonate species is likely a potential driving force to increase sulfate production in the atmosphere."

Figure 1—How many trials were performed here? Why was this DRIFTS experiment not performed for TiO_2/CaO, to account for any changes in speciation after extraction? To me, the data presented in Figure 1b–c don't necessarily show that $CaCO_3$ is enhancing the photochemistry over that of

TiO_2 alone via carbonate radical … how does the surface area of these mixed films compare to that of the single-component films? What is the surface water content of each? Is it possible that the surface reaction environment is different? What is the S(VI)/S(IV) ratio under each condition? What does "yield" mean in the caption?
Response to Q: No less than three times unless the first two trails are highly consistent.

IC data we supplied in the supporting information (previous version) is complement evidence to support our argument in the main text. Together with DRIFTS analysis of sulfur species over TiO_2, $CaCO_3$, TiO_2+$CaCO_3$, in combination with IC analysis of sulfur species over TiO_2+CaO and TiO_2+$CaCO_3$, carbonate ions are speculated to play a different role in enhancing sulfate production in dark and irradiation cases. Therefore, we do not further perform the DRIFTS experiments for TiO_2/CaO particles.

In our experiments, we applied grounded TiO_2, grounded $CaCO_3$ as well as grounded TiO_2+$CaCO_3$ particles for all experiments and BET measurements. Our BET measurement results show that the BET surface area of grounded TiO_2 (50 % wt.) +$CaCO_3$ (50 % wt.) particles (23.52 m^2 g^{-1}) is slightly lower than the averaged surface area of TiO_2 (56.44 m^2 g^{-1}) and $CaCO_3$ particles (1.25 m^2 g^{-1}). Therefore, a total exposed surface area of 50 % wt. TiO_2 + 50 % wt. $CaCO_3$ is almost comparable to that sum of 50 % of TiO_2 and 50 % of $CaCO_3$, and surface area is not the fundamental force to increase sulfate production.

Similarly, we specify RHs that enable to form the monolayer water over various particles to compare hygroscopicity among different types of particles. For TiO_2, over 11 % of RH can have the particles form monolayer water (Haghighatmamaghani et al., 2019) while a monolayer of water forms on the surface of $CaCO_3$ particles when RH is over 52 % (Li et al., 2010). On this basis, increased water content due to the presence of $CaCO_3$ is the not reason that increases the sulfate production over the TiO_2+$CaCO_3$ mixture upon irradiation.

While we can not ensure that there is no change of properties during the grinding process, a mixture of 50 % wt. TiO_2 + 50 % wt. $CaCO_3$ is prone to present properties that combine both TiO_2 and $CaCO_3$ particles. Considering this, the DRIFTS analysis compares the spectra of 50 % wt. TiO_2 + 50 % wt. $CaCO_3$ mixture and linear superposition of spectra of TiO_2 and $CaCO_3$ components can reflect the underlying synergistic effect between TiO_2 and $CaCO_3$ particles.

By analyzing IC data, the ratios of S(IV) to S(VI) over TiO_2, $CaCO_3$, 50 % wt. TiO_2 + 50 % wt. $CaCO_3$ were determined to be 0, 1.94, and < 0.003, respectively. On the other hand, we compare the net S(VI) production for each particle, and TiO_2: $CaCO_3$: TiO_2 (50 % wt.) + $CaCO_3$ (50 % wt.) ≈ 1.87:0.28:14.60. Our results suggest that $CaCO_3$ and TiO_2 produce much less S(IV)+S(VI) than TiO_2: $CaCO_3$: 50 % wt. TiO_2 + 50 % wt. $CaCO_3$, indicating that there is an abnormal reaction channel that significantly increases sulfate production when these two components contact with each other.

L151—What does "a strong interaction" mean? What does "weak interplay" mean? These terms are vague/imprecise. Why did grinding not lead to a decrease in size of the $CaCO_3$ particles?

Response to Q: “A strong interaction” means that TiO_2 particles strongly adhere to $CaCO_3$ particles whereas “weak interplay” means that TiO_2 particles poorly adhere to $CaCO_3$ particles. We have changed those two terms to “Compact contact” and “Loose contact”.

Consistent with the SEM observations in the early study (Christidis et al., 2004), the continuous grinding process brings a negligible change in crystal size of calcite within 15 min, probably due to the instinct hardness of calcite. In our study, particles were ground for 10 min for each mixture. Therefore, grinding does not lead to an evident change in the size of $CaCO_3$ particles.

We have changed the term “yield” to “production”.

L155—Is it possible that the overall exposed surface area of the system was larger after grinding, or that aggregates were disrupted, and that this was the cause of the results in Figure S8 rather than anything relating to the specific interface/interactions between TiO_2 and $CaCO_3$?
Response to Q: Thanks for your thoughtful comments. We have considered this issue already. In our experiments, we applied ground TiO_2, ground $CaCO_3$ as well as ground TiO_2+$CaCO_3$ particles for all experiments and BET measurements. Our results show that the BET surface area of ground TiO_2+$CaCO_3$ particles is almost identical to the average value of BET surface area of ground TiO_2 and ground $CaCO_3$ particles. Therefore, the total exposed surface area is almost not changing and it is not the fundamental force to increase sulfate production.

L157—What is “fast production”, exactly? This term is used throughout the manuscript, but in the absence of kinetic data / multiple timepoints, I do not have a sense of what “fast” means here.
Response to Q: We calculated SO_2 uptake coefficients for both $CaCO_3$, TiO_2, and TiO_2+$CaCO_3$, which were determined by the sulfate production rate using multiple timepoints. More details could be found in the experimental section. Seven and Ten timepoints during the heterogeneous reaction were applied for calculating the kinetics in “TiO_2 +SO_2+(CO_2)” and “TiO_2+($CaCO_3$)+SO_2” reaction systems, respectively. Hence, we mentioned the concept “fast” in the context.

L164—What exactly is meant by “the rapid SO_2 oxidation pathway”? This echoes my previous comment (L157).
Response to Q: We have changed “the rapid SO_2 oxidation pathway” to “the increased sulfate production”.

L169—What mechanism do the authors propose for the enhancement observed upon addition of $CaCO_3$ to SiO_2/Al_2O_3? Overall, I find this paragraph confusing; there are a lot of results presented in this manuscript that are briefly discussed / glossed over, and to fully convince the reader that all possibilities have been considered, all results should be discussed in terms of how they fit / do not fit with the overall/big-picture interpretation presented by the authors.
Response to Q: Thanks for your suggestion, we thus put more effort to discuss the results shown in our graph and give more interpretation to convince the readers that we have fully considered the possibility that would affect the conclusion/big-picture we deduced.

For this data, more discussion is presented as “In Fig. 4, the introduction of TiO_2 components (≈

1 % wt.) into SiO_2-Al_2O_3 leads to 81.6 % enhancement of sulfate production because of the photolabile ROS. On the other hand, merely 24.8 % wt. increase of sulfate yield was observed once ≈ 8 % wt. of $CaCO_3$ was incorporated into SiO_2-Al_2O_3 dust particles. This can be attributed to the alkaline environment created by $CaCO_3$, which is believed to increase SO_2 adsorption (Al-Hosney and Grassian, 2005) and sulfate production accordingly. Surprisingly, mixing of ≈ 1 % mass fraction of TiO_2 and ≈ 8 % wt. of $CaCO_3$ into SiO_2-Al_2O_3 gives rise to a 235 % increase in sulfate formation relative to that of SiO_2-Al_2O_3. It represents that there is nearly an extra 100 % enhancement of sulfate production due to the presence of TiO_2 and $CaCO_3$ in the atmospherically relevant mass fraction. These results lead to the hypothesis that the observed synergistic effect on heterogeneous oxidation of SO_2 is likely to take effect in the atmosphere."

L174—"thus likely involving the reaction mechanism proposed in this work"—I do not follow this statement.

Response to Q: We attempt to express that alpha-Fe_2O_3 may produce electron-hole pairs upon irradiation, and further react with (bi)carbonate ions to form carbonate radicals. In this case, the $CO_3^{\cdot -}$ initiated SO_2 oxidation is also likely to occur in alpha-Fe_2O_3 particles.

L184—Recent work by Abou-Ghanem and co-workers (ES&T 2020) has shown that Ti in mineral dust differs substantially from commercial TiO_2. In this context, I don't think it is reasonable to state that 1% TiO_2 is "atmospherically relevant" without qualification of some sort. I also don't know what "authentic dust simulants" means here.

Response to Q: Thanks for your thoughtful comments. We have gone through the literature you recommended and it indeed helps us to have a better understanding of titanium-containing dust particles (Abou-Ghanem et al., 2020). While we may not ensure that the mass percentage (%) of TiO_2 in Ti-containing mineral dust particles always goes above 1%, the mass percentage of TiO_2 in authentic PM collected from aerosol sampling sites was analyzed and determined to be 5 % (Engelbrecht et al., 2009). On this basis, we believe 1 % of TiO_2 is plausible to be found in the atmosphere.

On the other hand, we also considered the crystal phase of TiO_2. Anatase and rutile are two of the three naturally occurring TiO_2 polymorphs whereas the third brookite is an uncommon phase of TiO_2 (Abou-Ghanem et al., 2020; Jaffe and Howard, 1996). In our experiment, commercial-available TiO_2 particles comprise both anatase and rutile. Combing with a possible 5 % of TiO_2 found in the PM, we suppose 1 % mass fraction of anatase and rutile TiO_2 is likely to exist in the PM.

We have changed the term "authentic dust simulants" to "mineral dust simulants", which refers to the simulants that include major crustal components, i.e. SiO_2 and Al_2O_3.

L186—What does "fast oxidation channel" mean? What does "beyond the conventional regime of alkaline neutralization of H_2SO_4" mean?

Response to Q: We have changed to "increased sulfate production". We want to say that the conventional reaction mechanism involving alkaline carbonate salt increases sulfate production mainly through the neutralization process. In this study, we propose that an alkaline environment is not the fundamental driving force to increase sulfate production, and carbonate salt serves as the precursor of carbonate radical, contributing to the increased sulfate yield. This is beyond the conventional reaction scheme.

L190—Which “mineral dust” was used here? Sulfate “yield” on what surface? The CO_2 is atmospherically relevant, but what about the SO_2 concentrations? This (the concentration dependence) should be discussed in the main text, rather than shown only in the supplementary information, because the experiments shown in Figure 1 were conducted at 10 ppm SO_2. Why was this the case, and how might the results obtained under these highly unrealistic conditions differ from those in the real atmosphere?

Response to Q: Mineral dust proxies TiO_2 were used here, and we have clarified the information in the main text; that is “Its influence on photochemical SO_2 uptake on mineral dust proxies TiO_2 was thus studied.”

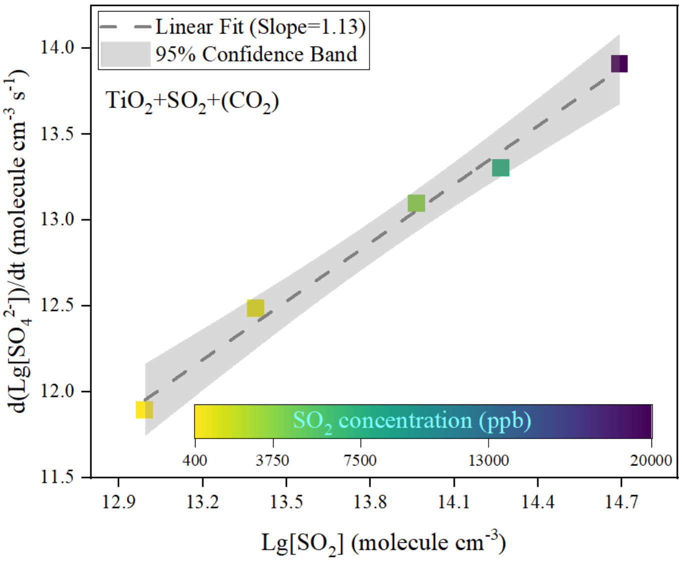

Fig. R3. Reaction order determination. The lg-Lg curve of the sulfate production rate of TiO_2 in the presence of CO_2 (400 ppm) upon varied SO_2 concentration exposure (400-20000 ppb, RH= 30 %) under irradiation (30 mW cm^{-2}) plotted against the concentration of SO_2 molecules exposed.

Thanks for your suggestion. We understand your concern about the gap between the lab and realistic conditions regarding SO_2 concentration. Therefore, we also conducted the SO_2 concentration dependence experiments for “TiO_2+CO_2+SO_2” system, and the pseudo-first reaction order (1.13) was determined in the selected concentration range (400-20000 ppb), indicating that the reaction kinetic obtained in the ppm level is slightly overlooked compared to that conducted in the ppb range. While we note that the difference in SO_2 concentration between the lab and atmospheric conditions remains, employing hundreds of ppb SO_2 in the laboratory simulation to obtain the kinetic parameter of sulfate formation is acceptable (Liu and Abbatt, 2021; Liu et al., 2020a). Taken above, we tentatively believe that uptake coefficients estimated under ppm level are valid, and these datasets derived from laboratory chambers are able to be generalized to the atmosphere condition.

For 10 ppm we employed in “TiO_2+$CaCO_3$” reaction system, we have performed SO_2 dependence experiment as well. We have replied to this question in your early comment.

L193—I don’t follow these arguments regarding the effects of gas-phase CO_2. How can these observations be directly related to observations with carbonate particles? I would think that the effect of CO_2 might relate to a competitive adsorption effect rather than being directly comparable to the effect of pre-existing (solid) carbonate on SO_2 uptake …

Response to Q: Thanks for your suggestion. We have changed the original sentence to “CO_2 suppresses both S(IV) and S(VI) products under the dark probably due to the competitive adsorption effect, as we observed over Al_2O_3 particles (Liu et al., 2020b).”

L203—What is the speciation of this TiO_2? Elemental Ti content is not necessarily an accurate predictor of photoreactivity.

Response to Q: Thanks for your comments. Though we do not do the specimen of TiO_2 in these mineral dust particles, the results from previous literature are able to provide some useful information.

Only the anatase phase of TiO_2 is observable in Kaolin (K-Ga-2) through differential thermal analysis, and chemical analysis shows that TiO_2 accounts for 2.08 % wt. of the total mass of K-Ga-2 (Johnson et al., 1982), consistent with early observation where anatase is general phase found in Kaolin clay (Weaver and Minerals, 1976). For Illite (IMt-2), TiO_2 is in rutile phase and accounts for 0.87 % wt. of total mass (Gailhanou et al., 2012). TiO_2 phases of anatase and rutile altogether account for Ti-containing components in Arizona test dust (ATD) particles (Joshi et al., 2017), where the 0.3 % wt. of TiO_2 is determined in the work of Joshi and coworkers and 0.5-1 % of TiO_2 is provided by supplier.

Anatase TiO_2 exhibits more efficient production of hydroxyl radicals than rutile TiO_2 in the presence of adsorbed hydroxyl groups and water layers (Buchalska et al., 2015), with more efficient production of carbonate radicals correspondingly. This gives an alternative explanation why in the presence of CO_2 under irradiation Kaolin (K-Ga-2) exhibits a pronounced increase of sulfate production than Illite (IMt-2) and Arizona test dust (ATD). The content and proportion of the active phase of TiO_2 altogether contribute to a pronounced increase of sulfate production, as you suggested in this comment in which Ti content is not necessarily an accurate predictor of photoreactivity. We have added relevant discussion in the main text; that is “On the other hand, TiO_2 content is not necessarily an accurate predictor of photoreactivity, the content and proportion of active phase of TiO_2 in K-Ga-2 altogether contribute to a more pronounced increase in sulfate production relative to other two clays (see detailed discussion in supplement text 18).”

L205–210—I find this argument difficult to follow. Are these results scaled to the surface area presented by each of these samples? I do not see how they can be quantitatively compared in this manner otherwise.

Response to Q: Although a comparison of sulfate production among these three dust particles is not the scope and intention of this graph, we understand your concern.

To address the problem, we made a rearrangement of the graph (Fig. R4), and sulfate production in each mineral dust is scaled by the mass for a quantitative comparison.

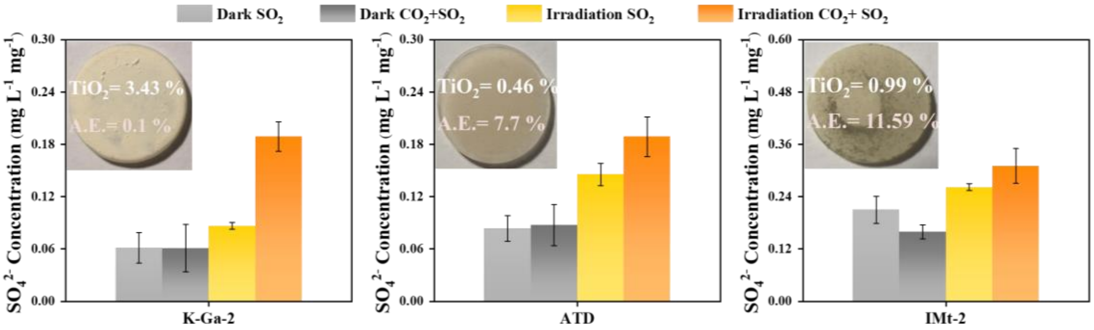

Fig. R4. Laboratory studies of sulfate production on authentic dust and clay membranes **(a)** K-Ga-2 **(b)** ATD as well as **(c)** IMt-2 under the dark and irradiation (30 mW cm^{-2}) upon exposure to 4.91×10^{14} molecules cm^{-3} SO_2/N_2+O_2 and 2.46×10^{18} molecules cm^{-3} CO_2+ 4.91×10^{14} molecules cm^{-3} SO_2/N_2+O_2 at RH of 30 %. Noting that sulfate yield in three cases was normalized by the mass of dust particles employed for heterogeneous reaction.

L231—Where is the evidence that “two water layers” “absorb” (adsorb?) on dust particles? On line 225, I find the terms being used here imprecise … what do “capture SO_2 in the gas phase first” and “then stabilize it as adsorbed S(IV)” mean?

Response to Q: Thanks for your careful check on our manuscript. It should be “adsorb”.

In the early context, we have added relevant citations to support our point that two water layers are prone to adsorb on dust particles; that is “As the RH increases beyond 10 % -15 %, multilayer water coverage occurs, reaching approximately two monolayers at RH of 30 % (Mogili et al., 2006).” In our experiments, employing RH of 30 % is tentatively assumed to provide two water layers over dust particles.

As we do not have direct evidence to validate the two water layers adsorbed on the dust surface, we thus put this sentence in a mild tone; that is “two water layers are likely to absorb on dust particles.”

We have revised the expression to “the resulting hydroxyl groups react with gaseous SO_2 to form adsorbed $S(IV)_{ad}$ species.”

L247—These aniline results should be presented in the main text. What does “a promoted degradation” mean?

Response to Q: Thanks for your suggestion, and we have put this result in the main text. The degradation rate of aniline is increased. We have changed it to “An increased degradation rate of aniline”.

L245—I find the paragraph starting on this line extremely difficult to follow. Specifically, I can’t decipher the argument relating to the scavengers. In addition, how do these conditions (dust suspension in water) compare to the conditions explored in the previous sections of the manuscript (solid particles)? Is it reasonable to use information gathered in aqueous suspensions to interpret results obtained at the surface of solid mixtures? The potential limitations/biases in this approach should be addressed in the text.

Response to Q: We understand your concern about the inconsistency between aqueous media and water layers on humidified dust particles. We have noted this issue, and thus introduce the relevant background information in this paragraph, i.e. “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 its physical and chemical properties (Cwiertny et al., 2008) (Peters and Ewing, 1997). In this work, heterogenous SO_2 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_2 oxidation, and mechanism studies performed in the aqueous phase are persuasive to some extent.”

Following this, we performed scavenger experiments to further validate our hypothesis that carbonate radical ions provide an alternative pathway to enhance sulfate production. Isopropanol (i-PrOH), known as the scavenger of hydroxyl radicals, was applied. In the absence of carbonate ions in TiO_2 suspension, hydroxyl radicals are a major contributor to oxidizing S(IV) to S(VI). Therefore, a great loss of sulfate production can be observed when carbonate ions are absent in the reaction system after adding i-PrOH. On the contrary, the introduction of carbonate ions reduces the loss of sulfate production, indicating that carbonate radical ions take effect and provide an alternative route to oxidize S(IV) to S(VI) even with i-PrOH.

L305—I do not understand the logic underlying these proposed reactions (in particular, equations 6–8). Where is the evidence for these species?

Response to Q: Through NTAS and ESR analysis, we produce experimental evidence that $SO_3^{\cdot-}$ increases due to the presence of $CO_3^{\cdot-}$. In fact, $SO_3^{\cdot-}$ chemistry has been extensively investigated by numerous studies looking at atmospheric chemistry (Gankanda et al., 2016; Hung and Hoffmann, 2015; Hung et al., 2018). When both oxygen and aqueous medium are available, these chain reactions (Eqs. 6–8) that we proposed in the main text are the most plausible pathway to take place in the reaction system of our concern.

$$SO_3^{\cdot-} + O_2 \rightarrow SO_5^{\cdot-} \qquad \text{(Eq. 6)}$$

$$SO_5^{\cdot-} + SO_3^{2-} \rightarrow SO_4^{\cdot-} + SO_4^{2-} \qquad \text{(Eq. 7)}$$

$$SO_4^{\cdot-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^{\cdot-} \qquad \text{(Eq. 8)}$$

In Gankanda’s work, they proposed the chain reactions (Eqs. 6–8) over mineral dust particles although they do not observe intermediate $SO_3^{\cdot-}$ and $SO_5^{\cdot-}$ (Gankanda et al., 2016). In the review of Grassian’s group (Rubasinghege et al., 2010), they also suggest $SO_3^{\cdot-}$ chemistry, including chain reactions (equations 6–8), can account for sulfate production over mineral dust particles.

While we do not provide direct evidence for these species, previous relevant works allow us to speculate on these reaction steps. We noted that we should introduce necessary background information on $SO_3^{\cdot-}$ chemistry to readers. This would help them to follow the reaction mechanism we proposed in the main text. Specially, we have added background information in the main text;

that is "Based on the above results, one may deduce that the interplay between carbonate radical and sulfite ions is a crucial step giving rise to the increased $SO_3^{\cdot-}$ (Eq. 5), which is reported to account for rapid atmospheric sulfate formation through chain propagation reactions (Eqs. 6-8) (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 (Gankanda et al., 2016; Rubasinghege et al., 2010)."

L325—I do not at all follow how these concentrations (for carbonate/hydroxyl radicals) were chosen here. The selected references do not make sense to me—one title is "The carbonate radical is a site-selective oxidizing agent of guanine in double-stranded oligonucleotides." How is this relevant to the argument regarding the relative concentrations of these oxidizing species?
Response to Q: Thanks for your careful check on our manuscript, and we have removed this reference from the current manuscript.

We have cited another reference relevant to our argument; that is "Oxidative Transformations of Contaminants in Natural and in Technical Systems". In this work, Sulzberger and coworkers suggest that the concentration of carbonate radicals can be two orders of magnitude higher than that of hydroxyl radicals in aqueous media, consistent with the concentration gap between carbonate radicals and hydroxyl radicals through the partitioning process from gas-phase determined in our reaction system (over 1.8 orders of magnitude, Fig. 9). While the net concentrations of carbonate hydroxyl radicals in the water layers of humified particles are very likely to be different from that found in the bulk aqueous media, concentration inputs of two radicals with the gap of two orders could reflect the relative contribution of carbonate radicals and hydroxyl radicals to sulfate production based on literature and our experimental trails.

L350–367—I think that this section would be much strengthened by addition of discussion regarding the way(s) in which performing experiments at such elevated SO_2 concentrations may have altered the surface pH of the particles employed.
Response to Q: Thanks for your suggestion. The detailed discussion has been added to the main text as follows:

"Considering that 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 SO_2 oxidation pathway initiated by $CO_3^{\cdot-}$ (see a more detailed discussion on determining equivalent exposure time in supplementary text 22)."

"Besides, 20 ppb is assumed to be atmospherically relevant concentration to calculate "equivalent exposure time" in this study whereas an even low concentration (several or a few tens ppb of SO_2) is monitored in the field observation (He et al., 2014; Watanabe et al., 2020). Therefore, reduction 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."

L369—What does a "non-negligible contribution to sulfate aerosol formation" mean? Compared to what?

Response to Q: We have changed the statement to “underlying pathway for sulfate aerosol formation”

L375—This information should be presented in the methods.
Response to Q: Thx for your suggestion, and we have put the relevant information into the method section.

L378—I do not understand how the maximum OH and carbonate radical concentrations were determined here (in this paragraph). Also, are there any other possible reasons (other than carbonate radical release) why the aniline loss may have been larger in the presence of CO_2?
Response to Q: In the reaction system we have been considering, carbonate radical ions are the most plausible oxidants that lead to the degradation of aniline.

In fact, without the involvement of TiO_2 particles, the degradation rate for “Aniline+Photolysis+CO_2+Air+Irradiation” system (-6.33×10^{-5} s^{-1}) is slightly slower than that for “Aniline+Photolysis+Air+Irradiation” system (-7.18×10^{-5} s^{-1}). While we can not explain the difference, this result however suggests the carbonate radical ion that is derived from the interaction between TiO_2 and (bi)carbonate under irradiation is the driving force in accelerating the loss of aniline. After all, carbonate radical is reported to react fast with aniline. If the presence of CO_2 prohibits aniline photolysis or air stripping processes, that means aniline degradation due to carbonate radicals contributes more than we are now considering.

More methodologies, sample preparation as well as measurement details including experimental set-up and description of measurements could be found in the experimental section. The major discussion on determining the maximum concentrations of hydroxyl and carbonate radical ions were demonstrated as follows:

“In the reaction system containing TiO_2 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 molecular in the presence of TiO_2 film can be described by Eq. **4** (Wang et al., 2004):

$$k_{\mathrm{obs}}=\frac{\mathrm{d[An]}}{\mathrm{dt}}=r_A+r_U+r_{ROS}=r_A+r_U+k_{\mathrm{ROS+AN}}[\mathrm{ROS}][\mathrm{An}] \qquad \textbf{[4]}$$

Where k_{obs} is the observed degradation rate of aniline, [An] is the concentration of aniline, denoted as [An] hereafter, and r_A, r_U, r_{ROS} stand for aniline removal rates resulting from air stripping, UV photolysis, ROS oxidation. $k_{\mathrm{ROS,\,An}}$ 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, e.g. “An+TiO_2+Air+Irradiation”, “Aniline+TiO_2+N_2+Irradiation”, etc. Upon irradiation, the dust proxy TiO_2 produces hole-electron pairs, further forming ·OH radicals and superoxide radicals ($O_2^{\cdot-}$) in the presence of absorbed water and oxygen molecules. Thus, a complement experiment using N_2 was adopted to investigate the role of $O_2^{\cdot-}$ in consuming aniline. As shown in Fig. 9a, a slight change in the degradation rate of aniline after stripping oxygen from the air, indicating that $O_2^{\cdot-}$ 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 $O_2^{\cdot-}$ by adding benzoquinone (BQ) into TiO_2 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 expression (Eqs. 5-7):

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

Integration of Eq. **S3** yields

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

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

Together with the reported second-order rate constant ($k_{\cdot OH,\ An}$ = 6.5×10^{9} $M^{-1}s^{-1}$) (Samuni et al., 2002), the steady-state OH radical concentration $[\cdot OH]_{ss\text{-}max}$ in buffered An solution can be calculated from eq. (1). The observed degradation rate constant of k_{exp} can be obtained from the slope of the semi-log plot of An degradation as shown in Eq. (2). The maximum steady-state concentration of ·OH radical ions supplied by the partitioning process from gas phases was thus estimated to be 2.15×10^{-15} M for the TiO_2+Air system.

When CO_2 (400 ppm, atmospheric relevant concentration) is introduced into a flow-cell chamber, an increased degradation rate of An is seen, which can be attributed to the generation of active carbonate radical ions (Fig. 9b). Similar to the method we adopted for the estimation of $[\cdot OH]_{ss\text{-}max}$, reference experiments were conducted to determine the rates for air stripping and UV photolysis processes in the "TiO_2+Air+CO_2" 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) $k_{\cdot OH,\ TBA}$= (6×10^{8} M^{-1} s^{-1}) while showing a rather low reaction rate with carbonate radicals (Liu et al., 2015) ($k_{CO_3^{\cdot-},TBA}$<1.6×10^{2} M^{-1} s^{-1}). Subsequently, we determined $[CO_3^{\cdot-}]_{ss}$ using the previous protocol (Huang and Mabury, 2000) with known $k_{CO_3^{\cdot-},\ AN}$ (5.4×10^{8} M^{-1} s^{-1}) (Wojnarovits et al., 2020). In the extreme case, assuming that all hydroxyl radical ions were fully trapped by absorbed and dissolved HCO_3^-/CO_3^{2-} over TiO_2 film and gaseous water molecular in the humidified airflow, the maximum steady-state $CO_3^{\cdot-}$ radical concentration was determined to be 1.39 × 10^{-13} M for "TiO_2+Air+CO_2" system, matching well with the early study where the concentration of carbonate radical can be two orders of magnitudes than ·OH over the water surface (Sulzberger et al., 1997)."

L391—I don't understand how carbonate radical ions "strengthen" the oxidative capacity of TiO_2-containing dust particles.

Response to Q: Here is a typo, and we have changed "carbonate radical ions" to "(Bi)carbonate ion". In this work, we show that increased sulfate production can be attributed to the formation of carbonate radical ions over dust particles that contain active component TiO_2 in the presence of bi(carbonate) ions upon irradiation. Following this, we deduce that (bi)carbonate ions strengthen the oxidative capacity of TiO_2-containing dust particles with regard to SO_2 oxidation.

L410—How were S(IV)/S(VI) ratios preserved after sampling/during extraction/analysis?

Response to Q: Thanks for your question. You have raised the question in the early comment. For your convince, we have pasted the answer here.

"The content of S(IV) species is low relative to S(VI) species. In the early study, Dixon and Aasen determined both S(IV) including sulfite and HMS as well as S(VI) species in collected PM (Dixon and Aasen, 1999). They extracted sample using mixing methanol with a preserving solution to prevent the unexpected conversion of S(IV) to S(IV). In all their considered sample, nearly 1/3 of samples are beyond detection limit or not detected. For others, S(IV) species are on the order of ng m^{-3} whereas S(VI) species are on the order of μg m^{-3}, thus giving rise to more than two orders of magnitudes gap between S(IV) species and S(VI) species. This is consistent with observation where S(IV) is not detectable in the rain water due to a rather low sulfite concentration, which is beyond the detection limit of ion chromatography (Jin et al., 2020). The above results suggest the content of S(IV) is much lower than that of S(VI).

Hence, while we did not employ specific preservation procedures to prohibit the conversion of S(IV) to S(VI), we believe the unexpected S(IV) oxidation during the sampling/extraction steps gives a slight influence on determining S(VI) species."

L422—What does "undesired processes" mean?

Response to Q: We attempt to express some collected samples may experience a heterogeneous reaction process during the mixed periods that combine both daytime and nighttime hours, which is the undesired case. This is because it will bring bias and uncertainty to examining the relationship between sulfate and (bi)carbonate ions in two periods.

We note this is a confusing phrase that would frustrate readers to follow, and we thus have revised the sentence to "Some of the collected sample, experiencing heterogeneous reaction that takes place during the day(nigh)-night(day) shifts periods, inevitably being assigned to the sulfate ions measured in separate sampling hours, thus reducing the correlation coefficients."

L446—I do not understand how the negative correlations discussed here and the CO_2 suppression results are related to one another.

Response to Q:

In our sampling, we mainly focus on the PM collected from the first four sampling stages (particles size ⩾3.3 μm). Previous field observation suggests mineral dust particles are dominant (45 %) in coarse inorganic mass fraction of PM (2.5 μm ≤ particles size ≤ 10 μm) (Bougiatioti et al., 2013).

In some sense, competitive adsorption between CO_2 and SO_2 over PM is supported by our early observations where CO_2 inhibits the SO_2 uptake on Al_2O_3 particles regardless of low and high water content formed, more precisely upon exposure of humified CO_2+SO_2/N_2+O_2 flow (5% and 95 %) (Liu et al., 2020b). Al_2O_3 is the major crust constituent found in the mineral dust (≈15 %) (Usher et al., 2003). We produce experimental evidence that there is competitive adsorption between CO_2-derived (bi)carbonate and sulfate species, and this gives rise to the reduction of SO_2 uptake on humified Al_2O_3 particles. Besides, SiO_2 particles are the most dominant constituent of mineral dust particles (≥ 60 %) (Ji et al., 2015). We supplied the data showing that CO_2 of atmospherically relevant concentration decreases the sulfate production over SiO_2 particles in the presence of gaseous H_2O_2 (Fig. R5). H_2O_2 is introduced into the reaction system as SiO_2 has rather lower SO_2 uptake coefficients ($< 1\times10^{-7}$) than other crust constituents, e.g. (α-Al_2O_3 ≈ 1.6×10^{-4} and α-Fe_2O_3

≈7.0×10^{-5}) (Crowley et al., 2010; Usher et al., 2002). The difference in sulfate production in two reaction systems ("SiO_2+SO_2" and "SiO_2+CO_2+SO_2") can not be easily observed otherwise. The heterogeneous reaction of SO_2 has been investigated over black carbon particles as well, and active sites are believed to drive sulfate production (He et al., 2017; Xu et al., 2015). While less knowledge is available for heterogeneous reactions on organic fraction of PM, our early study focusing on the sulfate production over atmospheric Humic-Like Substances (HULIS) reported that SO_2 consumes active sites of HULIS (Liu et al., 2020c). On this basis, CO_2 is likely to behave the same as SO_2 does and competitive adsorption between CO_2 and SO_2 is expected over HULIS as well, or maybe over other organic matters with similar physicochemical properties.

Taken from the above discussion, we speculate the competitive adsorption between different trace gases is likely to occur over particulate matter, especially for trace gas SO_2 of several to dozens of ppb level in the presence of CO_2 of 400 ppm level.

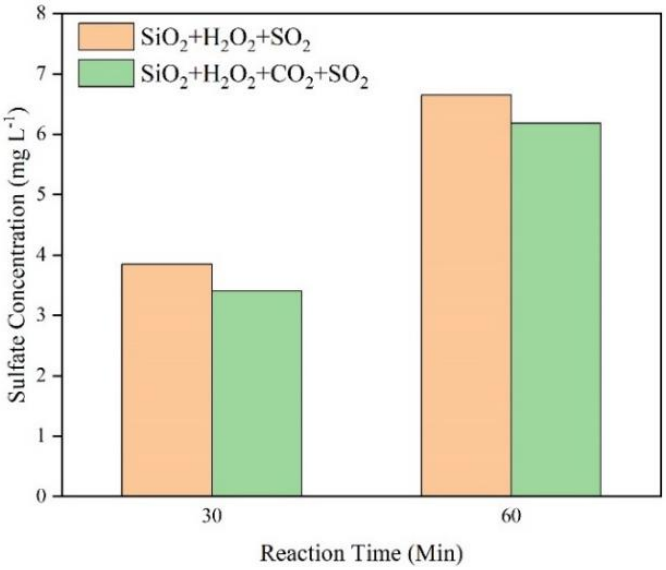

Fig. R5. Sulfate concentration quantified by IC on mineral dust particles after exposure to gaseous SO_2 under irradiation for 30 min in presence of H_2O_2 gas flow. Reaction conditions: Total flow rate = 52.5 mL min^{-1}, $SO_2 = 2.21\times10^{14}$ molecules cm^{-3} and $CO_2 = 9.83\times10^{15}$ molecules cm^{-3}. To produce gaseous H_2O_2 flow, an air flow was humidified in a bubbler loaded with 100 mM H_2O_2. The detailed protocol is similar to the one we applied for sulfate production over TiO_2 particles (Supplement Text 3). We performed two sets of experiments with a duration time of 30 min and 60 min, respectively.

L469—I don't understand the statement regarding "CO_2-derived bicarbonate species". Would the authors expect CO_2 to occupy PM surface sites? What about CO_2 dissolving in an aqueous layer? How do the authors know that the bicarbonate species are CO_2-derived?
Response to Q: Yes, we suppose the CO_2-derived bicarbonate species occupy PM surface sites, giving rise to the negative correlation between sulfate and (bi)carbonate ions.

When liquid water content (LWC) of particulate matter is sufficiently low, sites of particle surface dominate the SO_2 uptake. On the other hand, aqueous-like media largely determines the SO_2 oxidation rate if LWC over PM is high (Wang et al., 2020). Competitive adsorption occurs in both above two cases, where the former can be explained by the maximum surface coverage that allows for gas uptake (Al-Hosney et al., 2005; Grassian, 2008). In the latter one, PM with high LWC sometimes comes from the PM with low LWC. Fresh particulate matter is usually dry when emitted into the atmosphere and suppression of SO_2 adsorption and sulfate formation correspondingly in the early emission stage. These particles become wet by adsorbing water over time (Khlystov et al., 2005). Adsorbed sulfate under dry conditions enters into the semi-aqueous layer, i.e. water layers over humidified PM. Since bi(carbonate) species hinder sulfate production in the early dry stage, the overall negative correlations to sulfate species are thus observed even after considering the later wet period, where CO_2 shows a negligible effect on SO_2 adsorption and subsequent oxidation to sulfate.

Alkaline (bi)carbonate salt particles behave unlike adsorbed/dissolved (bi)carbonate species regarding SO_2 uptake. The former favors SO_2 adsorption (Al-Hosney and Grassian, 2005) and subsequent oxidation by oxidants, e.g. O_3 (Li et al., 2006), and is expected to positively correlate to sulfate production. On the contrary, competitive adsorption between adsorbed CO_2 (HCO_3^-/CO_3^{2-}) and SO_2 reduces the sites over dust particles, likely showing the negative correlation to sulfate.

Considering that negative correlations between sulfate and (bi)carbonate ions are observed, we deduce that CO_2-derived anions are the dominant bi(carbonate) source observed in the collected sample. We have added relevant discussion into the current manuscript, allowing readers to follow.

“This is also supported by lab-based observations where CO_2-derived (bi)carbonate species are demonstrated to suppress sulfate production over two dominant mineral dust components aluminum oxide (Liu et al., 2020b) and silicon dioxide (Fig. S15 and supplement 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_2 adsorption and sulfate formation is possible in the early emission stage before PM becomes wet, thus contributing to the overall negative correlation.”

L493—To what extent do the authors think that gas-phase carbonate radicals contribute to overall atmospheric oxidative capacity? I am not entirely convinced of its production in these experiments (as the evidence is indirect).
Response to Q: Thanks for your question. You raise a really good suggestion and we would like to place our great effort on directly probing the gas-phase $CO_3^{\cdot-}$ coming from dust particle surfaces in the future work.

At present, direct observation of gas-phase $CO_3^{\cdot-}$ ejected from dust particles is not available for our lab experiment set-up. Therefore, indirect measurements using probe molecules of carbonate radicals were conducted to validate our assumption.

In the reaction system in which we designed to probe gas-phase $CO_3^{\cdot-}$; that is probe molecule (phosphate buffer solution pH = 7.0 + aniline) beneath TiO_2-coated film upon 310 nm UV irradiation in the presence of air flow or air+CO_2 flow (the intervening gap between probe molecules and TiO_2-coated film is less than 2 mm)), the formation of new active intermediates due to CO_2 is very likely to account for accelerated degradation of aniline. While we can not provide a direct observation of $CO_3^{\cdot -}$ (g), at least in the current reaction system we are now considering, $CO_3^{\cdot -}$ (g) is the most plausible active intermediate to account for promoted aniline degradation.

Taken above, in combination with current knowledge of the formation scheme of $CO_3^{\cdot -}$, we thus speculate that gas-phase $CO_3^{\cdot -}$ ejected from dust particles contribute to the increased atmospheric oxidative capacity.

Similarly, we put this conclusive statement in a conservative tone to avoid disputed arguments coming from the community; that is “To be important, gas-phase carbonate radical ions are speculated to be formed the in the atmospherically relevant CO_2 concentration (400 ppm) when mineral dust particles are irradiated.”

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