

EGU21-3649

Isotopic evidence for importance of atmospheric acidity on sulfate formation in the Mt. Everest region

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Acknowledgements.

Sampling: The staff working at the Qomolangma Station for Atmospheric and Environmental Observation and Research, Chinese Academy of Sciences.

Data: CNR-ISAC (Institute of Atmospheric Sciences and Climate of the National Research Council of Italy) and Ev-K2-CNR Chartered Association (O3 data).

European Centre for Medium-range Weather Forecast for the ERA-Interim reanalysis dataset (<https://www.ecmwf.int/en/forecasts/datasets/reanalysis-datasets/era-interim>).

The NOAA Air Resources Laboratory for the provision of the HYSPLIT transport and dispersion model and/or READY website (<https://www.ready.noaa.gov>) used in this publication.

Funding: Japan Society for the Promotion of Science (JSPS) KAKENHI (Grants JP18F18113 [N.Y.], JP18K19850 [S.H.], JP19H01143 [S.H.], JP20H04305 [S.H.], JP16H05884 [S.H.], and JP17H06105 [N.Y.]).

NSF AGS 1644998. Tibetan Plateau Scientific Expedition and Research Program (STEP) (No. 2019QZKK0605); The National Natural Science Foundation of China (Nos. 41705132 [S.K.], 41630754 [S.K.], 42021002 [M.L.]).

Accepted in ACP (April 19th)



Atmospheric Chemistry and Physics

<https://doi.org/10.5194/acp-2020-1279>

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Abstract

Discussion

Metrics

12 Jan 2021

Review status: a revised version of this preprint was accepted for the journal ACP and is expected to appear here in due course.

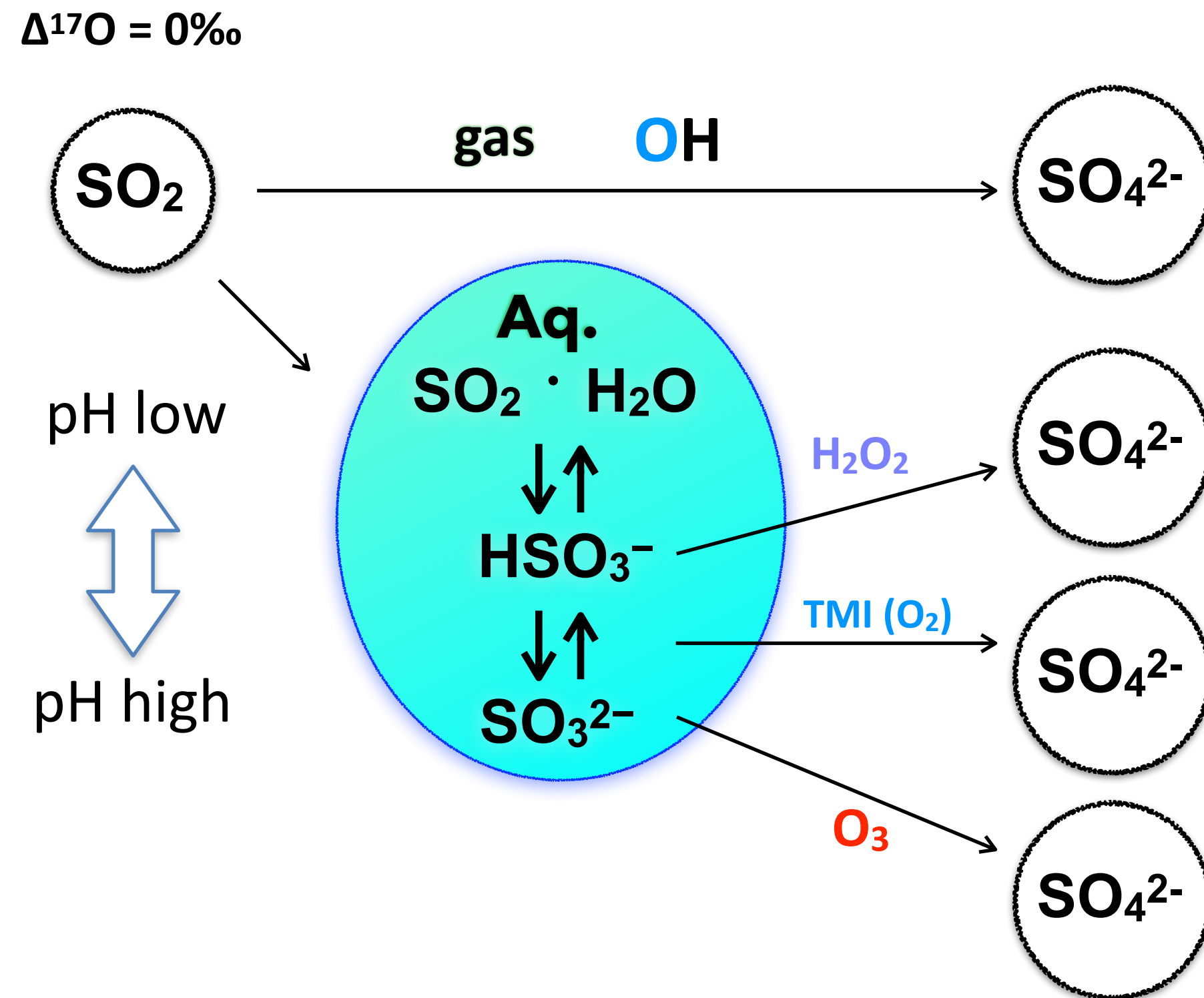
Isotopic constraints on atmospheric sulfate formation pathways in the Mt. Everest region, southern Tibetan Plateau

Kun Wang^{1,2,8}, Shohei Hattori², Mang Lin^{2,3,11}, Sakiko Ishino^{2,4}, Becky Alexander⁵, Kazuki Kamezaki^{2,10}, Naohiro Yoshida^{2,7,9}, and Shichang Kang^{1,6,8}

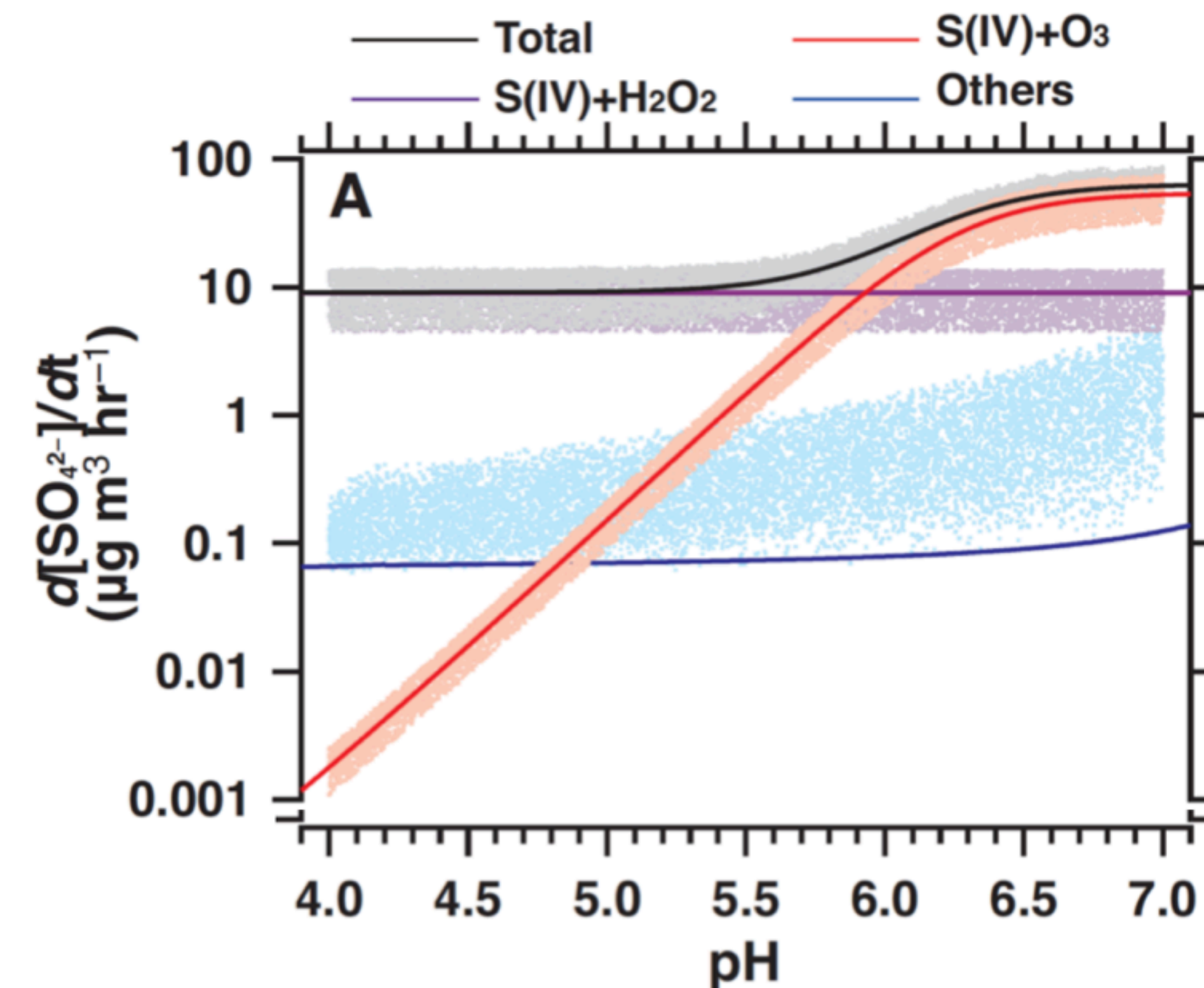
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Acidity (e.g. cloud pH) as factor controlling sulfate formation

Atmospheric sulfate formation occurs in both gas-phase and liquidphase.



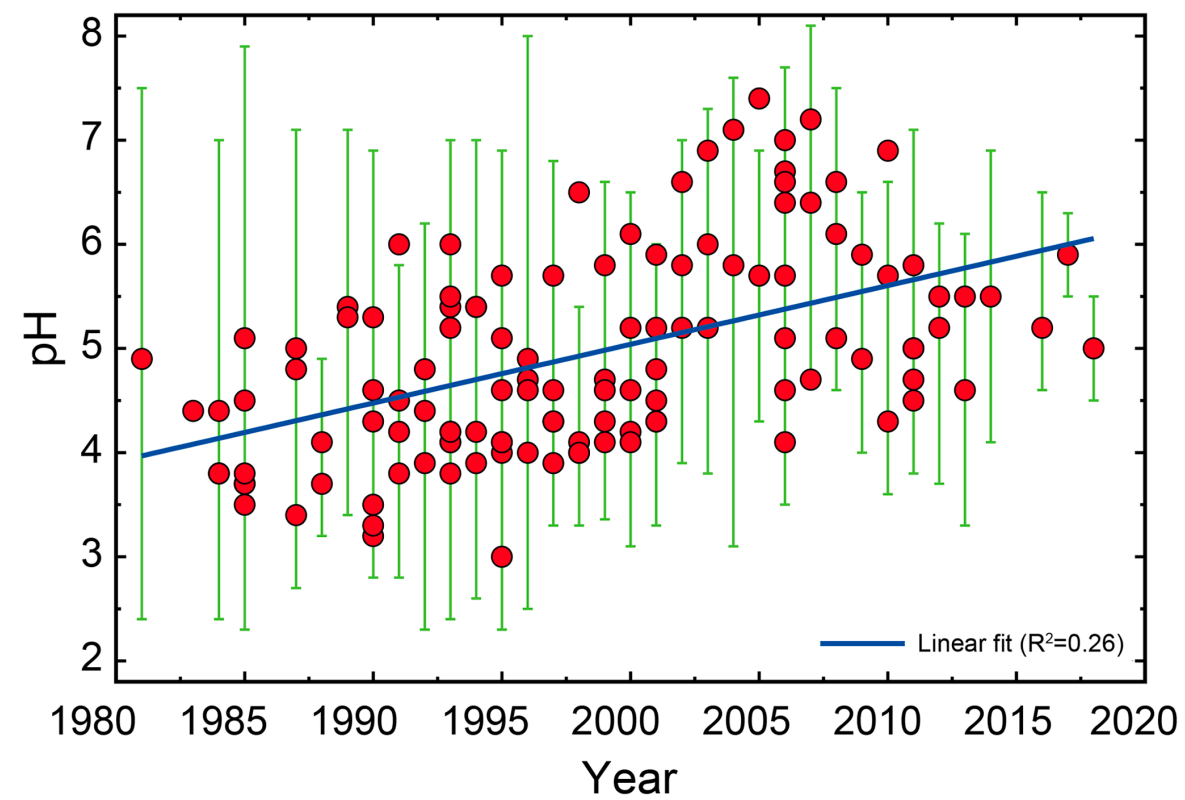
Acidity-induced enhancement of sulfate formation



The aqueous oxidation of S(IV) by O_3 is only significant at high pH conditions greater than $\text{pH} = 5$, due to the strong pH dependence of S(IV) species in solutions (Calvert et al., 1985; Seinfeld and Pandis, 2016). Since the pH in modern cloud water is typically within the range of 3 to 5 (Pye et al., 2020 and references therein), the aqueous oxidation of S(IV) by O_3 is thus considered to be unimportant when compared to the oxidation by H_2O_2 .

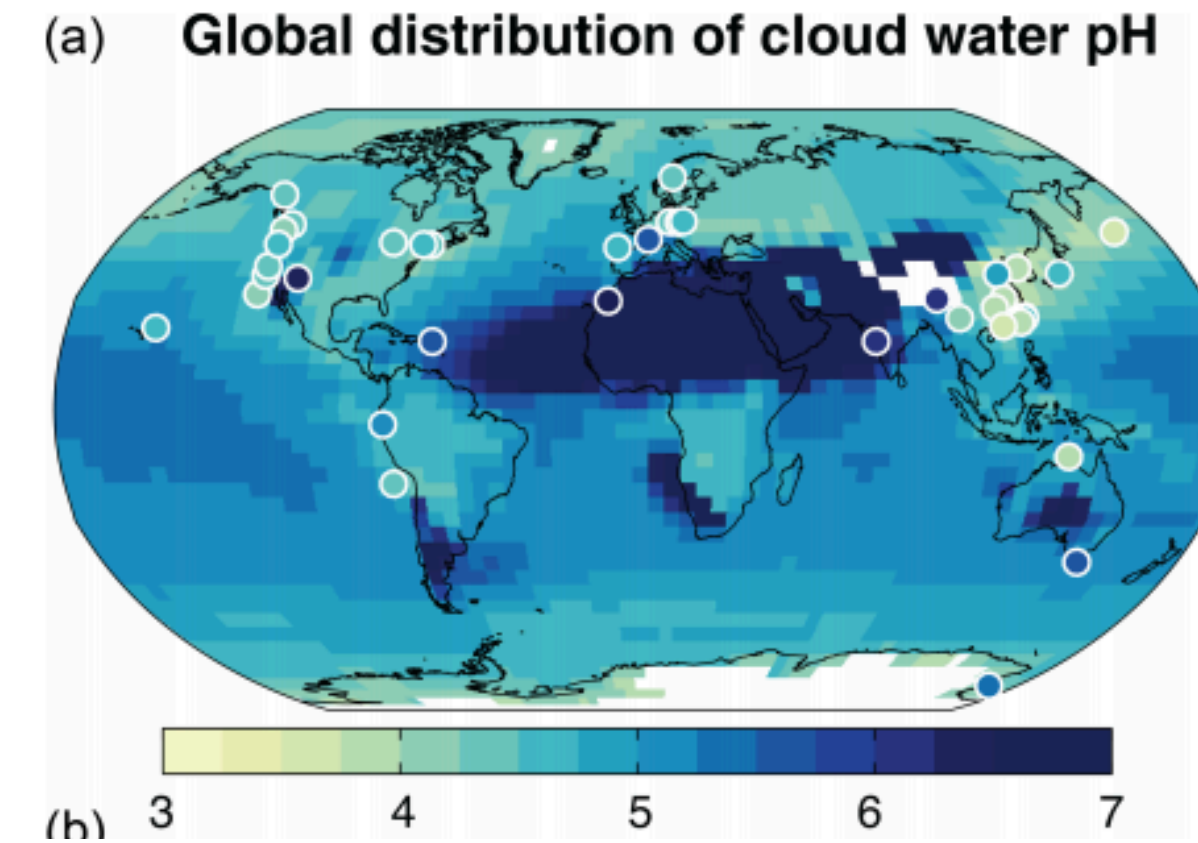
Heterogeneous distribution of cloud water pH in the atmosphere

Decrease of acidity (increase in pH) after 1980s



From Shah et al. 2020 ACP

High pH in dusty region



Is the acidity-dependent sulfate formation pathway ($S(IV)+O_3$ in liquid-phase) really important?

Observation $\longleftrightarrow$ Modeling

There is **no observational evidence** for sulfate formation pathways based on a comparison between observed and modeled sulfate concentrations.

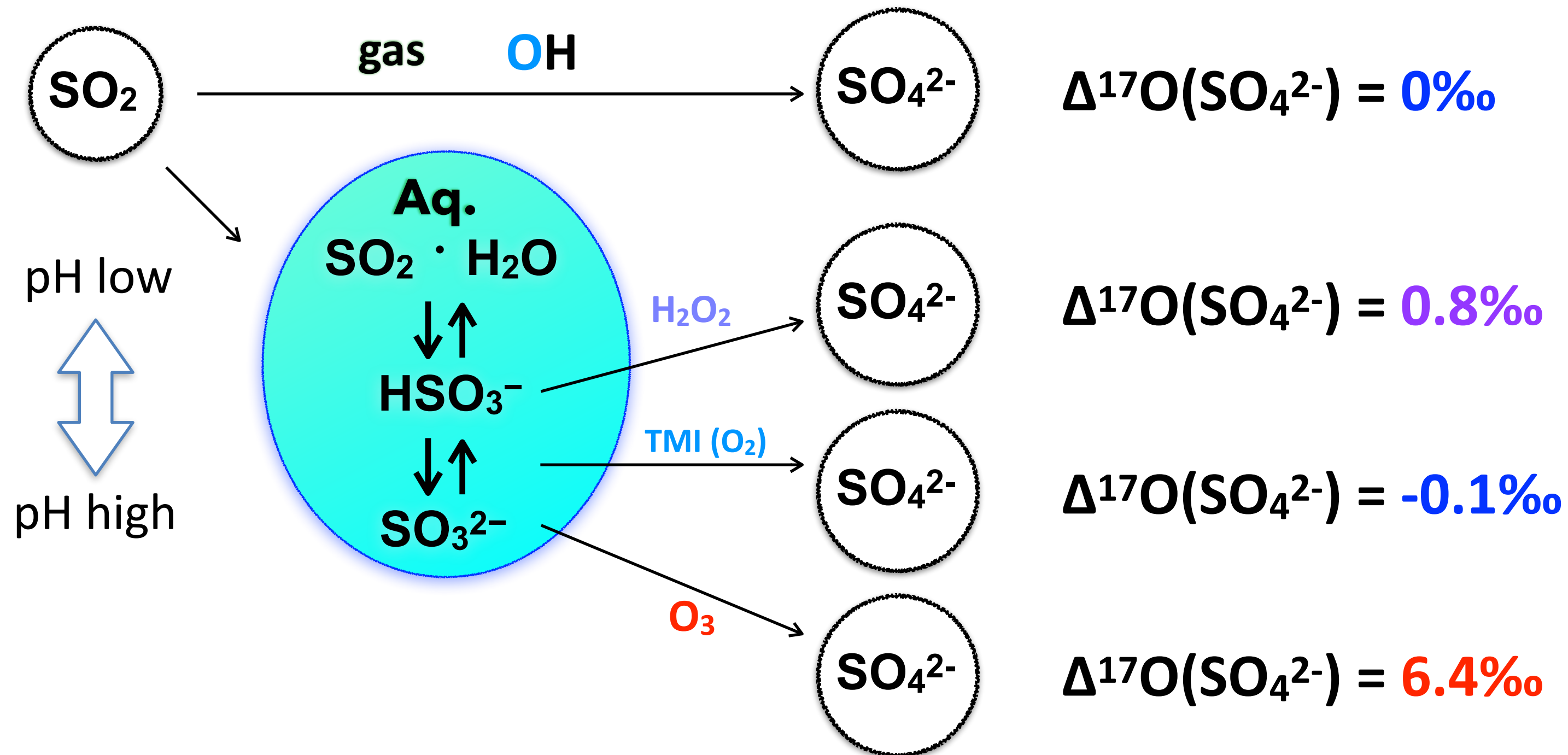
Motivation:
Tracing atmospheric process

$\Delta^{17}\text{O}$ in sulfate: tracer of formation pathway

Simplified definition: $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$

$\Delta^{17}\text{O}(\text{O}_3) = 26\text{‰}$, $\Delta^{17}\text{O}(\text{OH}) = 0\text{‰}$

$\Delta^{17}\text{O} = 0\text{‰}$

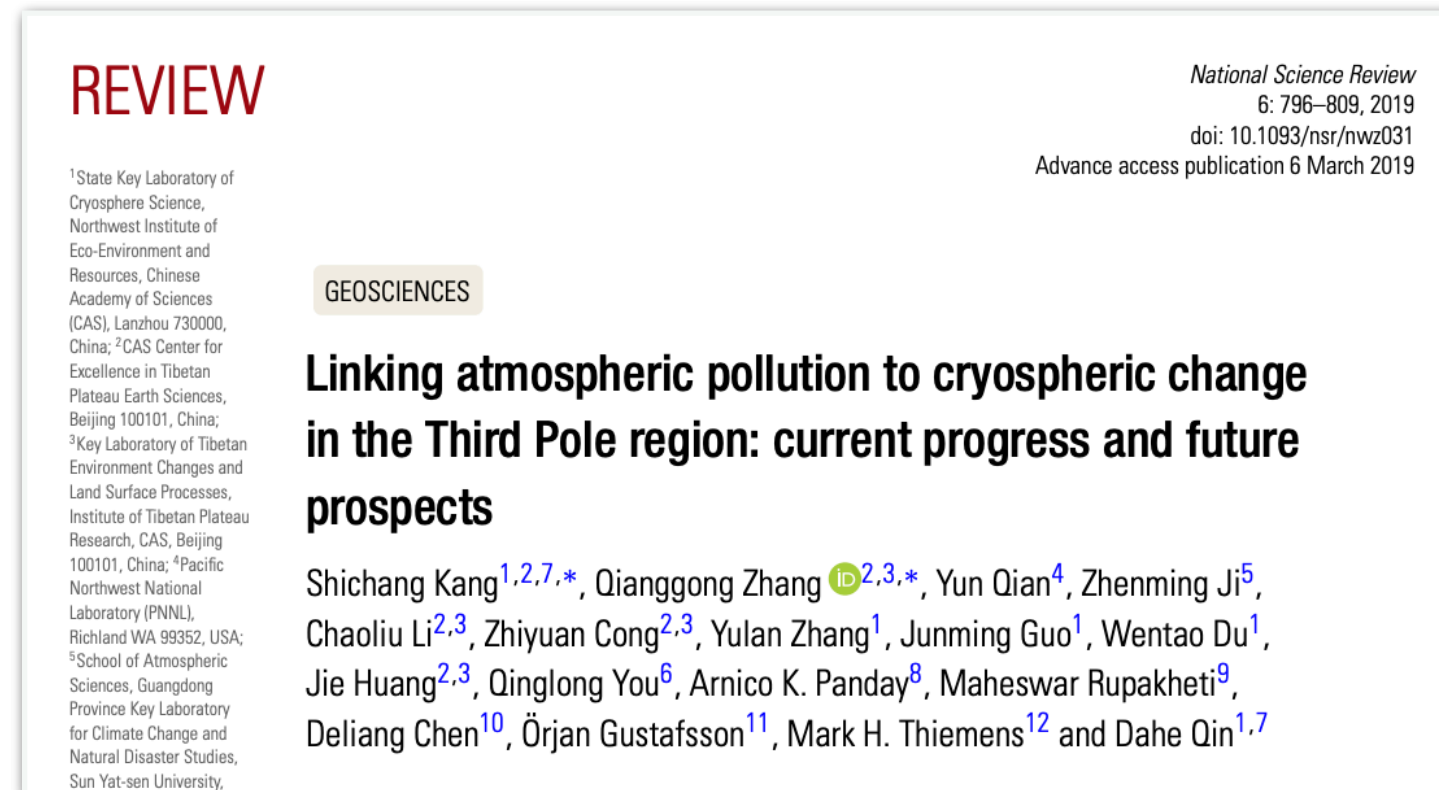


$$f_{\text{O}_3, \text{max}} = (\Delta^{17}\text{O}_{\text{nss-SO}_4^{2-}} - \Delta^{17}\text{O}_{\text{SO}_4^{2-}(\text{TMI})}) / (\Delta^{17}\text{O}_{\text{SO}_4^{2-}(\text{O}_3)} - \Delta^{17}\text{O}_{\text{SO}_4^{2-}(\text{TMI})})$$

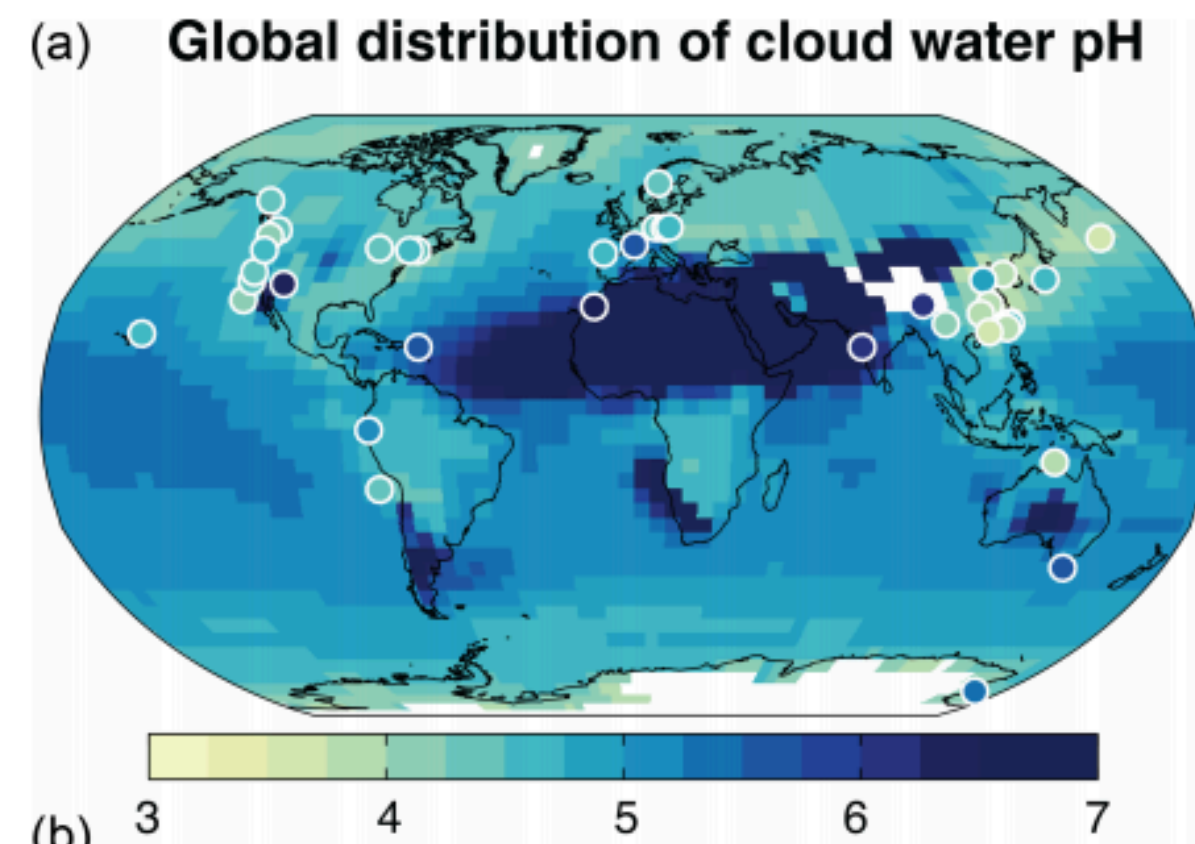
$$f_{\text{O}_3, \text{min}} = (\Delta^{17}\text{O}_{\text{nss-SO}_4^{2-}} - \Delta^{17}\text{O}_{\text{SO}_4^{2-}(\text{H}_2\text{O}_2)}) / (\Delta^{17}\text{O}_{\text{SO}_4^{2-}(\text{O}_3)} - \Delta^{17}\text{O}_{\text{SO}_4^{2-}(\text{H}_2\text{O}_2)})$$

Third Pole

The Tibetan Plateau (hereafter referred to as TP), covering an area of $\sim 2.5 \times 10^6 \text{ km}^2$ and having an average elevation of over 4000 m above sea level (a.s.l.).



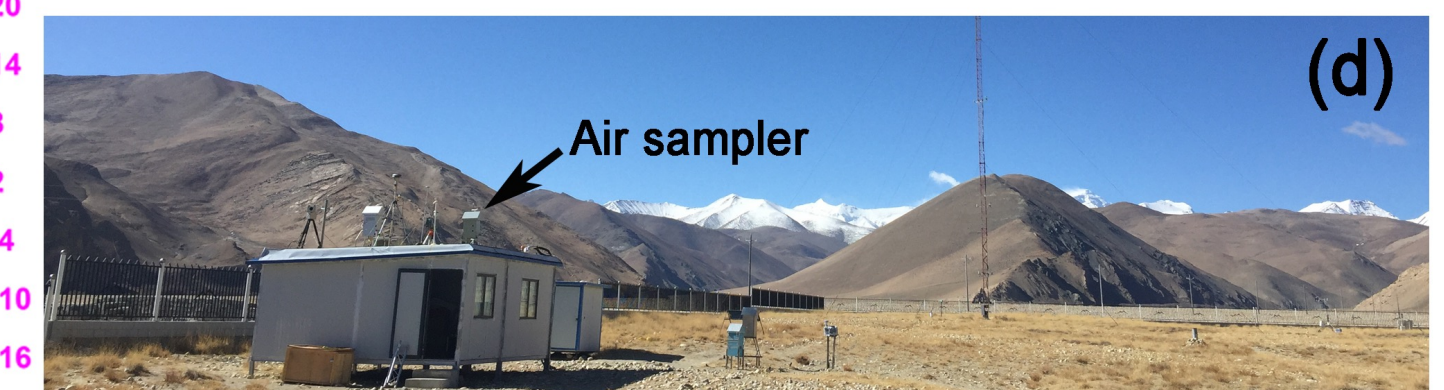
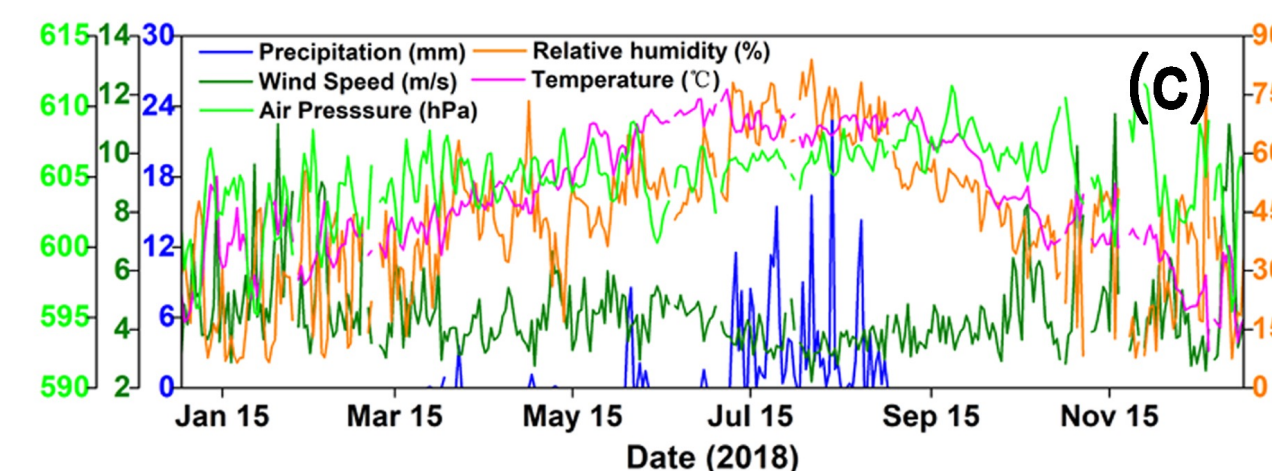
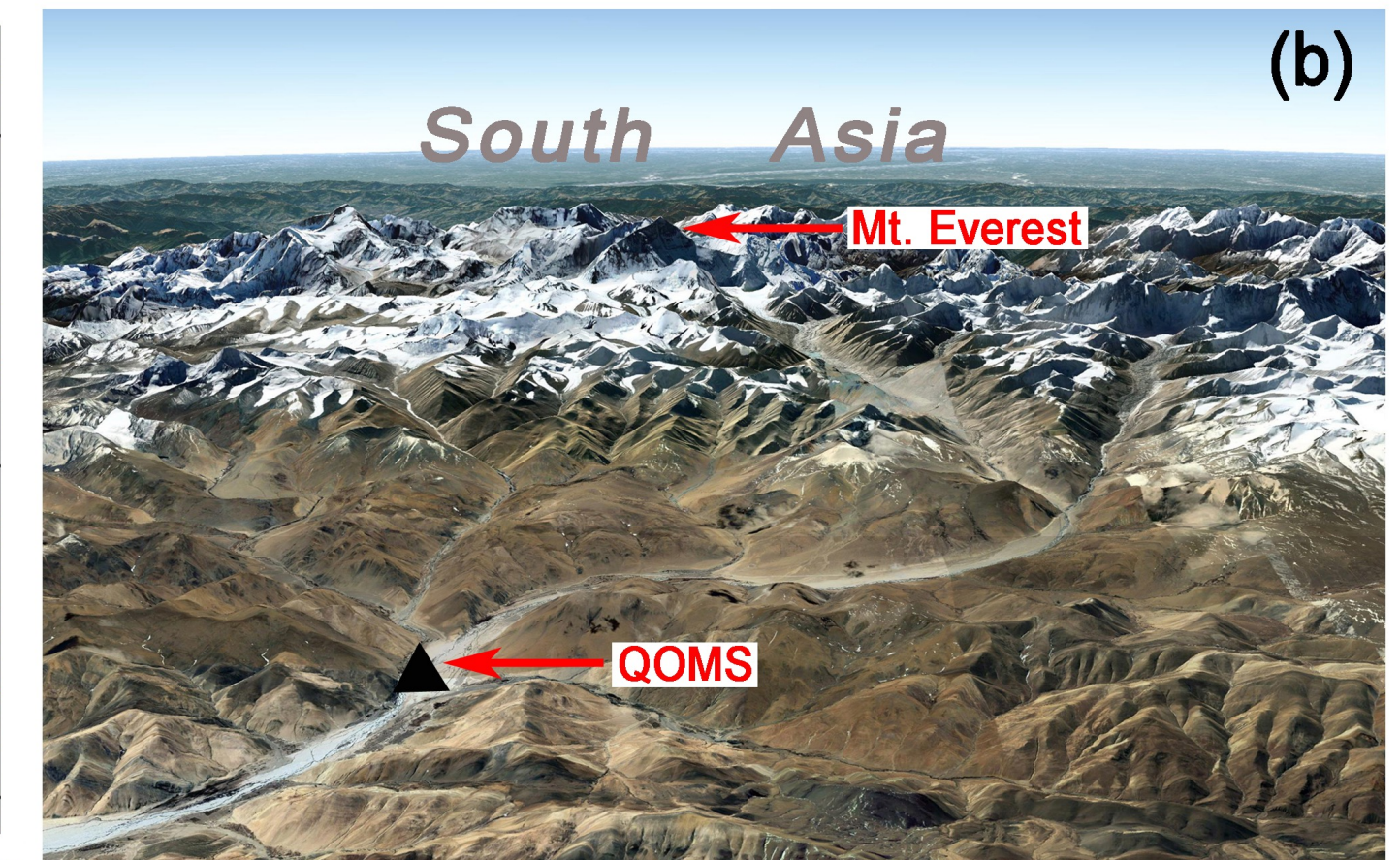
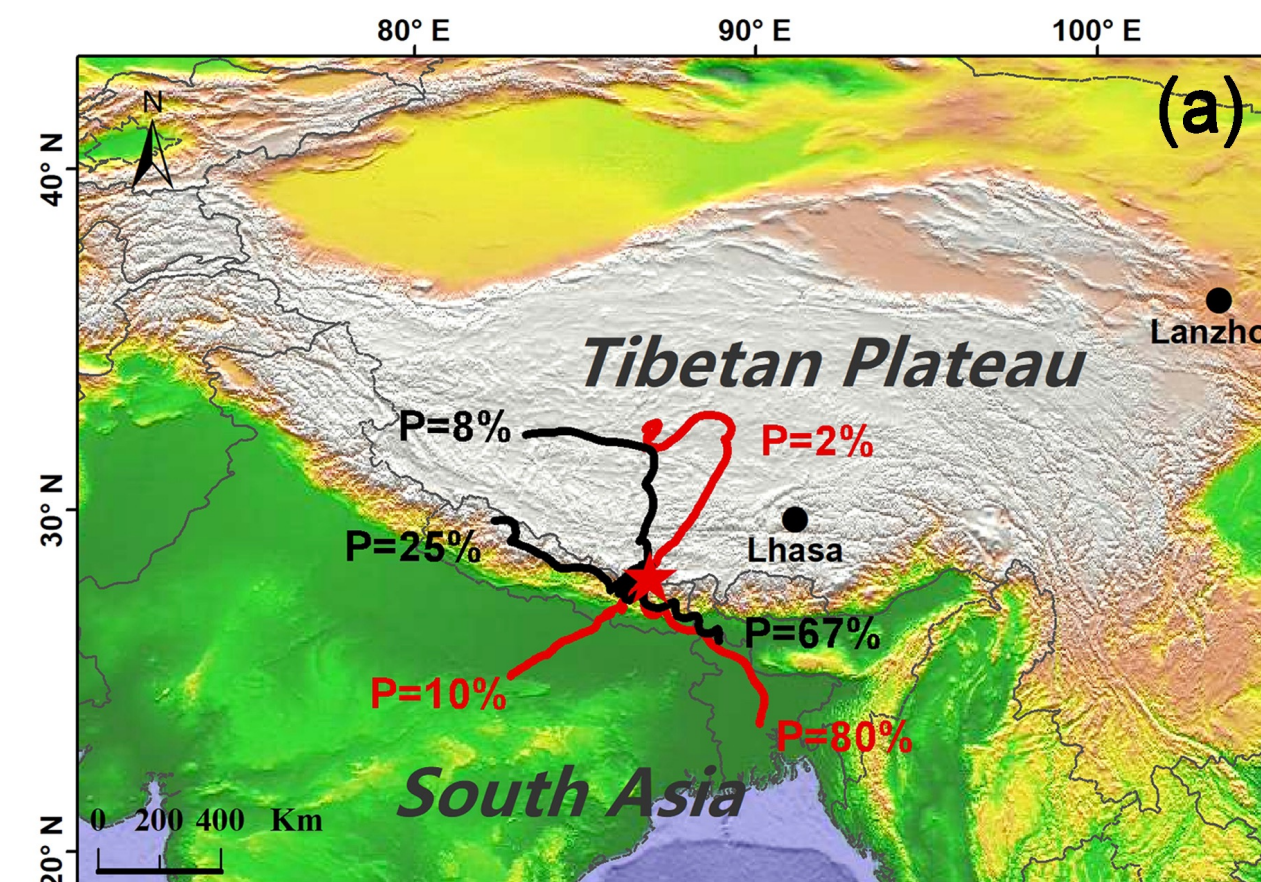
[Kang et al. 2019 National Science Review]



From Shah et al. 2020 ACP

This study: Qomolangma Atmospheric and Environmental Observation and Research Station, CAS (QOMS)

QOMS (28.21°N, 86.56°E, 4276 m a.s.l.)



[Figure 1, Wang et al. accepted in ACP]

Good site to test importance of atmospheric acidity (high pH in dusty region) for sulfate formation.

Comparison with global chemical transport model

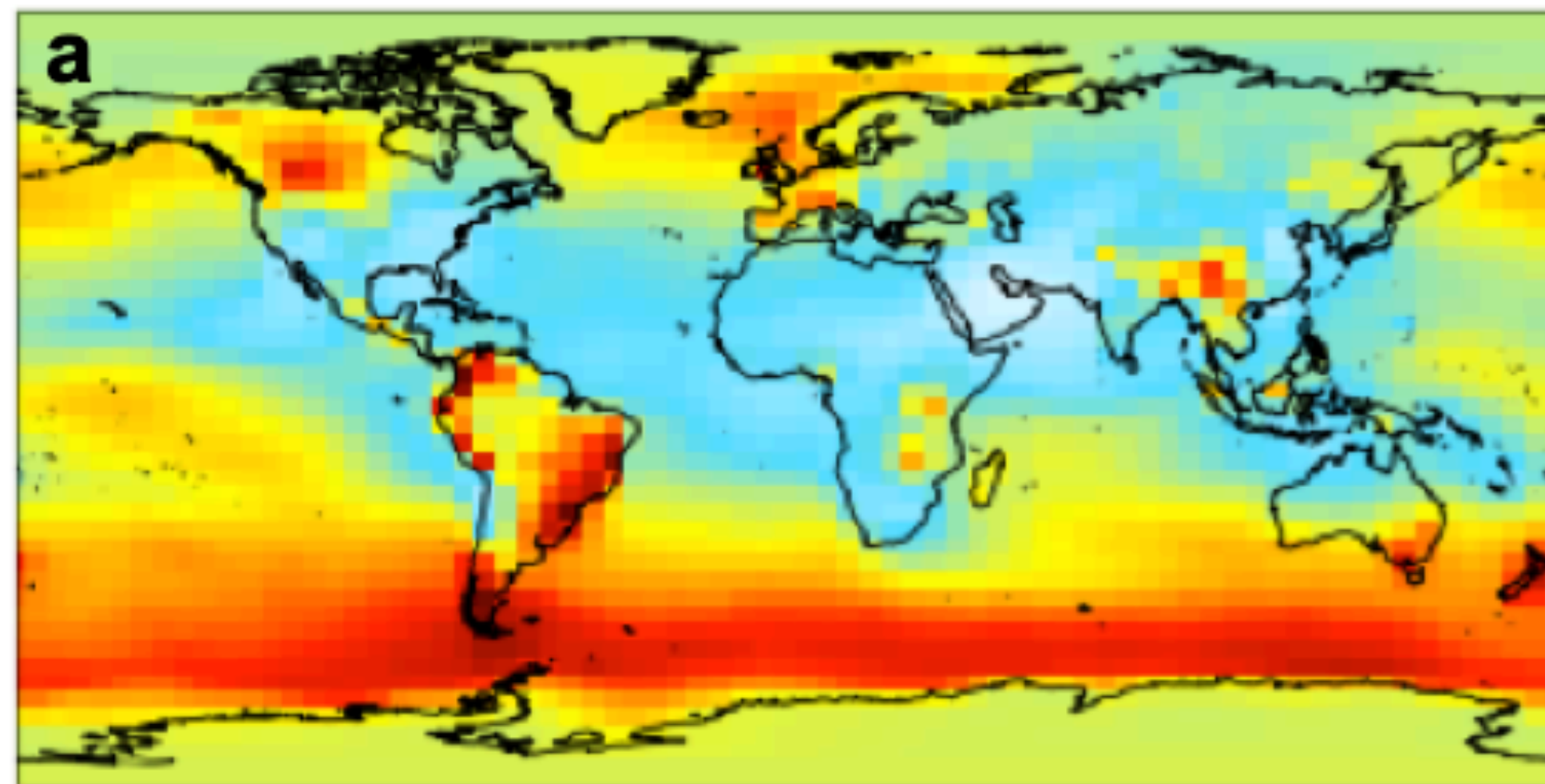
GEOS-Chem

(<http://acmg.seas.harvard.edu/geos/>)

After v12.5, bulk cloud water pH is calculated iteratively using concentrations

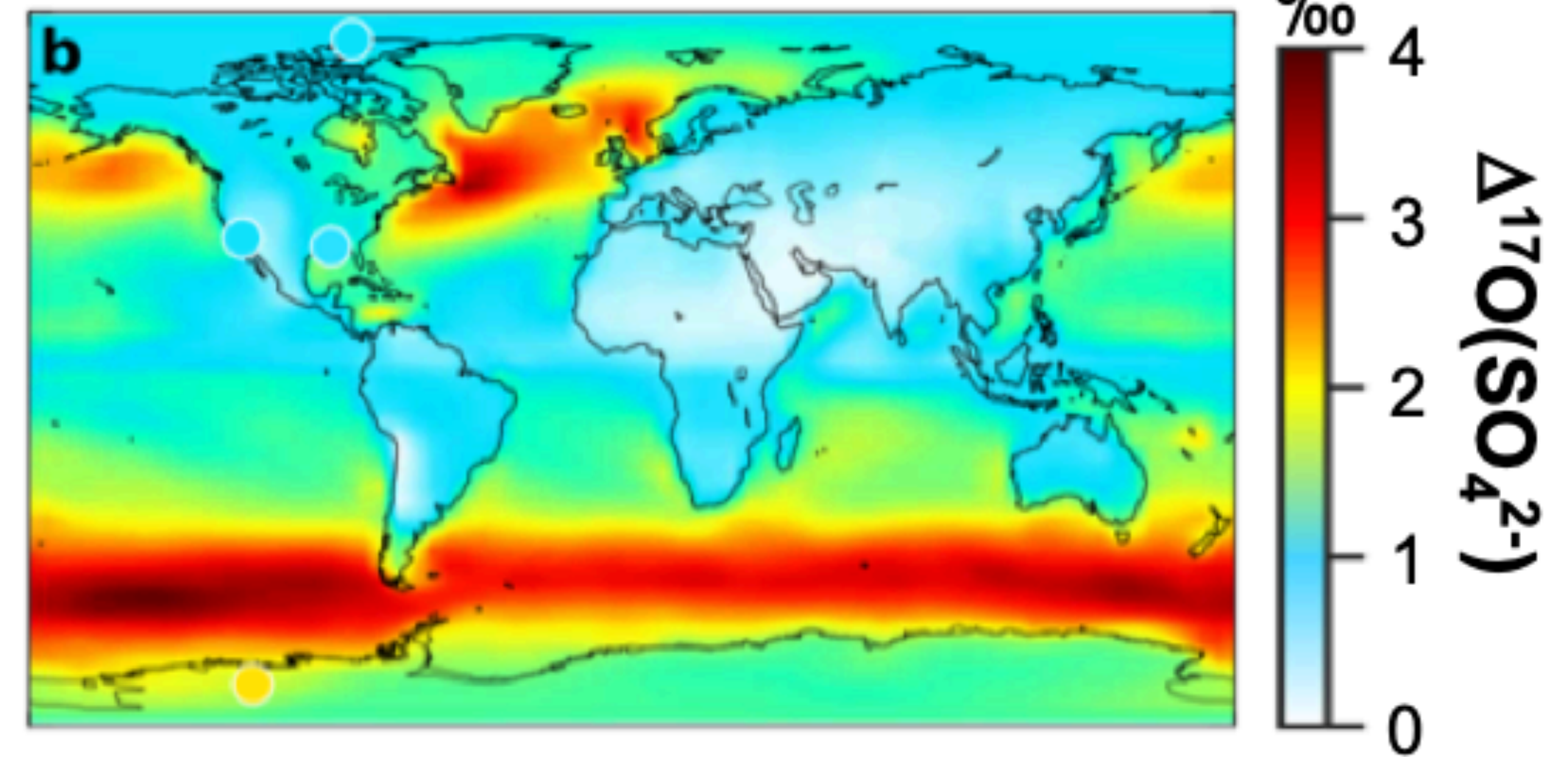
- Version: 12.5.0 updated with cloud water pH calculations
- Grid: 4 x 5 horizontal grid with 47 vertical layers
- Calculated year: 2013 (Met data: MERRA2)
- SO_4^{2-} produced by each oxidation pathway is transported as a separate “tracer” in the model.

Interactive cloud water pH calculation



v. 12.5 (this study)

pH fixed (4.5 for NH, 5 for SH)



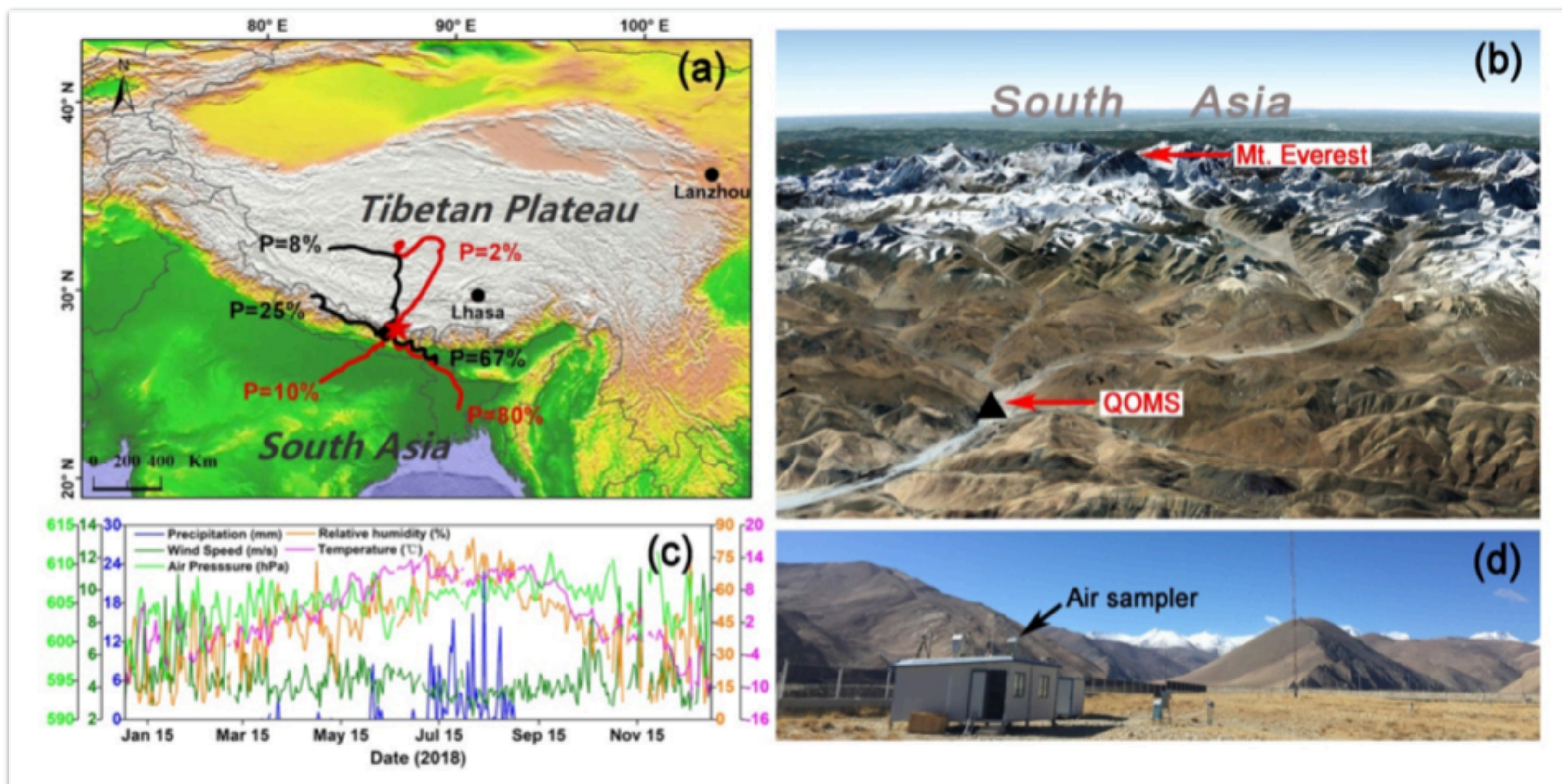
v. 11 (Sofen et al. 2011)

Hattori, Alexander, Savarino, *Springer Nature*,
Handbook of Isotopologue Biogeochemistry, submitted

$\Delta^{17}\text{O}$ of sulfate is expected to be high in dusty region.

Methods: Site, sampling, measurements

The TSP samples were collected by a high-volume air sampler (Laoying-2031, LAOYING Institute, China) mounted on the roof of an instrument room (Fig. 1d). Each sample was collected on a pre-baked (450 °C for 4 h) quartz filters (Whatman Inc., UK), and covered 4-7 d at a flow rate of 1.05 m³ min⁻¹.



Ion concentrations, isotopic measurements for $\Delta^{17}\text{O}$ of sulfate at Tokyo Tech., Japan.

Results: seasonal trend of ion species and BC

Concentrations of the main water-soluble ionic species (e.g., SO_4^{2-} , NO_3^- , Ca^{2+} , K^+) extracted from TSP samples in the Mt. Everest region show very similar and clear seasonal variations (Fig. 2a), with high in pre-monsoon and low in monsoon season. It is likely result from the scavenging effect of precipitation in the monsoon season and more frequent dust storms in the pre-monsoon season.

Mineral dust is considered to be the only significant source of primary sulfate in our study due to frequently occurring dust storms as well as the significant correlations between SO_4^{2-} and Ca^{2+} in both seasons ($r = 0.825$, $p < 0.01$ for pre-monsoon; $r = 0.908$, $p < 0.01$ for monsoon) (Fig. 2b).

Correction to non-dust (nd) SO_4^{2-}

Here we adopt a k value of 0.18, corresponding to a molar ratio of 0.075, which has been widely used in previous studies for the estimation of the terrigenous sulfate (Lin et al., 2020; Kunasek et al., 2010; Patris et al., 2002).

$$[\text{nd-SO}_4^{2-}] = [\text{bulk-SO}_4^{2-}] - k \times [\text{Ca}^{2+}]$$

$$\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{SAS}} = [\text{bulk-SO}_4^{2-}] / [\text{nd-SO}_4^{2-}] \times \Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{bulk}}$$

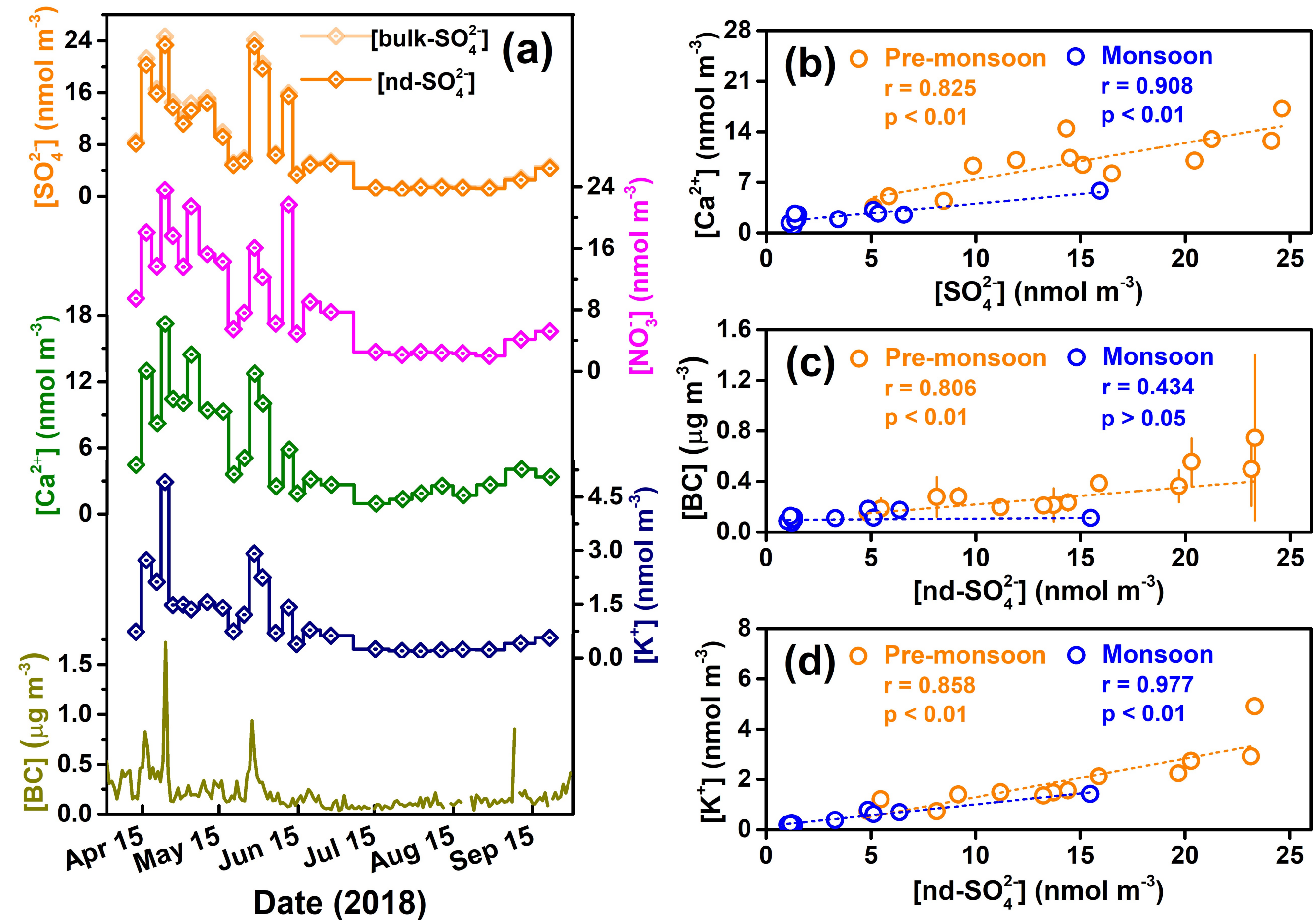
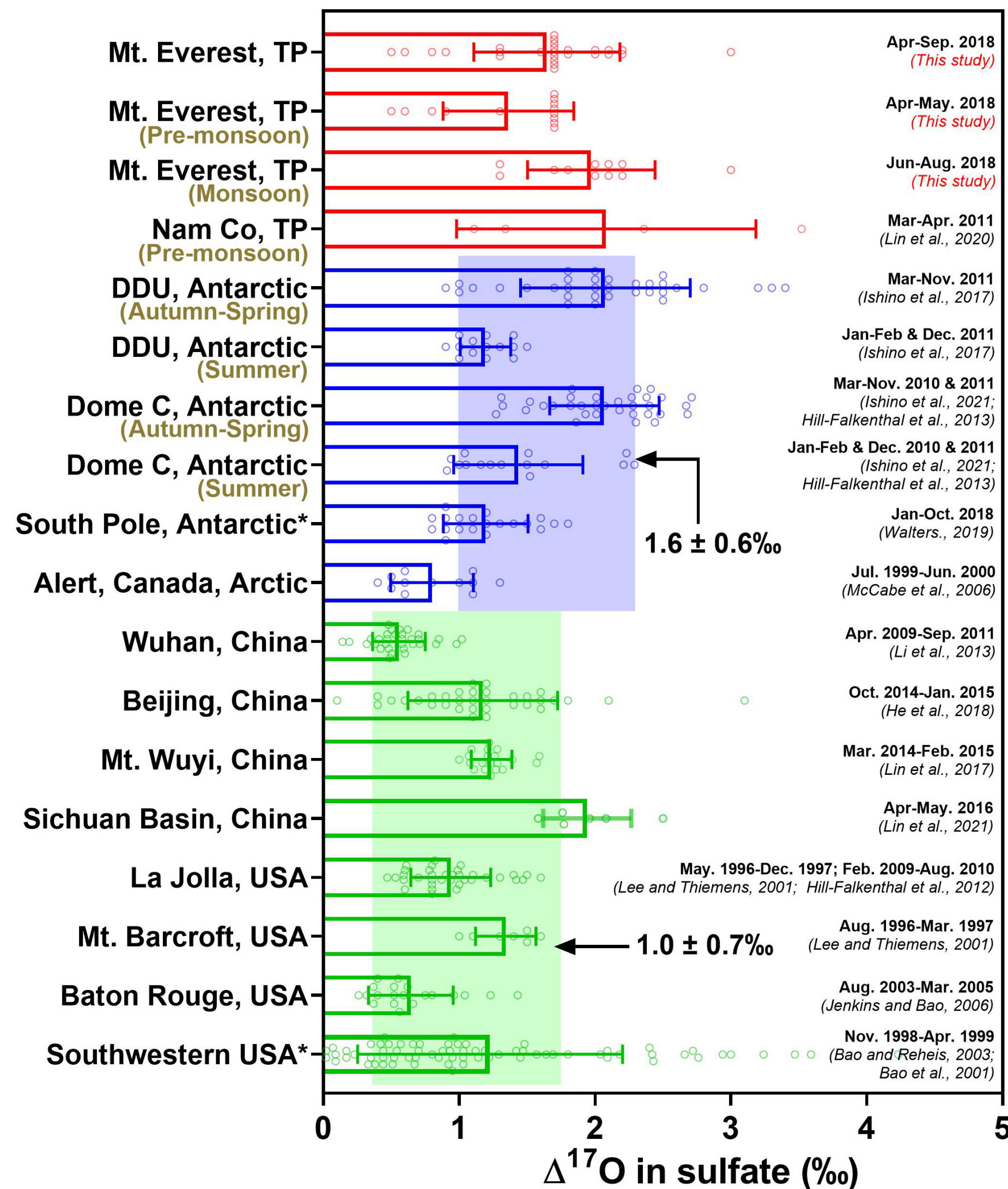


Figure 2: (a) Temporal variations in concentrations of major ions in TSP samples collected from the Mt. Everest region across the entire study period, and (b-d) correlations between $[\text{bulk-SO}_4^{2-}]$ and $[\text{Ca}^{2+}]$, $[\text{nd-SO}_4^{2-}]$ and $[\text{BC}]$, as well as $[\text{nd-SO}_4^{2-}]$ and $[\text{K}^+]$ in the pre-monsoon and monsoon seasons. The error bars in Fig. 2(c) stand for 1σ -uncertainty.

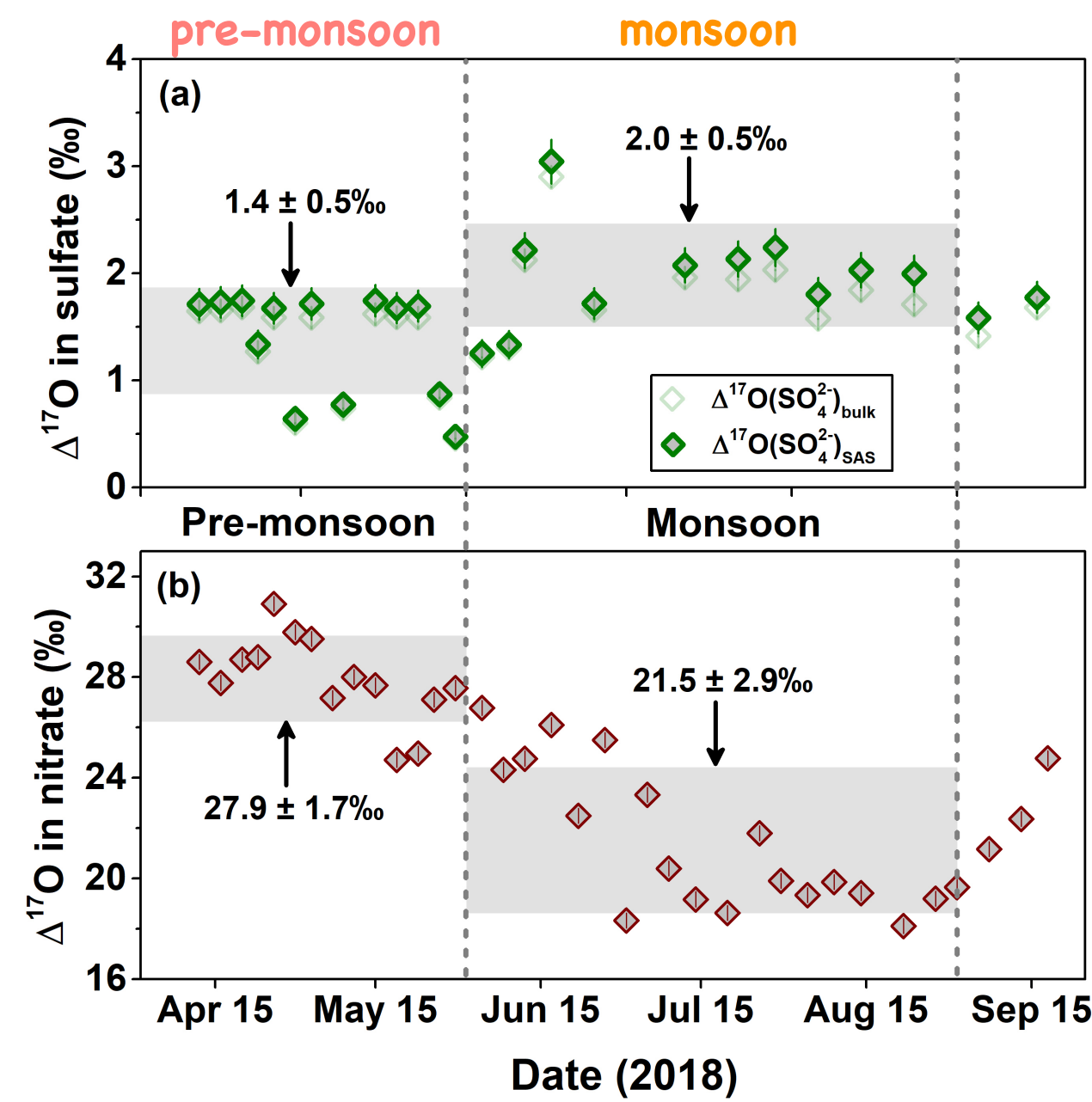
Results: comparison with other place



← Our observed $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ data in the Mt. Everest region (averaged at $1.7 \pm 0.5\text{‰}$) show higher values than those obtained from most of previous measurements at the similar latitude, and are comparable to those from the polar regions. Though the increase of $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{SAS}}$ values from pre-monsoon season (i.e. spring) to monsoon season (i.e. summer) is opposite to typical seasonality observed in polar regions.

↓ $\Delta^{17}\text{O}(\text{NO}_3^-)$ in the same samples (Wang et al., 2020a) shows a typical seasonality (Fig. 4) reflecting the 315 sunlight-driven seasonal changes in the photochemical oxidants, which has been reported in many previous studies conducted from diverse geographic sites (e.g., Michalski et al., 2003; Savarino et al., 2007; Guha et al., 2017; Wang et al., 2019b). Thus, the clear seasonal trend of high $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{SAS}}$ in warm season and low $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{SAS}}$ in cold season observed in the Mt. Everest region imply the existence of characteristic factor controlling sulfate formation.

Reverse seasonality between sulfate and nitrate



$\Delta^{17}\text{O}$ of sulfate in the Tibet region is high.
Importance of S(IV)+O₃ pathway

Discussion: Why is the S(IV)+O₃ reaction important?

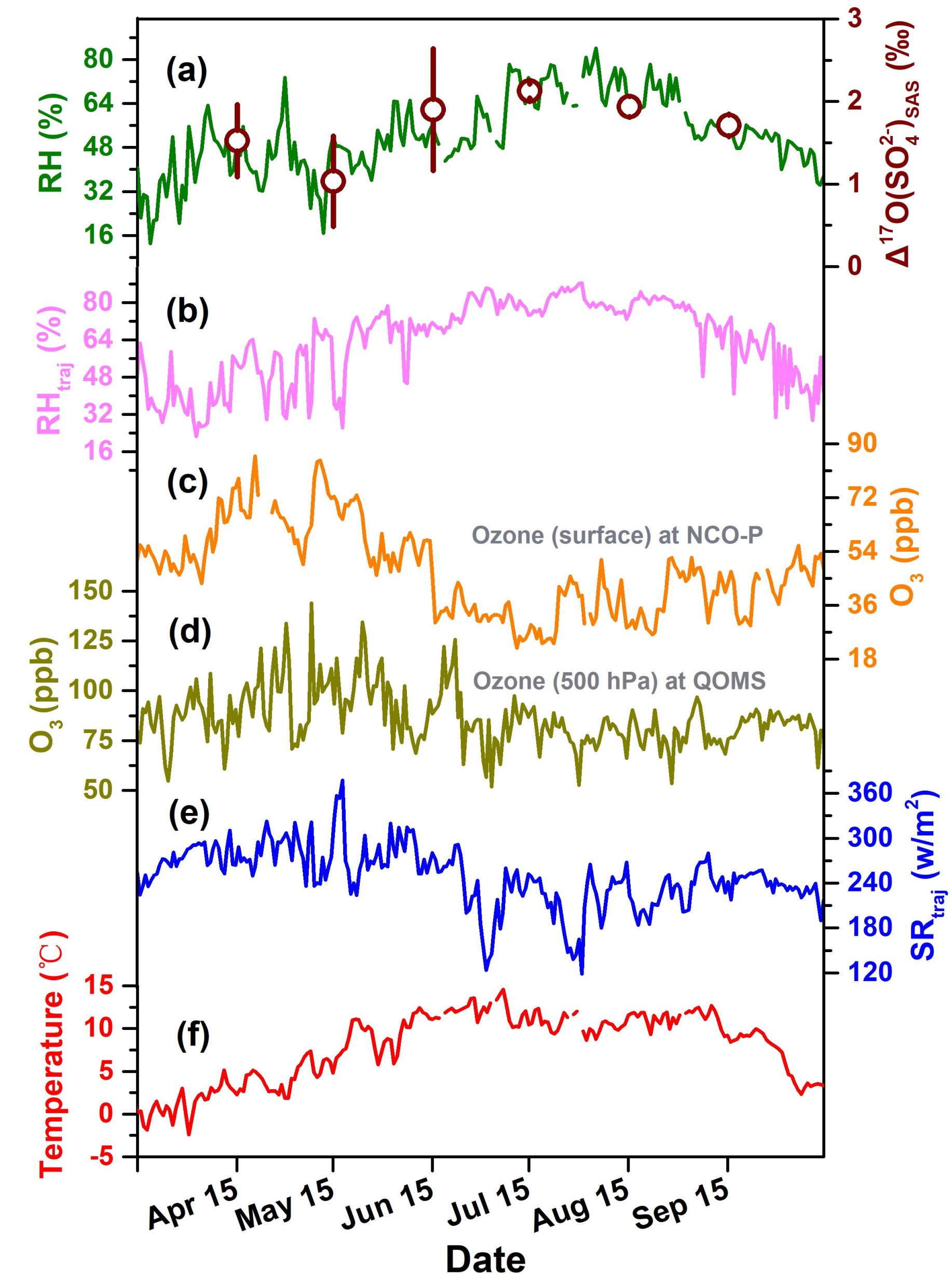
The reverse seasonality of $\Delta^{17}\text{O}(\text{SO}_4^{2-})$

- Correlated with Relative Humidity
- Not correlated with O₃ concentration

High RH results the dilution of acidity of cloud droplet, increasing cloud water pH. The adsorption of SO₂ is thought to be one of the important rate-determining steps for SO₂ oxidation on dust surface suggesting that the heterogeneous reactions on dust surface are very dependent on the SO₂ uptake coefficient, which is further determined by RH (Bauer and Koch, 2005; Li et al., 2006).

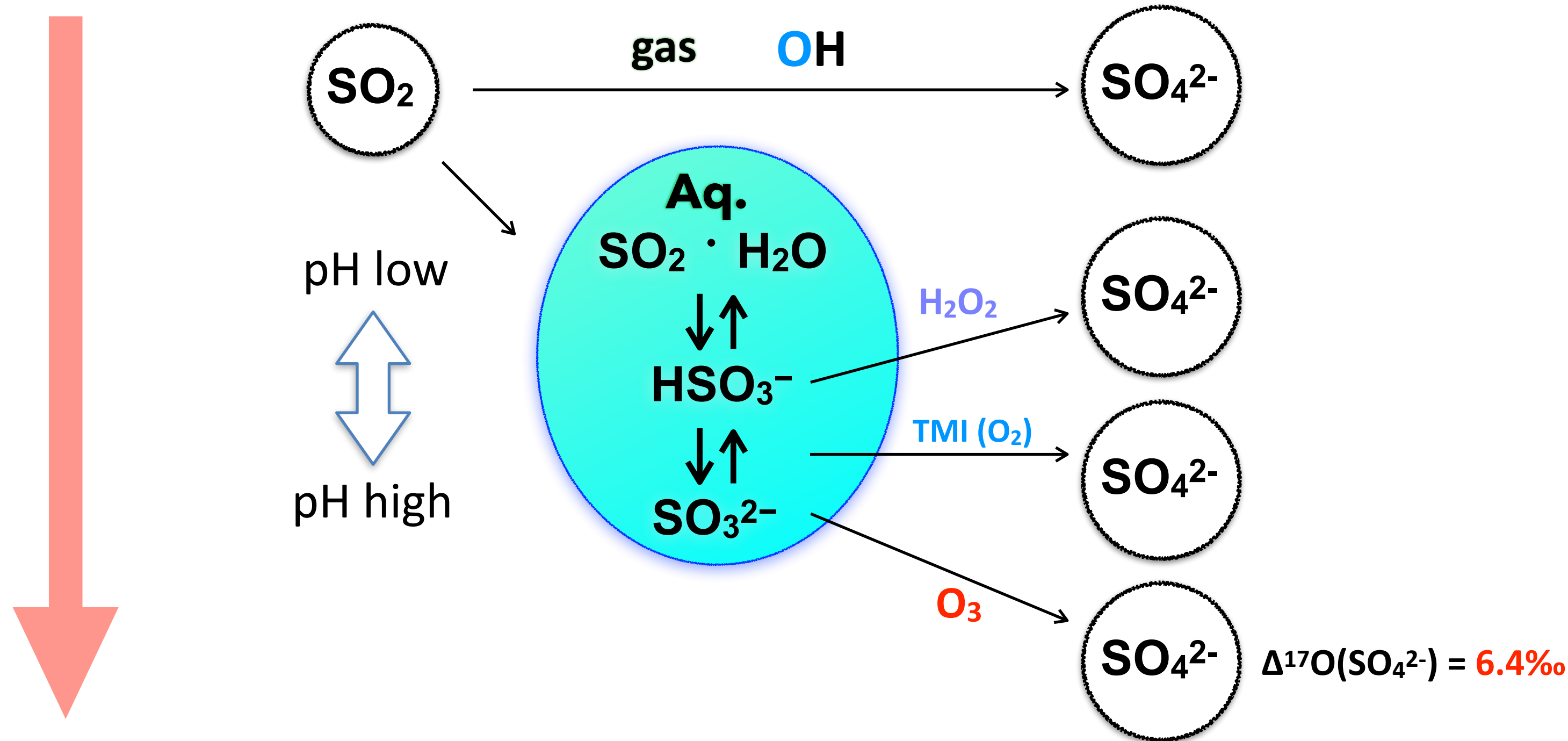
Or, by increasing the hygroscopicity of atmospheric aerosols, RH can promote SO₂ oxidation on the surface of dust aerosols. Thus, RH should play a crucial role in the heterogeneous oxidation processes.

Importance of **liquid phase** chemistry?



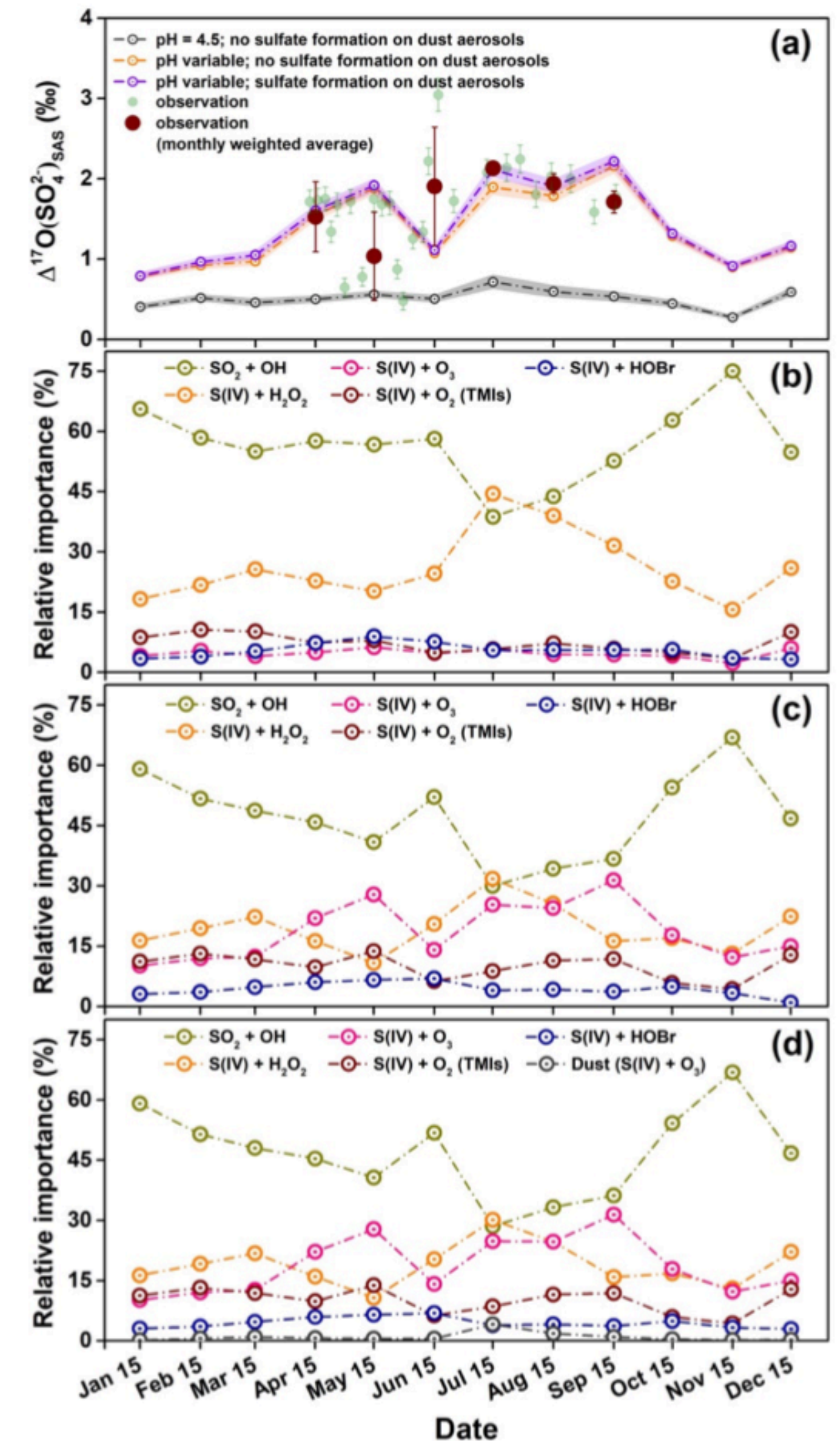
Results: comparison with model

The observed high $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{SAS}}$ is reproduced only when considering interactive pH calculation in the model. In turn, fixed pH model (= 4.5) underestimate $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{SAS}}$.



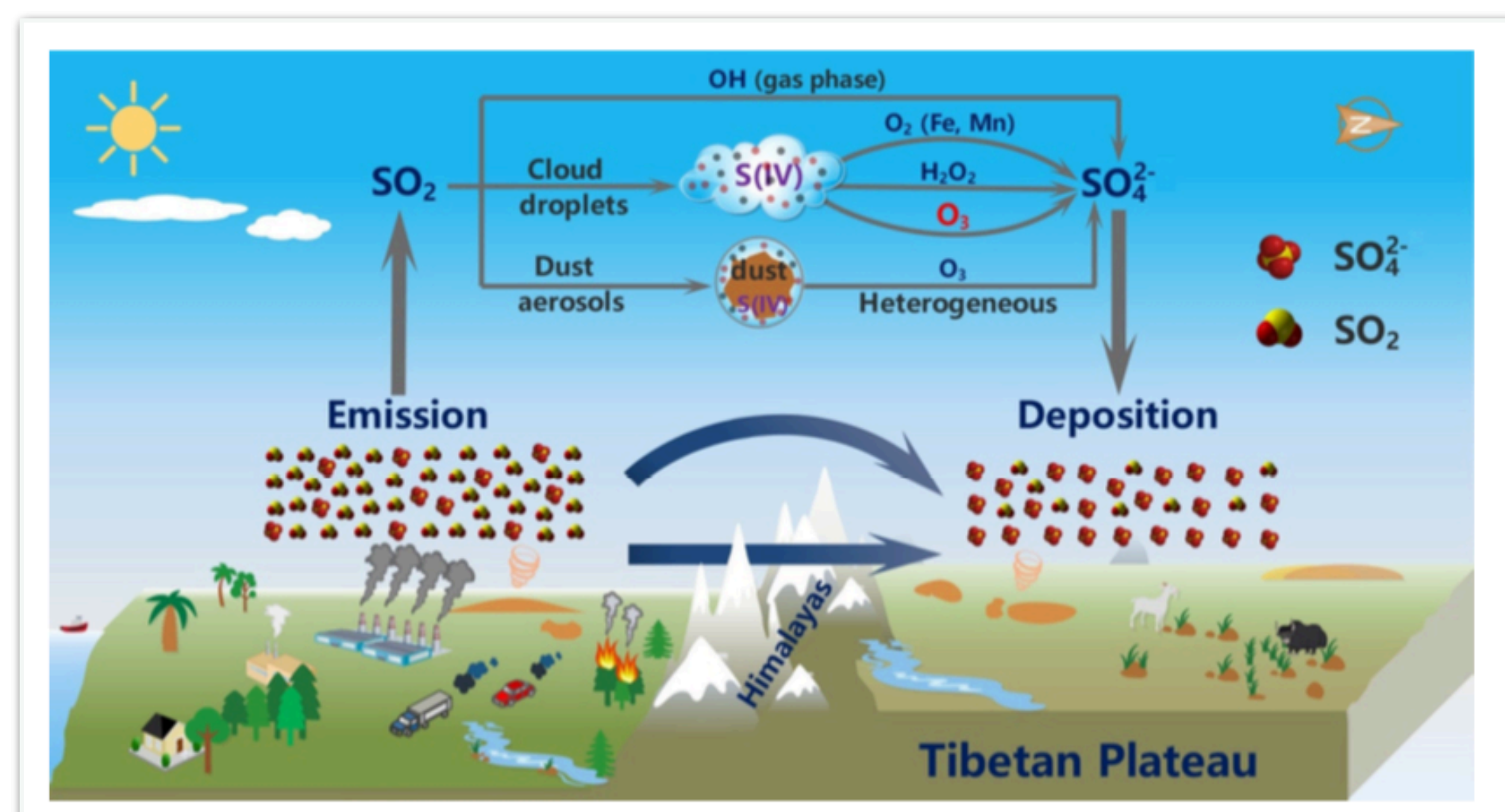
The aqueous oxidation of S(IV) by O_3 is only significant at high pH conditions greater than pH = 5, due to the strong pH dependence of S(IV) species in solutions (Calvert et al., 1985; Seinfeld and Pandis, 2016).

Evidence for importance of atmospheric acidity (high pH in dusty region) for sulfate formation.



Conclusions: importance of atmospheric acidity

Overall, our study provides observational evidence that atmospheric acidity plays an important role in controlling sulfate formation pathways particularly for dust-rich environments. Such identification of key processes provides an important basis for better understanding of the sulfur cycle in the Tibet Plateau, which is further meaningful to accurately evaluate the environment and climatic changes within this region.



This study: An evidence of acidity-driven sulfate formation at Mt. Everest region

Wang, K., Hattori, S., Lin, M., Ishino, S., Alexander, B., Kamezaki, K., Yoshida, N., and Kang, S.: Isotopic constraints on atmospheric sulfate formation pathways in the Mt. Everest region, southern Tibetan Plateau, **Atmos. Chem. Phys.** <https://doi.org/10.5194/acp-2020-1279>, accepted, 2021.

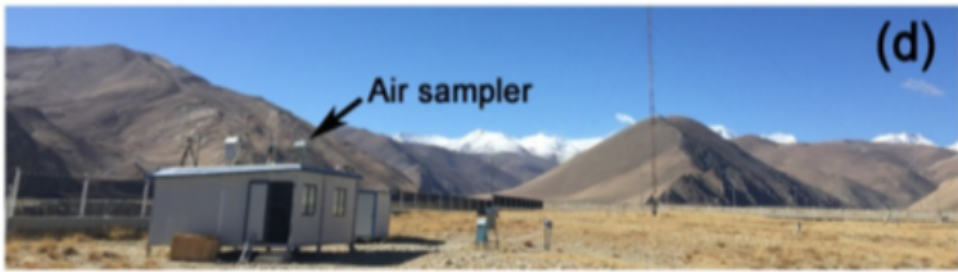
Next paper about acidity-driven sulfate formation

Hattori, S., Y. Iizuka, B. Alexander, S. Ishino, K. Fujita, S. Zhai, T. Sherwen, N. Oshima, R. Uemura, A. Yamada, N. Suzuki, S. Matoba, A. Tsuruta, J. Savarino, and N. Yoshida, Isotopic evidence for acidity-driven enhancement of sulfate formation after SO_2 emission control, **Science Advances**, accepted.

May 5th, 2021. Stay tuned!

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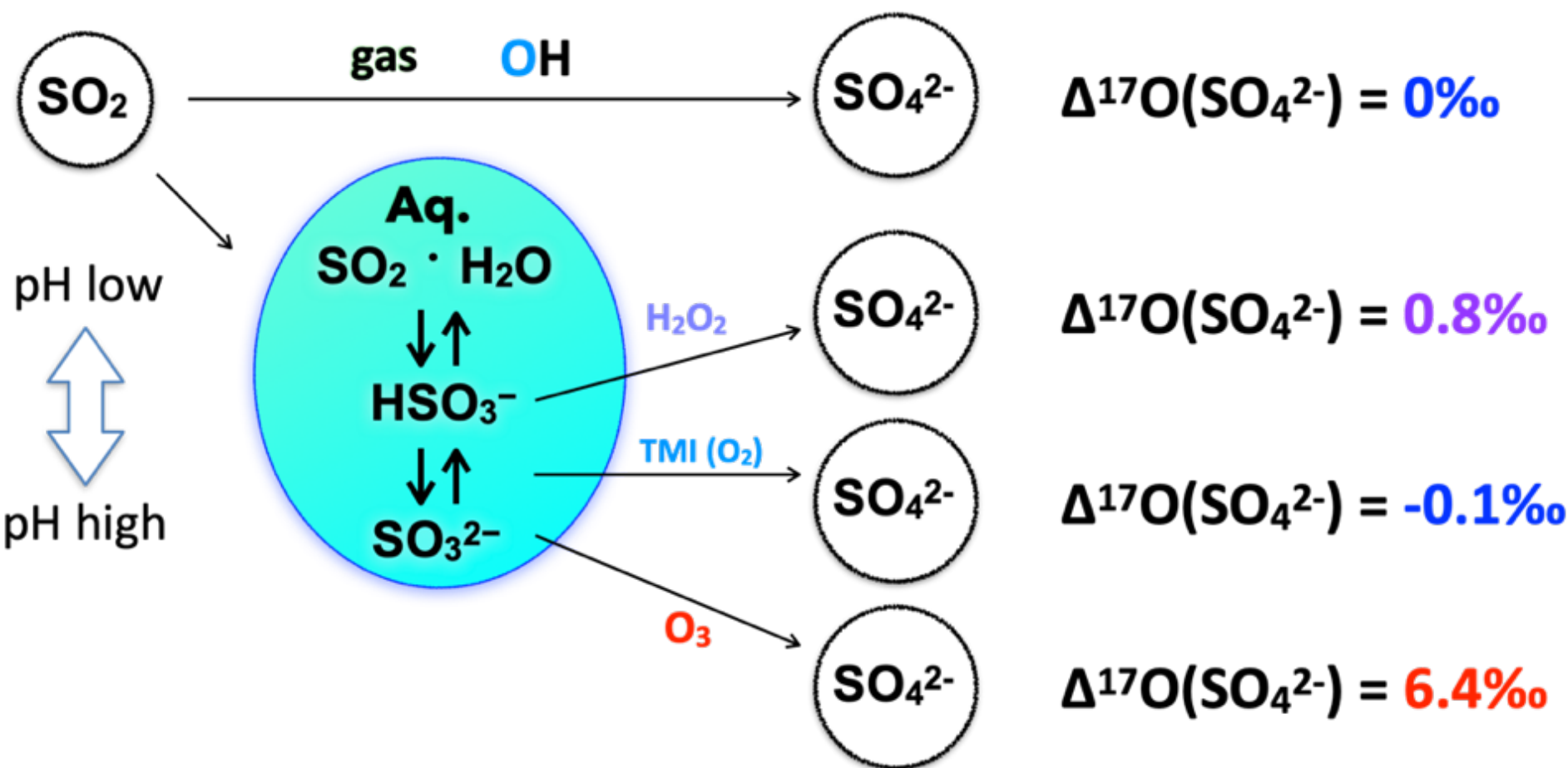
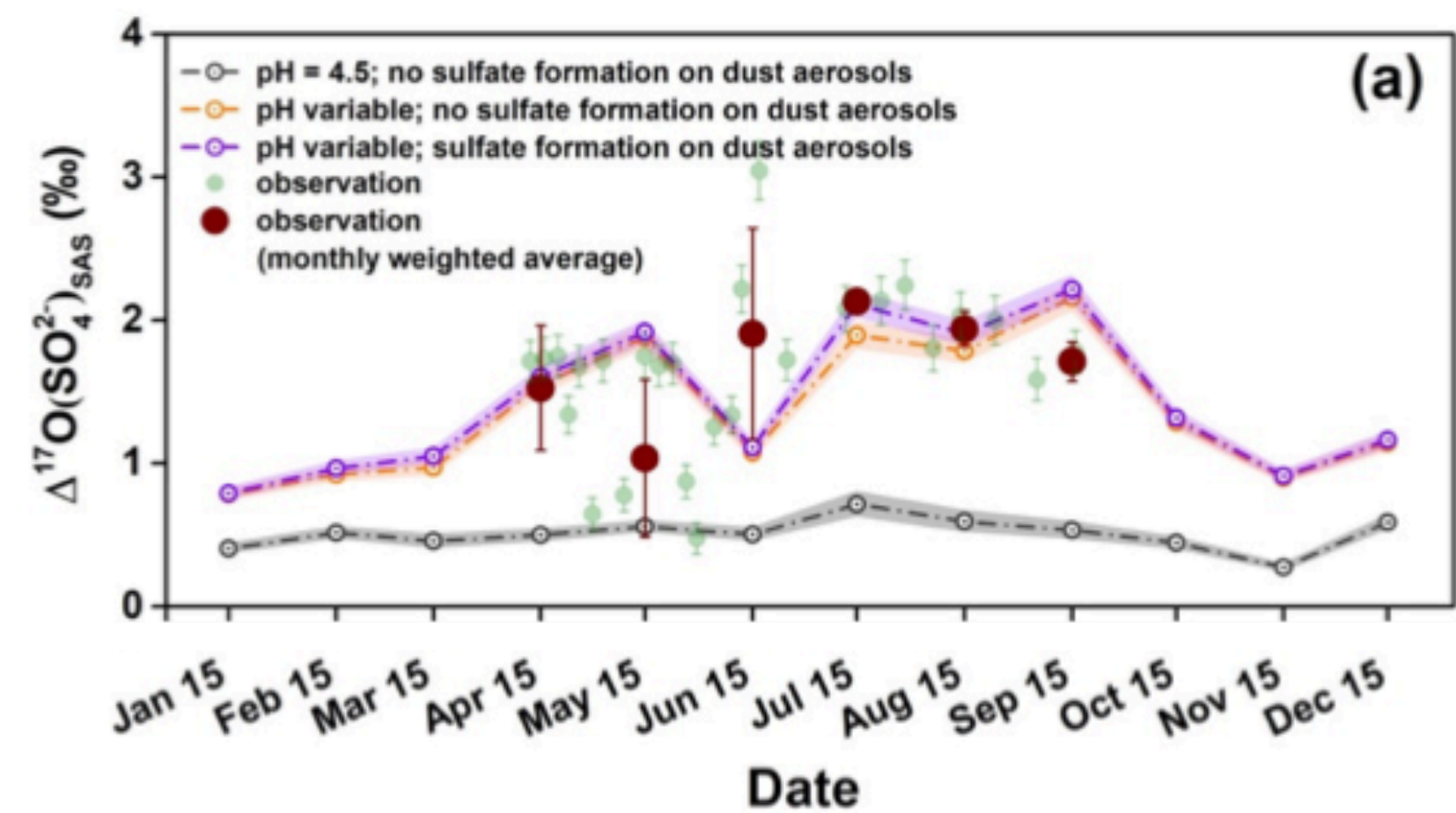


Isotopic evidence for importance of atmospheric acidity on sulfate formation in the Mt. Everest region

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The high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ is found in Mt. Everest region

High $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ is only possible in high pH condition.



Summary: Acidity-driven sulfate formation evidenced by ^{17}O -excess