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Philippe Ciais, Jean Jouzel. Deuterium and oxygen 18 in precipitation: Isotopic model, including mixed cloud processes. *Journal of Geophysical Research*, 1994, 99 (D8), pp.16.793-16.803. 10.1029/94JD00412 . hal-02923778

HAL Id: hal-02923778

<https://hal.science/hal-02923778>

Submitted on 3 Feb 2021

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Deuterium and oxygen 18 in precipitation: Isotopic model, including mixed cloud processes

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Abstract. Modeling the isotopic ratios of precipitation in cold regions meets the problem of “switching” from the vapor-liquid transition to the vapor-ice transition at the onset of snow formation. The one-dimensional model (mixed cloud isotopic model (MCIM)) described in this paper focuses on the fractionation of water isotopes in mixed clouds, where both liquid droplets and ice crystals can coexist for a given range of temperatures. This feature is linked to the existence of specific saturation conditions within the cloud, allowing droplets to evaporate while the water vapor condensates onto ice crystals. The isotopic composition of the different airborne phases and the precipitation is calculated throughout the condensation history of an isolated air mass moving over the Antarctic ice sheet. The results of the MCIM are compared to surface snow data both for the isotopic ratios and the deuterium excesses. The sensitivity of the model is compared to previous one-dimensional models. Our main result is that accounting specifically for the microphysics of mixed stratiform clouds (Bergeron-Findeisen process) does not invalidate the results of earlier modeling studies.

1. Introduction

The study of the deuterium and oxygen 18 distributions in natural waters proves to be very useful in such fields as cloud physics, climatology, hydrology, and paleoclimate studies. Usually, data acquisition is combined with the modeling of isotopic fractionations occurring at various stages of the water cycle and the interpretation takes advantage of the relationships which exist between isotopic distributions and various, generally climate-related parameters. The purpose of isotopic models is to predict the global scale deuterium and oxygen 18 distributions in water vapor, clouds, and precipitations. For both isotopes, the isotopic mass ratios (R) are conventionally expressed in the δ scale relative to the $SMOW$ standard:

$$\delta = \frac{R - R_{SMOW}}{R_{SMOW}} \times 1000 \text{ (units ‰)}$$

Isotopic models fall in two categories. Dynamically simple models deal with processes occurring in isolated air masses. They are generally based on Rayleigh condensation models assuming immediate removal of precipitation [Dansgaard, 1964; Friedman *et al.*, 1964; Taylor, 1972; Siegenthaler and Matter, 1983; Jouzel and Merlivat, 1984]. Though being indispensable tools in understanding field isotope data and their relationships with climatic variables, these simple models do not account for the complexity of the dynamical processes involved in the formation of precipitation. To deal with these latter aspects, the isotopic cycles have been

introduced into general circulation models (GCMs), that consider this dynamical complexity [Joussaume *et al.*, 1984; Jouzel *et al.*, 1987]. Besides those two approaches, an intermediate two-dimensional isotopic model has been developed by Fisher [Fisher and Alt, 1985; Fisher, 1990]. Both simple models and GCMs are very complementary and are now being developed in parallel.

One of the advantages of simple models is their ability to account for the complexity of cloud microphysics and its interplay with the various fractionation processes occurring at each phase change of the water in the atmosphere, while those processes can only be parameterized in dynamically complex models. As reviewed by Jouzel [1986], this complexity is due to the following reasons: Two types of isotopic fractionations are involved. An equilibrium fractionation, arising from lower saturation vapor pressure of heavy species HDO and $H_2^{18}O$ compared to the main component $H_2^{16}O$, and a kinetic effect resulting from differences in the molecular diffusivities in air of these molecules. Liquid and solid phases have to be treated separately, because, unlike liquid droplets, the cloud solid (ice crystals, large ice particles, or hailstones) is not isotopically homogeneous. Ice crystals are out of isotopic equilibrium due to low diffusion of molecules in solid and the variable history of the air mass producing the solid. Liquid droplets whose radius is less than $30 \mu m$ can be considered at any time in isotopic equilibrium with the surrounding water vapor [Jouzel *et al.*, 1975]. Raindrops of radius larger than $30 \mu m$ are out of isotopic equilibrium because of their large isotopic relaxation times.

With this in mind, Jouzel *et al.* [1980] and Federer *et al.* [1982] have incorporated into a cloud model the equations describing the isotopic fluxes among vapor, droplets (cloud water), raindrops (rainwater), ice crystals (cloud ice), graupels, and hailstones. This model represents a very elaborate description of isotopic processes occurring in clouds, but its use is limited to the study of isolated convective clouds and

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it would not be appropriate for describing the isotopic history of an air mass from its oceanic source to, for example, the polar ice caps. Also, it does not adequately account for the two important following points: First, one has to consider a drop size spectrum rather than a fixed radius drop population, as partially addressed by *Federer et al.* [1982]. However, this point is important only for convective clouds and will not be further discussed here. Second, if both liquid droplets and ice crystals are to coexist for a given range of temperatures, then neither the droplets nor the crystals will be in isotopic equilibrium [*Jouzel and Merlivat*, 1984].

This is due to the so-called Bergeron-Findeisen process which plays a key role in the formation of ice crystals [*Rogers*, 1979]. This physical mechanism discussed by *Bergeron* [1935] had been formulated as early as 1911 by *Wegener* (quoted by *Mason* [1971]): "The vapor tension will adjust itself to a value in between the saturation values over ice and water. The effect of this must then be that condensation will take place continually until the liquid phase is entirely consumed." In mixed clouds, i.e., clouds containing both liquid water and ice, the environment should thus be undersaturated with respect to the liquid phase while supersaturated with respect to the solid phase. If so, the liquid droplets tend to evaporate, while two phase transitions can lead to ice formation: direct deposition of vapor onto the existing crystals by inverse sublimation and freezing of supercooled droplets. Ice crystals usually begin to appear in clouds when the temperature drops below -15°C , while supercooled droplets end at temperatures as low as -40°C , the homogeneous freezing threshold [*Rogers*, 1979].

From an isotopic point of view, the Bergeron-Findeisen process may be neglected in convective clouds, as noted by *Federer et al.* [1982], but probably not in stratiform clouds where the formation of polar precipitation takes place [*Jouzel and Merlivat*, 1984]. The fact that the vapor pressure is likely above the saturation pressure over ice had already been accounted for by *Jouzel and Merlivat* [1984] through the formulation of a kinetic fractionation during ice formation. We will adopt their description of the isotopic effects at the vapor-ice phase transition. Besides, during the Bergeron-Findeisen process in mixed clouds the vapor pressure is also below the saturation pressure over liquid water. Therefore droplets will not be in isotopic equilibrium with respect to the vapor, which requires to account for a kinetic fractionation associated to the vapor-liquid transition.

Hereinafter, we present an isotopic cloud model which fully includes such nonequilibrium processes. This so-called mixed cloud isotopic model (MCIM) is directly in the line of those developed by *Jouzel and Merlivat* [1984] for the solid phase (referred hereinafter as RMK model) and by *Merlivat and Jouzel* [1979] for the liquid phase. These models are now currently used in interpreting the isotopic content of polar snow concerning the isotope-temperature relationship. Combined with these two models, the MCIM will provide a full description of isotopic processes occurring in an air mass from its oceanic origin up to the cold ice sheet regions. The deuterium excess (a linear combination of both isotopes defined as $d = \delta D - 8 \delta^{18}\text{O}$) will also be examined with the MCIM. The study of d makes it possible to infer climatic information about the conditions of temperature and humidity prevailing at the evaporative ocean source of the vapor [*Jouzel et al.*, 1982; *Johnsen et al.*, 1989; *Dansgaard et al.*,

1989; *Petit et al.*, 1991; *Fisher*, 1991]. Kinetic fractionation effects are slightly greater in proportion for oxygen 18 than for deuterium. As d couples both isotopes, it is a very relevant parameter to examine in the MCIM which deals specifically with kinetic fractionations. We will explore the properties of d in the MCIM as in the work of *Petit et al.* [1991].

2. Description of the Model

Vapor, Liquid, and Ice in the Mixed Cloud Isotopic Model (MCIM)

The variable T refers to the cloud temperature (or condensation temperature), the natural working variable of one-dimensional isotopic models. For model-data comparison we converted the observations from ground to cloud temperature using the empirical linear function derived by *Jouzel and Merlivat* [1984] over the Antarctic ice sheet ($T_{\text{cloud}} = 0.67 \times T_{\text{ground}} - 1.2$). Figure 1 describes the condensation history of an air mass according to three hypotheses. Figure 1a is a Rayleigh distillation for which the condensed phase is removed as soon as it forms in the cloud. Figure 1b is the model of *Jouzel and Merlivat* [1984] (RMK model) where some liquid remains in the cloud above T_s . Figure 1c is the MCIM model of this paper. From the ocean evaporation to the apparition of the first ice crystal at T_s , the MCIM is strictly identical to the model of *Jouzel and Merlivat*. Specifically, the moist air is lifted up till its dew point is reached, then starts the condensation process; a certain amount of liquid is kept into the cloud and the vapor is saturated with the liquid (the liquid is in isotopic equilibrium). In the interval (T_s, T_w) the Bergeron-Findeisen process occurs. Ice appears in the system at T_s , but in contrast to the RMK model, supercooled droplets are still present down to T_w . Below T_w the liquid has entirely disappeared and the cloud is only composed of ice and vapor. At that point, due to successive removal by precipitation, the amount of airborne ice in the cloud is very low. The system is then fairly close to the Rayleigh distillation conditions.

Supersaturation Function

The water vapor partial pressure in the cloud (e_w) drives the amount of the different airborne phases. According to the Bergeron-Findeisen hypothesis, the value of e_w lies between the saturation over liquid water (e_l^s) and the saturation over ice (e_i^s). This is shown in Figure 2. Instead of the water vapor partial pressures, we prefer to speak in terms of supersaturation, a commonly used variable in this type of studies. The supersaturation of the vapor with respect to the ice (S_i) is defined as

$$S_i = \frac{e_w}{e_i^s} \quad (1)$$

There are only very few measurements of S_i in polar clouds [*Miller and Schverdferger*, 1972; *Miller*, 1973]. The exact temperature dependence of S_i over the Antarctic cannot be constrained by observations. Therefore the function $S_i(T)$ was prescribed in the model for three separate temperature domains. For $T > T_s$, we assume that the vapor is exactly saturated with respect to the liquid droplets in the cloud. This is expressed by

$$S_i = \frac{e_i^s}{e_i^s} \quad (2)$$

For $T < T_w$, dealing with the vapor-ice transition only, S_i is taken to be a linear function of the cloud temperature. This choice is somewhat arbitrary but has proven robust enough to describe correctly the variability of the observed δ in snow, including the behavior of the deuterium excess

Figure 1. Three generations of one-dimensional isotopic models: (a) classical Rayleigh distillation with a switch between formation of liquid and formation of snow at $T = T_s$. (b) RMK model of Jouzel and Merlivat [1984]. Above T_s , some liquid is kept in the cloud, but below T_s the model is a Rayleigh distillation. (c) MCIM model. Above $T = T_s$, the model is identical to the RMK. Between $T = T_s$ and $T = T_w$, both ice crystals and supercooled droplets coexist in the system, according to the Bergeron-Findesein process. Below $T = T_w$, there is no more liquid in the cloud and the model approaches a Rayleigh distillation with ice and vapor.

Figure 2. Short-dashed curve, partial pressure of water vapor in the MCIM model as a function of cloud temperature. The partial pressure plotted here corresponds to a supersaturation of $S_i = 1.02 - 0.0038 \times T$ below $T = T_w$. In between (T_s, T_w) the partial pressure obeys the Bergeron-Findesein hypothesis. Solid curve, saturation pressure for the vapor-ice transition. Long-dashed curve, saturation pressure for the vapor-liquid transition.

[Johnsen et al., 1989; Fisher, 1991; Petit et al., 1991]. In the standard run of the MCIM model, S_i corresponds to the “preferred case” of Petit et al. [1991].

$$S_i = p + q \times T \quad (3)$$

$$p = 1.02, \quad q = -0.0038$$

In a recent paper, Fisher [1991] outlined that the function S_i probably takes very different values from one storm to the other, or even within the same cloud. Expression (3) should be seen as an average supersaturation relative to several precipitation events, from which we simulate the mean values of δ and d in snow. Finally, in the interval (T_s, T_w) which defines the limits of the Bergeron-Findesein process, we impose continuity both for S_i and its derivative. Gradually, S_i becomes lower than the curve describing the saturation over liquid water at T_s and reaches the curve (equation (3)) of supersaturation over ice at T_w . Figure 3 shows the shape of the S_i function of temperature. One cannot entirely dismiss the possibility that as far as liquid water is available to evaporate, the vapor pressure is maintained exactly at its saturation value over the liquid. Such a possibility can be accounted for by adjusting the value of p and q (Figure 3). In any case, the discontinuity in the supersaturation that occurred in previous works when switching from equation (1) to equation (3) at the onset of the formation of snow does not exist any longer. One of the principal advantages of the MCIM is to fill the modeling gap of intermediate temperatures (T_s, T_w) by accounting for mixed cloud processes.

Cloud Model

In this section we describe how the mass transfers among vapor, liquid water, and ice are formulated in the MCIM for the Bergeron-Findesein process. Figure 4 summarizes the microphysical mechanisms interplaying among the different phases. The liquid droplets disappear because of evaporation and freezing, whereas the vapor condenses into ice. At

Figure 3. Supersaturation function (S_i) of the vapor with respect to cloud ice in the MCIM model. Vertical arrows are the boundaries of the Bergeron-Findesein domain (T_s , T_w). Solid curve, S_i for the vapor-ice transition at equilibrium. Long-dashed curve, S_i for the liquid-vapor transition at equilibrium. Short-dashed curve, intermediate S_i , characteristic of the Bergeron-Findesein process. Such an intermediate S_i function is assumed to be linear below $T = T_w$ ($S_i = 1.02 - 0.0038 \times T$).

each step, the precipitation processes remove a fraction of the cloud liquid water and of the cloud ice. We assume that the condensation history of the moist air mass follows three assumptions: (1) no mixing with the outside air, (2) no large raindrops, (3) no isotopic fractionation when freezing a droplet into an ice particle (the freezing characteristic time of droplets must be short compared to their evaporative characteristic time). The mixing ratios of the vapor, the cloud liquid droplets, and the cloud ice are denoted as m_v , m_l , and m_i . The removal of liquid (ice) by precipitation is noted $f_l(f_i)$, the evaporative flux of droplets P_{lv} , the freezing of liquid droplets P_{li} , the condensation of vapor into ice P_{vi} . Note that the term “liquid precipitation” refers only to the fact that they are derived from the cloud liquid. In a real cloud, especially above an ice sheet, droplets falling to the surface are likely to collide on ice crystals and freeze immediately, hence reaching the ground under solid state [Pruppacher and Klett, 1978; Rogers, 1979; Johnsen et al., 1989]. This freezing nevertheless will not affect their isotopic ratio, as long as the surface temperature is low enough to prevent secondary evaporation during the fall of the droplets. The mass balance of the system is expressed by

$$dm_v + dm_l + dm_i + f_l + f_i = 0 \quad (4)$$

Water vapor. The mixing ratio of the vapor (m_v) is controlled by the air pressure (P) and the water vapor partial pressure (e_w) which is a function of temperature. This is expressed by

$$m_v = \frac{18 \times e_w}{29 \times P - 18 \times e_w} \quad (5)$$

Liquid water. The liquid mixing ratio (m_l) is controlled by the evaporation, the freezing and the precipitation of the cloud droplets. The formulation of P_{lv} and P_{li} is detailed below. The liquid precipitation (f_l) is adjusted in such a manner that m_l decreases continuously from $m_l = m_{l0}$ at T

$= T_s$ (m_{l0} is the amount of liquid present in the cloud when the Bergeron-Findesein process begins) to $m_l = 0$ at $T = T_w$. For each condensation step, the variation in the liquid mixing ratio is expressed by

$$dm_l = -P_{lv} - P_{li} - f_l \quad (6)$$

Ice crystals. Ice is formed in the cloud by the freezing of liquid droplets and by the condensation of vapor. It is removed according to the precipitation flux (f_i). The evolution of the ice mixing ratio (m_i) obeys to

$$dm_i = P_{vi} + P_{li} - f_i \quad (7)$$

The solid precipitation (f_i) is left adjustable in our model, which serves to control the amount of cloud ice. Specifically, we used

$$f_i = C_{1\text{prec}}(m_i) \quad \text{if } f_i < dm_i \quad (8)$$

$$f_i = C_{2\text{prec}}(dm_i) \quad \text{if } f_i \geq dm_i \quad (9)$$

The global sensitivity of the model to f_i is examined below. The formulation of equations (8) and (9) has no physical basis. Both precipitation coefficients $C_{1\text{prec}}$ and $C_{2\text{prec}}$ are just a convenient way to fix the amount of cloud ice in a plausible manner (see Figure 5). Typically, the precipitation coefficient $C_{1\text{prec}}$ goes from 0.2 in a mixed cloud up to 1 in a Rayleigh distillation. The precipitation coefficient $C_{2\text{prec}}$ is chosen at around 1.01 in a standard run of the MCIM. For the mass balance equation of the system to be entirely determined, we now have to provide an estimate for the fluxes describing the transfers that occur among the three phases.

Evaporation of liquid water. Cloud droplets evaporate because of the undersaturated conditions during the Bergeron-Findesein process. The evaporation flux (P_{lv}) is assumed to be proportional, first to the departure from saturation over liquid water and second to the liquid mixing ratio. As a consequence the more the distance from the saturation increases, the greater the evaporative flux will be. This is

Figure 4. Mass transfers between the different constituents in the cloud. Dashed lines point out fluxes which are associated with an isotopic fractionation. Such fluxes involve mass transfer due to diffusion processes. The precipitation (removed from the cloud) and the freezing of liquid droplets are rapid processes and they do not yield any isotopic fractionation.

expressed by equation (10) below, in which the evaporation coefficient C_e is left adjustable. In the standard run, C_e is set to 10^{-4} .

$$P_{lv} = C_e(1 - S_l)m_l \quad (10)$$

S_l , supersaturation of the vapor with respect to the cloud liquid, is defined by

$$S_l = \frac{e_w}{e_l^s} \quad (11)$$

Freezing of liquid water. The freezing of a fraction of the droplets occurs as the temperature decreases [Bigg, 1953]. The corresponding flux (P_{li}) relates to the liquid mixing ratio according to equation (12). The freezing coefficient C_f has to be adjusted by trial and error. In the standard run of the model, we used $C_f = 10^{-4}$. The isotopic model is not very sensitive to the value of C_f when C_f varies between 0 and $\approx 10^{-3}$.

$$P_{li} = C_f(m_l) \quad (12)$$

Condensation of vapor. The condensation of vapor molecules on ice crystals (P_{vi}) is deduced from the decrease in the vapor mixing ratio at each condensation. This is expressed by

$$P_{vi} = -\frac{\partial m_v}{\partial T} dT \quad (13)$$

Isotopic Cloud Model

We now examine the isotopic implications of equations (4) to (13). The Bergeron-Findeisen process consists of two phase transitions, both out of equilibrium (evaporation of droplets, condensation of vapor into ice). The isotopic effects associated with each transition are different, although they all yield an isotopic depletion of the vapor.

Isotopic fractionation during the Bergeron-Findeisen process. For the vapor-ice transition in an environment where the vapor is supersaturated over ice, an extra kinetic effect is superimposed to the classical equilibrium fractionation coefficient α_i [Jouzel and Merlivat, 1984]. We used their formulation of the total fractionation coefficient (α_{ki}).

$$\alpha_{ki} = \alpha_i \alpha_k \text{ with } \alpha_k = \frac{S_i}{\alpha_i(D/D')(S_i - 1) + 1} \quad (14)$$

The value of α_k depends on the supersaturation function $S_i(T)$. In a recent work, Fisher [1991] improved the formulation of α_k by considering the dependence of all the variables on the ambient air temperature. This improvement produces virtually no changes in the model results for either isotope and only a small change in the predicted deuterium excess. Hence for the sake of comparison with previous studies, we chose to keep the original formulation of Jouzel and Merlivat [1984] in the MCIM. Using the convention $R_{SMOW} = 1$, we expressed the condensation of isotopic species in the vapor onto ice crystals:

$$P'_{vi} = \alpha_{ki}(1 + \delta_v)P_{vi} \quad (15)$$

As the liquid-vapor transition occurs when the vapor is undersaturated with respect to the liquid, the pertaining fractionation coefficient also includes additional kinetic ef-

Figure 5. Mixing ratios of the different constituents in the cloud for the standard run of the MCIM model. Vertical arrows mark the boundaries of the Bergeron-Findeisen domain (T_s , T_w). The cloud already contains some liquid at high temperatures ($T > T_s$). Ice starts forming at $T = T_s$, but it is subsequently removed by precipitation. Liquid droplets disappear completely at $T = T_w$ as the result of successive freezing and evaporation.

fects. As far as the liquid phase of the system is composed of small droplets with a mean radius that does not exceed 30 μm [Jouzel et al., 1975], the liquid and vapor phases may be considered to be in pseudoequilibrium and it suffices to replace the equilibrium fractionation coefficient (α_l) by its pseudoequilibrium value (α_{kl}). The general derivation of α_{kl} for a droplet either growing in a supersaturated environment or evaporating in an undersaturated environment (our case of interest) is detailed in the Appendix:

$$\alpha_{kl} = S_l(D'f') \left[S_l \left(\frac{D'f'}{\alpha_l} - \frac{AD'f'}{\alpha_l} + ADf \right) + \frac{AD'f'}{\alpha_l} - ADf \right]^{-1} \quad (16)$$

Using (16), the liquid isotopic composition is given by

$$(1 + \delta_l) = \alpha_{kl}(1 + \delta_v) \quad (17)$$

Finally, no isotopic change is associated with the freezing of liquid because the freezing is rapid (the time needed to freeze a droplet is much lower than its e -folding isotopic relaxation time). This is expressed by

$$P'_{li} = (1 + \delta_l)P_{li} \quad (18)$$

Complementary equations (19) to (23) consist of those directly derived from the definition of isotopic ratios. Equation (24) describes the mass balance of isotopic species. Equations (25) and (26) for isotopes are related to (6) and (7) for the dominant species.

$$m'_v = (1 + \delta_v)m_v \quad (19)$$

$$m'_l = (1 + \delta_l)m_l \quad (20)$$

$$m'_i = (1 + \delta_i)m_i \quad (21)$$

$$f'_l = (1 + \delta_l)f_l \quad (22)$$

$$f'_i = (1 + \delta_i)f_i \quad (23)$$

$$dm'_v + dm'_l + dm'_i = -f'_l - f'_i \quad (24)$$

$$dm'_i = -P'_{lv} - P'_{li} - f'_l \quad (25)$$

$$dm'_i = P'_{vi} + P'_{li} - f'_i \quad (26)$$

The mean isotopic composition of the total precipitation ($\bar{\delta}$) is a composite term which includes the precipitation derived from airborne liquid and from airborne ice. This is expressed by

$$(1 + \bar{\delta}) = \frac{f'_l + f'_i}{f_l + f_i} \quad (27)$$

The system of equations is solved by differentiating equations (19) to (21), combining them into the isotopic mass balance equation (24) to obtain the infinitesimal variation in δ of the vapor and in δ of the ice between two successive condensation steps. This leads to (26) and (27).

$$\frac{d\delta_v}{(1 + \delta_v)} = \frac{-1}{(m_v + \alpha_{kl}m_l)} (m_l d\alpha_{kl} - P_{lv}\alpha_{kl} + P_{vi}\alpha_{ki} + dm_v) \quad (28)$$

$$d\delta_i = \frac{1}{m_i} [-(1 + \delta_i)(P_{li} + P_{vi}) + (1 + \delta_v)\alpha_{ki}P_{vi} + (1 + \delta_v)\alpha_{kl}P_{li}] \quad (29)$$

Equations (28) and (29), together with (17), determine completely the isotopic composition of each airborne phase in the cloud. The composition of the precipitation derives from (27). The results of the MCIM are discussed in section 3. The sensitivity of the model is discussed with respect to the supersaturation and to the specificities of mixed cloud processes. The influence of evaporative conditions at the mois-

ture source on the MCIM deuterium excess is discussed in section 4.

3. Results and Sensitivity Study of the MCIM Model

Results

Mixing ratios. Figure 5 shows the mixing ratios of the vapor, the cloud liquid, and the cloud ice. The vapor is progressively converted into ice and its mixing ratio m_v decreases during the air parcel history. The liquid mixing is equal to m_{l0} at the onset of the Bergeron-Findeisen process (T_s), but droplets are partly frozen and partly evaporated so that m_l is equal to zero at T_w . Ice forms in the cloud starting at T_s as a result of droplets freezing and vapor condensation. If no precipitation occurred, ice crystals would accumulate in the cloud and eventually represent the whole airborne condensed phase. This is not the case because the precipitation (f_i) causes m_i to decrease at low temperatures. At the lower end of the Bergeron-Findeisen domain (T_w), the amount of ice in the cloud is already so reduced that the system practically follows the conditions of a Rayleigh distillation.

Simulated δ s. Figure 6a shows δ of all airborne phases in the MCIM, as a function of temperature. Because the fractionation pertaining to the vapor-liquid transition is lower than for the vapor-ice transition, the newly formed liquid has a lower δ than the newly formed ice. Moreover, the airborne ice sequestered in the cloud keeps a memory of previous condensation steps (with a higher δ), whereas the liquid is fully equilibrated with the vapor at each step. This drives the δ value of airborne ice above the δ of airborne liquid (Figure 6a). Generally, δ in precipitation lies between δ of the liquid and δ of the ice. The MCIM δ in precipitation agrees well with observations in Antarctica, both at low temperatures (between -20°C and 40°C) and intermediate temperatures (between 0°C and 20°C). Realistic, very negative, δD values close to -400‰ are obtained when the cloud temperature reaches -40°C . Such an agreement of one-dimensional isotopic models with observations at low temperatures is not a specific performance of the MCIM (the model of Jouzel and Merlivat, for instance, is also quite satisfying from this point of view). However, for intermediate temperatures, the agreement with observations is slightly improved in the MCIM compared to previous models. This is because there is no discontinuity in δ at T_s in the MCIM.

Sensitivity of the MCIM model to the saturation conditions of the vapor in the cloud. Figure 6b displays δD in precipitation versus temperature simulated by the MCIM for three different assumptions on the saturation conditions of the vapor. Specifically, we tested three possibilities for the vapor in the cloud (1) in between saturation with ice and saturation with respect to liquid (Bergeron-Findeisen hypothesis), (2) saturated with respect to liquid, and (3) saturated with respect to ice. Between T_s and T_w the simulated δD values do not differ by more than 20‰ between extreme cases (2) and (3). For temperatures below T_w this discrepancy increases up to 60‰ . Figure 6b suggests a better agreement of the simulated δD with the observations when the supersaturation takes its values between cases 1 and 3. Figure 6c shows the behavior of the deuterium excess in the MCIM for cases (1), (2), and (3). The d values increase

Figure 6. (Opposite) (a) Deuterium content (δD) in the different constituents of the cloud as a function of cloud temperature. The curves correspond to the standard run of the MCIM model where the supersaturation below $T = T_w$ is given by $S_i = 1.02 - 0.0038 \times T$. The δD of the vapor is lower by approximately 100‰ than δD of any airborne condensed phase. The δD of the liquid is lower than δD of the ice, mostly because the cloud ice keeps an isotopic memory of ice formed at previous condensation steps. The δD in precipitation lies in between δD of solid and δD of liquid as the precipitation removed from the system is derived from both condensed phases. (b) Deuterium in precipitation versus cloud temperature for different saturation conditions (S_i) in the MCIM model. 1. Bergeron-Findeisen hypothesis where S_i takes intermediate values between saturation over ice and saturation over liquid. Curve 1 plots the standard run of the MCIM model ($S_i = 1.02 - 0.0038 \times T$). Curve 2: the vapor is at saturation with respect to cloud liquid. Curve 3: the vapor is at saturation with respect to cloud ice. Triangles are observations made by *Lorius and Merlivat* [1977] in East Antarctica (ground temperatures have been turned into cloud temperatures using $T_{\text{cloud}} = 0.67 \times T_{\text{ground}} - 1.2$). (c) Excess in precipitation versus δD in precipitation for different saturation conditions (S_i) in the MCIM model. Curves 1, 2, and 3 correspond to Figure 6a. Triangles are observations compiled by *Petit et al.* [1991].

inland, as effectively observed in Antarctica, except when the vapor is kept at saturation with the liquid as in case (2). This suggests that the vapor is probably never at saturation with the liquid in polar clouds. Also, when the vapor is kept at saturation with the solid, the MCIM overestimates d values ($d = +40$ to $+50\text{‰}$). Figure 6c suggests that only an intermediate supersaturation analogous to case (1) yields a correct agreement with the data. We made several runs of the MCIM using various slopes for $S_i(T)$ as in the work of Fisher [1991]. These runs showed that d in the MCIM is very sensitive to S_i . The sensitivity of the MCIM to the supersaturation was similar in magnitude, although slightly lower, than in the works of Jouzel and Merlivat [1984] or Fisher [1991]. For instance, an increase in S_i from 1.2 to 1.5 at -40°C has the effect to increase the value of d in the MCIM by $+10\text{‰}$. The best agreement with the observations was found in the supersaturation range 1.15 to 1.25. Such a range appears plausible in view of the few existing observations [Miller and Schwerdtfeger, 1972; International Atomic Energy Agency (IAEA), 1969–1986].

Sensitivity of the Model

We have shown that the sensitivity of the MCIM to the supersaturation was similar to previous one-dimensional isotopic models. We now examine features that are specifically new in the MCIM. First, droplets and ice crystals coexist between T_s and T_w . Second, a nonzero amount of condensed phase is kept within the cloud. The first point is addressed by varying the nature (liquid or solid) of the airborne condensed phase. The second point is examined by testing different amounts of condensate in the cloud, which is equivalent in comparing the MCIM with the model of Jouzel and Merlivat (Rayleigh distillation).

Coexistence of liquid and ice. We define the nature of the airborne condensed phase as the relative proportion of liquid droplets versus ice crystals during the Bergeron-Findeisen process. The variable ρ is constructed as the ratio of the droplets to the total airborne condensed phase in between (T_s , T_w). Provided that the precipitation intensity is maintained constant, ρ depends only on the evaporation and on the freezing of the droplets (coefficients C_e and C_f). In the real world, ρ certainly differs among clouds and may possibly take any value between 0 and 1. We limited ourselves to three test cases. We considered a typical mixed cloud ($\rho = 0.5$), a cloud made only with ice ($\rho = 0$), and a cloud made only with liquid ($\rho = 1$). In all three cases the total amount of condensed phase is the same.

The δ - T relations: Figure 7a shows δD versus T , respectively, for $\rho = 0$, $\rho = 0.5$, and $\rho = 1$ (considering $\delta^{18}\text{O}$ instead of δD does not change the conclusions). The gradient $\delta D - T$ changes by no more than 1‰C^{-1} between extreme cases $\rho = 0$ and $\rho = 1$. This translates into a difference of 25‰ in δD of precipitation at -40°C . The existing datasets of δ in surface snow do not allow to sort out this effect. Also, due to a less efficient fractionation for the liquid-vapor transition than for the vapor-ice transition, δ of the condensed phase decreases more rapidly with T when the cloud contains a higher amount of liquid. Below T_w , we deal with ice crystals only and the system approaches a Rayleigh distillation. In this range of temperature the MCIM gives a $\delta D - T$ gradient of 6.5‰C^{-1} , a value close to Rayleigh-type models which is in fair agreement with the empirical gradient of 6.04‰C^{-1} proposed by Lorius and Merlivat

Figure 7. Sensitivity of the MCIM isotopic model to different compositions (liquid/solid) for the total airborne condensed phase (parameter ρ in section 3). The total amount of the airborne phase is the same in all experiments. (a) δD in precipitation versus temperature. (b) Excess in precipitation versus δD in precipitation. Vertical arrows are boundaries of the Bergeron-Findeisen domain (T_s , T_w).

[1977] in East Antarctica. Our conclusion is that the nature of the condensed phase formed under the Bergeron-Findeisen conditions does not strongly influence the $\delta - T$ relationship.

The $\delta D - \delta^{18}\text{O}$ relationship: Although the gradients $\delta D - \delta^{18}\text{O}$ obtained in the MCIM for the three cases of ρ were all fairly similar (not shown), d proved to be more sensitive (Figure 7b). It is observed that between cases $\rho = 0$ and $\rho = 1$, d differs by several per mils. However, an “all liquid” configuration ($\rho = 1$) must be improbable, considering that supercooled droplets are far from the equilibrium with the vapor. Besides, d obtained in the model for a mixed cloud ($\rho = 0.5$) and for an “all ice” cloud ($\rho = 0$), was not very different, even at low temperatures.

Amount of condensed phase kept in the cloud. We examine now the consequences of keeping in the cloud various quantities of a condensed phase during the Bergeron-Findeisen process. In the MCIM the total airborne condensed phase is entirely controlled by the precipitation intensity. A systematic removal of the condensed phase formed at each condensation represents the extreme case of Rayleigh distillation conditions, whereas no removal would correspond to a hypothetical closed system [Jouzel, 1986]. We constructed the variable ω in such a manner that $\omega = 0$ in a Rayleigh distillation and $\omega = 1$ for a closed system where all the condensed phase is kept in the cloud. By setting the values of f_i and f_l , ω can be varied within the interval [0, 1].

The $\delta - T$ relations: The gradients $\delta D - T$ obtained for various amounts of condensed phase are shown in Figure 8a. It is clear that the gradient $\delta D - T$ is sensitive to ω (a higher ω drives a smaller gradient $\delta D - T$). This can be

understood as a “memory” of the airborne phase formed at previous steps which progressively accumulates into the cloud. If more airborne phase is kept (ω is higher), the precipitation has a higher δ . Within the interval (T_s, T_w) the gradient $\delta D - T$ changes by a factor 3 when passing from Rayleigh to closed system conditions. However, a closed system cloud type is only approached in the inner core of very strong convective clouds, and the most frequent values of water content found in all types of stratiform clouds are within the narrow range of $0.05\text{--}0.25\text{ gm}^{-3}$, generally less for stratiform clouds in polar regions [Mason, 1971]. As an example, Miller [1973] infers from crystal growth calculations that a crystal mass density of 5.10^{-9} gm^{-3} can be expected at the top of the inversion layer over the Antarctic plateau. Multiplying this estimate by a factor as large as 1000 would still leave ω very low. In Antarctica as well as in Greenland [Johnsen *et al.*, 1989], δ measured in snow is consistent only with low values of ω in isotopic models. This may explain the overall good performances of previously used Rayleigh-type isotopic models, despite their simplistic characteristics.

The δD – $\delta^{18}\text{O}$ relationships: The gradients $\delta D - \delta^{18}\text{O}$ simulated by the MCIM for different values of ω do not deviate significantly from the meteoric water line, which suggests an observational gradient $\delta D - \delta^{18}\text{O}$ close to 8 [Craig and Gordon, 1965]. Regarding the deuterium excess, as long as ω does not exceed 10 to 15%, the MCIM is able to match correctly the observations, including the deuterium excess of inland Antarctica that can be as large as +20‰ [Petit *et al.*, 1991]. Again, a reasonable agreement with the d

Figure 8. Sensitivity of the MCIM isotopic model to different amounts of total airborne condensed phase (total is equal to liquid plus ice). The amount of total condensed phase is varied by changing the value of ω in section 3 ($\omega = 0$ means Rayleigh distillation, $\omega = 1$ means closed system without precipitation). (a) δD in precipitation versus temperature. (b) Excess in precipitation versus δD in precipitation.

Figure 9. Response of d in precipitation to the evaporative source temperature (T_e). The response is plotted at different condensation temperatures going from $T_C = -20^\circ\text{C}$ to $T_C = -40^\circ\text{C}$. Note that d is more sensitive to T_e when going inland. The results obtained using the MCIM isotopic model (solid curves) are compared to those obtained using the RMK model of Jouzel and Merlivat (dashed curves).

observations can be reached only when the system is close to the Rayleigh conditions at low temperature.

4. Influence of the Evaporative Source Conditions on d Values in Precipitation

Previous works have outlined the fact that d in polar precipitation is largely determined by the source conditions, specifically by the following three parameters: sea surface temperature (T_e), relative humidity (H), and wind speed (W). This has motivated attempts to use d as a proxy of ocean surface conditions [Jouzel *et al.*, 1982; Johnsen *et al.*, 1989; Petit *et al.*, 1991]. In this section we examine the sensitivity of the MCIM model to the source conditions and compare it with previous one-dimensional isotopic models (RMK model).

Sea surface temperatures. Petit *et al.* [1991] pointed out that the sea surface temperature (SST) largely determines d values in Antarctic snow. They also demonstrated that warmer SST result in higher d in snow, especially at inland sites (mean surface temperatures lower than -30°C). The question is how the implementation of the Bergeron-Findeisen process modifies these conclusions. For both the MCIM and the RMK models, Figure 9 shows d versus T_e at different in situ condensation temperatures. Globally, the sensitivity of the MCIM model to T_e is similar to that of the RMK. Whatever the in situ temperature the maximum discrepancy between both models indeed does not exceed 2‰ for the excess. Using the partial derivative $\sigma_t = \partial d / \partial T_e$, which measures the response of d in precipitation to changes in SST, we found that T_e is about 3 times more important in governing the excess in snow at -40°C than at -20°C . The difference in σ_t obtained in the RMK and MCIM models, respectively, at a given temperature is small.

Relative humidity and wind speed. In agreement with Petit *et al.*, the MCIM model produces lower deuterium excesses in response to increased source humidity. The sensitivity of d to changes in H being assessed by the value

of $\sigma H = \partial d / \partial H$ at a given condensation temperature, we found that σH in the MCIM decreases by a factor 2 between coastal (-20°C) and inland locations (-40°C). In other terms the memory kept by d of changes in H at the source is larger on the coast than over the central ice sheet regions. When it comes to the comparison of the MCIM to the RMK model, the response of d to H is very similar. The wind speed above the ocean surface triggers the initial fractionation coefficient, an effect which is expected to be preserved through the cooling history and seen in d of precipitation. However, the excess is not a monotone function of the wind speed, so that low and high wind speed values can yield identical d values [see *Petit et al.*, 1991]. In addition, the high-frequency variability of the wind is likely to smooth out its influence on the deuterium excess. We will not discuss in detail this problem. In summary, regarding the response of d to the source conditions, the results of the MCIM model fully endorse the conclusions of the detailed sensitivity study presented by *Petit et al.* [1991].

Conclusion

The main difference between the MCIM isotopic model presented in this study and the previous one-dimensional isotopic models consists in a more refined description of the microphysical processes occurring at low temperatures. Below 0°C and down to -15° to -30°C , we allow a certain fraction of the preexisting liquid, formed at higher temperatures, to remain in the cloud. Simultaneously, the solid phase that progressively appears is not systematically removed. In this case, the water vapor mixing ratio takes an intermediate value between saturation over ice and saturation over water. Droplets evaporate, whereas the vapor tends to condense on the growing ice crystals. The predicted $\delta - T$ gradients and d in precipitation compare well with the available data in Antarctic surface snow, but they are not very sensitive to the quantity of liquid or solid kept in the cloud. On the other hand, in accordance with previous models, d in the MCIM remains strongly dependent on changes in the supersaturation function. The impact of climatic changes at the evaporative moisture source on the d values shows quite similar features than those previously obtained using Rayleigh-type models. In summary, taking into account realistically the processes that lead to the formation of the precipitation does not imply reassessing the climatic information previously derived from the deuterium excess.

Nevertheless, the present study concerns a given air parcel and does not simulate the conditions of the wide scale poleward moisture transport. In particular, we did not discuss the nature of the trajectory, nor the eventual mixing of the air during the isotopic history. The fact that the δ in snow, at a given location, results from several precipitation events, possibly characterized by different origins [Fisher, 1990], has also not been envisaged. Simulations of the water isotope cycle using GCMs [Joussaume et al., 1984; Jouzel et al., 1987] seems a promising approach for solving these problems as their results may help to constrain the moisture transport of the present one-dimensional model. In addition, GCMs make it possible to take into consideration the geographical variability of δ in the original oceanic vapor, which plays a key role in governing the d values.

Appendix: Pseudoequilibrium Fractionation Coefficient for Liquid-Vapor Phase Transition out of Saturation

We infer the pseudoequilibrium fractionation factor α_{kl} from the isotopic evolution of a liquid droplet growing from the surrounding vapor as a result of molecular collisions. Growth by coalescence has not been taken into account because its contribution becomes important only if the droplet radius exceeds $30\ \mu\text{m}$. The saturation with respect to the liquid-vapor equilibrium is expressed by S_l , defined by

$$S_l = \frac{e_w}{e_l^s} \quad (\text{A1})$$

Values of S_l lower than 1 account for liquid droplets placed in undersaturated vapor, which corresponds specifically to the conditions of the Bergeron-Findeisen process and has for consequence the progressive disparition of the droplets by evaporation. The rate of change in the isotopic ratio of a droplet in such an environment is expressed by (A2) [Stewart, 1975]:

$$\frac{dR_L}{dt} = \frac{3\rho_{\text{sat}}}{a^2\rho_{\text{drop}}} \left[D'f' \left[S_L \left(R_v - \frac{R_L}{\alpha_L} \right) + \frac{A}{\alpha_L} (R_L)(S_L - 1) \right] - ADf(R_L)(S_L - 1) \right] \quad (\text{A2})$$

where

- a droplet average radius;
- ρ_{drop} droplet average density;
- ρ_{sat} vapor density at saturation;
- D diffusivity of water vapor in the air;
- f ventilation coefficient of the water vapor [Kinzer and Gunn, 1951, p. 74];
- D', f' same for isotopic species;
- A droplet vapor heat transfer coefficient [Jouzel, 1974, p. 38];
- α_L equilibrium fractionation coefficient [Majoube, 1971].

Equation (A2) depends on the isotope ratios of the droplets and the surrounding vapor, R_L and R_v , respectively, in such a manner that it can be rewritten under the form

$$\frac{dR_L}{dt} = a_1 R_L + a_2 R_v \quad (\text{A3})$$

The expression of the factors a_1 and a_2 is given by

$$a_1 = \frac{3\rho_{\text{sat}}}{a^2\rho_{\text{drop}}} \left[-\frac{D'f'}{\alpha_L} \left(S_L + \frac{AD'f'}{\alpha_L} \right) \cdot (S_L - 1) - ADf(S_L - 1) \right]$$

$$a_2 = \frac{3\rho_{\text{sat}}}{a^2\rho_{\text{drop}}} (D'f') S_L$$

Assuming a constant isotopic ratio for the vapor (R_v), (A2) has the solution

$$a_1 R_L + a_2 R_v = (a_1 R_L + a_2 R_v)_{t=0} e^{a_1 t} \quad (\text{A4})$$

The term $\tau = (a_1)^{-1}$ is the e -folding isotopic relaxation time of the droplet. The range of possible values for τ in cloud droplets has been studied by Jouzel [1974], who reached the conclusion that τ does not exceed a few seconds as long as the droplet radius remains smaller than 30 μm . In the case of larger drops found in convective clouds, τ would be significantly higher and the drop would no longer be in isotopic equilibrium. As we address here processes occurring in a stratiform cloud, it is reasonable to postulate that $t \gg \tau$. Hence the droplets are isotopically equilibrated, although they are not saturated with respect to the vapor (we call that "pseudoequilibrium" in section 3). Therefore the right member of (A4) is equal to zero, which yields the expression of the pseudoequilibrium fractionation factor α_{kl} :

$$\alpha_{kl} = \frac{R_l}{R_v} = S_l(D'f') \left[S_l \left(\frac{D'f'}{\alpha_l} - \frac{AD'f'}{\alpha_l} + ADf \right) + \frac{AD'f'}{\alpha_l} - ADf \right]^{-1} \quad (\text{A5})$$

One can note that α_{kl} depends both on the equilibrium fractionation factor α_l and on S_l which characterizes the departure from saturation conditions with respect to the liquid-vapor transition. In the limit case where the population of droplets is in thermodynamic equilibrium ($S_l = 1$), (A5) simplifies into $\alpha_{kl} = \alpha_l$.

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(Received February 19, 1993; revised February 7, 1994; accepted February 8, 1994.)