Preparation and calibration of ^{17}O-enriched nitrite isotope standards

Toward reliable Δ^{17}O measurements of atmospheric NO_2 and HONO

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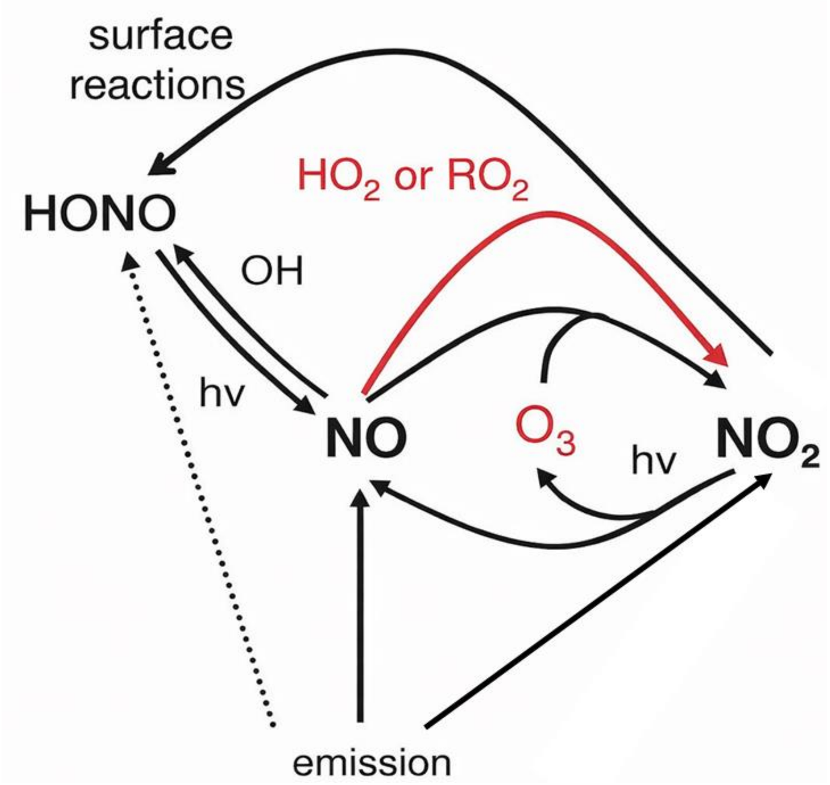
Reactive nitrogen has profound effects on atmospheric chemistry

Coupling between atmospheric reactive nitrogen cycling and radical cycling

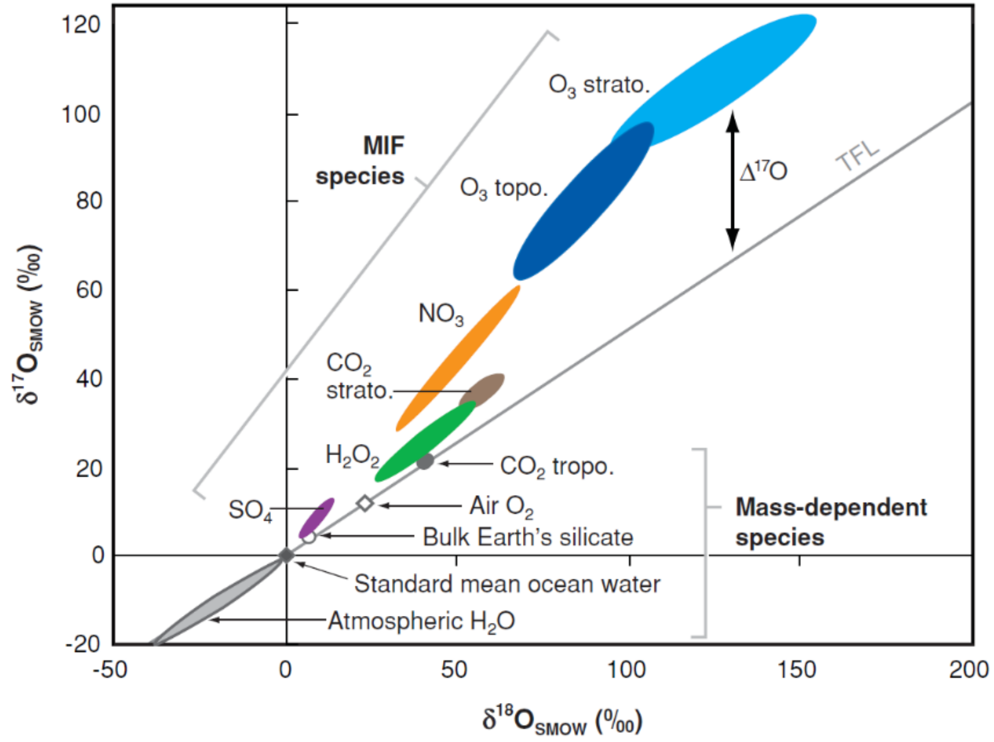


- Atmospheric oxidation capacity (AOC) controls the oxidation of key greenhouse gases (e.g., CH_4) and the formation of secondary pollutants (O_3 and $PM_{2.5}$), regulating their transformation and removal.

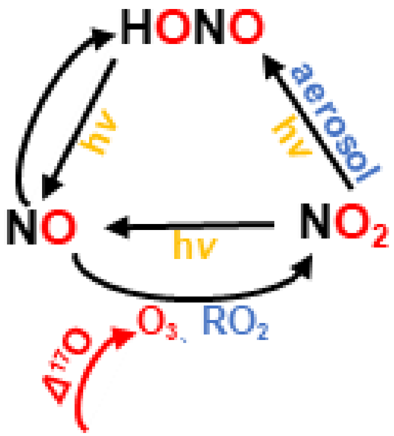
- The photochemical cycling of reactive nitrogen (NO_x, HONO) influences O_3, OH, and peroxy radicals, thereby shaping AOC.

Understanding the sources and transformation mechanisms of reactive nitrogen is essential for exploring changes in atmospheric oxidative capacity.

$\Delta^{17}O$ is a powerful tracer of reactive nitrogen oxidation pathways



(Thiemens., 2006)



- ➢ O_3 dominated reactions give higher $\Delta^{17}O$
- ➢ RO_2 dominated reactions give lower $\Delta^{17}O$

Oxidant	$\Delta^{17}O$	reference
O_3	~26.2 ‰	(Vicars et al., 2014)
RO_2, OH	~0	(Michalski et al., 2006)

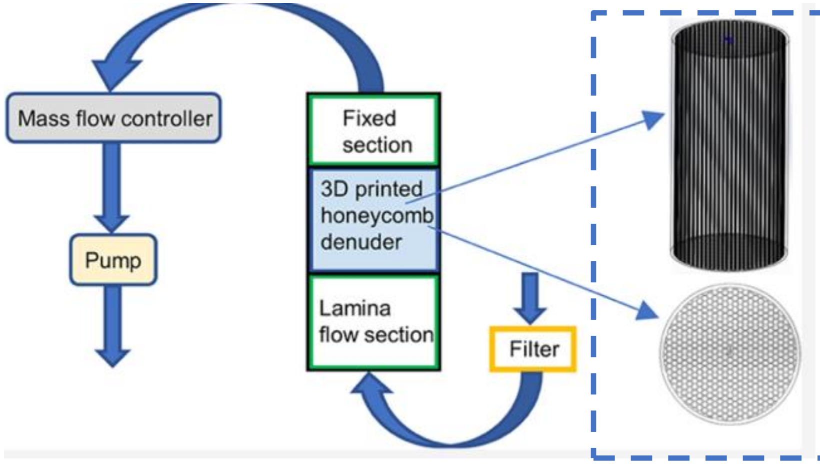
The definition of the oxygen mass independent signal (O-MIF)： $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$

$\Delta^{17}O$ of atmospheric NO_2 and HONO:

- ➢ **The formation mechanisms of NO_2 and HONO;**
- ➢ **Oxidants concentration;**
- ➢ **Atmospheric oxidation capacity**

The principle of the denuder sampling methods

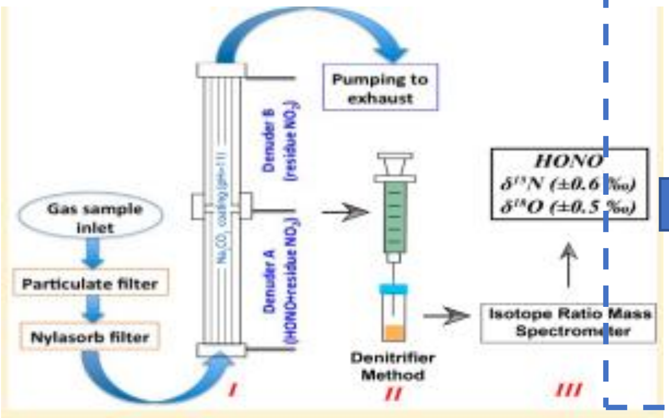
The denuder sampling devices were used to collect atmospheric NO_2 and HONO for isotope analysis



Guaiacol/KOH coating

$NO_2 \longrightarrow NO_2^-$

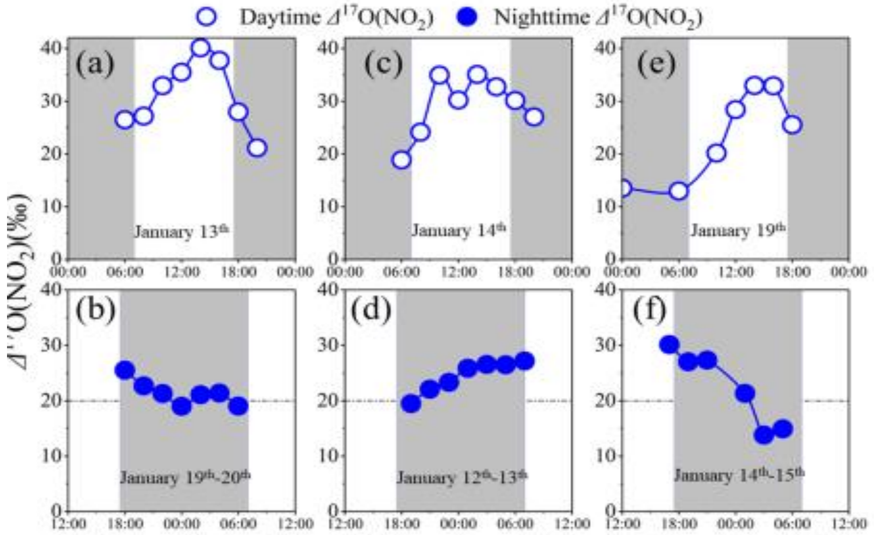
(Zhou et al., 2022)

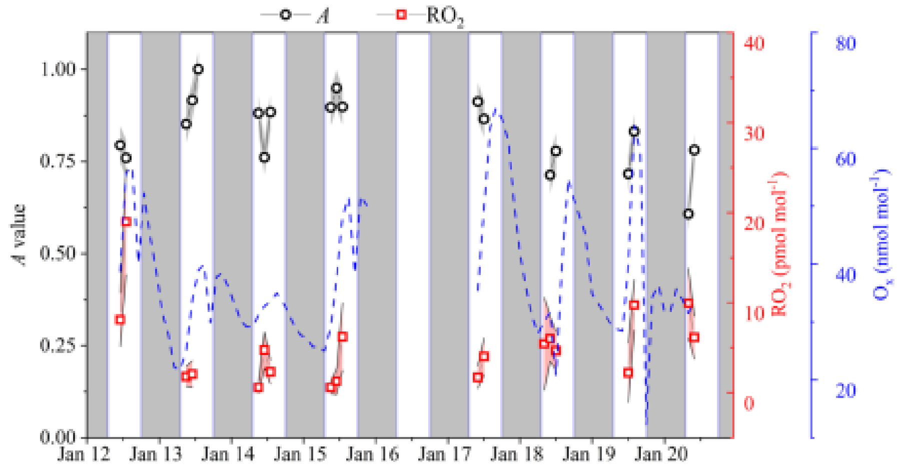


Na_2CO_3/glycerol coating

$HONO \longrightarrow NO_2^-$

(Chai et al., 2018)





(Zhang et al., 2025)

The key bottleneck is the lack of reliable nitrite $\Delta^{17}O$ standards

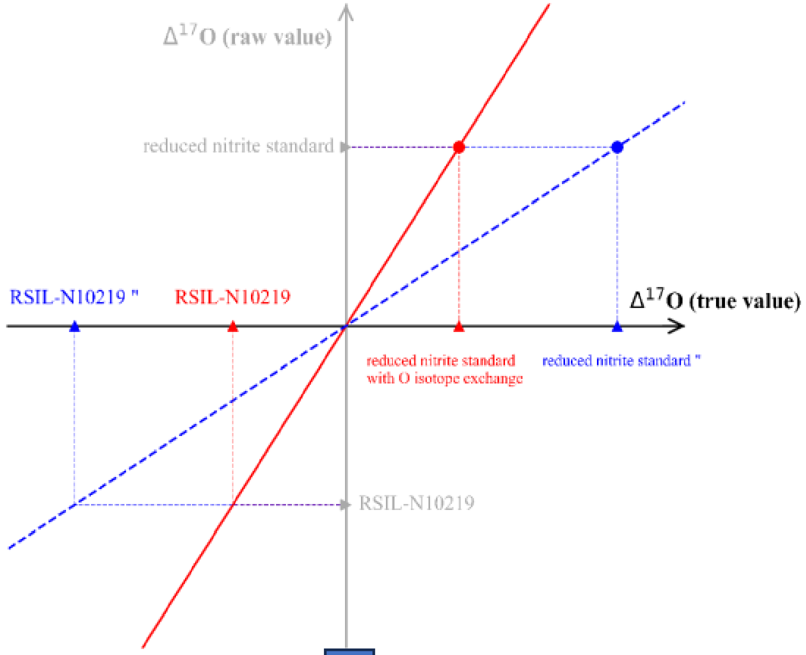
Chemical coating convert NO_2/HONO to NO_2^-

↓

NO_2^- sample and isotope standard identical treatment
(using the azide method convert NO_2^- to NO2)

↓

Acquire the $\Delta^{17}O$ value of NO_2^- sample based on the isotope calibration curve



Three international nitrite isotope standards

Nitrite standard	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)
RSIL-N10219	2.8	88.5	non-zero
RSIL-N7373	-79.6	4.5	zero
RSIL-N23	3.7	11.4	zero

- The adopted true $\Delta^{17}O$ value of RSIL-N10219 ranges from -7‰ ~-12.9‰, which will introduce significant uncertainty in calibration
- Atmospheric NO_2 has positive $\Delta^{17}O$ signals

Objectives of this study

- **Prepare nitrite isotope standards with positive $\Delta^{17}O$ signals**
- **Developed a new calibration approach suitable for accurate $\Delta^{17}O$ signal determination of the RSIL-N10219 and the newly homemade nitrite standards**

Precise evaluation of regional atmospheric $\Delta^{17}O(NO_y)$ variation

^{17}O-enriched nitrite standards were prepared by oxygen exchange with water

Step1：Prepare ^{17}O-enriched Water

400 uL ^{17}O-enriched mother solution + 1L Mili-Q water ($\Delta^{17}O$ = 76.5‰)

Step2：Isotope exchange

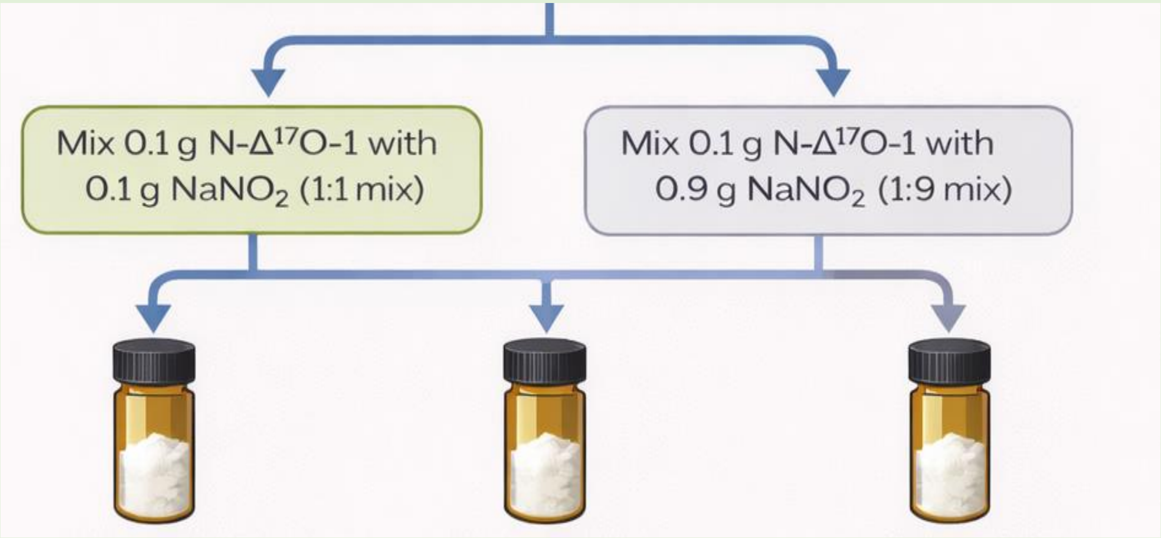
- Take 10 mL of prepared water dissolve 2 g ultrapure $NaNO_2$
- Transfer to 100 mL tinted Schott bottle
- Incubate at 85°C for 2 months

Step3：Drying and collection

Pour into 40 mL beaker || Dry at 85°C for 24 hours || Collect powder with scalpel || Homogenize with mortar || Dry at 105°C for 5 hours

Step 4：Create standards

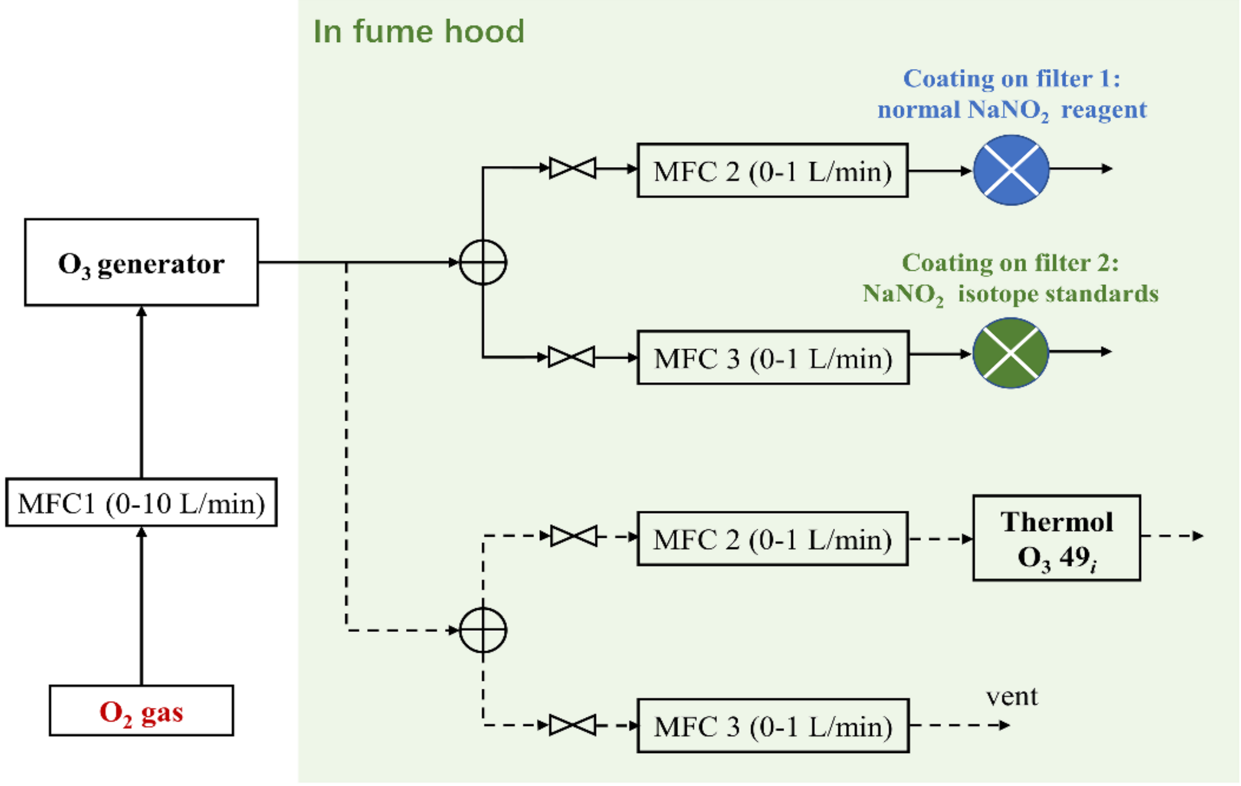
- Yield: 1.8 g pure nitrite
- Store in dark/dry conditions (RT)
- **Label: N-$\Delta^{17}O$-1**



N-$\Delta^{17}O$-1 **N-$\Delta^{17}O$-2** **N-$\Delta^{17}O$-3**

Parallel O_3 oxidation method enables the calibration of nitrite $\Delta^{17}O$

Schematic diagram of the O_3 oxidation experimental setup



solid line： ozone oxidation streams
dotted line： O_3 concentration measurement

Reaction： $NO_2^- + O_3 \rightarrow NO_3^- + O_2$

$$\Delta^{17}O(NO_3^-)_1 = \frac{2}{3} \times \Delta^{17}O(NO_2^-)_{normal} + \frac{1}{3} \times \Delta^{17}O(O_3^*)$$

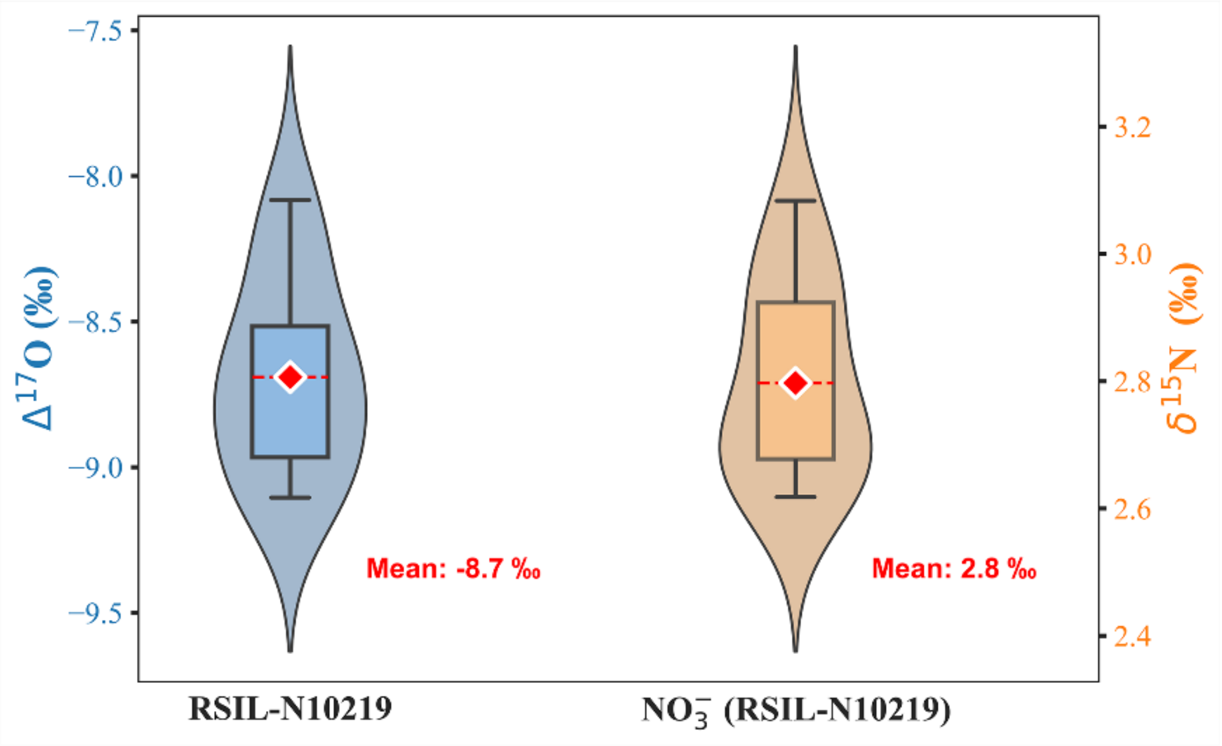
$$\Delta^{17}O(NO_3^-)_2 = \frac{2}{3} \times \Delta^{17}O(NO_2^-)_{std} + \frac{1}{3} \times \Delta^{17}O(O_3^*)$$

$$\Delta^{17}O(NO_2^-)_{std} = \frac{3}{2} \times (\Delta^{17}O(NO_3^-)_2 - \Delta^{17}O(NO_3^-)_1)$$

The $\Delta^{17}O(NO_3^-)_1$ and $\Delta^{17}O(NO_3^-)_2$ represent the $\Delta^{17}O$ values of nitrate produced from the ozone oxidation of either normal nitrite reagent or nitrite standard, respectively .

The $\Delta^{17}O$ calibration results of RSIL-N10219

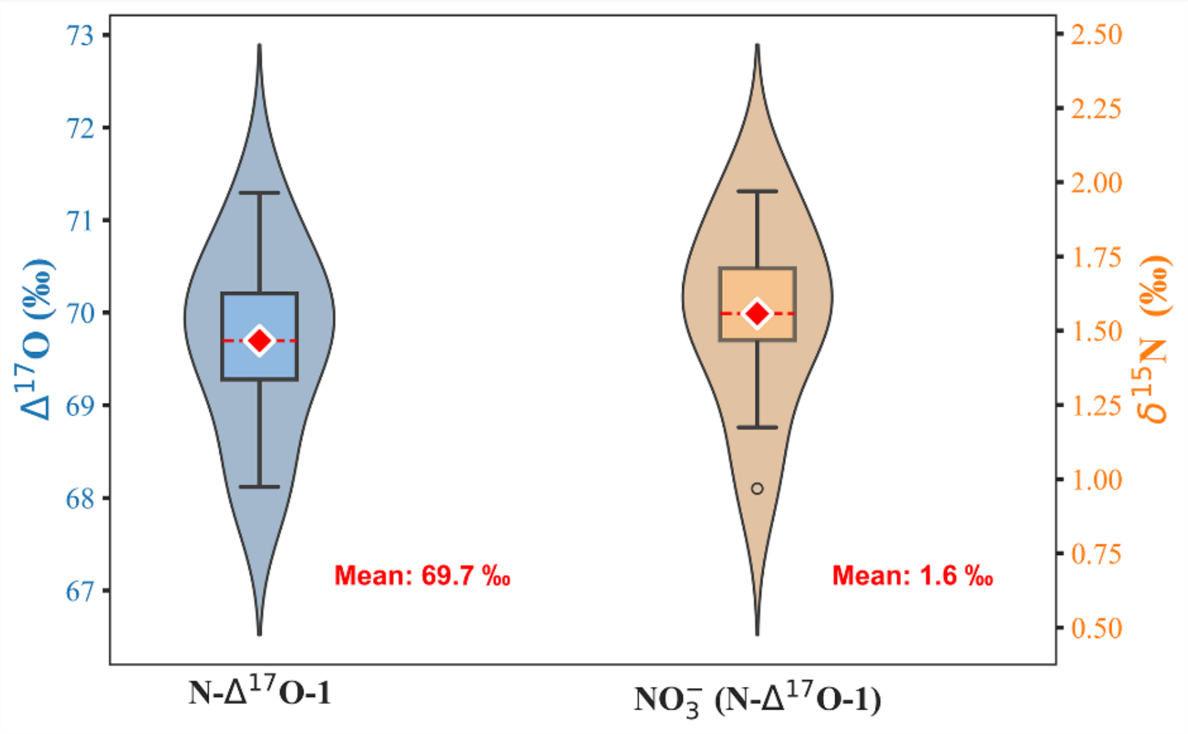
The $\Delta^{17}O$ calibration results of RSIL-N10219 obtained from 11 different groups of O_3 oxidation experiments



- The mean $\Delta^{17}O$ value of RSIL-N12019 is (-8.7 ± 0.3) ‰ (1σ, n=11).
- The measured $\delta^{15}N$ value of NO_3^- produced by the O_3 oxidation of RSIL-N10219 is (2.80 ± 0.15) ‰ (± 1σ, n=11), in good agreement with the recommended $\delta^{15}N$ value of RSIL-N10219 (2.80 ‰)
- The $\Delta^{17}O$ of the generated ozone vary in a wide range from 26.1 ‰ to 32.5 ‰

The $\Delta^{17}O$ calibration results of N- $\Delta^{17}O$ -1

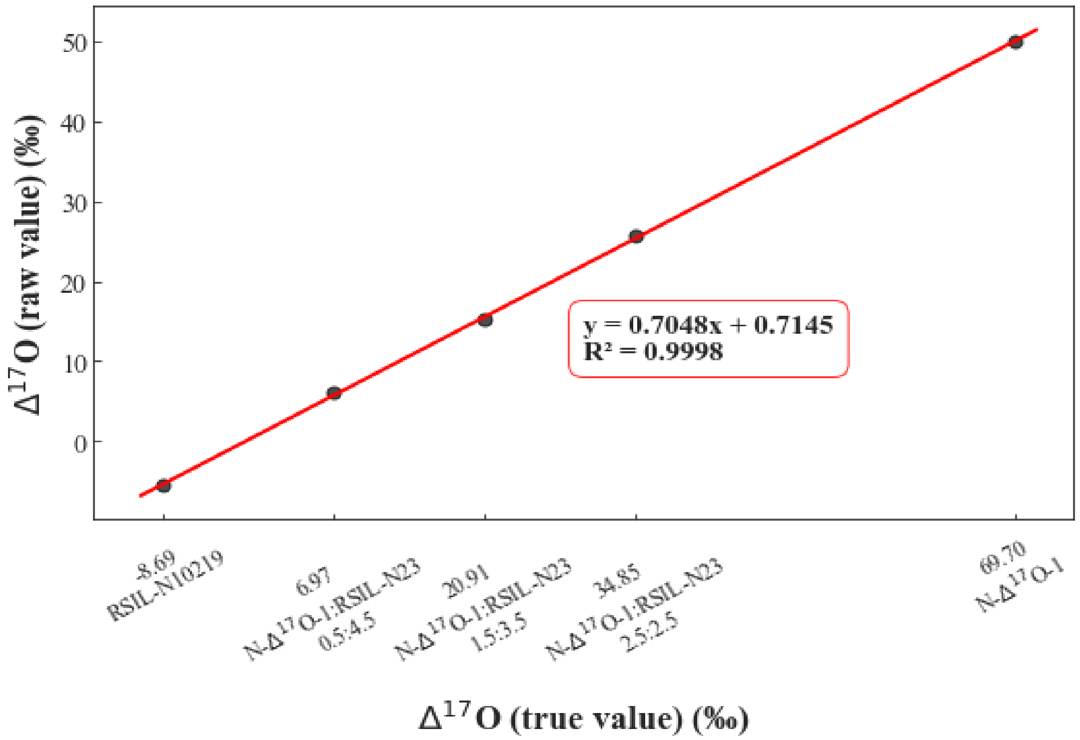
The $\Delta^{17}O$ calibration results of N-Δ17O-1 obtained from 10 different groups of O_3 oxidation experiments



- The $\Delta^{17}O$ of N-$\Delta^{17}O$-1 was determined as 69.7 ± 1.0‰ (n = 10), showing good reproducibility.
- The measured value is lower than the $\Delta^{17}O$ of ^{17}O-enriched water (76.5‰), suggesting incomplete isotope exchange between NO_2^- and water during the standard preparation process.

The $\Delta^{17}O$ calibration results of N-$\Delta^{17}O$-2 and N-$\Delta^{17}O$-3

$\Delta^{17}O$ values of N-$\Delta^{17}O$-2 and N-$\Delta^{17}O$-3 were determined using RSIL-N10219 and N-$\Delta^{17}O$-1 as references.



$\delta^{15}N$ and $\delta^{18}O$ measurements of the homemade ^{17}O-enriched nitrite samples

type	standard name	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)	n
reference	RSIL-N10219	2.8	88.5	-8.7	/
	RSIL-N7373	-79.6	4.5	0	/
	RSIL-N23	3.7	11.4	0	/
	RSIL-N1:1	-38.4	46.5	-4.35	/
sample	N-$\Delta^{17}O$-1	1.0 ± 0.1	60.9 ± 0.4	69.5 ± 0.5	10
	N-$\Delta^{17}O$-2	0.8 ± 0.3	38.0 ± 0.1	34.1 ± 0.1	6
	N-$\Delta^{17}O$-3	0.5 ± 0.1	20.1 ± 0.3	6.6 ± 0.1	8

- Calibration curves show excellent linearity (R^2 = 0.9998), confirming method reliability.
- The $\Delta^{17}O$ values are 34.5 ± 0.3‰ (N-Δ17O-2) and 6.4 ± 0.1‰ (N-Δ17O-3).
- These agree well with expected values from 1:1 and 1:9 mixing ratios (34.9‰ and 6.97‰).

Conclusions

- Reliable ^{17}O-enriched nitrite standards were previously lacking.
- Here, we developed new nitrite standards with positive $\Delta^{17}O$ values and established the O_3 oxidation method for $\Delta^{17}O$ signal calibration.
- This enables accurate $\Delta^{17}O$ measurements of atmospheric NO_2 and HONO, and provides a powerful tool to better constrain atmospheric oxidation processes.

T Zhou, S Albertin, Z Jiang, J Savarino, J Duan, Z Yu, Y Yu, Z Zhang, Yichao Wu, Shihao Liu, Zeqian Liu, Slimane Bekki, Nicolas Caillon, Lei Geng*, Preparation and Calibration of ^{17}O-Enriched Nitrite Isotope Standards, ACS Earth and Space Chemistry, https://doi.org/10.1021/acsearthspacechem.5c00399 (2026)