Isotopic Analysis:

We have extensively tested the use of low concentration (i.e. high volume) samples with the denitrifier method. It is critically important when running very low concentrations to include reference materials that are very close in concentration to the samples for correcting the raw data (i.e. there is a “volume” effect that is accounted for by using samples and references of the same volume). Below are two tables (Tables S1 and S2) of data obtained with internal quality control samples. These nitrate solutions are treated as samples, run at different concentration in different runs, and then corrected to the reference materials discussed in the manuscript text. In Table S1, results from a potassium nitrate (KNO_3) solution are shown for different injection volumes. Agreement for both the $\delta^{15}N(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ over a variety of low concentrations and across different sample runs is excellent. Table S2 shows results from a mixture of the reference materials USGS34 and USGS35. Again, the solution is treated as a sample and corrected in each run; agreement for $\Delta^{17}O(NO_3^-)$ across runs is excellent.

Table S1. Results of an internal quality control, KNO_3. The $\delta^{15}N(NO_3^-)$ mean is 58.37±0.62 ‰, with the range of 57.52-59.59 ‰. The mean of $\delta^{18}O(NO_3^-)$ is 30.65±0.52 ‰, with the range of 29.55-31.50 ‰.

$\delta^{15}N(NO_3^-)$	$\delta^{18}O(NO_3^-)$	Injected volume (mL)	Concentration (μM)
59.39	30.43	20.00	0.50
58.19	30.85	20.00	0.50
58.37	30.80	20.00	0.50
57.52	31.13	16.67	0.60
58.77	30.62	16.67	0.60
58.12	30.59	13.33	0.75
57.66	31.50	13.33	0.75
58.73	30.16	13.33	0.75
58.39	31.31	10.31	0.97
57.71	31.00	10.00	1.00
58.26	31.01	10.00	1.00
58.48	30.82	10.00	1.00
57.70	30.45	10.00	1.00
57.57	31.04	10.00	1.00
58.96	29.93	10.00	1.00
59.59	29.77	10.00	1.00
59.31	30.16	10.00	1.00
58.70	30.88	10.00	1.00
58.27	29.55	10.00	1.00
57.76	31.01	6.67	1.50

Table S2. Results of $\Delta^{17}O$ for USGS35/34 mixture, an internal quality control. The mean $\Delta^{17}O(NO_3^-)$ of 11.45±0.44 ‰ and the range of 10.88-12.21 ‰.

$\Delta^{17}O(NO_3^-)$	NO_3^- amount (nmol)	Concentration (μM)	Injected volume (mL)
11.26	50.00	5.00	10.00
10.89	50.00	5.00	10.00
10.88	50.00	3.00	16.67
11.06	50.00	3.00	16.67
11.78	50.00	2.00	25.00
10.94	50.00	2.00	25.00
11.62	50.00	1.50	33.33
11.71	50.00	1.00	50.00
12.21	50.00	1.00	50.00
11.83	50.00	1.00	50.00
11.59	45.00	3.00	15.00
11.37	45.00	2.00	22.50
11.23	40.00	1.00	40.00
11.20	40.00	1.00	40.00
12.20	40.00	1.00	40.00

Table S3. Isotopic fractionation from the field experiment observations by Erbland et al. (2013) and modeled here following the theoretical approach of Frey et al. (2009). No $^{18}\varepsilon$ data were reported by Erbland et al. (2013).

Temperature,	Field Experiment		Temperature,	Model	
^{o}C	$^{15}\varepsilon$, ‰	$^{18}\varepsilon$, ‰	^{o}C	$^{15}\varepsilon$, ‰	$^{18}\varepsilon$, ‰
-10	-3.6±1.1	-	0	12.6	1.1
-20	-0.3±1.2	-	-13	13.2	1.0
-30	0.9±3.5	-	-33	14.2	0.8
			-53	15.3	0.7
			-73	16.8	0.6

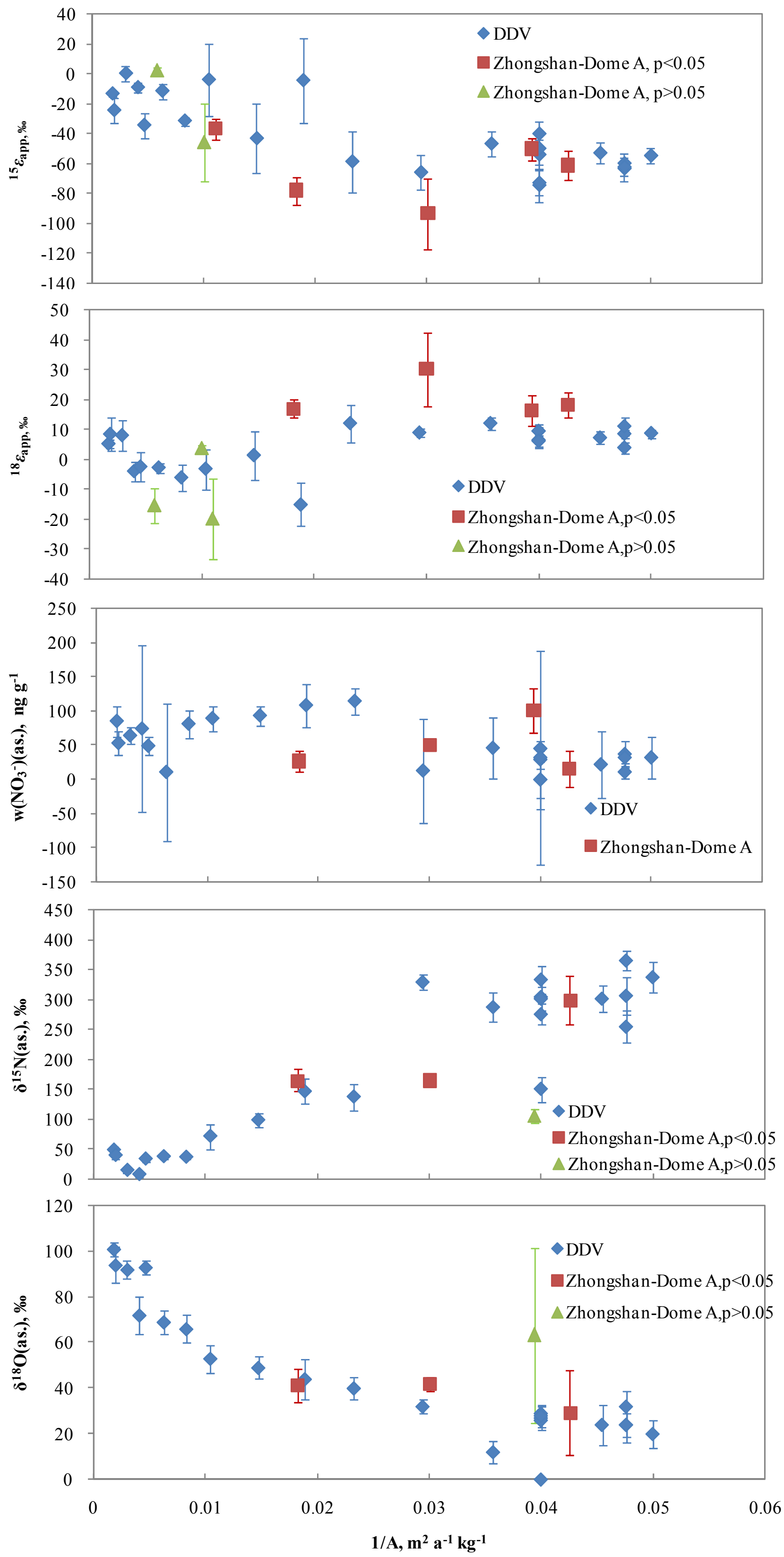

Fig. S1. Comparison of current study data with the data of Erbland et al. (2013). The snow samples on the traverse of D10-Dome C-Vostok (referred to as DDV in the figure) were collected only to the depth of ca. 20 cm for most of the snowpits (Frey et al., 2009; Erbland et al., 2013). We thus only compare the apparent fractionation constants (ε_{app}) and asymptotic values (as.) from the depth interval of 0-20 cm to make a direct comparison with those in Erbland et al. (2013). It is noted that all of the data from Erbland et al. (2013) were used to make the figure. For the apparent fractionation constants, all of the seven pits in this study were included in the figure, with red squares and green triangles representing $p<0.05$ and $p>0.05$ (t-test), respectively. In terms of the asymptotic values, based on the fact that $w(NO_3^-)$, $\delta^{15}N(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ varied significantly along the profiles in the pits P1-P3 (Fig. 3 in the manuscript), the calculation of asymptotic values were not performed for P1-P3. The asymptotic values of P4-P7 were included in the figure, with red squares and green triangles representing $p<0.05$ and $p>0.05$, respectively.

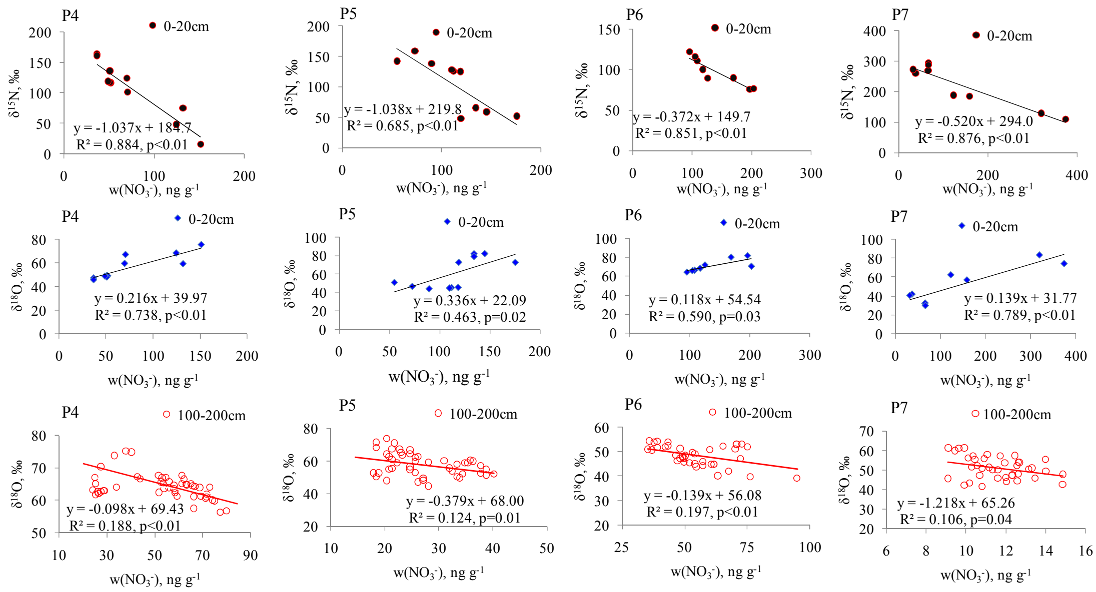

Fig. S2. Linear relationships between $w(NO_3^-)$ and $\delta^{18}O$ and $\delta^{15}N$ of NO_3^- in the near surface (top and middle rows) and at depth (bottom row) snow ranges. Least squares regressions are shown and are all significant at p<0.05.

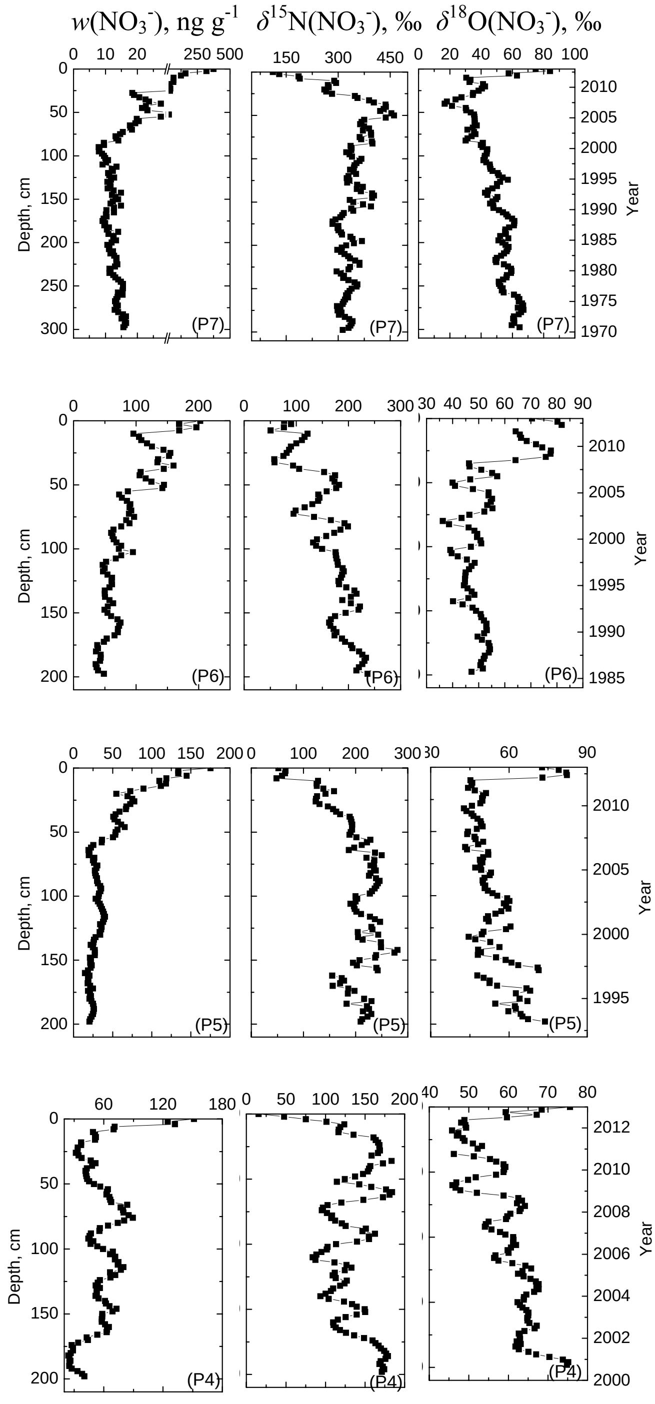

Fig. S3. Rough dating of the group II inland snowpits, from measured snow accumulation rate and snow density (for details see the main text).

References:

Erbland, J., Vicars, W., Savarino, J., Morin, S., Frey, M., Frosini, D., Vince, E., and Martins, J.: Air-snow transfer of nitrate on the East Antarctic Plateau - Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium in summer, Atmos. Chem. Phys., 13, 6403-6419, 2013.

Frey, M. M., Savarino, J., Morin, S., Erbland, J., and Martins, J.: Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, Atmos. Chem. Phys., 9, 8681-8696, 2009.