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1 SO₂ photo-oxidation on mineral dust: The missing link to
2 explain $\Delta^{33}\text{S}$ anomalies in urban sulfate aerosols

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12

13 **KEYWORDS**

14 Sulfur Mass-Independent Fractionation (S-MIF), UV radiation, Air Pollution, Particulate Matter,
15 Model-Observation Reconciliation

16 **ABSTRACT**

17 Sulfate aerosols exert a net cooling effect on the earth-atmosphere system, yet their radiative
18 forcing remains associated with largest of uncertainties in the assessment of climate change. One
19 of the contributing factors is the poor understanding of the sulfate formation pathways, which are
20 thought to be following mostly the mass-dependent fractionation model (i.e., $\Delta^{33}\text{S} \sim 0$). However,
21 globally, urban sulfate aerosols exhibit significant non-zero $\Delta^{33}\text{S}$ compositions (from -0.6‰ to
22 +0.6‰), resulting in sulfur mass-independent fractionation (S-MIF) processes. The origin(s) of
23 these S-MIF anomalies remain(s) unclear. Here, we conducted dual-isotope ($\Delta^{33}\text{S}$, $\delta^{34}\text{S}$) probing
24 of sulfate aerosols from summertime megacity Delhi in South Asia. A shift towards concomitantly
25 high $\Delta^{33}\text{S}$ (from +0.2‰ to +0.5‰) and low $\delta^{34}\text{S}$ (from +5‰ to +1‰) values was observed with
26 the influx of mineral dust. The Fe-to-Al tracer showed significant correlations with sulfate loadings
27 ($R^2=0.84$) and $\Delta^{33}\text{S}$ signatures ($R^2=0.77$). As such, we postulate that the SO_2 photo-oxidation on
28 mineral dust generates S-MIF anomaly $\sim +0.35 \pm 0.10$ ‰, thereby also explaining the previously
29 observed $\Delta^{33}\text{S}$ values worldwide. Together, the findings help deconvolute S-isotope dynamics in
30 urban regions wherein, contrary to prevailing paradigm, non-anthropogenic factor (i.e., mineral
31 dust) is found to influence the aerosol sulfate-induced pollution affecting air quality/human health.

32 **SYNOPSIS**

33 Sulfate-related pollution in urban regions—affecting air quality/human health—could be linked to
34 non-anthropogenic factor i.e., mineral dust.

35 INTRODUCTION

36 Sulfur (S) is one of the essential elements for life. The sulfur biogeochemical cycle
37 contributes to controlling the redox state of Earth's surface and links the atmosphere, biosphere,
38 hydrosphere, and the lithosphere¹. Yet, the sulfur cycle is massively disrupted by human activities¹⁻
39 ³. The majority of natural and anthropogenic S is released directly as SO₂ (gas) or oxidized into
40 SO₂ in the atmosphere². On a global scale, ~50% of SO₂ (natural and anthropogenically emitted)
41 is oxidized to sulfate while the rest is lost to dry and wet scavenging³. The pathway taken by SO₂
42 to form sulfate has major implications for both the radiative effects and the environment— in gas-
43 phase reactions occurring predominantly with hydroxyl radicals (OH), the end-product sulfuric
44 acid (g) leads to new particle formations eventually altering the cloud albedo and lifetime⁴. In the
45 heterogenous phase reactions occurring primarily in cloud droplets via several oxidants, the major
46 ones being O₂+TMI (Transition Metal Ion), H₂O₂, O₃ and NO₂, the end-product sulfate particles
47 contribute towards modifying the aerosol size distribution and cloud condensation nuclei activity⁵.
48 On a global scale, the sulfate aerosols contribute to a negative effective radiative forcing (ERF) of
49 -0.90 (-0.24 to -1.56) W m⁻² (IPCC, 2021). As such, the net cooling effect of sulfate aerosols
50 partially counteracts the warming effects of greenhouse gases (e.g., CO₂, CH₄)^{3,6}. However, the
51 magnitude and expected future changes in sulfate aerosol radiative forcing remains one of the
52 largest uncertainties associated with assessments of climate change⁶.

53 To this end, S-isotope geochemistry can be used towards addressing these uncertainties as
54 it provides powerful information for deconvolution of both emission sources and atmospheric
55 processes⁷⁻⁹. Sulfur has four stable isotopes, ³²S, ³³S, ³⁴S and ³⁶S whose natural abundances are
56 approximately 95%, 0.75%, 4.2% and 0.015%, respectively^{10,11}. The S-stable isotopes undergo
57 fractionation during kinetic and equilibrium reactions which causes the reactant (SO₂) and the

58 product (sulfate) to have distinct isotope compositions^{12,13}. In general, the isotope ratios of any two
59 isotopes can be scaled to each other based on the mass i.e., “mass dependent fractionation (MDF)”
60 model⁹. More specifically, the fractionation factors determined for MDF processes follow a
61 relation ${}^{3y}a = ({}^{34}a)^{3yb}$ wherein ${}^{3y}a$ could be ${}^{33}a$ or ${}^{36}a$ and ${}^{3y}b$ is ${}^{33}b$ or ${}^{36}b$ and the $3yb$ is the relative
62 fractionation of ${}^{3y}S/{}^{32}S$ and ${}^{34}S/{}^{32}S$ ¹³. The ${}^{33}b$ and ${}^{36}b$ values were experimentally determined to be
63 0.515 and 1.889¹⁴. Any deviation from this relationship implies the occurrence of “Mass
64 Independent Fractionation (MIF)”¹⁵. The S-MIF is expressed as $\Delta^{33}S = (\delta^{33}S+1) - (\delta^{34}S+1)^{0.515}$
65 and $\Delta^{36}S = (\delta^{36}S+1) - (\delta^{34}S+1)^{1.889}$. Considerable debate exists in the interpretation of S-MIF
66 signals observed in atmospheric aerosols from urban locations^{e.g.,16-18}.

67 The origin of S-MIF in nature has been primarily attributed to photochemical reactions in
68 the presence of UV radiation —SO₂ absorption at 190-220 nm i.e., photolysis, and SO₂ absorption
69 at 250-330 nm i.e., photo-oxidation¹⁵. These mechanisms have been suggested to account for the
70 S-MIF observed in the Archean sediments as well as in modern aerosols^{15,17}. However, to date the
71 reported S-MIF values ranging from -0.6‰ to +0.6‰ evidenced in urban aerosols from polluted
72 regions (e.g., Beijing, Montreal; Supporting Information (SI) Figure S1) have not been fully
73 explicable with the S-isotope variations in emission sources (e.g., biomass or fossil fuel
74 combustion with $\Delta^{33}S$ upto $\sim \pm 0.2\%$) or atmospheric oxidation processes (e.g., homogenous and
75 heterogenous reactions displaying $\Delta^{33}S \sim 0\%$)¹⁶⁻¹⁸. While a stratospheric origin of sulfate aerosols
76 has been conceived to perpetuate $\Delta^{33}S$ in urban aerosols¹⁷, this is not the case for all locations and
77 cannot fully resolve the signals reported worldwide¹⁶. Taken together, this invokes the necessity
78 for additional oxidation pathways or reactions to be identified for the conversion of SO₂ to sulfate
79 affecting the $\Delta^{33}S$ in atmospheric aerosols¹⁶. As such, it could be a contributing factor for the
80 uncertainties associated with the radiative forcing of sulfate aerosols on a global scale, and

81 especially in one of the most polluted regions of the world with rising SO₂ levels i.e., S Asia¹⁹. We
82 therefore conducted dual-isotope fingerprinting ($\Delta^{33}\text{S}$, $\delta^{34}\text{S}$) of ambient sulfate aerosols in
83 summertime megacity Delhi in S Asia. Combining chemical, isotopic, and meteorological
84 information enabled resolving the origin of S-MIF anomalies in one of the most polluted regions
85 in the world.

86

87 **MATERIALS AND METHODS**

88 **Sampling.** Aerosol PM₁₀ samples (n=44) were collected using an Envirotech Air Pollution
89 Monitoring 550 aerosol sampler, operated at 1 m³ hr⁻¹ with a sampling duration of 24 hours
90 (sample collection started at 6 am and continued till 6 am of the next day; see SI Table S1). Sample
91 collection was made between April-May 2021 atop a five-storey residential building in the Anand
92 Vihar area of Delhi. The area is surrounded by parks and greenery. The sampling period covers
93 the summer season. Delhi has a semi-arid climate and summer temperatures are on average 45±3
94 °C²⁰. Aerosol samples were collected on pre-combusted (450 °C for 6 h) PALLFLEX tissue quartz
95 filters (25 cm×20 cm). Filter blanks were collected approximately three times per month. Samples
96 were stored in a freezer at -20 °C prior to analysis.

97 **Chemical and Isotope Measurements.** The concentration of water-soluble ions and metals, as
98 well as the S-isotope compositions were measured using an ion chromatography Metrohm IC
99 (Professional 850) and QQQ-ICP-MS, and a MC-ICP-MS instrument respectively. Measurements
100 were carried out at the University of Tours (for water-soluble ions) and Centre de Recherches
101 Pétrographiques et Géochimiques, CRPG (for S-isotopes) in France, and the Université du Québec
102 à Montréal, UQAM (for metals) in Canada, respectively. Further details on the procedure,

103 measurements, analytical uncertainties, quality control and reproducibility are provided in SI Note
104 S1.

105

106 **RESULTS AND DISCUSSION**

107 **Summertime aerosol characteristics and multi-S-isotope compositions in S Asia.** The
108 megacity Delhi—located in the heart of the Indo-Gangetic Plain—suffers from acute air pollution
109 crisis²⁰. High average PM₁₀ concentrations were found during the study period, 90±30 µg/m³ in
110 the months of April and 200±80 µg/m³ in May 2021 (SI Table SI). This is attributable in general
111 to features such as several types of anthropogenic activities, collocated emission sources, location
112 and topography, population density, and socio-economic development²⁰⁻²². Furthermore, long-
113 range transport of dust from the adjoining Thar Desert and Arabian regions is also known to
114 contribute towards episodic dust storms and high PM levels during summer²⁰.

115 The water-soluble inorganic ions (e.g., SO₄²⁻, K⁺) together contributing as much as 50% to
116 the PM₁₀ concentrations serve as tracers for combustion sources and secondary formation
117 processes²⁰⁻²³. Concentrations of one such component, aerosol sulfate, ranged from 1 to 23 µg/m³
118 (Figure 1a) implying a fractional contribution of upto 20% in the PM₁₀ aerosols. The multi-S
119 isotope compositions from Delhi ranged from 0.5‰ to 5‰ for δ³⁴S, from 0.2‰ to 0.5‰ for Δ³³S
120 during summer of 2021 (SI Table S2). In contrast to the observations of low Δ³³S (< 0.1‰) in the
121 city of Montreal and high Δ³³S (~0.5‰) in its corresponding sub-rural background¹⁶, here we find
122 such higher values in the city. This however is in accordance with the finding from Beijing (i.e., E
123 Asia) where a gradient shifting from ~0‰ to positive Δ³³S values (~0.5‰) has been reported
124 during the summer^{16,17,23}. For δ³⁴S, the values are in general lower than those reported for Montreal

125 and Beijing during summer^{16,23}, with values lower than 1‰ also being encountered in Delhi during
126 the latter part of the summer. A shift towards concomitantly high $\Delta^{33}\text{S}$ and low $\delta^{34}\text{S}$ values was
127 observed with proceeding of the summer season (Figure 1a) and could be driven by change in the
128 sources and/or atmospheric processes.

129 **Evaluation of plausible factors contributing to the sulfate $\Delta^{33}\text{S}$ dynamics.** The measurements
130 of multiple S-isotope composition reported here constitute the first for S Asia. The span of the
131 $\Delta^{33}\text{S}$ values in the present study is such that it cannot be explained by the model proposed by Harris
132 et al. (2013). Their model, relying upon the seasonal isotope variations induced by three major
133 oxidation pathways (OH, H_2O_2 , O_2+TMI), accounts for a maximum $\Delta^{33}\text{S}$ -value of 0.05‰ during
134 summer¹⁸. This implies that the additional $\Delta^{33}\text{S}$ dynamics observed in summertime Delhi could
135 either be linked to changes in origin and/or possibly other chemical reactions.

136 The anthropogenic emission sources could modulate the $\Delta^{33}\text{S}$ values^{17,23,24}. In particular,
137 biomass burning and/or biofuel combustion have been shown to affect the urban $\Delta^{33}\text{S}$ signatures²³.
138 However, for the summer samples, a poor correlation was found between $\Delta^{33}\text{S}$ and K^+ (a tracer for
139 biomass burning) (SI Figure S2). Coal combustion was found to be a large source of aerosol sulfate
140 in Delhi based on source-apportionment using $\delta^{34}\text{S}$ (see SI Note S2), however, lab-based studies
141 have shown both SO_2 and sulfate formed from coal combustion do not carry any $\Delta^{33}\text{S}$ ¹⁷. Iron
142 extraction from Archean banded-iron formation (BIF) is another source of atmospheric S that
143 produces non-zero $\Delta^{33}\text{S}$ ¹⁶. However, no such activities exist in and around the city^{20,21}. Taken
144 together this suggests that anthropogenic activities do not cause the observed $\Delta^{33}\text{S}$ isotope
145 anomalies.

146 Stratospheric intrusions have been implicated for the $\Delta^{33}\text{S}$ observed in urban aerosols¹⁷.
147 However, HYSPLIT model-based back trajectories do not show air masses arriving from the upper

148 troposphere (> 10-15 km) to the sampling location (SI Figure S3). This is consistent with the study
149 of Lin et al. (2016) who also estimated a very low (< 1%) input of stratospheric SO₄ in their study²⁵.
150 Even with such an input only upto +0.1‰ of the Δ³³S anomaly may be explained, but not the entire
151 range witnessed here. Furthermore, such intrusions are more common during the monsoon season
152 than during the summer season in the Indian sub-continent²⁶, which is further corroborated by the
153 low cloud optical thickness and high cloud top pressure measurements during the summer of 2021
154 at Delhi (SI Figure S4). We therefore turn our attention to the possibility of chemical reactions/
155 mechanisms in order to explain the origin of the Δ³³S values observed in our sulfate aerosols.

156 **Linking chemical and dual S-isotope signals to deconvolute sulfate formation.** Recently, the
157 role of mineral dust in the formation of secondary aerosol sulfate has been called into contention¹⁶.
158 The mechanisms behind the formation of secondary aerosol sulfate mediated by mineral dust
159 remain elusive^{16,27}. For instance, they may include oxidation of SO₂ by the superoxide radical
160 anion formed on semi-conducting metal oxides like Al₂O₃, Fe₂O₃ and TiO₂ by UV radiation,
161 oxidation by NO₂¹⁶. Interestingly, our chemical analyses indicate significant contributions of
162 mineral dust in the PM₁₀ aerosols in Delhi as samples present Fe/Al ratios (i.e., the conventional
163 reference for upper continental crust)^{28,29} from as low as 0.2 during April to as high as 1.4 during
164 May (all > 0.05; Figure 1a), similar to the ones characterizing desert dusts (from 0.48 to 1.74)²⁹.
165 We elected to discuss the Fe/Al ratio which is more representative of mineral dust than the Ca²⁺/Al
166 ratio, mainly a tracer for carbonate mineral^{28,29}.

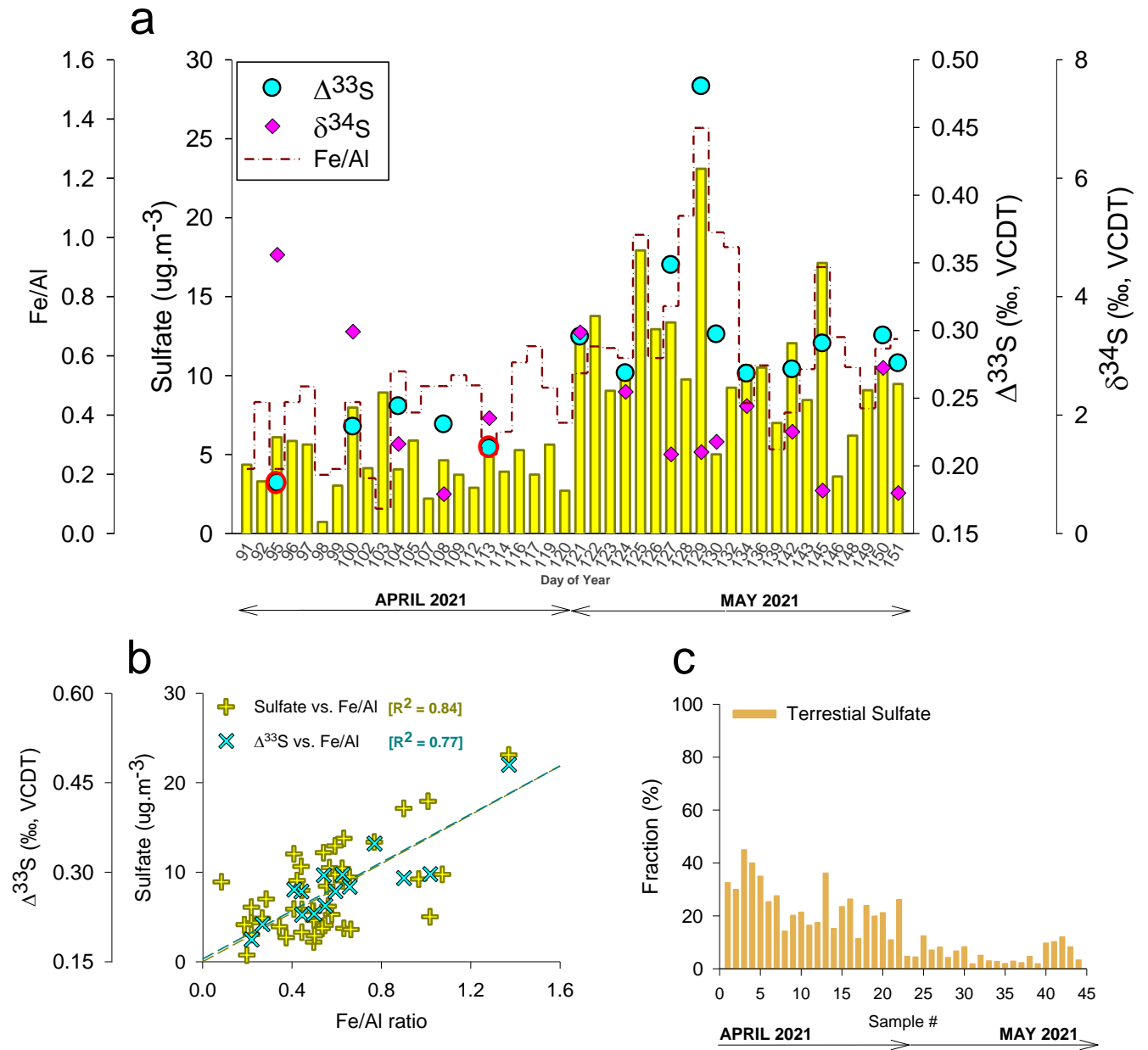
167 Higher Fe/Al ratios were observed with the progression of the summer season concomitant
168 with the influx of mineral dust from the Thar desert in western India, as evidenced by air mass
169 analysis and satellite data (SI Figures S3, S5). We find strong correlations between the Fe/Al ratios
170 and the sulfate loadings (R²=0.84) and Δ³³S values (R²=0.77) respectively, highlighting a potential

171 link between the sulfate formation, S-isotope variations and mechanisms involving mineral dust.
172 In fact, the higher $\Delta^{33}\text{S}$ anomalies ($> 0.2\text{‰}$) observed in the month of May were concomitant with
173 5-times higher loadings of mineral dust relative to those of April 2021. Taken together, this implies
174 that the low $\Delta^{33}\text{S}$ values ($< 0.2\text{‰}$) are indeed not greatly affected by mineral dust contribution and
175 can be explained as arising from a combination of different sources/origins and other homogenous
176 and heterogenous oxidation pathways (upto $\sim +0.20\text{‰}$) or even stratospheric intrusions^{17,18,23}. But
177 the higher $\Delta^{33}\text{S}$ values (as well as sulfate concentrations) observed in Delhi during summer of 2021
178 were strongly modulated by the presence of mineral dust.

179 Weak winds combined with a shallow boundary layer can lead to the contribution of high
180 fine mode resuspended road dust (whose composition remains unknown). This has been observed
181 in E Asia during the haze episodes³⁰. However, such meteorological conditions are more
182 favourable for wintertime S Asia than summer^{20,22}. The terrigenous sulfate source fraction ($f_{\text{ter-S}}$)
183 is useful for accounting the contribution of local resuspended dust (from within the city). Here,
184 based on ratio of SO_4^{2-} -to- Ca^{2+} concentrations in regional soil to the same in sampled aerosol, we
185 accounted for the $f_{\text{ter-S}}$ in summertime Delhi samples (Figure 1c; see also Note S2). We find that
186 the $f_{\text{ter-S}}$ decreased from $20\pm 5\%$ on average in April to $< 5\pm 2\%$ during May of 2021. This decrease
187 in $f_{\text{ter-S}}$ is concomitant with the increase in the Fe-to-Al ratio. This implies that influx of mineral
188 dust from nearby desert region in W India modulated the formation of aerosol sulfate and thereby
189 the observed high $\Delta^{33}\text{S}$ values (as desert dust carries no S-MIF)¹⁶ as the summer progressed. This
190 also points to the fact that the $\delta^{34}\text{S}$ signature of mineral dust from the Thar desert might be slightly
191 lower than that from deserts in China, Morocco, Tunisia and Jordan, with $\delta^{34}\text{S}$ ranges between 5
192 and 13‰ ¹⁶.

193 **Implications of mineral dust on sulfate-induced urban air pollution.** Overall, the present
194 findings suggest that $\Delta^{33}\text{S}$ is a reliable tracer for better constraining the formation of sulfate
195 aerosols in the presence of mineral dust. Comparing with previous observations from a sub-rural
196 background site in Montreal (referred to as station 98 in Au Yang et al., 2019), we find overlapping
197 characteristics in both $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ (Figure 2). Here, we conjecture that the high $\Delta^{33}\text{S}$ values
198 recorded at station 98 are indeed explicable by the SO_2 photo-oxidation on mineral dust pathway
199 in line with the hypothesis by Au Yang et al. . Furthermore, with an estimated $\Delta^{33}\text{S}$ fingerprint of
200 $+0.35\pm 0.10\text{‰}$ for this pathway, we are able to also explain the $\Delta^{33}\text{S}$ values previously observed in
201 other urban locations such as in E Asia (Figure 2) hinting at a plausible global significance of this
202 pathway. The implications of the findings here are twofold (i) even a small contribution from
203 mineral dust-mediated SO_2 photo-oxidation may have a large effect on the observed $\Delta^{33}\text{S}$ signals
204 in aerosols, (ii) regions with low SO_2 production but high input of mineral dust e.g., remote oceanic
205 regions²², can still act as emission regions of sulfate aerosols, thereby affecting the aerosol
206 radiative forcing. It remains to be seen if this pathway sustains during vertical transport of SO_2
207 where competing mechanisms such as aqueous phase oxidation and/or stratospheric intrusions
208 become more relevant³¹.

209 For South Asia, the rising SO_2 levels present a threat to several of the sustainable
210 development goals for the region such as access to clean air and freshwater^{32,33}. For accurate
211 predictions of future scenarios of the influence of SO_2 on the region it is imperative to account for
212 all sources and formation pathways of sulfate. We therefore consider that the findings here would
213 aid in that direction and contribute towards reducing the model-observation discrepancies in
214 modeling global and regional sulfate aerosol dynamics wherein the sensitivity of the simulations
215 remains highly dependent on the accounted oxidation pathways³⁴.



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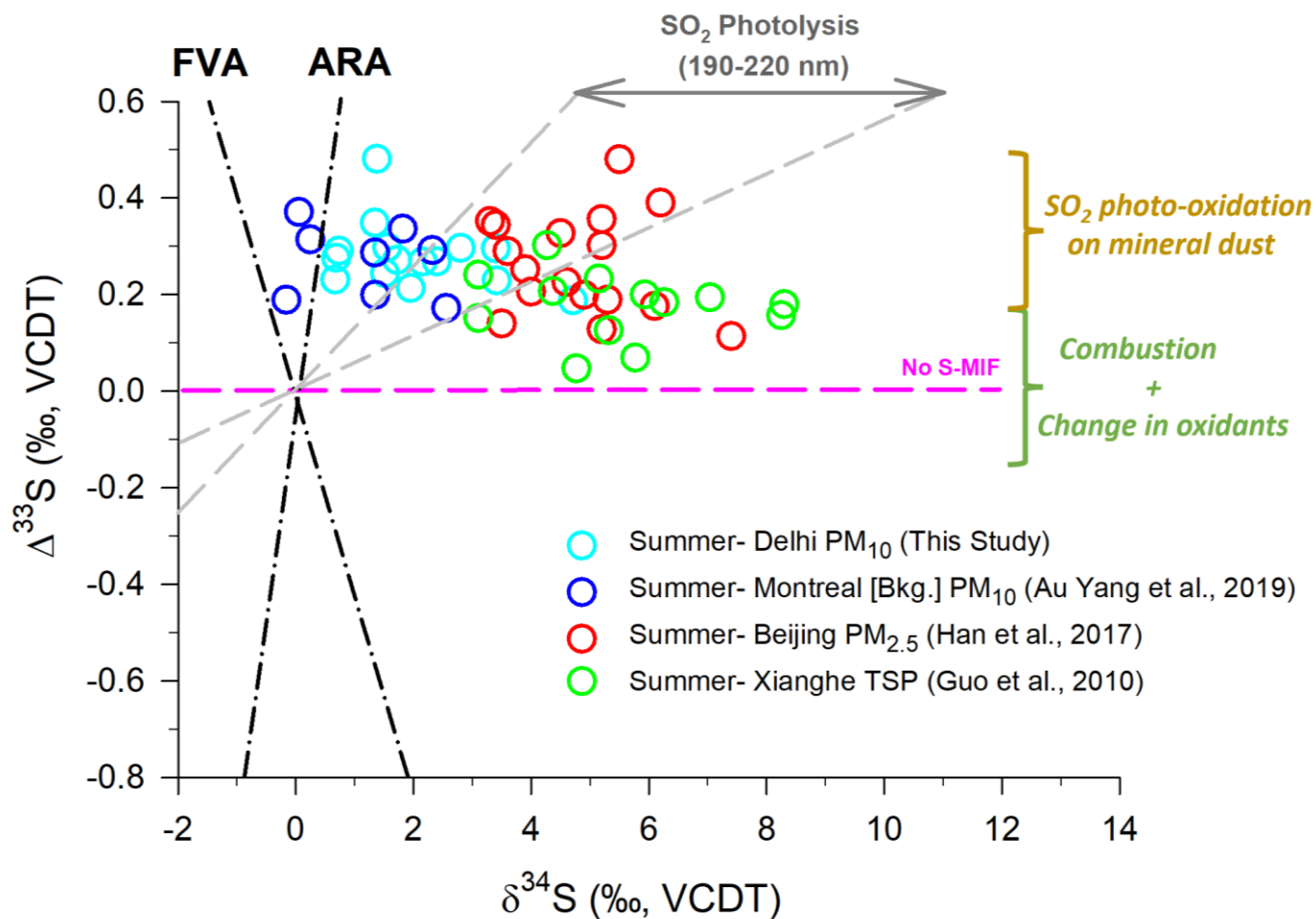
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219 **Figure 1.** (A) Temporal changes in the sulfate concentrations, $\Delta^{33}\text{S}$, $\delta^{34}\text{S}$ and Fe/Al ratios,

220 (B) Correlation of the $\Delta^{33}\text{S}$ signals, sulfate loadings with the influx of mineral dust (see also, SI

221 Table S1-S2, SI Figures S3-S5), (C) Calculated terrestrial sulfate fraction in the PM₁₀ samples (see

222 also SI Note S2). Samples with red circles (Day 95, 113) refer to the ones collected only during
223 the nighttime (6 pm to 6 am). As such, these were restricted to 12 h collections.



224

225

226 **Figure 2.** Relation between $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ for sulfate in Delhi PM₁₀ during sampling and their
 227 comparison with aerosols collected from Beijing²³ and Xianghe in E Asia³⁵ and sub-rural
 228 background site in Montreal, Canada¹⁶. ARA represents the Archean Reference Array based on
 229 the data from Neoproterozoic and Paleoproterozoic rocks in Australia and Africa³⁶. FVA represents the
 230 felsic volcanic array³⁷. The gray field represents experiment data from SO₂ photolysis in the
 231 190–220 nm region (Xenon arc lamp)¹⁵.

232 **ASSOCIATED CONTENT**

233 **Supporting Information.** Notes S1-S2 include discussions on the chemical and isotope
234 measurements, source apportionment calculations. Figures S1-S5 include air mass analysis,
235 satellite data-derived maps, correlations. Tables S1-S2 list the sampling details and concentrations
236 of water-soluble ions, metals, and multiple S-isotope compositions.

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241 **Author Contributions**

242 S.D. designed research and was supported by D.W., Z.C and G.P.; S.D., B.S., and G.P performed
243 the chemical and isotopic measurements, respectively; All co-authors analyzed data; S.D., wrote
244 the paper with input from all co-authors.

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249 **Notes**

250 The authors declare no competing financial interests.

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255 **REFERENCES**

- 256 1. Thode, H. G. Sulphur isotopes in nature and the environment: an overview. *Stable isotopes:*
257 *natural and anthropogenic sulphur in the environment* **1991**, *43*, 1-26
258 https://scope.dge.carnegiescience.edu/SCOPE_43/SCOPE_43_1_Chp1.pdf (accessed
259 2021.12).
- 260 2. Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to*
261 *Climate Change*; John Wiley & Sons, 2016.
- 262 3. *Climate change 2007: The Physical Science basis*; <https://www.ipcc.ch/report/ar4/wg1/> ,
263 2007.
- 264 4. Kulmala, M.; Riipinen, I.; Sipilä, M.; Manninen, H. E.; Petäjä, T.; Junninen, H.; Dal Maso,
265 M.; Mordas, G.; Mirme, A.; Vana, M.; Hirsikko, A. Toward direct measurement of
266 atmospheric nucleation. *Science* **2007**, *318*, 89-92.
- 267 5. Mertes, S.; Galgon, D.; Schwirn, K.; Nowak, A.; Lehmann, K.; Massling, A.; Wiedensohler,
268 A.; Wieprecht, W. Evolution of particle concentration and size distribution observed
269 upwind, inside and downwind hill cap clouds at connected flow conditions during
270 FEBUKO. *Atmos. Environ.* **2005**, *39*, 4233–4245.
- 271 6. Arias, P.; Bellouin, N.; Coppola, E.; Jones, R.; Krinner, G.; Marotzke, J.; Naik, V.; Palmer,
272 M.; Plattner, G. K.; Rogelj, J.; Rojas, M. *Climate Change 2021: The Physical Science Basis.*
273 *Contribution of Working Group14 I to the Sixth Assessment Report of the*
274 *Intergovernmental Panel on Climate Change; Technical Summary* **2021**.

- 275 7. Nriagu, J. O.; Coker, R. D.; Barrie, L. A. Origin of sulphur in Canadian Arctic haze from
276 isotope measurements. *Nature* **1991**, *349*, 142-145.
- 277 8. Shen, Y.; Buick, R.; Canfield, D. E. Isotopic evidence for microbial sulphate reduction in
278 the early Archaean era. *Nature* **2001**, *410*, 77–81.
- 279 9. Farquhar, J.; Bao, H.; Thiemens, M. Atmospheric influence of Earth's earliest sulfur
280 cycle. *Science* **2000**, *289*, 756-758.
- 281 10. Ding, T.; Valkiers, S.; Kipphardt, H.; De Bievre, P.; Taylor, P.; Gonfiantini, R.; Krouse, R.
282 Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials
283 and V-CDT with a reassessment of the atomic weight of sulfur. *Geochim. Cosmochim. Acta*
284 **2001**, *65*, 2433–2437.
- 285 11. Coplen, T. B. Guidelines and recommended terms for expression of stable-isotope-ratio and
286 gas-ratio measurement results. *Rapid Comm. Mass Spec.* **2011**, *25*, 2538–2560.
- 287 12. Ono, S.; Wing, B.; Johnston, D.; Farquhar, J.; Rumble, D. Mass-dependent fractionation of
288 quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles,
289 *Geochim. Cosmochim. Acta* **2006**, *70*, 2238–2252.
- 290 13. Dauphas, N.; Schauble, E. A. Mass fractionation laws, mass independent effects, and
291 isotopic anomalies. *Ann. Rev. Earth Pl. Sci.* **2016**, *44*, 709–783.
- 292 14. Eldridge, D.; Guo, W.; Farquhar, J. Theoretical estimates of equilibrium sulfur isotope
293 effects in aqueous sulfur systems: Highlighting the role of isomers in the sulfite and
294 sulfoxylate systems. *Geochim. Cosmochim. Acta* **2016**, *195*, 171–200.

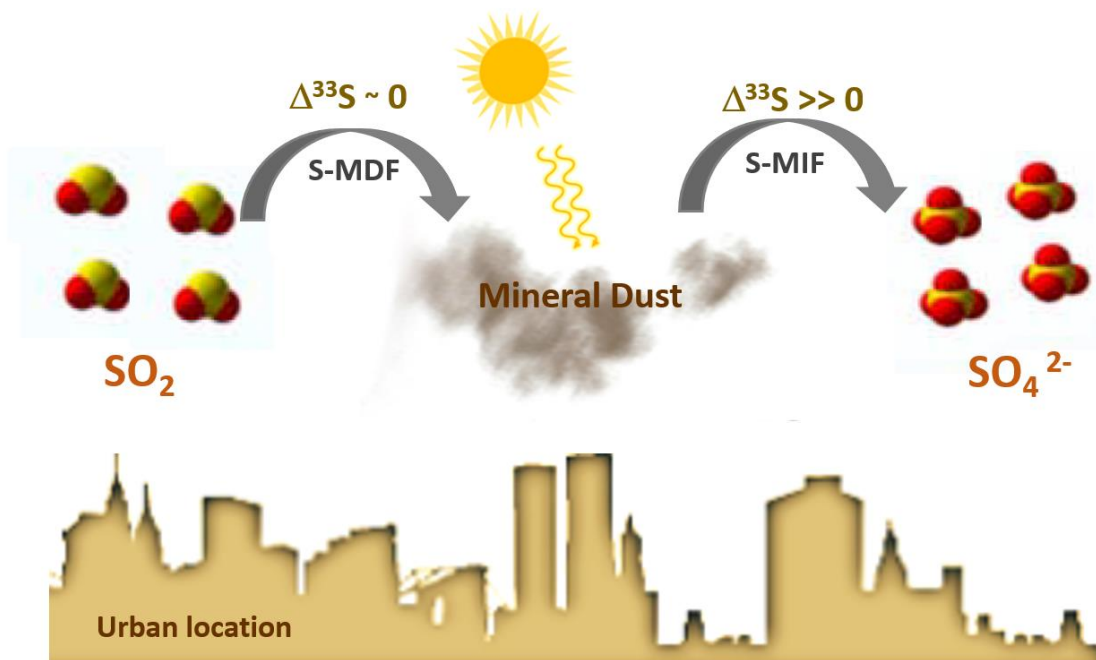
- 295 15. Whitehill, A. R.; Jiang, B.; Guo, H.; Ono, S. SO₂ photolysis as a source for sulfur mass-
296 independent isotope signatures in stratospheric aerosols. *Atmos. Chem. Phys.* **2015**, *15*,
297 1843-1864.
- 298 16. Au Yang, D.; Cartigny, P.; Desboeufs, K.; Widory, D. Seasonality in the $\Delta^{33}\text{S}$ measured
299 in urban aerosols highlights an additional oxidation pathway for atmospheric SO₂. *Atmos.*
300 *Chem. Phys.* **2019**, *19*, 3779-3796.
- 301 17. Lin, M.; Zhang, X.; Li, M.; Xu, Y.; Zhang, Z.; Tao, J.; Su, B.; Liu, L.; Shen, Y.; Thiemens,
302 M. H. Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and
303 implications for the modern and Archean atmospheres. *Proc. Natl. Acad. Sci. U. S. A.* **2018**,
304 *115*, 8541-8546.
- 305 18. Harris, E.; Sinha, B.; Hoppe, P.; Ono, S. High-precision measurements of ³³S and ³⁴S
306 fractionation during SO₂ oxidation reveal causes of seasonality in SO₂ and sulfate isotopic
307 composition. *Environ. Sci. Technol.* **2013**, *47*, 12174–12183.
- 308 19. Dahiya, S.; Myllyvirta, L. Global SO₂ Emission Hotspots Database: Ranking the World's
309 Worst Sources of SO₂ Pollution. Greenpeace Environment Trust,
310 [https://www.greenpeace.org/india/en/publication/3951/global-so2-emission-hotspots-](https://www.greenpeace.org/india/en/publication/3951/global-so2-emission-hotspots-database-ranking-the-worlds-worst-sources-of-so2-pollution-2/)
311 [database-ranking-the-worlds-worst-sources-of-so2-pollution-2/](https://www.greenpeace.org/india/en/publication/3951/global-so2-emission-hotspots-database-ranking-the-worlds-worst-sources-of-so2-pollution-2/)(accessed 2021.12)
- 312 20. Hama, S. M.; Kumar, P.; Harrison, R. M.; Bloss, W. J.; Khare, M.; Mishra, S.; Namdeo, A.;
313 Sokhi, R.; Goodman, P.; Sharma, C. Four-year assessment of ambient particulate matter
314 and trace gases in the Delhi-NCR region of India. *Sustain. Cit. Soci.* **2020**, *54*, 102003.

- 315 21. Gurjar, B. R.; Nagpure, A. S. Indian megacities as localities of environmental vulnerability
316 from air quality perspective. *J. Smart Cities* **2016**, *1*,15-30.
- 317 22. Dasari, S.; Andersson, A.; Bikkina, S.; Holmstrand, H.; Budhavant, K.; Satheesh, S.; Asmi,
318 E.; Kesti, J.; Backman, J.; Salam, A.; Bisht, D. S. Photochemical degradation affects the
319 light absorption of water-soluble brown carbon in the South Asian outflow. *Sci. Adv.* **2019**,
320 *5*, eaau8066.
- 321 23. Han, X.; Guo, Q.; Strauss, H.; Liu, C.; Hu, J.; Guo, Z.; Wei, R.; Peters, M.; Tian, L.; Kong,
322 J. Multiple sulfur isotope constraints on sources and formation processes of sulfate in
323 Beijing PM_{2.5} aerosol. *Environ. Sci. Technol.* **2017**, *51*, 7794–7803.
- 324 24. Lee, C. W.; Savarino, J.; Cachier, H.; Thiemens, M. Sulfur (³²S, ³³S, ³⁴S, ³⁶S) and oxygen
325 (¹⁶O, ¹⁷O, ¹⁸O) isotopic ratios of primary sulfate produced from combustion processes.
326 *Tellus B* **2002**, *54*, 193–200.
- 327 25. Lin, M.; Zhang, Z.; Su, L.; Hill-Falkenthal, J.; Priyadarshi, A.; Zhang, Q.; Zhang, G.; Kang,
328 S.; Chan, C. Y.; Thiemens, M. H. Resolving the impact of stratosphere-to-troposphere
329 transport on the sulfur cycle and surface ozone over the Tibetan Plateau using a cosmogenic
330 ³⁵S tracer. *J. Geophys. Res. Atmos.* **2016**, *121*, 439–456.
- 331 26. Fadnavis, S.; Chattopadhyay, R. Linkages of subtropical stratospheric intraseasonal
332 intrusions with Indian summer monsoon deficit rainfall. *J. of Climate* **2017**, *30*, 5083-5095.
- 333 27. Harris, E.; Sinha, B.; Foley, S.; Crowley, J. N.; Borrmann, S.; Hoppe, P. Sulfur isotope
334 fractionation during heterogeneous oxidation of SO₂ on mineral dust. *Atmos. Chem. Phys.*
335 **2012**, *12*, 4867– 4884.

- 336 28. Paris, R.; Desboeufs, K. V.; Formenti, P.; Nava, S.; Chou, C. Chemical characterisation of
337 iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX: implication for
338 iron solubility. *Atmos. Chem. Phys.* **2010**, *10*, 4273–4282.
- 339 29. Formenti, P.; Schütz, L.; Balkanski, Y.; Desboeufs, K.; Ebert, M.; Kandler, K.; Petzold, A.;
340 Scheuven, D.; Weinbruch, S.; Zhang, D. Recent progress in understanding physical and
341 chemical properties of African and Asian mineral dust. *Atmos. Chem. Phys.* **2011**, *11*, 8231–
342 8256.
- 343 30. Tian, S. L.; Pan, Y. P.; Wang, Y. S. Size-resolved source apportionment of particulate
344 matter in urban Beijing during haze and non-haze episodes. *Atmos. Chem. Phys.* **2016**, *16*,
345 1-19.
- 346 31. Lin, M.; Biglari, S.; Zhang, Z.; Crocker, D.; Tao, J.; Su, B.; Liu, L.; Thiemens, M. H.
347 Vertically uniform formation pathways of tropospheric sulfate aerosols in East China
348 detected from triple stable oxygen and radiogenic sulfur isotopes. *Geophys. Res. Lett.*
349 **2017**, *44*, 5187-5196.
- 350 32. Fadnavis, S.; Müller, R.; Kalita, G.; Rowlinson, M.; Rap, A.; Li, J. L. F.; Gasparini, B.;
351 Laakso, A. The impact of recent changes in Asian anthropogenic emissions of SO₂ on
352 sulfate loading in the upper troposphere and lower stratosphere and the associated radiative
353 changes. *Atmos. Chem. Phys.* **2019**, *19*, 9989-10008.
- 354 33. Fadnavis, S.; Sabin, T. P.; Roy, C.; Rowlinson, M.; Rap, A.; Vernier, J. P.; Sioris, C. E.
355 Elevated aerosol layer over South Asia worsens the Indian droughts. *Sci. Rep.* **2019**, *9*, 1-
356 11.

- 357 34. Paulot, F.; Paynter, D.; Ginoux, P.; Naik, V.; Horowitz, L.W. Changes in the aerosol direct
358 radiative forcing from 2001 to 2015: observational constraints and regional
359 mechanisms. *Atmos. Chem. Phys.* **2018**, *18*, 13265-13281.
- 360 35. Guo, Z.; Li, Z.; Farquhar, J.; Kaufman, A. J.; Wu, N.; Li, C.; Dickerson, R. R.; Wang, P.
361 Identification of sources and formation processes of atmospheric sulfate by sulfur isotope
362 and scanning electron microscope measurements. *J. of Geophys. Res. Atmos.* **2010**, *115*,
363 D00K07.
- 364 36. Mast, M. A.; Turk, J. T.; Ingersoll, G. P.; Clow, D. W.; Kester, C. L. Use of stable sulfur
365 isotopes to identify sources of sulfate in Rocky Mountain snowpacks. *Atmos. Environ.* **2001**,
366 *35*, 3303–3313.
- 367 37. Philippot, P.; van Zuilen, M.; Rollion-Bard, C. Variations in atmospheric sulphur chemistry
368 on early Earth linked to volcanic activity. *Nat. Geosci.* **2012**, *5*, 668–674.

SO₂ Photo-oxidation on mineral dust surface generates S-MIF



Sulfur Mass-Dependent Fractionation : S-MDF
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