First, we would like to thank Greg Michalski for the contribution of constructive comments, which are very helpful to further improve this work. The review expresses above all concerns regarding our proposed theoretical considerations to explain post-depositional fractionation of stable isotopes in nitrate. These are mainly discussed in sections "4.2.1 Evaporation" and "4.2.2 Photolysis" of the ACPD manuscript. We address comments regarding both sections below and note where this will affect our conclusions. Corresponding changes will be included in the revised version of the manuscript.

Section 4.2.1 Evaporation

The purpose of this section was to estimate qualitatively sign and order of magnitude of the isotopic fractionation constant ε for nitrate stable isotopes upon sublimation or evaporation. The main criticisms were (1) the case of stable water isotopes is not a good analog for nitric acid (HNO_3) equilibrium phase fractionation and (2) the molecular model of a simple harmonic oscillator (SHO) is too simplistic to estimate the sign of ε for HNO_3 equilibrium phase fractionation.

Regarding (1) we concur in that the structure of our argument was misleading in that we started out with the water isotope analog as a first hypothesis only to reject it later by showing that HNO_3 equilibrium phase fractionation is likely controlled by the degree of protonation. In order to avoid confusion we will therefore omit any reference to stable water isotopes.

Regarding (2) the review pointed us to Monse et al. (1969), a publication we were unaware of at the time we submitted our manuscript. These authors modeled normal vibrational frequencies and the reduced partition function ratios (RPFR) of various oxynitrogen compounds with single oxygen or nitrogen isotopic substitutions. In our manuscript we considered of all the possible oxygen substitutions only the case of $H^{18}ONO_2$, where the rare oxygen isotope is protonated. In this case Monse et al. (1969) calculated a red-shift of 12 cm^{-1} in the O-H stretch mode and of 24 cm^{-1} in the O-NO stretch mode, (Monse et al., 1969, Tab. II). This indicates that the oxygen isotope substitution should increase mostly the N-O bond strength, consistent with our proposed SHO model. This in turn will lead to negative ε values or depletion of $H^{18}ONO_2$ (Tab.1). However, we agree that in order to assess the likelyhood of dissociation and concurrent fractionation the entire

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molecule and all possible substitutions need to be taken into account rather than only individual bonds.

We therefore update our model and assume that evaporation of NO_3^- occurs in two steps, 1) recombination (protonation) to form HNO_3 followed by 2) evaporation of HNO_3, each of which induce isotopic fractionation.

Regarding step 1 we evaluate isotopic exchange equilibria of HNO_3 in aqueous solution, considering (i-ii) single oxygen (^{18}O case only) and (iii) nitrogen isotope substitution:

(i) $H^{18}ONO_2 + {}^{16}ONO_2^- \rightleftharpoons H^{16}ONO_2 + {}^{18}ONO_2^-$
(ii) $HON^{18}OO + ON^{16}OO^- \rightleftharpoons HON^{16}OO + ON^{18}OO^-$
(iii) $HO^{15}NO_2 + O^{15}NO_2^- \rightleftharpoons HO^{14}NO_2 + O^{15}NO_2^-$
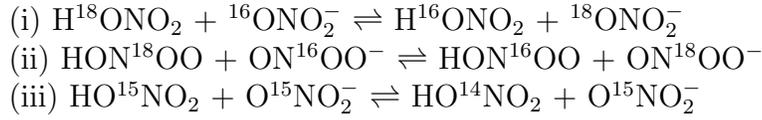
According to the statistical mechanical theory of Urey (1947) the ratios of the reduced partition functions Q can be used to estimate the respective equilibrium fractionation factors α, if thermodynamical equilibrium can be assumed:

$$^{18}\alpha_{H^{18}ONO_2/^{18}ONO_2^-} = \frac{Q_{H^{18}ONO_2}/Q_{H^{16}ONO_2}}{Q_{^{18}ONO_2^-}/Q_{^{16}ONO_2^-}} \tag{1}$$

$$^{18}\alpha_{HON^{18}OO/ON^{18}OO^-} = \frac{Q_{HON^{18}OO}/Q_{HON^{16}OO}}{Q_{ON^{18}OO^-}/Q_{ON^{16}OO^-}} \tag{2}$$

$$^{15}\alpha_{HO^{15}NO_2/O^{15}NO_2^-} = \frac{Q_{HO^{15}NO_2}/Q_{HO^{14}NO_2}}{Q_{O^{15}NO_2^-}/Q_{O^{14}NO_2^-}} \tag{3}$$

We used the model results of Monse et al. (1969) to calculate the corresponding $\varepsilon = \alpha$-1 for the temperature range at Dome C (Tab.1). We observe the following: first, oxygen substituted species show both isotopic enrichment and depletion upon protonation, the sign of ε depending on the internal molecular position of the rare isotope (Tab.1). As indicated above these results are consistent with our SHO approach indicating depletion in the case of $H^{18}ONO_2$ and not enrichment as stated by the review. In fact, the comment cites wrongly the isotope-exchange equilibrium for $H^{18}ONO_2/NO^{18}O^-$ (Tab. V in Monse et al., 1969), and not for nitrate. However, to estimate the overall effect $HON^{18}OO$ needs to be also included. To do this we assume a statistical distribution of the internal molecular position of the rare oxygen isotope and find that ε values are positive (Tab.1), but significantly smaller

than those observed in lab and at Dome C (Table 1 in the ACPD manuscript). Second, nitrogen substituted species show also enrichment in the protonated nitrate (Tab.1). Based on this, protonation, step 1 in our model, should lead to enrichment of all stable isotopes in HNO_3, and therefore to depletion in NO_3^-.

Step 2 in our evaporation model, the evaporation of the HNO_3 molecule, is expected to lead to enrichment of the heavier isotopes in HNO_3 remaining in the condensed phase (e.g. Urey, 1947). For example, for the hydrogen-bonded oxygen isotope substitution the HNO_3 liquid-vapor equilibrium can be written as follows:

$$H^{18}ONO_{2,(g)} + H^{16}ONO_{2,(aq)} \rightleftharpoons H^{16}ONO_{2,(g)} + H^{18}ONO_{2,(aq)}$$
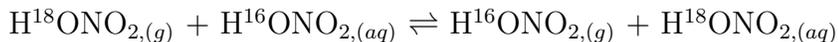
Subscripts (g) and (aq) refer to the gaseous and aqueous phase, respectively. Experimental data for this system are not available and *ab initio* estimates prove to be difficult to do. One of the main reasons for strong fractionation and enrichment of the heavy isotopes in the aqueous phase is the formation of hydrogen bonds. Therefore, the success of *ab initio* calculations of liquid-vapor phase equilibria will depend largely on the choice of solvation model and hydrogen-bridge network (e.g. Oi, 2003). A recent first attempt for the case of pure water showed only unsatisfactory agreement between model and experiment (Oi, 2003). While an estimate for HNO_3 seems feasible, it is clearly beyond the scope of this work.

Since the aqueous phase equilibrium fractionation is likely the controlling step in the overall process, evaporation/sublimation should then deplete both the heavy oxygen and nitrogen isotopes in the NO_3^- ion remaining in the snow phase. Observations show however very strong enrichment of the nitrogen isotope, indicating only a minor contribution of evaporation to post-depositional fractionation. We note that lab experiments are urgently needed to determine the evaporative fractionation constant for the nitrate stable isotopes and to confirm our model.

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Table 1: Reduced partition function ratios (RPFR) of selected oxynitrogen compounds calculated by Monse et al., (1969) were used to compute ε values for the HNO_3 exchange equilibria in the temperature range typical for Dome C.

T (°C)	-33	-53	-73
$Q_{H^{18}ONO_2}/Q_{H^{16}ONO_2}$	1.12209	1.13932	1.16077
$Q_{HON^{18}OO}/Q_{HON^{16}OO}$	1.13949	1.15943	1.18413
$Q_{^{18}ONO_2^-}/Q_{^{16}ONO_2^-}$	1.13275	1.15193	1.17568
$Q_{HO^{15}NO_2}/Q_{HO^{14}NO_2}$	1.22732	1.25856	1.29734
$Q_{O^{15}NO_2^-}/Q_{O^{14}NO_2^-}$	1.21019	1.23956	1.27957
		$\times 10^3$	
1. $^{18}\varepsilon_{H^{18}ONO_2/^{18}ONO_2^-}$	-9.4	-10.9	-12.7
2. $^{18}\varepsilon_{HON^{18}OO/ON^{18}OO^-}$	6.0	6.5	7.2
weighed average of 1. and 2.[a]	0.8	0.7	0.6
$^{15}\varepsilon_{HO^{15}NO_2/O^{15}NO_2^-}$	14.2	15.3	13.9

[a] assuming a statistical distribution of ^{18}O

Section 4.2.2 Photolysis

As suggested, we included in our analysis the model results of Monse et al. (1969) for single oxygen isotope substitution in NO_3^-. In the case of the NO_3^- with no rare isotope substitution, model and aqueous phase observations show excellent agreement, whereas the vibrational frequencies for the KNO_3 salt are slightly lower (Tab.2). In addition, the model shows a much larger decrease in ZPE than observed for the salt (Tab.2), resulting also in a more negative ε value. Overall, this does not change our conclusion that PHIFE fails to explain the oxygen isotope fractionation, likely due to matrix effects.

The review raises then questions regarding some of the assumptions underlying the application of the theory of Photo Induced Fractionation Effects (PHIFE) to NO_3^- in snow. We agree that the case of NO_3^- is different compared to gaseous nitrous oxide and water discussed previously (Yung and Miller, 1997; Miller and Yung, 2000), in that direct photo-dissociation likely does not take place. In addition, the quantum yield of the major photolysis channel of NO_3^- is not unity, but has been measured on ice to be about 1.89×10^{-3} at Dome C conditions (Chu and Anastasio, 2003).

This will mostly affect the accuracy of the ZPE-shift model used to estimate the absorption cross section of the various NO_3^- isotopologues. Another limitation is that the ZPE-shift model cannot account for changes in shape and intensity of absorption spectra upon isotopic substitution (Miller and Yung, 2000). *Ab initio* calculations of the UV absorption spectrum provide likely a more accurate estimate, but have also their shortcomings (see Miller and Yung, 2000), and are beyond the scope of this work.

In summary, we expect isotopic substitution to make a difference in the UV absorption spectrum of NO_3^- and therefore think that PHIFE is a valid first modeling approach for ε of $^{15}N(NO_3^-)$, noting that there are uncertainties in the absorption estimates and ε. Lab experiments are needed to confirm the predictions. It should be emphasized that the model indicates a strong sensitivity of ε to the spectrum of actinic flux, consistent with existing lab and field observations.

Table 2: Normal vibrational frequencies of NO_3^- isotopologues used to calculate photolytic fractionation factors ε.

	NO_3^{-} [a]	NO_3^{-} [b]	$N^{18}OO_2^{-}$ [b]	NO_3^{-} [c]	$N^{18}OO_2^{-}$ [c]
ν_i, cm^{-1}					
ν_1	1049.2	1049.5	1029.2	1049.0	1030.0
ν_2	830.9	831.0	827.5	834.3	822.6
ν_3	1375.6	1375.9	1361.2	1357.5	1370.0
ν_4	1375.6	1375.9	1375.6	1357.5	1370.0
ν_5	716.8	717.1	700.7	715.9	699.6
ν_6	716.8	717.1	707.9	715.9	699.6
ZPE, cm^{-1}	3032.5	3033.2	3001.0	3015.0	2995.9
ΔZPE, cm^{-1}			-32.1		-19.1

[a] aqueous phase observations (Begun, 1960).
[b] model calculation, no solvent included (Monse et al., 1969).
[c] average frequencies observed on microcrystalline KNO_3 (Chakraborty, 1999).

SUMMARY

In a revised manuscript we will state assumptions and uncertainties in our model, which indicates that photolysis is the dominating loss process at Dome C. However, a definite answer can only come from lab measurements of the photolytic and evaporative fractionation constants, planned in the near future. These will then provide constraints for quantitative partitioning in evaporative and photolytic NO_3^- loss from snow. We will change our conclusions accordingly.

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