Multiple Sulfur Isotope Study of Aerosol Samples and its implication

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Outline

✓ Background

✓ $^{34}\text{S}$ Sulfur Isotope & Implication

✓ $^{33}\text{S}$ Sulfur Isotope & Implication
Background

• Multiple sulfur stable isotopes: $^{32}\text{S}(95.02\%),\; ^{33}\text{S}\; (0.75\%),\; ^{34}\text{S}\; (4.21\%),\; ^{36}\text{S}\; (0.02\%)$

• $^{34}\text{S}$ is widely used due to high abundance in nature
  Atmospheric particle/$\text{SO}_2$/precipitation/sea water

• $\delta^{34}\text{S}$ retains its special signal, used for:
  regional source appointments
  evaluating $\text{SO}_2$ oxidation pathways
Background

- $^{33}\text{S}$ and $^{36}\text{S}$ are seldom adopted for low abundance and restriction in monitoring instruments; mainly used in geology field;

- $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (abnormal sulfur isotopes) are tracers for atmospheric evolution and chemical reaction processes.
Compositional Notation

Background

Express compositions as ratios of isotopic ratios using

\[ \delta^{34}\text{S} = \left[ \frac{(34\text{S} / 32\text{S})_{\text{sample}}}{(34\text{S} / 32\text{S})_{\text{ref}}} - 1 \right] \times 1000 \]

\[ \delta^{33}\text{S} = \left[ \frac{(33\text{S} / 32\text{S})_{\text{sample}}}{(33\text{S} / 32\text{S})_{\text{ref}}} - 1 \right] \times 1000 \]

Standard: Canyon Diablo iron meteorite (CDT)

\[ \Delta^{33}\text{S} \quad \text{is measured–predicted} \quad \frac{33\text{S}}{32\text{S}} \text{ in a sample} \]

\[ \Delta^{36}\text{S} \quad \text{is measured–predicted} \quad \frac{36\text{S}}{32\text{S}} \text{ in a sample} \]

\[ \Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times \left[ (1 + \delta^{34}\text{S}/1000)^{0.515} - 1 \right] \]

\[ \Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \times \left[ (1 + \delta^{34}\text{S}/1000)^{1.90} - 1 \right] \]

|\Delta^{33}\text{S}| \sim 0, \text{ Mass-dependent; } |\Delta^{33}\text{S}| \geq 0.1\%, \text{ Mass-independent}
published data compilation from studies by Hoering, Rumble, Ono, Hu, Papineau, Mojzsis, Whitehouse, Baublys, Ohmoto, Farquhar, Johnston
**Measured Method**

- Sulfate is converted to Barite, then reduced to silver sulfide ($\text{Ag}_2\text{S}$) by wet chemistry

- $\text{SF}_6$ is produced by the reaction of silver sulfide ($\text{Ag}_2\text{S}$) with $\text{F}_2$ gas

- $\text{SF}_6$ goes through cryogenic & gas chromatographic purification line

- $\text{SF}_6$ is measured by dual-inlet Thermo Finnigan MAT253 at UMD

- The precision for $\delta^{34}\text{S}$ & $\Delta^{33}\text{S}$ are 0.1 ‰ and 0.008‰
Observation: $\delta^{34}$S Sulfur Isotope & Implication

Ternary mixing model: a dominant component & two subordinate components (high and low in $\delta^{34}$S)
Observation \( \delta^{34}\text{S} \) Sulfur Isotope & Implication

Sulfur Isotopic Composition of Aerosol Sulfate
Implication  $\delta^{34}\text{S}$ Sulfur Isotope & Implication

Backward trajectories ending on 1 Mar

The larger $\delta^{34}\text{S}$ on 1 Mar is due to the mixing of sea salt.
Observation $\delta^{34}\text{S}$ Sulfur Isotope & Implication
Interpretation $\delta^{34}S$ Sulfur Isotope & Implication

Observation $\Delta^{33}S$ Sulfur Isotope & Implication

- $\Delta^{33}S$ presents a seasonal variation
- Mass-dependent in March, obvious mass-independent in summer.
Observation: $\Delta^{33}S$, $\Delta^{36}S$

Positive $\Delta^{33}S$ values and negative $\Delta^{36}S$ values
Interpretation $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$—SO$_2$ photochemistry

SO$_2$ photochemistry is only present candidate for anomalous S isotope effects in the rock record

Farquhar et al.  
Interpretation \( \Delta^{33}S, \Delta^{36}S \)—SO\(_2\) photochemical reactions

- Wavelength dependency of sulfur MIF during SO\(_2\) photolysis
- KrF laser (248 nm) is a major way
Interpretation _Δ^{33}S_

✓SO₂ photolysis (mainly at 248 nm) occurs only in stratosphere in present atmosphere for high O₃ and O₂

✓Δ^{33}S we measured in aerosol sulfate should be related to input of sulfate from the stratosphere
CAPE (Convective available potential energy) is used to predict atmospheric instability and severe weather. Positive relationship proves sulfur anomalies in aerosol are related to sulfate from stratosphere.
Interpretation \(\Delta^{33}S\)

- Extremely High \(\Delta^{33}S\) on August 13, 14, and 15 lead us to further investigate the origin of sulfur isotope anomaly.
• Deep convective clouds active at Xianghe during the time
Thanks for your attention