Anomalous isotopic fractionation during broadband SO_2 photochemistry: comparative systematics of ^{16}O- and ^{18}O-rich SO_2

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Sulfur Isotope Fractionation

♦Measured as deviation of an isotopic ratio compared to a reference isotopic ratio, typically Vienna Canyon Diablo Troilite (VCDT) for sulfur

e.g., $\delta^{34}S = [^{34}S/^{32}S]_{meas}/[^{34}S/^{32}S]_{ref} - 1$

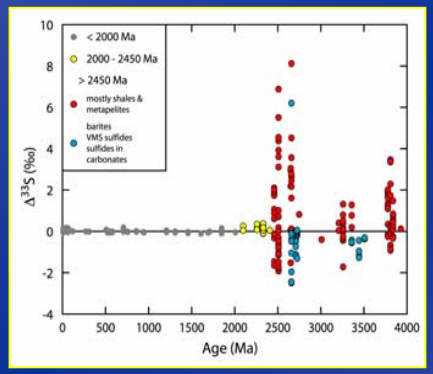
♦Mass-dependent fractionation: Solid-earth geological processes and biological processes tend to fractionate sulfur isotopes in proportion to their masses, such that

$\delta^{33}S \sim 0.515 \times \delta^{34}S$ and $\delta^{36}S \sim 1.90 \times \delta^{34}S$

♦Anomalous (non mass-dependent) sulfur isotope signatures are found in the ancient geological record
♦$\Delta^{33}S$ and $\Delta^{36}S$ quantify the deviation of a given sample's isotopic signature from a mass-dependent fractionation line. For example:

$\Delta^{33}S = \ln(\delta^{33}S_{meas}+1) - 0.515 \times \ln(\delta^{34}S_{meas}+1)$

♦This anomalous sulfur fractionation implies constraints on the history of atmospheric oxygen levels [1]



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Laboratory Experiments

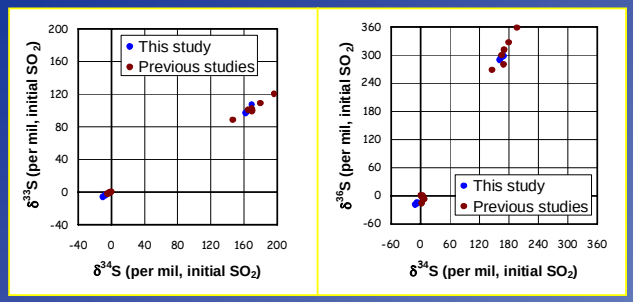
♦Gas-phase SO_2 photochemistry
♦Broadband UV radiation, 180 - 360 nm
♦Experiments produce large anomalous sulfur isotope fractionation
♦May provide a viable explanation for the ancient sulfur isotopic signatures observed [1]

Effects of Isotopic Substitution

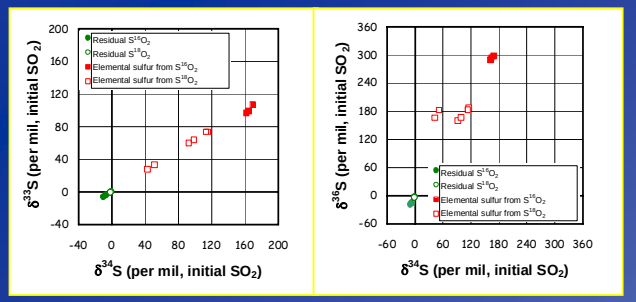
♦Both primary and secondary photoprocesses are sensitive to intermolecular isotopic substitution [2,3]
♦Zmolek et al. saw significant differences in photopolymerization effects in $(^{13}CS_2)_x$ vs. $(^{12}CS_2)_x$ [3]
♦The current study investigates whether oxygen isotopic substitution in SO_2 affects sulfur isotope fractionation resulting from UV photolysis
♦Experiments were performed with both ^{16}O-rich and ^{18}O-rich SO_2

Results

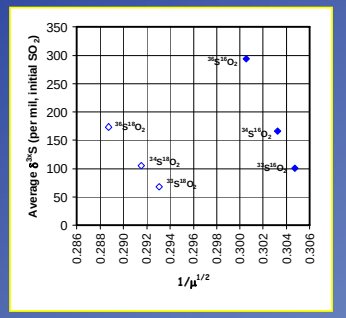
♦Three-isotope plots shown are normalized to an initial SO_2 composition of $\delta^{33}S = \delta^{34}S = \delta^{36}S = 0$
♦Results with ^{16}O-rich SO_2 are consistent with those of previous photolysis experiments performed at the University of Maryland Department of Geology



♦Results with ^{18}O-rich SO_2 indicate reduced sulfur isotope fractionation compared to ^{16}O-rich case



♦The degree of enrichment for a given sulfur isotope is correlated with $1/\mu^{1/2}$, where μ is the reduced mass of a particular O-S isotopic combination



♦Isotopic composition of additional experimental products waiting to be measured
♦Results are preliminary; physical mechanism responsible for the relative fractionation effects of different SO_2 isotopomers is under investigation

References

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[3] P. Zmolek et al. (1999) J. Phys. Chem. 103 2477-2480