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Snow accumulation rate and atmospheric oxidation pathway proxies from nitrate isotopes in East Antarctica

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Nitrate is naturally deposited in Antarctic snow and is detectable at low concentrations throughout our deepest ice cores. However, nitrate is photoreactive under ultraviolet light and experiences significant post-depositional loss. This nitrate loss favors $^{14}\text{NO}_3^-$ over $^{15}\text{NO}_3^-$, and the resulting isotopic fractionation can be used as a proxy for duration of sunlight exposure. Here, we present nitrate isotope data ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) sampled from shallow snow cores and pits across East Antarctica. Our >30 sampling sites extend from coastal Adélie Land onto the high East Antarctic Plateau at Dome C and beyond, covering annual snow mass balances that range from 240 mm/yr to less than 30 mm/yr (water equivalent). The $\delta^{15}\text{N}$ of nitrate at these sites show an inverse relationship with snow accumulation rate, with $\delta^{15}\text{N} \approx 20\text{‰}$ at the coastal sites with the highest accumulations and $\delta^{15}\text{N} \approx 150\text{-}250\text{‰}$ at the driest inland sites. This relationship develops because newly deposited nitrate is buried below the level of light penetration by new snow relatively quickly at high accumulation sites, but nitrate at drier sites can be exposed to sunlight for several years. After burial below the reach of sunlight, the $\delta^{15}\text{N}$ signature of nitrate is preserved and thus offers a new proxy for snow accumulation rate in East Antarctic ice cores. In contrast, the oxygen isotopes of nitrate isotopically exchange with surrounding ice after burial, which complicates their interpretation. However, our large sample set allows an estimation of the rate of isotopic exchange at various sites, and the original isotopic values at the time of deposition may be approximated after correcting for this rate of exchange. These oxygen isotope values likely reflect in part the atmospheric oxidation history of the nitrate and its nitrogen oxide progenitor, but further study is needed to fully understand nitrate oxygen isotope dynamics.