On the origin of the occasional spring nitrate peak in Greenland snow

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S1: Record of weekly snow accumulation at Summit

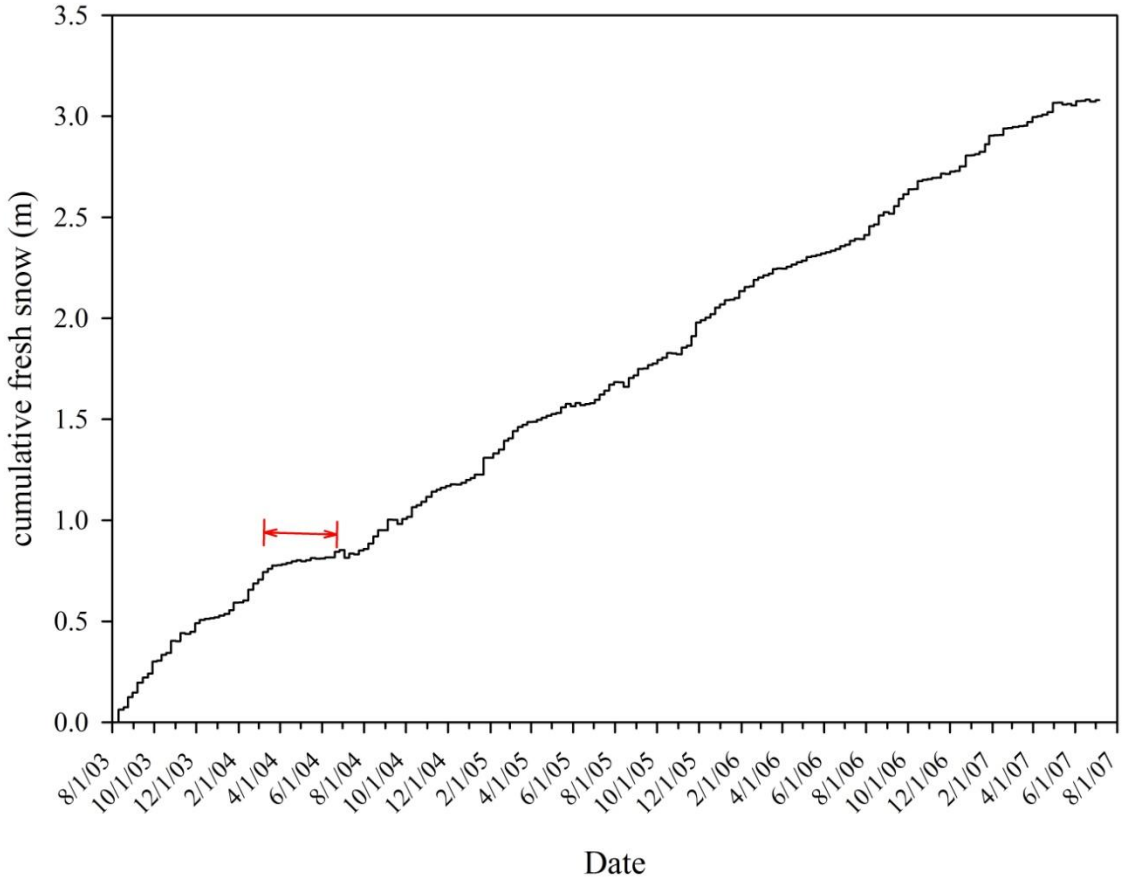

Figure S1. Cumulative snow accumulation at Summit, Greenland from 2003 to 2007. The red arrow indicates the period of 2004 late spring to summer when minimum snow accumulated.

S2: Effect of acidity on the timing of Cl^-/Na^+ peak

The Cl^-/Na^+ peak is a good summer layer indicator in the preindustrial period when atmospheric acidity reaches the highest level in summer (due to the summer peaks of sulfate and nitrate). However, in the industrial era, the timing of the Cl^-/Na^+ peak differs due to seasonal changes in atmospheric acidity before and after the industrial revolution. Here we discuss why the Cl^-/Na^+ peak is affected by atmospheric acidity. The Cl^-/Na^+

calculation can be expressed by the following equation:

$$Cl^-/Na^+ = \frac{ssCl^- + Cl^-_{ex}}{Na^+} = \frac{ssCl^-}{Na^+} + \frac{Cl^-_{ex}}{Na^+} \qquad \text{Equation 1}$$

where $ssCl^-$ represents sea-salt chloride, and Cl^-_{ex} is excess chloride originating from acid-sea salt displacement (Laskin et al., 2012; Legrand and Delmas, 1988) and/or potential anthropogenic emissions in the Northern Hemisphere. Assuming Na^+ in Summit snow is solely from sea salt, the first term in E1 is then equal to 1.79 (the mass ratio of Cl^-/Na^+ in standard sea water). Therefore, variability in the value of Cl^-/Na^+ in snow/ice cores is determined by the second term of E1, Cl^-_{ex}/Na^+. In the preindustrial period, Na^+ reaches the lowest level in summer when the acidity is the highest (due to summer peaks of nitrate and non-sea-salt sulfate), so that Cl^-/Na^+ peak almost precisely falls in summer (**Figure S2, bottom)**. However, in the industrial era, the non-sea-salt sulfate (and acidity) peak becomes irregular, with a major peak in winter (**Figure S2, bottom)**. This leads to the shift of annual Cl^-/Na^+ peak toward the main non-sea-salt sulfate (winter) peak. An shown in **Figure S2**, the affect of the winter non-sea-salt sulfate peak (acidity effect) on the Cl^-/Na^+ peak is clearly indicated in the industrial era (indicated as green arrows).

There are additional reasons why Cl^-/Na^+ peak is not a good summer indicator, especially in the industrial period with relatively high atmospheric and snow acidity. Cl^- is subject to post-depositional process which is influenced by many factors including snow acidity (Röthlisberger et al., 2003). This process could induce further uncertainties when using Cl^-/Na^+ peak to identify the summer snow layer.

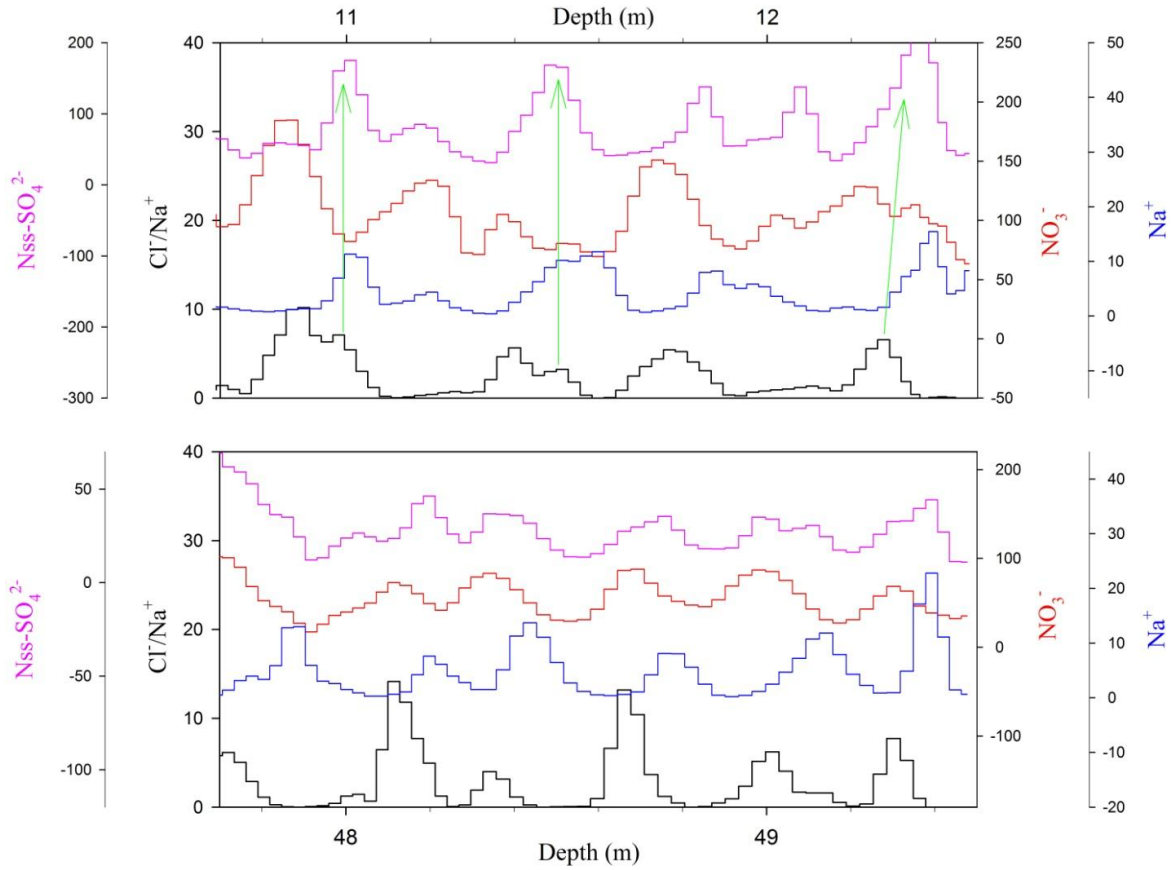

Figure S2. Concentrations of NO_3^-, nss-SO_4^{2-} and Na^+, and Cl^-/Na^+ in the firn core. Top: the industrial period (depth interval of 10.75 to 12.5 m, covering the years of 1984 to 1987); Bottom: the preindustrial period (depth interval of 47.75 to 49.5 m, covering the years of 1879 to 1884).