**Supplementary discussion**

**S1. Factors determining $\Delta^{17}_O$ in atmospheric nitrate**

Atmospheric nitrate is the oxidation product of NO$_x$ (NO$_x$ ≡ NO + NO$_2$). NO$_x$ is emitted from natural sources including biomass burning, lightning and soil bioactivity, and anthropogenic sources mainly from fossil fuel combustion$^{40}$. During NO$_x$ cycling, NO is oxidized to NO$_2$ primarily by O$_3$, HO$_2$ and RO$_2$. Terminal reactions that oxidize NO$_2$ to HNO$_3$ are different between day- and nighttime. During the daytime, NO$_2$ is photolyzed to produce NO + O, or is oxidized to HNO$_3$ by OH. In the daytime, cycling of NO$_x$ between NO and NO$_2$ is at least 3 orders of magnitude faster than its loss by oxidation to HNO$_3$, so that NO$_x$ achieves isotopic equilibrium with O$_3$, HO$_2$, and RO$_2$$^{41}$. At night, the oxidation of NO$_2$ by O$_3$ to form NO$_3$ is important for HNO$_3$ formation. NO$_3$ can then react with dimethyl sulphide (DMS) or volatile organic compounds (VOC) to form HNO$_3$, or with NO$_2$ to form N$_2$O$_5$ which hydrolyzes to HNO$_3$ on the surface of aerosols. In the present day, NO$_2$ + OH contributes to 76% of global, tropospheric nitrate formation, with N$_2$O$_5$ hydrolysis as the second largest contributor (18%)$^{41}$. Reactive bromine (BrO) also plays a role in both NO$_x$ cycling and nitrate formation in polar regions$^{42-43}$ and in the marine boundary layer$^{44}$, although its global importance is not well-quantified$^{41}$.

The O-17 excess ($\Delta^{17}_O$) value of oxygen isotopes is a mass-independent fractionation signal created during O$_3$ formation and transferred to other oxygen-bearing compounds during oxidation reactions$^{45}$. It is conventionally known that fractionation of isotopes in physical-chemical processes is mass-dependent, from which changes in isotopic ratios of polyisotopic elements (e.g., oxygen and sulphur) are scaled in proportion to their relative mass difference. Therefore, mass-dependent fractionation gives an approximate relationship of $\delta^{17}_O \approx 0.52 \times$
δ^{18}O. During the photochemical production of O₃, due to the asymmetric effect associated with the recombination of O₂ and O (intermediate products of O₃ formation)⁴⁶, the isotope fractionation deviates from the mass-dependent relationship, leading to an excess of O-17 which is calculated by Δ^{17}O = δ^{17}O – 0.52 × δ^{18}O. For most other physical and chemical processes, oxygen isotopes obey mass-dependent fractionation producing zero Δ^{17}O, the Δ^{17}O value of most other oxygen-bearing molecules in the atmosphere is explicitly determined by the degree of the interactions between their precursors with O₃.

The Δ^{17}O of NO₂ (Δ^{17}O(NO₂)) is determined by the relative abundance of O₃/(HO₂ + RO₂) during NOₓ cycling reactions, while the Δ^{17}O of nitrate (Δ^{17}O(NO₃⁻)) is determined by both Δ^{17}O(NO₂) and the oxidant (OH or O₃) involved in the oxidation of NO₂ to HNO₃⁴¹. If more O₃ is involved in the production of nitrate, higher Δ^{17}O values in nitrate will result. Because two thirds of oxygen atoms in nitrate is from NO₂, Δ^{17}O(NO₃⁻) is most sensitive to the value of Δ^{17}O(NO₂), and hence the variability of Δ^{17}O(NO₃⁻) is dominated by variability in the relative O₃/(HO₂ + RO₂) abundance⁴⁷. This makes Δ^{17}O(NO₃⁻) a good proxy for the relative abundance of O₃ and (HO₂ + RO₂). In contrast, δ^{18}O(NO₃⁻) is influenced by the relative abundance of oxidants involved in nitrate formation and δ^{18}O of water. Unlike Δ^{17}O, the δ^{18}O of oxidants and water varies over space and time. These multiple dependencies make δ^{18}O(NO₃⁻) much more difficult to interpret as a proxy for oxidant levels. Hastings et al.,⁴⁸ uses δ^{18}O(NO₃⁻) to look for changes in nitrate formations pathways (day- vs. night-time reactions), rather than to explore changes in past oxidant levels. The former is possible because of the large difference between δ^{18}O of water (which determines δ^{18}O(OH), the main day-time oxidant) and O₃ (the main night-time oxidant).
The Δ\(^{17}\)O value of tropospheric O\(_3\) is currently in debate. Measurements using nitrite-coated filters to collected tropospheric O\(_3\) by Vicars et al.\(^{49-50}\) suggest that Δ\(^{17}\)O of tropospheric O\(_3\) is ~ 25 ‰. This is at the lower range of other observations\(^{51}\), and is not consistent with the result of laboratory and model experiments by Michalski et al.\(^{52}\) who suggest Δ\(^{17}\)O of O\(_3\) is ~ 35 ‰. Because adopting the value of 35 ‰ predicts a better agreement between measured and modeled Δ\(^{17}\)O(NO\(_3^–\)) values in the global atmosphere, in this study, we use 35 ‰ as the Δ\(^{17}\)O value of O\(_3\) when estimating Δ\(^{17}\)O(NO\(_3^–\)) in different climate using the ICECAP model.

In the following discussions, we utilize the ICECAP model to explore the effects of tropospheric precursor emissions and chemistry change on the NO\(_x\) cycling and terminal reactions from NO\(_2\) to HNO\(_3\) in different climates (i.e., Holocene and LGM), thereby discerning the causes of changes in Δ\(^{17}\)O(NO\(_3^–\)) from one climate to the other.

**S1.1 The NO\(_x\) cycling**

Globally, the value of Δ\(^{17}\)O(NO\(_2\)) is determined by the relative importance of O\(_3\) versus RO\(_2\) and HO\(_2\) oxidation of NO to NO\(_2\). Tropospheric O\(_3\) production depends on emissions of precursor gases including VOCs, CO and NO\(_x\) that are sensitive to temperature and other meteorological conditions. Lower temperatures in colder climates will reduce O\(_3\) precursor emissions\(^{53-55}\), which tends to decrease global tropospheric O\(_3\) production in the glacial period compared to the Holocene\(^{54}\). The response of the HO\(_x\) family to precursor emissions is more complicated. Production of HO\(_x\) is primarily sensitive to O\(_3\) photolysis frequencies and water vapor abundances. The relative partitioning of HO\(_x\) between OH and (RO\(_2\)+HO\(_2\)) is controlled by the relative abundances of NO versus CO+VOCs. Therefore, variations in (RO\(_2\)+ HO\(_2\)) reflect the convolution of these parameters, and vary relatively independently from tropospheric O\(_3\) itself\(^{53}\). Models generally predict higher OH in the glacial period compared to the Holocene\(^{47}\).
especially in the high latitudes due to reduced sinks (CO and VOCs) and higher surface UV albedos caused by enhanced snow and ice cover\textsuperscript{53}. The effect of changing OH alone on $\Delta^{17}$O(NO$_3^-$) is considered to be relatively small, as the variability of $\Delta^{17}$O(NO$_3^-$) is most sensitive to the relative abundances of O$_3$ and (HO$_2$ + RO$_2$).

In the polar regions, BrO can also be important over short time periods for oxidizing NO to NO$_2$, such as polar spring associated with ozone depletion events\textsuperscript{42,56}. Because BrO is produced from Br reacting with O$_3$, during ozone depletion events, there is an anti-correlation between O$_3$ and BrO abundances\textsuperscript{57}. BrO obtains its oxygen atom from O$_3$ and thus possesses and transfers the same $\Delta^{17}$O to NO$_2$ when oxidizing NO as does O$_3$, making these two pathways isotopically indistinguishable. In the northern mid- to high-latitudes, the ICECAP model predicts that annual-mean BrO oxidation in NO$_x$ cycling is less than 1% in the Holocene, and ~2.2% and 1.4% in the cold and warm LGM, respectively. Due to the small influence of BrO in NO$_x$ cycling in all time periods in the ICECAP model, we ignore the effect of BrO in NO$_x$ cycling in our analysis.

Using the ICECAP model, we estimate changes in tropospheric O$_3$ abundance due to changing O$_3$-precursor emissions and chemistry alone from the Holocene to the LGM (Figure 3). As expected, tropospheric O$_3$ abundance decreases in the glacial period due to reductions in temperature-dependent emissions of O$_3$-precursors. The ICECAP model also calculates decreases in tropospheric (HO$_2$ + RO$_2$) from the Holocene to the LGM (Figure 3b). The decreases in HO$_2$ are due both to reductions in primary HO$_x$ production from reduced water vapor abundances in colder climates, as well as a shift of HO$_x$ partitioning toward OH and RO$_2$ due to relative changes in NO$_x$, VOC, and CO abundances\textsuperscript{53}. The decreases in modeled RO$_2$ in the glacial climates are mainly due to the reduction of VOCs.
The ratio of \( \frac{O_3}{(H_2O + RO_2)} \), which determines \( \Delta^{17}O(No_2) \), is plotted in Figure 3d. Although large spatial variability exists, in general the \( \frac{O_3}{(H_2O + RO_2)} \) ratio decreases in the LGM compared to the Holocene in the northern mid- to high-latitudes. In particular, in the northern mid- to high-latitudes (30 to 90°N), the ratio decreases by 6.6% and 15.6% on average in the warm and cold LGM scenarios, respectively, compared to the Holocene. Based on the model predicted tropospheric \textit{in-situ} \( O_3 \) and \( (H_2O + RO_2) \) abundances in the LGM and Holocene, we further calculate the conversion rates of NO to \( NO_2 \) via \( O_3 \), \( H_2O \) and \( RO_2 \) oxidation, and the fraction of \( O_3 \) oxidation of NO in \( NO_2 \) formation in each climate. The latter explicitly determines \( \Delta^{17}O(No_2) \). Following \textit{Alexander et al.}⁴¹, we use the A-value to represent the fraction of \( O_3 \) oxidation in \( NO_2 \) formation:

\[
A = \frac{k_1 \cdot [NO] \cdot [O_3]}{k_1 \cdot [NO] \cdot [O_3] + k_2 \cdot [NO] \cdot [H_2O] + k_3 \cdot [NO] \cdot [RO_2]}
\]

(1)

Where \( k_1, k_2 \) and \( k_3 \) are the reaction rate constants from \textit{Atkinson et al.}⁵⁸. A smaller A-value leads to lower \( \Delta^{17}O(No_2) \) and thus lower \( \Delta^{17}O(No_3^-) \). As shown in Figure 3c, the A-values are lower in the glacial period compared to the Holocene in the northern hemisphere. In comparison with the \( O_3/(H_2O + RO_2) \) ratio, the A-value also takes into account the effect of changes in the temperature-dependent reaction rate constants between different climates, and thus better estimates the effect of tropospheric chemistry changes on \( \Delta^{17}O(No_3^-) \).

Therefore, if only tropospheric chemistry is taken into account, the A-value is expected to decrease from the Holocene to the LGM (Supplementary Table 1). This should lead to lower \( \Delta^{17}O(No_2) \) and thus \( \Delta^{17}O(No_3^-) \) values in the LGM if other factors are the same, opposite to the observed trend in our ice-core observations.

\textbf{S1.2. The terminal reactions (NO}_2 \rightarrow \text{HNO}_3}
Terminal reactions oxidizing NO$_2$ to HNO$_3$ can be in general categorized as daytime (OH) and nighttime (O$_3$) reactions. The relative importance of OH and O$_3$ for the oxidation of NO$_2$ to HNO$_3$ is to first order determined by the length of day versus night, which changes seasonally but does not change over the time scales considered here. The importance of OH and O$_3$ in the oxidation of NO$_2$ to HNO$_3$ is also influenced by the abundances of these oxidants, as well as by the aerosol surface area (influencing the rate of N$_2$O$_5$ hydrolysis) and abundance of DMS or VOC (influencing the rate of NO$_3$ + DMS/VOC). Thus, in addition to the relative abundance of O$_3$/(HO$_2$ + RO$_2$), $\Delta^{17}$O(NO$_3^-$) is also influenced by O$_3$/OH, aerosol surface area, and DMS and VOC concentrations. Although these are of secondary importance relative to O$_3$/(HO$_2$ + RO$_2$), their effects on climate-driven variability in observed $\Delta^{17}$O(NO$_3^-$) must be considered. For example, the rate of nitrate formed through N$_2$O$_5$ hydrolysis is mainly affected by aerosol composition, surface area, temperature and relative humidity$^{41,59}$. If this pathway increases significantly in the colder climates due to increased atmospheric dust and sea-salt aerosol abundances or decreases in air temperature$^{60}$, larger $\Delta^{17}$O(NO$_3^-$) would be expected, as is observed. In addition, observations of $\Delta^{17}$O(NO$_3^-$) in atmospheric nitrate in the Arctic$^{42,56}$ and tropical marine boundary layer$^{61}$ suggest that BrONO$_2$ hydrolysis is also a significant nitrate formation pathway, and could even be episodically dominant such as during the polar ozone-depletion events$^{42}$. Increases in BrONO$_2$ hydrolysis in the glacial climate would tend to increase $\Delta^{17}$O(NO$_3^-$), as is observed.

In order to estimate changes in the relative importance of the oxidation pathway of NO$_2$ to nitrate from the Holocene to the glacial period, we use the ICECAP model to estimate changes in the production rates of HNO$_3$ over the glacial-interglacial time scale due to precursor emissions and chemistry alone. The ICECAP model underestimates the glacial atmospheric sea-salt aerosol
abundance likely due to the lack of a sea-salt aerosol source from the sea-ice surface, which may cause a modeled underestimate of the HNO$_3$ production rate through N$_2$O$_5$ hydrolysis in the glacial period, as well as the concentration of reactive bromine$^{62}$ and thus BrONO$_2$ hydrolysis. However, the main NO$_x$ source region for nitrate in Greenland is in the northern mid-latitudes (30-60 °N), where the influence of sea ice on sea salt aerosols is relatively small. In ICECAP, the annual mean production rates of HNO$_3$ through NO$_2$ + OH, NO$_3$ + DMS/VOC, N$_2$O$_5$ and BrONO$_2$ hydrolysis, as well as the relative importance (i.e., fraction) of each pathway for annual mean HNO$_3$ production, in the northern mid-latitudes in each climate scenario are listed in Supplementary Table 1. In ICECAP, the rate of HNO$_3$ production for all pathways is decreased in the LGM climate compared to the Holocene, mainly due to reduced emissions of NO$_x$.

Additionally, in the extra-tropics, the net decrease in simulated aerosol particle abundances in the cold climates relative to the Holocene decreases N$_2$O$_5$ hydrolysis loss frequencies. This decrease in aerosol abundance primarily reflects emission-driven reductions in organic aerosol and its precursors$^{53}$, despite increases in mineral dust$^{63}$. Similarly, climate-driven reductions in biogenic DMS and VOC emissions in the cold climates reduce the rate and importance of NO$_3$ + DMS/VOC. The reduced aerosol abundance in the cold climates also decreases BrONO$_2$ hydrolysis rate, despite increases in BrO concentration in the model.

Since nitrate production rate from all pathways decreased in the LGM compared to the Holocene, the changes in the relative importance of each pathway which influences Δ$^{17}$O(NO$_3^-$) is then determined by the relative degree of decreases in each pathway. As shown in Supplementary Table 1, while the relative importance of NO$_2$ + OH, N$_2$O$_5$ hydrolysis and NO$_3$ + DMS/VOC in general decreases in the LGM compared to the Holocene, that of BrONO$_2$ hydrolysis increased significantly from the Holocene (~7.7 %) to the LGM (23.1 % and 14.2 %).
in the cold and warm LGM, respectively). In ICECAP, the abundance of BrO increases in the LGM compared to the Holocene, primarily due to decreases in HO2 which is the largest sink of BrOx (= Br + BrO), in addition to increases in reactive Br production from HOBr photolysis. The increases in BrO concentrations buffer the decreases in BrONO2 hydrolysis rates caused primarily by reduced NOx emissions and aerosol abundances. This explains why the production from BrONO2 hydrolysis decreases by a smaller degree than the other terminal pathways in the LGM compared to the Holocene. Fractional increases in BrONO2 hydrolysis will tend to increase Δ17O(NO3−) in cold climates, consistent with the observed trend in Δ17O(NO3−).

Using the ICECAP model calculated fraction of each nitrate formation pathway, the Δ17O(NO3−) value is calculated according the following equation:

\[ \Delta^{17}O(NO_3^-) = f_1 \cdot \Delta^{17}O_1 + f_2 \cdot \Delta^{17}O_2 + f_3 \cdot \Delta^{17}O_3 + f_4 \cdot \Delta^{17}O_4 \]  

(2)

Where \( f_x \) and \( \Delta^{17}O_x \) represent the fraction and \( \Delta^{17}O \) value of each terminal reaction. \( x = 1, 2, 3, 4 \), refers to OH oxidation, NO3 + DMS/VOC reaction, and N2O5 and BrONO2 hydrolysis, respectively.

\( \Delta^{17}O_x \) is calculated by following equations:

\[ \Delta^{17}O_1 = \frac{2}{3} \cdot A \cdot \Delta^{17}O(O_3^+) \]  

(3)

\[ \Delta^{17}O_2 = \frac{2}{3} \cdot A \cdot \Delta^{17}O(O_3^+) + \frac{1}{3} \cdot \Delta^{17}O(O_3^+) \]  

(4)

\[ \Delta^{17}O_3 = \frac{4}{6} \cdot A \cdot \Delta^{17}O(O_3^+) + \frac{1}{6} \cdot \Delta^{17}O(O_3^+) \]  

(5)

\[ \Delta^{17}O_4 = \frac{2}{3} \cdot A \cdot \Delta^{17}O(O_3^+) + \frac{1}{3} \cdot \Delta^{17}O(O_3^+) \]  

(6)

Where \( \Delta^{17}O(O_3^+) \) is the isotopic anomaly transferred to NO2 which is approximately 48‰ when \( \Delta^{17}O \) in bulk \( \Delta^{17}O \) is ~35‰52, and \( A \) is the A-value as expressed in Equation (1).
The ICECAP model-calculated mean values of $\Delta^{17}\text{O}(\text{NO}_3^-)$ in the northern mid- to high-latitudes in each climate scenario are listed in Supplementary Table 1. Due to the decreased $A$-values in the LGM compared to the Holocene, $\Delta^{17}\text{O}(\text{NO}_3^-)$ in the LGM decreases by 2.5 ‰ to 3.3 ‰, despite the increases in the relative importance of BrONO$_2$ hydrolysis. Modeled increases in the relative importance of BrONO$_2$ hydrolysis alone from the Holocene to LGM increase $\Delta^{17}\text{O}(\text{NO}_3^-)$ by 2.5 ‰ and 1.0 ‰ in the cold and warm LGM, respectively, partially counteracting decreases in $\Delta^{17}\text{O}(\text{NO}_3^-)$ driven by decreases in O$_3$ oxidation relative to HO$_x$ oxidation. The model may underestimate the strength of BrONO$_2$ hydrolysis in the LGM in part because sources of bromine don’t change with climate in ICECAP. In order for increases in the relative importance of BrONO$_2$ hydrolysis to explain the observed 6.2 ‰ glacial-interglacial change in the ice-core $\Delta^{17}\text{O}(\text{NO}_3^-)$ record, it must account for 70 - 82 ‰ of total nitrate production in the northern mid- to high-latitudes in the glacial period. This fraction is large over the broad spatial and temporal scales considered here, as BrONO$_2$ hydrolysis contributes only $(20 \pm 10)$ ‰ to total nitrate production even in high halogen environments (i.e., tropical marine boundary layer) in the present day atmosphere$^{44}$. In the polar regions after polar sunrise when O$_3$ depletion events occur$^{64}$, BrONO$_2$ hydrolysis may dominate local nitrate production$^{42}$. However, these short-lived episodes are constrained to polar springtime and do not represent the major nitrate production pathways over the larger spatial and temporal scales currently recorded in Greenland ice cores.

In sum, although the relative importance of BrONO$_2$ hydrolysis for nitrate production in the LGM may contribute to the observed glacial increase in $\Delta^{17}\text{O}(\text{NO}_3^-)$, it is unlikely that increases in BrONO$_2$ hydrolysis alone can explain the magnitude of the observed change in $\Delta^{17}\text{O}(\text{NO}_3^-)$ between the Holocene and the LGM. However, the direction and magnitude of the
sensitivity of reactive halogen chemistry to climate has not been explored, and changes in reactive halogen chemistry may play an important role in the observed trend in $\Delta^{17}$O(NO$_3^-$).

**S.2. The effects of stratospheric-sourced O$_3$ from STT**

An additional source of O$_3$ from the stratosphere through Stratosphere-to-Troposphere Transport (STT) will tend to increase $\Delta^{17}$O(NO$_3^-$) through 1) increasing the $A$-value, and 2) enhancing the relative importance of pathways that produce nitrate with larger $\Delta^{17}$O(NO$_3^-$), i.e., the nighttime reactions and BrONO$_2$ hydrolysis. Changes in total O$_3$ concentrations would affect the steady-state concentration of NO$_2$, and thus the production rates of HNO$_3$ from all of the terminal reactions. However, since all terminal reactions would be enhanced by the same factor due to the increased NO$_2$ concentration assuming a linear response, the relative contribution of each terminal reaction should then stay the same and no effect on $\Delta^{17}$O(NO$_3^-$) should be expected. In contrast, increases in total O$_3$ concentration will enhance the nighttime reactions (NO$_3$ + DMS/VOC and N$_2$O$_5$ hydrolysis) through promoting NO$_3$ production by NO$_2$ + O$_3$, and BrONO$_2$ hydrolysis through promoting BrO production by Br + O$_3$, while not directly influencing NO$_2$ + OH oxidation. Therefore, increases in total O$_3$ concentrations in the troposphere will increase $\Delta^{17}$O(NO$_3^-$) by increasing the $A$-value and by increasing the relative importance of nighttime reactions and BrONO$_2$ hydrolysis, assuming HO$_x$ is relatively constant. Our multiple model sensitivity studies suggest that over major climate transitions$^{53,65}$, production of total HO$_x$ (OH + HO$_2$ + RO$_2$) is most sensitive to O$_3$ photolysis frequencies (influenced by stratospheric O$_3$ column abundance which determines the surface UV levels) and water vapor abundances. It is less sensitive to tropospheric ozone concentrations ([O$_3$]) because (1) photolysis frequency variability in space and time is much greater than tropospheric [O$_3$] variability, (2) OH production is also limited by water vapor abundance (most O$^1$D is immediately quenched back to
O$_3$), and (3) water vapor abundance is dominated by physical processes (e.g., evaporation rate) and thus independent of O$_3$ abundance. The partitioning of HO$_x$ between HO$_2$ + RO$_2$ and OH is then set by the relative abundances of NO to VOCs and CO. Therefore, chemical factors other than tropospheric ozone abundances exert greater influences on tropospheric (HO$_2$ + RO$_2$), and therefore O$_3$ and (HO$_2$ + RO$_2$) do not necessarily co-vary in time.

We do however note that the strength of the Brewer-Dobson Circulation (BDC), through which STT is largely affected, influences the spatial distribution of stratospheric ozone and hence UV levels in the troposphere. Therefore, all else being equal, with a stronger BDC in the glacial climate, surface UV levels will decrease in the mid- to high-latitudes and increase in the tropics. This should further reduce the total HO$_x$ production in the mid- to high-latitudes, and thus HO$_2$ + RO$_2$ abundances in the northern mid- to high-latitudes assuming all other factors are the same. This also tends to increase the tropospheric O$_3$/(HO$_2$+RO$_2$) ratio, in addition to direct stratospheric O$_3$ input, consistent with the observations of increased $\Delta^{17}$O(NO$_3^-$) in the glacial time.

In summary, if the stratospheric-sourced O$_3$ is enhanced in the LGM compared to the Holocene, $\Delta^{17}$O(NO$_3^-$) in the LGM will be increased, qualitatively consistent with the observations. In the section that follows, we estimate the required increases in stratospheric-sourced O$_3$ through STT from the Holocene to the LGM in order to explain the observed 6.2‰ glacial-interglacial difference in $\Delta^{17}$O(NO$_3^-$).

### S.3. The required increase in stratospheric-sourced O$_3$ to explain the observations

In order to estimate the increase in stratospheric-sourced O$_3$ required to explain the observed increase in glacial $\Delta^{17}$O(NO$_3^-$), we define $\lambda$ as the ratio of total O$_3$ in the troposphere to O$_3$ originating from in-situ production only:
where \([O_3]_i\) represent in-situ \(O_3\) concentration and \([O_3]_{strat}\) represents the concentration of stratospheric-sourced \(O_3\).

The \(A\)-value from equation 1 becomes:

\[
A = \frac{k_j \cdot [NO] \cdot [O_3]_i \cdot \lambda}{k_j \cdot [NO] \cdot [O_3]_i + k_2 \cdot [NO] \cdot [HO_2] + k_2 \cdot [NO] \cdot [RO_2]}
\]  

(8)

Assuming a linear response to increases in total \(O_3\) concentrations in the troposphere, the production rates of nighttime reactions (i.e., \(NO_3 + DMS/VOC\) and \(N_2O_5\) hydrolysis) and \(BrONO_2\) hydrolysis would be enhanced by a factor of "\(\lambda\)" relative to the values reported in Supplementary Table 1. Subsequently, \(f_x\), i.e., the fraction of each nitrate production pathway relative to total nitrate production, is a function of "\(\lambda\)."

In order to explain the observed 6.2‰ glacial-interglacial difference in \(\Delta^{17}O(NO_3^-)\), we need:

\[
6.2\%_o = \Delta^{17}O(NO_3^-)_{LGM} - \Delta^{17}O(NO_3^-)_H
\]

(9)

Where 'LGM' represents WB or CM (the cold or warm LGM climate, respectively) and \(H\) represents the Holocene.

Substituting equations (3)-(6) into equation (2), we obtain:

\[
\Delta^{17}O(NO_3^-)_H = \frac{2}{3} \cdot A_H \cdot \Delta^{17}O(O_3^+) + \frac{1}{3} \cdot \Delta^{17}O(O_3^+) \cdot (f_{2,H} + f_{4,H}) + \frac{1}{6} \cdot \Delta^{17}O(O_3^+) \cdot f_{3,H}
\]

(10)

\[
\Delta^{17}O(NO_3^-)_{LGM} = \frac{2}{3} \cdot A_{LGM} \cdot \Delta^{17}O(O_3^+) + \frac{1}{3} \cdot \Delta^{17}O(O_3^+) \cdot (f_{2,LGM} + f_{4,LGM}) + \frac{1}{6} \cdot \Delta^{17}O(O_3^+) \cdot f_{3,LGM}
\]

(11)

Where \(f_{x,H}\) and \(f_{x,LGM}\) represent the fractional importance of each nitrate production pathway in the Holocene and LGM respectively, and \((x = 2, 3, 4)\) are the terminal reaction
pathways NO$_3$ + DMS/VOC, N$_2$O$_5$ hydrolysis and BrONO$_2$ hydrolysis, respectively. $f_{x,H}$ and $f_{x,LGM}$ are functions of $\lambda_H$ and $\lambda_{LGM}$, respectively:

$$f = \frac{R2 \cdot \lambda}{R1 + \lambda \cdot (R2 + R3 + R4)}$$

(12)

where R1-R4 represent the production rate of each terminal nitrate formation pathway, as shown in Supplementary Table 1.

Substituting equations (8) and (12) into (10) and (11), and combining the resulting equations with equation (9), we get one equation with two unknowns, $\lambda_H$ and $\lambda_{LGM}$. All other terms are calculated in ICECAP. This equation is simplified as the following:

$$6.2\% = F(\lambda_{LGM}) - F(\lambda_H)$$

(13)

Where $F(\lambda_{LGM})$ and $F(\lambda_H)$ are functions of the unknown terms $\lambda_{LGM}$ and $\lambda_H$, respectively.

Assuming that the stratosphere to troposphere flux of O$_3$ has not changed significantly over the industrial era, we can use present-day stratospheric-sourced O$_3$ to represent [O$_3$]$_{strat,H}$. In ICECAP, the present day annual mean tropospheric O$_3$ concentration originating from the stratosphere in the northern mid- to high-latitudes is $0.32 \times 10^{12}$ molecule/cm$^3$ (13.6 ppbv), representing ~ 22% of total ozone concentration in this region over the entire troposphere. This fraction is within the range of stratospheric contribution to tropospheric ozone estimated by other models (e.g., Hess and Lamarque$^{66}$, and Hess et al.$^{67}$).

[O$_3$]$_{LH}$ in ICECAP is $0.49 \times 10^{12}$ molecule/cm$^3$ (20.8 ppbv), so that $\lambda_L$ is 1.66 according to equation (7). The $A$-value in the Holocene from the ICECAP model and calculated in Equation (8) is $A_H = 0.74$, compared to 0.65 when including only \textit{in-situ} produced O$_3$ in the troposphere. Including both stratospheric-sourced O$_3$ and \textit{in-situ} produced O$_3$ in the troposphere, the
calculated mean $\Delta^{17}\text{O}(\text{NO}_3)$ value northern mid- to high-latitudes in the Holocene is 28.9 $\%\text{o}$, which is consistent with the observed $\Delta^{17}\text{O}(\text{NO}_3)$ value of $(29.4 \pm 0.7)\%\text{o}$ in the Holocene.

With known $\lambda_{4t} = x$, we can then solve equation (13) for $\lambda_{LGM}$, resulting in values of $\lambda_{LGM} = 4.10$ and 3.29 for the warm and cold LGM, respectively. In ICECAP, tropospheric, annual-mean $[\text{O}_3]_i$ is 0.36 and 0.30 molecule/cm$^3$ (15.5 and 12.8 ppbv) for the warm and cold LGM, respectively, in the northern mid- to high-latitudes. According to equation (7), $[\text{O}_3]_{\text{strat}}$ is then 1.12 and 0.69 molecule/cm$^3$ (47.9 and 29.5 ppbv) in the warm and cold LGM in this region, respectively, representing 75.6 % and 69.7 % of the total tropospheric ozone abundance in each glacial scenario. We then can calculate the changes in stratospheric-sourced $\text{O}_3$ between the LGM and Holocene using the following equation:

$$z = \frac{[\text{O}_3]_{s_{LGM}} - [\text{O}_3]_{s_{H}}}{[\text{O}_3]_{s_{H}}}$$

where 'z' represents the fractional change in stratospheric-sourced $\text{O}_3$ from the LGM to the Holocene. Equation 14 yields $z = 252\%$ and $118\%$ for the warm and cold LGM climate, respectively. This means that the tropospheric concentration of stratospheric-sourced $\text{O}_3$ must increase by 251 % and 118 % in the warm and cold LGM compared to the Holocene, respectively, in the northern mid-to high-latitudes, in order to explain the entirety of the observed change in $\Delta^{17}\text{O}(\text{NO}_3)$. The calculated stratospheric-sourced $\text{O}_3$ is higher in the warm LGM than the cold LGM. This is because the relative importance of BrONO$_2$ hydrolysis is increased more in the cold than warm LGM (Supplementary Table 1), leading to less stratospheric-soured $\text{O}_3$ needed to explain the ice core $\Delta^{17}\text{O}(\text{NO}_3)$ record.

We note, however, the calculated 118-252 % increase in stratospheric-sourced $\text{O}_3$ through STT from the Holocene to LGM is probably a high-end estimate. The chemistry simulated by
ICECAP may underestimate the role of N$_2$O$_5$ and BrONO$_2$ hydrolysis in the LGM due to the lack of a sea-salt aerosol source from the sea ice. Sea salt aerosols promote N$_2$O$_5$ and BrONO$_2$ hydrolysis and is also important for the production of reactive bromine which leads to BrONO$_2$. Additionally, and increased BDC in cold climates will tend to increase the stratospheric O$_3$ column abundance in the mid- to high-latitudes, resulting in a decreased HO$_x$ production rate and an increased O$_3$/HO$_x$ ratio. In sum, there are large uncertainties regarding the magnitude of our estimated increase in stratospheric-sourced O$_3$, and we expect that our calculated 118-252% increase in stratospheric-sourced O$_3$ is an upper limit. However, the observed glacial interglacial variability in $\Delta^{17}$O(NO$_3^-$) is difficult to explain from tropospheric chemistry alone. More observational and modeling work is needed to reduce the uncertainty. We also note the estimated increase in stratospheric-sourced O$_3$ may be a result of a variety of processes, caused not only by an enhanced BDC but also increased stratospheric O$_3$ abundance due to lower CH$_4$ and N$_2$O abundances in the glacial climate, and/or increases in synoptic-scale processes such as tropopause folding events$^{68-69}$. More research is required to examine the causes, and to assess the magnitude, of the observed increases in STT in the glacial climate.

S4. Other potential factors influencing $\Delta^{17}$O(NO$_3^-$)

S4.1. Effects of post-depositional processing of snow nitrate on GISP2 $\Delta^{17}$O(NO$_3^-$)

Post-depositional processing of snow nitrate occurs in the air-snow interface, and includes evaporation or desorption of HNO$_3$ from snow and the UV photolysis of snow nitrate$^{70-71}$. The latter is recognized as the main process influencing the preservation of nitrate and its isotopic signal in snow and ice cores$^{72-73}$. The main photo-product, NO$_x$, is quickly transported from the snowpack to the overlying atmosphere through wind pumping$^{74-76}$, where it is re-oxidized to nitrate. Reformation of nitrate from the photo-products in the condensed phase of snow grains
(i.e., the disorganized layer of snow grain surface) also occurs if the nitrate being photolyzed is trapped inside the snow grain instead of on its surface\textsuperscript{77}.

The recycling in the air-snow interface replaces the regional atmospheric $\Delta^{17}$O(NO$_3^-$) signal with a local signal by reforming nitrate under local tropospheric oxidant conditions. Because UV photolysis of snow nitrate only happens during periods of sunlight (mainly in the summer months), this tends to lower $\Delta^{17}$O in the reformed nitrate compared to the originally deposited nitrate\textsuperscript{78}, but overall the snow $\Delta^{17}$O(NO$_3^-$) still represents atmospheric conditions. In contrast, recycling in the condensed phase erases the atmospheric signal preserved in $\Delta^{17}$O(NO$_3^-$) by exchanging oxygen atoms with water that possesses zero $\Delta^{17}$O, and therefore forms nitrate with very low $\Delta^{17}$O(NO$_3^-$) compared with the originally deposited nitrate\textsuperscript{72}. The degree of post-depositional processing of snow nitrate is influenced mainly by surface UV intensity, snow accumulation rate, and snow UV light-absorbing impurities (UV-LAI) (e.g., organics, dust and black carbon)\textsuperscript{73,76,79}. Field observations from East Antarctic snowpits\textsuperscript{72} indicate that at sites with snow accumulation rates greater than 0.1 m ice a$^{-1}$, the effect of nitrate recycling in the condensed phase on snow $\Delta^{17}$O(NO$_3^-$) is negligible under present day Antarctic snow UV-LAI concentrations. The reason seems to be that nitrate trapped inside snow grains will not be effectively photolyzed until the snow stays in the photic zone long enough so that photolabile nitrate is attenuated\textsuperscript{77}.

For the GISP2 ice core, the snow accumulation rate falls below 0.1 m ice a$^{-1}$ frequently during the glacial climate (Figure 2b). This appears to suggest that $\Delta^{17}$O(NO$_3^-$) in the GISP2 ice core may lose its atmospheric signal by some degree in the glacial climate. However, in the glacial period, snow UV-LAI concentrations are much higher than that in Antarctic snow in the present day\textsuperscript{60} which tends to decrease the depth of the photic zone and will limit recycling in the
condensed phase by lowering the amount of time snow nitrate spends in the snow photic zone. This is evident by the $\delta^{15}\text{N(NO}_3^-)$ record from the GISP2 ice core$^{80}$. The highest glacial $\delta^{15}\text{N(NO}_3^-)$ value in GISP2 core (38.9 ± 0.3‰) is equivalent to the asymptotic $\delta^{15}\text{N(NO}_3^-)$ value (the value after nitrate is buried below the photic zone)$^{72}$ at sites with snow accumulation rates of 0.12 - 0.16 m ice a$^{-1}$. This suggests that in the glacial period, even though snow accumulation rates at Summit sometimes fall below 0.1 m ice a$^{-1}$ over the time period reported here, nitrate recycling in the condensed phase is negligible due to the shallower photic zone caused by higher LAI concentrations.

In addition, based on the record of $\delta^{15}\text{N(NO}_3^-)$ in the GISP2 ice core$^{80}$, we have estimated that the degree of post-depositional processing of snow nitrate is greater in the last glacial period compared to the Holocene. This effect alone will drive $\Delta^{17}\text{O(NO}_3^-)$ to be lower in the glacial period compared to the Holocene, which is the opposite of what is observed. Therefore, trends in the $\Delta^{17}\text{O(NO}_3^-)$ record from the GISP2 ice core over the time periods considered here cannot be the result of changes in post-depositional processing. It is however possible that the higher degree of post-depositional processing in the glacial climate is muting the effect of changes in oxidants on the record, making the observed changes in $\Delta^{17}\text{O(NO}_3^-)$ a lower limit proxy for climate-driven variability in oxidant abundances.

**S4.2. Potential effects of stratospheric denitrification**

Stratospheric denitrification refers to the sedimentation process of Polar Stratospheric Clouds (PSCs) containing nitric acid trihydrate. Research on nitrate in Antarctic snow$^{81}$ has suggested that stratospheric denitrification associated with the winter polar vortex could result in a late winter/early spring nitrate concentration maximum in snow. This is supported by measurements of $\Delta^{17}\text{O(NO}_3^-)$ in the boundary layer and surface snow in East Antarctica$^{82}$, which
show a strong influence of stratospheric nitrate which possesses higher $\Delta^{17}$O(NO$_3^-$) than nitrate formed in the troposphere. In the present climate, due to the warmer winter and the weaker and less persistent Arctic vortex compared to Antarctica, denitrification occurs less frequently and less extensively in the Arctic$^{83}$. There is currently no observational evidence that suggests that significant stratospheric nitrate input occurs in the Arctic troposphere, consistent with model simulations that the stratospheric contribution of nitrate to Greenland is negligible$^{41}$.

In the glacial period, due to decreased greenhouse gas burdens, the stratosphere is predicted to be warmer than the Holocene, and with a weaker polar vortex compared to today$^{84}$ despite dynamical changes in atmospheric circulation in the northern high latitudes due to the growth of continental ice sheet. Thus, the contribution of stratospheric nitrate to Greenland is expected to be weaker in the glacial period compared to the Holocene. This will tend to lower ice-core $\Delta^{17}$O(NO$_3^-$) in the glacial period, opposite to the observations. Thus, it is unlikely that variability in stratospheric denitrification in the Arctic can explain the observed variability in $\Delta^{17}$O(NO$_3^-$) reported here.

**Supplementary Table 1.** Annual mean production rate and fraction of each terminal reaction from NO$_2$ to HNO$_3$, the A-value and the calculated $\Delta^{17}$O(NO$_3^-$) value in northern mid-to high-latitudes in each climate scenario predicted by ICECAP, using tropospheric O$_3$ from *in situ* production only (i.e., the effect of stratospheric-sourced ozone is not included).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>OH oxidation</th>
<th>NO$_3^+$DMS/VOC</th>
<th>N$_2$O$_5$ hydrolysis</th>
<th>BrONO$_2$ hydrolysis</th>
<th>A-value</th>
<th>$\Delta^{17}$O (NO$_3^-$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holocene</td>
<td>4085.9</td>
<td>72.6</td>
<td>500.4</td>
<td>434.1</td>
<td>0.74</td>
<td>24.4 (28.9)</td>
</tr>
<tr>
<td>Cold-LGM</td>
<td>426.7</td>
<td>64.3</td>
<td>15.8</td>
<td>153.5</td>
<td>0.51</td>
<td>21.9 (35.1)</td>
</tr>
<tr>
<td>Warm-LGM</td>
<td>871.2</td>
<td>73.8</td>
<td>32.9</td>
<td>166.2</td>
<td>0.54</td>
<td>21.1 (35.1)</td>
</tr>
</tbody>
</table>

*Values in parenthesis are the calculated A-value and $\Delta^{17}$O(NO$_3^-$) with the effects of STT of O$_3$. 
References:


