Geophysical Research Abstracts
Vol. 15, EGU2013-14110, 2013
EGU General Assembly 2013

SO_2 photolysis and photoexcitation produces ^{33}S and ^{36}S mass independent fractionation, linking sulfur isotope anomalies in cryospheric sulfate to explosive volcanic eruptions entering the stratosphere

Matthew S. Johnson (1), Shohei Hattori (2), Sebastian O. Danielache (3), Johan A. Schmidt (1), Akinori Yamada (4), Yuichiro Ueno (2), Shinkoh Nanbu (3), and Naohiro Yoshida (2)

(1) Department of Chemistry, University of Copenhagen, Denmark, (2) Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, (3) Faculty of Science and Technology, Sophia University, Japan, (4) Department of Earth and Planetary Science, University of Tokyo, Japan

We report measurements of the ultraviolet absorption cross-sections of $^{32}SO_2$, $^{33}SO_2$, $^{34}SO_2$ and $^{36}SO_2$ recorded from 250 to 320 nm at 293 K with a resolution of 8 cm^{-1}. The cross-sections were used in a photochemical model to obtain fractionation constants to compare with photochemical chamber experiments. We conclude that planetary atmospheres will exhibit isotopic fractionation from both photoexcitation and photodissociation, and that experiments in the literature have isotopic imprints arising from both the B1B1-X1A1 and the C1B1-X1A1 bands. 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_2, that links the two yielding a useful metric of the explosivity of historic volcanic events. A plume model of S(IV) to S(VI) 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 $^{32}SO_2$, $^{33}SO_2$, $^{34}SO_2$ and $^{36}SO_2$ from 250–320 nm. The model demonstrates that UV photoexcitation is enhanced by altitude while mass-dependent oxidation such as SO_2 + 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 $\Delta^{33}S/\delta^{34}S$ and $\Delta^{36}S/\Delta^{33}S$ 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.