Response Letter (For Referee 2)

Comment from Referee 2:

"The authors provide a strong case that carbonate radical reactions could contribute substantially to the atmospheric production of sulfate from SO_2. I have no argument with all of the very extensive laboratory and theoretical studies. It makes good sense. However, when we get to the field study data, the hypothesis does not seem to hold up. In Figure 5 we are presented with the experimental "correlation" of sulfate and carbonate ions in daylight and at night. To call the correlation "weak" is being very generous. In fact, I would argue there is no demonstrated correlation at all. I think the authors ought to re-write their paper conclusion to highlight the lack of any observed correlation, even though there ought to be one based on all of the laboratory work. They could speculate on why the field study failed to find the expected relationship, and suggest more field studies to resolve the issue."

Author general reply:

Thanks for your valuable suggestions, which greatly helped us to improve the manuscript. According to your comments, we have revised the discussion on field measurement and rewritten the conclusion section to highlight the significance of the findings in this work. Besides, we would like to give a special thank you for your careful check on our manuscript, pointing out the grammar issues listed as follows. We have revised all of the problems that you've pointed out, and they were all fully revised and highlighted in blue in the current version of the manuscript.

Response to the weak correlation between sulfate and carbonate ions in the field observation:

We note that weak correlation coefficients were obtained from current field observations with regard to the relationship between sulfate and bi(carbonate) ions in PM. This is because sulfate ions found in PM come from both primary sources and secondary sources, locally or non-locally. To confirm which source is more dominant in our PM sample, we collected and analyzed meteorological information 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^{-1} (Fig. R8). All plots shown in Fig. R1 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^{-1})(Witkowska et al., 2016; Wu et al., 2020). On this basis, the local source is expected to be the dominant contributor to local air pollution and the mass growth of collected PM.

It is generally accepted that under stagnant meteorological conditions (wind speed < 1.5 m s^{-1}), for the coarse-mode (2.5 μm ~ 10 μm) of sulfate, the heterogeneous reaction of SO_2 on the dust surfaces is believed to be a major contributor (Liu et al., 2017). In this case, for ambient PM considered in this study (3.3 μm ~ 9.0 μm) under the low wind speed (0.76 ± 0.73), local heterogeneous chemical pathway mainly contributes to sulfate ions, while long-term transport is less important. Nevertheless, in our field observations, 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 $PM_{3.3}$-$PM_{9.0}$, respectively, during daytime hours. A plausible explanation is that although less significant, local primary emission source also brings bias and uncertainty to the correlation analysis. Shanghai is a coastal city, and sulfate species such as K_2SO_4

and Na_2SO_4 from the sea salt contribute to the local PM as well (Long et al., 2014). On the other hand, this novel SO_2 oxidation channel is 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.

For those large particles (LP), that refer to the particles with a diameter large than 9 µm in this work, sulfate ions show a rather weak or even no correlation to (bi)carbonate ions during the night-time and day-time hours (Fig 7a and 7c). This is likely correlated to the short lifetime of LP. Generally, the aerosol lifetime is on the order of less than an hour to several 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 µm, $PM_{2.5}$ has a lifetime prolonged to nearly one day or longer (Liu et al., 2020). Therefore, $PM_{3.3}$-$PM_{9.0}$ are expected to have a relatively long lifetime, on the order of several hours or longer, which enables the heterogeneous reaction process to become a more important contributor to overall sulfate ions 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. Similarly, 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 period.

Taken all, a weak correlation between sulfate ions and (bi)carbonate ions observed for $PM_{3.3}$-$PM_{9.0}$ in this work correlates to non-chemical primary emission and complicated $CO_3^{\cdot -}$ regime of heterogenous sulfate production in the atmosphere. For LP, they have a relatively short lifetime, and thus further weaken the $CO_3^{\cdot -}$ initiated SO_2 oxidation channel to occur, leaving the correlation coefficient much low. While we note that the correlation coefficients between sulfate and (bi)carbonate are not promising in this work, field measurements of sulfate and (bi)carbonate ions shed light on their distinct correlations during the daytime and nighttime hours. This is the first time that relationships between those ions are explored separately in these two periods. Overall, carbonate radical is likely to impact the sulfate formation in the atmosphere during daytime hours. Detailed and systematic SO_2 oxidation triggered by $CO_3^{\cdot -}$ needs further investigations to enable a better interpretation of correlations between these inorganic ions at the given meteorological conditions and physico-chemical properties.

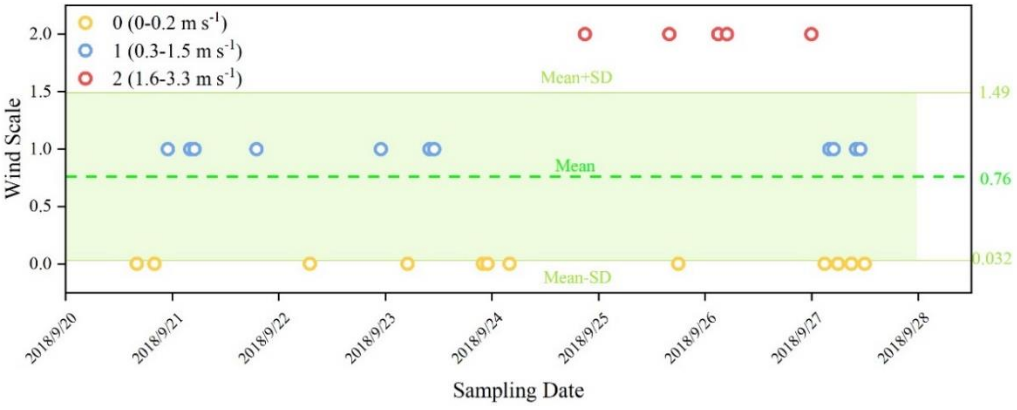

Fig. R1. Daily variations of wind scales from 20 September to 28 September in 2018, Yangpu Sipiao Station, Shanghai.

Detailed correction in the manuscript:

"Complement field sampling and analysis were further conducted to examine our hypothesis that intermediates $CO_3^{\cdot-}$ *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^{-1} *(Fig. S18). All plots shown in Fig. S18 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^{-1}*)(Witkowska et al., 2016; Wu et al., 2020), indicating that local source is a dominant contributor to local air pollution.*

It is generally accepted that under stagnant meteorological conditions (wind speed < 1.5 m s^{-1}*), for the coarse-mode (2.5 μm ~ 10 μm) of sulfate, 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), in which* TiO_2 *was found at mass mixing ratios ranging from 0.1 to 10 % depending on the exact location where particles were uplifted (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 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, more attention was paid to PM collected in stages 1-4 (particles with their dimension ⩾ 3.3 μm). As (bi)carbonate ions are known as key precursors in producing* $CO_3^{\cdot-}$ *and accelerate sulfate formation, quantifications of those relevant water-soluble ions were thus conducted (supplement text 23 and 24).*

We further considered the relationships between sulfate ions and (bi)carbonate ions by means of linear regression analysis. However, under the low wind speed (0.76 ± 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. A plausible explanation is that although less significant, local primary emission source also brings certain bias and uncertainty to the correlation analysis. Shanghai is a coastal city, and sulfate species such as* K_2SO_4 *and* Na_2SO_4 *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 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 concentration of water-soluble ions determined in these samples (relatively small size) may not come from the net contribution of heterogenous reaction processes in absolute day-time and night-time periods. Some of the undesired processes that take place during day(nigh)-night(day) shifts may also contribute to the concentration of sulfate ions in separate sampling hours.*

For those large particles (LP), that refer to the particles with a diameter large than 9 μm in this work, sulfate ions show a rather weak or even no correlation to (bi)carbonate ions during the night-time and day-time hours (Fig. S19). This is likely due 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 μm,* $PM_{2.5}$ *has a lifetime prolonged to nearly one day or longer (Liu et al., 2020). Therefore,* $PM_{3.3}$*-*$PM_{9.0}$ *are expected to have a relatively long lifetime, on the order of several hours, which enables the heterogeneous reaction process to become a more important contributor to overall sulfate ions 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. Similarly, 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.*

While we note that the correlation coefficients between sulfate and (bi)carbonate are not promising 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. 7 and Fig.S19, 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 our previous lab study where* CO_2*-derived (bi)carbonate species are demonstrated to block the active sites for yielding sulfate over mineral dust proxy aluminum oxide (Liu et al., 2020). Instead, positive correlations are seen for those ions within PM sampled during the daytime hours regardless of size ranges and carbonate types (*HCO_3^- */*CO_3^{2-}*). 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, 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 the highly correlated relationship between* Ca^{2+} *and* SO_4^{2-} *water-soluble ions (Liu et al., 2020) during the carbonate-enriched dust storm episodes, together with persistent reports on the significant role of photochemical channels in increasing the sulfate concentration during the daytime (Kim et al., 2017; Wei et al., 2019; Wu et al., 2017) indirectly reflects the possibility of accelerated* SO_2 *oxidation triggered by photo-generated active intermediates associated with carbonate species.*

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 day-time hours. Detailed and systematic SO_2 *oxidation channel triggered by* $CO_3^{\cdot -}$ *needs further investigations to enable a better interpretation of correlations between these inorganic ions at the given meteorological conditions of sampling and physico-chemical properties of PM." **(Main Text, Page 15-17, Line 397-463)***

Response to the request for rewiring the conclusion section:

We have fully revised the conclusion section, with detailed modifications shown as follows:

Detailed correction in the manuscript:

"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_2 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 irradiation or bi(carbonate) ions under dark conditions is summarized and elucidated in Fig. 8. During the night-time hours at 298 K (ambient temperature) CO_2-derived (bi)carbonate species are prone to have a slightly negative effect on sulfate formation due to the competitive adsorption between CO_2 and SO_2. For alkaline carbonate salt, it favors sulfate formation through the neutralization process. On the other hand, during the day-time hours, both CO_2-derived (bi)carbonate species and carbonate salt work as the precursor of $CO_3^{\cdot-}$, 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 earlier studies (Chen et al., 2021; Dupart et al., 2012), we observed the production of gas-phase $CO_3^{\cdot}$ ions when mineral dust particles are irradiated in the presence of CO_2 (atmospherically-relevant concentration 400 ppm). This observation implies that the increased sulfate yield in part comes from promoted gas-phase secondary sulfate aerosol triggered by $CO_3^{\cdot-}$ (g).

By means of ROS scavenger experiments, direct observation of carbonate radical using NTAS analysis, oxygen isotope assay, ESR spectra as well as DFT calculations, $CO_3^{\cdot-}$-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 evidenced to serve as a minor pathway over TiO_2-containing mineral dust particles. In addition, a weak correlation between sulfate ions and (bi)carbonate ions observed for $PM_{3.3}$-$PM_{9.0}$ in this work correlates to non-chemical primary emission and complicated $CO_3^{\cdot-}$ regime of sulfate production in the atmosphere. Nevertheless, 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. This trend agrees with the experimental observations.

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 (bi)carbonate ions.

To be important, carbonate radical ions are observed to be formed in the gas phase in the atmospherically relevant CO_2 concentration (400 ppm) when mineral dust proxies are irradiated. This will help the formation of external sulfate aerosol formation. Since both sulfate aerosol and CO_2 are well known to affect the radiation budget and solar energy balance on the earth (Cheung et al., 2011; Möller, 1964), their overall influence on the global climate considering the increased yield of sulfate aerosol triggered by CO_2, the precursor of carbonate radical, needs further investigation. Therefore, our study highlights the necessity for a comprehensive understanding of *the $CO_3^{\cdot-}$ 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 first 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."* ***(Main Text, Page 15-17, Line 465-501)***

The paper is well written, but I found some English grammar issues:
Response to grammar issue: We have revised the all mentioned grammar issues (G_1-G_7) listed below, and the revised part has been highlighted in the current version of manuscript.

G_1: Line 35 "such as" amines. **Response:** Revised

G_2: Line 92 and elsewhere: "phy-chemical" ought to be physico-chemical. **Response:** Revised

G_3: Line 95 change "better applicability in" to "simulate" **Response:** Revised

G_4: Line 97 "This result allows us to consider that in addition to alkaline environment alternative important force resulting in the remarkable increase of sulfate yield upon irradiation is expected within the carbonate-containing system." Change to "This result allows us to assert that the carbonate-containing system contains another important mechanism for sulfate generation beyond the production of an alkaline environment."

G_5: Line 223 "stemmed' should be "produced" **Response:** Revised

G_6: Line 238 "none" should be "no"Line 270 "complement" should be "complementary" **Response:** Revised

G_7: Line 292 "photo-response" should be "photo-generated. **Response:** Revised

Reference:

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