

JGR Atmospheres



RESEARCH ARTICLE

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Key Points:

- Regional characteristics of atmospheric sulfate formation were probed by ^{17}O -excess ($\Delta^{17}\text{O}$) of sulfate at inland and coastal East Antarctica
- Specifically, high $\Delta^{17}\text{O}$ in spring–summer at inland suggests that chemical destruction of methanesulfonate (MS^-) on the Antarctic Plateau produces sulfate
- Existing gap between $\Delta^{17}\text{O}$ of sulfate in the atmosphere and ice can be reconciled by MS^- destruction in snow

Regional Characteristics of Atmospheric Sulfate Formation in East Antarctica Imprinted on ^{17}O -Excess Signature

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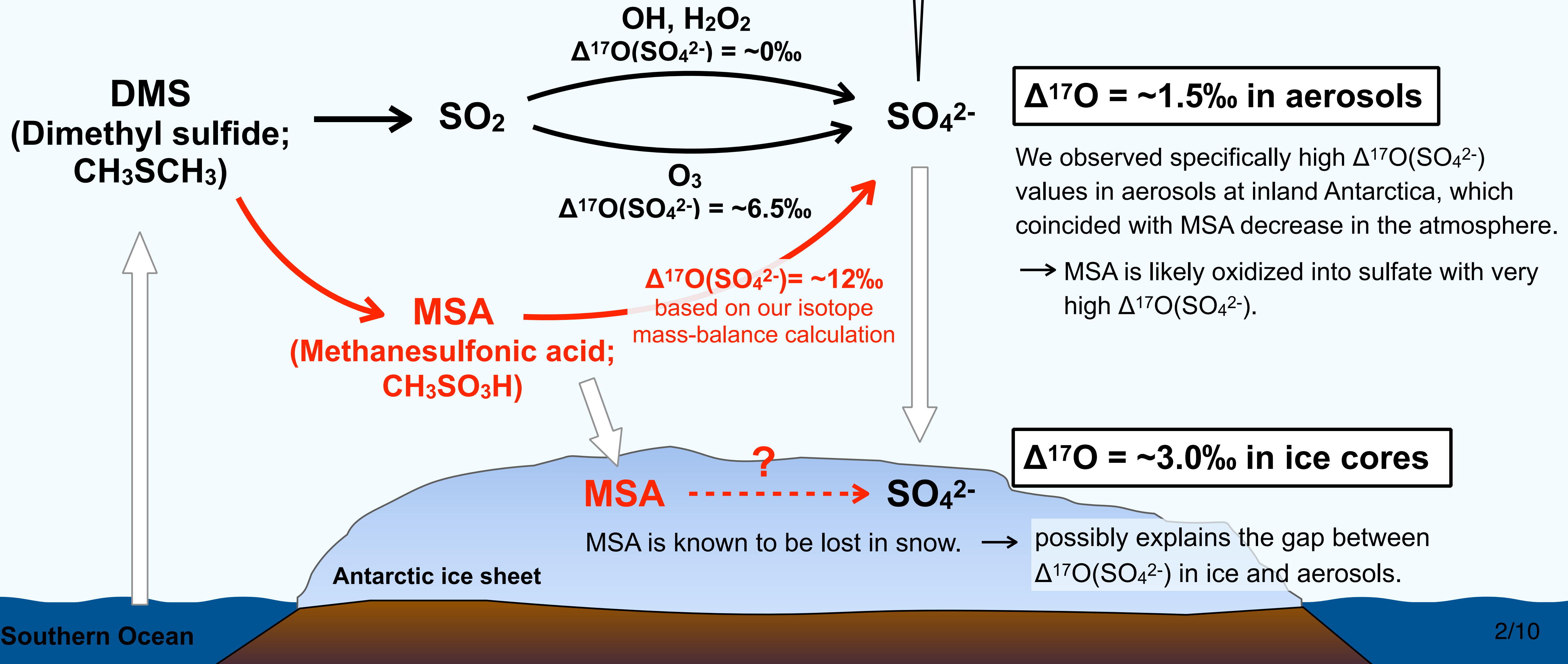
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Summary: Oxidation of MSA likely largely impacts $\Delta^{17}\text{O}(\text{SO}_4^{2-})$.

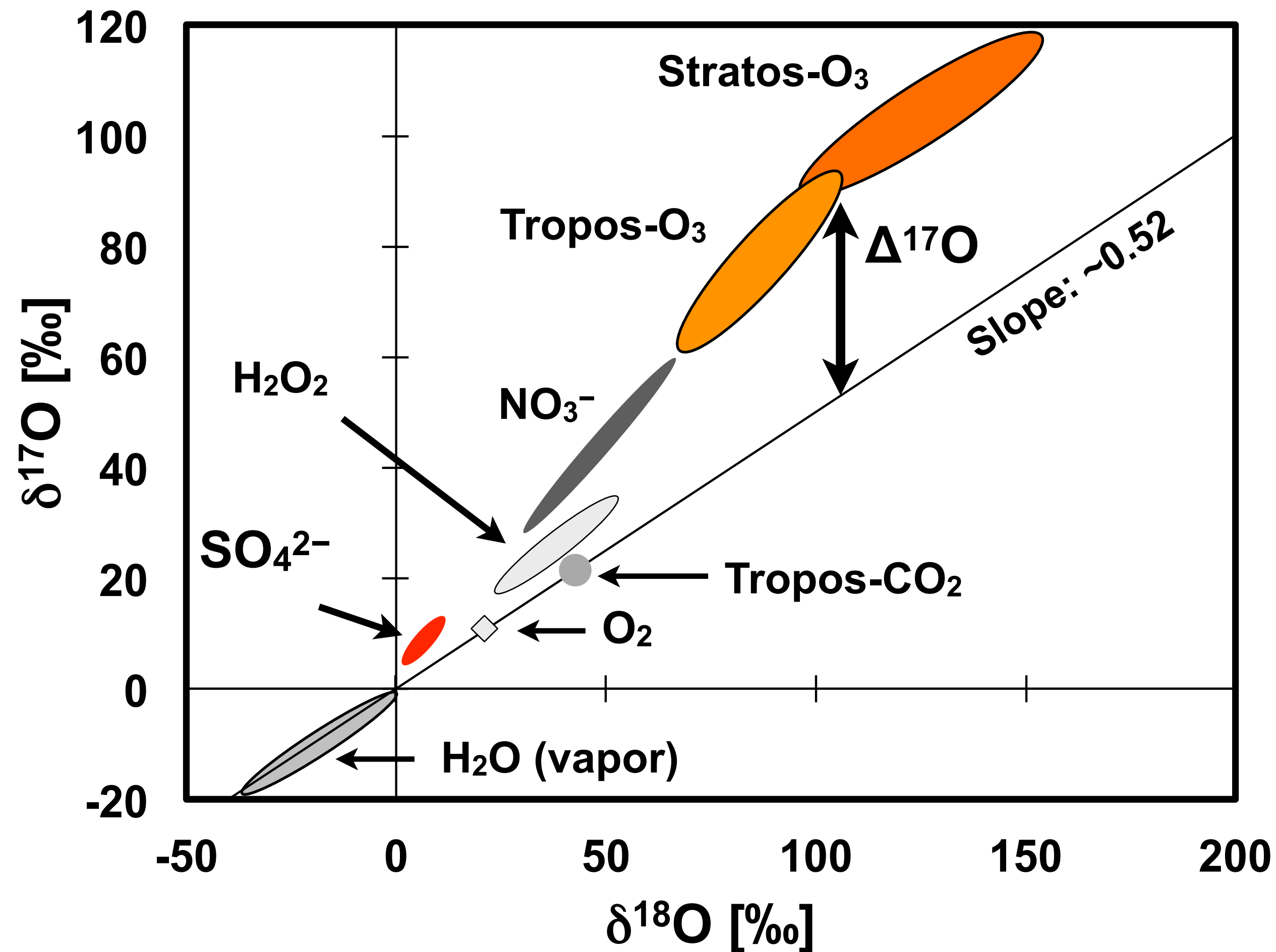
$\Delta^{17}\text{O}(\text{SO}_4^{2-})$ reflects the oxidants chemistry involved in sulfate formation.

→ Those preserved in Antarctic ice cores might tell the past oxidants chemistry? But there is an unexplained gap between ice and air.

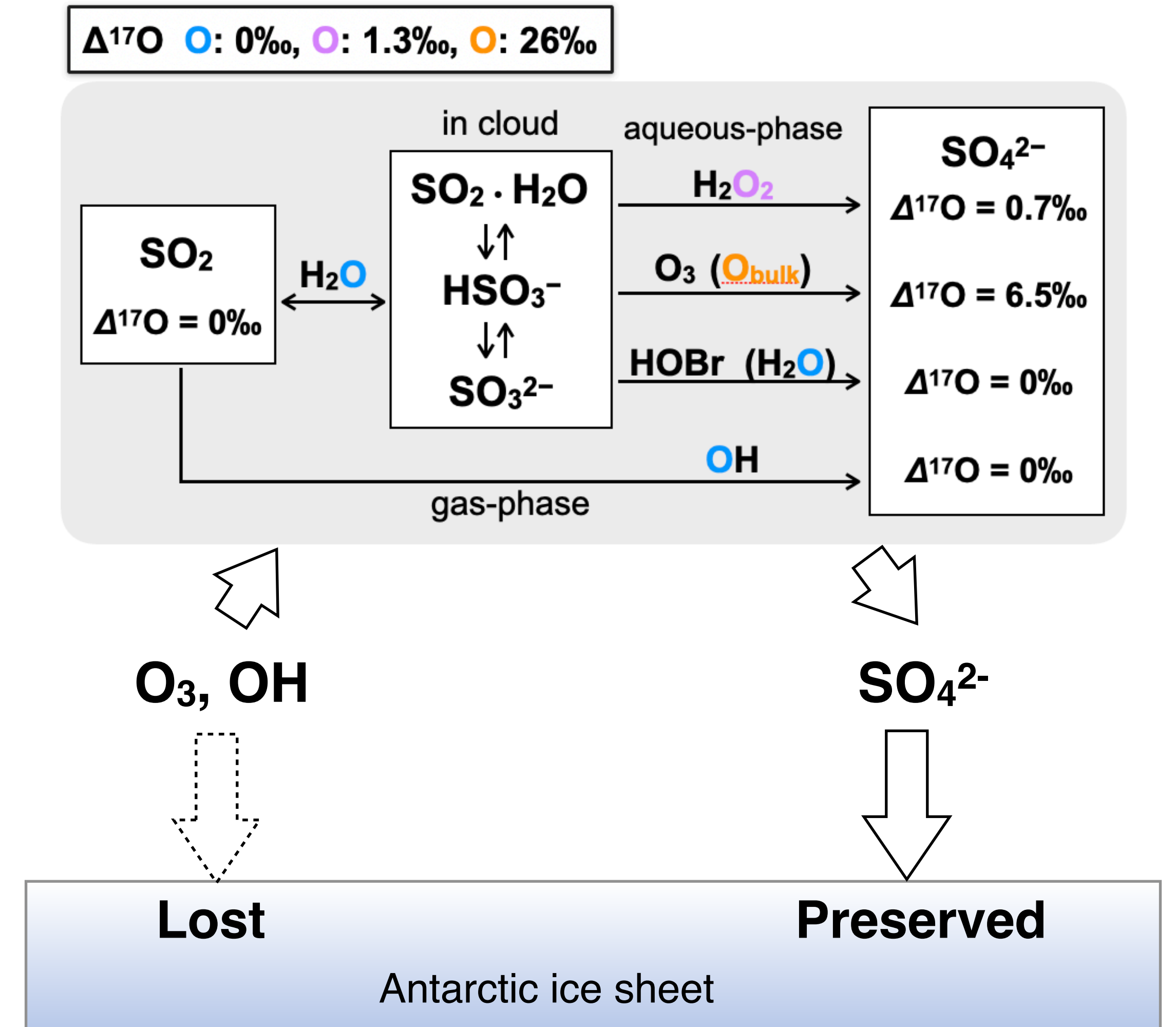


Background: ^{17}O -excess of atmospheric sulfate ($\Delta^{17}\text{O}(\text{SO}_4^{2-})$)

Simplified definition: $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$



[after [Thiemens, 2006](#)]



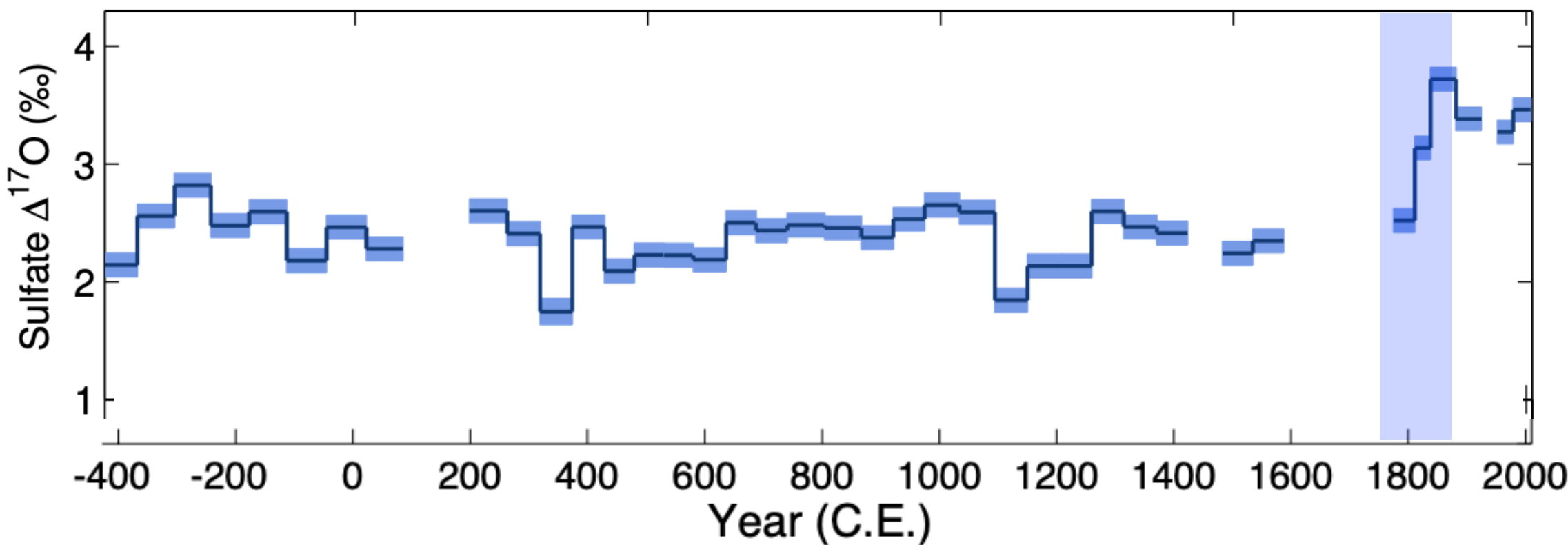
$\Delta^{17}\text{O}(\text{SO}_4^{2-})$ might tell the past oxidants chemistry.

[e.g., [Alexander et al., 2002](#)]

Background: $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in the Antarctic ice and atmosphere

1. An unexplained ice-core $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ record

Previous study with WAIS-Divide ice cores [Sofen et al., 2014]

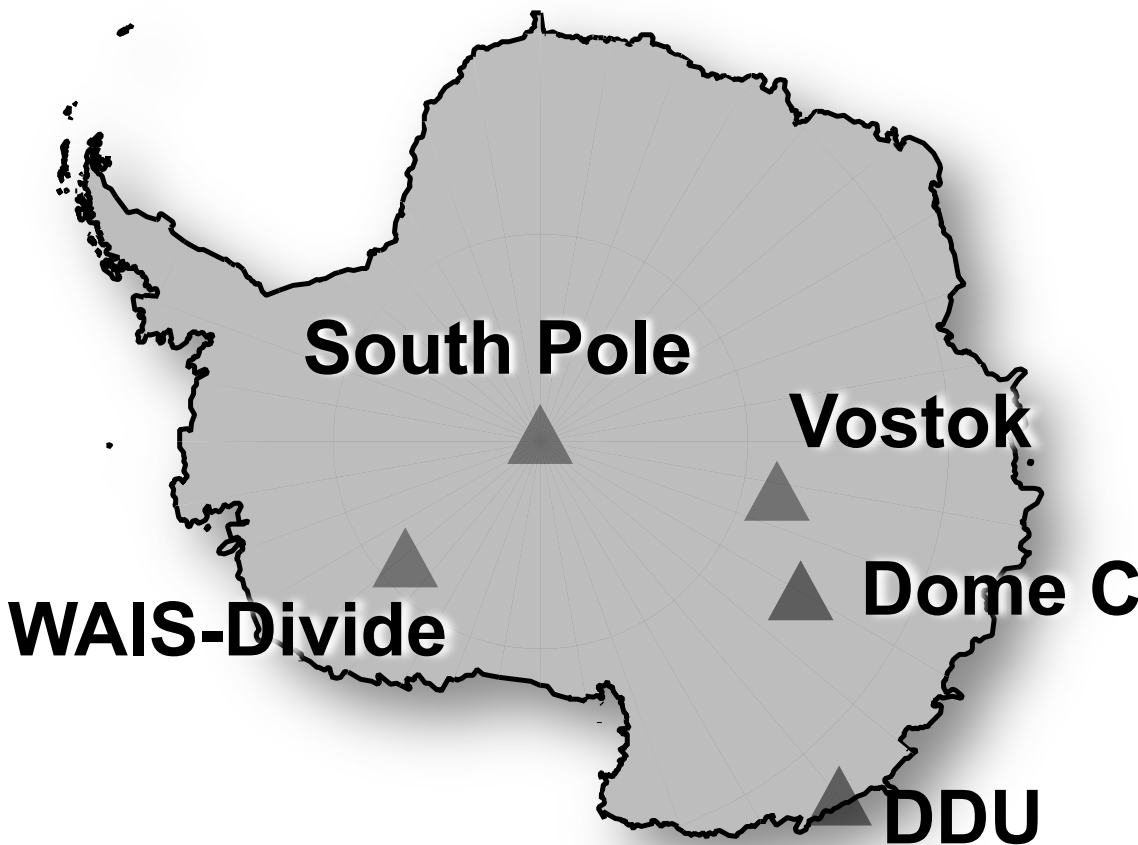


“ The sulfate $\Delta^{17}\text{O}$ record exhibits a 1.1 ‰ increase in the early 19th, which suggests that an additional 12–18 % of sulfate formation occurs via aqueous-phase production by O_3 , relative to that in the gas phase. ... However, assuming OH, H_2O_2 , and O_3 are the main oxidants contributing to sulfate formation, Monte Carlo box model simulations require a large (260%) increase in the O_3 / OH mole fraction ratio over the Southern Ocean in the early 19th century to match the sulfate $\Delta^{17}\text{O}$ record. This unlikely scenario points to a deficiency in our understanding of sulfur chemistry and suggests other oxidants may play an important role in sulfate formation in the mid- to high-latitude marine boundary layer. “ [Sofen et al., 2014]

2. A significant gap between $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in ice and air

Sample type	Site	Time period	$\Delta^{17}\text{O}(\text{SO}_4^{2-})$	
			Mean	Surface
Aerosols	Dome C ^a	Jan.-Dec., 2010	1.3±0.1	+1.5‰ ↓
	South Pole ^b	Jan.-Dec., 2010	1.2±0.3	
	DDU ^c	Jan.-Dec., 2011	1.4±0.2	
Ice cores	WAIS ^d	1774~2005 C.E.	2.8±0.3	2.9
	Dome C ^e	2.5~9.4 kya	3.3±0.6	2.9
	Vostok ^e	5.7~11.2 kya	2.9±0.6	3.1

[^aHill-Falkenthal et al., 2013; ^bWalters et al., 2019; ^cIshino et al., 2017; ^dKunasek et al., 2010; ^eAlexander et al., 2002, 2003]

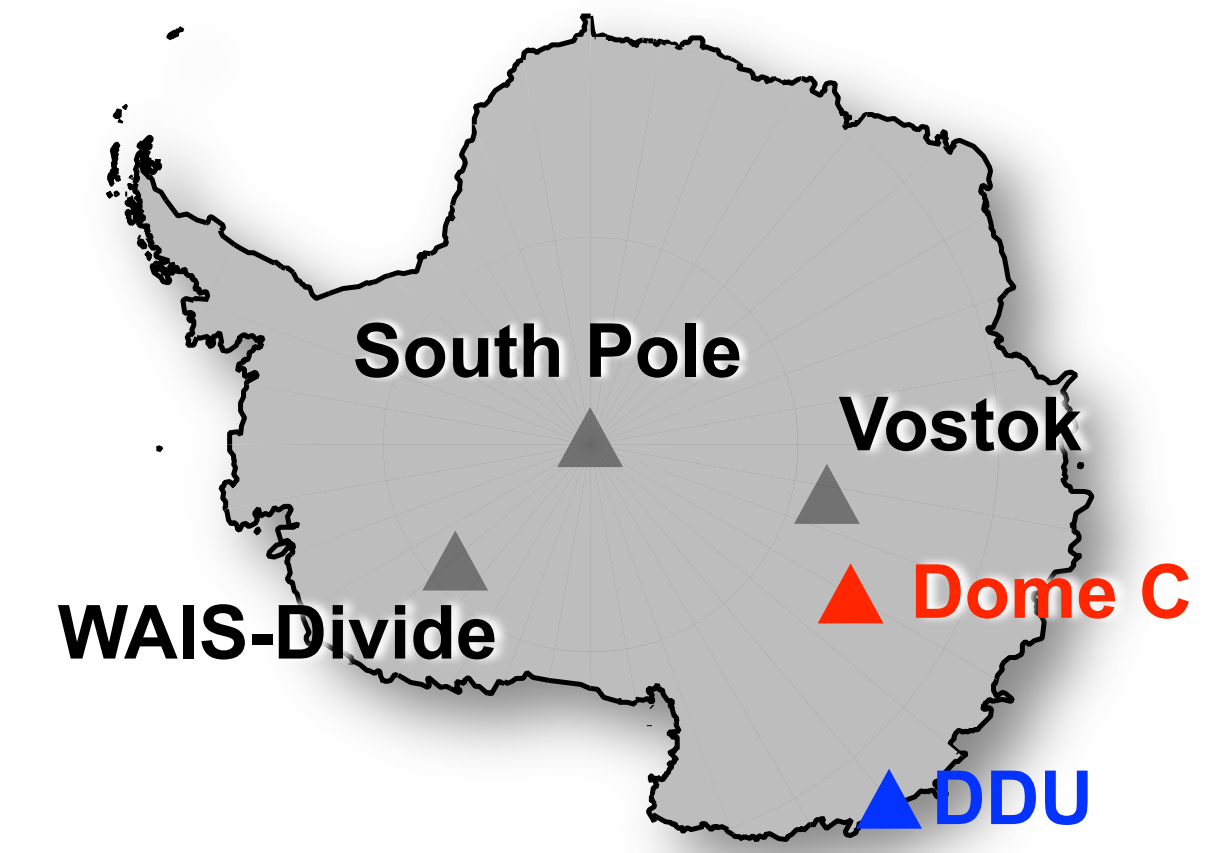


Any missing post-depositional processes for sulfate?

Methods

Aerosol samples collection by HVAS

- **Dome C** (75°06'S, 123°12'E, 3233 m): Total suspended particles
- **Dumont d'Urville** (66°40'S, 140°01'E, 40 m): Fine (< 1 μ m) and Coarse (> 1 μ m)
* $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ was measured for Fine particles only, while concentrations were for Fine and Coarse
- **Time resolution: 7 to 10 days per sample**
- **Time period: January - December, 2011**



Chemical analyses

1. Ion extraction and quantification by IC

- Dome C samples @ Tokyo Tech [[Ishino et al., 2019](#)]
- DDU samples @ IGE [[Jourdain and Legrand, 2002](#)]

2. $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ measurement

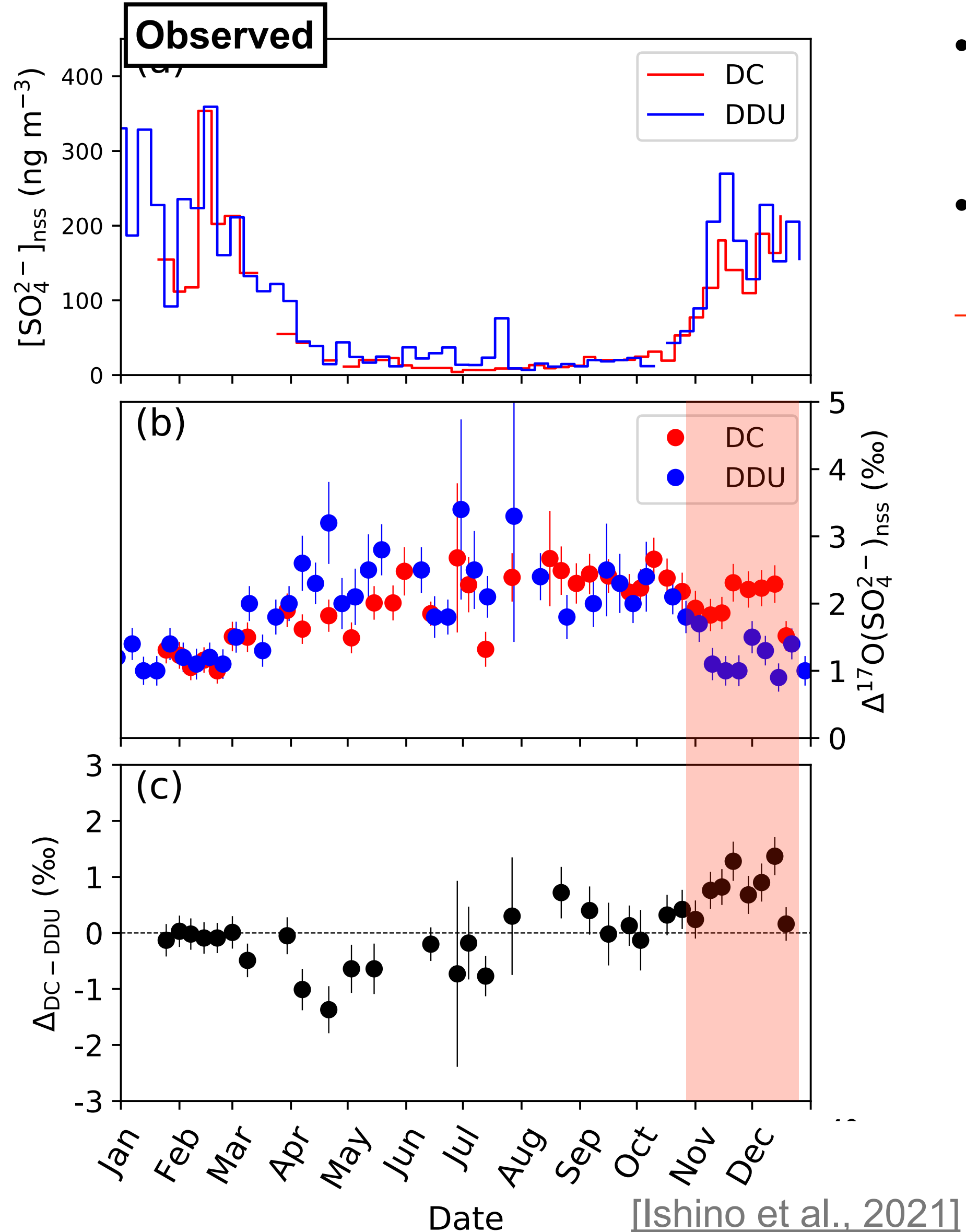
- The method developed by [[Savarino et al., 2001](#)] and updated by [[Schauer et al., 2012](#); [Geng et al., 2013](#)] was set up at Tokyo Tech [[Ishino et al., 2017](#)].
- ~1 μmol of SO_4^{2-} was separated from other anions using IC
- H_2SO_4 obtained from IC was converted to Ag_2SO_4 .
- Ag_2SO_4 pyrolysis into SO_2 and O_2 using TC/EA
- Measure O_2 ($m/z = 32, 33, 34$) using IRMS (MAT253, Thermo Fischer Scientific)

GEOS-Chem global chemistry transport model

(<http://acmg.seas.harvard.edu/geos/>)

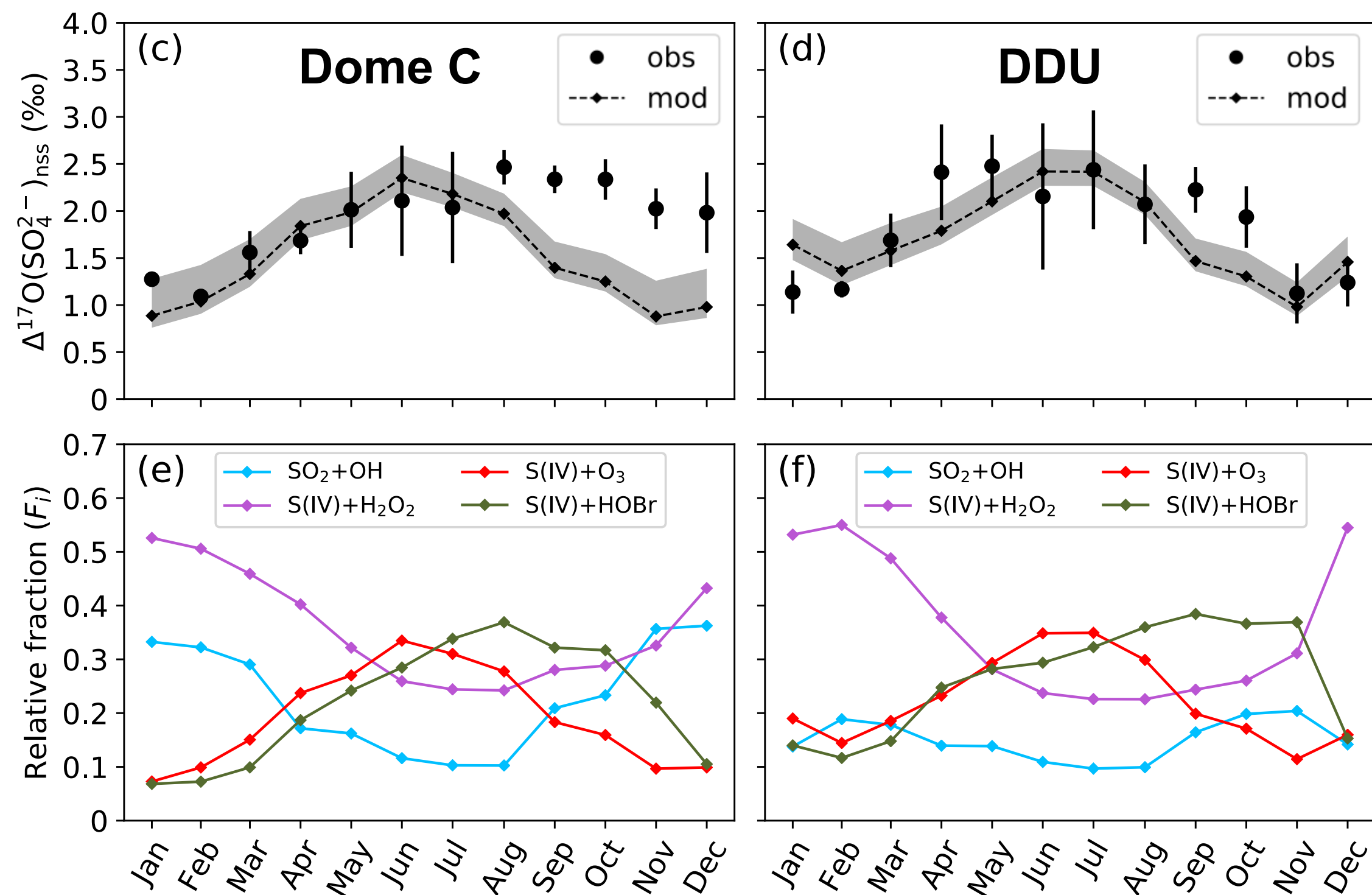
- Version 11-02d: Updated halogen chemistry including $\text{S(IV)} + \text{HOBr}$ [[Chen et al., 2017](#)]
- Additionally introduced reactive bromine emissions from sea-salts produced via blowing snow sublimation over sea ice [[Huang et al., 2020](#)]
- Grid: 4° x 5° horizontal grid with 47 vertical layers up to 0.01hPa
- Met data: MERRA2
- Year: 2011
- SO_4^{2-} produced by each oxidation pathway is transported as a separate “tracer” in the model.

Results: Observed and modeled $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in aerosols



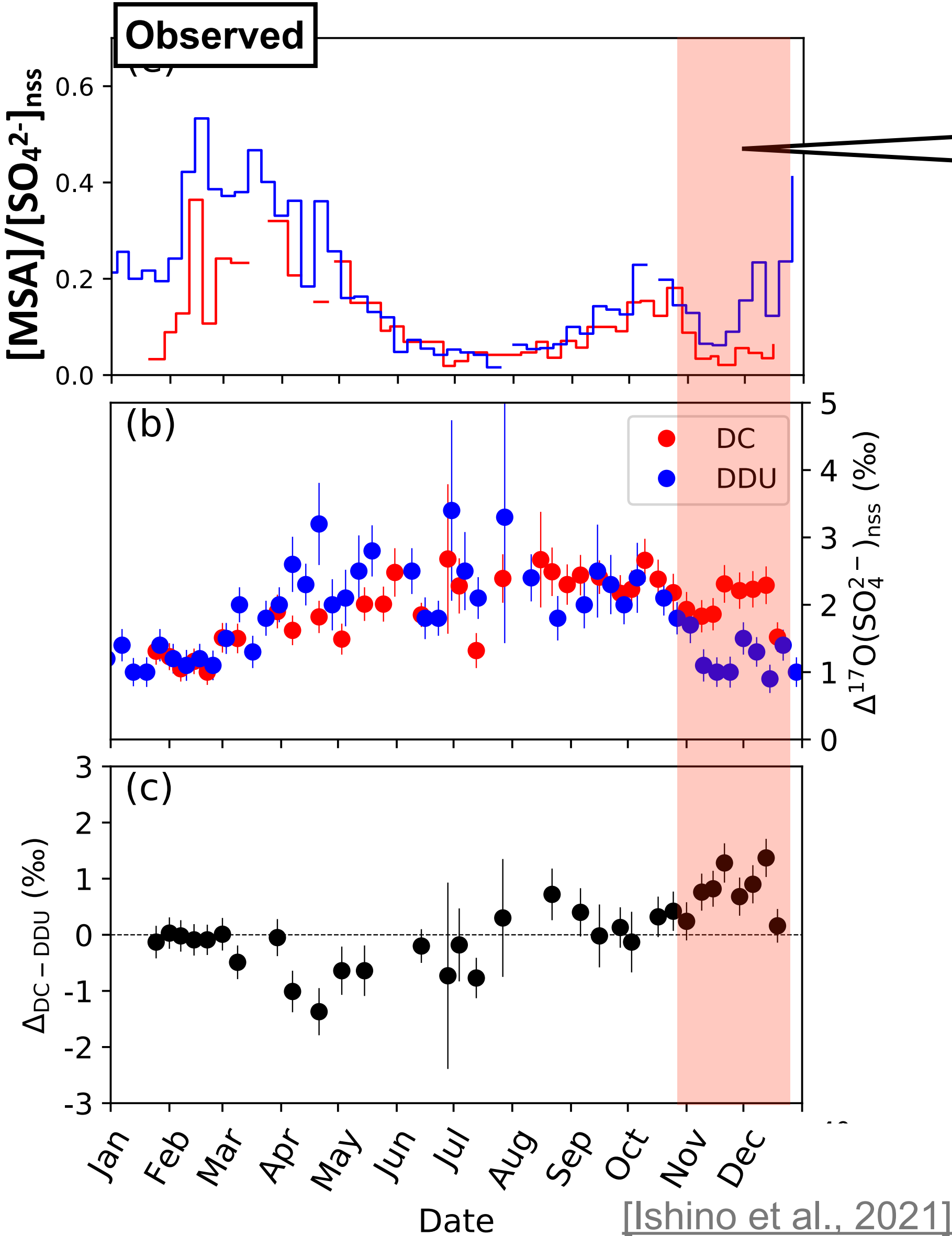
- General seasonality at both sites: summer minima ($\sim 1.0\text{‰}$) and winter maxima ($\sim 2.5\text{‰}$) owing to sunlight-driven changes in the relative importance of O_3 vs. OH and H_2O_2 oxidation.
- BUT in summer (Oct.-Dec.), $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ at inland (Dome C; $2.0 \pm 0.3\text{‰}$) are significantly higher than those at the coastal site (DDU; $1.3 \pm 0.3\text{‰}$).
- Specific processes causing high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in inland Antarctica?

Modeled The model also cannot produce high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in summer at inland...



* $\Delta_{\text{DC-DDU}} = \Delta^{17}\text{O}(\text{SO}_4^{2-}) \text{ at DC} - \Delta^{17}\text{O}(\text{SO}_4^{2-}) \text{ at DDU}$

Discussion: Specifically high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ at inland than at coast in summer



An efficient chemical destruction of **methanesulfonic acid (MSA)** over the Antarctic plateau associated with high photochemical activity in this period.

[Legrand et al., 2017]

→ Does this reaction produce sulfate?
What is expected $\Delta^{17}\text{O}$?

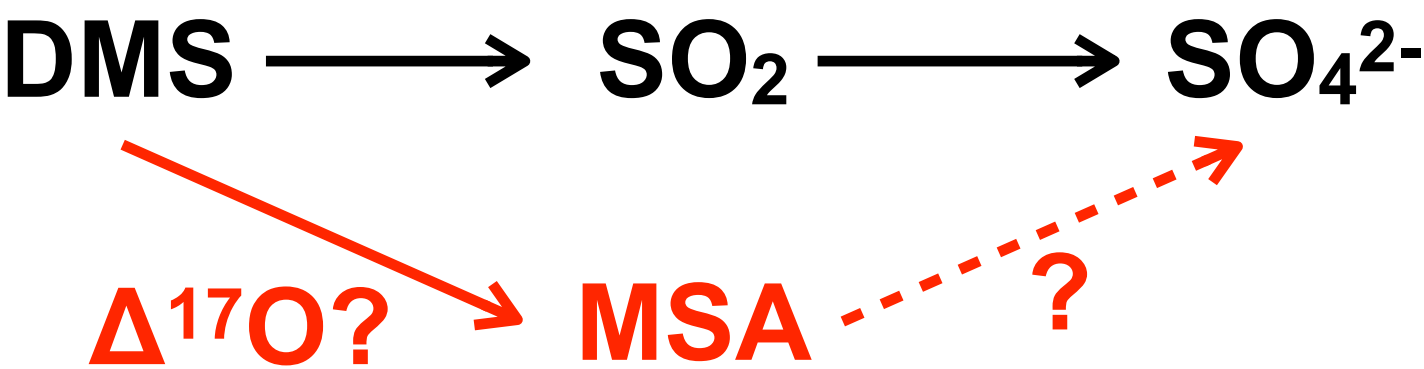
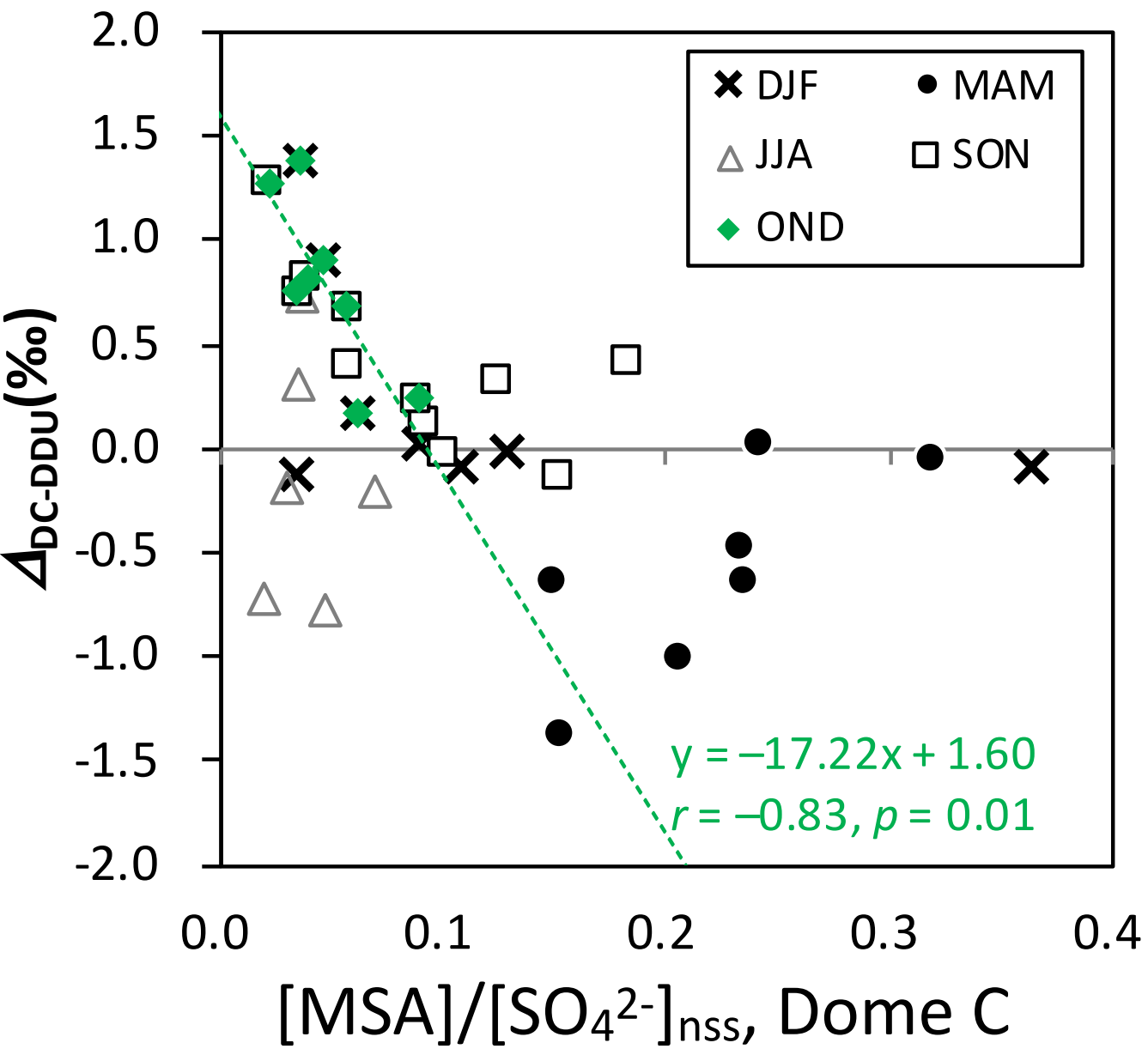


Table S1. Correlations of $\Delta_{\text{DC-DDU}}$ to other atmospheric components at Dome C during Oct.-Dec.

Components	r	p
$[\text{SO}_4^{2-}]_{\text{total}}$	0.08	0.85
[MSA]	-0.69	0.06
[Cl ⁻]	0.36	0.39
[NO ₃ ⁻]	0.35	0.40
[Na ⁺]	-0.80	0.02
[Mg ²⁺]	-0.71	0.05
[Ca ²⁺]	0.12	0.77
[O ₃]	0.81	0.02
[H ⁺]	0.33	0.43
$[\text{MSA}]/[\text{SO}_4^{2-}]_{\text{nss}}$	-0.83	0.01
$[\text{SO}_4^{2-}]_{\text{ss}}/[\text{SO}_4^{2-}]_{\text{total}}$	-0.61	0.11
$\delta^{34}\text{S}_{\text{nss}}$	-0.36	0.39

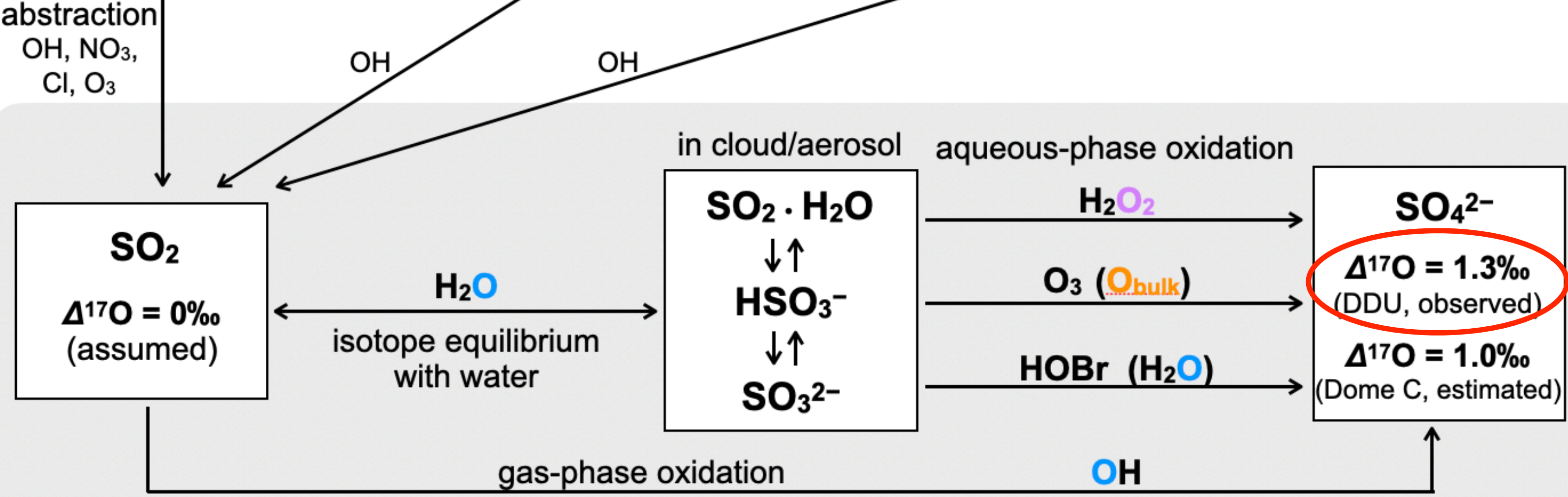
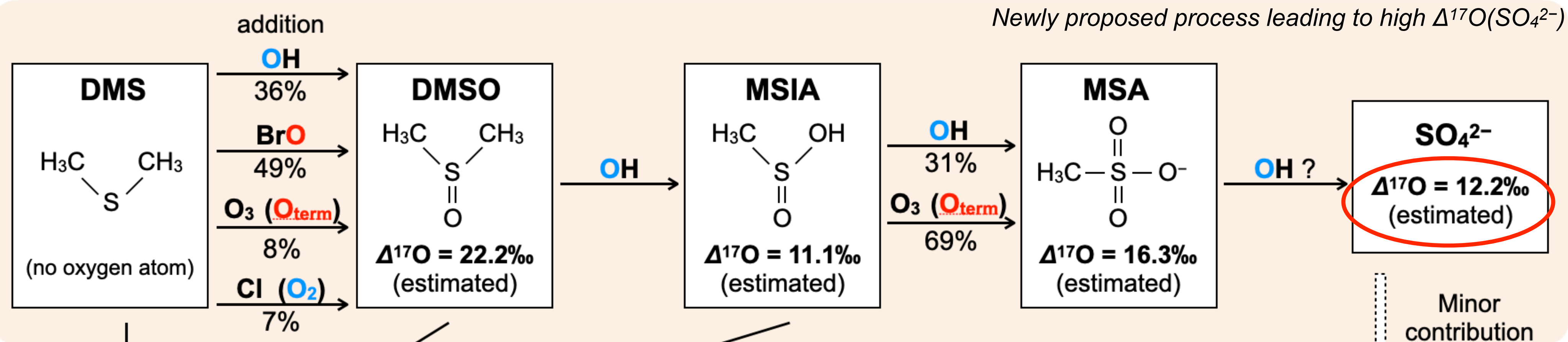


* $\Delta_{\text{DC-DDU}} = \Delta^{17}\text{O}(\text{SO}_4^{2-}) \text{ at DC} - \Delta^{17}\text{O}(\text{SO}_4^{2-}) \text{ at DDU}$

Discussion: Isotope mass-balance calculation for $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ produced from MSA

Assumed $\Delta^{17}\text{O}$ of oxidants ●: 39‰, ●: 26‰, ●: 1.3‰, ●: 0‰

* Relative contributions of each pathway (%) were estimated by the model of [Chen et al. \(2018\)](#) and averaged within the troposphere in 60°-90°S during October-December.



- Minor contribution
- $[\text{MSA}]/[\text{SO}_4]_{\text{nss}}$ at DDU = ~ 0.14
 - $[\text{MSA}]/[\text{SO}_4]_{\text{nss}}$ at DC = ~ 0.05
 - > $\sim 9\%$ of sulfate at DC may be produced by MSA oxidation.

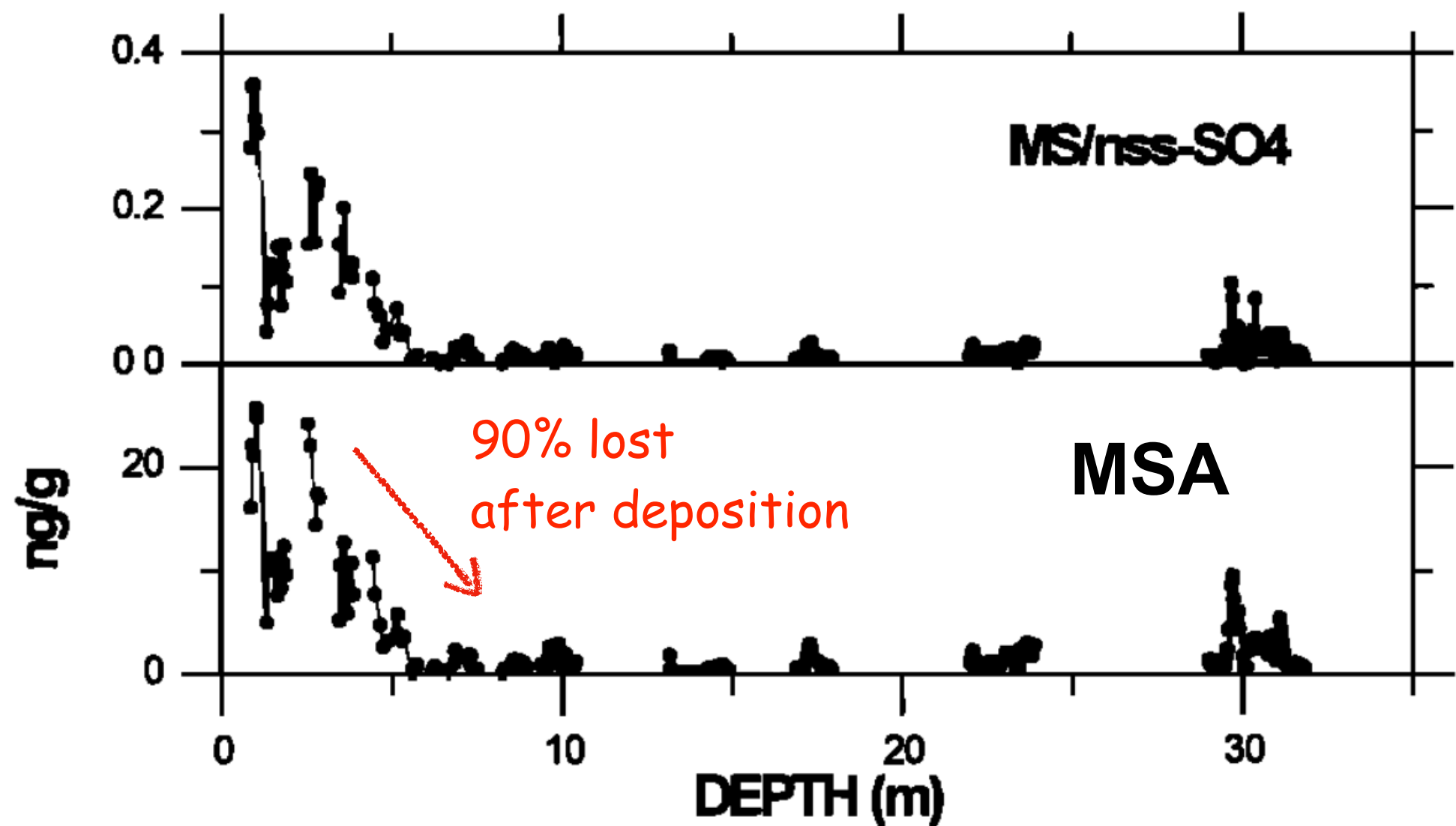
$1.3 \times 0.91 + 12.2 \times 0.09 = 2.3\text{‰}$
Fairly consistent with the observed value at DC.

Recognized processes affecting $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ [\[Ishino et al., 2021\]](#)

MSA oxidation is the most likely process responsible for high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ at inland in summer. 8/10

Implication: Post-depositional increase in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ due to MSA oxidation?

Vertical profile of MSA in snow at Vostok [Wagnon et al., 1999]



- $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ produced by MSA oxidation = 12.2‰ [slide 8]
 - Annual mean $[\text{MSA}]/[\text{SO}_4]_{\text{nss}}$ at DC = 0.11 [Legrand et al., 2017]
 - 90% of MSA is lost after deposition to snow [Wagnon et al., 1999]
- > $12.2\text{‰} \times 0.11 \times 0.09 = 1.2\text{‰}$

In good agreement with the ~1.5‰ difference between ice and atmosphere $\Delta^{17}\text{O}(\text{SO}_4^{2-})$.

A significant gap between $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in ice and air

Sample type	Site	Time period	$\Delta^{17}\text{O}(\text{SO}_4^{2-})$	
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Aerosols	Dome C ^a	Jan.-Dec., 2010	1.3±0.1	
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[^aHill-Falkenthal et al., 2013; ^bWalters et al., 2019; ^cIshino et al., 2017; ^dKunasek et al., 2010; ^eAlexander et al., 2002, 2003]

+1.5‰

$\Delta^{17}\text{O}(\text{SO}_4^{2-})$ records in ice cores seem to be largely perturbed by MSA oxidation in snow.

Conclusions

We observed specifically high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ at inland ($2.0 \pm 0.3 \text{ ‰}$) than the coastal site ($1.3 \pm 0.3 \text{ ‰}$) during summer (Oct. to Dec.).

Evidences that

- Those high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ values coincide with chemical destruction of MSA in aerosols at inland.
- Our isotope mass-balance calculation gives $\Delta^{17}\text{O}(\text{MSA})$ of $\sim 16 \text{ ‰}$, and $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ produced from MSA oxidation of $\sim 12 \text{ ‰}$. suggest MSA oxidation into sulfate is the most likely process responsible for the high $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ observed.

If contributing to the known post-depositional loss of MSA in snow, this process should also cause a significant post-depositional increase in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ over 1 ‰ , that can reconcile the discrepancy between $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in the atmosphere and ice.

$\Delta^{17}\text{O}(\text{SO}_4^{2-})$ recorded in Antarctic ice cores has been proposed as a potential tool for assessing the past oxidants chemistry in the atmosphere, BUT the signature seems to be largely perturbed by MSA oxidation in snow after deposition.

→ Future works are needed. Investigating the relationship between $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ and $[\text{MSA}]/[\text{SO}_4^{2-}]$ in snow over Antarctica to see to what extent the signature modified?, if can information of the past oxidants be extracted?, etc...

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