



Supplement of

**Measurement report: Nitrogen isotopes ($\delta^{15}\text{N}$) and first
quantification of oxygen isotope anomalies ($\Delta^{17}\text{O}$, $\delta^{18}\text{O}$) in
atmospheric nitrogen dioxide**

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This file contains the data used in this manuscript: Table S1 for Figure 1, Table S2 for Figure 2, Table S3 for Figure 2 and Figure 3, Table S4 for Figure 3, Table S5 for Figure 4, Table S6 for Figure 5, Table S7 for Figure A1, and Table S8 for figure B1.

Table S1. Mean values of NO_2^- collected on the first denuder tube of the sampling cartridge vs. NO_2^- produced by the gas standard generator.

NO_2^- expected /nmol	NO_2^- collected /nmol
1226.1	1281.7
150.3	139.4
32.5	22.3
115.3	124.9
893.3	869.1

Table S2. Summary table of ambient NO , NO_2 , O_3 and O_x hourly mean mixing ratios over the collection periods.

Date & local time	NO /nmol mol ⁻¹		NO_2 /nmol mol ⁻¹		O_3 ^(*) /nmol mol ⁻¹	O_x ^(*) /nmol mol ⁻¹
	Mean	SD	Mean	SD	Mean	Mean
14/05/2019 21:00	0	0.9	5.1	1.5	50.9	57.4
14/05/2019 22:00	0	0.9	5.6	1.6	54	57.5
14/05/2019 23:00	0	1.0	4.7	1.4	52	55.9
15/05/2019 00:00	0	0.9	3.3	0.9	53.7	55.1
15/05/2019 01:00	0	1.1	4.2	1.2	51	53
15/05/2019 02:00	0	1.0	4.1	1.2	50	51.8
15/05/2019 03:00	0.2	1.0	4.2	1.2	42.6	44.9
15/05/2019 04:00	0	1.2	4.1	1.2	35.6	39.4
15/05/2019 05:00	0	1.3	5.9	1.7	31.8	36.7
15/05/2019 06:00	0	1.1	10.9	3.2	26.8	35.2
15/05/2019 07:00	5.9	3.4	14.7	4.3	15.3	34.2
15/05/2019 08:00	2.7	1.7	21.3	6.2	20.1	42.4
15/05/2019 09:00	1.1	0.9	5.5	1.6	35.2	46.4
15/05/2019 10:00	1	1.3	4.5	1.3	40.4	46.7
15/05/2019 11:00	0.4	1.0	4	1.2	41.6	46.1
15/05/2019 12:00	0.7	1.2	3.1	0.9	42.2	46.2
15/05/2019 13:00	0.7	1.1	3.8	1.1	43.9	47.8
15/05/2019 14:00	0.8	0.9	2.5	0.7	47.6	51.2
15/05/2019 15:00	0.5	1.2	2.4	0.7	49.1	52.1
15/05/2019 16:00	0	1.3	2.9	0.8	50.3	53.3
15/05/2019 17:00	0	1.1	2.9	0.8	50.7	54.3
15/05/2019 18:00	0	1.3	2.9	0.9	50.2	54.3
15/05/2019 19:00	0	1.5	2.7	0.8	51	54.5
15/05/2019 20:00	0	1.0	3	0.9	49.9	53
15/05/2019 21:00	0	1.3	4.1	1.2	46.4	50.4
15/05/2019 22:00	0	1.6	4.3	1.2	44.8	48.3
15/05/2019 23:00	0	1.0	5.4	1.6	42.7	46.5
16/05/2019 00:00	0	0.7	10.4	3.0	39.2	43.2
16/05/2019 01:00	0	1.0	12.4	3.6	32.2	38.5

16/05/2019 02:00	0	0.8	12.5	3.6	27.5	35.6
16/05/2019 03:00	0	0.9	8.9	2.6	21.6	29.7
16/05/2019 04:00	0	1.1	7.6	2.2	22.1	27.2
16/05/2019 05:00	0	1.2	7.7	2.2	18.8	24.4

(*) Data monitored at the local air quality monitoring site of Saint-Martin d'Hères located a kilometre south of the sampling site (<https://www.atmo-auvergnerhonealpes.fr/>).

Table S3. Summary table of the global solar radiation flux during the sampling period (measured at 200 meters from the sampling site by the IGE weather station with a Skye SP1110 pyranometer).

Date & time UTC+2	Global radiation /W m ⁻²
14/05/2019 21:00	6.145
14/05/2019 21:10	2.651
14/05/2019 21:20	0.681
14/05/2019 21:30	0.125
14/05/2019 21:40	0.062
14/05/2019 21:50	0.054
14/05/2019 22:00	0.039
14/05/2019 22:10	0.033
14/05/2019 22:20	0.058
14/05/2019 22:30	0.037
14/05/2019 22:40	0.053
14/05/2019 22:50	0.053
14/05/2019 23:00	0.033
14/05/2019 23:10	0.037
14/05/2019 23:20	0.04
14/05/2019 23:30	0.059
14/05/2019 23:40	0.038
14/05/2019 23:50	0.051
15/05/2019 00:00	0.029
15/05/2019 00:10	0.044
15/05/2019 00:20	0.039
15/05/2019 00:30	0.042
15/05/2019 00:40	0.053
15/05/2019 00:50	0.044
15/05/2019 01:00	0.033
15/05/2019 01:10	0.04
15/05/2019 01:20	0.049
15/05/2019 01:30	0.061
15/05/2019 01:40	0.054
15/05/2019 01:50	0.054
15/05/2019 02:00	0.049
15/05/2019 02:10	0.053
15/05/2019 02:20	0.061
15/05/2019 02:30	0.042
15/05/2019 02:40	0.049

15/05/2019 02:50	0.076
15/05/2019 03:00	0.047
15/05/2019 03:10	0.043
15/05/2019 03:20	0.069
15/05/2019 03:30	0.032
15/05/2019 03:40	0.105
15/05/2019 03:50	0.075
15/05/2019 04:00	0.048
15/05/2019 04:10	0.057
15/05/2019 04:20	0.067
15/05/2019 04:30	0.067
15/05/2019 04:40	0.063
15/05/2019 04:50	0.074
15/05/2019 05:00	0.06
15/05/2019 05:10	0.058
15/05/2019 05:20	0.055
15/05/2019 05:30	0.054
15/05/2019 05:40	0.058
15/05/2019 05:50	0.187
15/05/2019 06:00	1.043
15/05/2019 06:10	3.229
15/05/2019 06:20	6.328
15/05/2019 06:30	10.42
15/05/2019 06:40	15.44
15/05/2019 06:50	21.05
15/05/2019 07:00	59.7
15/05/2019 07:10	91.9
15/05/2019 07:20	114.4
15/05/2019 07:30	
15/05/2019 07:40	166.2
15/05/2019 07:50	171.5
15/05/2019 08:00	225.2
15/05/2019 08:10	255.4
15/05/2019 08:20	283.5
15/05/2019 08:30	312.3
15/05/2019 08:40	341.1
15/05/2019 08:50	370.4
15/05/2019 09:00	399.1
15/05/2019 09:10	427.8
15/05/2019 09:20	457.5
15/05/2019 09:30	485.9
15/05/2019 09:40	511.6
15/05/2019 09:50	539.8
15/05/2019 10:00	565.7
15/05/2019 10:10	591.2
15/05/2019 10:20	616.1
15/05/2019 10:30	639.6
15/05/2019 10:40	661.6

15/05/2019 10:50	684.3
15/05/2019 11:00	706.5
15/05/2019 11:10	726.6
15/05/2019 11:20	745.7
15/05/2019 11:30	759.6
15/05/2019 11:40	774.3
15/05/2019 11:50	791.4
15/05/2019 12:00	805
15/05/2019 12:10	819
15/05/2019 12:20	831
15/05/2019 12:30	843
15/05/2019 12:40	860
15/05/2019 12:50	867
15/05/2019 13:00	871
15/05/2019 13:10	885
15/05/2019 13:20	891
15/05/2019 13:30	894
15/05/2019 13:40	892
15/05/2019 13:50	874
15/05/2019 14:00	900
15/05/2019 14:10	903
15/05/2019 14:20	894
15/05/2019 14:30	897
15/05/2019 14:40	797.6
15/05/2019 14:50	914
15/05/2019 15:00	935
15/05/2019 15:10	732.4
15/05/2019 15:20	740.1
15/05/2019 15:30	882
15/05/2019 15:40	754.4
15/05/2019 15:50	876
15/05/2019 16:00	618.8
15/05/2019 16:10	481.7
15/05/2019 16:20	180.2
15/05/2019 16:30	581
15/05/2019 16:40	286.7
15/05/2019 16:50	373.9
15/05/2019 17:00	266.9
15/05/2019 17:10	354.6
15/05/2019 17:20	
15/05/2019 17:30	454
15/05/2019 17:40	417.4
15/05/2019 17:50	428.2
15/05/2019 18:00	242.1
15/05/2019 18:10	176.8
15/05/2019 18:20	345.6
15/05/2019 18:30	270.5
15/05/2019 18:40	364.6

15/05/2019 18:50	345.9
15/05/2019 19:00	321.2
15/05/2019 19:10	303.6
15/05/2019 19:20	271.8
15/05/2019 19:30	232.7
15/05/2019 19:40	184.7
15/05/2019 19:50	163.5
15/05/2019 20:00	134.5
15/05/2019 20:10	103.8
15/05/2019 20:20	29.35
15/05/2019 20:30	21.2
15/05/2019 20:40	16.09
15/05/2019 20:50	10.76
15/05/2019 21:00	5.791
15/05/2019 21:10	2.16
15/05/2019 21:20	0.542
15/05/2019 21:30	0.107
15/05/2019 21:40	0.052
15/05/2019 21:50	0.055
15/05/2019 22:00	0.063
15/05/2019 22:10	0.075
15/05/2019 22:20	0.059
15/05/2019 22:30	0.046
15/05/2019 22:40	0.06
15/05/2019 22:50	0.064
15/05/2019 23:00	0.052
15/05/2019 23:10	0.041
15/05/2019 23:20	0.047
15/05/2019 23:30	0.051
15/05/2019 23:40	0.068
15/05/2019 23:50	0.039
16/05/2019 00:00	0.043
16/05/2019 00:10	0.06
16/05/2019 00:20	0.051
16/05/2019 00:30	0.063
16/05/2019 00:40	0.053
16/05/2019 00:50	0.052
16/05/2019 01:00	0.051
16/05/2019 01:10	0.066
16/05/2019 01:20	0.028
16/05/2019 01:30	0.057
16/05/2019 01:40	0.026
16/05/2019 01:50	0.049
16/05/2019 02:00	0.045
16/05/2019 02:10	0.051
16/05/2019 02:20	0.067
16/05/2019 02:30	0.057
16/05/2019 02:40	0.06

16/05/2019 02:50	0.07
16/05/2019 03:00	0.063
16/05/2019 03:10	0.043
16/05/2019 03:20	0.062
16/05/2019 03:30	0.06
16/05/2019 03:40	0.054
16/05/2019 03:50	0.061
16/05/2019 04:00	0.054
16/05/2019 04:10	0.071
16/05/2019 04:20	0.057
16/05/2019 04:30	0.074
16/05/2019 04:40	0.061
16/05/2019 04:50	0.069
16/05/2019 05:00	0.043
16/05/2019 05:10	0.035
16/05/2019 05:20	0.059
16/05/2019 05:30	0.047
16/05/2019 05:40	0.08
16/05/2019 05:50	0.232
16/05/2019 06:00	1.266

Table S4. Summary table of sampling periods (dates and local times) and calibrated NO₂ isotopic measurements ($\pm 1\sigma$) of $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$.

Local sampling date & time (start - end)	$\delta^{15}\text{N}(\text{NO}_2)$ ($\pm 0.1 \text{ ‰}$)	$\delta^{18}\text{O}(\text{NO}_2)$ ($\pm 1.8 \text{ ‰}$)	$\Delta^{17}\text{O}(\text{NO}_2)$ ($\pm 0.3 \text{ ‰}$)
14 May 2019 21:00 - 00:00	-11.7	75.6	27.4
15 May 2019 06:00 - 09:00	-4.9	97.6	31.8
15 May 2019 09:00 - 12:00	-10.1	114.5	39.2
15 May 2019 12:00 - 15:00	-11.8	90.9	35.8
15 May 2019 15:00 - 18:00	-11.0	86.9	31.1
15 May 2019 18:00 - 21:00	-11.1	77.1	29.7
16 May 2019 00:00 - 05:00	-11.1	62.2	20.5

Table S5. Summary table of daytime sampling periods (dates and local times), RO₂ mixing ratios estimated from Eq.(6) and $T_{\text{NO}+\text{O}_3}$ estimated from Eq.(4) using measured $\Delta^{17}\text{O}(\text{NO}_2)$ in this study.

Local sampling date & time (start - end)	RO ₂ / $\mu\text{mol mol}^{-1}$		$T_{\text{NO}+\text{O}_3}$	
	Mean	SD	Mean	SD
15 May 2019 06:00 - 09:00	8.0	0.8	3.4	0.0
15 May 2019 09:00 - 12:00	0.0	1.0	3.6	0.1
15 May 2019 12:00 - 15:00	8.0	0.9	4.9	0.0
15 May 2019 15:00 - 18:00	24.7	0.8	7.1	0.0
15 May 2019 18:00 - 21:00	28.3	0.8	7.2	0.0

Table S6. Values from the SIAR model simulation used for NO_x emission source partitioning

NO _x emission source	Soil	Natural gas combustion	Vehicle exhaust
Median	0.06	0.38	0.57
Mean	0.07	0.36	0.57
First quartile (Q1/25th percentile)	0.03	0.29	0.52
Third quartile (Q2/75th percentile)	0.09	0.45	0.63
Interquartile range (IQR)	0.06	0.16	0.11
Maximum (Q3+1.5*IQR)	0.19	0.69	0.79
Minimum (Q1-1.5*IQR)	0.00	0.04	0.35

Table S7. Data for calibration of ¹⁸O and ¹⁵N with nitrite standards at 100 nmol measured by the chemical azide method. The measured $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{raw}}$) and $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\text{raw}}$) values of NO₂⁻ standards are plotted against their certified reference $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{std}}$) and $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\text{std}}$) values.

Standard	$\delta^{18}\text{O}_{\text{raw}}$ (‰)	$\delta^{15}\text{N}_{\text{raw}}$ (‰)	$\delta^{18}\text{O}_{\text{std}}$ (‰)	$\delta^{15}\text{N}_{\text{std}}$ (‰)
RSIL-N7373	17.81	-43.6	4.5	-79.6
	22.59	-44.24	4.5	-79.6
	23.32	-44.27	4.5	-79.6
	24.37	-44.49	4.5	-79.6
	25.01	-44.63	4.5	-79.6
RSIL-N23	23.73	-2.88	11.4	3.7
	25.86	-2.93	11.4	3.7
	29.58	-2.91	11.4	3.7
	31.6	-2.99	11.4	3.7
RSIL-N10219	95.02	-3.42	88.5	2.8
	98.19	-3.53	88.5	2.8
	98.29	-3.47	88.5	2.8
	99.02	-3.55	88.5	2.8

Table S8. Temporal evolution of $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ differences between measurements of RSIL standards (prepared in the KOH/guaiacol eluted matrix) and their certified reference values.

Standard	Date of analysis	$\delta^{17}\text{O}_{\text{res}}$ (‰)	$\delta^{18}\text{O}_{\text{res}}$ (‰)	$\Delta^{17}\text{O}_{\text{res}}$ (‰)	
RSIL-N7373	29/04/2019	0.6	0.9	0.1	
		0.8	1.4	0.0	
		0.9	1.7	0.0	
	07/05/2019	0.6	0.6	0.3	
		0.6	1.4	-0.2	
		0.3	0.0	0.3	
	20/05/2019	0.7	1.4	0.0	
		0.9	1.8	0.0	
	RSIL-N10219	29/04/2019	1.5	3.9	-0.6
2.5			5.4	-0.3	
07/05/2019		1.3	3.7	-0.6	
		1.5	3.5	-0.4	
		1.2	3.3	-0.5	
20/05/2019		3.1	6.4	-0.3	
		2.8	6.1	-0.3	
RSIL-N23		29/04/2019	0.4	0.8	-0.1
			0.1	0.2	0.0
	0.9		1.5	0.1	
	07/05/2019	0.8	1.3	0.2	
		0.8	1.3	0.1	
		0.6	1.4	-0.1	
	20/05/2019	1.2	1.6	0.4	
		1.2	2.4	-0.1	