Science Bulletin 66 (2021) 323–326

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Short Communication

Isotopic signatures of stratospheric air at the Himalayas and beyond

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ARTICLE INFO

Article history:
Received 27 May 2020
Received in revised form 9 September 2020
Accepted 10 September 2020
Available online 12 November 2020

Downward transport of stratospheric air significantly modifies the chemical and radiation budget of the Earth's atmosphere. The Tibetan Plateau including the Himalayas is the largest and highest plateau on Earth and one of the most climatically important, sensitive, and complex regions in the world. Its topography and thermal heating affect the evolution of the Asian monsoon system via its uplift, leading to complex stratospheric-tropospheric interactions that play an important role in the global mass budget [1]. In addition, the plateau is impacted by both naturally and anthropogenically sourced chemicals and is the source area of many major Asian rivers providing a sustainable water supply and food security for billions of people [2]. Constraining the intensity and integrated flux of stratosphere-to-troposphere transport and potential influences on atmospheric chemistry and deposition at the Tibetan Plateau and surrounding regions is therefore central to quantification of their consequences for the hydrosphere and cryosphere near term and in the future.

The strong springtime stratosphere-to-troposphere transport at the Himalayas has been previously recognized [1] but poorly understood due to a dearth of direct field-based measurements of chemical tracers exclusively originating in the stratosphere. Previous attempts to quantify stratospheric influences using ozone (O_3) measurements have embedded uncertainties because O_3 produced in the troposphere via a host of photochemical reactions obfuscates the stratospheric signal [3]. Cosmogenic ^{35}S was recently demonstrated as a sensitive chemical tracer to detect stratospheric air in the planetary boundary layer (PBL) [4]. ^{35}S is a radioactive isotope (half-life: ~87 d) predominately produced in the stratosphere via the spallation of ^{40}Ar by high energy cosmic rays (immediately oxidized to radioactive sulfur dioxide in ~1 s following its cosmogenic origin). Due to the shorter oxidation lifetime of sulfur dioxide (SO_2) than sulfate removal lifetime, most radioactive SO_2 is oxidized to radioactive sulfates ($^{35}SO_4$) during downward transport, and ^{35}S occurs as $^{35}SO_4$ in natural aerosol and snow samples [3–5]. Enrichment of stratospherically sourced $^{35}SO_4$ in ground-level aerosols and snow is consequently a unique chemical signature for quantifying the influence of high-altitude air masses on the Earth's surface. In a pilot study, an unexpectedly high $^{35}SO_4$ concentration was measured in a fresh snow sample collected at Mount Everest during the spring of 2013 [3], potentially indicating a strong stratospheric influence over the Himalayas as noted by previous climatological studies [1]. It was suggested that the downward entrained stratospheric air at the Himalayas including Mount Everest may occasionally transport downwind via the westerly jet (Fig. 1a) [3].

To test the hypothesis that the Himalayas are an important conduit for downward transport of stratospheric air to the troposphere and delineate the extent of stratospheric influence, we report new and comprehensive $^{35}SO_4$ measurements simultaneously made at Mount Everest and the downwind regions (Southeast China) during the 2016 Mount Everest Scientific Expedition Sampling Campaign (April–May 2016) (methods in Supplementary materials online). This new study is focused on quantifying the average contribution of stratospheric air to the Earth's surface on a relatively long time-scale (months) with potentially new insights into climate and paleoclimates, rather than resolving rapid and deep stratospheric intrusion processes at a short weather time scale (hours to days) as shown in our previous work [3].

We observe significant enrichments of stratospherically sourced ^{35}S in atmospheric sulfates collected at Mount Everest and downwind in Southwest China (~2000 km from Mount Everest) (Fig. 1b). These values are higher than existing measured and simulated

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https://doi.org/10.1016/j.scib.2020.11.005
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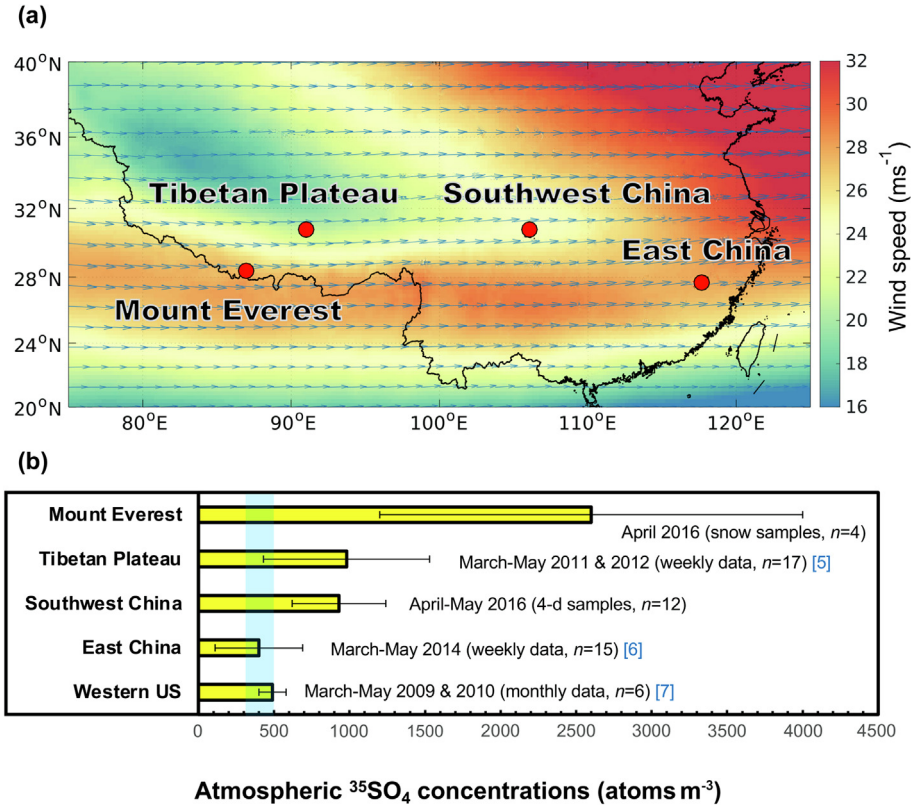

Fig. 1. Sampling sites and springtime atmospheric $^{35}SO_4$ concentrations. (a) Maps showing locations of atmospheric $^{35}SO_4$ sampling sites in this and previous studies. The base map is the mean wind field in the upper troposphere (250 hPa) during the study period (April–May 2016) based on the ERA5 reanalysis data. (b) Springtime $^{35}SO_4$ concentrations measured at five different mid-latitude sites. The average $^{35}SO_4$ concentration at Mount Everest is estimated from blowing snow samples (see methods in Supplementary materials online for details). Data from Nam Co at the Tibetan Plateau [5], Mount Wuyi at East China [6], and La Jolla at Western United States [7] are also included. Error bars stand for one standard deviation. Shaded blue vertical bars indicate steady-state $^{35}SO_4$ concentrations at mid-latitudes simulated in previous studies [4,6,7].

$^{35}SO_4$ concentrations for mid-latitude regions [5–7]. In most stratospheric intrusion events, "fresh" stratospheric air only reaches the free troposphere because vertical transport from the free troposphere to the stable PBL is inefficient. If the PBL turbulence becomes strong, "aged" stratospheric air masses in the free troposphere may be entrained to the PBL, and the stratospheric signal in the PBL is diluted by efficient mixing in the troposphere. In these "aged" stratospheric air masses, $^{35}SO_4$ concentrations are approximate ~1000 atoms m^{-3} based on previous measurements in 4-d samples [7]. In some rare cases, complex coupling of tropopause folds, long-range transport, and turbulent PBL dynamics facilitates the direct penetration of stratospheric air from the stratosphere to the PBL. An extremely high $^{35}SO_4$ concentration (~7000 atoms m^{-3}) was observed in a 4-d sample influenced by "fresh" stratospheric air in a deep stratospheric intrusion event [4]. In light of these previous measurements [4,7], we rule out the possible influences of "fresh" stratospheric air at Southwest China because of the absence of extremely high $^{35}SO_4$ concentrations (>5000 atoms m^{-3}) in our 4-d samples during the sampling campaign. This interpretation is consistent with previous global climatological investigations showing that deep stratospheric intrusions occurring directly across Southwest China are dynamically unlikely [1]. Alternatively, relatively high $^{35}SO_4$ concentrations (1000–2000 atoms m^{-3}) in 6 (of 12) samples reveal that Southwest China may be frequently (~50%) influenced by "aged" stratospheric air that originated from the Himalayas and mixed into the PBL of our study region from the free troposphere. Our interpretation is supported by the spatial distribution of mean wind field in the upper troposphere during our study period (Fig. 1a), which displays a strong westerly jet over the Himalayas and Southwest China, a pattern similar to that observed during stratospheric intrusion episodes identified in our previous study [3]. Our first-order estimation of intrusion frequency may be further improved in the future using sophisticated mesoscale meteorological simulations that incorporate ^{35}S tracer to match our observations.

A consideration is the possible influence of the PBL structure. If the observed high $^{35}SO_4$ concentrations were due to a stable PBL, simultaneous accumulation of stable sulfates in the stable PBL should have been observed, and ^{35}S specific activities (SA; defined as the concentration ratio of radioactive $^{35}SO_4$ to total sulfates) would not increase (or may even decrease). Simultaneously increased sulfate concentrations are however not found in ^{35}S-enriched samples (Fig. S1a online), and samples characterized by high ^{35}S concentrations also have high ^{35}S SA (Fig. S1b online). These observations strongly support our interpretation that the observed enrichment of ^{35}S is a result of enhanced stratospheric influences rather than changes in the stability of the PBL. Overall, our data indicate that stratospheric air frequently intruded into the troposphere at the Himalayas during our study period, mixed with tropospheric air in the upper troposphere and transported to a large geographic region on the side of the westerly jet (Fig. 1a). The interannual variations of springtime tropopause pressure and potential vorticity at 200 hPa over the Himalayas in the 21st century do not display unusually strong stratospheric intrusions activated in 2016 (Fig. S2 online). Consequently, we suggest that the stratospheric influence at the Himalayas and its downwind region is likely an annual occurrence. The significant high-altitude influences on the Earth's highest plateau and its surrounding region may enable us to define unrecognized chemistry and potentially climate information not only at present but also in the past.

To evaluate the stratospheric influence on atmospheric chemistry, we additionally measured the ^{17}O anomaly (defined as non-zero values of $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) in sulfates (methods in Supplementary materials online). The $\Delta^{17}O(SO_4)$ value is controlled by the oxygen isotopic composition of oxidizing reagents responsible for SO_2 oxidation in the troposphere (e.g., OH radicals, O_2, H_2O_2, O_3), among which H_2O_2 and O_3 are the only two known species contributing to positive $\Delta^{17}O(SO_4)$ (Fig. 2a) [8–10]. $\Delta^{17}O$ values in non-dust sulfate aerosols from Southwest China (1.58‰–2.50‰) and the Tibetan Plateau (1.11‰–3.52‰) are generally higher than those from East China (<1.6‰) [11–13]. Given the relatively small $\Delta^{17}O$ values in atmospheric H_2O_2 (~1.3‰) [8], tropospheric O_3 possessing large $\Delta^{17}O$ values (~26‰) [9] is a likely source of anomalously enriched ^{17}O in our collected sulfates (Fig. 2a). If the anomalous enrichment of ^{17}O was a consequence of oxidation pathway shifts related to O_3 in both sites, a positive correlation between O_3 mixing ratios and $\Delta^{17}O(SO_4)$ values as observed in the Tibetan Plateau (Fig. 2b) should have also been observed in Southwest China. However, an opposite relation in Southwest China is observed in the relatively limited dataset (Fig. 2b). We note that high O_3 mixing ratios in the sampling site at the highly populated Southwest China are generally accompanied by high pollution events (characterized by $PM_{2.5}$ concentrations) rather than downward transport of high-altitude air masses (characterized by ^{35}S SA) (Fig. S1c, d online). In pollution events, low $\Delta^{17}O(SO_4)$ values (<1.6‰) have been observed in East China due to enhanced direct sulfate emissions from combustion ($\Delta^{17}O = 0$) and secondary sulfate formation dominated by aqueous H_2O_2 and heterogeneous O_2 (or NO_2) oxidation [11–13]. Given the removal lifetime of sulfate in the free troposphere (>1 week) [7,11] is longer than the time scale of the eastward transport of air masses from the Himalayas to Southwest China through the prevailing westerlies (<1 week) (Fig. 1b), we favor the explanation that sulfate with highly anomalously enriched ^{17}O in Southwest China is the result of additional inputs of high-$\Delta^{17}O$ sulfates transported from its upwind region (the Tibetan Plateau) instead of a shift to the O_3 oxidation pathway directly occurring at the sampling site. The high $\Delta^{17}O$ values in non-dust sulfate aerosols originating in the Tibetan Plateau are explained in part by a large fraction of mineral dust in aerosols, which facilitate heterogenous SO_2 oxidation by O_3 at the mineral surface to produce high-$\Delta^{17}O$ sulfates as a result of increased pH values [3]. Local-scale pollution is likely the major factor accounting for the decrease of $\Delta^{17}O(SO_4)$ values in Southwest China, also known as the dilution effect [14].

A major finding of our new measurements at the Tibetan Plateau and Southwest China is that aerosol samples with high concentrations of stratospherically produced ^{35}S also have high $\Delta^{17}O$ values (Fig. 2c), pointing to the possibility of additional influences from high-altitude air masses. Such an apparent positive correlation between ^{35}S SA and $\Delta^{17}O$ values in sulfate aerosols has been noted by early studies conducted in the Western United States and Antarctic Plateau, indicating that $\Delta^{17}O(SO_4)$ and sulfate oxidation chemistry may depend on sulfate formation altitudes [14,15]. The detailed atmospheric processes responsible for altitude-dependent $\Delta^{17}O(SO_4)$ remain an open question at present because global $^{35}S(SO_4)$-$\Delta^{17}O(SO_4)$ measurements are limited [11,14,15].

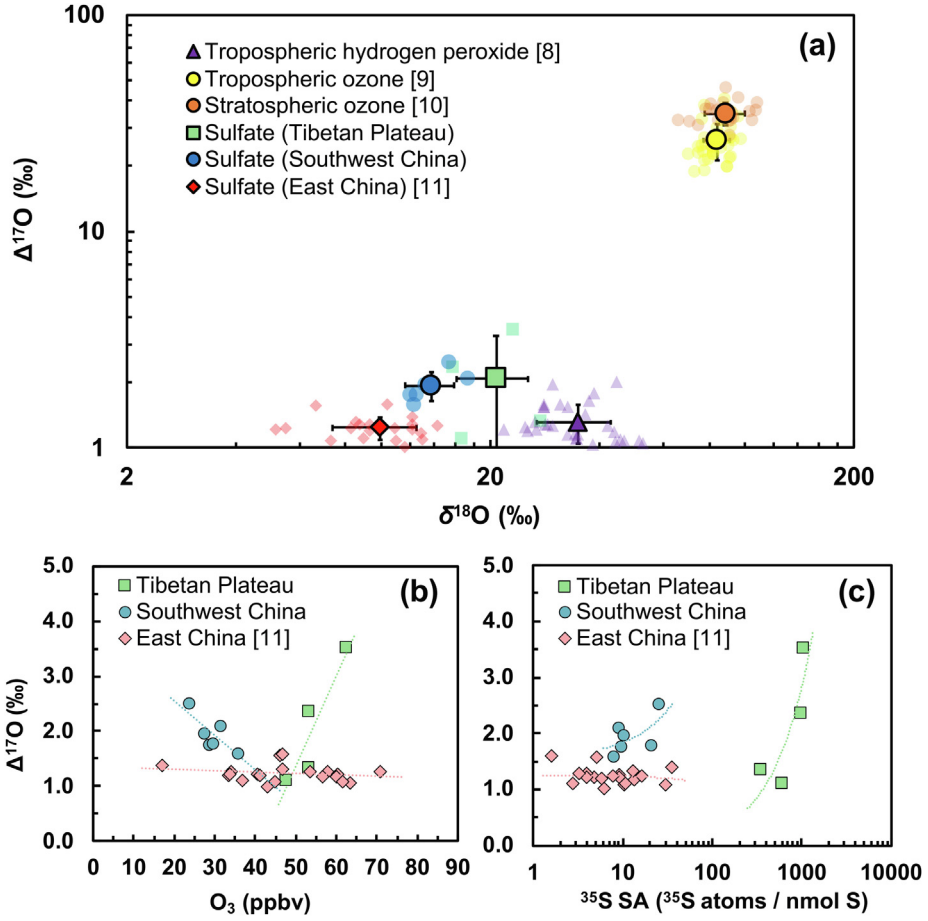

Fig. 2. Triple oxygen isotopic compositions of sulfate aerosols. (a) $\Delta^{17}O$-$\delta^{18}O$ log–log plot for sulfate aerosols collected in Southwest China, East China [11], and the Tibetan Plateau. Measurements of tropospheric H_2O_2 [8], tropospheric [9] and stratospheric O_3 [10] are also included for comparison. Filled symbols represent the mean of all samples (symbols in a light color). Error bars stand for one standard deviation of all samples. Relationships between $\Delta^{17}O$-O_3 (b) and $\Delta^{17}O$-^{35}S (c) specific activities in our study. Previous measurements in East China [11] are also shown.

The altitude-dependent $\Delta^{17}O(SO_4)$ observed in the Tibetan Plateau and its downwind regions may be linked to large $\Delta^{17}O$ anomalies in high-altitude O_3 molecules and OH radicals. A detailed discussion on the altitude-dependent $\Delta^{17}O(SO_4)$ is available in our previous works [11,14,15] and the Supplementary materials (online). Isotopic measurements of sulfate aerosols directly collected at Mount Everest are currently underway to provide deeper insight into the exact chemical mechanism for the observed altitude-dependent $\Delta^{17}O(SO_4)$. Nevertheless, given the extreme slow reaction rate (half-life: ~10^9 years) of oxygen isotope exchange between sulfate and water under normal conditions at the Earth's surface, our existing data imply that $\Delta^{17}O(SO_4)$ has the potential of tracing the sulfate formation source altitude in the Tibetan Plateau and surrounding regions in both present days and past.

Overall, using cosmogenic ^{35}S, we have shown that the Himalayas and its extensive downwind areas are more affected by stratospheric air than other regions, and these stratospheric influences are also likely recorded by triple oxygen isotopes in atmospheric sulfates. Our data provide observationally based constraints in quantifying air pollution, tropospheric chemical and radiation budgets in these regions in present days. Given that snow and glacier melting in this region (the headwaters of many Asian rivers) is highly relevant to changes in the atmosphere, further researches focusing on elucidation of the interaction between stratosphere-troposphere-cryosphere-hydrosphere-biospheres at the Himalayas and surrounding regions to understand possible consequences of frequent stratospheric intrusions for water availability, quality, and food security are urgently needed. Additionally, long-term paleo-records of stratosphere-troposphere interaction, atmospheric circulation, uplift of the Tibetan Plateau, and relevant impacts on climate and atmospheric chemistry may be potentially obtained using relatively long-lived cosmogenic isotopes (e.g., ^{10}Be, ^{14}C, and ^{36}Cl) and triple oxygen isotopes in atmospherically deposited sulfates, which are demonstrated to be altitude-dependent in this study. If appropriate tree-ring, ice or sedimentary records in these regions can be co-employed, these isotopic proxies would improve our understanding of paleo-climate and paleo-altimetry of the world's highest plateau.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

The isotopic analysis was conducted at University of California San Diego (UCSD). The work of data analysis and paper writing was conducted at Guangzhou Institute of Geochemistry of Chinese Academy of Sciences and supported by Key Research Program of Frontier Sciences of Chinese Academy of Sciences (ZDBS-LY-DQC035) and the National Natural Science Foundation of China (42021002) to Mang Lin. The sampling work was partially supported by Chinese Academy of Sciences (XDA20040501) and the National Natural Science Foundation of China (41630754, 41721091) to Shichang Kang. Constructive and critical comments by anonymous reviewers are acknowledged. We thank Nadia Biglari for her assistance in purifying a part of samples for triple oxygen isotopic analysis, Prof. Lin Su for preparation of Fig. 1a, Prof. Jianzhong Xu for providing Mount Everest $PM_{2.5}$ data, and all members from 2016 Mount Everest Scientific Expedition Team for field assistance. All data reported in this study are provided in Supplemental materials (online). This is contribution No. IS-2931 from Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). Map in this article was reviewed by Ministry of Natural Resources of the People's Republic of China (GS(2020)5323).

Author contributions

Mang Lin, Shichang Kang, and Mark H. Thiemens designed research. Mang Lin, Kun Wang, Shichang Kang, Youping Li, Zhongyu Fan, and Mark H. Thiemens collected samples. Mang Lin carried out isotopic analysis, analyzed data, and wrote the manuscript.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2020.11.005.

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