A Case Study on Drivers of the Isotopic Composition of Water Vapour at the Coast of East Antarctica

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Key Points:

- Direct air mass advection from the ice sheet leads to strongly depleted vapour isotopic compositions at a ship close to the Mertz glacier.
- Both isotopic distillation due to cloud formation and sublimation of surface snow drive the vapour isotopic composition over the ice sheet.
- Ocean evaporation can quickly overwrite the isotopic signature of air masses shortly before arrival at the ship.

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Abstract

Stable water isotopes (SWIs) contain valuable information on the past climate and phase changes in the hydrologic cycle. Recently, vapour measurements in the polar regions have provided new insights into the effects of snow-related and atmospheric processes on SWIs. The purpose of this study is to elucidate the drivers of the particularly depleted vapour isotopic composition measured on a ship close to the East Antarctic coast during the Antarctic Circumnavigation Expedition in 2017. Reanalysis data and backward trajectories are used to model the isotopic composition of air parcels arriving in the atmospheric boundary layer (ABL) above the ship. A novel approach is developed to account for moisture exchanges with the snow surface. The model generally reproduces the observed trend with strongly depleted vapour δ^{18}O values in the middle of the 6-day study period. This depletion is caused by direct air mass advection from the ice sheet where the vapour is more depleted in heavy SWIs due to distillation during cloud formation. The time spent by the air masses in the marine ABL shortly before arrival at the ship is crucial as ocean evaporation typically leads to an abrupt change in the isotopic signature. Snow sublimation is another important driver because the air masses and the sublimation flux will differ substantially in their isotopic composition if the air masses cross the ocean-snow boundary or descend from higher atmospheric levels. Although our model makes strong simplifications, it is a useful and computationally efficient method for understanding SWI dynamics at polar sites.

Plain Language Summary

Stable water isotopes are useful to reconstruct historical temperature conditions from ice cores. This method is possible because phase changes of water alter the isotopic composition. For example, if an air mass cools down, forms clouds, and produces rain or snowfall, the water vapour preferentially looses heavy water molecules. This study aims to explain a remarkable vapour isotopic signal measured on a ship close to the East Antarctic coast during six days in 2017. We model the isotopic composition of air parcels along their pathways to the ship and develop a novel approach to represent moisture exchange with the snow surface. The modelled vapour isotopic composition at the ship reaches a distinct minimum, similar to the measurements, when the air parcels move directly from the ice sheet to the ship. As expected, the vapour isotopic composition is lower over the ice sheet than over the ocean, largely due to cloud formation. However, moisture uptake from the snow surface and from the ocean shortly before arrival at the ship can strongly and abruptly influence the isotopic signature of the air masses. Although our model is not perfect, it helps to improve the interpretation of isotope measurements at polar sites.

1 Introduction

Stable water isotopes (SWIs) are widely used as both tracers in the global hydrologic cycle (Koeniger et al., 2010; Elliot, 2014) and as climate proxies in ice cores (Lorius et al., 1979; Grootes et al., 1994; EPICA community members, 2004). Several processes affect the vapour and snow isotopic composition, starting from the process of ocean evaporation in the source region (Craig & Gordon, 1965; Merlivat & Jouzel, 1979), transport processes (Helsen et al., 2006), cloud formation and precipitation (Jouzel & Merlivat, 1984; Ciais & Jouzel, 1994), and post-depositional processes (Cuffey & Steig, 1998; Johnsen et al., 2001; Jouzel et al., 2003; Krinner & Werner, 2003; Helsen et al., 2005, 2007).

Isotopic fractionation during cloud formation gives rise to isotopic distillation of atmospheric vapour. As a result, snowfall and surface snow on the Antarctic Ice Sheet generally become more depleted in heavy SWIs with increasing distance from the coast and elevation (Masson-Delmotte et al., 2008). Isotopic fractionation also plays an important role in phase changes at the Earth's surface. While the fractionation effects are well understood in the case of ocean evaporation, they are subject of current research

in the case of snow sublimation. Traditionally, it was assumed that sublimation occurs layer by layer without fractionation (Friedman et al., 1991; Neumann & Waddington, 2004; Town et al., 2008). However, recent experimental studies found evidence of fractionation during sublimation. For example, Hughes et al. (2021) sampled near-surface vapour and snow in northeast Greenland with a high temporal resolution on clear-sky summer days. These measurements demonstrated that alternating periods of sublimation and vapour deposition can lead to clear diurnal cycles in the vapour isotopic composition, which are consistent with changes in the snow isotopic composition. Similar diurnal cycles in the vapour isotopic composition were reported for Dome C on the Antarctic plateau and explained by local sublimation and vapour deposition (Casado et al., 2016). These findings are supported by controlled experiments in cold laboratories, showing that snow-vapour exchange at the surface and in the pore space alters the isotopic compositions of snow and vapour (e.g., Sokratov & Golubev, 2009; Ebner et al., 2017). Equilibrium fractionation explains a large part of these SWI dynamics although changes in d-excess in both vapour and surface snow indicate some influence of kinetic fractionation (Casado et al., 2016; Hughes et al., 2021; Wahl et al., 2021).

The isotopic composition of atmospheric vapour observed at a specific site is influenced by weather changes on different time scales. At Thule Air Base, coastal northwest Greenland, Akers et al. (2020) observed a strong seasonal cycle in vapour isotopic composition controlled by shifts in sea-ice extent, which define the distance to marine moisture sources. Synoptic weather events led to variations over multiple days, superimposed on the seasonal cycle. At Syowa station, coastal East Antarctica, Kurita et al. (2016a) also found a strong influence of synoptic weather systems, causing advection of marine or glacial air masses with distinct isotopic signatures. At other coastal polar sites, shifts between these air masses manifest themselves in pronounced diurnal cycles in the vapour isotopic composition, at least in summertime high-pressure periods. An example is Dumont d'Urville, coastal East Antarctica, where strong katabatic winds advect dry air with strongly depleted δ^{18}O values from the interior of the ice sheet during the coldest hours of the day (Bréant et al., 2019). Similar diurnal cycles can be observed at Kangerlussuaq, southwest Greenland, where an ice-free strip of land alternatingly experiences katabatic winds and a see breeze (Kopec et al., 2014).

Apart from measurements, models are an important tool for understanding the dynamics of SWIs in the atmosphere and the driving processes. There are two modelling approaches: (1) Lagrangian models which simulate moist processes and isotopic fractionation along air parcel trajectories (Jouzel & Merlivat, 1984; Ciais & Jouzel, 1994; Helsen et al., 2006; Sinclair et al., 2011; Christner et al., 2017); and (2) Eulerian models, such as general circulation models (GCMs), which consider the temporal change on a fixed three-dimensional grid (e.g., Joussaume et al., 1984; Pfahl et al., 2012). Eulerian models provide a more accurate representation of the spatial variability of the isotopic composition of water vapour across the hydrologic cycle by accounting for the mixing of air masses of different origins and the highly variable pathways water vapour may take between evaporation and condensation. For example, GCMs are able to satisfactorily reproduce the global and seasonal variations in the isotopic composition of precipitation (Noone & Sturm, 2010; Hoffmann et al., 2000). However, it is more difficult to discern the effect of individual processes on isotopic variability using Eulerian models as these processes can be isolated less easily, compared to the computationally more efficient Lagrangian models (Dütsch et al., 2018). Thurnherr et al. (2021) used a combination of both approaches to better understand vapour isotopic measurements along the ship route of the Antarctic Circumnavigation Expedition (ACE). The output of the Eulerian model COSMO$_{iso}$ was analyzed along backward trajectories starting at the position of the ship. This method demonstrated that the cold and warm sectors of extratropical cyclones, associated with evaporation and dew formation, respectively, were important drivers of the vapour isotopic composition over the open ocean.

In the present study, we develop a Lagrangian model to explain the vapour isotopic signal of a specific event during the ACE campaign. We investigate in detail a 6-day period in January 2017, in which the ship stayed close to the Mertz glacier, East Antarctica, and the values of vapour $\delta^{18}O$ reached a pronounced minimum. The objectives are to (i) reproduce the $\delta^{18}O$ values of water vapour observed at the Mertz glacier using a Lagrangian model with simple isotope dynamics and (ii) better understand the influences of air mass origin and isotopic fractionation during moisture exchange with the Earth's surface and during cloud formation. Our model accounts for equilibrium fractionation but neglects kinetic effects during all phase changes apart from ocean evaporation. As some other models still neglect isotopic fractionation during snow sublimation, we analyze how sensitive the modelled vapour $\delta^{18}O$ is with respect to the assumptions that snow sublimation is or is not associated with equilibrium fractionation. Although our model represents some processes less accurately than the COSMO$_{iso}$-based modelling framework of Thurnherr et al. (2021), we are able to directly distinguish the effects of individual processes with a lower computational effort. The novelty of our Lagrangian isotope model is the fact that it computes the isotopic composition of sublimating surface snow by accounting for the history of snowfall and surface-atmosphere exchange, considering a multi-layer snowpack. The last aspect is an advantage over the COSMO$_{iso}$ model, which treats the snowpack as a single homogeneous layer.

2 Data and Methods

2.1 Water Vapour Measurements at the Mertz Glacier

The ACE campaign took place between November 2016 and April 2017. A continuous time series of water vapour isotopic composition was recorded at the position of the ship at a height of approximately 13.5 m a.s.l. using a cavity ring-down laser spectrometer with a high temporal resolution of 1 s. More details and an overview of this time series can be found in Thurnherr, Kozachek, et al. (2020). Here, we focus on the period from 27th January to 1st February 2017 as it includes two consecutive days with exceptionally depleted values of $\delta^{18}O$ and δD. This event occurred while the ship was anchored close to the outlet of the Mertz glacier and coincided with low values of specific humidity and high values of d-excess (Figure 5 in Thurnherr, Kozachek, et al., 2020), typical of continental Antarctic interior air masses (Bréant et al., 2019).

2.2 Modelling Approach

We developed a model, which considers the most common three SWIs ($H_2{}^{16}O$, $H_2{}^{18}O$, $HD{}^{16}O$) although we only present $\delta^{18}O$ in the results. The model consists of two parts: (i) *Model Sublimation* computes the isotopic composition of surface snow, which determines that of the sublimation flux; (ii) *Model Air Parcel* quantifies the vapour isotopic composition along air parcel trajectories, considering vapour exchange with the snow or ocean surface and vapour removal due to cloud formation (Figure 1). For the phase changes of snow sublimation, vapour deposition, and condensation, we only consider equilibrium fractionation as a first-order approximation and use temperature-dependent formulas for the fractionation factors from Merlivat and Nief (1967), Majoube (1970), and Majoube (1971). To evaluate the importance of fractionation during sublimation, we compare two simulations, which assume that snow sublimation is associated with equilibrium fractionation (Run E) or not associated with any fractionation (Run N). In both simulations, kinetic fractionation is only taken into account in the process of ocean evaporation by applying the widely-used Craig-Gordon formula in its original form (Craig & Gordon, 1965; Horita et al., 2008).

The next sections explain the input data and main characteristics of the two model parts while further methodological details and equations can be found in Texts S1 to S3 in the Supporting Information. Important model constants and parameters are listed in
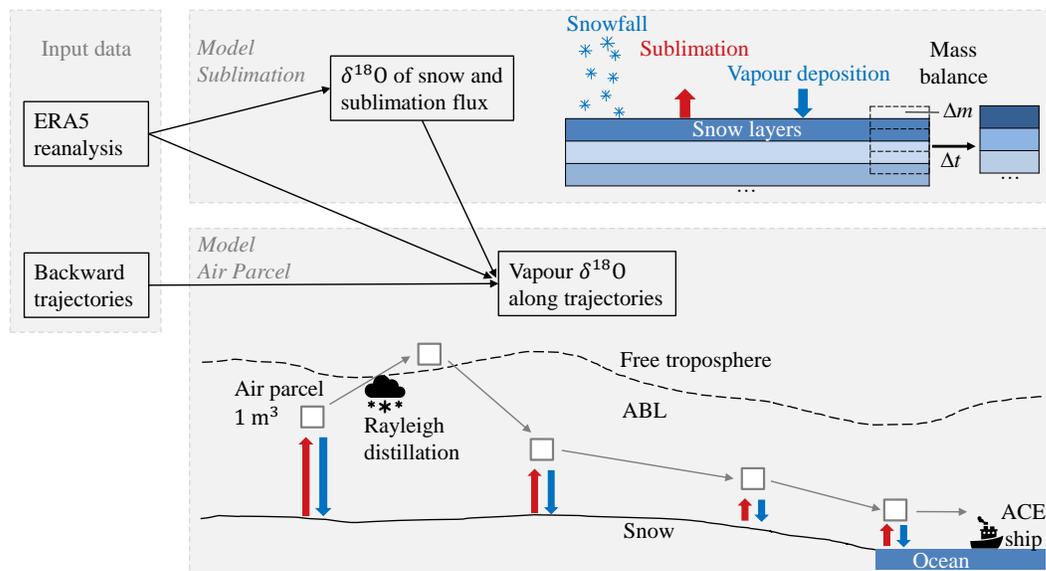
Figure 1. Schematic illustration of the modelling approach. The net accumulation of snow mass in one time step (Δt), denoted by Δm, may be positive or negative.

Table S1. For brevity, we refer to the surface water vapour flux as the surface flux from here on. All time information in this paper is given in UTC time while local time at the outlet of the Mertz glacier corresponds to UTC+10 h.

2.2.1 Input Data

The model uses ERA5 reanalysis data produced by the European Centre for Medium-Range Weather Forecasts (ECMWF) with spatial and temporal resolutions of $0.25° \times 0.25°$ and 1 h, respectively (Hersbach et al., 2018). The following variables were retrieved: land-sea mask, mean snow evaporation rate (for grid cells with land fraction > 0.5 and latitude $< 60°$ S), mean evaporation rate (for grid cells with land fraction ≤ 0.5, considered as liquid ocean surface), air temperature and dew point temperature at 2 m height, surface temperature, atmospheric pressure, and snowfall rate. Snow evaporation, i.e., sublimation, and ocean evaporation are based on the common Monin-Obukhov bulk parameterization assuming constant roughness lengths on the ice sheet ($z_{0m} = 0.0013$ m, $z_{0T} = z_{0q} = 0.00013$ m) and dynamic roughness lengths for the ocean depending on a wave model (ECMWF, 2016). In addition to the snow surface, drifting and blowing snow particles contribute to the sublimation flux (Sigmund et al., 2021) and consequently they may change their isotopic composition. However, drifting and blowing snow is not represented in the ERA5 reanalysis and there is little knowledge about isotopic effects of this process. In the main analysis, we use data for latitudes south of $30°$ S from July 2016 to February 2017. The first six months serve as a spin-up period to reduce uncertainties arising from the initialisation of the snow isotopic composition. For purposes of validation, we compare results of *Model Sublimation* with isotope measurements at Dome C, East Antarctica, published by Casado et al. (2016, 2018). To this end, ERA5 data for the grid cell including Dome C ($75°$ S, $123.25°$ E) and the period from January 2013 to January 2016 are used.

Model Air Parcel additionally assimilates 10-day backward air parcel trajectories taken from Thurnherr, Wernli, and Aemisegger (2020). These trajectories were calculated with the Lagrangian analysis tool LAGRANTO (Wernli & Davies, 1997; Sprenger

& Wernli, 2015) using the 3D-wind fields from the ECMWF operational analyses. Every hour, a set of trajectories was launched from up to 56 vertical levels between 0 and 500 hPa above sea level along the ACE cruise track. For each trajectory, the time step was 3 h. In this study, the following variables were extracted for trajectories arriving at the ship in the period from 27th January to 1st February 2017: air pressure at heights of the air parcel and the ABL, specific humidity, and air temperature.

2.2.2 Model Sublimation

In the case of snow sublimation, the isotopic composition of the surface flux depends on that of the surface snow (e.g., Wahl et al., 2021). The latter is initialized with typical values for snowfall depending on the temperature and the effects of snowfall and surface flux on the snow isotopic composition are simulated with time. The snowfall $\delta^{18}O$ is parameterized as a linear function of the daily running mean air temperature because in the literature, this relationship is derived from daily mean values. We apply the same linear function to snowfall over the whole Antarctic continent although different $\delta^{18}O$-temperature slopes have been measured at different sites. In our baseline simulation, the function for snowfall $\delta^{18}O$ is taken from Stenni et al. (2016), henceforth Stenni16, and characterized by an intermediate slope of 0.45‰ K^{-1}. Sensitivity tests are performed using functions from Landais et al. (2012) and Fujita and Abe (2006), henceforth Landais12 and FA06, respectively, with low and high slopes of 0.35‰ K^{-1} and 0.78‰ K^{-1}, respectively (Texts S2 and S4 in the Supporting Information).

The snowpack is modelled as a series of 100 layers, each with the same thickness and a constant density of 350 kg m^{-3}. For the location of Dome C, we tested three values for the snow layer thickness (0.1 cm, 1 cm, and 10 cm) and compared the surface snow $\delta^{18}O$ with measurements of Casado et al. (2018). A thickness of 1 cm led to the best agreement and was therefore selected for the remaining analysis (Text S4 and Figure S1 in the Supporting Information). We assume that the snowpack always exists in grid cells south of 60° S with a land fraction greater than 0.5. If the snowfall and surface fluxes add or remove snow mass at the surface, a simple mixing mechanism will guarantee that the thickness and mass of the snow layers remain constant. More precisely, a part of each layer is mixed with an adjacent layer to compensate for the mass gain or loss at the surface (Figure 1). We neglect changes in snow density and assume that snow added by snowfall or vapour deposition has the same density as the snowpack. The mixing mechanism is a vastly simplified version of a realistic vapour transport mechanism (Jafari et al., 2020). In reality, the interplay between ventilation, isotope diffusion within the snowpack and recrystallisation can cause a continuous replacement of the interstitial water vapour in the surface snow layer. However, it is still an open question how the combination of these processes can quantitatively change the isotopic compositions of snow and the water vapour in the ABL. Therefore, our model is based on the following assumptions: (1) no isotope diffusion within the snow layers; (2) no impact of snow metamorphism on the isotopic profile; (3) fractionation only at the uppermost snow layer because of its direct contact with the atmosphere; and (4) no ventilation within the snow layer.

In the case of vapour deposition, the isotopic composition of the surface flux depends on that of the atmospheric vapour. *Model Sublimation* estimates the latter as the mean of two hypothetical values for vapour, which is in isotopic equilibrium with the surface snow or with potential snowfall, respectively. This simple estimate accounts for the fact that both local snow sublimation and the distillation process during air mass transport can influence the vapour isotopic composition. However, the importance of both influences varies in reality depending on weather conditions. Figure S2b and Text S4 in the Supporting Information show that the simple estimate for vapour $\delta^{18}O$ reproduces the mean value measured by Casado et al. (2016) at Dome C in a 24-d period in austral summer 2014/2015 (mean bias error of −0.2‰) although the temporal variability is strongly underestimated. On the basis of this comparison, we expect uncertainties of

a few ‰ in our simple estimate of the vapour isotopic composition. This estimate is only used to compute the effect of a limited amount of vapour deposition in *Model Sublimation* and to initialize some of the air parcels. Vapour deposition plays a limited role because the total mass removed from all modelled air parcels due to vapour deposition is 22 times lower than the total mass taken up by all parcels due to snow sublimation.

2.2.3 Model Air Parcel

We consider air parcels with a constant volume of $1 \times 1 \times 1$ m^3, travelling along the trajectories that arrive within the ABL at the position of the ship. This criterion results in 6 to 24 trajectories per arrival time and an average value of 13 trajectories. The isotopic composition of each air parcel is initialized when the parcel resides in the ABL for the first time. If this situation occurs over snow (land fraction > 50 % and latitude south of $60°$ S), the isotopic composition of the parcel will be initialized as a function of the isotopic compositions of surface snow and potential snowfall (same assumption as used in *Model Sublimation* for atmospheric vapour). Over the ocean, the parcel is only initialized when it is influenced by evaporation because this condition allows us to estimate the initial isotopic composition of the parcel using the Craig-Gordon formula simplified with the global closure assumption (e.g. Dar et al., 2020). Under this assumption, the isotopic composition of atmospheric vapour equals that of the evaporate. If the trajectory crosses the ABL over land north of $60°$ S, the isotopic composition of the surface flux is not known and therefore the parcel will be initialized once over water or south of $60°$ S. An overview of the locations of initialization and the position of the ship is given in Figure 2. On average, the air parcels are initialized 5.3 days before arriving at the ship. The specific humidity of the parcel is initially taken from the trajectory data set and then modelled explicitly.
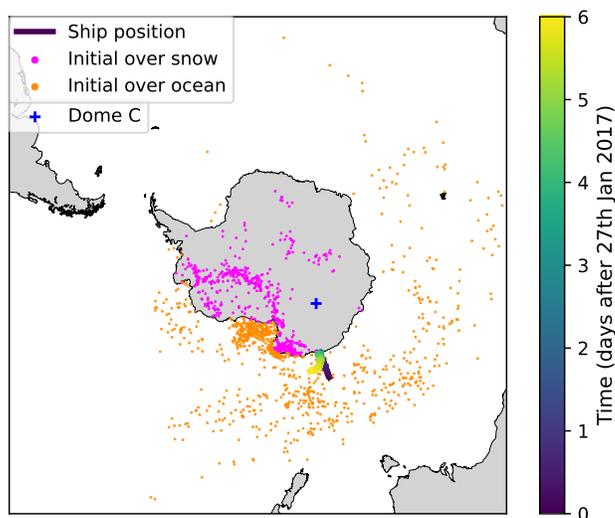

Figure 2.   Map with the position of the ship (colored line) during the study period, the initial locations of the modelled air parcels (dots), and the location of Dome C (blue cross).

Along the trajectory, the specific humidity and isotopic composition of the parcel can change due to the surface flux and cloud formation. The surface flux will only affect the parcel if it resides in the ABL. Assuming a well-mixed ABL with a height-constant vapour density, the moisture flux into or out of the parcel (J_{a}) due to the surface flux

276 (J) is computed as

$$J_{\mathrm{a}} = J \frac{d_{\mathrm{a}}}{d_{\mathrm{ABL}}} \;, \tag{1}$$

277 where $d_{\mathrm{a}} = 1$ m and d_{ABL} are the depths of the air parcel and ABL, respectively. The
278 specific humidity in *Model Air Parcel* agrees approximately with that in the trajectory
279 data set (Figure S3 in the Supporting Information). Considering all data points from
280 the initialization of the air parcels to the arrival at the ship, the specific humidity in *Model*
281 *Air Parcel* is characterized by a RMSE of 0.6 g kg^{-1} and a correlation coefficient of $\rho =$
282 0.94 when compared with the trajectory data set. Comparing only the values at the fi-
283 nal position of the air parcels (i.e., at the ship) with the trajectory data set, specific hu-
284 midity tends to be underestimated with RMSE $= 0.9$ g kg^{-1} and $\rho = 0.45$.

285 In the case of snow sublimation, the isotopic composition of the surface flux is taken
286 from *Model Sublimation*. In all other cases (ocean evaporation, condensation, or vapour
287 deposition), the isotopic composition of the surface flux depends and feeds back on that
288 of the air parcel (Text S3 in the Supporting Information). To guarantee an accurate feed-
289 back, the time step needs to be small enough, especially if the vapour mass taken up or
290 removed from the air parcel is in the same order of magnitude as the vapour mass con-
291 tained in the parcel. Therefore, the effects of ocean evaporation, condensation, or vapour
292 deposition are computed step-wise by dividing each 3-h time step into 32 sub-intervals
293 of equal length. This value was justified using an example situation, for which the num-
294 ber of sub-intervals was continuously increased by a factor of two until the isotopic com-
295 position of the parcel at the end of the 3-h step changed by less than 1 %. We assume
296 that there is no sea ice during the 6-day period in austral summer.

297 Isotopic fractionation during cloud formation is calculated using the classic Rayleigh
298 distillation model with equilibrium fractionation (Jouzel & Merlivat, 1984; Sinclair et
299 al., 2011). It assumes that the liquid or solid water phase is removed immediately after
300 its formation, i.e., the cloud water precipitates immediately. The equilibrium fraction-
301 ation factors used in the Rayleigh model are computed as in Sinclair et al. (2011), ac-
302 counting for mixed-phase clouds with a gradual, linear shift from the vapour-liquid to
303 the vapour-ice transition as the air temperature decreases from 0° C to −20° C. Changes
304 in air density along the trajectory influence the vapour mass contained in the parcel as
305 they imply exchange of air with the surrounding atmosphere. The model assumes that
306 this exchange of air does not have a direct effect on the isotopic composition of the par-
307 cel.

3 Results and Discussion

309 As the model only accounts for equilibrium fractionation in most phase change pro-
310 cesses, the simulated dynamics of δ^{18}O and δD are very similar. Therefore, we only present
311 results for δ^{18}O.

3.1 Comparison of Modelled and Measured Vapour Isotopic Composi-tions

314 Figure 3 compares the ensemble averaged vapour δ^{18}O of the air parcels with the
315 measurements on the ship close to the Mertz glacier. We show the baseline simulations
316 using the relationship of Stenni16 to parameterize the snowfall isotopic composition in
317 *Model Sublimation*. Similar to the measurements, the modelled vapour δ^{18}O at the ship
318 is approximately −15‰ in the beginning and at the end of the investigated 6-day pe-
319 riod and reaches a minimum of approximately −39‰ in the middle of the period. The
320 simulation considering equilibrium fractionation (Run E) leads to slightly more depleted
321 vapour isotopic compositions in the middle of the period, compared to the simulation
322 neglecting fractionation during snow sublimation (Run N). At other times, the vapour
323 isotopic composition is identical for both model runs. Overall, both runs achieve a sim-

324 ilar agreement with the measurements with the same root-mean-square error (RMSE)
325 of 5.2‰ and similar Pearson correlation coefficients of 0.82 (Run E) and 0.80 (Run N).
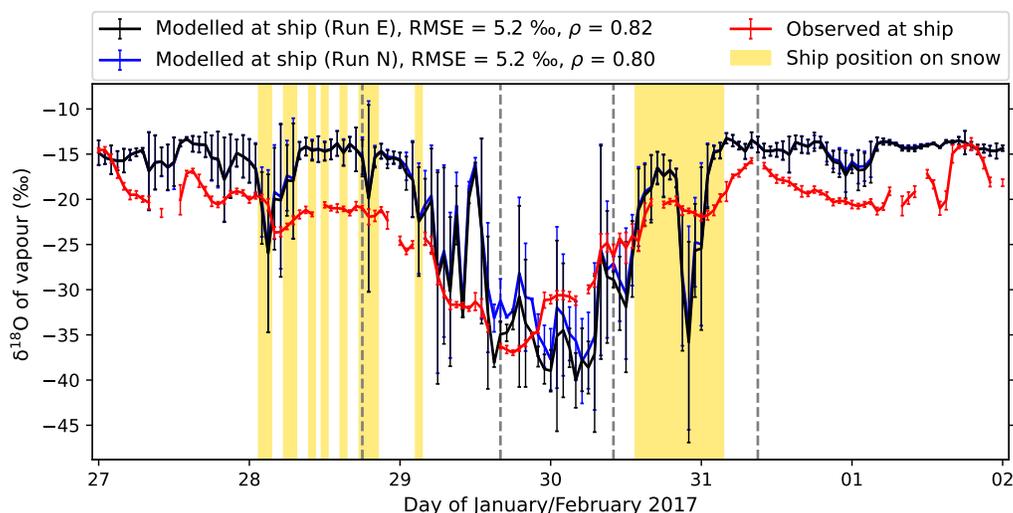

Figure 3. Modelled and measured $\delta^{18}O$ of atmospheric water vapour at the ship close to the Mertz glacier from 27th January to 1st February 2017. We show the modelled ensemble averages and standard deviations for multiple air parcels in the baseline simulations. The measurements represent 1-h mean values and standard deviations. In the legend, root-mean-square errors (RMSE) and Pearson correlation coefficients (ρ) are specified. The yellow shading indicates times when the ship was located in a grid cell modelled as snow surface; at the other times, the ship was in a grid cell treated as ocean surface. The vertical grey dashed lines indicate times analyzed in Figure 6.

326   In the first two and last two days of the period, the modelled $\delta^{18}O$ is generally more
327 enriched than the measured one with an average difference of 4‰. Possible reasons may
328 be (i) a bias in the initial isotopic composition of air parcels over the ocean due to the
329 global closure assumption or a bias in the surface water $\delta^{18}O$; (ii) the neglect of kinetic
330 fractionation during cloud formation; (iii) the neglect of mixing of air masses with dif-
331 ferent isotopic compositions, e.g., at weather fronts; and (iv) the simple assumption that
332 the vapour mass exchanged between the atmosphere and the surface is homogeneously
333 distributed in the ABL (Equation 1). This last assumption does not account for the fact
334 that the air and vapour densities decrease with height and that the air in the ABL may
335 not be perfectly mixed, especially in a stable ABL.

336   The largest mismatch between the model and the measurements is found on 29th
337 January at 12:00 and 30th January at 22:00 when the modelled time series shows two
338 strong peaks. The first (second) peak overestimates (underestimates) the measured $\delta^{18}O$
339 by approximately 15‰. Apart from the aforementioned shortcomings of the model, the
340 coarse spatial resolution may contribute to the temporary mismatch as the coastline is
341 not accurately represented. During the first (second) peak, the ship was located in a grid
342 cell treated as ocean (snow) surface (yellow shading in Figure 3). Consequently, the model
343 may overestimate (underestimate) the time spent by the air parcels in the marine ABL
344 shortly before arriving at the ship. If an air parcel with a strongly depleted $\delta^{18}O$ value
345 reaches the coast and takes up moisture from the liquid ocean surface, the isotopic sig-
346 nature of the parcel can change abruptly as the $\delta^{18}O$ value of the evaporation flux can
347 be depleted or enriched compared to the ocean water (Equation S13 in the Supporting

Information). Furthermore, sea ice may cover a part of the ocean close to the Antarctic cost even in austral summer, which is neglected in the model. Additionally, the ABL height provided with the trajectory data set may not always be accurate, which influences the modelled time period and magnitude of moisture exchange between the air parcels and the surface. Although there are some hours with a large model-measurement mismatch, the model is able to reproduce the general trend and timing of the vapour depletion event on 29th and 30th January 2017.

3.2 Sensitivity of the Isotopic Composition of the Air Parcels with Respect to That of Snowfall

It is important to note that changing the snowfall isotopic composition in *Model Sublimation* does not affect the isotopic composition of the air parcels during cloud formation. The isotopic composition of snowfall is only used to estimate that of surface snow, which determines that of the sublimation flux and influences the initial isotopic composition of the air parcels. Figure 4 shows how the modelled $\delta^{18}O$ at the ship changes when assuming different snowfall δ-temperature relationships in Run E (Equations S7 to S9). Differences in the $\delta^{18}O$ time series are mainly visible in the middle of the study period, suggesting that many air parcels are initialized over snow or influenced by sublimation at this time. The snowfall δ-temperature relationship of FA06 leads to a less pronounced minimum of $-34‰$ in the vapour $\delta^{18}O$ time series, compared with the baseline simulation using the relationship of Stenni16. On the contrary, the snowfall δ-temperature relationship of Landais12 leads to the most pronounced $\delta^{18}O$ minimum of $-45‰$. The best agreement with the measurements is obtained for the baseline simulation (RMSE = $5.2‰$, $\rho = 0.82$) although the agreement is still reasonable for the simulations using the relationships of FA06 (RMSE = $5.3‰$, $\rho = 0.80$) and Landais12 (RMSE = $5.7‰$, $\rho = 0.82$). The generalization of a site-dependent, idealized δ-temperature relationship for snowfall is a strong simplification in the model and contributes to deviations between the model and the measurements. Nevertheless, the associated sensitivity of the vapour $\delta^{18}O$ is small enough to draw useful conclusions about the dominant processes driving the isotopic signal.
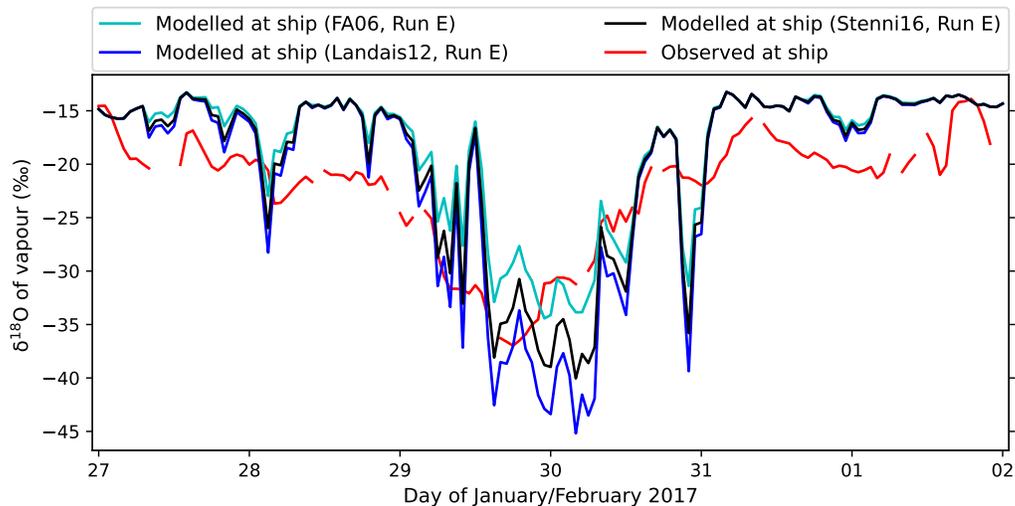

Figure 4. Effect of different snowfall δ-temperature relationships assumed in *Model Sublimation* on the modelled $\delta^{18}O$ of atmospheric water vapour at the ship in Run E. Modelled ensemble averages are compared with measured 1-h averages.

3.3 Drivers of the Vapour Isotopic Composition

Previous studies at other coastal polar sites have found distinct isotopic signatures for air masses advected from the ocean and those advected from the ice sheet (e.g., Kopec et al., 2014; Kurita et al., 2016a, 2016b). Therefore, it is a plausible hypothesis that shifts between such air masses largely explain the observed isotope dynamics close to the Mertz glacier. The more depleted isotopic composition of vapour over the ice sheet is generally thought to result from the distillation effect of cloud formation. However, snow sublimation including isotopic fractionation also influences the variability of the vapour isotopic composition. As the ocean is often a strong vapour source, the distance between the ship and the ice sheet may play an important role. In the marine boundary layer, a strong vertical humidity gradient, typically associated with cold air advection over a relatively warm ocean surface, leads to strong evaporation with enhanced equilibrium and kinetic fractionation. This effect can cause differences of several ‰ in the vapour $\delta^{18}O$ between cold and warm sectors of extratropical cyclones but it is unlikely to explain a large decrease of more than 10‰ (Thurnherr et al., 2021). We now investigate which of the aforementioned drivers play a dominant role in our case study.

On the first day and during most of the last two days of the study period, the ship moved towards and away from the ice sheet, respectively (Figure 2). Due to a longer distance to the ice sheet, it is likely that recent ocean evaporation caused the relatively enriched vapour $\delta^{18}O$ at this time. From 28th January 2017, 02:00, to 31st January 2017, 06:00, the ship stayed in close proximity to the ice sheet. In this phase, the $\delta^{18}O$ remained relatively enriched for one day and then dropped to very depleted values. The fact that only the most depleted $\delta^{18}O$ values in the time series are sensitive with respect to assumptions in *Model Sublimation* (Figures 3 and 4) is consistent with the hypothesis that processes over the ocean drove the vapour isotopic composition in the first and last two days of the period while processes over the Antarctic Ice Sheet influenced the isotopic signature in the middle of the period. Moreover, the small differences between Runs E and N demonstrate that isotopic fractionation during snow sublimation can only explain a very small part of the minimum in the $\delta^{18}O$ time series.

The initial isotopic composition of the air parcels can influence the model results, especially if the time between initialization and arrival at the ship is short. Air parcels initialized over the ocean start their trajectories with a fairly uniform $\delta^{18}O$ between approximately $-15‰$ and $-11‰$ (Figure 5a). These initial values are similar to the final isotopic composition modelled at the ship during the first two and last two days of the investigation period, suggesting that ocean evaporation is an important driver. As expected, air parcels initialized over snow have more variable and more depleted initial $\delta^{18}O$ values than those initialized over ocean. Interestingly, there are almost always some air parcels that are initialized over snow and the range of their initial $\delta^{18}O$ values remains similar throughout the period (approximately $-70‰$ to $-40‰$). However, when the most depleted $\delta^{18}O$ values are observed at the ship, almost all air parcels are initialized over snow. This fact supports the hypothesis that the air masses originate from the interior of the ice sheet at this time.

To asses the importance of different moisture exchange processes along the trajectories, we show in Figure 5b the ensemble-averaged total change of vapour mass in an air parcel due to specific processes. Except in the middle of the study period, moisture uptake from the ocean and moisture removal due to cloud formation clearly have the largest impact on the moisture budget of the air parcels. As expected, the magnitude of these moisture exchanges largely reflects the varying travel times of the air parcels and, in particular, the amount of time spent in the marine ABL (Figure 5c). Only in the middle of the study period, moisture uptake due to snow sublimation becomes the dominant term in the moisture budget of the parcels while the time spent in the marine ABL is close to zero. Although the parcels experience very little cloud formation at this time, the distillation effect of cloud formation may still be responsible for the very depleted $\delta^{18}O$ val-

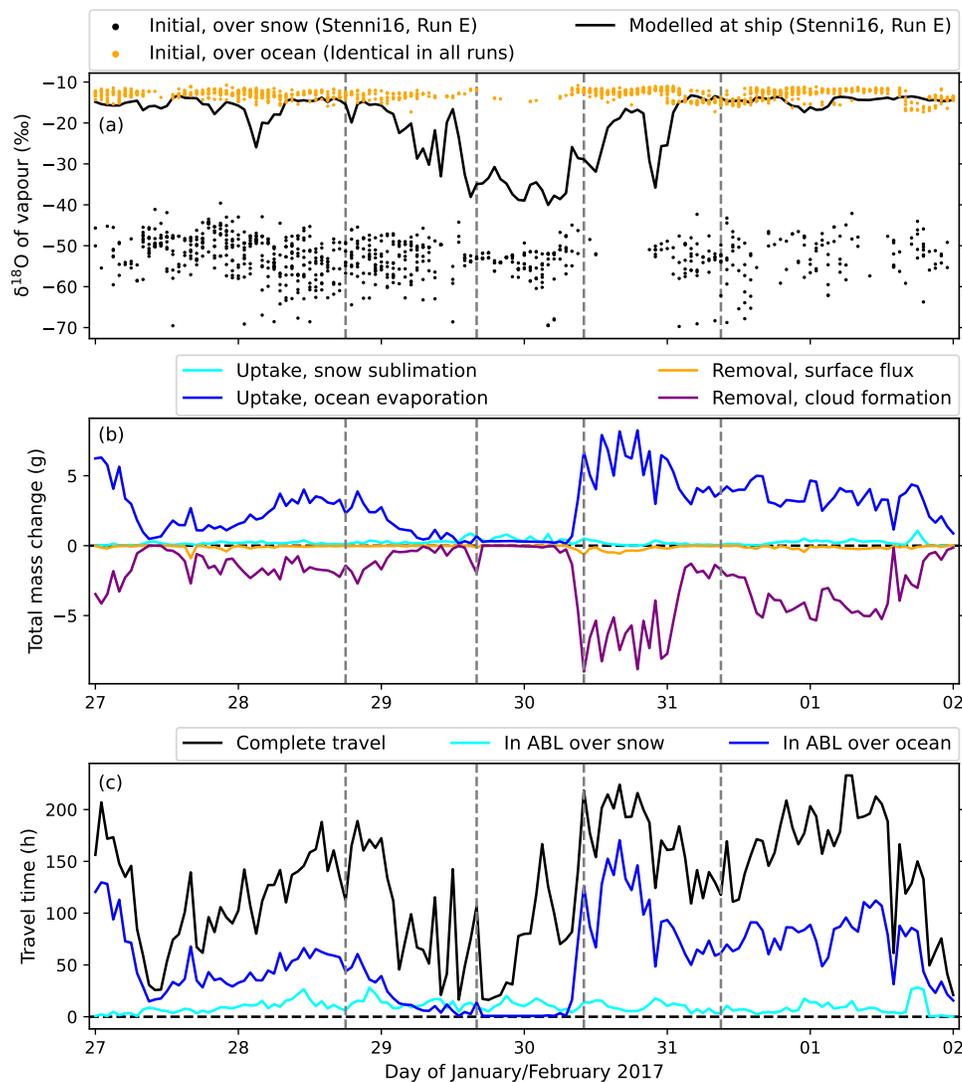**Figure 5.** (a) Comparison between initial $\delta^{18}O$ of individual air parcels and ensemble-averaged final $\delta^{18}O$ in Run E; (b) Ensemble average of the total change of vapour mass in an air parcel due to different processes between initialization and arrival at the ship; (c) Average travel time of the air parcels and average times spent in the boundary layers (ABLs) over snow and ocean. The vertical grey dashed lines indicate times analyzed in Figure 6.

430   ues as this effect is reflected by the temperature dependence of the initial isotopic com-
431   position of the air parcels over snow. Vapour removal due to the surface flux is gener-
432   ally the smallest term in the moisture budget and most of the time negligible. Overall,
433   Figures 3–5 show that the air masses with the most depleted $\delta^{18}O$ values originate from
434   the ice sheet and their isotopic signature is influenced by snow sublimation. This iso-
435   topic signature seems to only reach the ship if the air masses spend little time in the ma-
436   rine ABL shortly before their arrival such that ocean evaporation cannot overwrite the
437   signature.

438   To better understand which drivers act in which sections of the air parcel trajec-
439   tories, we present trajectory maps for four different arrival times in Figure 6. The ar-

rival times include situations with relatively enriched and depleted δ^{18}O values while the
ship was close to the ice sheet and the ensemble averaged travel time of the air parcels
was at least 4 days. Similar maps indicating locations where the parcels reside in the ABL
can be found in Figure S4 in the Supporting Information. Figures 6a and 6d show sim-
ilar situations leading to relatively enriched δ^{18}O values at the ship. In both situations,
the air parcels travel some distance in the marine ABL parallel to the Antarctic coast
before arriving at the ship. Almost half of the air parcels are initialized over the ice sheet
and exhibit strongly depleted δ^{18}O values around $-50‰$ until they enter the marine ABL.
Due to ocean evaporation, the δ^{18}O of the air parcels quickly increases and reaches val-
ues comparable to those of parcels initialized over the ocean.
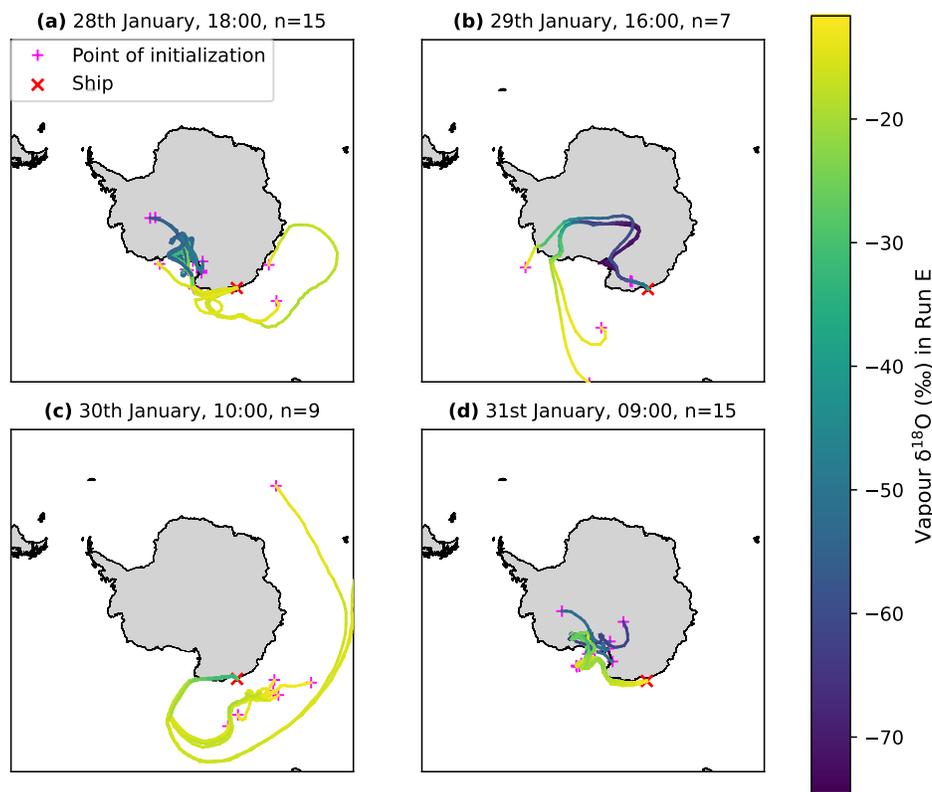
Figure 6. Vapour δ^{18}O along air parcel trajectories in the baseline simulation of Run E for
four different times of arrival at the ship (grey dashed lines in Figures 3 and 5). The number of
trajectories is denoted by n. Trajectories arriving at the ship at a lower height are plotted on top
of other trajectories.

Figure 6b refers to a situation with one of the most depleted δ^{18}O values measured
at the ship. Four of seven air parcels are initialized over the ice sheet and take a direct
and short route to the ship where they only take up moisture from the ocean in the last
time step. Their final δ^{18}O values are similar to those of the other three parcels that are
initialized over the ocean and travel over the interior of the ice sheet before taking the
same final route as the parcels initialized over snow. While the parcels are lifted over the
ice sheet, their isotopic composition becomes increasingly depleted due to the distilla-
tion effect of cloud formation and reaches extreme δ^{18}O values of approximately $-60‰$ to
$-75‰$. Only towards the end of the trajectories as the parcels move over the escarpment
zone of the ice sheet, they enter the ABL over snow (Figure S4b). At this time, approx-
imately 20 h before the arrival at the ship, snow sublimation adds vapour with a rela-

tively enriched δ^{18}O value to the parcels (Figure 7). The sublimation flux in the escarpment zone is relatively enriched in heavy SWIs compared to the air parcels because their isotopic composition was shaped at higher and colder levels over the interior of the ice sheet. Additionally, the parcel isotopic composition is particularly sensitive with respect to moisture uptake after most of the initial vapour mass was removed from parcels due to cloud formation. As a consequence, the moisture uptake in the escarpment zone increases the isotopic composition of the parcels abruptly. This increase caused by sublimation is similarly strong as another increase in the last time step, when the parcels reach the ocean and take up moisture from the water surface.
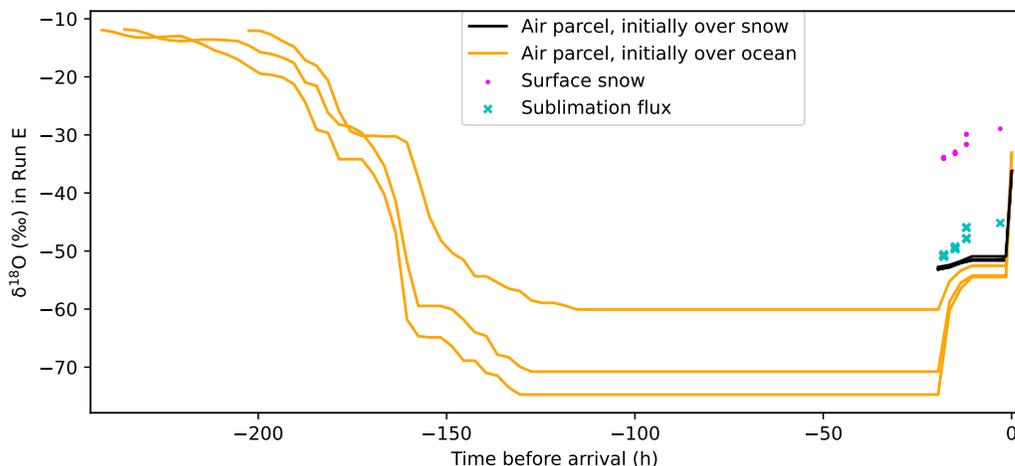
Figure 7. Vapour δ^{18}O as a function of time for the air parcel trajectories arriving at the ship on 29th January, 16:00, in the baseline simulation of Run E (corresponding to Figure 6b). The points and crosses show δ^{18}O values of the surface snow and sublimation flux, respectively, at locations where the air parcels reside in the ABL over snow.

The situation shown in Figure 6c leads to an intermediate δ^{18}O at the ship. All air parcels start their trajectories over the ocean and finally travel over the coastal zone of the ice sheet. Already over the ocean, cloud formation and condensation at the surface begin to decrease the δ^{18}O of the parcels. As soon as the parcels reach the ice sheet, their δ^{18}O continues to decrease because snow sublimation adds vapour with a more depleted δ^{18}O value to the air parcels. In this situation, the sublimation flux is more depleted in heavy SWIs compared to the parcels because the latter carry the isotopic signature of processes over the ocean.

4 Conclusions

We developed a Lagrangian isotope model with the aim to reproduce and explain the vapour δ^{18}O time series measured on the ACE ship close to the Mertz glacier in a 6-day period in austral summer 2017. The vapour mass and isotopic composition of air parcels was modelled along trajectories between an initial location in the ABL and the final location in the ABL at the ship. While isotope effects of cloud formation and ocean evaporation were represented with common approaches (classic Rayleigh distillation model and Craig-Gordon formula, respectively), the effect of snow sublimation was estimated using a novel approach, considering changes of the isotopic composition in a multi-layer snowpack due to snowfall, sublimation, and vapour deposition.

Similar to the measured values, the modelled vapour $\delta^{18}O$ at the ship reaches a pronounced minimum value of $-39‰$ in the middle of the study period. The RMSE of the baseline simulation amounts to $5.2‰$, which is reasonable considering the model limitations such as the neglect of kinetic fractionation in phase change processes apart from ocean evaporation and the neglect of mixing of air masses with different isotopic compositions. Our analysis confirms the hypothesis that the relatively enriched $\delta^{18}O$ values are associated with air masses advected from the ocean whereas the strongly depleted $\delta^{18}O$ values are caused by direct advection of air masses from the Antarctic Ice Sheet. This result is consistent with similar observations at other coastal polar sites in the literature. As expected, cloud formation leads to very depleted vapour isotopic compositions over the ice sheet. Snow sublimation can also significantly modify the isotopic composition of the air parcels depending on their origin. For example, air parcels originating from high levels over the interior of the ice sheet may carry a strongly depleted isotopic signature to the escarpment zone of the ice sheet and then experience an abrupt and strong enrichment in heavy SWIs due to a relatively enriched sublimation flux. However, the model options of considering or neglecting equilibrium fractionation during sublimation play a minor role. A critical factor for the vapour $\delta^{18}O$ at the ship is the time that the air parcels spend in the marine ABL shortly before arriving at the ship because ocean evaporation can quickly overwrite their isotopic signature.

Our modelling approach could be adapted for a study similar to Helsen et al. (2006) to simulate the vertical isotope profile in snow pits using backward trajectories for events of snow accumulation at an Antarctic site and deriving the isotopic composition of local snowfall from that of the air parcels. In contrast to the model of Helsen et al. (2006), our model accounts for the post-depositional effects of snow sublimation and vapour deposition. However, further improvements in our model such as the parameterization of kinetic fractionation during cloud formation and a more sophisticated vapour transport mechanism in the snowpack may be important for this purpose. Moreover, the deposition of drifting and blowing snow can contribute to snow accumulation and influence the isotopic composition of surface snow. To understand the latter effect, fundamental research is needed as the isotopic composition of drifting and blowing snow particles may be altered by sublimation, which has not been studied so far.

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Open Research

Model results were generated using Copernicus Climate Change Service information [2021] available at https://doi.org/10.24381/cds.adbb2d47 (Hersbach et al., 2018). The air parcel trajectories were downloaded from https://doi.org/10.5281/zenodo.4031705 (Thurnherr, Wernli, & Aemisegger, 2020). The calibrated isotope maesurements from the ACE campaign were downloaded from https://doi.org/10.5281/zenodo.3250790 (Thurnherr & Aemisegger, 2020). Validation data from the Dome C site containing $\delta^{18}O$ of surface snow and atmospheric vapour were retrieved from https://doi.org/10.5194/tc-12-1745-2018-supplement and https://doi.org/10.5194/acp-16-8521-2016-supplement, respectively (Casado et al., 2016, 2018). The python programming code and the main model output

including the data shown in the figures are available at
https://drive.switch.ch/index.php/s/ObsiN3bmBGagk9P (This data will be published
in a repository at the end of the peer review process). The figures were made with Mat-
plotlib version 3.5.1, available under the Matplotlib license at https://matplotlib.org/.

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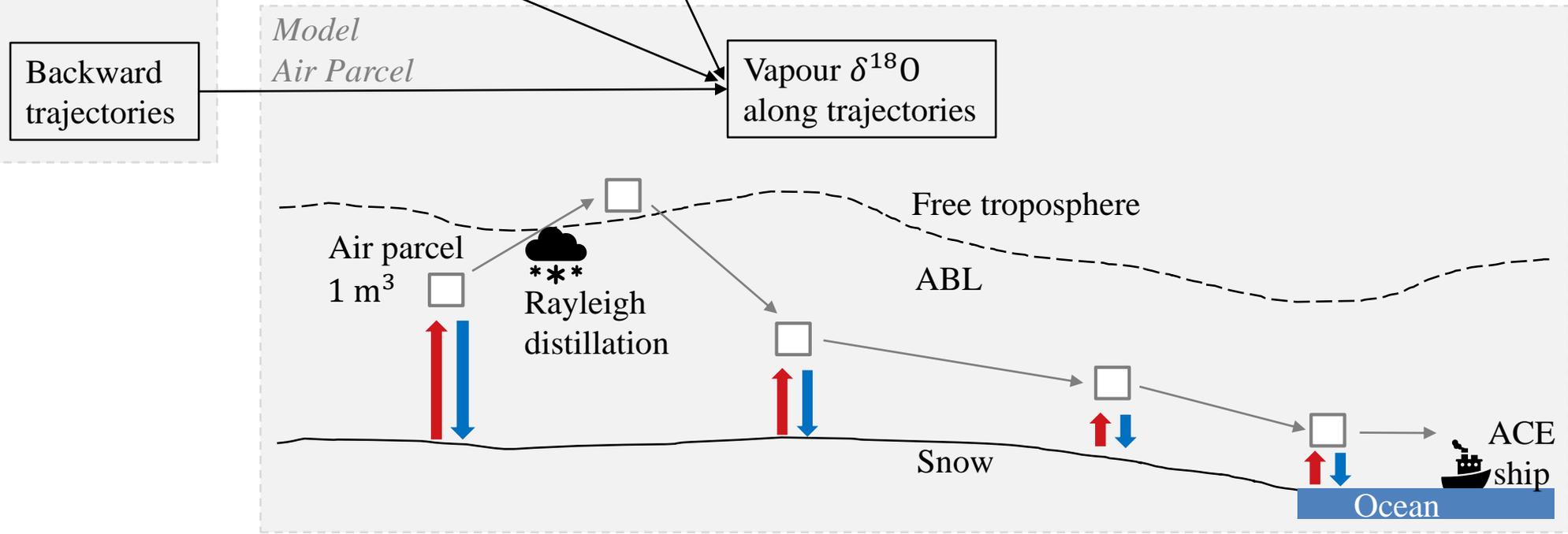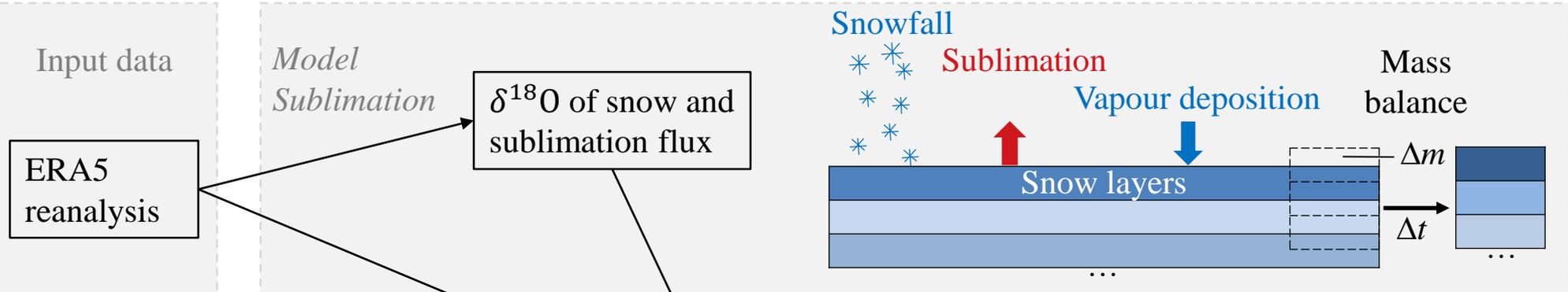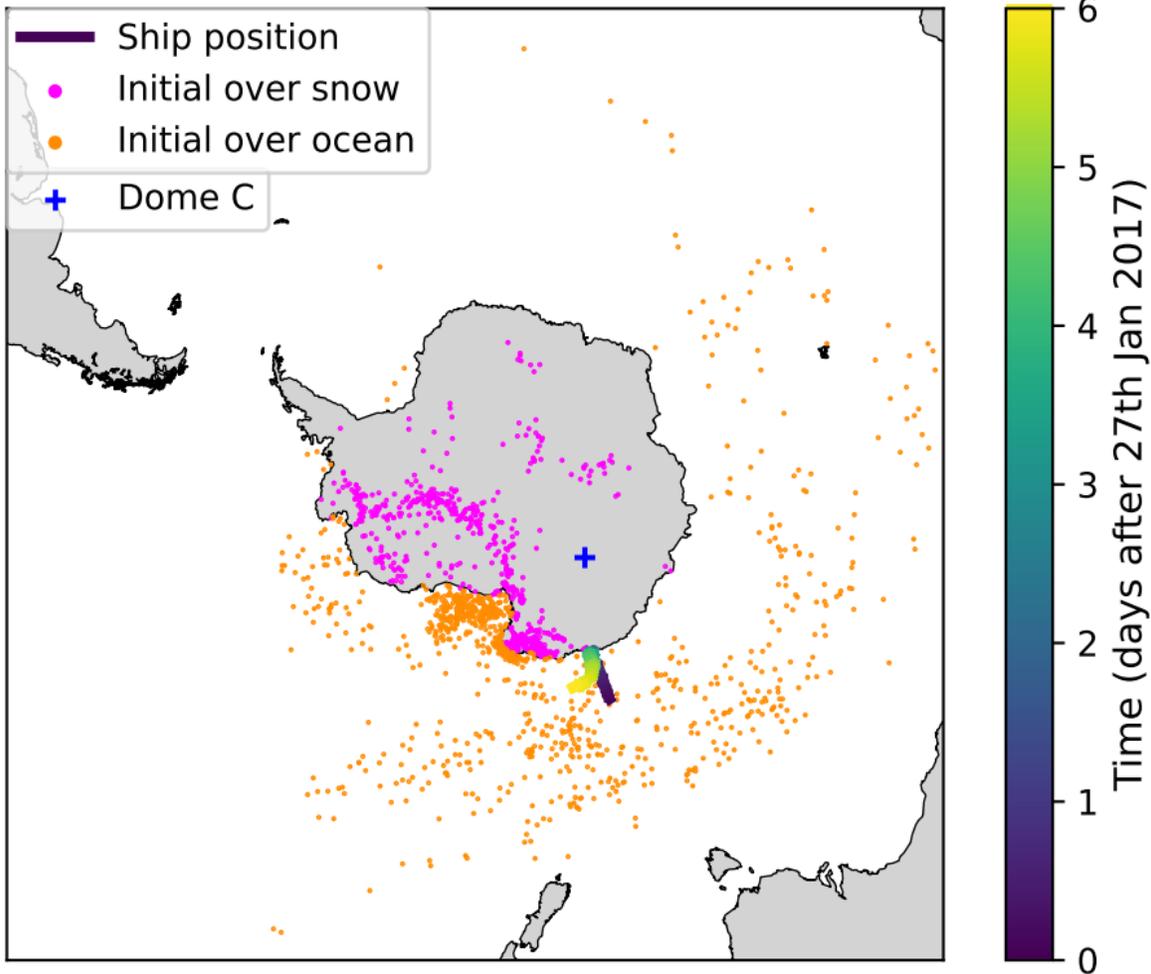
Figure 1.

Input data

Model Sublimation

$\delta^{18}O$ of snow and sublimation flux

Snowfall

Sublimation

Vapour deposition

Mass balance

Snow layers

Δm

Δt

...

...

Backward trajectories

Model Air Parcel

Vapour $\delta^{18}O$ along trajectories

Free troposphere

Air parcel 1 m³

Rayleigh distillation

ABL

Snow

ACE ship

Ocean

Figure 2.

Legend:
- Ship position
- Initial over snow
- Initial over ocean
- Dome C

Time (days after 27th Jan 2017)

Figure 3.

Legend:
- Modelled at ship (Run E), RMSE = 5.2 ‰, $\rho = 0.82$
- Modelled at ship (Run N), RMSE = 5.2 ‰, $\rho = 0.80$
- Observed at ship
- Ship position on snow

Y-axis: $\delta^{18}O$ of vapour (‰)

X-axis: Day of January/February 2017

Figure 4.

Figure 5.

(a)

- Initial, over snow (Stenni16, Run E)
- Initial, over ocean (Identical in all runs)
- Modelled at ship (Stenni16, Run E)

(b)

- Uptake, snow sublimation
- Uptake, ocean evaporation
- Removal, surface flux
- Removal, cloud formation

(c)

- Complete travel
- In ABL over snow
- In ABL over ocean

$\delta^{18}O$ of vapour (‰)

Total mass change (g)

Travel time (h)

Day of January/February 2017

Figure 6.

(a) 28th January, 18:00, n=15   **(b)** 29th January, 16:00, n=7
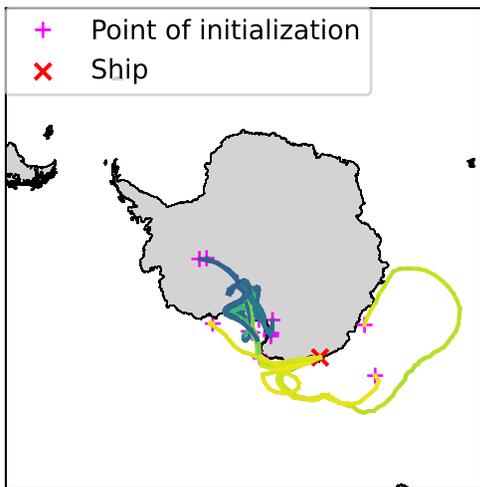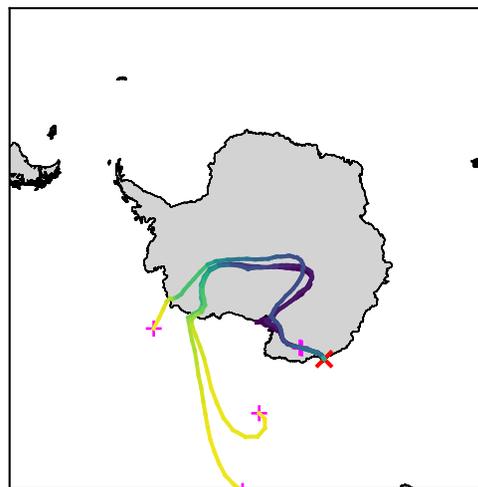
(c) 30th January, 10:00, n=9   **(d)** 31st January, 09:00, n=15

Point of initialization

Ship

Vapour $\delta^{18}O$ (‰) in Run E

Figure 7.