Nonequilibrium Fractionation During Ice Cloud Formation in iCAM5: Evaluating the Common Parameterization of Supersaturation as a Linear Function of Temperature

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Abstract Supersaturation with respect to ice determines the strength of nonequilibrium fractionation during vapor deposition onto ice or snow and therefore influences the water isotopic composition of vapor and precipitation in cold environments. Historically, most general circulation models formed clouds through saturation adjustment and therefore prevented supersaturation. To match the observed isotopic content, especially the deuterium excess, of snow in polar regions, the saturation ratio with respect to ice (Si) was parameterized, usually by assuming a linear dependence of Si on temperature. The Community Atmosphere Model Version 5 (CAM5) no longer applies saturation adjustment for the ice phase and thus allows ice supersaturation. Here, we adapt the isotope-enabled version of CAM5 to compute nonequilibrium fractionation in ice and mixed-phase clouds based on Si from the CAM5 microphysics and use it to evaluate the common parameterization of Si. Our results show a wide range of Si predicted by the CAM5 microphysics and reflected in the simulated deuterium excess of Antarctic precipitation; this is overly simplified by the linear parameterization. Nevertheless, a linear function, when properly tuned, can reproduce the average observed relationship between δD and deuterium excess reasonably well. However, only the model-predicted Si can capture changes in microphysical conditions under different climate states that are not due to changes in temperature. Furthermore, parametric sensitivity tests show that with the model-predicted Si, water isotopes are more closely tied to the model microphysics and can therefore constrain uncertain microphysical parameters.

Plain Language Summary The concentration of oxygen and hydrogen isotopes of water depends on meteorological processes such as evaporation from the ocean and cloud formation. Water isotope concentrations measured in ice cores and other natural archives are therefore used to reconstruct Earth’s past climate. In Antarctica, isotope concentrations strongly depend on the meteorological conditions during ice and mixed-phase cloud formation, especially the supersaturation with respect to ice. Isotope-enabled climate models, which are often used to support interpretations of isotope measurements, commonly prescribe supersaturation with respect to ice as a linear function of temperature. It is unknown how much this simplification affects the representation of water isotope concentrations in the models. Here we use a recently developed isotope-enabled climate model, which uses a physically based calculation of supersaturation, to evaluate the linear parameterization used in other models. We find that, even though it is less physically realistic, the linear parameterization can represent the average water isotope concentrations reasonably well. We also evaluate how model parameters related to supersaturation affect water isotopes. Our results suggest that water isotopes can potentially be used to improve climate models.

1. Introduction

Stable water isotopologues (H16O, HD16O, and H18O, hereafter referred to as stable water isotopes) have shown great potential as natural tracers of the global water cycle and have provided valuable insight into Earth’s past and present climate (e.g., Dansgaard et al., 1993; Markle et al., 2017; Moyer et al., 1996). The basis for their wide range of applications is isotopic fractionation, which occurs during phase transitions and is caused by the different thermodynamic properties of the isotopes: heavier water isotopes have higher binding energies and therefore preferentially go to the compound in which the molecules are bound most...
strongly. They also have slower diffusion velocities and therefore need more time to reach an equilibrium state. Due to these two effects, stable water isotopes experience equilibrium and nonequilibrium fractionation, respectively, and thereby continuously record the meteorological history of air parcels through changes in their relative concentrations. Equilibrium fractionation occurs during every phase transition involving the vapor phase and is roughly 8 times stronger for HD\(^{16}\)O than for H\(^{18}\)O, leading to a ratio close to 8:1 between \(\delta D\) and \(\delta^{18}O\) in atmospheric waters, where the \(\delta\) notation describes the concentration of HD\(^{18}\)O and H\(^{18}\)O relative to Vienna Standard Mean Ocean Water (VSMOW): \(\delta = \frac{[\text{H}]_{\text{sample}}}{[\text{H}]_{\text{VSMOW}}} - 1\); \(R^{18}O = [^{18}\text{O}]/[^{16}\text{O}]\); \(R^D = [\text{D}]/[\text{H}]\). Nonequilibrium fractionation occurs during phase transitions where diffusion is important, that is, (1) evaporation of water from the surface or from rain drops, when there is a strong gradient of humidity, and (2) ice and mixed-phase cloud formation, which usually occurs in an environment that is supersaturated with respect to ice (Rogers, 1979). Nonequilibrium fractionation is stronger for H\(^{18}\)O than for HD\(^{16}\)O and therefore leads to deviations from the ratio of 8:1, which are commonly quantified by the deuterium excess, \(d = \delta D - 8 \cdot \delta^{18}O\) (Dansgaard, 1964).

Due to the complexity of processes involving fractionation, measurements of stable water isotopes would be difficult to interpret without the help of numerical isotope models. Since Dansgaard (1964) developed a Rayleigh model simulating isotopic variations in an isolated air parcel to explain the temperature effect and the amount effect (i.e., increasing depletion of heavy isotopes with decreasing temperature and increasing precipitation amount), numerical models have been widely applied to link measured isotopic variations to physical processes. Following the pioneering work of Joussaume et al. (1984) stable water isotopes have been incorporated into many atmospheric general circulation models (AGCMs): iCAM (Lee et al., 2007; Nusbaumer et al., 2017), ECHAMwiso (Hoffmann et al., 1998; Werner et al., 2011), GISS ModelE (Schmidt et al., 2005), HadCM3 (Tindall et al., 2009), ICON-ART-Iso (Eckstein et al., 2018), IsoGSM (Yoshimura et al., 2008), and LMDZiso (Risi et al., 2010), among others. These AGCMs solve the full set of equations governing the dynamics and physics of the atmosphere on a global three-dimensional grid and simulate fractionation during all phase transitions in the hydrological cycle. In contrast to Rayleigh models, isotope-enabled AGCMs provide a spatially and temporally complete picture of global isotopic variations in water vapor and precipitation, limited only by their spatial resolution and the parameterization of unresolved processes. They have been widely applied to support interpretations of isotope measurements in paleoarchives. For example, Werner et al. (2000) showed with the help of ECHAMwiso that seasonality of precipitation explains the discrepancy between borehole and isotope-derived temperatures in Greenland, and Sime et al. (2009) showed with the help of HadCM3 that the relation between temperature and isotope ratios in Antarctic ice cores is nonlinear and that therefore interglacial climates may have been warmer than previously thought. At the same time, isotope tracers can be used to constrain physical parameterizations in the models that could otherwise not be detected because of compensating errors in the moisture, pressure, or temperature fields (Field et al., 2014; Nusbaumer et al., 2017; Risi et al., 2012). Historically, AGCMs use saturation adjustment to determine the rates of condensation, evaporation, deposition, and sublimation to or from both liquid and ice phase condensate. Thus, supersaturation is removed after each time step by converting excess vapor to liquid or ice clouds. However, no supersaturation means no nonequilibrium fractionation during ice cloud formation, and thus unrealistic deuterium excess values, especially at high latitudes. To solve this problem, supersaturation with respect to ice in these models is parameterized and accounted for in the microphysical transfers of the heavy water isotopes (HD\(^{18}\)O, H\(^{18}\)O) but not in the microphysical treatment of standard water (H\(^{18}\)O). In most AGCMs, the same parameterization as the one used in Rayleigh models is adopted, which describes the saturation ratio with respect to ice (SI) as a linear function of temperature (\(T\)) in the form of SI = \(a + b \cdot T\) (Jouzel & Merlivat, 1984; Petit et al., 1991). The intercept \(a\) is usually set to a value close to 1, implying saturation at \(T \approx 0\) °C, while the slope \(b\) is adjusted such that the simulated deuterium excess matches observations, usually of snow in Antarctica (e.g., Petit et al., 1991).

The resulting values for \(b\) range from \(b = -0.002\) (Nusbaumer et al., 2017) to \(b = -0.007\) (Schoennemann et al., 2014).

There are several limitations related to parameterizing supersaturation with respect to ice as a linear function of \(T\): (1) A one-dimensional linear function cannot reflect a potential wide range of supersaturations at a given \(T\); (2) since it is mostly tuned for present-day climate, the parameterization might not represent past climate conditions correctly, due to possible differences in the microphysics that influence supersaturation (e.g., different dust emissions or a different ratio of mixed-phase and ice clouds); and (3) since the isotope and microphysics parts of the model act independently in such a setup, an agreement between modeled
and observed isotope ratios reflects on the quality of the tuning process rather than the quality of the model (Mathieu et al., 2002).

The Community Atmosphere Model Version 5 (CAM5) (Neale et al., 2010) is one of a growing number of AGCMs whose microphysics scheme does not apply saturation adjustment for the ice phase and therefore allows supersaturation with respect to ice. This means that, although it is still used in the isotope-enabled version of CAM5 (iCAM5) (Nusbaumer et al., 2017), the parameterization of Si is not necessary. The aim of this study is therefore to adapt iCAM5 to compute nonequilibrium fractionation based on Si predicted by the microphysics scheme (Gettelman et al., 2010; Morrison & Gettelman, 2008), and with the help of this new model version (1) evaluate the parameterization of Si as a linear function of T and (2) test the sensitivity of stable water isotopes to microphysical parameters influencing the model-predicted Si. Thereby, we focus on Antarctica, where supersaturation during ice and mixed-phase cloud formation is especially important for isotopes in precipitation and compare simulations in two different climates, present day and the last glacial maximum. Both iCAM5 versions are validated against observations of isotopes in surface snow and ice cores from Antarctica.

2. Methods

2.1. Model

CAM5 (Neale et al., 2010) is the atmospheric component of the National Center for Atmospheric Research Community Earth System Model (CESM) (Hurrell et al., 2013). For stratiform cloud physics it uses the macrophysics scheme by Park et al. (2014) and the two-moment microphysics scheme by Morrison and Gettelman (2008), modified to allow supersaturation with respect to ice by Gettelman et al. (2010). In pure ice clouds (\(T < -37 \, ^\circ C\)), ice crystals can form via heterogeneous immersion freezing on mineral dust or by the homogeneous freezing of sulfate (Liu & Penner, 2005; Liu et al., 2007). Ice crystal formation in mixed-phase clouds (\(-37 \, ^\circ C < T < 0 \, ^\circ C\)) occurs via heterogeneous deposition nucleation and condensation freezing (Meyers et al., 1992) and also through contact freezing (Young, 1974). Moist convection is separated into deep convection (Zhang & McFarlane, 1995) and shallow convection (Park & Bretherton, 2009), and moist boundary layer turbulence is parameterized following Bretherton and Park (2009).

The implementation of stable water isotopes in CESM (Brady et al., 2019) follows the approach of previous modeling work (e.g., Joussaume et al., 1984; Hoffmann et al., 1998; Yoshimura et al., 2008). H\(_{18}\)O and HD\(_{16}\)O were added and tracked throughout the model’s hydrological cycle. Both heavy isotopes experience equilibrium and nonequilibrium fractionation during phase transitions. The equilibrium fractionation factors \((\alpha_{eq})\), which describe the ratios of saturation vapor pressures of the heavy isotopes (H\(_{18}\)O, HD\(_{16}\)O) and the light isotope (H\(_{16}\)O), are parameterized as functions of \(T\) following Horita and Wesolowski (1994) for the liquid/vapor transition, and following Majoube (1971) and Merlivat and Nief (1967) for the ice/vapor transition. The ratios of diffusivities of the light and heavy isotopes \((D/D_{iso})\), which are important for nonequilibrium fractionation, are taken from Merlivat (1978). In iCAM5 (Nusbaumer et al., 2017), fractionation during evaporation from the ocean is parameterized with the Craig and Gordon (1965) model using a wind speed-dependent formulation of the nonequilibrium fractionation factor (Merlivat & Jouzel, 1979). A similar approach is used for evapotranspiration from land in the isotope-enabled Community Land Model Version 4 (iCLM4) (Wong et al., 2017) that is coupled to iCAM5. Sublimation of surface snow or ice is assumed to occur without fractionation. The snow depth in iCLM4 is limited to a maximum snow water equivalent of \(H_{max} = 1\) m, and any precipitation that would increase the snow depth to \(H > H_{max}\) is routed directly to runoff (i.e., to the river component and ultimately to the ocean). This means that the isotopic composition of the snow pack is not updated in such regions. In the following, the implementation of fractionation during ice cloud formation, which is the focus of this study, is described in more detail. For a detailed description of other isotope parameterizations in iCAM5, see Nusbaumer et al. (2017).

2.1.1. Fractionation During Ice Cloud Formation

Because of the low diffusivities of water molecules in ice and the short lifetime of ice crystals in the atmosphere, vapor deposition onto ice or snow is assumed to follow a Rayleigh process, which describes isotopic fractionation in an open system, where the condensate is immediately removed. The isotope ratio of the condensate \((R_c)\) and the remaining vapor \((R_v)\) are then given by

\[
R_c = \alpha \cdot R_{v,0} \quad (1)
\]

\[
R_v = R_{v,0} \cdot f^{a-1} \quad (2)
\]
where \( R_{eq} \) is the initial isotope ratio in the vapor, \( f \) is the fraction of remaining vapor, and \( \alpha \) is the effective fractionation factor (including both equilibrium and nonequilibrium fractionation); \( \alpha \) is calculated following Jouzel and Merlivat (1984) and Blossey et al. (2010):

\[
\alpha = \frac{\alpha_{eq} \cdot Si}{\alpha_{eq} \cdot D_{eq} \cdot (SI - 1) + 1}
\]

with the tuning parameters \( a \) and \( b \) set to 1.0 and −0.002, respectively, in order to match observed precipitation deuterium excess over Antarctica (Nusbaumer et al., 2017).

To illustrate the impact of this parameterization, Figure 1 shows the evolution of \( \delta D \) and deuterium excess in water vapor (dashed lines) and condensate (solid lines) during Rayleigh condensation for three different parameterizations of \( SI \) as a function of \( T \). The black dot depicts the initial isotopic composition of the water vapor, and the thin lines connect the isotopic composition of the condensate with the isotopic composition of the vapor it originates from.

We evaluate the effects of nonequilibrium fractionation in the \( \delta D \) versus deuterium excess phase space, because it has been widely used in the past to analyze the effect of \( SI \) on isotopes (e.g., Petit et al., 1991; Risi et al., 2010). Since heavy isotopes condense more readily than light isotopes, the condensate has a higher \( \delta D \) than the vapor it originates from in all three air parcels. As more vapor condenses, the removal of heavy isotopes leads to lower \( \delta D \) in both vapor and newly forming condensate. The deuterium excess in vapor and condensate decreases first and then increases again. This curvature is due to an artifact of the traditional deuterium excess definition related to the nonlinearity of the \( \delta \) scale (where the change of \( \delta \) depends on \( \delta \) itself) and could be avoided by using a definition based on the \( \ln(R) \) scale (Dütsch et al., 2017; Markle et al., 2017). However, here we focus on the differences between the lines and therefore the curvature is of advantage, because it makes the differences more visible. Initially, at high \( \delta D \), a higher \( SI \) leads to a higher deuterium excess in the condensate and a lower deuterium excess in the remaining vapor, due to stronger nonequilibrium fractionation (i.e., HD\(^{18}\)O diffuses more readily onto the ice crystals than H\(^{2}\)\(^{18}\)O due to its lower diffusivity). However, because of the lower deuterium excess in the remaining vapor, the newly forming condensate has a lower deuterium excess as well, and after further deposition the Rayleigh lines of the condensate cross. For small fractions of remaining vapor, a higher \( SI \) therefore leads to a lower deuterium excess in the condensate. Such small fractions of remaining vapor are typically found at high latitudes or altitudes. Furthermore, a higher \( SI \) leads to an overall flatter slope between \( \delta D \) and deuterium excess. Thus, Figure 1 demonstrates that \( SI \) has a large impact on the deuterium excess in both vapor and condensate, and therefore a correct representation of \( SI \) in isotope models is important.

In contrast to most AGCMs, the microphysics scheme of CAM5 allows \( SI > 100\% \) (Gettelman et al., 2010), and the parameterization of \( SI \) is no longer necessary. Now vapor deposition onto ice and snow can be treated consistently for standard water (H\(^{18}\)O) and the heavy isotopes (HD\(^{18}\)O and H\(^{2}\)\(^{18}\)O). In this study, we therefore adapt the computation of nonequilibrium fractionation in iCAM5 to use \( SI \) predicted by the microphysics scheme (hereafter referred to as \( SI_{\text{eq} \text{al}} \)) instead of the parameterized \( SI \) (hereafter referred to as \( SI_{\text{param}} \)).

Note that the default iCAM5 setup limits nonequilibrium fractionation during ice and mixed-phase cloud formation to \( T < -20 \) °C, whereas in reality it can occur at \( T < 0 \) °C if \( SI > 100\% \). For consistency this −20 °C limit is kept in the modified iCAM5 version but will be the focus of sensitivity tests (see section 2.2.2).
2.2. Simulations

2.2.1. Control Simulations

We run four control (ctrl) iCAM5 simulations, one for each of the Si versions ($S_{param}$ and $S_{real}$) used in two different climates (present day and last glacial maximum). All four simulations use the finite-volume dynamical core with 1.9°N × 2.5°E horizontal resolution and a hybrid sigma-pressure vertical coordinate system with 30 levels. iCAM5 is coupled to the isotope-enabled land surface model iCCLM4 (Wong et al., 2017) and the isotope-enabled sea ice model iCICE4 (Brady et al., 2019), with prescribed sea surface temperatures and sea ice concentrations. Present-day climate simulations use year 2000 CE climate forcings, and sea surface temperatures and sea ice concentrations from Hurrell et al. (2008). Last glacial maximum simulations use year 19050 BCE (21000 BP(1950)) climate forcings, and sea surface temperatures and sea ice concentrations from Zhu et al. (2017). Aerosol emissions are based off historical data from Lamarque et al. (2010) and Lamarque et al. (2011). Ocean isotope ratios are assumed to be constant in time and space ($\delta^{18}O = 0$‰ and $\delta D = 0$‰ in present-day climate, and $\delta^{18}O = 1.13$‰ and $\delta D = 9.10$‰ during the last glacial maximum, which corresponds to the climatological global average from Zhu et al., 2017). For both climates, the simulations are branched from a 1-year spin-up simulation using $S_{param}$ and run for 10 years (Table 1). In addition to the $S_{param}$ simulations where the tuning parameter $b$ in equation (4) is set to the default value ($b = -0.002$), we run two simulations for present-day climate and last glacial maximum with $b = -0.004$ and $b = -0.006$, respectively. The results of these simulations will be shown in Figure 6 and in the supporting information.

2.2.2. Sensitivity Tests

Since stable water isotopes are sensitive to Si, and Si is predicted by the microphysics scheme in the $S_{real}$ simulations, isotopes can potentially be used to constrain microphysical parameters influencing Si in the model. This is especially useful because measurements of Si itself are sparse (Genthon et al., 2017). We select three microphysical parameters that significantly influence Si: the number of active aerosols for ice nucleation ($naai$), the Wegener-Bergeron-Findeisen time scale for the growth of ice crystals ($epsi$), and the sedimentation velocity of ice crystals ($ai$). To test the sensitivity of stable water isotopes to these parameters we run additional simulations for present-day climate, in which we scale the parameters by a factor $\beta$, where $\beta = 0.5, 2$.

Furthermore, we test the sensitivity of stable water isotopes to the temperature threshold ($T_{int}$) below which nonequilibrium fractionation occurs for both Si versions, also in present-day climate. In addition to the control simulations using $T_{int} = -20$ °C, we run simulations with $T_{int} = -10$ °C and $T_{int} = 0$ °C. All sensitivity simulations are branched from the present-day 1-year spin-up simulation using $S_{param}$ (and $\beta = 1$, $T_{int} = -20$ °C) and run for 5 years (Table 1).

### Table 1

| Control simulations (10 years) | Sensitivity simulations (5 years) |
|--------------------------------|----------------------------------|
| LGM, $S_{param}$, $b = -0.002$ | PD, $S_{param}$, $b = -0.002$, $naai$ ($x0.5, x2$) |
| LGM, $S_{param}$, $b = -0.004$ | PD, $S_{param}$, $b = -0.002$, $epsi$ ($x0.5, x2$) |
| LGM, $S_{param}$, $b = -0.006$ | PD, $S_{param}$, $b = -0.002$, $ai$ ($x0.5, x2$) |
| LGM, $S_{real}$ | PD, $S_{real}$, $b = -0.002$, $T_{int} = -10$ °C, $0$ °C |
| PD, $S_{param}$, $b = -0.002$ | PD, $S_{real}$, $naai$ ($x0.5, x2$) |
| PD, $S_{param}$, $b = -0.004$ | PD, $S_{real}$, $epsi$ ($x0.5, x2$) |
| PD, $S_{param}$, $b = -0.006$ | PD, $S_{real}$, $ai$ ($x0.5, x2$) |
| PD, $S_{real}$ | PD, $S_{real}$, $T_{int} = -10$ °C, $0$ °C |

Note. Control simulations are run for present-day climate (PD) and the last glacial maximum (LGM). Sensitivity simulations are run for present-day climate only. $T_{int}$ is the temperature threshold for nonequilibrium fractionation, $naai$ is the number of active aerosols for ice nucleation, $epsi$ is the Wegener-Bergeron-Findeisen time scale for the growth of ice crystals, and $ai$ is the sedimentation velocity of ice crystals.
2.3. $T$, $Si$, and Deuterium Excess in Vapor During Cloud Formation

Over Antarctica, most precipitation falls in the form of snow, which, in contrast to rain, does not experience strong fractionation during sublimation and thus carries its initial isotopic signal all the way to the ground. The deuterium excess in surface snow therefore strongly depends on the meteorological conditions ($T$ and $Si$), as well as the isotopic composition of the vapor ($\delta D_v$ and $\delta^{18}O_v$) at cloud formation. To determine these variables, we add four new diagnostic water tracers to iCAM5, whose deposition and condensation fluxes to ice and liquid clouds in the microphysics scheme are equal to the fluxes of standard water multiplied by $T$, $Si$, $\delta D_v$, or $\delta^{18}O_v$; blue: the flux of standard water multiplied by the tracer ratio; black: the flux of standard water. For example, in the case of rain evaporation, rain is the source and vapor is the destination, or in the case of snow melting, snow is the source and rain is the destination.

2.4. Observations

The simulated isotope ratios are compared with ice core measurements from five Antarctic sites: West Antarctic Ice Sheet Divide (WD) (Markle et al., 2017; WAIS Divide Project Members, 2013, 2015), European Project for Ice Coring in Antarctica (EPICA) Dronning Maud Land (EDML) (EPICA Community Members, 2006; Stenni et al., 2010), EPICA Dome C (EDC) (Jouzel et al., 2007; Stenni et al., 2010), Talos Dome (TAL) (Buiron et al., 2012; Landais et al., 2015; Stenni et al., 2011), and South Pole (SP) (Kahle et al., 2018), all placed on a common time scale by Buizert et al. (2018). The ice core data are averaged from 1000 BCE to 2000 CE for present-day climate and from 19000 to 16000 BCE (20950 to 17950 BP(1950)) for the last glacial maximum. The present-day simulations are additionally compared with measurements of Antarctic surface snow from Masson-Delmotte et al. (2008).

3. Results

3.1. Spatial Pattern of Deuterium Excess

Figure 3 shows the climatology of deuterium excess in precipitation for the four control simulations, and their differences (see supporting information Figures S1 and S2 for the $Si_{param}$ simulations with $b = -0.004$...
Figure 3. Climatology of deuterium excess in precipitation. (a–c) $S_{\text{param}}$ simulations (with $b = -0.002$), (d–f) $S_{\text{real}}$ simulations, and (g and h) difference between the $S_{\text{real}}$ and $S_{\text{param}}$ simulations. (a, d, and g) Present day (PD), (b, e, and h) last glacial maximum (LGM), and (c and f) difference between last glacial maximum and present day. Numbers to the left and right of the Earth denote the global and Antarctic averages, respectively. The ice core measurements are shown as dots.

and $b = -0.006$, respectively). In all four simulations, deuterium excess decreases with latitude over the ocean, reaching values close to 0‰ around 70° S (Figures 3a, 3b, 3d, and 3e). The decrease can partly be explained by an increasing fraction of snow in precipitation. Over Antarctica, deuterium excess is negative at the coast and positive further inland, reaching values of up to 20‰ close to the South Pole. Higher deuterium excess values inland can also be seen in the ice cores and are related in part to the nonlinear effect of the $\delta$ scale (Dütsch et al., 2017; Markle et al., 2017).

Figure 4. Precipitation-weighted occurrence frequency of $T$ and $S_i$ at cloud formation calculated from 6-hourly average precipitation fields over Antarctica for (a) present day (PD), (b) last glacial maximum (LGM), (c) the difference between last glacial maximum and present day. The frequencies are calculated separately for each $T$ bin of 1.2 °C. The solid lines are the precipitation-weighted mean $S_{\text{real}}$ for PD and LGM, and the dashed lines show $S_{\text{param}} = 1 - 0.002 \cdot T$, $S_{\text{param}} = 1 - 0.004 \cdot T$, and $S_{\text{param}} = 1 - 0.006 \cdot T$. The boxplots indicate at which $T$ and $S_i$ most precipitation forms (horizontal: $T$; vertical: $S_i$; blue: PD; red: LGM) with the whiskers showing the 5th and 95th percentiles.
Figure 5. Difference in precipitation deuterium excess between the $S_{\text{real}}$ simulations and $S_{\text{param}}$ simulations with $b = -0.002$ as a function of $T$ and $Si$ at cloud formation for (a–c) present day (PD) and (d–f) last glacial maximum (LGM): (a, d) total difference in precipitation deuterium excess ($d_p$), (b, e) difference resulting from fractionation during cloud formation ($d_p - d_v$), and (c, f) difference resulting from deuterium excess in vapor ($d_v$). Each dot is a 6-hourly average at a grid point over Antarctica. The sum of (b) and (c) is equal to (a), and the sum of (e) and (f) is equal to (d). The dashed and solid lines are $S_{\text{param}} = 1 - 0.002 \cdot T$ and the precipitation-weighted mean $S_{\text{real}}$, respectively.

In iCAM5, the deuterium excess during the last glacial maximum is generally lower over the ocean and higher over central Antarctica than in present-day climate (Figures 3c and 3f). The deuterium excess predicted by the different $Si$ versions differs substantially over Antarctica (Figures 3g and 3h) and over Greenland (not shown), indicating the presence of nonequilibrium fractionation during ice and mixed-phase cloud formation and therefore the sensitivity of precipitation isotopes to $Si$ in very cold regions. The model-predicted saturation ratio with respect to ice, $S_{\text{real}}$, leads to lower deuterium excess than $S_{\text{param}}$ with $b = -0.002$, similar deuterium excess as $S_{\text{param}}$ with $b = -0.004$, and higher deuterium excess than $S_{\text{param}}$ with $b = -0.006$. The differences are most pronounced during the last glacial maximum. At the coast of Antarctica, the $Si$ versions even show opposite trends between last glacial maximum and present-day climate. $S_{\text{real}}$ produces lower deuterium excess values during the last glacial maximum than in present-day climate, while $S_{\text{param}}$ produces higher or lower values, depending on the choice of $b$. The ice cores close to the coast of Antarctica also have lower deuterium excess values during the last glacial maximum than in present-day climate, in agreement with the $S_{\text{real}}$ simulations. $\delta^D$ and $\delta^{18}O$ alone do not differ much between the $S_{\text{param}}$ and $S_{\text{real}}$ simulations relative to their spatial and temporal variations (see supporting information Figures S3 and S4). This is because they are primarily governed by equilibrium fractionation.
Figure 6. Simulated climatological δD and deuterium excess in precipitation at each grid point over Antarctica and the five ice cores sites (linearly interpolated from the four surrounding grid points) compared to observations for (a,c) present day (PD) and (b,d) last glacial maximum (LGM). The top row (a,b) shows the simulations using Sireal, the bottom row (c,d) shows the simulations using Siparam with $b = -0.002$ (orange), $b = -0.004$ (purple), and $b = -0.006$ (green). The gray dots are the measurements from Masson-Delmotte et al. (2008), and the black markers are the ice core measurements. The solid lines are quadratic polynomial fits of the dots.

3.2. Relationship Between T and Si

Figure 4 shows at which $T$ and $Si$ most Antarctic precipitation forms in iCAM5 (using the diagnostic water tracers described in section 2.3). Ninety percent of Antarctic precipitation forms at $T$ between $-42$ and $-14$ °C in present-day climate (Figure 4a) and between $-50$ and $-20$ °C during the last glacial maximum (Figure 4b). $Si$ is mostly between 107% and 127% in present-day climate and between 107% and 130% during the last glacial maximum. Thus, despite much lower $T$, precipitation during the last glacial maximum does not form at significantly higher $Si$. The differences in occurrence frequency between the last glacial maximum and present-day climate also show a much more complex pattern than a simple shift to lower $T$ and higher $Si$ (Figure 4c).

In both climates, $Si$ is close to 100% at $T \approx 0$ °C and increases with decreasing $T$ as the ratio between the saturation vapor pressure over liquid water and ice increases. However, the increase of $Si$ with decreasing $T$ is not linear. The mean $Si$ increases nonlinearly with decreasing $T$ and is always higher than the default $Siparam$ with $b = -0.002$. Furthermore, for every depicted $T$ there is a wide range of possible $Si$ values, sometimes spanning more than 50%.

As Figure 5 shows, the differences between $Sireal$ and $Siparam$ also affect the deuterium excess. If $Sireal < Siparam$, the resulting deuterium excess in precipitation in the $Sireal$ simulations is always lower than in the $Siparam$ simulations with $b = -0.002$ (Figures 5a and 5d). If $Sireal > Siparam$, the signal is mixed: at relatively high $T$ ($> -37$ °C), the resulting deuterium excess in precipitation is higher in the $Sireal$ simulations than in the $Siparam$ simulations with $b = -0.002$; at relatively low $T$ ($< -37$ °C), it is generally lower in the $Sireal$ Simulations than in the $Siparam$ simulations with $b = -0.002$. This pattern is the result of two additive effects: the difference in the strength of nonequilibrium fractionation, and the difference in the isotopic composition of the vapor from which clouds form. Nonequilibrium fractionation is stronger for higher $Si$. 


and the difference between deuterium excess in precipitation ($d_p$) and deuterium excess in vapor ($d_v$) is larger in the $S_{\text{real}}$ simulations than in the $S_{\text{param}}$ simulations where $S_{\text{real}} > S_{\text{param}}$, and smaller where $S_{\text{real}} < S_{\text{param}}$ (Figures 5b and 5e). Because $S_{\text{real}}$ is usually higher than $S_{\text{param}}$ with $b = -0.002$, the stronger nonequilibrium fractionation removes more deuterium excess from the remaining vapor, and therefore, the deuterium excess in the remaining vapor is always lower in the $S_{\text{real}}$ simulations than in the $S_{\text{param}}$ simulations with $b = -0.002$ (Figures 5c and 5f). The opposite happens for $S_{\text{param}}$ with $b = -0.004$ and $b = -0.006$ (see supporting information Figures S5 and S6), because in these cases $S_{\text{real}}$ is usually lower than $S_{\text{param}}$. The effect of fractionation dominates at relatively high $T (> -37 \, ^\circ \text{C})$, leading to higher deuterium excess in the $S_{\text{real}}$ simulations where $S_{\text{real}} > S_{\text{param}}$ and vice versa, while the effect of the vapor dominates at relatively low $T (< -37 \, ^\circ \text{C})$, leading to lower deuterium excess in the $S_{\text{real}}$ simulations compared to $S_{\text{param}}$ with $b = -0.002$ for all $S_i$ (and higher deuterium excess compared to $S_{\text{param}}$ with $b = -0.004$ and $b = -0.006$).

### 3.3. Relationship Between $\delta D$ and Deuterium Excess

Figure 6 shows the relationship between $\delta D$ and deuterium excess in precipitation in the control simulations and observations. In addition to the $S_{\text{param}}$ simulation with the default $b = -0.002$, the simulations with $b = -0.004$ and $b = -0.006$ are shown in panels (c) and (d). Note the similarity between the polynomial fits and the Rayleigh lines in Figure 1 including the crossing points, indicating that the isotopic composition of precipitation over Antarctica can be approximated by a Rayleigh process.

The simulated $\delta D$ and deuterium excess values interpolated to the ice core sites tend to be more enriched along the polynomial fits compared to the observations. This may be related to the relatively coarse resolution and consequently lower topography. The advantage of the $\delta D$ versus deuterium excess phase space is that we can still infer what the deuterium excess would be at the ice core sites if $\delta D$ was lower.

The simulations using $S_{\text{real}}$ and $S_{\text{param}}$ with $b = -0.002$ and $b = -0.004$, respectively, all produce a reasonable relation between $\delta D$ and deuterium excess in present-day climate (Figures 6a and 6c). In contrast, the simulation using $S_{\text{param}}$ with $b = -0.006$ differs substantially from the observations, with too low deuterium excess values at lower $\delta D$ ($< -300\%$). All simulations underestimate deuterium excess at higher $\delta D$ ($> -300\%$), which might be related to evaporation from the ocean or land and is not further addressed in this study. The $S_{\text{param}}$ simulation with $b = -0.002$ produces lower deuterium excess values at higher $\delta D$ and higher deuterium excess at lower $\delta D$ compared to the $S_{\text{real}}$ simulation, which can be explained by the fact that the default parameterization mostly underestimates $S_i$ in iCAM5 as seen in Figure 4, leading to weaker nonequilibrium fractionation and a higher deuterium excess in the remaining water vapor (cf. Figure 1).

For the last glacial maximum there are only five observational data points, but they clearly fall within the range of values in the simulation using $S_{\text{real}}$ (except for EDC), while they are overestimated by the simulation using $S_{\text{param}}$ with $b = -0.002$ (Figures 6b and 6d). The simulation using $S_{\text{param}}$ with $b = -0.004$ produces

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**Figure 7.** Difference in precipitation-weighted occurrence frequency of $T$ and $S_i$ at cloud formation between the simulations with $\beta = 2$ and $\beta = 0.5$ calculated from 6-hourly average precipitation fields over Antarctica for (a) naal, (b) epsi, (c) ai. The solid line is the precipitation-weighted mean $S_{\text{real}}$, and the dashed lines show $S_{\text{param}} = 1 - 0.002 \cdot T$, $S_{\text{param}} = 1 - 0.004 \cdot T$, and $S_{\text{param}} = 1 - 0.006 \cdot T$. The boxplots indicate at which $T$ and $S_i$ most precipitation forms (horizontal: $T$, vertical: $S_i$, blue: $\beta = 0.5$, red: $\beta = 2$) with the whiskers showing the 5th and 95th percentiles.
Figure 8. δD and deuterium excess in precipitation in the sensitivity simulations for (a,d) naai, (b,e) epsi, (c,f) ai compared to observations (in present-day climate). The top row (a–c) shows \( S_{\text{param}} \) with \( b = -0.002 \), and the bottom row (d–f) shows \( S_{\text{real}} \). The colored dots are the climatological averages at each grid point over Antarctica (dark: \( \beta = 0.5 \); medium: \( \beta = 1 \) (ctrl); light: \( \beta = 2 \)), and the gray dots are the observations from Masson-Delmotte et al. (2008). The solid lines are quadratic polynomial fits of the dots.

more reasonable δD and deuterium excess values, but none of the \( S_{\text{param}} \) simulations capture the range of the ice core values as well as the \( S_{\text{real}} \) simulation does.

Thus, even though Figure 4 showed that \( S_i \) is not a linear function of \( T \), \( S_{\text{param}} \) can represent the 10-year average relationship between δD and deuterium excess reasonably well. However, there is no guarantee that this is true in all situations. The large variability of \( S_i \) at a given \( T \) might be important at shorter time scales, for example, for individual weather events, or in different regions, for example, in the upper troposphere. Therefore, we recommend using the more physically realistic \( S_{\text{real}} \) when possible.

3.4. Sensitivity Tests

3.4.1. Microphysical Parameters

This section addresses the sensitivity of the deuterium excess in Antarctic precipitation to the number of active aerosols for ice nucleation (\( \text{naai} \)), the Wegener-Bergeron-Findeisen time scale for the growth of ice crystals (\( \text{epsi} \)), and the sedimentation velocity of ice crystals (\( \text{ai} \)). By changing the properties of ice and mixed-phase clouds, these parameters directly influence \( S_i \). Furthermore, through feedbacks of clouds on climate, they indirectly influence \( T \) as well. In the \( S_{\text{param}} \) simulations, the deuterium excess is sensitive only to \( T \), because \( S_i \) is parameterized as a linear function of \( T \). In the \( S_{\text{real}} \) simulations, the deuterium excess is sensitive to both \( T \) and \( S_i \). Figure 7 shows how \( T \) and \( S_i \) are affected by the scaling of the microphysical parameters in present-day climate. Higher \( \text{naai} \) and \( \text{epsi} \) increase ice nucleation and deposition, respectively, and thus reduce supersaturation, leading to lower \( S_i \) at all \( T \) (Figures 7a and 7b). Higher \( \text{ai} \) enhances the
sedimentation of ice crystals, with a mixed effect on Si. Higher values of ai result in lower Si above −30 °C and higher Si below −30 °C (Figure 7c). On average, scaling all three microphysical parameters by β = 2 compared to β = 0.5 leads to higher T and lower Si. According to the Rayleigh lines in Figure 1, we therefore expect lower deuterium excess at high δD and higher deuterium excess at low δD in Antarctic precipitation for β = 2 than for β = 1 in both the Si\textsubscript{param} and the Si\textsubscript{real} simulations, and the opposite effect for β = 0.5.

As Figure 8 shows, the lower Si and higher T in the simulations with β = 2 indeed lead to a lower deuterium excess at high δD and a higher deuterium excess at low δD compared to the control simulation (vice versa for β = 0.5). For all three parameters, the relation between δD and deuterium excess is similar across the Si\textsubscript{param} simulations, because the effect of changes in β on T alone is relatively small. In contrast, the deuterium excess in the Si\textsubscript{real} simulations is very sensitive to changes in Si caused by changes in β. Since the initial isotopic composition of the vapor depends on processes that are not addressed in this study (e.g., evaporation from the ocean or land) we will not focus on the absolute values, but on the slope between δD and deuterium excess instead. While the slope between deuterium excess and δD is too steep compared to observations in the Si\textsubscript{real} control simulation, it is too flat in the Si\textsubscript{real} simulations with reduced naai and epsi, suggesting that the truth lies somewhere in between. Reducing ai leads to lower deuterium excess at low δD, but with a similar slope between deuterium excess and δD.

### 3.4.2. Temperature Threshold for Nonequilibrium Fractionation

Figure 9 shows how δD and deuterium excess depend on the temperature threshold below which nonequilibrium fractionation occurs during ice and mixed-phase cloud formation (T\textsubscript{ini}). Increasing T\textsubscript{ini} from −20 °C to −10 or 0 °C results in much lower deuterium excess values in the Si\textsubscript{real} simulations (Figure 9b), whereas the values in the Si\textsubscript{param} simulations do not depend strongly on T\textsubscript{ini} (Figure 9a). This can be explained by the difference between Si\textsubscript{real} and Si\textsubscript{param} at relatively high T (> −20 °C) (cf. Figure 4a). While Si\textsubscript{param} (with b = −0.002) only grows as large as 104% for T > −20 °C, Si\textsubscript{real} exceeds 110% in most instances when −20 °C < T < −10 °C. Therefore, Si\textsubscript{real} leads to stronger nonequilibrium fractionation than Si\textsubscript{param}, which leaves the remaining vapor (and consequently the newly forming condensate) depleted in deuterium excess. Interestingly, the effect of increasing T\textsubscript{ini} is highly nonlinear. The difference between the simulations with T\textsubscript{ini} = −20 °C and T\textsubscript{ini} = −10 °C is much larger than the difference between the simulations with T\textsubscript{ini} = −10 °C and T\textsubscript{ini} = 0 °C, suggesting that deposition onto ice and snow at T between −20 and −10 °C dominates the changes in both simulations with increased T\textsubscript{ini}.

![Figure 9](image-url)
4. Discussion

4.1. Implications

Even though our results show that $Si$ is clearly not a linear function of $T$, the $Si_{param}$ simulations, with the right tuning, produced a reasonable range of $\delta D$ and deuterium excess in Antarctic precipitation, both compared to observations and to $Si_{real}$ simulations. In part, this is not surprising, because the $Si$ function had been tuned for the simulations to match the observations. Nevertheless, this means that models parameterizing $Si$ as a linear function of $T$ are still a valid tool for supporting the interpretation of isotope measurements in paleoarchives. However, there may be situations where the large $Si$ variability independent of $T$ is important, for example, for individual weather events. This variability can be represented only if $Si$ is predicted by the microphysics scheme.

Furthermore, with $Si$ predicted by the microphysics scheme, isotopes can serve as an additional observational constraint on microphysical parameters. Previous studies have shown that CAM5 tends to produce too much ice and too little supercooled liquid water in mixed-phase clouds (Cesana et al., 2015; Kay et al., 2016; Komurcu et al., 2014; Wall et al., 2017). This means that even if $Si$ is simulated perfectly, the overestimated ice production can lead to too many nonequilibrium fractionation events and a lower deuterium excess in the remaining vapor, which is passed to precipitation forming further downstream. The ice bias in CAM5 can be caused by a too efficient Wegener-Bergeron-Findeisen process, that is, a too rapid growth of ice crystals at the expense of supercooled liquid water (Tan et al., 2016), and is often corrected for by decreasing the parameter $\epsilon Si$ (e.g., Sagoo & Storelvmo, 2017; Tan & Storelvmo, 2016). Our simulation with reduced $\epsilon Si$ has a flatter slope between $\delta D$ and deuterium excess, suggesting that $\epsilon Si$ might indeed be too high in the default CAM5 setup. Other studies have shown that CAM5’s ice nucleation scheme for mixed-phase clouds (Meyers et al., 1992) overestimates the concentration of ice nucleating particles at high latitudes (DeMott et al., 2010; Prenni et al., 2007; Xie et al., 2013), which also leads to too much ice in mixed-phase clouds. This is because the Meyers et al. (1992) scheme calculates ice nucleating particle concentration assuming a fixed dependence on $T$ and $Si$ based on measurements from the Sierra Nevada, where ice nucleating particles are much more abundant than at high latitudes, and does not take into account the spatial and temporal variability of ice nucleating particles. With most of Antarctic precipitation in our simulations forming in the mixed-phase cloud regime ($-37^\circ C < T < 0^\circ C$), naai is primarily predicted by the Meyers et al. (1992) scheme, and our results show that reducing naai improves the slope between $\delta D$ and deuterium excess as well. The overestimated ice fraction in mixed-phase clouds may also explain why allowing nonequilibrium fractionation at all $T < 0^\circ C$, instead of only at $T < -20^\circ C$, brings the simulated $\delta D$ and deuterium excess values much further away from observations: if the condensate was mainly liquid between $T = -20^\circ C$ and $T = 0^\circ C$, this threshold would only have a minor impact.

With the implementation of a new ice nucleation scheme (Shi et al., 2015; Wang et al., 2014), as well as a new microphysics scheme (Gettelman, 2015), the ice bias has been greatly improved in newer versions of CAM (Bogenschutz et al., 2018). We therefore expect a better agreement between the modeled and observed $\delta D$ and deuterium excess without the need for reducing naai, $\epsilon Si$, or deactivating nonequilibrium fractionation at $T > -20^\circ C$ in the isotope-enabled version of CAM6 that is currently under development.

4.2. Neglected Processes

One process that has been neglected in the discussion so far is evaporation from the ocean or land. Since evaporation is the only process involving strong nonequilibrium fractionation apart from ice and mixed-phase cloud formation, the deuterium excess is commonly used as a proxy for moisture source conditions (e.g., Jouzel et al., 1982; Uemura et al., 2012; Vimeux et al., 1999). From a Rayleigh perspective, moisture source conditions determine the initial isotopic composition of the air parcel, while meteorological conditions during cloud formation determine how the isotopic composition of the air parcel evolves. For Antarctic precipitation, moisture mainly originates from the ocean (Sodemann & Stohl, 2009). Previous studies have shown that the wind speed-dependent formulation by Merlivat and Jouzel (1979) that is used in iCAM5 for evaporation from the ocean does not represent nonequilibrium fractionation correctly (Bonne et al., 2019; Pfahl & Wernli, 2009; Uemura et al., 2010). This is why in this study we focus on the slope between $\delta D$ and deuterium excess and not on the absolute values. However, the isotopic composition of the initial vapor can also influence the slope, due to the nonlinearity of the $\delta$ scale (Dütsch et al., 2017; Markle et al., 2017). We test this with the Rayleigh equations (1) and (2) by adding $-10\%$ and $+10\%$ to the
Figure 10. Evolution of $\delta D$ and deuterium excess in water vapor (dashed lines) and condensate (solid lines) during Rayleigh condensation for three different initial deuterium excess values ($d_{i,0}$) and $S_i = 1 - 0.004 \cdot T$. The black dots depict the initial isotopic composition of the water vapor, and the thin lines connect the isotopic composition of the condensate with the isotopic composition of the vapor it originates from.

initial $\delta D$ of the air parcels, corresponding to an initial deuterium excess of $-10\permil$ and $+10\permil$, respectively. As Figure 10 shows, a higher initial deuterium excess in vapor unsurprisingly leads to a higher deuterium excess in the condensate, but the slope between $\delta D$ and deuterium excess is nearly independent of the initial values. We therefore expect very similar results with regards to the slope between $\delta D$ and deuterium excess for different formulations of fractionation during evaporation from the ocean or land.

By using the isotope ratios of precipitation from iCAM5, we also neglect potential postdepositional processes. Recent studies from Greenland and Antarctica show that isotopic exchanges between snow and water vapor (Steen-Larsen et al., 2014), fractionation during sublimation (Madsen et al., 2019; Ritter et al., 2016), and snow metamorphism (Casado et al., 2018) may alter the isotope ratios in surface snow, especially at low accumulation sites. Due to the snow depth limit of $H_{\text{max}} = 1\text{m snow water equivalent}$ in our version of CLM4 (see section 2.1), the simulated snow pack mainly reflects the initial isotopic composition instead of the signal from precipitation, and it is not possible to meaningfully account for postdepositional processes. In a revised version of CLM4 (van Kampenhout et al., 2017), the snow pack is allowed to refresh from the top, and any excess mass is removed from the lowest snow layer instead. Including this new treatment of snow in the isotope version of CLM4 (iCLM4) (Wong et al., 2017) will be the focus of future work.

5. Conclusions

The isotope version of the Community Atmosphere Model Version 5 (iCAM5) is one of a few isotope-enabled AGCMs whose microphysics scheme does not apply saturation adjustment for the ice phase and therefore allows supersaturation with respect to ice. In this study we adapted iCAM5 to compute nonequilibrium fractionation during ice and mixed-phase cloud formation based on the supersaturation predicted by the microphysics scheme (the real supersaturation, $S_{\text{real}}$) instead of the commonly applied parameterization of supersaturation with respect to ice as a linear function of temperature (the parameterized supersaturation, $S_{\text{param}}$).

A comparison between simulations using the real supersaturation and simulations using the parameterized supersaturation showed that a linear function oversimplifies the dependence of supersaturation with respect to ice on temperature and that differences between the real and the parameterized supersaturation are reflected in deuterium excess in Antarctic precipitation. The average relation between $\delta D$ and deuterium excess was nevertheless well reproduced by the simulations using the parameterized supersaturation, when properly tuned. Thus, a linear function of temperature tuned to match isotope measurements may be a reasonable approximation of supersaturation with respect to ice. However, for a more physically realistic treatment of nonequilibrium fractionation and to adequately represent microphysical changes that are independent of temperature, using the real supersaturation is preferable.

Our results also showed that with the real supersaturation stable water isotopes can constrain microphysical parameters that influence supersaturation with respect to ice in the model. Reducing the number of active aerosols for ice nucleation ($n_{\text{aai}}$) or the Wegener-Bergeron-Findeisen time scale for the growth of ice crystals ($\tau_{\text{epi}}$) improved the relation between $\delta D$ and deuterium excess compared to observations, which is in agreement with previous findings showing that CAM5 overestimates the fraction of ice in mixed-phase clouds.

In summary, while the parameterization of supersaturation with respect to ice as a linear function of temperature may lead to reasonable results with the right tuning, using the real supersaturation to compute nonequilibrium fractionation ties the isotopes more closely to the model microphysics, which on the one hand facilitates interpretations of isotope measurements in paleoarchives, and on the other hand makes isotopes more useful observational constraints.
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