Role of Dust and Iron Solubility in Sulfate Formation during the Long-Range Transport in East Asia Evidenced by $^{17}$O-Excess Signatures

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ABSTRACT: Numerical models have been developed to elucidate air pollution caused by sulfate aerosols ($\text{SO}_4^{2-}$). However, typical models generally underestimate $\text{SO}_4^{2-}$, and oxidation processes have not been validated. This study improves the modeling of $\text{SO}_4^{2-}$ formation processes using the mass-independent oxygen isotopic composition [$^{17}$O-excess; $\Delta^{17}$O($\text{SO}_4^{2-}$)], which reflects pathways from sulfur dioxide (SO$_2$) to $\text{SO}_4^{2-}$, at the background site in Japan throughout 2015. The standard setting in the Community Multiscale Air Quality (CMAQ) model captured $\text{SO}_4^{2-}$ concentration, whereas $\Delta^{17}$O($\text{SO}_4^{2-}$) was underestimated, suggesting that oxidation processes were not correctly represented. The dust inline calculation from sulfur dioxide (SO$_2$) in the hydroxyl (OH) radical and the aqueous-phase oxidation by hydrogen peroxide (H$_2$O$_2$), ozone (O$_3$), and O$_2$ catalyzed by transition-metal ions (TMIs) for $\text{SO}_4^{2-}$ formation are typically considered. However, typical CTMs often underestimate the burden of atmospheric $\text{SO}_4^{2-}$, particularly in China, suggesting that some $\text{SO}_4^{2-}$ formation in the atmosphere is missing. To date, heterogeneous $\text{SO}_4^{2-}$-production mechanisms particularly for aerosol surfaces$^\text{13-16}$ have been proposed to explain this missing formation such as the enhanced role of the oxidation by reactive nitrogen$^\text{17-20}$, H$_2$O$_2$,$^\text{21}$ TMI-catalyzed O$_2$,$^\text{22-24}$ and Mn-catalyzed oxidation.$^\text{25,26}$ Nonetheless, the observational evidence has not yet identified a specific mechanism. For example, while the importance of NO$_2$ for $\text{SO}_4^{2-}$ formation...
within the aerosol surface was proposed, follow-up studies have cast doubt on the impact of its reaction. Thus, these proposed reactions have been highly controversial arguments.

These pollution and haze events over China and their impact on the downstream region should be mitigated, mainly via the reduction of anthropogenic SO$_2$ emissions. However, according to reports in Western countries, atmospheric SO$_2$ has declined less rapidly than would be expected from decreases in SO$_2$ emissions. This unknown response has been attributed to chemical feedback mechanisms of a weakening H$_2$O$_2$ limitation on the S(IV) + H$_2$O$_2$ pathway and acidity-driven enhancement of the S(IV) + O$_3$ pathway under low SO$_2$ conditions in Western countries. Therefore, accurate CTMs for both concentration and oxidation processes are required to establish an effective emission regulation strategy for improving air quality, and the accurate implementations of atmospheric SO$_2$ formation mechanisms in CTMs are essential for elucidating present pollution and predicting future air quality. Yet, the atmospheric SO$_2$ formation pathways implemented in CTMs have been simply evaluated by total SO$_2$ masses and not validated by independent observational evidence.

One proven method to validate atmospheric SO$_2$ formation is the mass-independent oxygen isotopic composition ($\Delta^{17}$O) of SO$_2$, which reflects the formation pathway from SO$_2$ to SO$_2$. The comparison of observed and modeled $\Delta^{17}$O(SO$_2$) has enabled the recognition and quantification of SO$_2$ formation mechanisms, including TMI-catalyzed S(IV) + O$_3$ SO$_2$ formation by O$_3$ oxidation on sea salt aerosol, S(IV) oxidation by hypohalous acids, and acidity-driven changes in SO$_2$ formation pathways. For extreme pollution events in China, the importance of the heterogeneous chemistry of SO$_2$ production, which is not considered in typical CTMs, has been discussed based on $\Delta^{17}$O(SO$_2$). However, verification has been limited in China. Studies to reveal the SO$_2$ formation process in the long-range transport over East Asia using $\Delta^{17}$O(SO$_2$) have been limited.

SO$_2$ emissions in East Asia have recently begun to decrease. Without the validation of SO$_2$ formation processes in East Asia, studies using current typical CTMs may not adequately predict air quality and climate change, given the possible cause of chemical feedback mechanisms, which have been studied in Western countries. Therefore, the observation of $\Delta^{17}$O(SO$_2$) in regions downstream from intense emission sources, such as China, is critical for research into SO$_2$. The present study describes the annual observation of SO$_2$ and $\Delta^{17}$O(SO$_2$) in 2015 at the background site in Japan (NOTOGRO-based Research Observatory [NOTOGRO] located over the downstream region of China) (Figure 1). Regional CTMs analyses over East Asia are conducted with the Community Multiscale Air Quality (CMAQ) model with three different configurations (Exps. A, B, and C). The role of mineral dust as a supply of alkaline material, which is a unique aspect of the East Asian environment, is investigated because dust-driven higher pH alters acidity-dependent aqueous-phase SO$_2$ formation, such as TMI-catalyzed oxidation by O$_2$ and oxidation by O$_3$. In addition, the impact of TMs on SO$_2$ formation is examined because these are uncertain parameters for emissions and solubilities in the model. Through comparisons of observed and modeled SO$_2$ and $\Delta^{17}$O(SO$_2$) at NOTOGRO in Japan, this study clarifies the key factors controlling the formation process of long-range-transported SO$_2$ in East Asia.

2. METHODS

2.1. Observation of Aerosol and Oxygen Isotopic Composition in Japan. The atmospheric observations were performed at NOTOGRO at 37.45°N, 137.36°E (Figure 1). The Noto peninsula extends from the west coast of mainland Japan approximately 150 km into the sea of Japan, and NOTOGRO is located on the tip of this peninsula. The geographical location of NOTOGRO is ideal for capturing the atmospheric variation in East Asia because it is surrounded by the sea and isolated from major pollution sources in Japan.

The aerosol samples were collected by a high-volume air sampler (MODEL-120 SL, Kimoto Co., Ltd., Japan) mounted on the rooftop (~10 m above sea level) of NOTOGRO. Fine (<2.5 μm) and coarse (>2.5 μm) samples were collected on prebaked (450 °C for 4 h) quartz filters (2500QAT-UP, Pall Co., Ltd.; TE-230-QZ, Tisch Environmental Inc.). Sampling was performed at a flow rate of ~1.05 m$^3$/min, and the sampling interval was usually 1 or 2 weeks. After sampling, the filters were wrapped in aluminum foil, sealed in polyethylene bags, and stored in a clean freezer at ~20 °C prior to the measurement at the Tokyo Institute of Technology, Japan. In the laboratory, half of each filter was soaked in ultrapure water (30 mL) in a 50 mL centrifuge tube (Centricon plus-70, Millipore). The sample solution was separated from the insoluble materials and the filter by centrifuging in a centrifugal filter unit for 10 min. This method can recover >98% of the
Table 1. Modeling Experimental Design and Settings of Solubility for Anthropogenic and Dust TMIs

| modeling experiments | design                          | Fe anthropogenic (%) | Fe dust (%) | Mn anthropogenic (%) | Mn dust (%) |
|----------------------|--------------------------------|----------------------|-------------|----------------------|-------------|
| Exp. A               | the standard simulation         | 10                   | -           | 50                   | -           |
| Exp. B               | incorporation of dust inline calculation | 10                   | 1           | 50                   | 50          |
| Exp. C               | same as Exp. B, but increasing TMI solubilities | 54                   | 3           | 97                   | 50          |

“Note: dash means dust simulation was not implemented in Exp. A. In the aqueous-phase reaction of O₃ catalyzed by TMIs (AQ(O₃)), Fe(III), and Mn(II) are related. Fe(III) was assumed to be 10% of the total dissolved Fe during the day and 90% at night as the diurnal variation. Mn(II) was assumed to be the same for all dissolved Mn. These diurnal variations of Fe(III) and Mn(II) were the same in all three experiments.

initial water volume. The major anions were quantified using an ion chromatograph (Dionex ICS-2100, Thermo Fisher Scientific) with a guard column (Dionex IonPac AG19, Thermo Fisher Scientific) and a separation column (Dionex IonPac AS19, Thermo Fisher Scientific). The major cations were quantified using an ion chromatograph (881 Compact IC Pro, Metrohm) with a guard column (Metrosep C4-S-Guard/4.0, Metrohm) and a separation column (Metrosep C4-150/4.0, Metrohm). The uncertainties of measurement errors were estimated by analyzing five different concentration standards at intervals of every ~20 sample measurements, resulting in approximately 4% for both cation and anion measurements.

The measurement procedures for Δ¹⁷⁷Ο(SO₄²⁻) are described in our previous studies. Briefly, 1 or 2 μmol of H₂SO₄ separated by ion chromatography was chemically converted to Na₂SO₄ and 30% of H₂O₂ solution (1 mL) was added, and the mixture was dried. The Na₂SO₄ was converted to silver sulfate (Ag₂SO₄) using an ion-exchange resin. This Ag₂SO₄ powder was transported in a custom-made quartz cup, which was dropped into the furnace of a high-temperature conversion elemental analyzer (TC/EA, Thermo Fisher Scientific) at 1000 °C and thermally decomposed into O₂. The O₂ gas was introduced separately into an isotope ratio mass spectrometer to measure m/z = 32, 33, and 34. The Δ¹⁷⁷Ο(SO₄²⁻) measurements were corrected using our working standard B (Δ¹⁷⁷Ο(SO₄²⁻) = 2.4‰) with the same procedure described previously. In this correction for isotopic analysis, SD (1σ) for the corrected values for standard B was 0.11‰ based on measurements for the samples collected in 2015, and this 1σ uncertainty was used for the error of the isotopic measurements in the present study. The raw observation data are presented in the Supporting Information (Table S1). All data for SO₄²⁻ concentration and Δ¹⁷⁷Ο- (SO₄²⁻) are corrected using Na⁺ concentration to non-sea salt fraction of SO₄²⁻ (nss-SO₄²⁻) in a similar manner reported previously.

2.2. Regional Chemical Transport Modeling over East Asia. 2.2.1. Model Description. The regional air quality modeling was conducted with the CMAQ model version 5.3.1. In this study, the simulation domain covered the entirety of East Asia with a horizontal resolution of 36 km (Figure 1) and 44 nonuniform layers from the surface to 50 hPa. One gas-phase reaction and five aqueous-phase reactions in cloud are involved in SO₂ oxidation (i.e., SO₂⁻ formation) in the original CMAQ. The one gas-phase reaction is SO₂ oxidation by OH (GAS), and the five oxidants in the aqueous-phase reactions in cloud are H₂O₂ (AQ(H₂O₂)), O₃ (AQ(O₃)), O₃ catalyzed by TMIs (AQ(O₃)), peroxyacetic acid (PAA) (AQ(PAA)), and methyl hydrogen peroxide (MHP) (AQ(MHP)). In addition to these five oxidants in the original CMAQ, taking into account the elevated NO₂ concentration in Chinese pollutions, the aqueous-phase pathway in cloud via NO₂ was added in this study. This inclusion partly improved the model underestimation issue during winter in our previous study. Note that the production of SO₄²⁻ on the aerosol surface is not considered in this study because the specific Chinese haze events that occurred in limited areas are out of scope and our focus is on capturing SO₄²⁻ pollution over East Asia from the viewpoint of the background site in Japan.

Second, it is possible to implement the development of physical-based inline dust calculation after CMAQ version 5.2. Before this version, the effect of soil dust for neutralization and altering cloud drop pH could not be considered, even though one of the characteristics in East Asia is the role of mineral dust originating from the Taklamakan and Gobi Deserts, the Loess Plateau, and Inner Mongolia. However, dust is not implemented as the default setting of CMAQ, which hampers the pH-dependent SO₂⁻ formation, especially for AQ(O₃) and AQ(O₃). The impact on SO₂⁻ formation caused by the difference with or without implementation of inline dust calculation was tested in this study, as explained in Section 2.2.2. The details of the modeling description and chemical configurations are, respectively, given in the Supporting Information (Sections S1 and S2).

2.2.2. Model Experiments. In this study, we compared the three following experiments (Exp. A, Exp. B, and Exp. C) to investigate the role of mineral dust and solubilities of Fe and Mn for SO₂⁻ formation, as summarized in Table 1. In Exp. A, which is the original settings in the CMAQ model version 5.3.1, the solubilities of anthropogenic Fe and Mn were set as 10 and 50% and dust inline calculation was not implemented (Table 1).
In Exp. B, the modulation of pH by mineral dust was considered, and thus the newly developed dust inline calculation scheme in CMAQ was applied. In addition to pH changes by mineral dust, the dust-derived Fe and Mn were considered in Exp. B. The solubility of dust Fe and Mn was set as 1 and 50%, respectively (Table 1). The details of the dust inline calculation are given in the Supporting Information (Section S3).

In Exp. C, increased TMI solubilities were considered because one of the uncertainties in modeling settings still under debate is TMI solubilities. Based on a literature review, the range of TMI solubility for Fe and Mn are 0.03−1.297%, respectively. 

The result from the IMPACT global aerosol model also suggested the verification of increasing anthropogenic Fe solubility (Figures S1 and S2 in the Supporting Information), the solubility of dust Fe and Mn was increased from 1% in Exp. B to 3% in Exp. C (Table 1). Based on the integrated massively parallel atmospheric chemical transport (IMPACT) global aerosol model (Figures S1 and S2 in the Supporting Information), the solubility of dust Fe was increased from 1% in Exp. B to 3% in Exp. C (Table 1). The result from the IMPACT global aerosol model also suggested the verification of increasing anthropogenic Fe solubility (Figures S3 and S4 in the Supporting Information). The discussion of TMI solubilities is also given in the Supporting Information (Section S4).

2.2.3. Calculation of $\Delta^{17}O(SO_4^{2-})$ from Model Outputs. The diagnostic tool of the sulfur tracking method in CMAQ was used to output each oxidation process involved in $SO_4^{2-}$ formation. From these outputs in CMAQ, the modeled $\Delta^{17}O(SO_4^{2-})$ was derived based on eqs 1 and 2.

$$F_i = \left\{ \begin{array}{l} \frac{[SO_4^{2-}]}{[SO_4^{2-}]_{\text{GAS}}} + [SO_4^{2-}]_{\text{AQ(H,O,2)}} \\ + [SO_4^{2-}]_{\text{AQ(O2)}} + [SO_4^{2-}]_{\text{AQ(NO2)}} \\ + [SO_4^{2-}]_{\text{boundary}} + [SO_4^{2-}]_{\text{emission}} \end{array} \right\}$$

$$\Delta^{17}O(SO_4^{2-}) = 0 \times F_{\text{GAS}} + 0.8 \times F_{\text{AQ(H,O,2)}} + 6.4 \times F_{\text{AQ(O2)}} - 0.1 \times F_{\text{AQ(O2)}} + 0 \times F_{\text{AQ(NO2)}} + \text{Bkg} \times F_{\text{boundary}} + 0 \times F_{\text{emission}}$$

In these equations, $[SO_4^{2-}]_i$ is the $SO_4^{2-}$ concentration from each process and $F_i$ represents the fractional contribution for each process, where $i$ indicates the $SO_4^{2-}$ formation process.

The contributions of PAA and MHP were negligible (around 0.1% contribution throughout the year) and hence were omitted from this calculation. In this study, $\Delta^{17}O(SO_4^{2-})$ of 0‰ was set for the GAS and emission oxidation pathways, and the end members and their uncertainties for $\Delta^{17}O(SO_4^{2-})$ in the other oxidation pathways were set to 0.8 ± 0.2‰ for AQ(H$_2$O$_2$), 6.4 ± 0.3‰ for AQ(O$_2$), and −0.1‰ for AQ(O$_2$) (see our previous studies31,37,43 for the determination of the end members). The value of AQ(NO$_2$) was set as 0‰ according to He et al.13 and references therein. $\Delta^{17}O(SO_4^{2-}) = 0$‰ for $SO_4^{2-}$ produced by AQ(NO$_2$) is expected based on the following three mechanisms: radical chain mechanism,50 oxygen-atom transfer from OH$^-$,51 or from O$_2$.$^{52}$ Additionally, a detailed discussion of the uncertainties of the AQ(O$_2$) end member is given in the Supporting Information (Section S5 and Figure S5). The $SO_4^{2-}$ derived from the boundary conditions is considered the background existing $SO_4^{2-}$, and thus monthly values observed at Alert, Canada, ranging from 0.5 to 1.3‰ were used.

2.2.4. Statistical Analysis. The model performance for $SO_4^{2-}$ concentration and calculated $\Delta^{17}O(SO_4^{2-})$ was statistically evaluated. The metrics were correlation coefficient (R), normalized mean bias (NMB), and normalized mean error (NME).

$$R = \frac{\sum_i (O_i - \bar{O})(M_i - \bar{M})}{\sqrt{\sum_i (O_i - \bar{O})^2} \sqrt{\sum_i (M_i - \bar{M})^2}}$$

$$\text{NMB} = \frac{\sum_i (M_i - O_i)}{\sum_i O_i}$$

$$\text{NME} = \frac{\sum_i |M_i - O_i|}{\sum_i O_i}$$

Here, $N$ is the total number of paired observations (O) and models (M), and these averages are denoted as $\bar{O}$ and $\bar{M}$, respectively. The recommended metrics for $SO_4^{2-}$ concentration model performance goals for best performance of $R > 0.7$, NMB < ±10%, and NME < ±35% and model performance criteria for acceptable performance of $R > 0.4$, NMB < ±30%, and NME < ±50%.53
behaviors (Figure 2). The highest SO$_4^{2-}$ to winter (September) and spring (February) over East Asia was divided into three seasons, late winter to autumn to winter (Figure 3a). As the background site in Japan, Chichijima island located in the western North Pacific (i.e., south of Tokyo) showed higher concentration in winter and lower concentration in summer. The difference in the seasonal variation of SO$_4^{2-}$ concentration seen in NOTOGRO is caused by the outflow pattern in East Asia, as found in Figure 2. Overall, throughout the year, the statistical analyses showed that all three modeling experiments (Exps. A, B, and C) generally captured the SO$_4^{2-}$ concentration (Table 2).

The weekly observed Δ$^{17}$O(SO$_4^{2-}$) at NOTOGRO ranged from 0.46 to 1.98‰, and the monthly weighted average ranged from 1.0 to 1.5‰, except for a value of 0.70‰ in August (Figure 3b). These observed Δ$^{17}$O(SO$_4^{2-}$) values ranging from 1.0 to 1.5‰ were higher than those reported in the polluted region in China, where the observations from Beijing varied from 0.1 to 1.6‰ with a mean of 0.9 ± 0.3‰ and the data from Wuhan varied from 0.14 to 1.02‰ with a time-weighted average of 0.53‰. The observed higher Δ$^{17}$O-SO$_4^{2-}$ values at NOTOGRO are explained by either the greater importance of AQ(O$_2$) (Δ$^{17}$O(SO$_4^{2-}$) = 6.4 ± 0.3‰) or the lesser importance of pathways such as GAS (Δ$^{17}$O(SO$_4^{2-}$) = 0‰) and AQ(O$_2$) (Δ$^{17}$O(SO$_4^{2-}$) = −0.1‰). We note that the low Δ$^{17}$O(SO$_4^{2-}$) values with high SO$_4^{2-}$ concentration in August probably originated from volcanic eruptions in western Japan, which is discussed in Section 3.2.

**3. RESULTS AND DISCUSSION**

### 3.1. Observed and Simulated SO$_4^{2-}$ Characteristics over East Asia

The simulated spatial distribution of SO$_4^{2-}$ over East Asia was divided into three seasons, late winter to spring (February–May), summer (June–August), and autumn to winter (September–December), to characterize seasonal behaviors (Figure 2). The highest SO$_4^{2-}$ concentrations were found over mainland China, and the higher-concentration regions extended into the downstream region over the Korean Peninsula and Japan. This feature was dominant from spring to summer; therefore, the simulations in the downstream region of Japan detected the polluted air mass resulting from the long-range transport over East Asia. In contrast, from autumn to winter when the strong northwesterly wind field by the Asian monsoon was dominated, the SO$_4^{2-}$ concentration was low and was characterized by clean background conditions. The weekly and monthly average variations of SO$_4^{2-}$ concentration observed at NOTOGRO also showed higher concentrations from spring to summer and lower concentrations during autumn to winter (Figure 3a). As the background site in Japan, Chichijima island located in the western North Pacific (i.e., south of Tokyo) showed higher concentration in winter and lower concentration in summer. The difference in the seasonal variation of SO$_4^{2-}$ concentration seen in NOTOGRO is caused by the outflow pattern in East Asia, as found in Figure 2. Overall, throughout the year, the statistical analyses showed that all three modeling experiments (Exps. A, B, and C) generally captured the SO$_4^{2-}$ concentration (Table 2).

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### 3.2. Disagreement between Observed and Modeled Δ$^{17}$O in the Standard Model

In the standard CMAQ model experiment (Exp. A), although the modeled SO$_4^{2-}$ concentrations agreed with the observations (Figure 3a, black
line), the modeled $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) ranged from 0.21 to 1.24‰ and underestimated the observations over the period except in winter (Figure 3b, black line). In Exp. A, GAS was the dominant oxidation process, contributing more than 30% of SO$_{2}^{\text{aq}}$ formation during the period and reaching up to 80% during spring and summer. Following the GAS process, atmospheric acidity by dust-derived CaCO$_3$ was found in August, and the low $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) was due mainly to the high contribution of the GAS process ($\Delta^{17}$O(SO$_{2}^{\text{aq}}$) = 0‰). The importance of GAS in volcano-originated SO$_{2}^{\text{aq}}$ was suggested in this study, whereas the importance of AQ(O$_2$) was suggested to be the dominant process in volcanic plumes. This difference indicates that the oxidation processes contributing to SO$_{2}^{\text{aq}}$ formation inside plumes are different from those contributing to SO$_{2}$ oxidation after diffusion into the atmosphere. The discussion of this volcanic impact is given in the Supporting Information (Section S6 and Figure S6).

Overall, the underestimation of $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) in Exp. A indicates that the standard model parameterization in CMAQ is missing oxidation pathways that increase $\Delta^{17}$O(SO$_{2}^{\text{aq}}$).

### 3.3. Importance of Dust-Derived pH Increase in SO$_{2}^{\text{aq}}$ Formation

Given the importance of dust in SO$_{2}^{\text{aq}}$ formation and neutralization, the dust inline calculation was implemented in Exp. B. The supply of alkaline dust to the atmosphere increases the pH and thus increases the acidity-dependent reaction rates for AQ(O$_2$) and AQ(O$_2$)$_2$. In Exp. B, the dust-derived Fe and Mn were calculated in addition to anthropogenic Fe and Mn. Although Exp. B did not improve the estimation of SO$_{2}^{\text{aq}}$ concentration substantially compared with Exp. A (Figure 3a and Table 2), $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) for Exp. B ranged from 0.56 to 2.36‰ (Figure 3b, brown line; Table 2). For the relative contributions of the SO$_{2}^{\text{aq}}$ oxidation processes in the model, AQ(O$_2$) increased, whereas GAS decreased (Figure 3d). This switch can be explained by the neutralization of atmospheric acidity by dust-derived CaCO$_3$ and the increased pH obtained by including the inline dust calculation is consistent with previous works. The results in Exp. B showed better agreement with the observations of $\Delta^{17}$O-(SO$_{2}^{\text{aq}}$) (Table 2), and this improvement in $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) in Exp. B suggests that mineral dust supply is crucial in increasing the acidity-driven SO$_{2}^{\text{aq}}$ formation in East Asia. However, the overestimation of $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) from February to March and from October to December remained.

### 3.4. Importance of TMI Solubilities in SO$_{4}^{2-}$ Formation

To account for the remaining gap between the model and observed values of $\Delta^{17}$O(SO$_{2}^{\text{aq}}$), the increases in TMI solubilities in the polluted air were considered in Exp. C. In the standard model of Exp. A, although the anthropogenic emission of TMI is accurately considered based on the latest emission data set, the modeled estimates of solubilities of anthropogenic and dust Fe and Mn remain highly uncertain in cloud water, as pointed out previously. The increased Fe solubilities have been indicated based on global model comparisons with multiple field campaigns over the Northwest Pacific and also observed toward the downstream region of East Asia, mainly because fine mineral aerosols can be acidified due to air pollution. Thus, for Exp. C, we implemented the higher solubilities for both anthropogenic and dust Fe. Compared to the anthropogenic Fe solubility (10%) and Mn solubility (50%) considered in Exp. A and B, the maximum solubility for anthropogenic Fe (54%) and Mn (97%) over the literature was taken in Exp. C (Table 1). Note that the higher solubility of Fe in dust (3%) considered in Exp. C is generally consistent with that simulated by the IMPACT global aerosol model (Figures S1 and S2 in the Supporting Information).

The SO$_{4}^{2-}$ concentration in Exp. C did not increase substantially compared with that in Exp. A and B (Figure 3a and Table 2), but the overestimation in modeled $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) from February to March was clearly decreased in Exp. C (Figure 3b, orange line; Table 2) and ranged from 0.54 to 1.94‰. The improvement in $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) values was explained by the increased contribution of AQ(O$_2$) owing to the higher solubilities of Fe and Mn (Figure 3e), especially from October to December. Regarding the importance of the AQ(O$_2$) process, TMI concentrations have been discussed in China. In Beijing, TMI-catalyzed oxidation showed a clear distinguishing of higher/lower contribution during polluted/clean periods. In Wuhan, the enhanced role of TMI-catalyzed oxidation in winter was suggested due to higher PM$_{2.5}$ concentration. In contrast, this study highlights the role of TMI-catalyzed AQ(O$_2$) through the consideration of solubilities over the downstream region of East Asia, as evidenced by $\Delta^{14}$O(SO$_{2}^{\text{aq}}$). The importance of TMI solubilities, which led to the improvement of $\Delta^{17}$O(SO$_{2}^{\text{aq}}$), was found during February and March when SO$_{4}^{2-}$ concentration was higher and from October to December when SO$_{4}^{2-}$ concentration was lower. Therefore, it is concluded that the role of TMI-catalyzed AQ(O$_2$) by enhancing solubilities does not depend on the pollution level in this case. Overall, the increased pH obtained by including dust and the increase in TMI solubilities in Exp. C showed the best match for SO$_{4}^{2-}$ concentration and $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) among three experiments conducted in this study. The series of results strongly indicate the importance of dust and TMI solubilities for SO$_{4}^{2-}$ formation via changes in oxidation processes in downstream regions of East Asia, which was not discovered in previous studies that considered only SO$_{4}^{2-}$ mass.

### 3.5. Toward Closer Agreement between Observed and Modeled SO$_{4}^{2-}$ Formation

However, SO$_{4}^{2-}$ concentration was still underestimated from February to March (observed values: 3.58 ± 0.26 and 5.64 ± 1.71 μg/m$^3$; modeled values in Exp. C: 2.61 and 3.66 μg/m$^3$; Table S2 in the Supporting Information) and $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) values were overestimated, even in Exp. C (observed values: 1.24 ± 0.20 and 1.26 ± 0.33‰; modeled values in Exp. C: 1.94 ± 0.09 and 1.57 ± 0.08‰; Table S3 in the Supporting Information). Since the domestic contribution to SO$_{4}^{2-}$ in Japan is estimated to be small except in summer, the most plausible reason for missing processes is attributed to inadequate SO$_{2}^{\text{aq}}$ formation in polluted areas over China. Here, $\Delta^{17}$O(SO$_{2}^{\text{aq}}$) values of possible missing processes (defined as $\Delta^{17}$O(SO$_{2}^{\text{aq}}$)$_{\text{missing}}$) are calculated from the following mass-balance calculation

$$[\text{SO}_4^{2-}]_{\text{obs}} \times \Delta^{17}O(\text{SO}_4^{2-})_{\text{obs}} = [\text{SO}_4^{2-}]_{\text{model}} \times \Delta^{17}O(\text{SO}_4^{2-})_{\text{model}} + [\text{SO}_4^{2-}]_{\text{missing}} \times \Delta^{17}O(\text{SO}_4^{2-})_{\text{missing}}$$

where $[\text{SO}_4^{2-}]_{\text{obs}}$, $[\text{SO}_4^{2-}]_{\text{model}}$ and $[\text{SO}_4^{2-}]_{\text{missing}}$ are SO$_{4}^{2-}$ concentrations for observation, model, and missing processes (i.e., difference between the observation and model), respectively, and $\Delta^{17}O(\text{SO}_4^{2-})_{\text{obs}}$, $\Delta^{17}O(\text{SO}_4^{2-})_{\text{model}}$ and $\Delta^{17}O(\text{SO}_4^{2-})_{\text{missing}}$ are $\Delta^{17}$O(SO$_{4}^{2-}$) for the observation, model, and missing processes, respectively. Given that...
[SO$_4^{2-}$]$_{missing}$ is calculated by [SO$_4^{2-}$]$_{meas}$ minus [SO$_4^{2-}$]$_{model}$. 

$\Delta^{17}O$(SO$_4^{2-}$)$_{missing}$ can be obtained from eq 6. The calculated $\Delta^{17}O$(SO$_4^{2-}$)$_{missing}$ was $-0.63 \pm 0.52\%$ during February and 0.70 $\pm 1.01\%$ during March, respectively.

For the calculated $\Delta^{17}O$(SO$_4^{2-}$)$_{missing}$ of $-0.63 \pm 0.52\%$ during February, the result can be explained by SO$_4^{2-}$ formation via TMI-catalyzed oxidation by O$_2$. Mn-catalyzed oxidation, and other reactions (i.e., oxidation by NO$_2$) having $\Delta^{17}O$(SO$_4^{2-}$) close to 0. The interpretation is consistent with previous studies, which proposed these mechanisms as missing processes in Chinese haze. It is worthy to conclude that AQ(H$_2$O$_2$) does not explain this missing SO$_4^{2-}$ formation during February.

Conversely, for the calculated $\Delta^{17}O$(SO$_4^{2-}$)$_{missing}$ of 0.70 $\pm 1.01\%$ during March, this value is close to $\Delta^{17}O$(SO$_4^{2-}$). In terms of the SO$_4^{2-}$ formation process, faster H$_2$O$_2$ oxidation of SO$_4^{2-}$ formation in high solute strength was suggested in Chinese haze events. The current CTMs are based on kinetics research in dilute aqueous solutions and may miss such strengthened features in the atmosphere. The contribution of AQ(H$_2$O$_2$) was declined in Exp. C compared to that in Exp. A (Figure 3d) through increased dust-derived pH and enhanced TMI solubilities in this study. Because AQ(H$_2$O$_2$) does not depend on pH, faster oxidation by H$_2$O$_2$ in Chinese pollution would also affect the downstream region over East Asia even in the application of Exp. C. In this study, although we do not include reactions on the aerosol surface because our focus is not on the Chinese haze itself, the accurate modeling to capture the enhanced SO$_4^{2-}$ concentration in haze events will also improve SO$_4^{2-}$ behaviors in the downstream region if the long-range transport occurs.

To date, SO$_4^{2-}$ production mechanisms have been proposed to explain this missing formation in Chinese pollution and haze events, as introduced. Although this study cannot identify a single mechanism for this missing formation pathway, our results imply that the oxidation pathways for inadequate SO$_4^{2-}$ formation in polluted areas over China are not always identical. Based on our $\Delta^{17}O$(SO$_4^{2-}$) approach, these estimations for missing processes from the perspective of the downstream region in East Asia are the first supportable information for unexplained SO$_4^{2-}$ formation over China. A recent study proposed the dominance of Mn-catalyzed oxidation of SO$_4$ and negligible formation pathways by gas- and aqueous-phase reactions in Chinese haze because the meteorological condition of the stable boundary layer with weak turbulence prohibits their formations. Under such conditions dominated by the Mn-catalyzed oxidation pathway, the value of $\Delta^{17}O$(SO$_4^{2-}$) is expected to be close to 0%, however, the reported value of $\Delta^{17}O$(SO$_4^{2-}$) in Beijing haze from October 2014 to January 2015 ranged from 0.1 to 1.6% with a mean of 0.9 $\pm$ 0.3%. Therefore, the dominance of Mn-catalyzed oxidation and the negligible contributions from other processes will be required to be carefully examined. The validation of $\Delta^{17}O$(SO$_4^{2-}$) in the future study. To validate SO$_4^{2-}$ formation over East Asia covering from the haze above the atmosphere with intense emission sources to a background condition over the downstream region, further studies including laboratory experiments, measurements of both SO$_4^{2-}$ concentration and $\Delta^{17}O$(SO$_4^{2-}$), and numerical modeling are needed.

### 3.6. Implications for Future Air Quality and Climate Studies

We demonstrated the effect of the dust-derived increase in pH on SO$_4^{2-}$ production and the need to increase TMI solubilities in the modeling by constraining both SO$_4^{2-}$ concentration and $\Delta^{17}O$(SO$_4^{2-}$) at the background site in Japan over the downstream region. On the current typical CTMs, TMI solubilities are fixed as constant, which does not account for spatial (both horizontal and vertical) and temporal variations particularly found in upwind and downstream differences over East Asia (i.e., Figures S1–S4 in the Supporting Information). This study highlights the importance of TMI solubilities to determine the role of the SO$_4^{2-}$ formation process. Compared to the parameterization in this study, the assumptions of solubilities for dust Fe (0.45%) and Mn (5%) for the previous study conducting the modeling of $\Delta^{17}O$(SO$_4^{2-}$) in Beijing haze were significantly lower. This study improved SO$_4^{2-}$ formation in the model by implementing detailed emissions of Fe and Mn, pH-dependent rate constants for AQ(O$_2$) catalyzed by TMIs, and increasing in solubilities of Fe and Mn; however, solubilities were taken as fixed parameters in time and space; hence, the detailed spatiotemporal variations of solubilities have not been accurately investigated. Thus, we propose considering spatiotemporal variations of Fe and Mn solubilities for the CTMs. To evaluate this development of CTMs and understand SO$_4^{2-}$ formation processes, the coordinated observation of $\Delta^{17}O$(SO$_4^{2-}$) and TMI solubilities along trajectories of long-range-transported air mass from upwind to downstream in East Asia will be one significant approach. These accurately modeled SO$_4^{2-}$ formation processes over East Asia are necessary to test SO$_4$ emission regulation strategies along with carbon neutrality because the unknown response to SO$_4$ emission reduction has already been reported in Western countries.

The changes in SO$_4^{2-}$ oxidation processes also alter the size distribution of SO$_4^{2-}$ and hence direct and indirect radiative forcing closely related to climate aspects. The reduction of SO$_4^{2-}$ in future atmospheric conditions (i.e., higher CO$_2$ concentration and lower SO$_4$ concentration) will increase atmospheric warming compared with the current atmospheric conditions through the slow climate response. The reduction of SO$_4^{2-}$ will also reduce atmospheric acidity and alter the magnitude, distribution, and deposition mode of nutrients supplied to the ocean in the coming decades. As we verified the important role of Fe as the catalyst on the SO$_4^{2-}$ formation, the declined acidity in the future will relate to weakening the role of TMI-related SO$_4^{2-}$ formation in the downstream of dust sources over East Asia. Given that a significant emission reduction of CO$_2$ combined with a well-designed emission pathway of SO$_4$ is required, our findings on the role of dust and TMI solubilities and the way to improve the modeling of SO$_4^{2-}$ formation will contribute to better emission regulations required for air quality and climate change.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c03574.

Setup of regional chemical transport modeling (Section S1); configuration of CMAQ chemical mechanism for SO$_4^{2-}$ (Section S2); description of dust inline calculation over East Asia (Section S3); discussion on TMI solubilities (Section S4); uncertainty analysis of...
end member for $\Delta^{17}$O(SO$_4^{2-}$) of O$_3$ aqueous-phase oxidation (Section S5); discussion on volcanic impacts on SO$_4^{2-}$ concentration and $\Delta^{17}$O(SO$_4^{2-}$) (Section S6); Figures S1−S6 and Tables S1−S4 (PDF)

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**Author Contributions**

S.I. and S.H. designed the research; S.I. and S.H. performed the model development and modification; S.I., S.H., and A.I. conducted model analyses; S.H., Y.S., and A.M. contributed to field observations; S.H. and N.Y. contributed to the laboratory experiments; S.I. and S.H. analyzed the data; and S.I. and S.H. wrote the paper, which was commented on by all authors. S.I. and S.H. equally contributed to this study.

**Notes**

The authors declare no competing financial interest.

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