Multiple Sulfur Isotope Study of Aerosol Samples and its implication

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Outline

- ✓ Background
- ✓ ^{34}S Sulfur Isotope & Implication
- ✓ ^{33}S Sulfur Isotope & Implication

Background

- **Multiple sulfur stable isotopes: ^{32}S(95.02%), ^{33}S (0.75%), ^{34}S (4.21%) ,^{36}S (0.02%)**

- **^{34}S is widely used due to high abundance in nature**

  Atmospheric particle/SO_2/precipitation/sea water

- **$\delta^{34}S$ retains its special signal, used for:**

  regional source appointments

  evaluating SO_2 oxidation pathways

Background

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

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

Compositional Notation_Background

$(^{32}S, ^{33}S, ^{34}S \& ^{36}S)$

✓**Express compositions as ratios of isotopic ratios using**

$\delta^{34}S = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{ref} - 1\ ]*1000$

$\delta\ ^{33}S = [(^{33}S/^{32}S)_{sample}/(^{33}S/^{32}S)_{ref} - 1\ ]*1000$

Standard： Canyon Diablo iron meteorite (CDT)

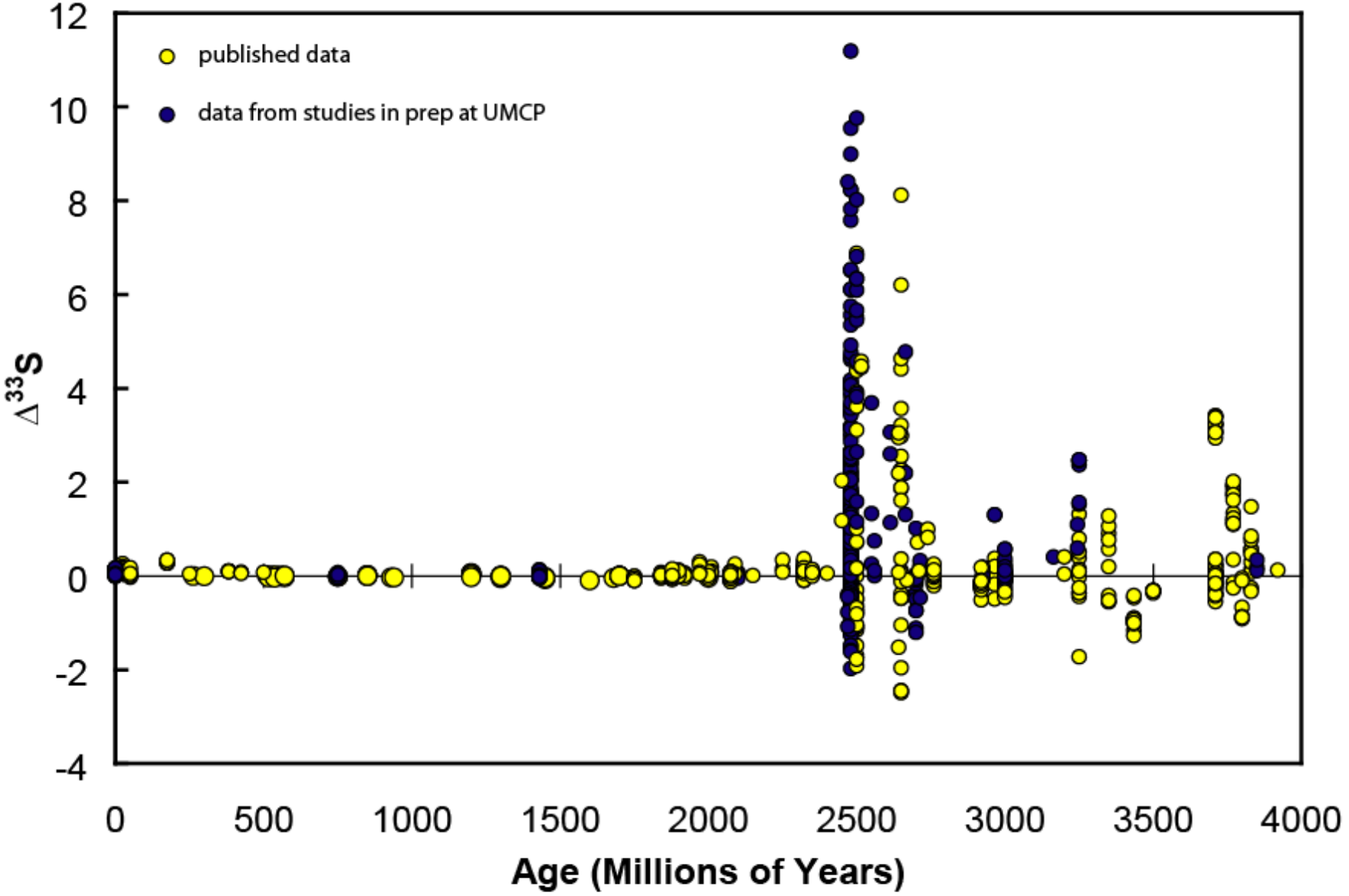
$\Delta^{33}S$ is **measured–predicted** $^{33}S/^{32}S$ in a sample

$\Delta^{36}S$ is **measured–predicted** $^{36}S/^{32}S$ in a sample

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

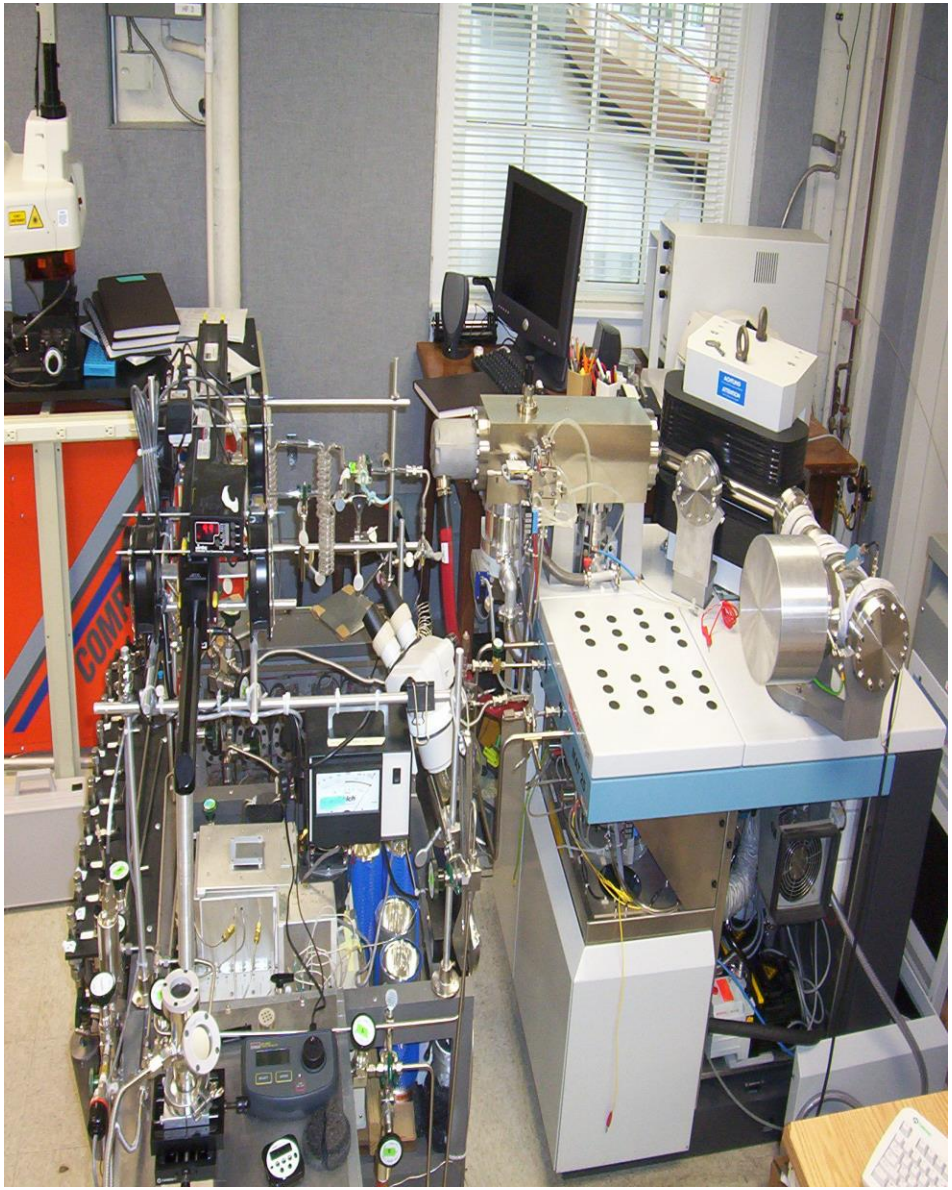
$\Delta^{36}S = \delta^{36}S - 1000 \times [(1 + \delta^{34}S/1000)^{1.90} - 1\ ]$

$|\Delta^{33}S| \sim 0$, Mass-dependent; $|\Delta^{33}S| \geq 0.1‰$, Mass-independent



published data compilation from studies by Hoering, Rumble, Ono, Hu, Papineau, Mojzsis, Whitehouse, Baublys, Ohmoto, Farquhar, Johnston

Measured Method _Background



✓Sulfate is converted to Barite, then reduced to silver sulfide (Ag_2S) by wet chemistry

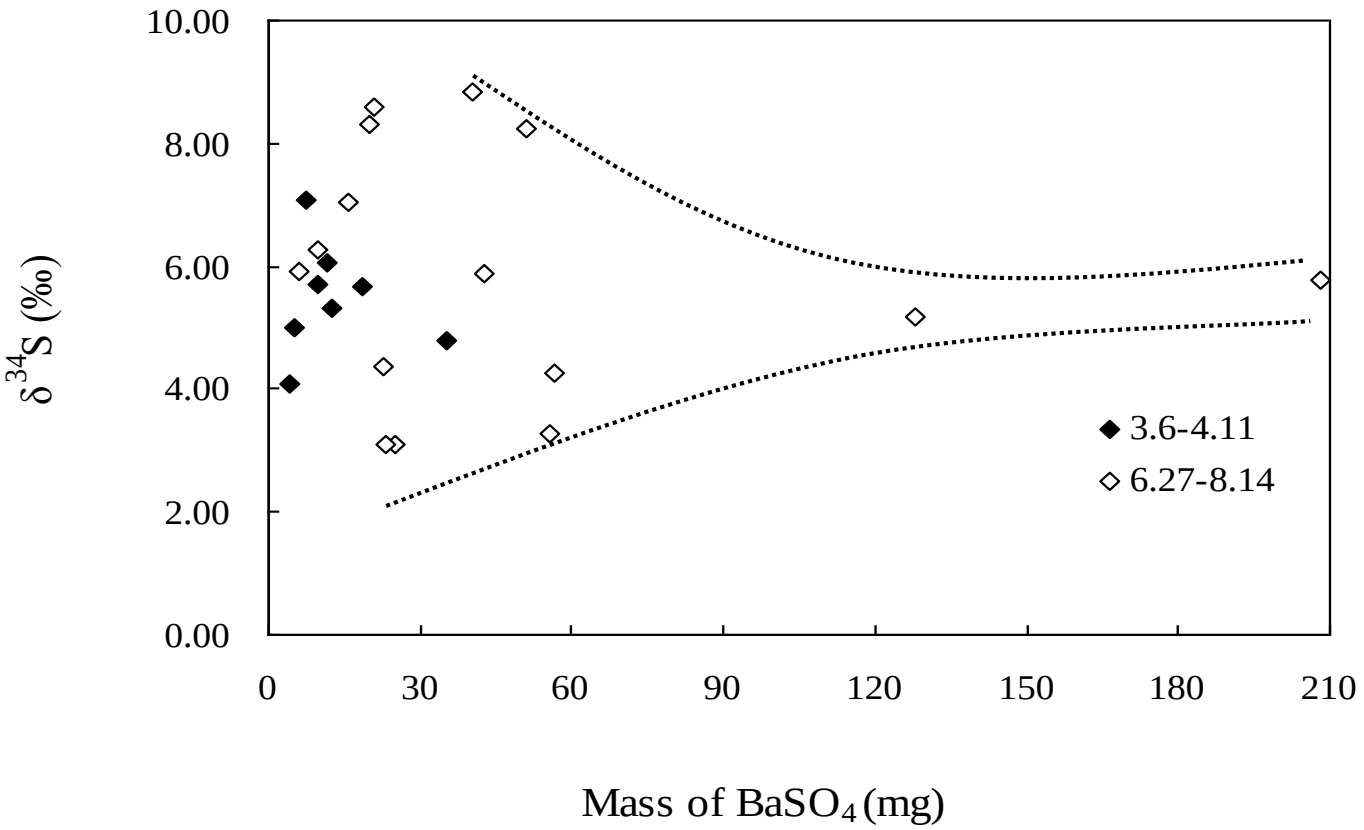
✓ SF_6 is produced by the reaction of silver sulfide (Ag_2S) with F_2 gas

✓SF_6 goes through cryogenic & gas chromatographic purification line

✓SF_6 is measured by dual-inlet Thermo Finnigan MAT253 at UMD

✓The precision for $\delta^{34}S$ & $\Delta^{33}S$ are 0.1 ‰ and 0.008‰

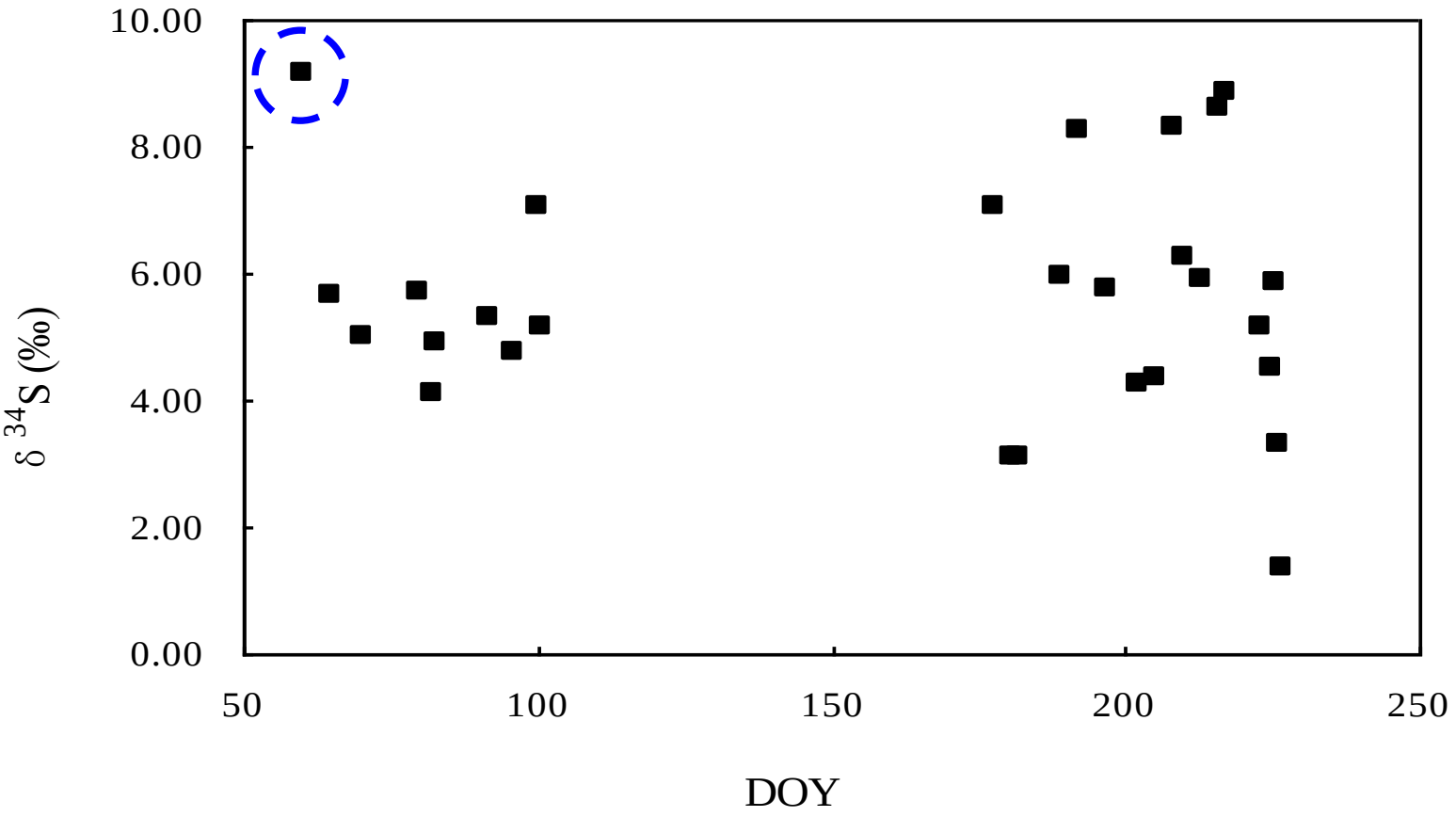
Observation_ $\delta^{34}S$ Sulfur Isotope & Implication



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

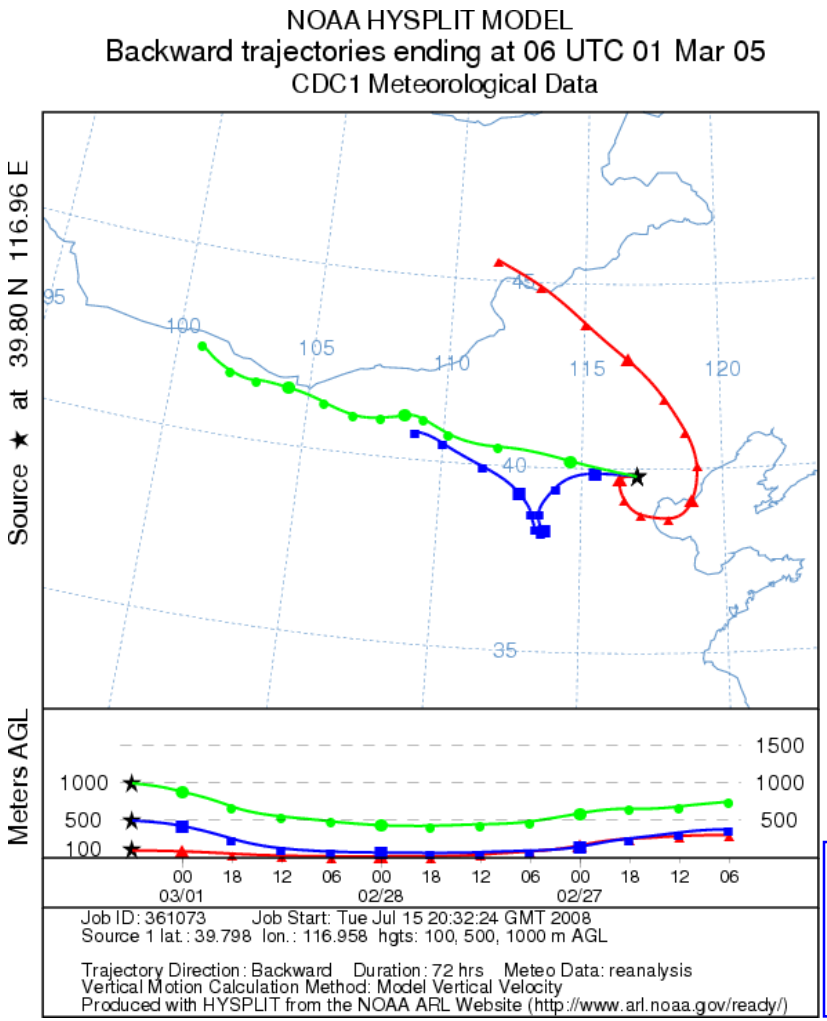
Observation_ $\delta^{34}S$ Sulfur Isotope & Implication

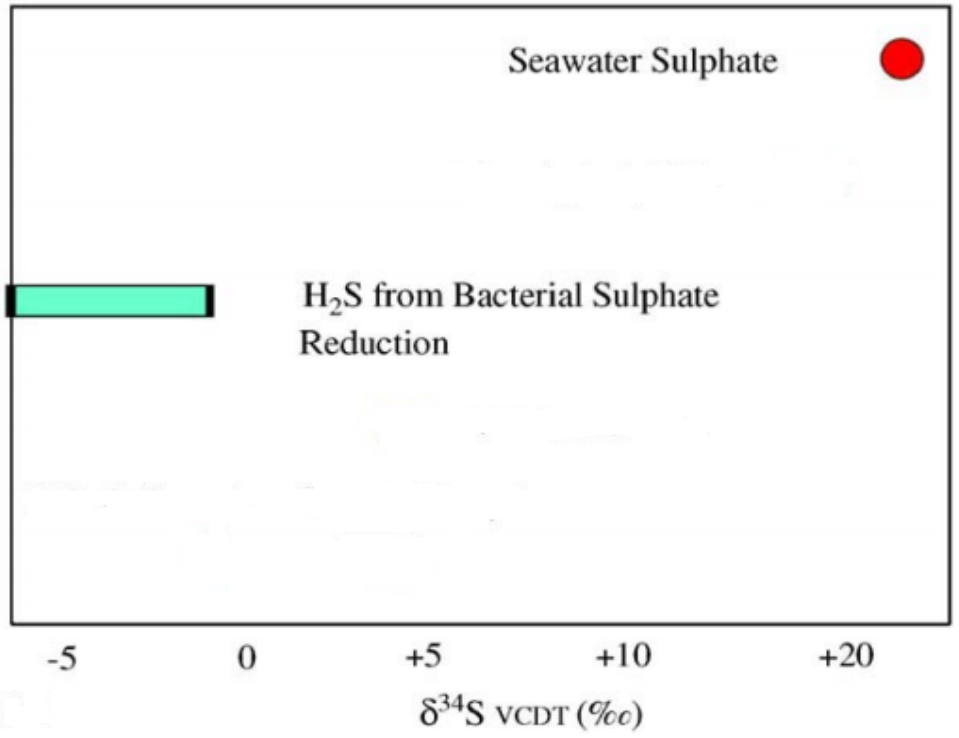
Sulfur Isotopic Composition of Aerosol Sulfate



Implication_ $\delta^{34}S$ Sulfur Isotope & Implication

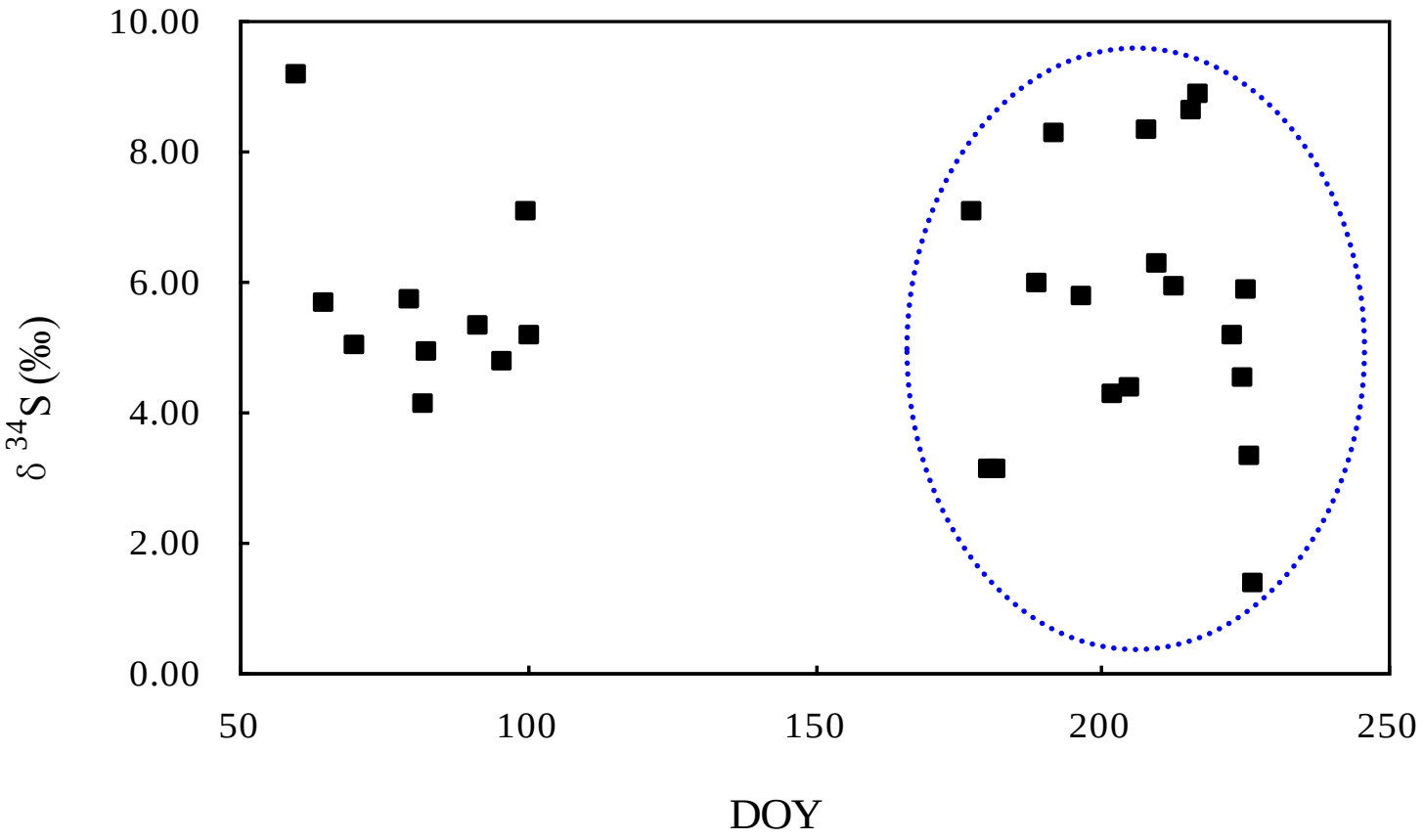
Backward trajectories ending on 1 Mar



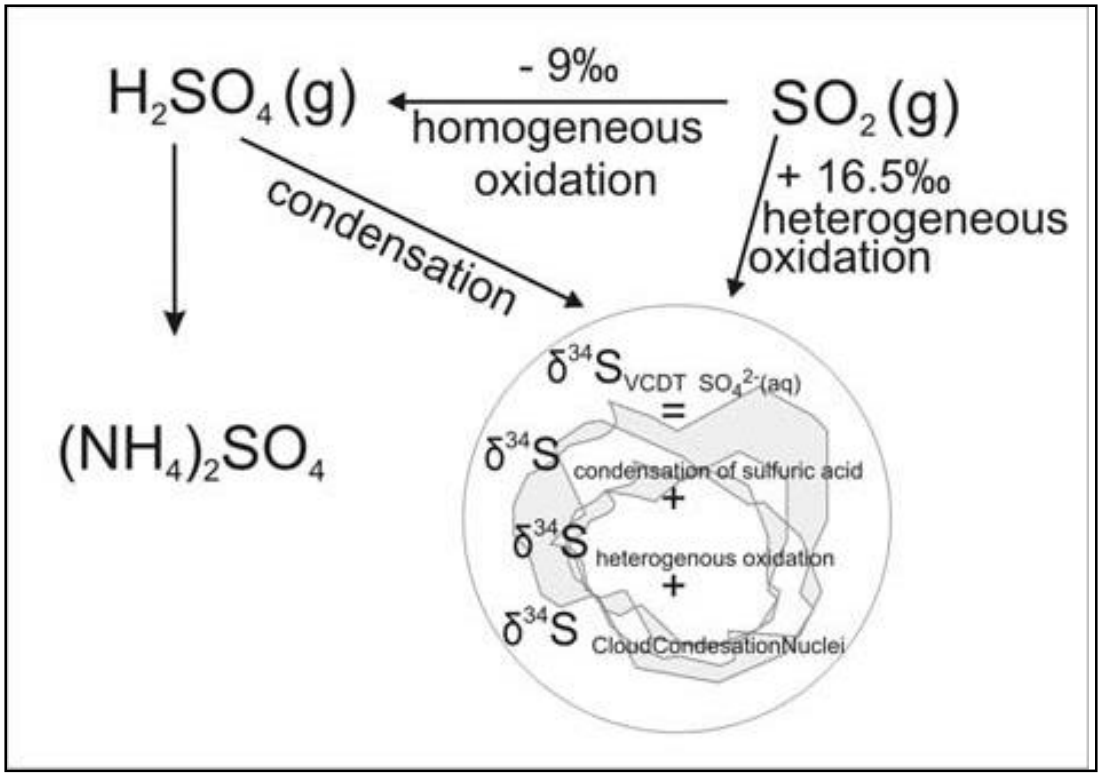


The larger $\delta^{34}S$ on 1 Mar is due to the mixing of sea salt

Observation_ $\delta^{34}S$ Sulfur Isotope & Implication

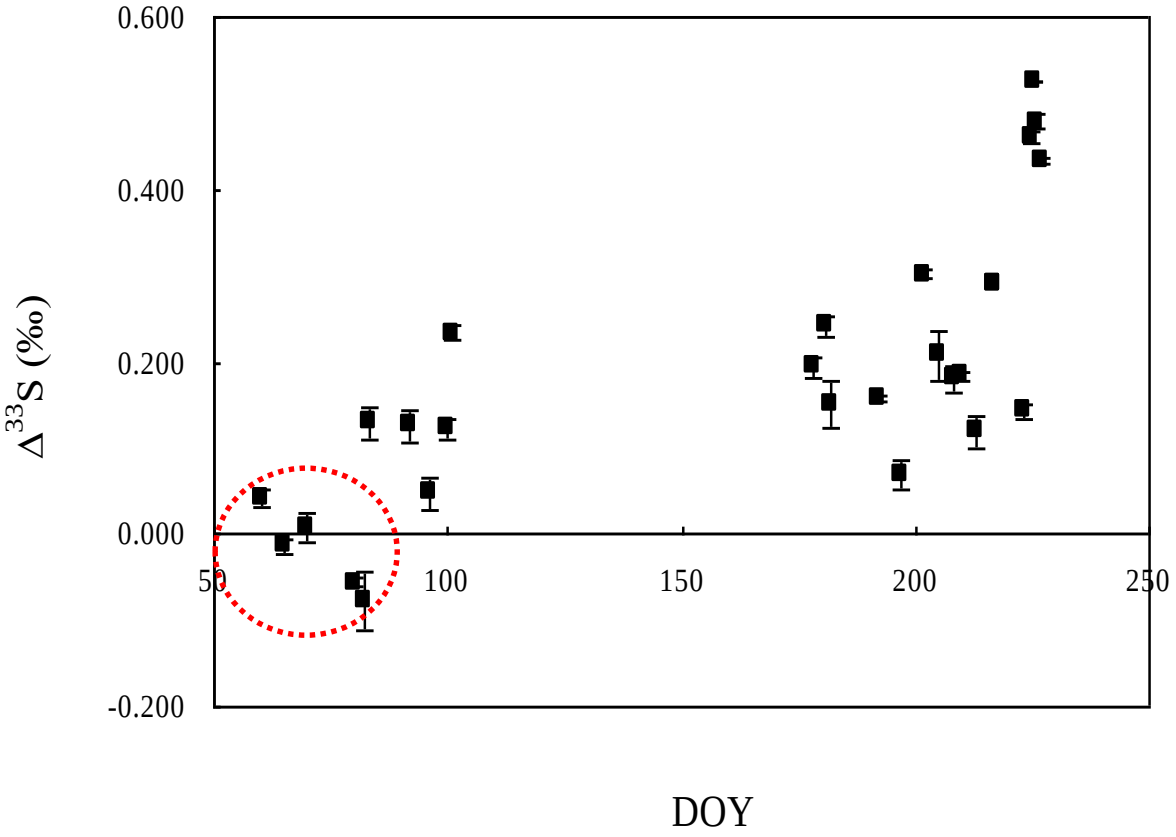


Interpretation _ $\delta^{34}S$ Sulfur Isotope & Implication



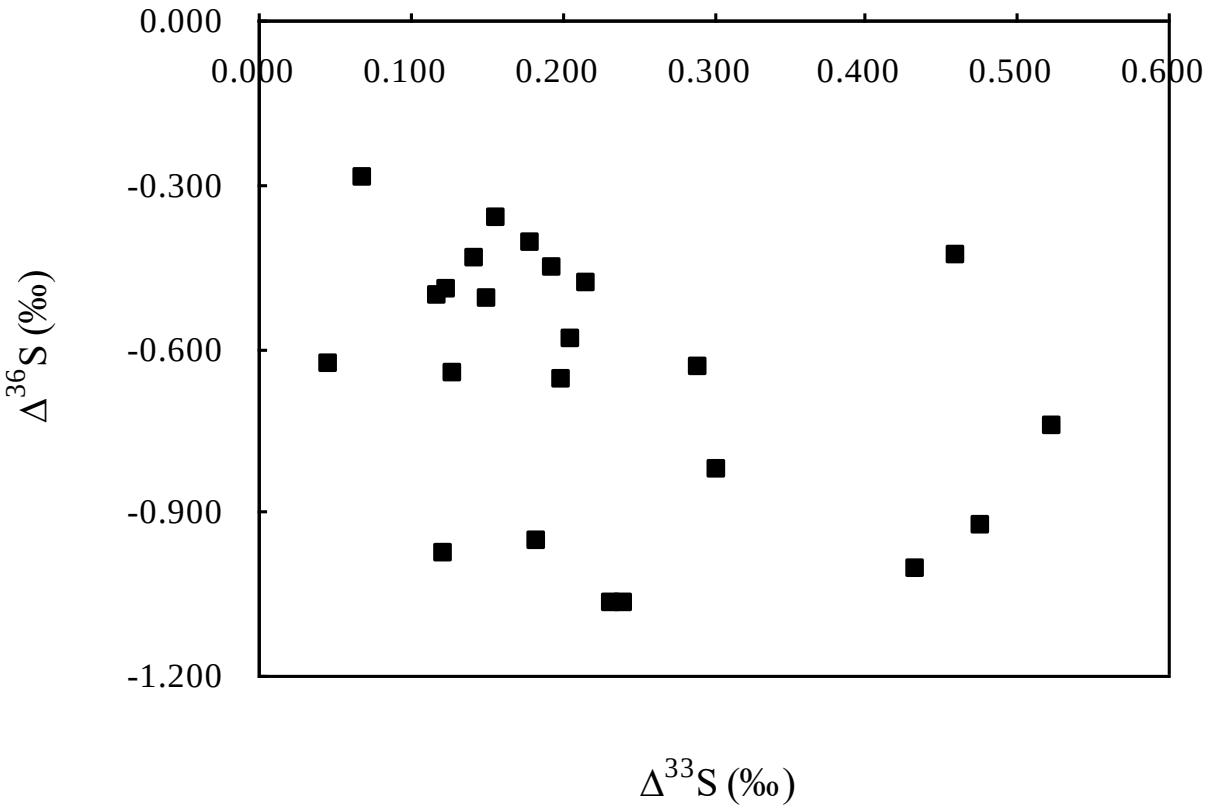
Winterholler et al. Atmos. Chem. Phys. Discuss. 8, 2008

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



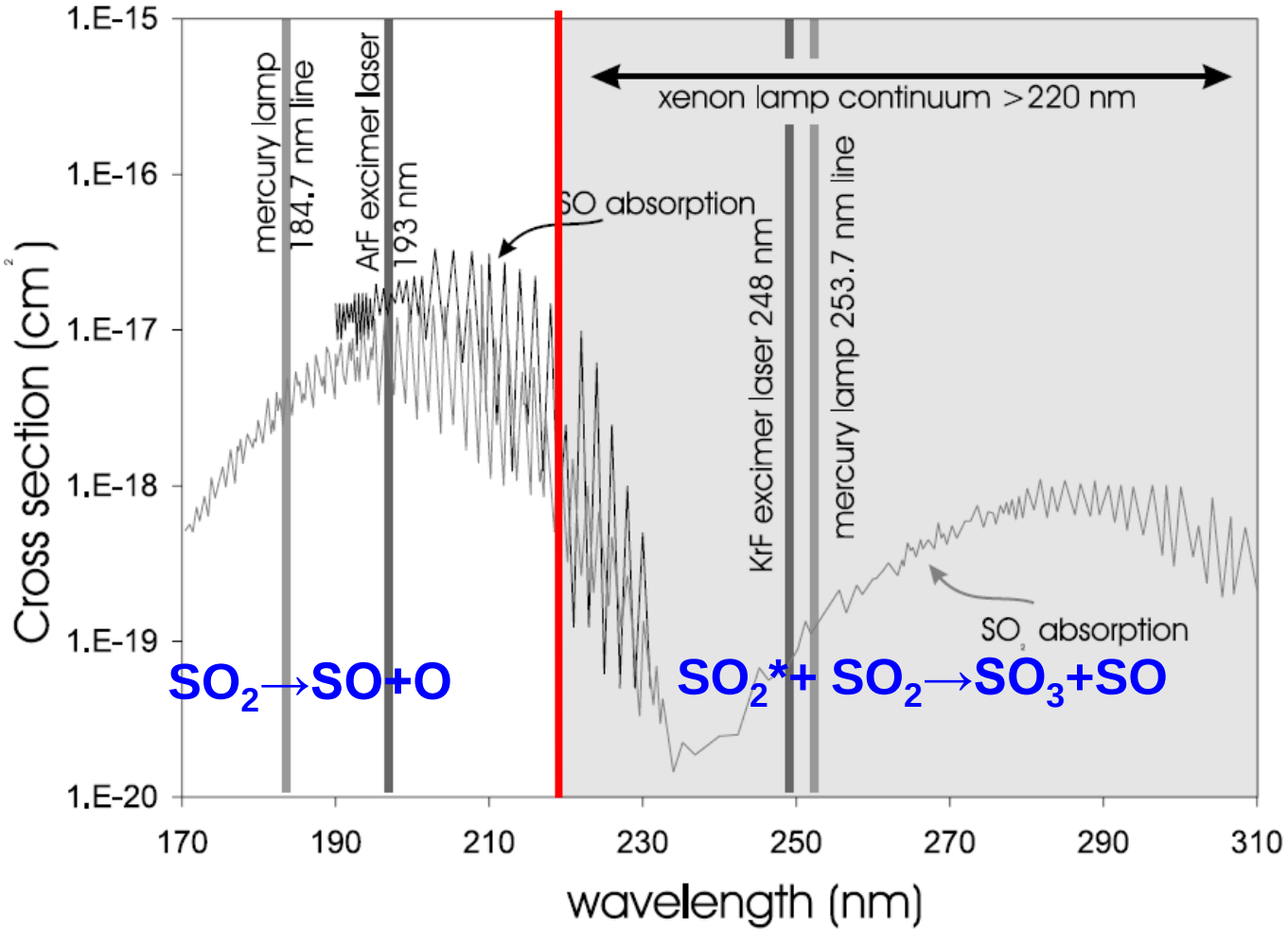
- $\Delta^{33}S$ presents a seasonal variation
- Mass-dependent in March, obvious mass-independent in summer.

Observation_ $\Delta^{33}S$, $\Delta^{36}S$



✓**positive $\Delta^{33}S$ values and negative $\Delta^{36}S$ values**

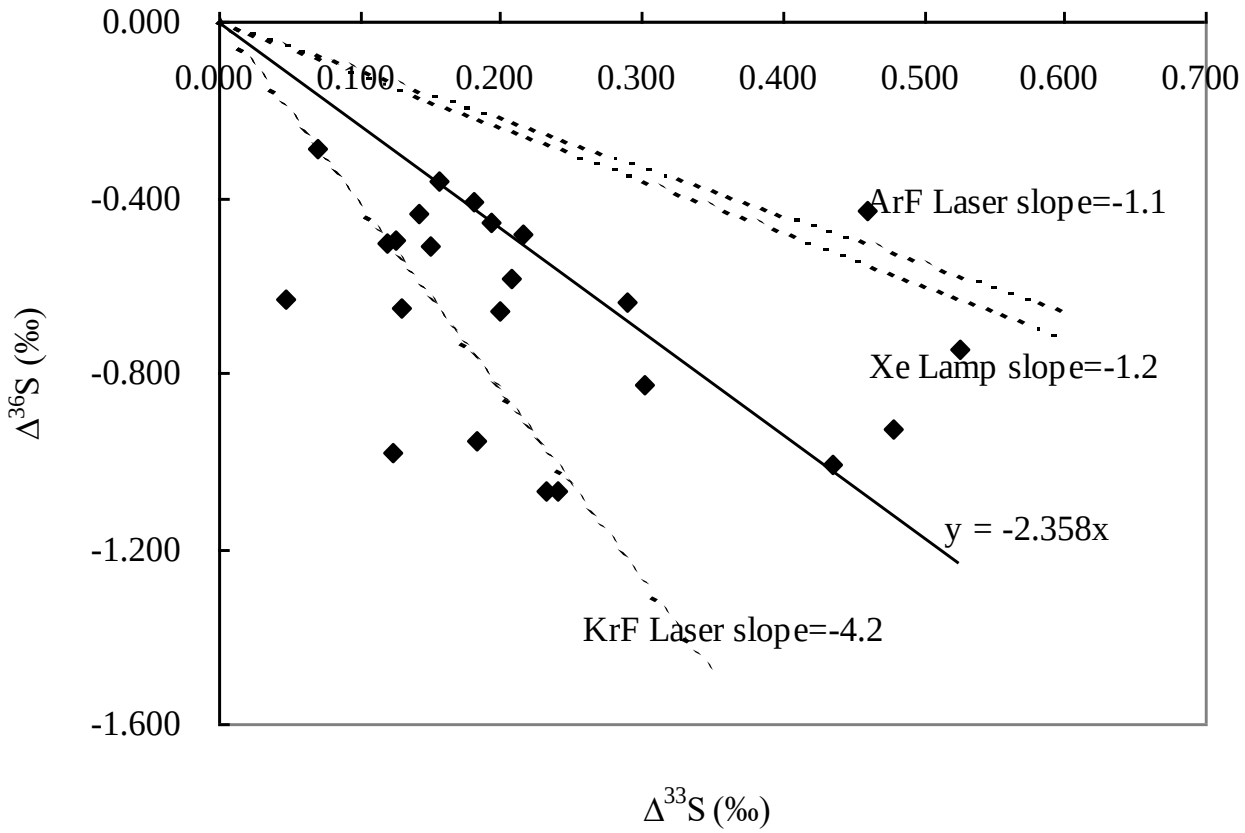
Interpretation_ $\Delta^{33}S$, $\Delta^{36}S$—SO_2 photochemistry



SO_2 photochemistry is only present candidate for anomalous S isotope effects in the rock record

Farquhar et al.
J. Geophys.Res., 106,2011

Interpretation_ $\Delta^{33}S$，$\Delta^{36}S$—SO_2 photochemical reactions



✓**Wavelength dependency of sulfur MIF during SO_2 photolysis**

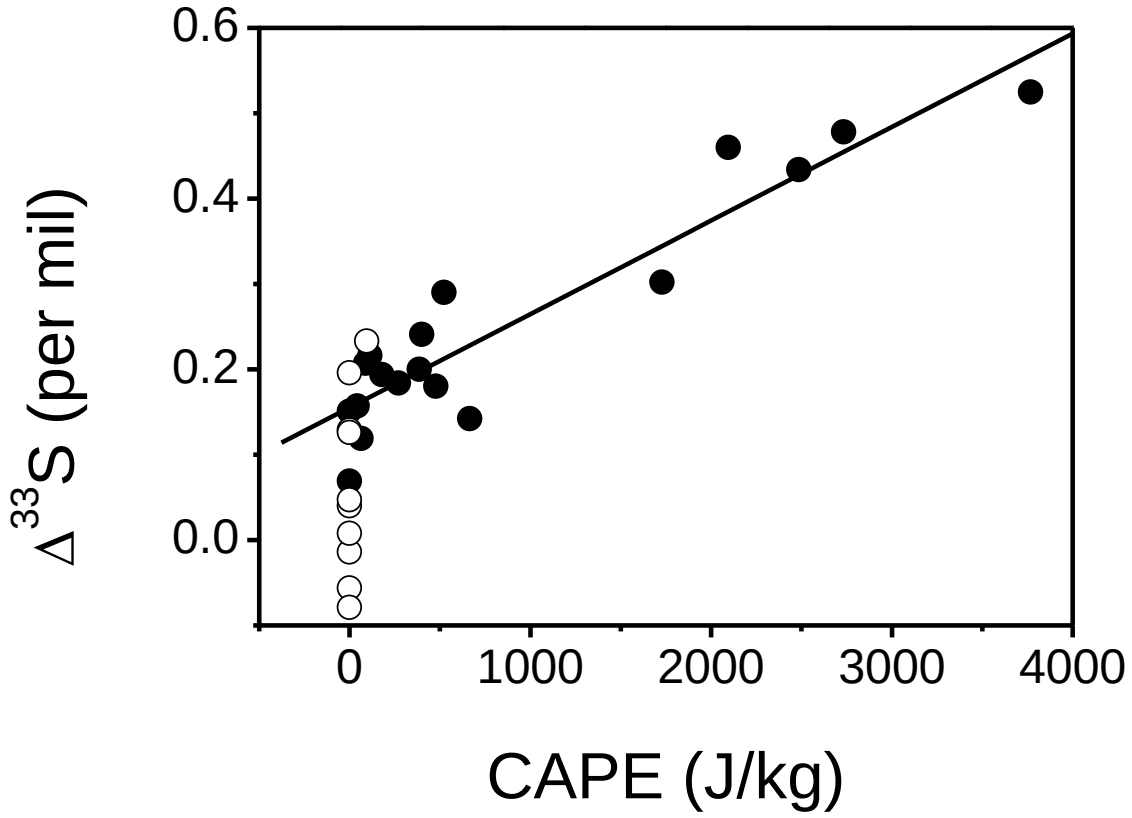
✓**KrF laser （248nm） is a major way**

Interpretation_ $\Delta^{33}S$

✓SO_2 photolysis (mainly at 248 nm) occurs only in stratosphere in present atmosphere for high O_3 and O_2

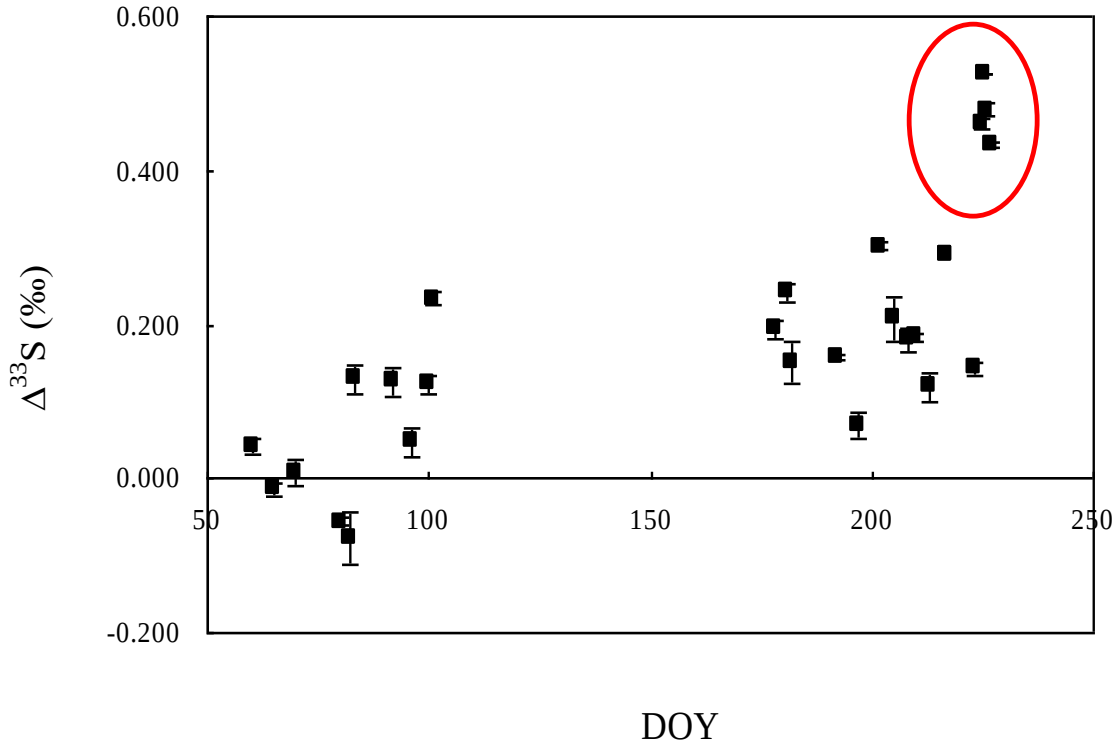
✓$\Delta^{33}S$ we measured in aerosol sulfate should be related to input of sulfate from the stratosphere

Interpretation_ $\Delta^{33}S$_CAPE



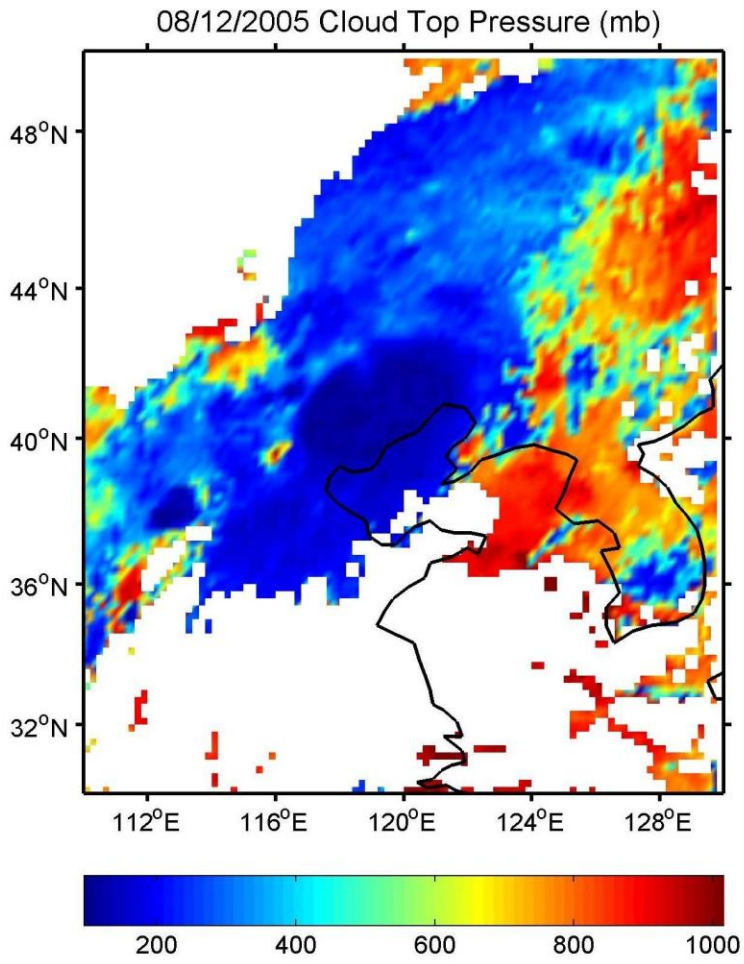
- CAPE (Convective available potential energy) is used to predict atmospheric instability and severe weather
- Positive relationship proves sulfur anomalies in aerosol are related to sulfate from stratosphere

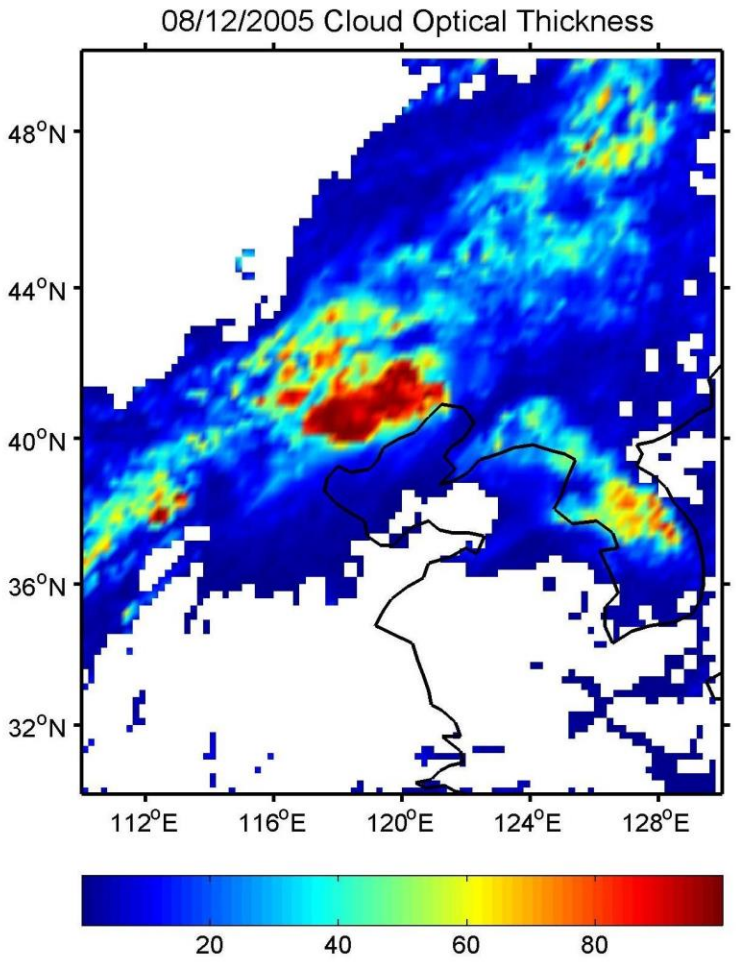
Interpretation_ $\Delta^{33}S$



- **Extremely High $\Delta^{33}S$ on August 13,14 and 15 lead us to further investigate the origin of sulfur isotope anomaly.**

Interpretation_ $\Delta^{33}S$_Satellite product （12 Aug.）





- **Deep convective clouds active at Xianghe during the time**


Thanks for your attention