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On the potential fingerprint of the Antarctic ozone hole in ice-core nitrate isotopes: a case study based on a South Pole ice core

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Text S1: Effect of the long-term changes in e-folding depth in the South Pole

The e-folding depth is determined by snow light absorbing impurities (LAIs), and snow physical properties (e.g., density, grain size) (Zatko et al., 2013). Over the studied period, snow LAIs are relatively constant as indicated by South Pole ice core records (Winski et al., 2021). Regarding snow physical properties, the grain size is inversely proportional to specific surface area (SSA) (Zatko et al., 2013), and both snow density and SSA are affected by wind speed and temperature (Kaspers et al., 2004; Domine et al., 2009). Although surface temperature at the South Pole were not changed significantly after the 1950s (below Figure S2), surface wind speed (below Figure S3) displays a decreasing trend since ~1970. In Polar Regions the wind action will increase the SSA of surface snow, however, it is the wind storm (>55km/h) that increase the SSA in Antarctica (Domine et al., 2009). Using the empirical relationship between surface snow density with temperature, wind speed and snow accumulation rate in Kaspers et al. (2004) and the parameters in Sugiyama et al. (2012) as follows:

$$\rho = 305 + 0.629\mathrm{T} + 0.150\mathrm{A} + 13.5\mathrm{W}$$

Where, ρ is surface snow density in kg/m^3, T is the annual average surface temperature in ℃, A is the accumulation rate in m w.e. a^{-1} and W is the annual wind speed in m s^{-1} at 10 m above the surface. The calculated surface snow density from 1957 to 2005 at the South Pole is plotted in Figure S4. As shown in the Fig.S4, snow density after the 1970s (i.e. the ozone hole period) is ~ 20 kg m^{-3} lower than before that. Using TARTES model and TRANSITS model, we calculated the changes in surface snow density would lead to an increase in e-folding depth by only ~1cm, corresponding to ~1 ‰ increase in the preserved $\delta^{15}N(NO_3^-)$. Therefore, the effects of the e-folding depth can be ignored in the South Pole.

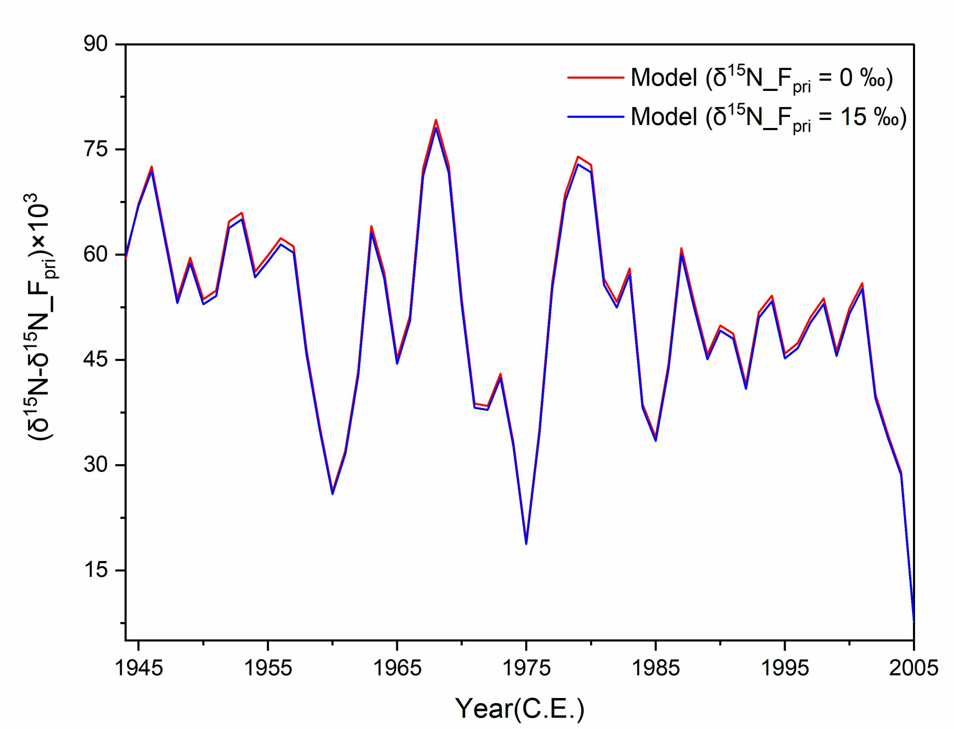

Figure S1. Modeled $\delta^{15}N(NO_3^-)$ changes (i.e., the differences between preserved $\delta^{15}N(NO_3^-)$ and that of F_{pri}) with different $\delta^{15}N(F_{pri})$. Note other parameters were kept same in these two scenarios.

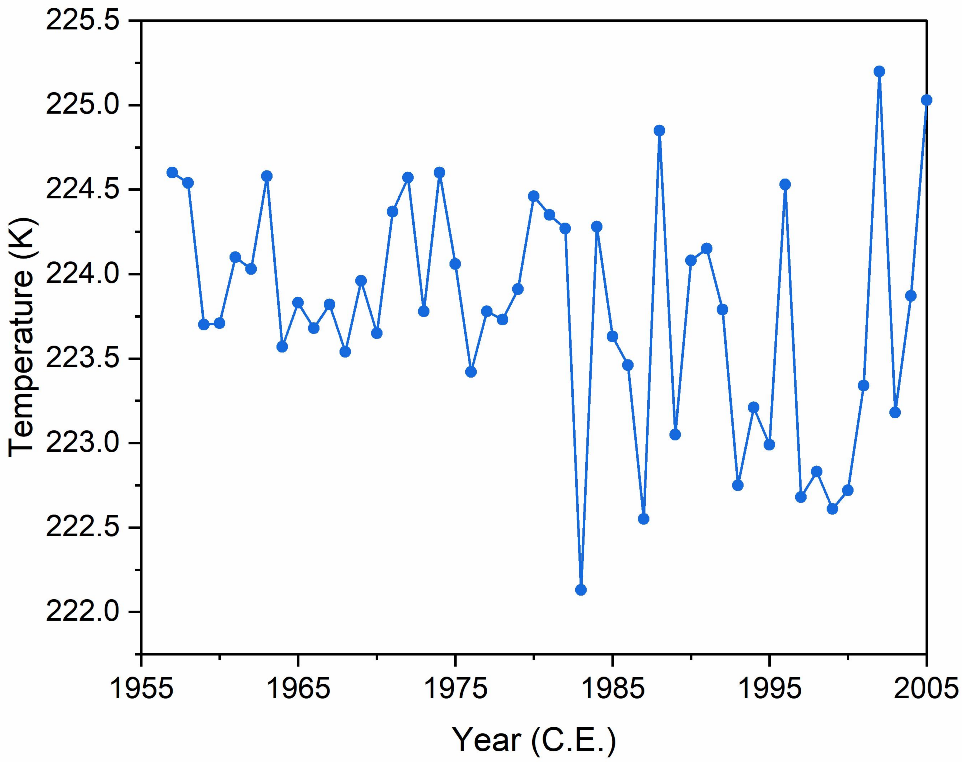

Figure S2. The annual mean atmospheric temperature from 1957 to 2005 at the South Pole. (https://ramadda.data.bas.ac.uk/repository/entry/show/?entryid=569d53fb-9b90-47a6-b3ca-26306e696706)

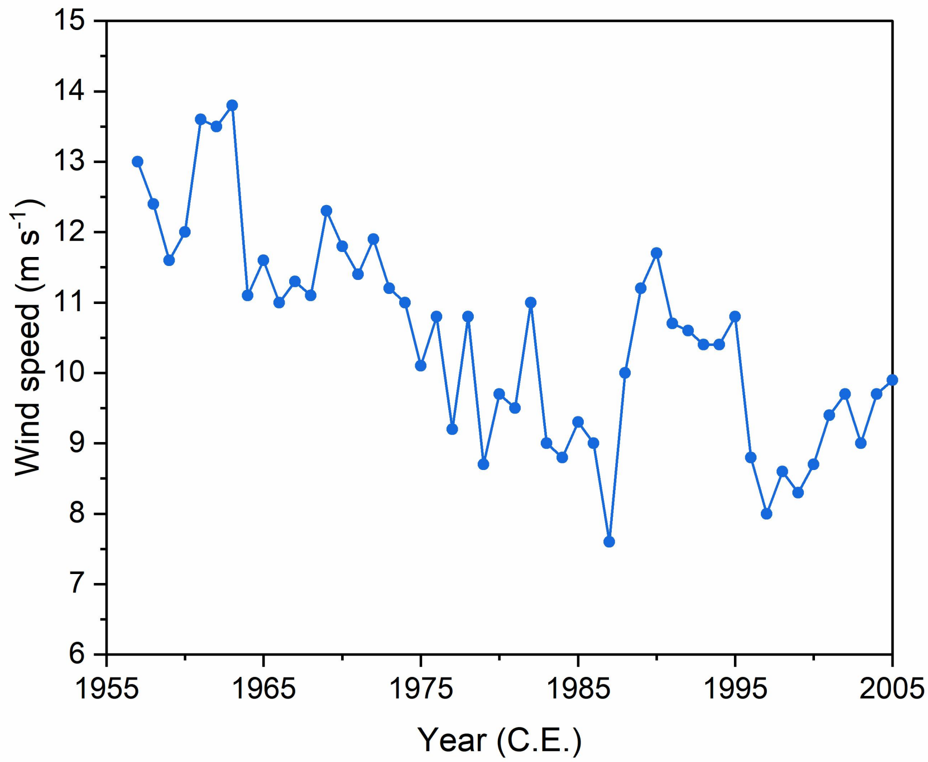

Figure S3. The annual mean wind speed from 1957 to 2005 at the South Pole. (https://ramadda.data.bas.ac.uk/repository/entry/show/?entryid=569d53fb-9b90-47a6-b3ca-26306e696706)

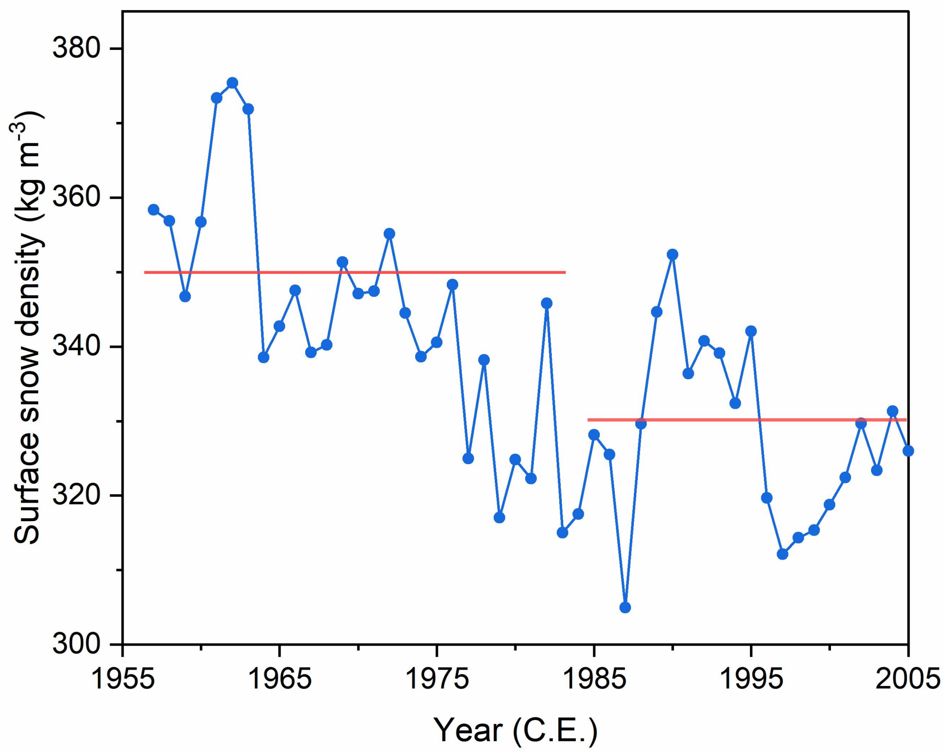

Figure S4. The calculated surface snow density from 1957 to 2005 at the South Pole. The red lines represent the mean surface snow density before and after 1970s, respectively.

Sample ID	Corresponding years (C.E.)
S1	2004-2005
S21	1983-1984
S23	1980-1981
S29	1973-1974
S32	1969-1970
S33	1967-1968
S35	1964-1965
S40	1958-1959
S41	1956-1957
S42	1954-1955
S43	1952-1953
S45	1949-1950
S47	1946-1947
S48	1944-1945

Table S1. The SP04C6 core samples that were combined with the adjacent ones and the corresponding years.

Parameter	Description	Value	Reference
h	Boundary layer height	81 m	Neff et al. (2018)
T	Temperature	-	NOAA observation
P	Pressure	-	NOAA observation
TCO	Total column ozone	-	NOAA observation
A	Snow accumulation rate	-	Measured in this research
ρ	Snow density	326 kg m^{-3}	Measured in this research
σ	Nitrate cross section	-	Berhanu et al. (2014)
Φ	Quantum yield	0.021	Meusinger et al. (2014)
O_3	Ozone concentration	-	NOAA observation
BrO	BrO concentration	-	Zatko et al. (2016)
$OH/HO_2/RO_2$	$OH/ HO_2/RO_2$ concentration	-	Zatko et al. (2016)
f_{cage}	Cage effect	0.15	Erbland et al. (2015)
F_{pri}	Primary input nitrate	$2.4*10^{-6}$ kg N m^{-2} yr^{-1}	Zatko et al. (2013)
FS/FPI	Fluxes FT and FS ratio	0.5	Erbland et al. (2015)
f_{exp}	Nitrate export fraction	0.2	Erbland et al. (2015)
$\gamma(NO_3^-)$	Atmospheric nitrate concentration	$5.4*10^{-11}$ kg N m^{-2} yr^{-1}	Erbland et al. (2015)
$10^3\times\Delta^{17}O(FS)$	$\Delta^{17}O$ in stratospheric input flux	42	Erbland et al. (2015)
$10^3\times\delta^{15}N(FS)$	$\delta^{15}N$ in stratospheric input flux	19	Erbland et al. (2015)

$10^3\times\Delta^{17}O$ (FT)	$\Delta^{17}O$ in tropospheric input flux	30	Erbland et al. (2015)
$10^3\times\delta^{15}N$(FT)	$\delta^{15}N$ in tropospheric input flux	0	Erbland et al. (2015)

Table S2. Parameters and variables used in the TRANSITS model.

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