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Poster Session Day 1

A numerical analysis of $\Delta^{36}S/\Delta^{33}S$ dependence on definitions of sulfur mass-independent fractionation: Implication for modern stratospheric sulfates

Yoshiaki Endo[1], Mimi Chen[2] & Mark W. Claire[3]

[1] Earth & Planetary Sciences, Tokyo Institute of Technology, Japan
[2] Peking University, China
[3] Blue Marble Space Institute of Science
*Presenting Author Email: endo.y.ac@m.titech.ac.jp

Mass-independent fractionation of stable sulfur isotopes (MIF-S) is believed to be a unique tracer of modern stratospheric eruptions as well as the Archean Earth's reducing atmosphere. The $\Delta^{36}S/\Delta^{33}S$ ratio has been suggested as a strong constraint to the photochemical origin(s) of MIF-S data, because the variation of $\Delta^{36}S/\Delta^{33}S$ ratio is commonly thought insignificant when mass-independently-fractionated sulfur species (i.e., non-zero $\Delta^{33}S$ or $\Delta^{36}S$ values) are mixed with mass-dependently-fractionated sulfur species (i.e., $\Delta^{33}S = \Delta^{36}S = 0‰$). The $\Delta^{36}S/\Delta^{33}S$ ratio, however, does not always remain constant during mixing, for the equations that define $\Delta^{33}S$ and $\Delta^{36}S$, which by definition represent deviations from mass-dependent behavior, are not linear. Several different definitions (linear, exponential, and logarithmic expressions) have been widely applied for $\Delta^{33}S$ and $\Delta^{36}S$, which make the $\Delta^{36}S/\Delta^{33}S$ ratio a definition-dependent value. Given that each definition has advantages and disadvantages, attention should be paid to the robustness of the $\Delta^{36}S/\Delta^{33}S$ ratio they predict. To examine the robustness of $\Delta^{36}S/\Delta^{33}S$ ratio, we performed numerical and analytical analyses of its definition dependence and the behavior during two-component mixing (Endo et al., 2024). Our results suggest that the calculated $\Delta^{33}S$ and $\Delta^{36}S$ derived from different definitions vary with $|\delta^{34}S|$: at larger $|\delta^{34}S|$, the deviations become more prominent, and when $|\delta^{34}S|$ is larger than ~34‰, the discrepancy of $\Delta^{36}S$ values determined by different definitions is over 1‰, which leads to significant definition-dependent variation in $\Delta^{36}S/\Delta^{33}S$ at identical $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$ values. This definition-dependence of $\Delta^{36}S/\Delta^{33}S$ is negligible for most natural samples that show small $^{34}S/^{32}S$ fractionation. However, particular attention should be paid when dealing with processes that yield not only significant MIF but also large ^{34}S isotopic fractionations, such as SO_2 photolysis. Among the tested expressions, the linear definitions are the most convenient to model two-component mixing when the $\delta^{34}S$ difference between the end members is large, because $\Delta^{33}S$ and $\Delta^{36}S$ values of the mixture can strictly fall on the linear arrays in $\Delta^{33}S$ versus $\Delta^{36}S$ spaces. By applying the linear expression, the $\Delta^{36}S-\Delta^{33}S$ distributions observed in the modern stratospheric records can be reproduced by SO_2 photolysis experiments.

Reference:
Endo, Y., Chen, M., & Claire, M. W. (2024). Chem. Geol., 661, 122157.