Response to Reviewer #3's comments

General comments

1) *This manuscript describes a closed box model assuming no atmospheric mixing and simulations of the effect of a mean diurnal cycle at Dome C (using observations) and Dome A (using atmospheric reanalyses and assumptions as inputs). The current title does not reflect the content and the conclusions are not well supported by the analyses and the underlying assumptions in the modelling methodology.*

Response: Thanks for reviewing the manuscript and the valuable comments. In the revised manuscript, we have addressed the issue of "no atmospheric mixing" by including exchanges between the boundary layer and free troposphere. Additionally, the calculations of isotope mass balance have also been modified following the new model structure. Using this modified model, we have conducted new simulations at Dome C and Dome A. The discussion has been reformulated in the revised manuscript based on the new simulated results and the feedback from the reviewers.

2) *The long introduction gives a good scene setting for the study, which addresses an important topic, but fails to describe the modelling framework in the context of other studies, and fails to provide a clear comparison of the meteorological and snow conditions between Dome C and Dome A (and what are the similarities and differences that need to be accounted for in comparing results for these two sites, for diurnal variations, clear and cloud sky, and winter vs summer conditions).*

Response: We would like to express our gratitude to the reviewer for this comment. In response to the comment, we have made some revisions to the manuscript. Specifically, in the revised manuscript, we have added a comparison of the meteorological and snow conditions between Dome C and Dome A in Section 2.2.2. The comparison of isotopic values for these two sites were also conducted at the result section (Section 3.2). Additionally, we have included a new paragraph in Section 4 to discuss the similarities and differences in diurnal variations between these two sites. We hope that these revisions will enhance the clarity and comprehensiveness of our work.

The added statement in Section 4 is as follows:

"The diurnal amplitude of water vapor δD across East Antarctic interior region appears to vary spatially. The modeled value of 28.79‰ at Dome A is slightly less than the averaged observations of 36±6‰ at Kohnen station and the in-situ measurements of 38±2‰ at Dome C (Ritter et al., 2016; Casado et al., 2016). The difference between the two latter locations can be explained by a smaller amplitude of diurnal temperature cycle (8.7°C) at Kohnen station, relative to that in Dome C (11.1°C). However, there still exists a discrepancy in water vapor δD amplitude when the peak-valley gap of diurnal temperature cycle is the same at Dome A and Dome C. Such an anomaly pattern can be attributed to atmospheric dynamical conditions linked with wind speed. At Dome A, the daily mean wind speed of 2.8 m/s is lower than 3.3 m/s in Dome C and 4.5 m/s in Kohnen station during summer. A small wind speed corresponds to the relatively weak air convection in horizontal orientation. Due to the coupling between upper and lower atmospheric layer, vertical turbulent mixing may decrease with the weakened air convection in the atmospheric near-surface layer (Casado et al., 2018).

This change can attenuate molecular exchange between surface snow and water vapor. In parallel, the decrease of vertical turbulence may result in a less efficient turbulent diffusion of water molecules and an elevated contribution of molecular diffusion during air-snow exchange. Changes in water vapor diffusion pathways increase kinetic fractionation and reduce effective isotopic fractionation of water isotopes, leading to a muted fluctuation of modelling water vapor δD in combination with less mass exchange. The surface snow δD displays the synchronization change and different amplitude in diurnal cycles, in accordance with the comparisons of water vapor δD between Dome A and Kohnen Station. The similar trend of snow δD is originated from similar temperature variations on a diurnal scale, because surface snow isotopic composition is mainly influenced by temperature-controlled fractionation of water isotopes during air-snow vapor exchange. This relationship also suggests that the difference in temperature amplitude could be playing a role in the unequal amplitude of snow δD.”

3) *The description of the model has flaws in the equations for latent heat flux and possibly in the use of relative humidity in the atmosphere and not relative to surface temperature for fractionation coefficients. The information provided in supplementary information is very difficult to understand.*

Response: Thanks for this comment. We found that the formulations used in the latent heat flux calculation is not correct, following Berkowicz and Prahm (1982) (B&P82) and the suggestion from the reviewer #2. In addition, the fractionation coefficients calculations should rely on the humidity with respect to the surface layer and surface temperature, rather than relative humidity and air temperature.

In the revised manuscript, we first have made modifications to the calculations of latent heat flux. Specifically, we have revised the calculations as follows:

$$Ex = LE/Ls = -\rho_a u^* q^* \qquad (1)$$

where ρ_a is dry air density varying with observed air temperature (T_a) and pressure (P_a), L_s is sublimation heat constant, u* and q* are friction velocity and specific humidity turbulent scale, respectively. Where u* and q* are respectively defined as:

$$u^* = \frac{k u_z}{log\left(\frac{z}{z_0}\right) - \Psi_M\left(\frac{z}{L}\right)} \qquad (2)$$

$$q^* = \frac{k(q_a - q_s)}{log\left(\frac{z}{z_0}\right) - \Psi_M\left(\frac{z}{L}\right)} \qquad (3)$$

We would also like to apologize for any confusion caused by our imprecise description of the relative humidity correction and fractionation coefficients. In the new version of the supplementary information, the text description for the relative humidity correction have been rewritten to be more clear and accurate. Additionally, we would like to clarify that it is the surface snow temperature (T_s) that controls isotopic fractionation during air-snow vapor exchange. Thus, the surface temperature were used to calculate fractionation coefficients, instead of air temperature. We will make the necessary corrections to the related description in Section 2.1.1 of the revised manuscript.

The revised supplementary information for humidity correction are as follows:

“The raw data of relative humidity (RH) at height z is the relative humidity with respect to the water surface (RH_w), measured with the HMP35D humidity probe (Xiao et al., 2008; Ding et al., 2022). The RH_w can be expressed as a percentage:

$$RH_w = e_w / e_w^s \times 100\% \qquad (S2)$$

where e_w is the water vapor pressure of air (Pa), and e_w^s is the saturated vapor pressure with respect to the water surface at the air temperature (Pa) which can be calculated using the Clausius-Clapeyron equation. When calculating the effective fractionation factor (α_f) in the model (Eq: (15) in the main text), the RH_w were converted to the relative humidity over ice at the temperature of the air (RH_i). The conversion between RH_i and RH_w was proposed based on the calibration procedures of Anderson et al. (1984). The details are as follows: 1) The RH_w observations were firstly rescaled using the maximum RH_w of all measured values at each air temperature point (T_a),

$$RH_w^{'} = RH_w (T_a) / RH_w^{max} (T_a) \qquad (S3)$$

2) $RH_w^{'}$ values were then converted to RH_i using Eq: (S4) :

$$RH_i = (e_w^s (T_a) / e_i^s (T_a)) \times RH_w^{'} \qquad (S4)$$

where e_i^s represents the saturated vapor pressure with respect to ice at the air temperature (Pa). Like e_w^s, e_i^s was calculated by the Clausius-Clapeyron equation. Based on Eq: (S3) and Eq: (S4), we obtained RH_i as the final result.

In addition, the relative humidity of the air with respect to the surface temperature (h) in Eq: (14) can also be converted from RH_w observations. The first step of procedures for h conversion is the rescaling RH_w based on Eq: (S3), same to the RH_i conversion. The second step is h calculation using the saturated vapor pressure with respect to ice at the surface temperature (Eq: (S5)).

$$h = (e_w^s (T_a) / e_i^s (T_s)) \times RH_w^{'} \qquad (S5)$$

4) *The choice of performing simulations driven by a mean diurnal cycle instead of using the actual wealth of observations is unclear and the implications should be discussed. I am puzzled by how wind effects are accounted for when averaging conditions.*

Response: Thanks for this comment. We chose to use the mean stacked conditions to conduct simulation since we wanted to highlight the effects of air-snow exchange in a general case. But in order to avoid confusion, in the revised manuscript, the simulations were conducted using continuous meteorological input for each individual day during the studied period at Dome C. This allowed us to calculate the average diurnal changes in water vapor isotopic composition and snow isotopes. However, for the Dome A case, the selected days for clear-sky, cloudy, and winter conditions were not continuous, making it difficult to conduct simulations as was done for Dome C. Instead, we were only able to use the model for one day to simulate the diurnal changes in snow and water vapor isotopes, after a week of spin-up time (as shown in Figures 4-6 in the revised manuscript). This allows to evaluate the effects of air-snow exchange under representative meteorological conditions.

In addition, we also reconsidered the effect of wind speed on simulations during atmosphere-snow water vapor exchange. In the revised manuscript, a new case simulation was presented to test the effect of wind speed variability on atmosphere-snow water vapor exchange. Specifically, we analyzed the response of water vapor and snow isotopic composition to the conditions of 1) a significant diurnal cycle of wind versus that with averaged wind speed. The results, as shown in Figure 1, suggest that strong variability in wind speed will enlarge the variations in latent heat, leading to a more significant diurnal change in water vapor isotopes and snow isotopes, but the for a longer time, there would be days with diurnal wind cycle both smaller or bigger than the mean, so the result with the mean wind pattern is more representative.

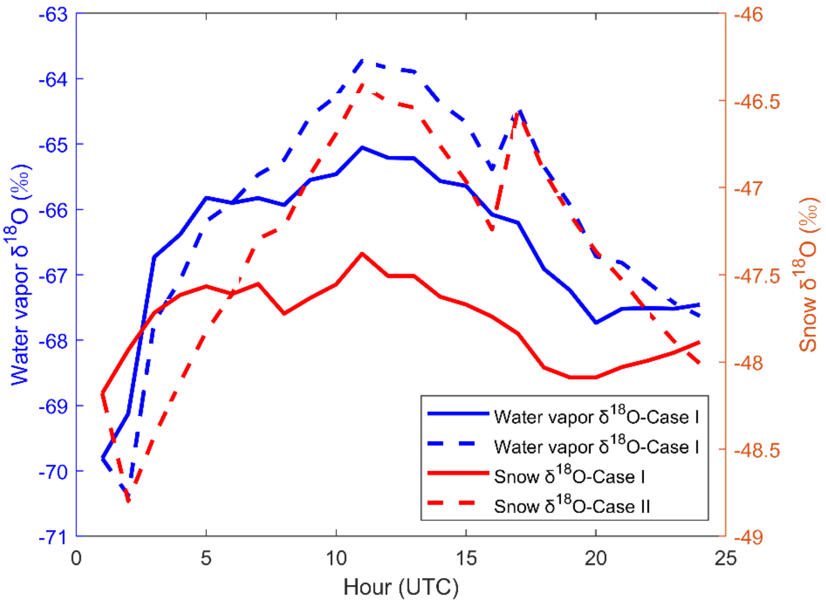

Figure 1: The comparison of water vapor isotopic composition between two simulated cases at Dome A. The simulations in two cases were driven using the averaged wind speed (Case I) and the strong diurnal changes in wind speed (Case II).

5) *There should be at least a more detailed comparison between the Dome C and Dome A characteristics (including comparison of meteorological conditions and ERA5 results at both sites), instead of current Table 1 (where assumptions versus observational based information should be differenciated).*

Response: Thanks for this suggestion. In the revised manuscript, we have added content to compare the meteorological conditions at Dome C and Dome A in Section 2.2.2, and the impacts of these conditions on the modeled water vapor and snow isotopes are discussed in Section 4.

6) *The assumptions displayed in Figure 1 should be discussed in the context of available information, including the Richardson number, regarding atmospheric exchanges (the closed box assumption validity).*

Response: Thanks for the valuable suggestion. We have incorporated these into the revised manuscript by discussing the assumptions related to the occurrence conditions of the air-mass renewal process associated with the Richardson number, as well as the isotopic fractionation during sublimation and deposition. Additionally, we have addressed the setting of initial conditions through some original and new sensitivity tests.

Here, we will provide the discussion of the occurrence conditions of the air-mass renewal process in the supplementary information:

"To determine the correlation between mixing occurrence conditions and Richardson numbers, we ran simulations for Dome C, taking into account mixing when $Ri<0$ and $Ri<0.1$. As shown in Figure 2, the case with $Ri<0$ did indeed underestimate the water vapor isotopic composition in the near-surface atmospheric layer during the cooling time. Based on this comparison, we incorporated mixing into the modeling once $Ri<0.1$."

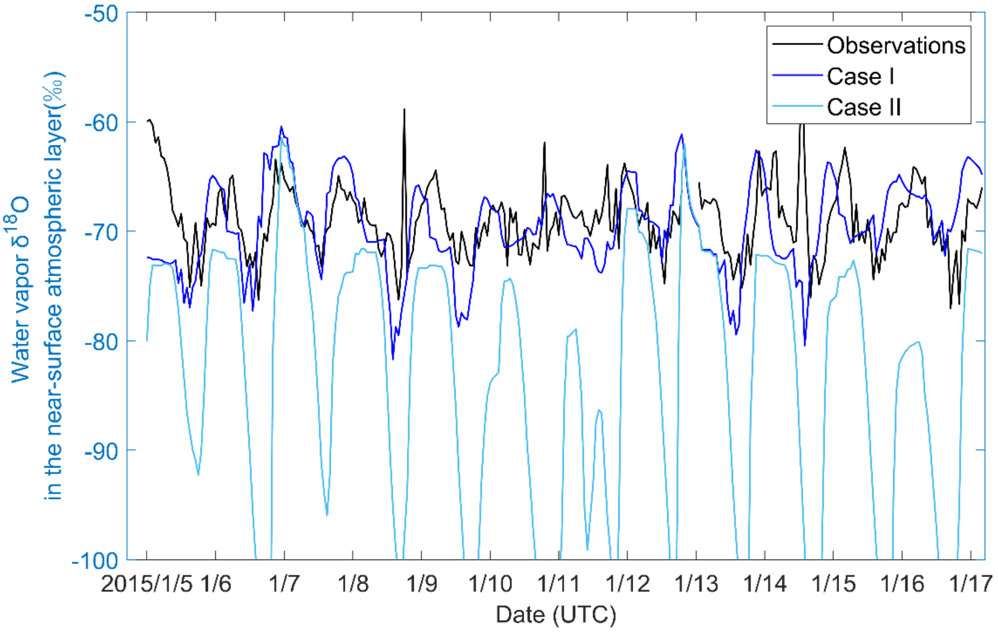

Figure 2: The comparison of water vapor isotopic composition between the simulated and observed changes at Dome C. Two simulated cases are presented here to discuss the occurrence condition of mixing. In the case I, the mixing is assumed to happen when $Ri<0$ in the cooling phase. The case II for the occurrence conditions of mixing is $Ri<0.1$ in the cooling phase.

7) *The authors should reflect on what their model explicitely implies in terms of behaviour, and what is effectively "validated" from their approach which does not resolve the diurnal variations in snow measured at Dome C. This physics-based approach is missing.*

Response: Thank you for bringing this to our attention. We have resolved the issue by making modifications to the physical mechanism of our model (Figure 1), as outlined in our previous response to general comments. We then conducted simulations under Dome C conditions and three different cases at Dome A using the updated model. The simulated results for a 24-hour period are presented in Figures 3-6 of the main text (at the end of this response). The new results indicate that the changes in snow isotopic composition are significantly greater than the original δ^{18}O simulations of 0.02‰ at Dome C. During a typical night, such as the frost event on January 6-7, 2015, the diurnal changes of the newly simulated results between the maximum and minimum can reach 2‰ for snow δ^{18}O (as shown in Figure 3). This magnitude is consistent with the observations for snow isotopes from Casado et al. (2018).

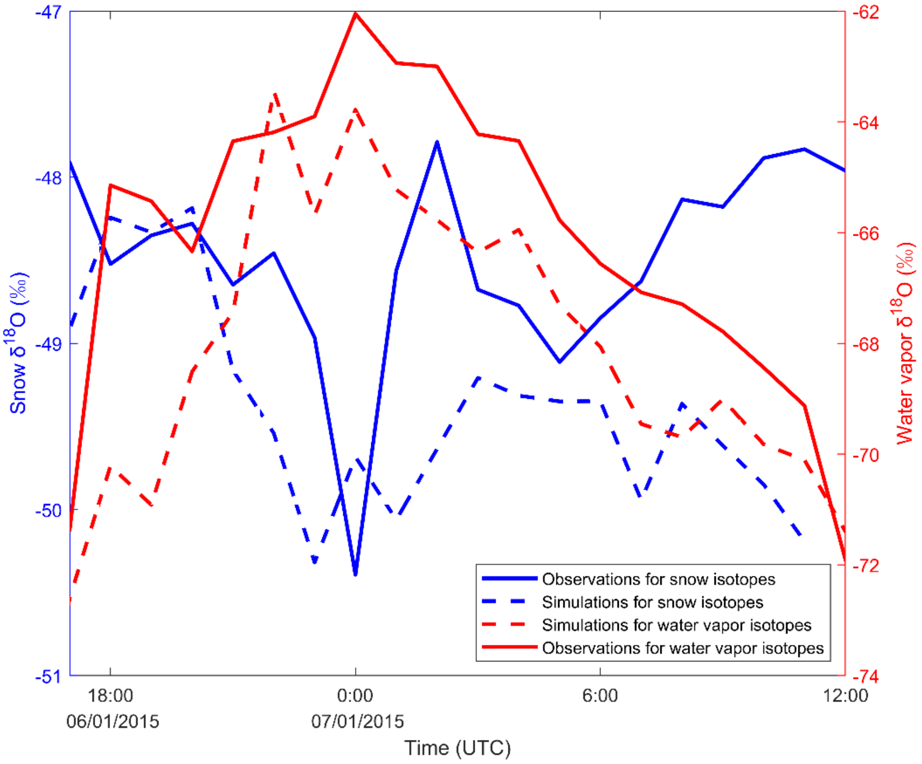

Figure 3: The changes of snow isotopes and water isotopic composition in the near surface atmospheric layer during the 6-7th Jan, 2015 at Dome C.

8) *For these reasons, major revisions are needed, first to ensure accurate equations in the model, and then to reflect on the limitations and suitability of the core assumptions of the closed box model to address these questions, and third regarding the average diurnal cycle approach, and fourth regarding the detailed comparison between Dome C and Dome A (well beyond "validating" and "applying" this model at the two sites).*

Response: Thank you for the helpful comment. Several significant changes were made to the model structure to reflect reviewer's suggestions. Specifically, we have added a third box to represent the free atmosphere layer. The calculations and equations were also updated to reflect the modifications made to the physical mechanism of the model. We also have presented new assumptions for initial conditions and air mass renewal occurrence conditions, which enable the model to run effectively. Furthermore, the simulations were continuously conducted using meteorological observations recorded hourly. Finally, we have included a comparison between Dome C and Dome A in the Discussion section of the revised manuscript (Details can be seen in response to Comment #2 and Comment #6). After all of these modifications, in addition to that arisen by other reviewers, the main conclusion of the manuscript stays the same: The diurnal variations in atmospheric water vapor $\delta^{18}O$ and δD can reach 4.75±2.15 ‰ and 28.79±19.06 ‰ under summer clear-sky conditions at Dome A, with corresponding diurnal variations in surface snow $\delta^{18}O$ and δD by 0.81±0.24 ‰ and 1.64±2.71 ‰, respectively. After 24-hour simulation, snow water isotopes were enriched under clear-sky conditions. However, there is no or very little enrichment for snow water isotopes under cloudy conditions. Under winter conditions at Dome A, the model still indicates the diurnal change in atmospheric and surface snow water isotopes are not significant, but the model predicts more or less depletions in snow $\delta^{18}O$ and δD in the period of 24-hour simulation, opposite to the results under summer clear-sky conditions. This suggests that the air-snow vapor exchange tends to enlarge snow water isotope seasonality.

Supplementary response

The revised figures in the main text are as follows:

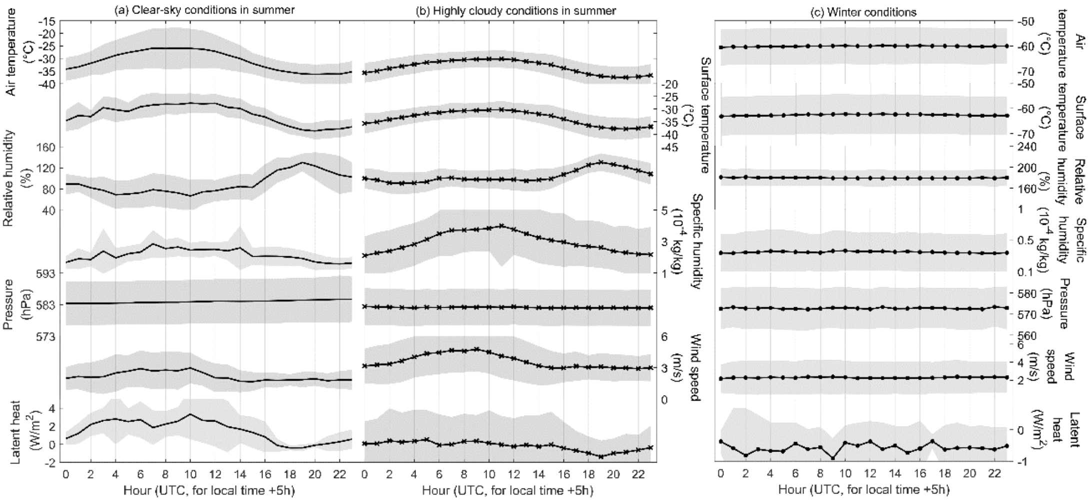

Figure 2: Stacks of diurnal cycles of meteorological parameters and the calculated latent heat under summer clear-sky conditions (a), summer highly cloudy conditions (b), and winter conditions (c) at Dome A. The hourly data for air temperature, relative humidity, air pressure and wind speed were averaged by AWS observations over those selected days. The diurnal variations for other three parameters were calculated based on hourly observations. In each panel, the solid line with marks represents the average and the grey shadow is the standard deviation. The background color of pink and blue corresponds to the period dominated by sublimation and deposition, respectively, in a diurnal cycle.

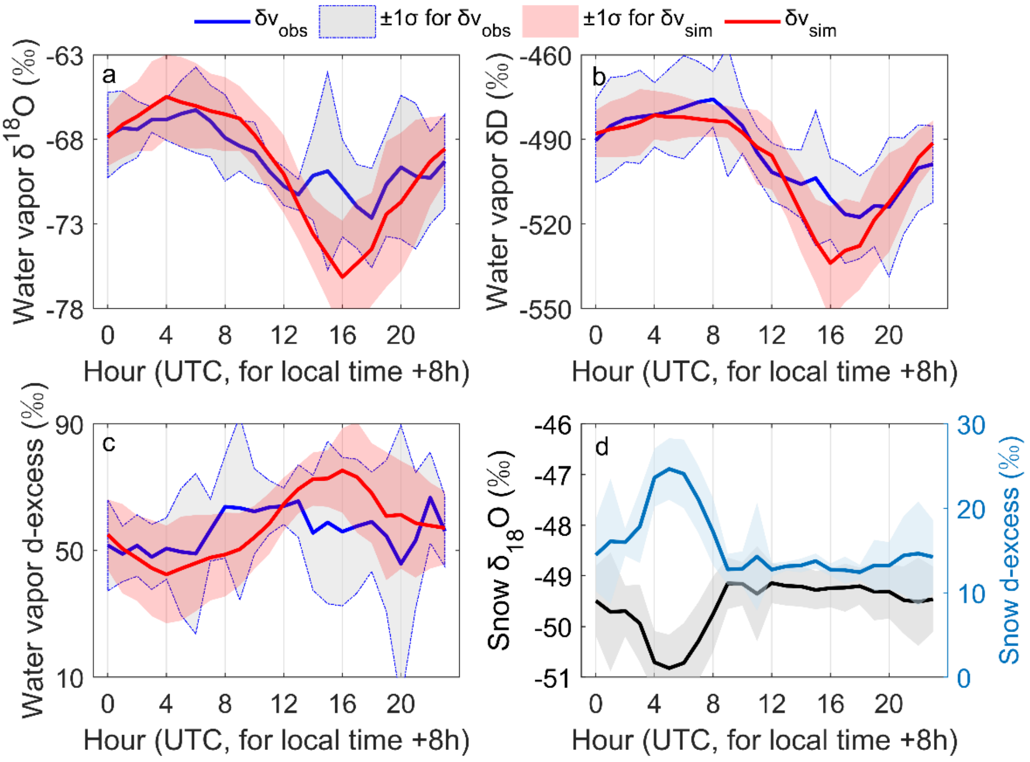

Figure 3: Model simulated diurnal variations of water vapor and snow isotopic compositions at Dome C along with the observations. (a) water vapor δ^{18}O, (b) water vapor δD, (c) water vapor d-excess and (d) snow isotopes. In panels (a)-(c), blue solid line represents the observations of water vapor isotopic composition (δv$_{obs}$) with the light grey shaded area as the uncertainties (±1σ). The red solid line and the light red shaded area depicts the modeled variations of water isotopic composition (δv$_{sim}$) and correspondingly uncertainties (±1σ). In panel (d), the diurnal variations of modeled snow δ^{18}O and d-excess are shown as the black solid line and light blue solid line, respectively. Their uncertainties are also displayed with shaded areas like δv$_{obs}$ and δv$_{sim}$ in first three panels. The method for uncertainties estimation can be seen in SI (Texts S2).

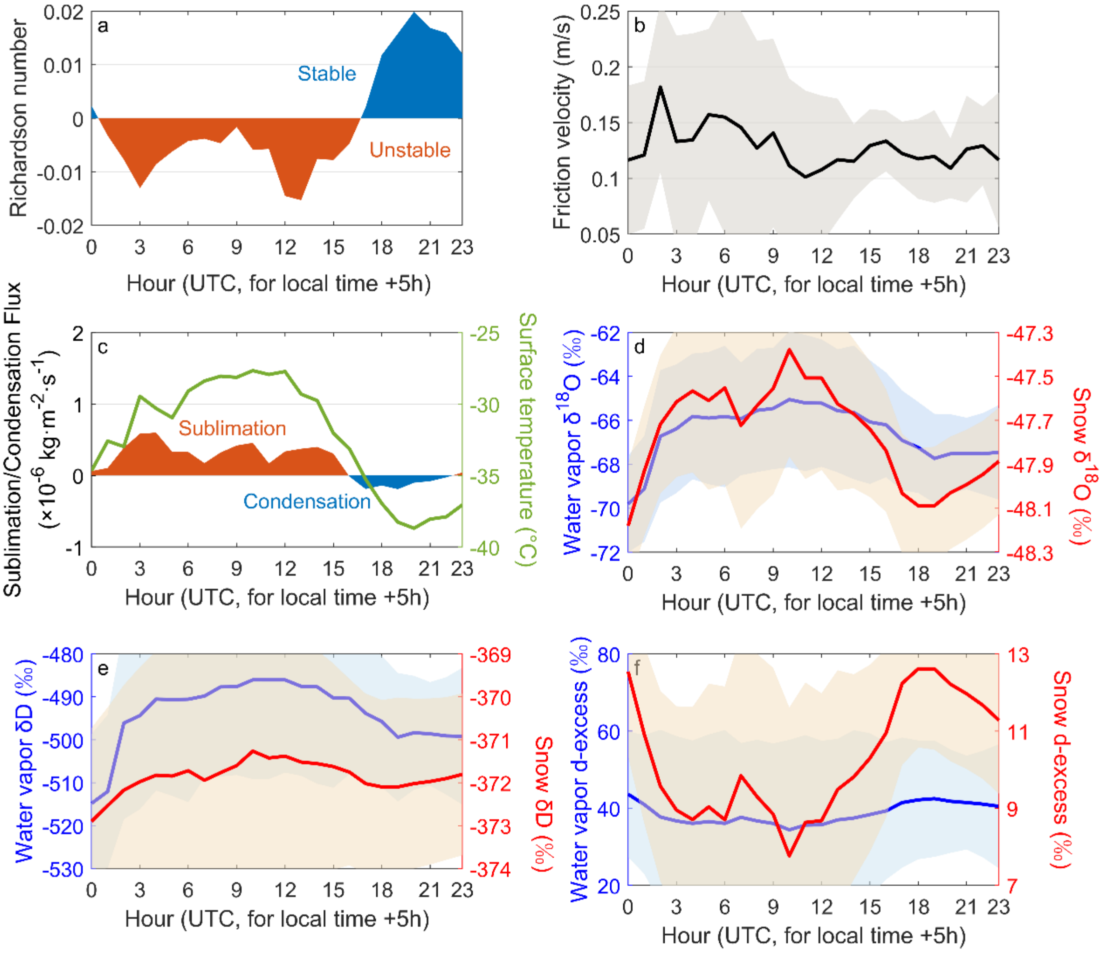

Figure 4: The simulated hourly mean vapor exchange flux and variations in atmospheric water vapor and snow isotopes under summer clear-sky conditions at Dome A: (a) Richardson number, (b) friction velocity, (c) vapor exchange flux, (d) snow and water vapor δ^{18}O, (e) snow and water vapor δD, (f) snow and water vapor d-excess. The uncertainties for each variable are displayed by shaded area in each subpanel.

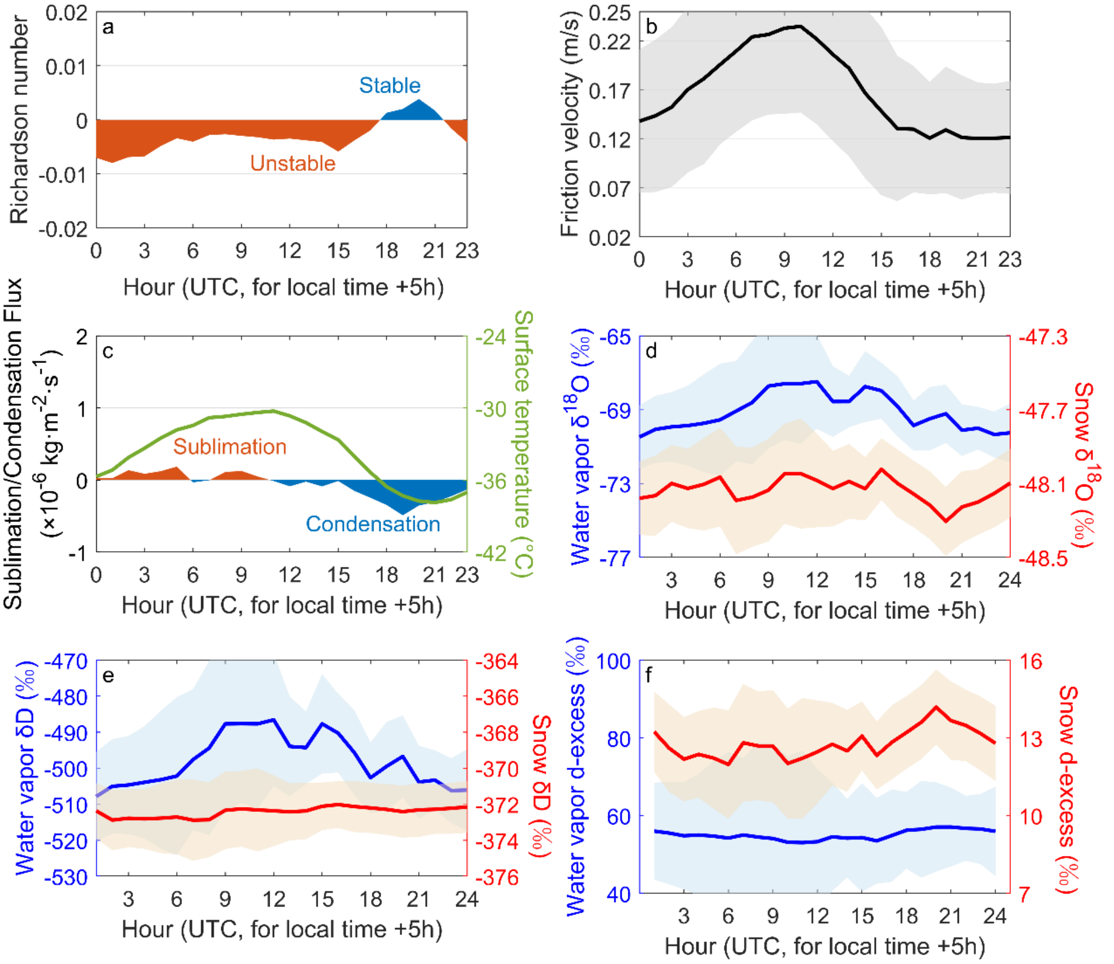

Figure 5: Same to Figure 4 but for Dome A under highly cloudy conditions in summer.

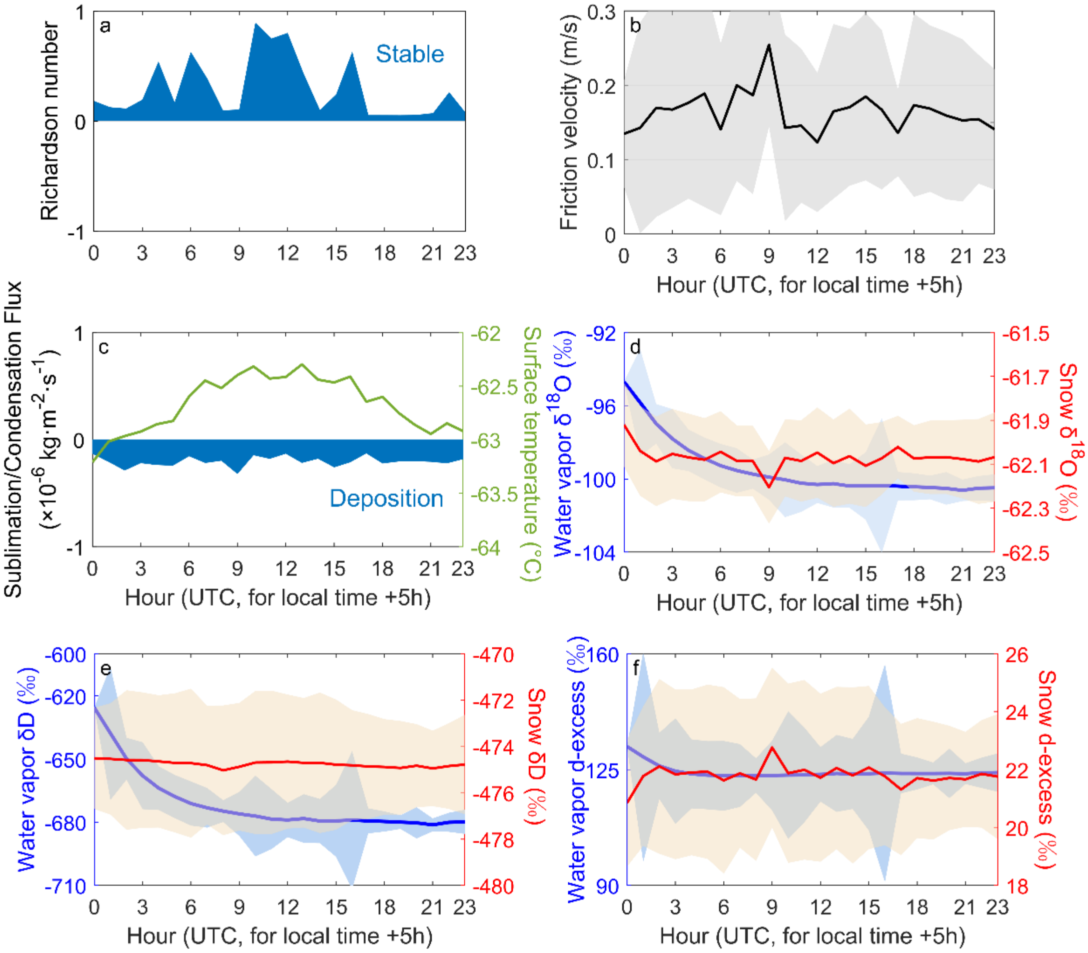

Figure 6: Same to Figure 4 but for Dome A under winter conditions.

End of the responses to Reviewer #3

Reference

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