

## SO<sub>2</sub> photoexcitation mechanism links sulfur MIF in polar sulfate to climate-impacting volcanism

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Natural climate variation such as that due to volcanoes is the basis for identifying anthropogenic climate change. However, knowledge of the history of volcanic activity is inadequate, in particular concerning the explosivity of specific events. Stable sulfur isotope abundances contain additional information and recent studies show a correlation between volcanic plumes that reach the stratosphere and mass-independent anomalies in sulfur isotopes in glacial sulfate. We describe a new mechanism, photoexcitation of SO<sub>2</sub>, links the two yielding a useful metric of explosivity of historic volcanic events. A plume model of SO<sub>2</sub> to sulfate conversion was constructed including photochemistry, entrainment of background air and sulfate deposition. Isotopologue-specific photoexcitation rates were calculated based on the UV absorption cross sections of <sup>32</sup>SO<sub>2</sub>, <sup>32</sup>SO<sub>2</sub>, <sup>32</sup>SO<sub>2</sub> and <sup>32</sup>SO<sub>2</sub> from 250 to 320 nm. The model demonstrates that UV photoexcitation is enhanced by altitude while mass-dependent oxidation such as SO<sub>2</sub> + OH is suppressed by in situ plume chemistry, allowing the production and preservation of a mass-independent sulfur isotope anomaly in the sulfate product. The model accounts for the amplitude, phases and time development of  $\Delta^{33}\text{S} / \delta^{34}\text{S}$  and  $\Delta^{36}\text{S} / \Delta^{33}\text{S}$  found in glacial samples. For the first time we are able to identify the process controlling mass-independent sulfur isotope anomalies in the modern atmosphere. This mechanism is the basis of identifying the magnitude of historic volcanic events.