Article

Acidity-driven gas-particle partitioning of nitrate regulates its transport to Arctic through the industrial era

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Anthropogenic NO_x emissions have altered the biogeochemical nitrogen cycle since the Industrial Revolution, yet Arctic ice core nitrate (NO₃⁻) records are inconsistent with post-1970s NO_x emission reductions. Here we show a NO₃⁻ deposition history covering 1800–2020 using an ice core from the southeastern Greenland dome with high snow accumulation. The ice core NO₃⁻ concentrations are particularly disconnected from NO_x source regions during the peak pollution period and post-1990s. A global chemical transport model reproduced these discordances between total NO₃⁻ and NO_x emissions by altering gaseous HNO₃ and particulate NO₃⁻ (p-NO₃⁻) ratios and subsequently NO₃⁻ lifetime. This result and correlations with acidity parameters recorded in the ice core, suggest that acidity-driven gas-particle partitioning of NO₃⁻ regulates its transport to Arctic regions alongside changes in NO_x emissions. In the future, despite NO_x reductions, the increase in proportion of p-NO₃⁻ with longer atmospheric lifetime becomes crucial to control the Arctic NO₃⁻ burden.

 NO_3^- and its precursors ($NO_x = NO + NO_2$) play important roles for both the atmosphere (i.e., particulate matter¹, climate system^{2,3}, and oxidative capacity through the formation of ozone (O_3)⁴) and biosphere^{5,6}. Global atmospheric models all agree that anthropogenic activities have resulted in a dramatic increase in atmospheric NO_3^- burden through the Industrial Era^{2,7,8}, although the magnitude of the increase remains highly uncertain owing to order of magnitude variability in atmospheric NO_3^- burden among models^{9,10}. Despite efforts to curb NO_x emissions in recent decades, the unexpectedly slow particulate NO_3^- reduction in a wide area of the Northern Hemisphere underscores the importance of understanding atmospheric NO_3^- dynamics beyond precursor NO_x emission¹¹⁻¹⁴.

Atmospheric NO₃⁻ exists as gaseous HNO₃ and particulate NO₃⁻ (p-NO₃⁻). While both forms can undergo wet and dry depositions¹⁵, HNO₃ is more readily removed due to its high solubility, whereas the p-NO₃⁻, generally in the form of NH₄NO₃ in fine-mode particles, is less prone to local deposition and supports long-range transport¹⁶. Thus, the shift in gas-particle partitioning toward p-NO₃⁻, driven by physical

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factors, such as liquid water content and temperature and by chemical factors like atmospheric acidity-especially changes in aerosol pH-can influence the distribution and deposition pattern of NO₃^{-12,17-19}. In recent decades, the persistent accumulation of atmospheric p-NO₃⁻ due to atmospheric neutralisation has been observed in the vicinity of anthropogenic NO_x source regions^{12,14,20}. These studies have primarily focused on the persistence of particulate matter from the perspective of air quality in major source regions, often highlighting the buffering effect of gas-particle partitioning in maintaining p-NO₃⁻ concentrations despite reductions in NO_x and SO₂ emissions. In contrast, over longer timescales-particularly since the Industrial Revolution, including periods of dramatic atmospheric acidification-the impact of this buffering mechanism on the longrange transport, spatial distribution, and deposition of NO₃⁻ in remote regions sensitive to environmental changes (e.g., the Arctic) remains poorly understood.

Greenland ice cores are archives for reconstructing changes in atmospheric species in response to anthropogenic activities in the Northern Hemisphere^{21–23}. The atmospheric NO_3^- in the Arctic region is mainly removed through wet deposition²⁴⁻²⁶ and deposits on the ice sheet. However, NO₃⁻ concentration (hereafter [NO₃⁻]) in Greenland ice cores are influenced not only by atmospheric deposition²³ but also by post-depositional processes such as photolytic loss and subsequent recycling²⁷⁻²⁹. In addition, snow accumulation in central Greenland (e.g., Summit site) is dominated by summer snow³⁰, introducing seasonal bias to NO3⁻ deposition associated with seasonally distinct NOx sources. Due to these uncertainties, while the increase in Greenland ice core [NO₃⁻] since the Industrial Revolution is attributed to anthropogenic activities²¹, a decrease in ice core $[NO_3^-]$ has not been clearly observed despite the suppression of NO_x emissions since the 1970s³¹, and these factors have not yet been comprehensively interpreted at a mechanistic level.

The ice core from the Greenland SE-Dome region (67.18°N, 36.37°W, 3170 m a.s.l.), drilled to 90 m in 2015 (SE-Dome I³²) and to 250 m in 2021 (SE-Dome II³³), is contextually highly desirable owing to its high accumulation rate at $\sim 1 \,\mathrm{m\,yr^{-1}}$ in water equivalents^{34,35}, the highest among Antarctic and Greenland ice domes. The SE-Dome region is characterised by minimal post-depositional NO₃⁻ loss, as regions with snow accumulation rates exceeding 50 cm yr⁻¹ in water equivalents typically bury deposited NO₃⁻ within approximately half a month^{34,36}. Furthermore, regional snow accumulation is constant throughout the year³⁴ (Supplementary Fig. S1), suggesting a negligible seasonal bias for NO₃⁻ deposition. Here, we reconstructed seasonally resolved NO₃⁻ deposition history from the SE-Dome II ice core covering 220 years (1800 to 2020 AD) from pre-industrial times (PI) to present-day (PD). By comparing the well-preserved atmospheric SE-Dome II NO₃⁻ records with NO_x emission inventories from source regions, we determined that, in addition to precursor NO_x emission changes, variations in atmospheric acidity influence the magnitude of NO₃⁻ transport and deposition to Arctic regions by altering the gasparticle partitioning.

Results

Annual average $[NO_3^{-}]$ from 1800 to 2020 in SE-Dome II ice core Annual $[NO_3^{-}]$ in the SE-Dome II ice core are presented in Fig. 1a. Pursuant to a previous study³⁷, the present study focused on concentrations, which more accurately reflect atmospheric abundance in high accumulation areas than the flux. The annual $[NO_3^{-}]$ of the SE-Dome II was 24.4 ± 9.2 µg kg⁻¹ on average for 1801–1850 (PI), increasing from the 1850s to reach a maximum of 72.0 ± 18.9 µg kg⁻¹ from 1971 through 2000. After the 2000s, $[NO_3^{-}]$ decreased slightly but maintained high values (65.7 ± 14.1 µg kg⁻¹) between 2011 and 2020. NO_3^{-} flux trends in the SE-Dome I ice core for 1960–2014³¹ showed similar interannual variability (see Supplementary Notes (SN) 1, Supplementary Fig. S2), ensuring the robustness of our data. By defining the 1970–2000 period as the peak of anthropogenic NO_3^- deposition in Greenland [pollution peak (PP)]²³, with 1800–1850 as the PI baseline, a [NO_3^-] ratio of 2.91 between these periods was obtained.

Comparison between ice core NO₃⁻ and NO_x emission inventory To focus on the variation in anthropogenic NO₃⁻, which is primarily influenced by human activities such as fossil fuel combustion, industrial emissions, and agriculture-related fertilisation, the [NO₃⁻] trend was normalised after subtracting the 1800–1850 (PI) average, which represents the baseline level of natural NO₃⁻ (see Methods). Figure 1b shows the comparison between normalised [NO₃⁻] and anthropogenic NO_x emission inventories from the Former Soviet Union (FSU), North America (NA), and Europe (EU) and provides a trendline with their combination (TRAJ). Despite the increase in Asian NO_x emissions after the 2000s, the Asian contribution to NO₃⁻ in the SE-Dome region remained minimal and did not affect the main conclusion of this study (see SN 2 and Supplementary Fig. S3).

Normalised $[NO_3^-]$ peaked at approximately 3 at PP (1970–2000) (Fig. 1b). The normalised NO_x emission inventories for EU, NA, and TRAJ showed similar increases of 3–4 in PP but were relatively higher at up to 5 for FSU. The NO_x emissions from TRAJ regions roughly agree with the $[NO_3^-]$ increase from PI to PP, indicating that the $[NO_3^-]$ trend from 1800 to 2020 was primarily driven by anthropogenic NO_x emissions from surrounding countries, although the peak $[NO_3^-]$ remains slightly lower than that of the surrounding regions. $[NO_3^-]$ began increasing from 1870 to 1920 before the increase in NO_x emissions (Fig. 1b). This discrepancy and its cause have been discussed elsewhere³⁸(see SN 3).

The $[NO_3^-]$ and NO_x emission trends thus show general agreement; however, the $[NO_3^-]$ increase in the SE-Dome from 1920 to 1970 was more gradual than the corresponding rise in NO_x emissions (Fig. 1b). Conversely, the $[NO_3^-]$ decrease after the 1990s was slower than the significant reductions in NO_x emissions (Fig. 1b). This slow response of $[NO_3^-]$ to drastic changes in NO_x emission is a contrasting result to the case of $[SO_4^{2-}]$ in ice cores that corresponds well with that of SO_2 emission in surrounding countries³⁹. This result highlights that there are other factors controlling the magnitude of NO_3^- transported to the Arctic region from the precursor NO_x emissions.

The PP/PI ratios of $[NO_3^-]$ in other Greenland ice cores were about 2 or lower (Supplementary Figs. S2, S4, see SN 4) possibly due to geographical reasons (e.g., distance from the source regions), post-depositional NO_3^- losses²³ and/or seasonal bias due to summertime snow accumulation³⁰. Notably, the $[NO_3^-]$ trends among several Greenland ice cores during the Industrial Era were similar to those of the SE-Dome ice core; $[NO_3^-]$ increased more slowly from 1940 to 1970 and decreased more slowly after the 1990s than NO_x emissions (Supplementary Fig. S2). This similarity ensures the spatial robustness of the discordance between $[NO_3^-]$ and NO_x over Greenland, not merely a local phenomenon at the SE-Dome site (see SN 4).

Correlation between $\Delta(NO_3^- - NO_x)$ and ice core chemistry

We investigated the 30 years running mean of the difference between normalised ice core [NO₃⁻] and the annual normalised NO_x emissions [Δ (NO₃⁻ – NO_x)] (Fig. 2a). The Δ (NO₃⁻ – NO_x) showed negative and positive values during 1920–1970 and 1990–2020, respectively. To identify the factors explaining the pattern and discordance between NO_x emission to [NO₃⁻] records, Δ (NO₃⁻ – NO_x) was compared with the various chemical and meteorological factors that could affect the transport behaviour of atmospheric NO₃⁻ (Fig. 3 and Supplementary Fig. S5, and SN 5). In this correlation assessment, the period prior to 1920 was excluded due to the low [NH₄⁺] data (often below the detection limit), the lack of meteorological data before 1900, and the aforementioned issue with the reliability of NO_x emission inventory between 1870 and 1920 (see SN 3).



Fig. 1 | **Annual [NO₃⁻] at the SE-Dome and NO_x emission inventory from 1800 to 2020.** a Annual (grey dot) and 30-year running average (black) of $[NO_3^-]$. **b** Normalised 30-year running average of $[NO_3^-]$ (black), and anthropogenic NO_x emissions from North America (NA, orange), Europe (EU, purple), and the Former Soviet Union (FSU, light blue). Trajectory-based blend (TRAJ, green) from the Former Soviet Union: North America: Europe = 1:4:2 according to the air-mass origins calculated via quantitative back-trajectory analysis³¹.

Among the variables, the $\Delta(NO_3^- - NO_x)$ after 1920 was significantly (p < 0.01) correlated with the atmospheric acidity-related parameters and cation species preserved in the ice core: ionic balance [H⁺] (r = -0.41, Fig. 3a), [nss-SO₄²⁻] (r = -0.52, Fig. 3b), gas ratio (GR, defined as ([NH₄⁺]-2[nss-SO₄²⁻])/[NO₃⁻]¹⁵) (r = 0.65, Fig. 3c) and [Ca²⁺] (r = 0.60, Fig. 3d), while the lack of a significant correlation to meteorological factors, such as air temperature over the North Atlantic regions (r = 0.17) and NAO index (r = 0.25) (Supplementary Fig. S5). These results imply that the change of the $\Delta(NO_3^- - NO_x)$ were related to chemical processes after NO_x emissions, rather than changes in atmospheric dynamics nor meteorological conditions.

NO₃⁻ exists in two forms. HNO₃ and p-NO₃⁻, which have different lifetimes and deposition velocities, and changes in their partitioning can significantly influence the amount of NO₃⁻ transported over long distances^{12,17,18}. This gas-particle partitioning is primarily governed by the acidity and liquid water content of fine-mode aerosols^{40,41}. In fact, as shown in Fig. 3a, b, $\Delta(NO_3^- - NO_x)$ showed a stronger correlation with [nss-SO₄²⁻], the main driver of fine-mode aerosol acidity¹⁵, than that with [H+], which does not necessarily represent the acidity of finemode aerosols due to the influence of coarse-mode ions, such as Ca2+ and Na⁺ originating from mineral dust and sea salt⁴². Furthermore, the observed higher correlation with GR (Fig. 3c), which is a simple representation of free ammonia available for NH₄NO₃ particle formation^{15,43}, further supports the above-mentioned process driven by changes in atmospheric acidity. Other acidity-related parameters, such as [NH₄⁺]/[nss-SO₄²⁻], also showed significant correlations (Supplementary Fig. S5, see SN 5). The more accurate proxy of free ammonia, adjusted gas ratio (adjGR, defined as ([NH₃] + [NO₃⁻])/ $([HNO_3] + [NO_3^{-}]))^{44}$, is not applicable because it requires separate p-NO₃⁻ and HNO₃ concentrations, which are not available from [NO₃⁻] in the ice core representing a mixture of both.

The correlation with $[Ca^{2+}]$ (Fig. 3d), primarily from mineral dust, suggested that the uptake of HNO₃ by coarse-mode dust particles also led to efficient dry deposition of NO₃⁻ onto the ice sheet. However, the correlation with $[Ca^{2+}]$ became significantly stronger only after the 1990s, when $[Ca^{2+}]$ and insoluble dust concentration in the SE-Dome I ice core began to rise as a result of emissions from local coastal Greenland⁴⁵. Notably, limited amount of Ca²⁺ in the ice core available to pair with NO₃⁻ (Supplementary Fig. S6 and SN 6) indicates that this process was of secondary importance in explaining $\Delta(NO_3^- - NO_x)$.



Fig. 2 | Ice core and model comparison of temporal changes in the difference between normalised $[NO_3^-]$ and NO_x emission ($\Delta(NO_3^- - NO_x)$) and acidity related parameters. a $\Delta(NO_3^- - NO_y)$ derived from ice core records (solid lines) and GEOS-Chem simulations (dashed lines). The solid lines were calculated using the ice core [NO3-] compared with CEDS NOx emissions from North America (NA, orange), Europe (EU, purple), and trajectory-based blend (TRAJ, green) regions. The dashed lines were calculated from the modelled NO₃⁻ deposition in the SE-Dome grid compared with CEDS NOx emissions in the model for Eastern North America (ENA, orange), Western Europe (WE, purple), and TRAJ regions (TRAJ, blue-green). **b** Gas ratio (GR): ([NH₄⁺]-2[nss-SO₄²⁻])/[NO₃⁻] for ice core observation (grey, annual data; black, 30 years running average), and ([NH4+] + [NH3] -2[nss-SO42-])/([p- $NO_3^{-1} + [HNO_3]$) from the modelled annual mean tropospheric concentrations over TRAJ region (blue-green). c Modelled planetary boundary layer mean aerosol pH for fine-mode particles over the TRAJ region (blue-green). Markers and shadows in (b, c) represent median and inter-quartile range, respectively, of variables over the model grids in the TRAJ region (- 90° to 30°E and 45° to 90°N, n = 300).

Acidity-driven partitioning of HNO_3 and p-NO_3^- in the GEOS-Chem model

To examine the importance of gas-particle partitioning between HNO₃ and p-NO₃⁻ in changes in transport and deposition patterns of total NO₃⁻ in response to anthropogenic emissions, global tropospheric chemistry was simulated using the GEOS-Chem chemical transport model. In the historical experiment, the meteorological fields were fixed to those in 1986 and only emissions were varied from 1800 to 2019 (see Methods), and responses of spatial and temporal variations of atmospheric NO₃⁻ were investigated. Throughout the entire period, atmospheric total NO₃⁻ (sum of HNO₃ and p-NO₃⁻) deposition at the SE-Dome site in the model was predominantly derived from wet deposition (Fig. 4w and Supplementary Fig. S7), consistent with observations in the Arctic^{24–26}. Figure 2a shows the modelled $\Delta(NO_3^- - NO_x)$ values using sum of wet and dry NO3⁻ depositions in the SE-Dome grid and NO_x emissions from different source regions (ENA, WE, and TRAJ). The modelled $\Delta(NO_3^- - NO_x)$ values were relatively constant until 1950, decreased until 1986, and increased up to PD, aligning with the observed post-1950 trend (Fig. 2a). This pattern covaried with the modelled GR values (Fig. 2b), and consequently aerosol pH in TRAJ region (Fig. 2c). We note that the temporal variations in aerosol pH are consistent with those reported by Zhai et al.⁴⁶, showing a more gradual increase in pH after the PP compared to the change from PI to PP. Thus, the modelled $\Delta(NO_3^- - NO_x)$ trends largely reproduced those observed in the SE-Dome ice core (Fig. 2a) and confirmed a connection with the



Fig. 3 | Scatter plots of the difference between normalised [NO₃⁻] and normalised NO_x emission in the TRAJ region [Δ (NO₃⁻ – NO_{x TRAJ})] as functions of atmospheric acidity related parameters in the SE-Dome II ice core. Δ (NO₃⁻ – NO_{x TRAJ}) was compared to (**a**) ionic balance [H⁺]

 $\{ ([NO_3^{-}] + [CI^{-}] + 2[SO_4^{2-}]) - ([NH_4^{+}] + [Na^{+}] + 2[Ca^{2+}]) \} (\mu mol kg^{-1}), (b) [nss-SO_4^{2-}] (\mu g kg^{-1}), (c) gas ratio (GR) (mol mol^{-1}), and (d) [Ca^{2+}] (\mu g kg^{-1}). The colour scale represents the year. Regression lines were fitted for the periods 1800–2019 (grey) and 1920–2019 (black).$

partitioning of HNO₃ and p-NO₃⁻ between acidity related parameters and Δ (NO₃⁻ – NO_x).

Based on this result, we investigated the changes in transport and deposition patterns of NO_3^{-} in the model (Fig. 4). The modelled surface p-NO₃⁻ to total-NO₃⁻ ratio (ε) in ENA, WE, and TRAJ regions commonly declined during PP (1973, Fig. 4j) and increased after NO_x reduction (2013, Fig. 4n). Reflecting a faster dry deposition rate of HNO₃ than that of p-NO₃⁻¹⁶, the changes in ε values resulted in the increased dry deposition ratio to total NO3⁻ deposition from PI (1850 and 1900, Fig. 4 c and g) to PP (1973, Fig. 4k) and its decrease to PD (2013 and 2019, Fig. 40 and s) in these three regions (Fig. 4w). Because of the changes in deposition velocity, the lifetime (τ_{NO3}) of t-NO₃⁻ also decreased until 1973 (Fig. 4l), followed by an increase through PD (2019) (Fig. 4t), as shown in Fig. 4x. These results are consistent with the role of gasparticle partitioning in nitrate transport discussed by Geng et al.¹⁹, in the regard that HNO₃ is more abundant than p-NO₃⁻ and its fraction increased during PP. However, our findings suggest that the rapid dry deposition of HNO₃ near source regions limits its long-range transport, altering the overall magnitude of NO₃⁻ transported over long distances. This contrasts with the mechanism proposed by Geng et al.¹⁹, which assumes that low- $\delta^{15}N$ HNO₃ is preferentially transported and preserved in ice cores. Further research is needed to fully verify these differences. Overall, the model represents the evolution of atmospheric acidity leading to the changes in gas-particle partitioning of HNO₃ and p-NO₃⁻, reasonably explaining changes in NO₃⁻ transport and the $\Delta(NO_3^- - NO_x)$.

Notably, the changes in ε and dry deposition ratio were less pronounced in WE than those in ENA (Fig. 4v and w). The intriguing differences between ENA and WE are likely due to variations in relative humidity and acidity, which regulate their dry deposition velocity as discussed by Nenes et al.¹⁶ (see Supplementary Fig. S7 and SN 7). The tropospheric concentration of peroxyacetyl nitrate (PAN), a dominant species in atmospheric reactive nitrogen whose thermal decomposition is possibly a non-negligible NO_x source in the Arctic region⁴⁷, responded linearly to anthropogenic NO_x emissions (Supplementary Fig. S8) and did not serve as an explanatory factor to the variability of the modelled Δ (NO₃⁻ – NO_x) (see SN 8).

Potential factors controlling NO_3^- transport and limitations of the model

Nonetheless, there are still limitations in the model regarding the effects of acidity and the associated gas-particle partitioning. Indeed, certain discrepancies remain between observation and model results in this study (see Fig. 2a and Supplementary Fig. S9 and SN 9), with the most critical issue being the overestimation of the modelled NO_3^- deposition in SE-Dome region compared to the observed ice core $[NO_3^-]$ after 1920s by approximately a factor of 2 (Supplementary Fig. S9c). This could be associated with a long-standing problem of an overestimate of t- NO_3^- in the remote atmosphere in the model¹⁸, with recent studies suggesting that this may be attributed to an underestimation of the rainout and washout processes for nitric acid and nitrate⁴⁸. Incorporating these deposition processes into the future model is expected to reduce the discrepancy between the model and ice core NO_3^- concentrations.

However, other limitations exist in this study, which will need to be addressed in future research. The gas-particle partitioning in GEOS-Chem used in this study was governed by the aerosol thermodynamic model ISORROPIA II, which mainly accounted for the formation of finemode NH₄NO₃^{49,50}. With these models, a large uncertainty remained in the pH calculations, particularly regarding cation components, such as Na⁺ and Ca²⁺ as pointed out by Pye et al. ¹⁵. Notably, [Ca²⁺] and [Na⁺] had increased in the SE-Dome ice core since 1990 (Supplementary Fig. S6), but these components were not accurately considered in the model. Furthermore, the model did not capture possible changes in the formation of coarse-mode p-NO₃⁻ on mineral dust or sea salt, such as in the form of Ca(NO₃)₂ and NaNO₃, which proceeded efficient dry deposition compared to fine-mode particles^{S1}. They could both decrease and increase the modelled ice core [NO₃⁻] concentrations.



Fig. 4 | **Modelled historical changes in NO₃⁻ transport and deposition patterns. a**-**t** Spatial distributions in annual mass-weighted average of tropospheric total NO₃⁻ (t-NO₃⁻) (**a**, **e**, **i**, **m**, **q**), particulate NO₃⁻ (p-NO₃⁻) ratio to t-NO₃⁻ (ε) in the surface layer (**b**, **f**, **j**, **n**, **r**), dry deposition ratio to t-NO₃⁻ deposition (**c**, **g**, **k**, **o**, **s**), and atmospheric lifetime of t-NO₃⁻ (τ_{NO3} , defined as the column amount divided by the deposition flux) (**d**, **h**, **l**, **p**, **t**) in 1850 (**a**-**d**), 1900 (**e**-**h**), 1973 (**i**-**l**), 2013 (**m**-**p**), and

2019 (**q**-t). **u**-**x** Regional averages of tropospheric t-NO₃⁻ concentration (**u**), surface ε (**v**), dry deposition ratio (**w**), and τ _{NO3} (**x**). Different line colours in (**u**-**x**) represent variables averaged over different regions: 10-day back trajectory region from SE-Dome (TRAJ, bluegreen), Eastern North America (ENA, orange), Western Europe (WE, purple), and SE-Dome grid (magenta), as indicated in (**a**).

The decrease could occur by shortening the overall lifetime through an increase in the coarse-mode $p-NO_3^-$ fraction during transport, while the increase could be due to promoting dry deposition over the Greenland ice sheet. We note that the model sensitivity test considering HNO₃ uptake on dust particles¹⁸ resulted in less than a 2% decrease in t-NO₃⁻ depositions in the SE-Dome grid. However, this is a conservative estimate, due to the uncertainties in the uptake coefficient and the absence of high-latitude dust sources in the model⁵² (see SN 9).

Other parameters must also be taken into account for factors beyond changes in atmospheric acidity. The model used in this study was unlikely to accurately capture decadal changes in aerosol liquid water content, which is another key factor influencing the gas-particle partitioning of NO₃⁻⁴¹, due to the fixed meteorological field including temperature and humidity (see Methods and SN 9). Although PAN was not necessarily critical in reproducing the variation of the Δ (NO₃⁻ – NO_x) values in this model, considering the impacts of the recent global warming, especially in the Arctic, temperature-dependent PAN decomposition could influence the spatiotemporal variability of PAN-derived NO_x and NO₃⁻ deposition (see SN 8). In addition, the GEOS-Chem model version used in the present study did not account for recent findings, such as increased reactive nitrogen lifetime due to NO₃⁻ photolysis⁵³⁻⁵⁵, although this process itself does not completely explain the discrepancy (SN 9).

Overall, while this study broadly reproduced the $\Delta(NO_3^- - NO_x)$ values and highlighted the importance of atmospheric acidity in modifying gas-particle partitioning, factors including those mentioned above should be carefully considered in future models to accurately capture the magnitude of long-range transport of reactive nitrogen to remote regions like the Arctic. The reconstructed NO_3^- deposition in SE-Dome II provides a valuable archive to constrain these uncertainties.

This study reconstructed the variations from the pre-industrial era to the present using NO_3^- records from SE-Dome ice core, which is characterised by minimal post-depositional NO_3^- loss and seasonal biases. It demonstrated that these NO_3^- variations reflect not only

changes in NO_x emissions in the source regions but also shifts in gasparticle partitioning driven by changes in atmospheric acidity. In particular, we revealed that changes in atmospheric acidity alter the atmospheric lifetime of total nitrate (t-NO₃⁻), thereby controlling its long-range transport and subsequent deposition patterns in remote regions. While the dampening of atmospheric $p-NO_3^-$ reduction caused by increased NH₃ and decreased SO₂ emissions is now recognised in major anthropogenic regions in the world^{11-14,17,20}, our results suggest that the scale of this impact may be hemispheric as evidenced in long-term aerosol p-NO₃⁻ observations at Alert⁵⁶. This trend in anthropogenic emission change is predicted to continue through 2050 under the Shared Socioeconomic Pathways (SSP) 2-4.5 scenario⁵⁷. Furthermore, the SE-Dome ice-core record indicates that NO₃⁻ has become the dominant inorganic anion in the Arctic aerosols since the 1990s, mirroring decreased SO₂ emissions and SO₄²⁻ concentrations (Supplementary Fig. S6). Considering that the net climate impacts of reactive nitrogen due to aerosol scattering of solar radiation and oxidants supply for regulating greenhouse gas lifetimes³, the persistent $t-NO_3^-$ loading in the Arctic atmosphere is a critical issue in this climatically sensitive region⁵⁸. In addition, air quality and climate concerns involve impacts on O₃ burden due to the significant role of p-NO₃⁻ photolysis in O₃ formation in remote and Arctic regions⁵³⁻⁵⁵.

With regard to accurate future predictions and assessments of atmospheric NO₃⁻, minimising uncertainties associated with transport and deposition patterns of NO₃⁻ in chemical transport models is crucial. However, the inter-model variability of NO₃⁻ simulation remains larger than that for SO₄²⁻, largely owing to the different representations of gas-particle partitioning for both fine-mode and coarse-mode p-NO₃⁻ among models¹⁰. Although our comparison of ice core observations and GEOS-Chem modelling suggests good overall agreement, feedback from acidity-driven changes in NO₃⁻ lifetime by modifying gas-particle partitioning may be overestimated in the model. Multi-phase chemistry dependent on atmospheric acidity remains a significant challenge in atmospheric chemistry, with high uncertainty for atmospheric dry NO₃⁻ deposition¹⁵.

Reducing this uncertainty requires refining atmospheric acidity modelling, gas-particle partitioning, and HNO_3 and $p-NO_3^-$ atmospheric lifetimes. An increased dust supply from the Greenland margin areas after $2000^{45.52}$ could add significant uncertainty to the deposition pattern of NO_3^- through the HNO_3 acid uptake. The $[NO_3^-]$ record from the SE-Dome II ice core, reported herein, provides a uniquely well-preserved and high temporal resolution archive essential for validating such key model parameters.

Methods

SE-Dome II ice core and age scale

We used a 250 m depth ice core obtained at a dome site on the SE-Dome (67.18°N, 36.37°W, 3170 m a.s.l³³.). The annual mean temperature at the SE-Dome was – 20.9 °C³². For a timescale, we used the age scale for 1800–2020 determined by Kawakami et al.³⁵. The age scale was carefully evaluated using independent age markers and its precision was within a half year and could thus produce precise ion concentrations and/or flux in annual resolution.

Analytical method of ion concentrations

In a cold room (class 10000) at the Institute of Low Temperature Science, Hokkaido University, Japan, the ice core was divided into 50 mm-depth sections, except for the top 5 m, where the low firn density necessitated 100 mm sections, using a clean ceramic knife, put into a cleaned polyethene bottle, and melted at + 20 °C in a clean room. Ion concentrations (Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, Ca²⁺, and NH₄⁺) were measured using ion chromatography [Thermo Scientific ICS-2100 (Thermo Fisher Scientific, Waltham, MA, USA); Dionex CS-12A column (Thermo Fisher Scientific) and 20 mM MSA eluent for cations; Dionex AS-18A column (Thermo Fisher Scientific) and 23-mM KOH eluent for anions]. The injection volume was 1000 µL for anions and 500 µL for cations. The analytical precision for ion concentration measurements was 10%, and the detection limit was $0.1 \,\mu g \, kg^{-1}$ for NO₃⁻. A total of 4948 samples, covering AD 1800 to 2020, were analysed, corresponding to 23 samples per year on average. In several samples, the Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, Ca²⁺, and NH₄⁺ concentrations were below the detection limit and were thus regarded as zero. To confirm that analytical errors did not cause any large peak in ion concentrations, samples with significantly different values from two adjacent samples, based on a 3-point running standard deviation $(>3\sigma)$, were re-measured with another ice sample from the same depth. Surface decontamination and sample melting were conducted within 1 week and 1 day, respectively, of the ion chromatography measurement.

Calculation of annual $[NO_3^-]$ and the related ion concentrations, normalised $[NO_3^-]$ and NO_x emissions

The $[NO_3^-]$ (n = 4948) were averaged per year (n = 221; from 1800 to 2020), as a boundary on 1 January from the age scale³⁵. The annual $[NO_3]$ average error was roughly 2% (10 / $\sqrt{22}$), depending on the analytical error (10%) and number of data averaged (n = 22). Annual $[Cl^{-}]$, $[SO_4^{2-}]$, $[Na^{+}]$, $[NH_4^{+}]$, and $[Ca^{2+}]$ were calculated in the same manner. Ionic balance (H⁺ concentration) was calculated as the difference of total anion minus total cation concentrations $\{[Cl^{-}] + 2[SO_4^{2^{-}}] + [NO_3^{-}] - ([Na^+] + [NH_4^{+}] + 2[Ca^{2^+}]) \text{ in } \mu \text{mol } \text{kg}^{-1}\}.$ Nonsea salt [SO₄²⁻] ([nss-SO₄²⁻], µmol kg⁻¹) were calculated by subtracting the sea-salt fraction ([ss-SO₄^{2–}] = 0.060 [Na⁺]) from total [SO₄^{2–}], i.e., $[nss-SO_4^{2-}] = [SO_4^{2-}] - [ss-SO_4^{2-}]$. GR was calculated by $[NH_4^+] - 2[nss-SO_4^{2-}]$ SO_4^{2-}])/[NO_3⁻] in molar ratio with assuming ice core [NO_3⁻] and [NH₄⁺] represent the sum of depositions of their gas and particulate form. Annual NO₃⁻ ion fluxes (n = 221; from 1800 to 2020) were based on the annual average [NO₃⁻] value multiplied by the annual accumulation rate determined by Kawakami et al.³⁵. The annual accumulation rate error depends on the density and timescale error used. This study used the timescale defined by Kawakami et al.³⁵, resulting in an error in density less than 1% per 1 mm, which is negligible compared with the $[\rm NO_3^-]$ error (2%).

In this study, to analyse the relative changes in anthropogenic NO₃, we distinguished between anthropogenic and natural sources of NO_3^- and normalised the data to allow for a comparable analysis of their changes. Anthropogenic NO₃⁻ primarily originates from NO_x emissions associated with industrial activities, such as the combustion of coal, oil, and natural gas. In addition, NO₃⁻ derived from soil NO_x emissions due to agricultural fertilisation was also considered an anthropogenic source. Natural NO₃⁻ sources includes lightning, biomass burning, and natural soil NO_x emissions. Whereas there is no observational evidence on the historical changes in natural NO₃⁻ sources, a modelling exercise considering all these anthropogenic and natural sources shows that more than 90% of global NO_x emission increases from PI to PD are driven by anthropogenic sources⁵⁹. Furthermore, a global database of biomass burning emissions shows that the significant increase of biomass burning since 1990s are mainly at the tropics of South America and Asia, and that in North America and Europe regions are largely unchanged⁶⁰. Therefore, we assumed that natural source NO₃⁻ remain constant throughout the entire period in the following process.

In the normalisation process, we first used the average ice core $[NO_3^-]$ during the pre-industrial period (1800–1850) as the baseline for natural source NO_3^- . For each year, the baseline was subtracted from the annual mean ice core $[NO_3^-]$ to estimate the anthropogenic NO_3^- contribution. We then normalised the annual anthropogenic NO_3^- values by dividing them with the average anthropogenic NO_3^- values over the entire period (1800–2020).

The anthropogenic NO_x emissions from multiple sectors, including agriculture, were obtained from the Community Emissions Data System (CEDS) inventory (http://globalchange.umd.edu/ceds/)^{61,62}. The annual NO_x emissions of NA (orange in Fig. 1), EU (purple in Fig. 1), and FSU (blue in Fig. 1) were extracted. These data were also normalised by dividing by the average values for the period 1800–2020, making the NO₃⁻ and NO_x emission datasets comparable, since natural NO_x emissions are not included in the CEDS data. The TRAJ line (green in Fig. 1) was calculated as a blend of NA:EU:FSU = 4:2:1 following the air-mass contribution from NA, EU, FSU of 0.2, 0.1, 0.05, respectively, when the whole was set as 1, based on the 7-d back trajectory analysis using the HYSPLIT model³¹.

Reanalysis climate data and index

The air temperature data were extracted from the Hudcurt5 reanalysis distributed by the Met Office Hadley Centre and the Climatic Research Unit at the University of East Anglia⁶³, and the relative humidity data from over-centennial atmospheric data assimilation (OCADA) reanalysis developed by the Meteorological Research Institute, Japan⁶⁴. The annual air temperature anomalies (1895–2019) and tropospheric average of relative humidity (1900–2015) were extracted at the SE-Dome site (67.4°N, 36.4°W) and North Atlantic Ocean region (50–60°N, 25–55°W). We used the annual NAO index (1836-2019) distributed by the NOAA-CIRES-DOE Twentieth Century Reanalysis (20CR) project⁶⁵ and the annual AO index (1950–2015) distributed by NOAA, Climate Prediction Centre⁶⁶ for a proxy of climatic spatial pattern in the North Atlantic Ocean and Arctic Ocean, respectively.

GEOS-Chem chemical transport model

GEOS-Chem is a global three-dimensional atmospheric chemistry transport model (www.geos-chem.org) developed by Bey et al.⁶⁷. GEOS-Chem version 12.5.0 (https://doi.org/10.5281/zenodo.3403111) driven by assimilated meteorological fields was used from the MERRA-2 reanalysis data product from NASA Global Modelling and Assimilation Office's GEOS-5 Data Assimilation System. To unravel variations driven by changes in anthropogenic emissions, a series of simulations

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dating from 1800 to 2019 (1800, 1825, 1850, 1975, 1900, 1925, 1950, 1960, 1973, 1986, 1999, 2013, and 2019) at a 25-year temporal resolution before 1950 and 13-year temporal resolution after 1960 were conducted. According to the method of Hattori et al.⁶⁸, the models consider the same meteorology (year 1986) but changing anthropogenic and biomass burning emissions. For anthropogenic emissions, including soil emissions from agricultural sectors, the CEDS inventory was used^{61,62}, same as the NO_x inventory used for the comparison to ice core NO3-. Emission species from CEDS included aerosols [black carbon (BC) and organic carbon (OC)], aerosol precursors, and reactive compounds [SO₂, NO_x, NH₃, CO, and non-methane volatile organic carbon (NMVOC)]. The biomass-burning emissions were used from the CMIP6 inventory (BB4CMIP) for individual years⁶⁰. Emission species from BB4CMIP included BC, CH₄, CO, NH₃, NMVOC, NO_x , OC, SO_2 , and HCl. Note that the year-to-year variability of NO_x emission from BB4CMIP has the relatively small impact (~1%) to NO3deposition at SE-Dome (see SN 9), ensuring our conclusion based on the modelling results is not influenced by the choice of year. Latitudinal CH₄ concentrations were prescribed for historical simulations. For years after 1979, CH₄ concentrations were based on the National Oceanic and Atmospheric Administration Earth System Research Laboratory (NOAA/ESRL) Global Monitoring Division flask observations http://esrl.noaa.gov/gmd/ccgg/trends_ch4/), and for years before 1979, the CMIP6 monthly mean surface CH₄ was used⁶⁹. Dry and wet depositions of gas and aerosol species were simulated based on the general schemes in GEOS-Chem⁷⁰⁻⁷². Peroxyacetyl nitrate (PAN), whose long-range transport and subsequent thermal decomposition supplies NO_x in the Arctic region⁴⁷, was simulated following Fischer et al.⁷³. The model was spun up for 1 year before each of the years simulated.

The thermodynamic partitioning of HNO₃ to fine mode p-NO₃⁻ was computed using ISORROPIA II^{49,50}. The module with assuming aerosol particles in the form of supersaturated solutions (i.e., the metastable state) and solving the forward problem using the total gas and aerosol concentrations of species as inputs (i.e., forward mode) to avoid the unrealistic aerosol pH⁷⁴. The gas-particle equilibrium partitioning was computed every 20 min timestep in each grid. Because the meteorological fields are fixed and only emissions are varied in the historical experiments, the physical parameters used to calculate partitioning, such as temperature and relative humidity, are the same across years. The coarse mode $p-NO_3^-$ is formed by the adsorption of HNO₃ on sea salt aerosols and is treated as a separate tracer than the fine mode p-NO₃⁻⁷⁵. The adsorption of HNO₃ on dust was not included in this study because of its limited impact within the dust outflow regions of the mid-latitude¹⁸ and a lack of high-latitude dust sources in the model^{18,52} (see SN 9).

The primary sources of NO₃⁻ to the Arctic region are Eastern North America (ENA) and Western Europe (WE). NO_x emissions were extracted over ENA (-90° to -60° E, 30° to 60° N, n = 56), WE (-15° to 40° E, 40° to 70° N, n = 72), and TRAJ (-90° to 30° E and 45° to 90° N, n = 300) (Fig. 4a) based on computed 10-d back trajectories according to a previous study⁶⁸. NO₃⁻ deposition, including both dry and wet depositions, was extracted from the SE-Dome grid (-37.5° to -32.5° E, 62° to 66° N, n = 1) and converted to ice core [NO₃⁻] by dividing by annual total precipitation. The modelled normalised [NO₃⁻] in the SE-Dome grid and NO_x emissions from source regions were calculated in the same manner as those for ice core observations (see section above). To do this for the modelled [NO₃⁻] and NO_x emissions, 220 annual values throughout the 1800–2019 period were calculated by interpolating the model results of the 13 discrete years.

GR from the model was calculated as $([NH_4^+] + [NH_3] - 2[SO_4^{-2}])/([p-NO_3^-] + [HNO_3])$, with considering gas and aerosol species separately unlike the ice core data, using the annual mean tropospheric concentrations over TRAJ region. Fine particle pH (recorded as

Chem_phSav in the model) was also extracted for the TRAJ region and averaged over the boundary layer. The ratio of $p-NO_3^-$ to $t-NO_3^-$ (ε) was calculated as $\varepsilon = [p-NO_3^-] / ([p-NO_3^-] + [HNO_3])$ for the surface layer in the model. The atmospheric lifetime of $t-NO_3^-$ (τ_{NO3}) was calculated in each horizontal grid by dividing the tropospheric column $t-NO_3^-$ amount by the $t-NO_3^-$ deposition flux.

Data availability

The ice core and model data generated in this study have been deposited in Figshare⁷⁶ (https://doi.org/10.6084/m9.figshare. 25941562) and the Hokkaido University Collection of Scholarly and Academic papers, HUSCAP (http://hdl.handle.net/2115/94521). Source data are provided with this paper. Physical and chemical data, including ion concentration and flux of the SE-Dome I ice core, are available from HUSCAP (https://eprints.lib.hokudai.ac.jp/dspace/handle/2115/67127). The other ice core data supporting the findings of this study are publicly available online as follows: Summit, NEEM, and EGRIP data were cited from https://doi.org/10.1073/pnas. 1319441111, https://doi.org/10.1594/PANGAEA.940553, and https://doi.org/10.1594/PANGAEA.940572.

Code availability

The GEOS-Chem model version used in this study is available at https://doi.org/10.5281/zenodo.5500717. The Python codes and associated raw model outputs used for analyses are available upon request to the corresponding authors.

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Author contributions

Y.I. and S.M. planned this study and conducted the SE-Dome ice core project administration. Y.I., M.M., K.K., M.S. and S.M. contributed to the measurement of ion concentrations. S.I. and S.H. conducted GEOS-Chem model simulations. Y.I., S.I., S.H. and S.M. conducted the data analyses. Y.I. S.I. and S.H. wrote the manuscript. Y.I. S.I. and K.F. prepared figures. Y.I., S.I., S.H., H.M., N.O. and S.M. acquired the funding. R.U., H.M., K.F., N.O., A. Spolaor, A. Svensson, B.M.V., H.O., O.S. and S.M. interpreted the results and provided comments on the manuscript. Y.I., S.I., and S.H. contributed equally to this work.

Competing interests

The authors declare no competing interests.

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Supplementary Notes, Figures, and Reference for:

Acidity-driven gas-particle partitioning of nitrate regulates its transport to Arctic through the industrial era

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Supplementary Notes (SN)

SN 1: Detailed description of NO₃⁻ concentrations from 1800 to 2020

The annual average concentrations and flux of NO_3^- in SE-Dome II ice core were calculated and compared with the data from SE-Dome I ice core¹ for the period of 1960-2014 (Fig. S2a). The NO_3^- fluxes in two SE-Dome ice cores I and II show an almost identical trend and interannual variability for 1960-2014, including the specific NO_3^- peaks in 1987 and 1992 (Fig. S2a). This synchronous trend supports homogeneous local deposition of NO_3^- in the SE-Dome region. Also, NO_3^- concentration and flux in SE-Dome II ice core show consistent variations throughout 1800-2020 because annual accumulation rate is almost constant during 1800-2020². This study uses NO_3^- concentration data ($[NO_3^-]$) for discussion, which more accurately reflects atmospheric aerosol abundance in high accumulation areas, such as in southern Greenland, compared to flux³.

In the main text, to focus on the long-term trend of $[NO_3^-]$ through 1800 to 2020, we mainly used the 30-year running mean values annealing the $[NO_3^-]$ peaks in several specific years. The $[NO_3^-]$ peaks were identified as the differences of more than 30 µg kg⁻¹ between the annual $[NO_3^-]$ and the 30-year running mean, deriving 1803, 1966, 1968, 1977, 1987, 1992, 2000, and 2012 (Fig. S2c). Most of the peaks coincided with the significant $[NH_4^+]$ peaks (Fig. S2c), suggesting they may be attributed to the forest fire events⁴, while the possibility of other sources or unusual atmospheric circulation patterns cannot be ruled out. The NO_x emission inventory by the Community Emissions Data System (CEDS)⁵ shows gradual trend and no such peak in a specific year, ensuring the use of the 30-year running mean values to analyse the changes associated with anthropogenic emission.

Taking advantage of the high accumulation ice core, we also calculated summer and winter $[NO_3^-]$ (Fig. S2b), while these are semi-quantitative values because of a half-year precision dating². $[NO_3^-]$ of a 3-months resolution was first calculated from the timescale described in Kawakami et al.². The seasonal boundaries were set to 1 March, 1 June, 1 September, and 1 December for spring (MAM), summer (JJA), autumn (SON), and winter (DJF). In the same manner as the annual data (see Materials and Methods in the main text), the error in the seasonal average of $[NO_3^-]$ was roughly 4% (10 / $\sqrt{6}$). However, Kawakami et al.² used tie points every half year, such that the seasonal timescale loses reliability when the boundaries were far from the tie points. In this study, we used summer and winter $[NO_3^-]$, which include the tie points.

Summer and winter average $[NO_3^-]$ displayed a trend similar to that for annual data, but with high and low values in summer and winter, respectively. This seasonality is consistent with previous studies from central Greenland⁶, while the source of increased summer $[NO_3^-]$ is under a debate. Based on the previous work from SE-Dome I ice core, the seasonal average snow accumulation rate during 1960-2014 suggested snow precipitation occurs evenly in four seasons

at the SE-Dome site⁷. Seasonal H_2O_2 cycle shape, an annual radiation change proxy, did not remarkably differ between 1800-1960 and 1960-2015², suggesting constant snow precipitation in this region throughout the respective year, even before 1960. These results indicate that [NO₃⁻] seasonality in the SE-Dome II core is caused by atmospheric variation with minimal seasonal accumulation bias.

SN 2: The influence from Asian NO_x emissions to SE-Dome region

The backward trajectory analysis indicates that the air-mass originates mainly from WE and ENA⁸, but the contribution to the Arctic NO₃⁻ from anthropogenic NO_x emissions from East Asian Countries (China, Korea, Japan, and Mongolia) remains to be a concern because it has been increasing since 1990s and can influence $\Delta(NO_3^- - NO_x)$ for that period. To examine this, we simulate the same model used in the main text with and without NO_x emissions from East Asia (90° to 145°E, 20° to 65°N) for the year 1850, 1973, and 2013. The input data and setup of the simulation are detailed in Materials and Methods in the main text. Fig. S3 shows the difference of annual total- NO_3^- (t- NO_3^- = HNO_3 + p- NO_3^-) deposition around Greenland in 2013 of 1) the base case with NO_x emissions from all countries (BASE, Fig. S3) and 2) the case with the anthropogenic NO_x emissions from East Asia turned off (noAsiaNO_x, Fig. S3). The result shows that $t-NO_3^-$ deposition at SE-Dome grid is 5.3% lower in the noAsiaNO_x simulation than BASE, indicating that 5.3% of the NO_3^- deposited in the SE-Dome region may have been transported from East Asia. Since 2013 was the year with the highest NO_x emissions from East Asia through 1800-2020 according to the emission database, it can be assumed that the contribution from East Asia to the SE-Dome NO₃⁻ is minor throughout the studied period, particularly for post-1940, the period of our focus in the main text. Indeed, the contributions from East Asia estimated for the year 1850 and 1973 were 9.1% and 2.0%, respectively.

There remain debates about the potential contributions of the dust and $SO_4^{2^-}$ transported from Asia to Greenland^{9–12}. Therefore, the Asian contribution of NO_3^- cannot be completely ignored. The validity of the percentage of Asia contribution estimated in this study (5.3%) may also be questioned by future improvements of aerosol transport models. However, to the present, NO_3^- records in Greenland ice cores have rarely been discussed due to the concerns on the postdepositional NO_3^- loss and seasonal biases in NO_3^- deposition, and thus the understanding on source apportionment is still limited. The extent of contribution from Asia to NO_3^- deposition in Greenland is a topic for future research.

SN 3: The discrepancy between ice core [NO₃⁻] and NO_x emission from 1870 to 1920.

 $[NO_3^-]$ in the SE-Dome II ice core rise from 1870 prior to increase of NO_x emissions, peaking before declining in 1920 (Fig. 1a). This pattern, consistent with other Greenland ice core

records^{13,14}, may reflect impacts from forest fires^{4,15,16} or anthropogenic emissions during the coal combustion era. However, emission data from CEDS for anthropogenic sources (Fig. 1b) and BB4CMIP for forest fires¹⁷ show a stable trend from 1870 to 1920. The CMIP6 inventory, combining CEDS and BB4CMIP, fails to document the known black carbon peak from North America between 1880-1920¹⁸, indicating a probable gap in NO_x emission records for the same period.

SN 4: Comparison of the normalised [NO₃⁻] with other Greenland ice cores

In Fig. S2d, we compared the trend in the SE-Dome $[NO_3^-]$ with those in other Greenland ice cores from Summit¹³, NEEM¹⁴, and EGRIP¹⁹. Here we evaluated the relative changes of $[NO_3^-]$ from the 1800-1900 average values (normalised $[NO_3^-]_{1800-1900}$ hereafter), instead of the period 1800-1850 as used in Fig. 1b, to better fit the available dataset by Röthlisberger et al.²⁰. This normalisation procedure gives a peak value of 2.71 during PP for the SE-Dome II ice core, which is clearly higher than those for Summit (2.02), NEEM (2.10), and EGRIP (1.91).

The high value of the SE-Dome II ice core can possibly be attributed to (i) geographical reasons (*e.g.* distance from the source regions), (ii) a minimal post-depositional effect of NO₃⁻ and (iii) a less seasonal bias of snow accumulation. Fig. S4c shows the NO₃⁻ concentration ratio between the period of 1970-2000 and 1800-1900 (R_{NO3}) compared to annual accumulation rate (C_{ann}), both from the series of Greenland ice cores^{13,14,19,20}. As the C_{ann} increases, the R_{NO3} increases exponentially, which is expressed as $C_{ann} = e^{AR_{NO3}}$ with a constant value A of 1.67 ($R^2 = 0.80$ and p < 0.001). On the other hand, the other factors of altitude, latitude, and annual air temperature show no significant correlation with R_{NO3} . These results suggest that the accumulation rate is a key factor determining the normalised [NO₃⁻], possibly due to the less post-depositional loss of NO₃⁻ at the higher accumulation site²¹. In addition, the normalised winter [NO₃⁻] (5.78) at PP is twice as large as that of summer (2.64) (Fig. S2b), possibly explaining the high R_{NO3} in the SE-Dome II ice core by the steady winter precipitation in the SE-Dome region, in contrast to the summer dominant snow accumulation at other coastal Greenland sites²² and Summit²³ (Fig. S1). These results suggest a good preservation of deposited NO₃⁻ in the SE-Dome II ice core.

Despite these differences in magnitudes, these three Greenland ice cores (NEEM, Summit, and EGIRP) exhibit qualitatively similar variations to those observed in the SE-Dome ice core (Fig. S2d). $[NO_3^-]$ levels remain fairly constant and low until around 1950, then increase, peaking between 1990 and 2000 (Fig. S2d). Although recent data are limited, $[NO_3^-]$ does not show a clear decline after their peaks, unlike NO_x emissions from source regions which peak around 1970–1980 and subsequently decrease (see Fig. 1b in the main text). Thus, the findings

observed in SE-Dome closely align with those from other ice cores, which indicates that these trends in ice core $[NO_3^-]$ result from regional to global scale phenomena such as long-range transport of anthropogenic NO_3^- from the Northern Hemisphere.

SN 5: Detailed description of correlations between $\Delta(NO_3^- - NO_x)$ and various chemical and meteorological parameters

The chemical and meteorological parameters used for comparison to $\Delta(NO_3^- - NO_x)$ (Fig. 2, 3, and S5) were chosen in the following reasons. As introduced in the main text, the atmospheric acidity is known to be a key factor affecting gas-particle partitioning of NO₃⁻ and thus its transport and deposition patterns^{24–27}. Therefore, we used the ion concentration data from the SE-Dome II ice core (non-sea-salt sulfate ([nss-SO₄²⁻]), [NH₄⁺], [Na⁺], and [Ca²⁺]) as well as proxies of atmospheric acidity²⁸. Nss-SO₄²⁻ and NH₄⁺ are major components of acidity and alkalinity, respectively, forming fine-mode particles together with NO₃^{-29,30}. Na⁺ and Ca²⁺ supplied from coarse-mode sea salt and mineral dust particles, respectively, also affect the acidity by the uptake of acids including HNO₃ and their subsequent deposition^{31,32}. Among the atmospheric acidity proxies summarized by Pye et al.²⁸, we avoid proxies that require gas- or particle-phase concentration of NO₃⁻ because ions preserved in ice cores represent mixture of them (i.e., t-NO₃⁻ (HNO₃ + p-NO₃⁻)). Consequently, three parameters were chosen for our analysis: ionic balance ([H⁺] = ([NO₃⁻] + [CI⁻] + [SO₄²⁻]) – ([NH₄⁺] + [Na⁺] + [Ca²⁺]) (in µeq kg⁻¹)), ammonium-to-sulfate ratio ([NH₄⁺]/[nssSO₄²⁻] (in mol mol⁻¹)), and gas ratio (GR = ([NH₄⁺] – 2[nssSO₄²⁻])/[NO₃⁻] (in mol mol⁻¹)).

The transport behavior of t-NO₃⁻ can be also affected by meteorological factors such as air temperature, humidity, precipitation, and air-mass transport pattern. Temperature and relative humidity are two determinant factors of liquid water content of aerosol surface and thus impact gas-particle partitioning of NO₃⁻³³. Here we used Hudcrut5 air temperatures since 1885³⁴ as well as relative humidity data from OCADA reanalysis since 1900³⁵ for the comparison to Δ (NO₃⁻ – NO_x). The data were extracted over the troposphere of North Atlantic Ocean region (50-60°N, 25-55°W) and SE-Dome site (67°N, 36°W). Annual accumulation rate in SE-Dome II ice core² was used as a proxy of precipitation. North Atlantic Oscillation (NAO) index since 1836 from 20CR ver.2³⁶ and Arctic Oscillation (AO) index since 1950³⁷ were used as proxies of air-mass transport pattern from NO_x source regions to the Arctic.

The correlation between the $\Delta(NO_3^- - NO_x)$ and the above proxies are shown in Fig. S5. As mentioned in the main text, given the $[NH_4^+]$ data lower than the detection limit and the lack of meteorological data before 1900, as well as the issue with the reliability of NO_x emission data between 1870 and 1920 (see SN 3), here we focus on the period of 1920-2019 (numbers shown in black in Fig. S5). With the criteria of p < 0.01 for the period of 1920-2019, the significant

correlations were found for 7 parameters out of 14: GR (Fig. S5g, r = 0.65), [Ca²⁺] (Fig. S5d, r = 0.60), [NH₄⁺]/[nssSO₄²⁻] ratio (Fig. S5f, r = 0.56), [nssSO₄²⁻] (Fig. S5a, r = -0.54), [H⁺] (Fig. S5e, r = -0.41), [Na⁺] (Fig. S5c, r = 0.37), and air temperature at SE-Dome site (Fig. S5j, r = 0.36). Six of them are indicators of atmospheric acidity derived from the ice core data. In contrast, the physical parameters except for the temperature at SE-Dome showed insignificant correlations. As concluded in the main text, these results imply that the change of the $\Delta(NO_3^- - NO_x)$ observed in the SE-Dome II ice core is the result of acidity-related processes, rather than changes in atmospheric dynamics nor meteorological conditions.

In addition to the parameters discussed in the main text, Na⁺ is also likely involved in the acidity-driven control of t-NO₃⁻ lifetime (Fig. S5c). Similar to the case of Ca²⁺, Na⁺ in SE-Dome II ice core shows a significant increasing trend since 2000s (Fig. S6). Given the role of sea salt particles for HNO₃ uptake³¹ and the efficient dry deposition of coarse-mode particles³⁸, the positive correlation between $\Delta(NO_3^- - NO_x)$ and Na⁺ suggests that the increased sea salt particles are locally facilitating the deposition of t-NO₃⁻ onto the Greenland ice sheet unlike the enhanced long-range transport in the form of p-NO₃⁻. Note that, however, given that the Na⁺ amount in the ice core is insufficient to pair with NO₃⁻ even after 2000s, this process is also likely of secondary importance in explaining the decadal changes in $\Delta(NO_3^- - NO_x)$, similarly to the case of Ca²⁺.

Air temperature at SE-Dome site showed a significant correlation with $\Delta(NO_3^- - NO_x)$ in the physical parameters (Fig. S5j). One possible explanation is that the partitioning of t-NO₃⁻ to HNO₃ is locally increasing in response to the recent Arctic warming, possibly resulting in the rapid local deposition of HNO₃. In addition, given that the recent Arctic warming is associated with the retreat of glacier and sea ice^{39,40}, the local t-NO₃⁻ deposition could be further facilitated by the recent increase in atmospheric mineral dust and sea salt particles forming coarse-mode p-NO₃⁻ as discussed above. Another possible consequence of the local temperature variation is the thermal decomposition of peroxyacetyl nitrate (PAN), that could increase local NO_x supply to form NO₃⁻ (see SN 8).

SN 6: Decadal average values of each ion concentration from 1800 to 2020 in SE-Dome ice core

Fig. S6 shows the decadal means of each ion concentration. For the period 1801-1850, both anion and cation concentrations are low and the total anion concentration is about 1.0 μ eq L⁻¹ while the total cation concentration is about 0.5 μ eq L⁻¹. For the period 1941-1990, the total anion concentration increased to 2.0 – 3.0 μ eq L⁻¹ due to the increase of anthropogenic NO₃⁻ and SO₄²⁻ while the total cation concentration less increased up to about 0.8 μ eq L⁻¹. For the period 1991-2020, the total anion concentration slightly decreases due to the emission control while the total concentration of cations reaches a maximum value of 1.0 - 1.8 μ eq L⁻¹ over the past 220

years. The NH₄⁺ increase during 1991-2020 is due to anthropogenic emission^{5,41}. The Na⁺ could be a result of increased local sea salt emission from open leads in the Arctic region⁴², while future investigation is needed. The Ca²⁺ could be a result of increased local dust emission from coastal region in Greenland⁴³. This increased cations (NH₄⁺, Na⁺ and Ca²⁺) with the decrease in SO₄²⁻ since 1990 would have increased the abundance of NH₄NO₃, NaNO₃, and Ca(NO₃)₂ decreased the [H⁺] (Fig. 3a), suggesting atmospheric oxidation chemistry related to atmospheric acidity has changed in a more neutral atmospheric environment⁸. The subsequent increase in the abundance of p-NO₃⁻ in the atmosphere is expected to increase atmospheric lifetime and have allowed longrange transport to the Arctic region, resulting in the dampened decrease of [NO₃⁻] in the SE-Dome II ice core (see main text).

We note that the transport mechanism of $p-NO_3^-$ can be different among the cations paired with NO_3^- . NH_4^+ and NO_3^- are both originated from gaseous species with forming NH_4NO_3 salts, making it small particles. On the other hand, most of Na^+ in the atmosphere are derived from sea salt and dust, and thus, $NaNO_3$ and $Ca(NO_3)_2$ formed by modification of NH_4NO_3 by sea salt and dust tends to form coarse particles. Given that coarse particles have a shorter atmospheric lifetime than fine particles, an increase in Na^+ and Ca^{2+} may result in less $p-NO_3^-$ transport from emission area to the polar regions than the case of an increase in NH_4^+ alone. On the other hand, dust nitrate including $Ca(NO_3)_2$ may enforce the long-range transport of NO_3^- in particulate state^{25,44}. Overall, future study is needed to estimate accurate $p-NO_3^-$ transportation with different cation pairs.

SN 7: Regional differences of HNO₃ and p-NO₃⁻ deposition patterns

As shown in Fig. S7, gas-particle partitioning and NO_3^- deposition patterns for the SE-Dome, ENA and WE, reveal distinct trends. In both ENA and WE, HNO₃ is the dominant species for NO₃⁻ deposition (Fig. S7h and i), with relative proportion of p-NO₃⁻ decreasing from PI to PP period, and then increasing up to the PD period, showing a consistent trend described in the main text. However, WE displays relatively higher ε values than ENA, with p-NO₃⁻ accounting for approximately 50% for atmospheric t-NO₃⁻ (Fig. S7j) and 20% of the total deposition in WE (Fig. S7l). Consequently, WE shows higher atmospheric t-NO₃⁻ concentrations compared to ENA but demonstrates lower local deposition (Figs. S7i and k compared to Figs. S7e and g), indicating a higher potential for long-range transport. Although our previous studies¹ have suggested that while ENA and WE contribute similarly in terms of air-mass trajectory, SE-Dome may experience a more significant influence from WE due to these differences in transport properties. This aligns with findings by Nenes et al.²⁷, which indicate that ENA tends to exhibit lower aerosol pH levels compared to WE, resulting in a greater total NO₃⁻ deposition flux in the United States compared to northern Europe. Although local deposition velocity differences are not the main focus of this study, they represent a critical factor in determining NO_3^- transport to polar regions that should be considered in the future study.

SN 8: Potential contribution of peroxyacetyl nitrate (PAN) to the Arctic nitrate and its influence to $\Delta(NO_3^- - NO_x)$ values

Peroxyacetyl nitrate (PAN), mainly formed in the urban atmosphere via a reversible reaction between oxidation products of NMVOCs and NO_2^{45} , is a principal reservoir of NO_x^{46} and thus a potentially important source of NO_2 in the Arctic region⁴⁷. Whereas NO_2 production by the thermal decomposition of PAN is strictly limited to ca. 1 pptv hr⁻¹ by the low temperature during winter and spring, it could supply non-negligible amount of NO_2 up to 10 pptv hr⁻¹ during summer⁴⁷. The local production of NO_3^- from this PAN-sourced NO_2 in the Arctic could be influenced by the global and Arctic warming⁴⁸, and partially explain the delayed peak in NO_3^- deposition in the ice cores. However, the compensating effect owing to the warming is expected between the reduction of PAN supply to the Arctic due to the enhanced decomposition during the long-range transport, and the increase of the local decomposition rate in the Arctic region.

The GEOS-Chem simulation in this study cannot quantify the impact of the temporal changes in PAN decomposition to the NO_3^- deposition in the ice core since we used the constant meteorological field of 1986, including temperature, throughout 1800 to 2019, to focus on the influence by the changes in atmospheric acidity (see Methods). As a result, the tropospheric PAN concentration around SE-Dome region shows a monotonous decreasing trend since 1973 (Fig. S8), with no delay from the NO_x emission reduction. This result indicates that PAN supply to the Arctic is reduced in response to emission reduction of precursors NMVOCs and NO_x in source regions, even without considering its enhanced decomposition enroute to the Arctic. Therefore, while remains to be an area of future research, the delayed peak of t-NO₃⁻ relative to NO_x emission reduction within our simulation is not explained by the changes in the local NO₃⁻ production through PAN decomposition, but by the acidity-driven process discussed in the main text.

SN 9: Model limitations and discrepancies between observation and model

Here we describe the limitations in the setup of our model simulations which add uncertainties in t-NO₃⁻ transport behavior and thus the decadal trend in Δ (NO₃⁻ – NO_x). First, we used the fixed meteorological field of 1986 with different emissions for corresponding years to focus on the changes in atmospheric acidity (see Methods in the main text). As a result, we did not consider decadal changes in temperature for modulating the gas–particle partitioning of NO₃⁻ in this study, although it depends on not only atmospheric acidity but also by temperature and liquid water content of aerosol^{27,33}. Since the Industrial Revolution, the Arctic region has experienced a temperature increase of approximately 2 to 3°C, and decadal mean surface air

temperatures were 0.7-0.95°C lower around 1970 than those around 1940 due to the impact of anthropogenic aerosols⁴⁹. This could have led to the more partitioning to p-NO₃⁻ and longer lifetime of t-NO₃⁻ during the PP period. This is the opposite effect to the observed negative $\Delta(NO_3^- - NO_x)$ in that period (Fig. 2a) and therefore possibly important for precisely reproduce its magnitude.

Second, we did not consider uptake of HNO₃ on mineral dust particles⁴⁴, based on a model sensitivity test with this process for the year 2013 showing only 1% reduction in total (sum of wet and dry) t-NO₃⁻ deposition at the SE-Dome grid compared to the base simulation. This is in line with Fairlie et al.⁴⁴, who successfully reproduced p-NO₃⁻ amount on dust in transpacific dust plumes but found that this process has the limited impact on atmospheric t-NO₃⁻ burden and cannot solve the long-standing problem of model's overestimate of t-NO₃⁻ by a factor of 2-3. However, we note that this is a modest estimate, because Fairlie et al.⁴⁴ adopted the uptake coefficient for HNO₃ on dust of ~10⁻³ for GEOS-Chem which is relatively low among a large uncertainty ranging 10^{-4} to $0.1^{50,51}$. Adopting higher values for the uptake coefficient could cause larger reduction of t-NO₃⁻ deposition at the SE-Dome by enhancing the deposition of p-NO₃⁻ with coarse dust particles enroute to Greenland. Furthermore, as shown from our ice core observation (Fig. 3d), HNO₃ uptake on dust could increase in ice core [NO₃⁻] by promoting the deposition of p-NO₃⁻ over the Greenland ice sheet. However, this process cannot be tested within the present study because the model does not account dust emissions from high latitude regions recently identified⁵².

Third, although HNO₃ uptake on sea salt particles are represented in our simulations, there lacks the representation of sea-ice sourced sea salt particles, such as sublimation of blowing snow⁵³ and emission from sea ice leads⁴². As discussed in SN 5 along with the positive correlation between the $\Delta(NO_3^- - NO_x)$ and Na⁺ (Fig. S5c), it is expected that the implementation of these sea-ice sourced sea salt particles to the model would increase NO₃⁻ deposition in the Arctic region including SE-Dome grid. The temporal changes of those processes in response to the intensification of surface winds and the sea ice reduction under the ongoing Arctic warming is unexplored area of research⁵⁴, indicating importance of continued studies for these processes in the future. Note that, however, our ice core observation suggests that this process is likely at lower priority in explaining the $\Delta(NO_3^- - NO_x)$ (see SN 5).

In addition, we have confirmed that the uncertainty comes from the year-to-year variability of biomass burning would be limited to ~1% for total NO₃⁻ deposition at SE-Dome grid, by comparing the simulation of continuous two years (2012 and 2013) with a large difference in NO_x emission from biomass burning¹⁷. p-NO₃⁻ photolysis on aerosols is another source of uncertainty, which can prolong the lifetime of total reactive nitrogen by regenerating NO_x^{55,56}. In the view of decadal changes, however, a modeling study by Shah et al.⁵⁷ has shown that this

process will be enhanced following the increase of $p-NO_3^-$ in the future. Therefore, the implementation of this process could enhance the magnitude of $\Delta(NO_3^- - NO_x)$, but unlikely impact the overall trend through the 200 years.

Thus, while the trends in $\Delta(NO_3^- - NO_x)$ can be generally explained by changes in atmospheric acidity, some of the remained model-observation discrepancies may be due to the influence of temperature or treatment of dust particles. These limitations would need to be considered in the future works in addition to the general model issues in representation of the atmospheric acidity as discussed in the main text.

Also, there are several additional points of discussion for the discrepancies between the model and the observation, in addition to a significant overestimate in ice core $[NO_3^-]$ (Fig. S9c), that could serve as model constraints. For instance in Fig. 2a, the observed $\Delta(NO_3^- - NO_x)$ between 1870 and 1920 is not reproduced by the model, indicating potential of inappropriate representations of anthropogenic or forest fire-related NO_x emissions over the period as discussed in SN 3. As another point, from 1925 to 1973, comparisons of $\Delta(NO_3^- - NO_x)$ between models and observations for ENA and WE are similar, yet there are discrepancies in TRAJ comparisons (Fig. 2a). This could be due to the inadequate representation of acidity-driven transport efficiency of NO₃⁻ from ENA and WE. It may be also due to the model's meteorological fields being fixed in 1986, not reflecting the actual air-mass contributions from ENA and WE (see also SN 7). Future works focusing on these model-ice core discrepancies would benefit in improving the dynamics of NO₃⁻ in the model and thus future projections.

Supplementary Figures (Fig. S)



Figure S1. The coefficient of variation (CV) of seasonal precipitation/accumulation in Greenland. The CV was calculated as dividing standard deviation of seasonal precipitation/accumulation (four seasons) by the annual mean for the period 2000-2020. The lower CV value indicates less seasonal bias. The Summit and SE-Dome accumulation data are Castellani et al.²³ and Furukawa et al.⁷, respectively. The coastal weather station data are from DMI reports²² (http://www.dmi.dk/laer-om/generelt/dmi-publikationer/). Also shown are the ice-core sites used in this study (black circles).



Figure S2. Comparison of NO_3^- records in the SE-Dome II ice core and previous studies. (a) Annual average concentration (black) and flux (red) of NO_3^- in SE-Dome II ice core. The blue line shows annual average flux of NO_3^- in the SE-Dome I ice core¹. (b) Annual (black), summer (red), and winter (blue) [NO_3^-] in the SE-Dome II ice core. (c) Annual mean [NH_4^+] and detrended [NO_3^-] in the SE-Dome II ice core. The detrended [NO_3^-] was calculated by subtracting 30 years running mean from the original values (Fig. 1a). (d) Normalised annual mean [NO_3^-]₁₈₀₀₋₁₉₀₀ in SE-Dome II ice core (black), Summit (light green), and NEEM (pink), and normalised decadal mean in EGRIP (brown). Summit, NEEM, and EGRIP data are cited from Geng et al.¹³, Sigl et al.¹⁴, and Erhardt et al.¹⁹, respectively.



Figure S3. Estimated contribution of Asian NO_x emission to $t-NO_3^-$ deposition (Gg yr⁻¹) around Greenland. (a) BASE and (b) noAsiaNO_x simulations (NO_x emissions from Asian countries turned off) in 2013. (c) Difference of $t-NO_3^-$ deposition between the two simulations calculated as (noAsiaNO_x – BASE)/BASE and shown in %.



Figure S4. The relationship between the NO₃⁻ concentration ratio (R_{NO3} , 1970-2000/1800-1900) to the ice core site conditions. R_{NO3} compared to (a) annual accumulation rate, (b) altitude, (c) latitude, and (d) annual mean temperature in the several ice cores in Greenland. The average R_{NO3} in the SE-Dome ice core is 2.71 (black star). Summit ($R_{NO3} = 2.02$, light green), NEEM ($R_{NO3} = 2.25$, pink), and EGRIP ($R_{NO3} = 1.98$, brown) data are cited from Geng et al.¹³, Sigl et al.¹⁴, and Erhardt et al.¹⁹, respectively. The other site data are cited from Röthlisberger et al.²⁰.



Figure S5. Correlations between $\Delta(NO_3^- - NO_x)$ and chemical and meteorological parameters. The 30-year running mean $\Delta(NO_3^- - NO_x)$ values were compared to (a) [nssSO₄²⁻], (b) [NH₄⁺], (c) [Na⁺], (d) [Ca²⁺], (e) ionic balance [H⁺], (f) ammonium-to-sulfate ratio [NH₄⁺]/[nssSO₄²⁻], (g) gas ratio (GR = ([NH₄⁺] - 2[nssSO₄²⁻])/[NO₃⁻] (in mol mol⁻¹)), (h) snow accumulation rate², (i, j) air temperature over the North Atlantic Ocean region (i) and SE-Dome grid (j) from Hudcrut5 dataset³⁴, (k, l) relative humidity over the North Atlantic Ocean region (k) and SE-Dome grid (l) from OCADA reanalysis³⁵, (m) NAO index³⁶, and (n) AO index. A color scale corresponds to year. Regression lines were obtained for the period of 1800-2019 (gray) and 1920-2019 (black).



Figure S6. Decadal mean values of anion and cation concentration in the SE-Dome II ice core (μ eq L⁻¹). Anion species include SO₄²⁻ (red), Cl⁻ (blue), and NO₃⁻ (yellow), and cation species include Na⁺ (green), NH₄⁺ (orange), and Ca²⁺ (gray).



Figure S7. Modeled regional differences of HNO₃ and p-NO₃⁻ deposition patterns. Annual mean tropospheric and surface concentrations of HNO₃ and p-NO₃⁻ (a, e, i), p-NO₃⁻ ratio to t-NO₃⁻ (ε) in surface layer and tropospheric mean (b, f, j), wet and dry depositions of HNO₃ and p-NO₃⁻ (c, g, k), and deposition ratios (d, h, l) for SE-Dome grid (a-d), ENA (e-h), and WE (i-l). Depositions are shown in cumulative of wet HNO₃ deposition (orange), dry HNO₃ deposition (khaki), wet p-NO₃⁻ deposition (blue), and dry p-NO₃⁻ deposition (lightblue).



Figure S8. Modeled tropospheric concentration and deposition of PAN in the SE-Dome grid. (a) Annual tropospheric mean concentrations of PAN (star) and t- NO_3^- (circle) in ppt in volume. (b) Same with Fig. S8c but with dry PAN deposition (brown).



Figure S9. Comparisons between ice core observed and modeled NO_x emission and NO_3^- deposition. (a) Normalised NO_x emission in CEDS and GEOS-Chem model. NO_x emission data from ASIA (blue) accounts for China, Japan, Korea, and Mongolia for CEDS data, and the region within 20 to 65°N in latitude and 90 to 145°E in longitude for the GEOS-Chem output. The definitions of other regions are shown in Fig. 4a in the main text. (b) Normalised [NO_3^-] and (c) non-normalised [NO_3^-] in the SE-Dome II ice core (grey dots: annual, black line: 30-year running average) and SE-Dome grid in the model (magenta).

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