Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean atmospheres

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The signature of mass-independent fractionation of quadruple sulfur stable isotopes (S-MIF) in Archean rocks, ice cores, and Martian meteorites provides a unique probe of the oxygen and sulfur cycles in the terrestrial and Martian paleoatmospheres. Its mechanistic origin, however, contains some uncertainties. Even for the modern atmosphere, the primary mechanism responsible for the S-MIF observed in nearly all tropospheric sulfates has not been identified. Here we present high-sensitivity measurements of a fifth sulfur isotope and multiple chemical species analysis approach provides strong evidence that S-MIF signatures in tropospheric sulfates are concomitantly affected by two distinct processes: an altitude-dependent positive $^{33}S$ anomaly, likely linked to stratospheric SO$_2$ photolysis, and a negative $^{36}S$ anomaly mainly associated with combustion. Our quadruple sulfur stable isotope measurements in varying coal samples (formed in the Carboniferous, Permian, and Triassic periods) and in SO$_2$ emitted from combustion display normal $^{33}S$ and $^{36}S$, indicating that the observed negative $^{36}S$ anomalies originate from a previously unknown S-MIF mechanism during combustion (likely recombination reactions) instead of coal itself. The basic chemical physics of S-MIF in both photolytic and thermal reactions and their interplay, which were not explored together in the past, may be another ingredient for providing deeper understanding of the evolution of Earth’s atmosphere and life’s origin.

As the tenth most abundant element in the universe, sulfur occurs as stable ($^{32}S$, $^{33}S$, $^{34}S$, and $^{36}S$) and radioactive isotopes (e.g., $^{35}S$ and $^{38}S$). The signature of mass-independent fractionation of quadruple sulfur stable isotopes [S-MIF or sulfur isotopic anomaly, quantified by $\Delta^{33}S = \delta^{33}S - [(1 + \delta^{34}S)^{0.515} - 1]$ and $\Delta^{36}S = \delta^{36}S - [(1 + \delta^{34}S)^{0.512} - 1]$ and traditionally expressed as per mil observed in Archean (~4 Ga to ~2.5 Ga) sediments has been interpreted as the products of UV photolysis of sulfur dioxide in an anoxic atmosphere and used to track the history of primitive Earth and evolution of early life. In this study, we present strong observational evidence that there is an additional process that produces similar anomalous sulfur isotope signatures. This previously unknown origin not only offers a tool for quantifying the present-day atmospheric sulfur budget and evaluating its influences on climate and public health but also implies that anomalous sulfur isotopic compositions in some of the oldest rocks on Earth might have been produced in a way different from that previously thought.

Significance

Anomalous sulfur isotopic compositions preserved in sedimentary rocks older than ~2.5 billion years have been widely interpreted as the products of UV photolysis of sulfur dioxide in an anoxic atmosphere and used to track the history of primitive Earth and evolution of early life. In this study, we present strong observational evidence that there is an additional process that produces similar anomalous sulfur isotope signatures. This previously unknown origin not only offers a tool for quantifying the present-day atmospheric sulfur budget and evaluating its influences on climate and public health but also implies that anomalous sulfur isotopic compositions in some of the oldest rocks on Earth might have been produced in a way different from that previously thought.

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in nature with a half-life of ideal age to track atmospheric processes (17). It is exclusively produced in the higher atmosphere by the spallogenic bombarding of 40Ar by high-energy cosmic rays. The ability of 35S to serve as a sensitive and unambiguous tracer in identifying sulfate aerosols originating from the higher atmosphere was recently demonstrated (19) and has been utilized in understanding sulfate formation pathways at different altitudes (20). Here we report all five (four stable and one radioactive) sulfur isotopes and all three stable oxygen isotopes (18O, 17O, and 16O) composition in sulfate along with other inorganic and organic compounds in the same aerosols collected at a midlatitude remote mountain site located in East Asia (Materials and Methods and SI Appendix, Fig. S1) to trace the origins of S-MIF signatures.

**Quadruple Sulfur Isotope Composition in Sulfate Aerosols, SO2, and Coal**

All sulfate aerosols measured in this study possess nonzero Δ33S and Δ36S values (Fig. 1), consistent with previous measurements (11–15). Because coal burning accounts for ~95% of sulfur emissions in China (21) and it has been speculated that sulfur isotopic anomalies of present-day aerosols might originate from coal (12), we first measured quadruple stable sulfur isotopes in various representative Chinese coal samples [formed in the Carboniferous, Permian, and Triassic periods, in which 90% of the total recoverable coal reserves across China were formed (22)] and ambient SO2 emitted from coal burning (Materials and Methods) to evaluate their contribution to nonzero Δ33S and Δ36S values in atmospheric sulfates. Our data indicate that sulfur isotope compositions in coal and SO2 are essentially normal within error, and their patterns in the Δ33S vs. Δ36S scatter plot notably differ from tropospheric sulfates (Fig. 1). It is therefore highly unlikely that nonzero Δ33S and Δ36S values in tropospheric sulfates directly originate from coal itself.

Slight differences in MDF exponents of varying SO2 oxidation processes could accommodate small variations of Δ33S in tropospheric SO2-derived sulfates (±0.1‰) (10) but cannot account for the relatively large nonzero Δ33S and Δ36S values in most atmospheric sulfates (including the data in this study) (−0.66‰ < Δ33S < 0.53‰; −1.6‰ < Δ36S < −0.1‰) (Fig. 1). In fact, the seasonal variation of Δ33S values observed in this study (SI Appendix, Fig. S2) does not match the model calculation that only considers MDF processes (10). Additionally, the statistically insignificant (P > 0.05) correlation between Δ33S, Δ36S, and Δ18O (= δ18O − 0.52 × δ34S) is an isotopic fingerprinting quantifying the relative contribution of SO2 oxidation processes (3) shown in this study (SI Appendix, Table S1) and by Romero and Thiemens (11) also supports our argument. Replicate analysis and interlaboratory comparisons for the same atmospheric samples in this work demonstrate that the observed nonzero Δ33S and Δ36S values are independently reproducible and in agreement (Materials and Methods), and the isotopic differences between SO2 and sulfate therefore further confirm that the nonzero Δ33S and Δ36S values in tropospheric sulfates are attributed to photolytic oxidation in the stratosphere or unknown S-MIF processes in the troposphere which require identification.

**Altitude-Dependent Δ33S in the Modern Atmosphere**

We observe that Δ33S is correlated with 35S specific activity (35S-SA) (Fig. 2 and SI Appendix, Fig. S2 and Table S1). The relationship between 35S-SA and Δ33S is best described by a log-linear function in this study, likely reflecting that their vertical profiles in the atmosphere are not exactly the same because of the complex nature of sulfur chemistry and different production processes of 35S (19) and Δ33S (16) at high altitudes. The age difference of air mass originating from the same altitude (i.e., decayed 35S but the same Δ33S) may also lead to the complex relationship but would not affect our major finding (i.e., positive relationship between 35S-SA and Δ33S) because the decay lifetime of 35S (~126 d) is significantly longer than the sulfate lifetime in the troposphere (days to weeks). Before this study, radioactive and multiple stable sulfur isotopes in sulfate aerosols were only simultaneously measured by Romero and Thiemens (11) in two samples collected from White Mountain in California. The sample possessing a greater 35S-SA in their pilot study displays a heavier Δ33S (0.16‰) than the other (0.10‰), consistent with our higher-sensitivity 35S measurements (17, 18).

An extremely low ratio of 35S in coarse to fine particles (0.04) supports the premise that sulfates collected in our remote mountain site were mainly affected by long-range horizontal and vertical transport (SI Appendix, SI Text). The altitude-dependent variation of Δ33S revealed by enrichment of stratospherically sourced 35S indicates that sulfate aerosols originating from the higher atmosphere possess a greater Δ33S value than the boundary layer. Ion-induced binary nucleation of H2SO4 and H2O by galactic cosmic rays was recently identified as a previously ignored process of new particle formations in the free troposphere (23). This process was subsequently found to be mass-dependent in laboratory experiments (24), and therefore it could not explain the Δ33S-Δ35S relation observed in this study. We do not rule out the possibility that there is an unknown SO2 oxidation mechanism which mass-independently enriches 35S in sulfate products in the free troposphere, but, at present, there is no evidence for the existence of such a process. Consequently, we favor the explanation by which downward transport of stratospheric sulfates is the most plausible source of positive Δ33S values in tropospheric sulfates (11–15).

Romero and Thiemens (11) first measured quadruple sulfur isotopes in tropospheric sulfate aerosols and noted that Δ33S in the stratosphere might be larger than traditionally thought. Our first-order estimation of Δ33S values in stratospheric sulfates at East Asia (>4‰) agrees with previous interpretations, although the value should not be viewed as a precise estimate since the relationship between 35S and Δ33S is nonlinear and complex (see SI Appendix, SI Text for details). Given large positive Δ36S values in sulfate products (and negative Δ35S values in residual SO2) in SO2 photolytic oxidation (in the presence of O3) (25) and...
frequent downward transport of stratospheric air at midlatitudes (19), it is plausible, and cannot be ruled out, that $\Delta^{33}$S values ($<2‰$) of stratospheric sulfates deposited in polar regions (a terminus in poleward transport from the tropics) are much smaller than stratospheric sulfates entrained downward at midlatitudes (where most of atmospheric sulfate measurements were made) as a result of Rayleigh fractionation of $\Delta^{33}$S during poleward transport. This view is consistent with results from a 2D dynamical/chemical model (26), although a different mechanism was used in that model ($SO_3$ photolysis, in which the $SO_2$ acquires positive $\Delta^{33}$S values), leading to an opposite trend. If this is true, the negative $\Delta^{33}$S values in sulfates deposited in the South Pole during volcanically quiescence times (16) (Fig. 3) may be explained. This hypothesis is also consistent with the decrease of $\Delta^{33}$S from positive to negative values found in cryospheric records during stratospheric volcano events (8), because more stratospheric $SO_2$ and sulfates can be transported to the polar regions during stratospheric volcano eruption than during volcanically quiescence times. Additionally, given the high temporal sulfur isotopic heterogeneity (8), it is not impossible that magnitudes of stratospheric S-MIF signatures preserved in the polar regions, even for snow pit samples (time scale: months), were smaller than atmospheric samples (time scale: days).

As argued above, the stratospheric origin of nonzero $\Delta^{33}$S values observed in most sulfate aerosols in East China and California (Fig. 1) may be therefore dynamically explained by a combination of (i) the Asian monsoon anticyclone that efficiently transports $SO_2$ to the lower stratosphere (27), (ii) the sulfate-enriched Asian Tropopause Aerosol Layer in the upper troposphere and lower stratosphere (28), and (iii) frequent, active, and intense stratospheric intrusions at midlatitudes of the Northern Hemisphere (19). Our findings therefore highlight the need for further simultaneous measurements (especially by aircraft or balloon collections) and 3D modeling of all five isotopes of sulfur in the modern atmosphere at varying geographic locales to understand the temporal and spatial sulfur isotopic heterogeneity, chemical transformation of sulfur-bearing species during transport, and their implication for tropospheric sulfur budget in the modern atmosphere.

**Combustion-Associated $\Delta^{36}$S in the Modern Atmosphere**

The most striking feature in the new data is that, unlike $\Delta^{33}$S, $\Delta^{36}$S is not clearly correlated with $^{35}$S-SA (Fig. 2 and SI Appendix, Fig. S2 and Table S1). The poor correlation ($r = -0.18$, $P = 0.55$) indicates that an additional process, apart from $SO_2$ photochemistry (4), is required to fully explain S-MIF seen in atmospheric sulfates. The sulfur oxidation ratio (SOR) is conventionally expressed as the molar ratio of sulfate to total sulfur in atmospheric sulfates. The sulfur oxidation ratio (SOR) is conventionally expressed as the molar ratio of sulfate to total sulfur (sulfate and $SO_2$) to quantify the degree of $SO_2$ oxidation (i.e., formation of secondary sulfate). A low SOR therefore indicates less secondary sulfates (i.e., a relatively large fraction of primary sulfates) in total sulfates. The excellent correlation ($r = 0.96, P < 0.000001$) between SOR and $\Delta^{36}$S (Fig. 2) suggests that $\Delta^{36}$S is linked to the formation of primary sulfate during fossil fuel and/or biomass combustion, with the most negative $\Delta^{36}$S at low SOR. The y intercept ($-1.7‰$), representing $\Delta^{36}$S in sulfates near the emission source (characterized by a near-zero SOR as a result of large amounts of $SO_3$), is close to the most negative $\Delta^{36}$S ($-1.9‰$) in primary sulfate aerosols emitted from biomass and diesel combustion (29) (Fig. 1). Alternatively, if the SOR equals 1, the $\Delta^{36}$S value in tropospheric secondary sulfate (0.1‰) is obtained, which matches $SO_2$ observations (Fig. 1). This quantitative agreement therefore supports the hypothesis that the large $^{36}$S anomaly is associated with combustion processes rather than
Our five-sulfur-isotope observation points to a previously underappreciated nonphotochemical channel for producing S-MIF (i.e., fossil fuel and/or biomass combustion). Recent theoretical studies suggested that S-MIF can occur in recombination reactions of elemental sulfur [e.g., $S + S_2 + M \rightarrow S_3 + M$], an analogy of $O_3$ formation that produces oxygen MIF (3) as a result of the symmetry effect (31, 32). Although the derived values should be quantitatively validated by laboratory experiments, the theoretical studies (31, 32) reemphasize the potential role of the symmetry effect in S-MIF, which has been noted since early studies (33) but was generally not considered in SO$_2$ photolytic reactions, because of the trace amount of gaseous S$_2$, S$_3$, and S$_4$ at ambient temperatures (34) and the difficulty of experimental investigation (31, 32). We argue that the elemental sulfur recombination reaction is strictly a thermal reaction, because elemental sulfur vapor (vapor pressure at 717.8 K: 1 atm) contains sulfur allotropes with two to eight sulfur atoms (35). In combustion processes, both S and S$_2$ are important short-lived intermediates (36). There are a host of potentially relevant reactions (e.g., $SH + S \rightarrow S_2 + H$) (36) that may be crucial in producing these small sulfur allotropes in gas phase, and the high molecular number density may facilitate elemental sulfur recombination reactions. We noted that large S-MIF would be emitted as primary sulfates ($\Delta^{33}S = -1.9^{\circ}\text{C}$) in smoldering combustion (Fig. 1) (29). Because of relatively low O$_2$ levels in this slow and persistent (up to years) type of combustion rather than flaming fires (37, 38), the fast oxidation reactions (e.g., $SH + O_2 \rightarrow SO + OH$, $SO + O_2 \rightarrow SO_2 + O$) (36) may be slightly restricted, and the above-discussed elemental sulfur related reactions may therefore become important. The potential role of such reactions in producing S-MIF signatures is highlighted and discussed by a recent study focusing on slightly negative $\Delta^{33}S$ values observed in the 19th century, a period with extensive and persistent global biomass burning (15). Our observation provides an additional dimension ($\Delta^{36}S$) to verify the combustion-associated S-MIF signature and to delineate its chemical physics. Given the complexity of combustion processes, a clearly defined $\Delta^{33}S - \Delta^{36}S$ relationship was not found in the early combustion experiment (29). The hypothesis proposed here and the corresponding $\Delta^{33}S - \Delta^{36}S$ relationship could be tested experimentally in the future to detail all parameters and mechanisms.

Significant correlations with SOR or biomass burning tracers are not observed with respect to $\Delta^{36}S$ (Fig. 2 and SI Appendix, Table S1), indicating that $\Delta^{36}S$ is less influenced by combustion processes than is $\Delta^{33}S$. Alternatively, the slightly negative $\Delta^{33}S$ values of primary sulfates emitted from combustion processes (13, 15, 29) (Fig. 1) may be masked by the apparent stratospheric signal (notably positive $\Delta^{33}S$ values) because our samples were collected in a midlatitude remote mountain site. Using the $y$-intercepts of $\Delta^{33S/35S}$SA and $\Delta^{36S}$/levoglucosan fitted curves in Fig. 2 ($\Delta^{33S} = 0.13 \pm 0.02^{\circ}\text{C}$, $\Delta^{36S} = -0.23 \pm 0.07^{\circ}\text{C}$, respectively), we estimate the $\Delta^{33S}/\Delta^{36S}$ ratio of background tropospheric sulfates at East Asia to be $-1.8 \pm 0.6$, a value matching tropospheric sulfates directly observed in a background station at the pristine Tibetan Plateau ($-1.8 \pm 0.9$, $n = 6$) (15) and stratospheric sulfates estimated from Plinian volcanic eruption ($-1.9 \pm 0.6$, $n = 13$) (8) and biomass burning ($-1.9 \pm 0.1$, $n = 3$) (16) records in polar regions (SI Appendix, Fig. S3). The consistency may imply the presence of a steady-state stratospheric component in the background troposphere of midlatitudes in the Northern Hemisphere as recently suggested by a decadal observation of stratospherically sourced $\Delta^{18}O$ in tropospheric CO$_2$ (39).

On the basis of our new five-sulfur-isotope measurements, we identify an altitude-dependent process producing a gradual $\Delta^{33S}/\Delta^{33S}$ slope and a combustion-related process producing a steep slope. The finding explains why inland California, a region more affected by the stratospheric air (19), possesses slightly higher $\Delta^{33S}$ ($0.20 \pm 0.15^{\circ}\text{C}$, $n = 22$) and much smaller $\Delta^{36S}$ ($-0.4 \pm 0.2^{\circ}\text{C}$, $n = 22$) values than the more polluted coastal California ($\Delta^{33S} = 0.16 \pm 0.14^{\circ}\text{C}$, $\Delta^{36S} = -1.0 \pm 0.4^{\circ}\text{C}$, $n = 17$) (Fig. 1). These two MIF end-members, together with the MDF end-member (e.g., tropospheric secondary sulfates (10)), resolve a 15-y-old mystery: the “decoupled” relationship between $\Delta^{33S}$ and $\Delta^{36S}$ in atmospheric sulfates (11) (Fig. 1). The unique isotopic fingerprinting discovered in this study has the potential to quantitatively identify and distinguish previously understudied sources of sulfates to the present-day troposphere (e.g., stratospheric sulfate, biomass burning, and incomplete residential coal combustion) (13, 15, 16, 40, 41) and their subsequent influences on public health and climate.

**Implications for the Understanding of the Archean S-MIF Record**

The variability of $\Delta^{33S}/\Delta^{33S}$ slopes in Archean sediments may be an indicator of a changing sulfur cycle on Earth during the appearance and evolution of early life (1, 2, 42), but fundamental chemistry reactions and corresponding biogeochemical processes remain elusive (42, 43). Because laboratory photolysis experiments showed that the $\Delta^{33S}/\Delta^{33S}$ slope is sensitive to the wavelength (SI Appendix, Fig. S3), experimental and modeling efforts have been...
focused on tuning atmospheric composition to reproduce the observed Archean array (44, 45). However, thermochemical sulfur fate reduction was proposed as an alternative or additional S-MIF mechanism to explain the Archean record (46), but this process was attributed to magnetic isotope effects (47), which only lead to $^{33}$S anomalies and contrast with observations in nature such as Archean rocks, ice cores, and present-day aerosols (Fig. 3). By comparison of sulfur isotopic signatures between modern and Archean record, recent studies suggest that varying atmospheric S-MIF processes (photolytic reactions of SO$_2$/OCS, and possibly recombination reactions of elemental sulfur) may have operated in both periods (15, 16, 48).

Our field-based observation has shown that, certainly for today, the isotopic anomalies in $^{32}$S and $^{36}$S appear decoupled in the measured natural samples, and their corresponding photochemical and nonphotochemical processes can be identified by simultaneous measurements of radiosulfur and combustion indices. The fitted $\Delta^{32}$S/$\Delta^{36}$S slope ($\pm 0.1$) in our selected aerosol samples (without samples strongly affected by combustion; see SI Appendix, SI Text and Fig. S2) is compatible with the relatively steep $\Delta^{32}$S/$\Delta^{34}$S slope of $\pm 3.6$ observed in some Paleocene (3.6 Ga to 3.2 Ga, an era characterized by intense volcanic activity (49)) purities (50) (Fig. 3), indicating that photochemical and nonphotochemical S-MIF processes may have concomitantly occurred in primitive Earth. In the Archean, it is widely accepted that S-MIF signatures are from photochemical reactions of sulfur-bearing species emitted from volcanoes, and therefore volcanic activity is required in all Archean S-MIF models (1, 43). Vventing and polymerization of gaseous S$_2$ is ubiquitous on Io (one of Galilean moons), the most volcanically active body in the solar system (51). At terrestrial volcanic vents and fumaroles, elemental sulfur deposits formed in high-temperature sulfur-bearing gases are commonly found (35, 52). Therefore, it is likely that basic reactions responsible for nonphotochemical S-MIF processes in combustion [probably recombination reactions (31, 32)], which are characterized by large $^{34}$S anomalies, may occur in terrestrial volcanoes throughout Earth’s history.

Existing data show a negative $\Delta$S value ($-0.9^{\circ}\text{C}$) and a near-zero $\Delta$S value ($0.03^{\circ}\text{C}$) in modern volcanogenic sulfate aerosols at the point of emission (53) (Fig. 3). This S-MIF signature, similar to combustion-associated $\Delta$S observed in this field-based study and previous laboratory experiments (29), likely resulted from thermochemical S-MIF processes as suggested previously, as a photochemical source is not possible. Steep $\Delta^{32}$S/$\Delta^{34}$S slopes are also observed in sulfates leached from Quaternary volcanic ash (54), and in some igneous rocks from the Eoarchean (4.0 Ga to 3.6 Ga), an era during which Earth might be intensively impacted by asteroid storm (the Late Heavy Bombardment) (55) (Fig. 3). These similarities emphasize the need for further sulfur isotopic measurements of present-day volcanic gases and solids formed in the gas phase to understand sulfur isotope partitioning in these thermal reactions and its implications for early Earth evolution. Given that both SO$_2$ photolysis and elemental sulfur polymerization are relevant to Archean volcanism, the Archean $^{33}$S and $^{36}$S anomalies could, in fact, come from the same volatiles but different reactions, which lead to varying $\Delta^{32}$S/$\Delta^{36}$S slopes in the Archean record (Fig. 3). These two distinct S-MIF processes and their interplay are not concomitantly explored in the past. The present data suggest that, with extended experimental and modeling efforts on providing the new chemical physics of S-MIF in elemental sulfur recombination reactions, the Archean S-MIF record and its implications for the atmospheric, oceanic, and microbial processes on primitive Earth may potentially yield deeper insight in the future.

**Materials and Methods**

Aerosol, SO$_2$, and coal samples were collected at a background mountain site in East Asia, a Chinese megacity (during the coal-burning season), and three coal mines across China, respectively (SI Appendix, Fig. S1). Eight isotopes ($^{28}$S, $^{32}$S, $^{33}$S, $^{34}$S, $^{35}$S, $^{16}$O, $^{17}$O, and $^{18}$O) in sulfur aerosols and quadruple stable sulfur isotopes ($^{32}$S, $^{33}$S, $^{34}$S, and $^{36}$S) were measured in two independent laboratories (University of California, San Diego and University of Science and Technology of China) using different fluorination methods and isotopic ratio mass spectrometers (IRMS) (Thermo Finnigan MAT 253), and were reported in isotope ratios defined as $d$ isotope = ($^{34}$S or $^{32}$S, $^{36}$S or $^{33}$S) in atmospheric sample in comparison of sulfur isotopic signatures between modern and meteorite analysis. Additionally, the International Atomic Energy Agency (IAEA) S1 has a sulfur isotopic composition on the VCDT scale of $\Delta^{32}$S = $-0.3^{\circ}\text{C}$, $\Delta^{33}$S = 0.10%, and $\Delta^{34}$S = $-0.80^{\circ}\text{C}$ (56). The IAEA S1 standard was routinely fluorinated and measured during the study period, and our values match the above-mentioned values and those obtained from another independent laboratory (University of Maryland (57)). Overall uncertainties (1 SD) of $d$ isotope, $\Delta$S, and $\Delta$S values in fluorination and isotopic measurements in both laboratories are less than 0.2‰, 0.01‰, and 0.2‰, respectively. Samples with sufficient sulfur and laboratory Ag$_3$S standards were replicated for full chemistry (reduction, fluorination, and isotopic measurements) in both laboratories for comparing the measured $\Delta^{32}$S and $\Delta^{34}$S values. Differences between two laboratories and replicated experiments are within the reported analytical uncertainties (SI Appendix, Tables S2 and S3). The high reproducibility of $\Delta$S and $\Delta$S for the same atmospheric sample in independent laboratories allows us to measure that these aerosol compositions were not an experimental artifact resulting from any unknown S-MIF fractionation process due to the chemically complex matrix in the atmospheric samples. Triple stable oxygen isotopes ($^{16}$O, $^{17}$O, and $^{18}$O) were measured at University of California, San Diego using a pyrolysis method (58) and an IRMS. Assuming the molar ratio of sulfur to sodium (a sea salt tracer) to be 0.0604 in sea salt spray, we estimated the sea salt content in each fine sulfate sample to be less than 1.5% (with an average of 0.9 ± 0.3%) (20). Therefore, all isotopic compositions reported in this study are not corrected for non–sea-salt sulfates. Concentration of water-soluble ions (Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, NO$_3^-$, and SO$_4^{\text{2-}}$), saccharic tracers for biomass burning (levoglucosan and mannosan), and non-carbonaceous species in the same aerosol samples were determined using two ion chromatographies ( Dionex ICS-1600 and ICS-2100), a high-performance anion exchange chromatography with pulsed amperometric detection (Dionex ICS-3000) technique (30), and a Desert Research Institute aerosol carbon analyzer (2001; Atomlytic Inc.) (59), respectively. Detailed sampling and analytical procedures can be found in SI Appendix, SI Text. All sulfur isotope data and relevant stratospheric/combustion tracer data reported in this study are presented in SI Appendix, Tables S2–S5.

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