

Interactive comment on “Air-snow transfer of nitrate on the East Antarctic Plateau – Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium” by J. Erbland et al.

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In the abstract, the authors suggest that the "However, the overall fractionation in $\Delta^{17}\text{O}$ is small thus allowing the preservation of an atmospheric signal." Overall fractionation might be understood to mean the difference between the $\text{D}(^{17}\text{O})$ of asymptotic nitrate and atmospheric nitrate. Perhaps the term "apparent $\text{D}(^{17}\text{O})$ fractionation constant" would be more appropriate, to be consistent with the remainder of the paper. Also, the sentence might be understood to mean that the atmospheric $\text{D}(^{17}\text{O})$ signature is preserved in ice core nitrate on the plateau. However, as Fig. 8 shows $\text{D}(^{17}\text{O})$ in asymptotic nitrate is up to 5-13 ‰ lower than $\text{D}(^{17}\text{O})$ in the top 2 cm, so this suggestion

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does not appear to hold water.

Referee #1 suggested measuring the isotope effect during nitric acid evaporation using H^{15}NO_3 . The authors replied to the reviewer that the equilibrium vapour pressure at in situ conditions would be too low to do this. They also cited thermodynamic calculations that discount the existence of a possible quasi-liquid layer below $-30\text{ }^\circ\text{C}$. Notwithstanding that any thermodynamic calculations would need to be verified by observations for a concentrated brine-nitrate-water mixture, their evaporation experiments were done at temperatures of $-30\text{ }^\circ\text{C}$ and above. In any case, the approach suggested by referee #1 would seem to be a sensible as a first step, this would seem to be viable and feasible approach to measure any associated isotopic fractionation, given the significant vapour pressure of nitric acid. Of course, the isotopic fractionation might vary with temperature and there may be secondary effects due to the interaction between HNO_3 and water in a mixture. However, such effects may be taken into account using thermodynamic calculations using the Gibbs-Duhem equation (Janco and Van Hook (1974), Chem. Rev. 74, 689-750).

NO_x and nitric acid and/or nitrate readily exchange nitrogen isotopes, leading to substantial enrichment of ^{15}N in the more oxidised phase (Brown and Begun (1959), Journal of Chemical Physics 30, 1206-1209), e.g. $+(64\pm 1)\text{ }^\circ\text{‰}$ for 1 M HNO_3 solutions. Isotopic exchange rates may be lower at lower concentrations, but the isotopic fractionation will presumably be similar, if not larger. Such nitrate concentrations do not appear to be unattainable and just as there are "cage effects" for oxygen isotopes, local conditions in the snow might be conducive to isotope exchange between nitrogen species. Intermediate species generated by nitrate photolysis might catalyse this exchange. Such equilibrium isotopic fractionation would add to any kinetic isotopic fractionation, which maybe attributed to absorption cross eection difference between nitric acid isotopologues. Have the authors undertaken any calculations or modelling to establish the potential significance of equilibrium isotope fractionation? They only seem to have considered equilibrium fractionation between HNO_3 and NO_3^- . This would seem to

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be a potentially relevant process, especially if, as stated by the authors, photoproducts undergo oxygen isotope exchange and NO_x has a longer lifetime than HNO₃.

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