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Kinetic ^{17}O effects in the hydrologic cycle: Indirect evidence and implications

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Abstract—The abundances of ^{18}O and deuterium in the present and past hydrologic cycle have proven to be an important tool in Earth systems science. In contrast, the abundance of ^{17}O in precipitation has thus far been assumed to carry no additional information to that of ^{18}O. Here, we demonstrate, using known constraints on oxygen isotope abundances from the O$_2$ cycle and existing data about the natural abundance of ^{17}O in water, that the relationship between the discrimination against ^{17}O and ^{18}O in water may vary. This relationship, presented here as $\theta = \ln(^{17}\alpha)/\ln(^{18}\alpha)$, is found to be 0.511 ± 0.005 for kinetic transport effects and 0.526 ± 0.001 for equilibrium effects, with very low temperature sensitivity. As a result, the $^{17}\Delta$ of precipitation is controlled primarily by kinetic effects during evaporation of the initial vapor and, in contrast to the deuterium excess, is independent of the temperature at the evaporation (and condensation) site. This makes $^{17}\Delta$ a unique tracer that complements ^{18}O and deuterium, and may allow for a decoupling of changes in the temperature of the ocean, that serves as the vapor source, from changes in the relative humidity above it. In addition, the $^{17}\Delta$ of ice caps is influenced by the kinetic effects in ice formation, and therefore measurement of ice $^{17}\Delta$ can be used as an additional constraint for better understanding and parameterization of these effects. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Natural variations in the abundances of the water isotopic species H$_2$^{16}O, H$_2$^{18}O and HDO are useful for studies of the hydrologic cycle and for monitoring global and regional climate change (Dansgaard, 1964; Gat, 1996). The relative abundances of the isotopologues change as a result of fractionation during evaporation, sublimation and condensation, as well as during transport processes in the atmosphere, soils, and plants.

Until recently, the abundance of H$_2$^{17}O in precipitation was assumed to carry no additional information to that of H$_2$^{16}O and H$_2$^{18}O. This is because processes in the hydrological cycle fractionate water in a mass-dependent way such that the enrichment in H$_2$^{17}O is about half of that in H$_2$^{18}O (Gat et al, 2000). In contrast, other atmospheric gases containing oxygen (e.g., CO$_2$, O$_2$, NO$_x$) show both mass-dependent fractionation and a mass-independent fractionation (with an enrichment in ^{17}O that is equal or higher than that in ^{18}O). The different ^{17}O/^{18}O relationships of the two types of fractionations makes the triple isotopes composition a unique tracer (Thiemens, 1999). Although such mass-independent fractionation is not known to occur in H$_2$O, we will show here that H$_2$^{17}O is still a useful tracer within the hydrologic cycle because of expected small variations (around 0.5) in the ^{17}O/^{18}O relationship in different mass-dependent processes. Similar variations were observed in different O$_2$ consumption processes (Angert et al., 2003), and are expected from theory to occur in all triple isotope systems (Matsuhisa et al., 1978; Young et al., 2002).

Two major mass-dependent processes control the isotopic composition of water on Earth. The first is the fractionation caused by the different saturation vapor pressures of the different water isotopologues, which is known as liquid-vapor (or solid-vapor) equilibrium fractionation. The second is the fractionation caused by the different diffusivities of water vapor isotopologues when they diffuse in air. This second type of mass-dependent fractionation is known as the water kinetic fractionation (not to be confused with other kinetic fractionations that involve breaking of molecular bonds).

In this paper we estimate the triple isotope relationships associated with equilibrium and kinetic fractionation of water based on existing H$_2$^{17}O measurements (Jabeen and Kusakabe, 1997; Meijer and Li, 1998; Miller, 2002), and on constrains imposed by the global O$_2$ isotopic budget (Luz et al., 1999; Angert et al., 2003) (O$_2$ isotopes are coupled to the water isotopes through photosynthesis). These relationships are then used to estimate the usefulness of water ^{17}O as a unique tracer.

2. NOTATION AND STANDARDS

The ^{17}O isotopic effects are expressed in terms of the parameter $^{17}\Delta$ (named "^{17}O excess" or "^{17}O anomaly"), which is the difference between a measured ^{17}O/^{16}O ratio and that "expected" based on the ^{18}O/^{16}O ratio of the sample. This notation requires two standard isotopic ratios (^{17}O/^{16}O and ^{18}O/^{16}O) and a reference mass-dependent relationship. Deviations of the ^{17}O/^{16}O and ^{18}O/^{16}O ratios from the reference ratios are expressed here in a modified delta notation (Hulston and Thode, 1965):

$$\delta'^{17}O = \ln\left(\frac{^{17}R}{^{17}R_{ref}}\right) = \ln(\delta^{17}O + 1) \qquad (1)$$

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$$\delta'^{18}O = \ln\left(\frac{^{18}R}{^{18}R_{ref}}\right) = \ln\left(\delta^{18}O + 1\right) \quad (2)$$

where ^{17}R stands for the isotope ratio $H_2^{17}O/H_2^{16}O$, ^{18}R stands for the isotope ratio $H_2^{18}O/H_2^{16}O$, and the subscript "ref" stands for the reference. The values of $\delta'^{17}O$ and $\delta'^{18}O$ are of order 10^{-2}, and when expressed in units of per mil (10^{-3}), they take on numerical values of order 10. The δ'^xO values differ only slightly from δ^xO, which is the usual notation. They are used here since fractionation lines are straight on such $\delta'^{17}O$ versus $\delta'^{18}O$ plots, and since moving between reference systems is considerably simpler (Miller, 2002; Angert et al., 2003). A disadvantage of the δ'^xO system relative to the δ^xO system is that mixing lines will not be straight.

The $^{17}\Delta$ value is calculated with reference to expected relative changes of $\delta'^{17}O$ and $\delta'^{18}O$.

$$^{17}\Delta = \delta'^{17}O - C \cdot \delta'^{18}O \quad (3)$$

Graphically, the ^{17}O excess ($^{17}\Delta$) can be represented on a $\delta'^{17}O$ versus $\delta'^{18}O$ plot (e.g., Fig. 1) as the vertical distance from the data point to a reference line. This reference line is defined by a standard ($^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios), and a reference slope (C). For the standard we choose mean seawater rather than V-SMOW, which is artificially produced to have the same $\delta^{18}O$ and δD as seawater, but not necessarily the same $\delta^{17}O$. It should be noted that because of the small range of the $\delta^{18}O$ in seawater, the range of $^{17}\Delta$ in it is expected to be extremely small. The reference slope (C) we use is taken as the slope for various natural water samples measured by Miller (2002), 0.525. The values of $^{17}\Delta$ are reported in per meg (10^{-6}) units.

The slope of a line passing between any two points ("A" and "B") on a $\delta'^{17}O$ versus $\delta'^{18}O$ plot, will be defined as λ (Meijer and Li, 1998):

$$\lambda \equiv \frac{\ln\left(^{17}R_A/^{17}R_B\right)}{\ln\left(^{18}R_A/^{18}R_B\right)} \quad (4)$$

The mass-dependent relationship will be presented as (Mook and de Vries, 2000):

$$\theta \equiv \frac{\ln\left(^{17}\alpha\right)}{\ln\left(^{18}\alpha\right)} \quad (5)$$

where $^{17}\alpha$ and $^{18}\alpha$ are the fractionation factors defined as $^xR_p/^xR_s$. The subscripts "p" and "s" stand for "product" and "substrate" respectively.

From the definitions above, it is clear that λ will have the same value as θ when "A" and "B" are the product and substrate of some isotopic fractionation processes (e.g., liquid water and vapor in isotopic equilibrium, or water vapor and the instantaneous fraction of it removed by molecular diffusion). In the special case of Rayleigh distillation, the relationship between θ and the slope resulting from Rayleigh distillation (λ_R) is given by Angert et al. (2003):

$$\theta = \frac{\ln\left(1 + \lambda_R^{18}\varepsilon\right)}{\ln\left(1 + ^{18}\varepsilon\right)} \quad (6)$$

where $^x\varepsilon = {}^x\alpha - 1$. Farquhar et al. (2003) recently noted that a continuum exists between true Rayleigh distillation and pure
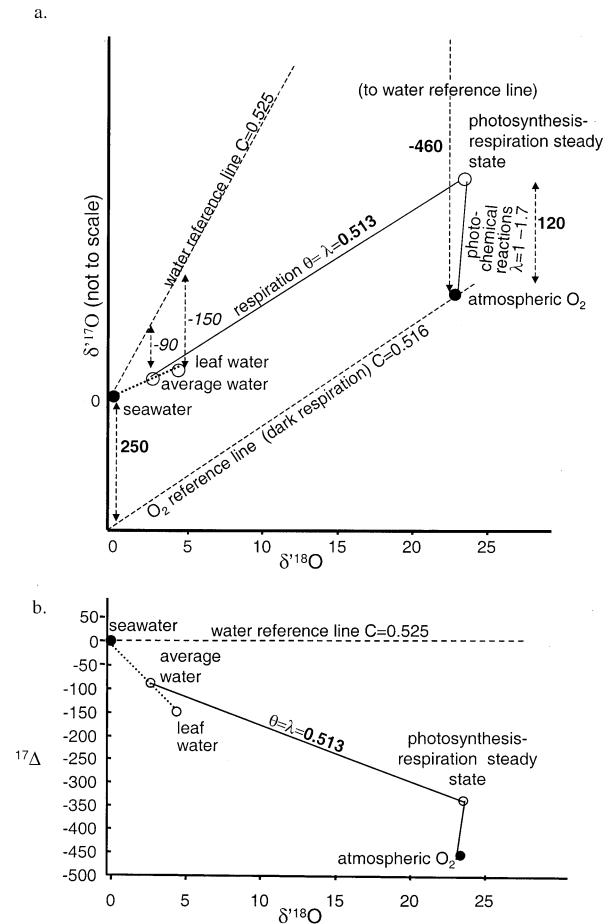

Fig. 1. (a) Schematic representation ($\delta'^{17}O$ not to scale) of the relationships between the hydrological cycle and the O_2 cycle in three isotopes space. The isotopic composition of atmospheric O_2 is controlled by photosynthesis and respiration. O_2 is produced, without fractionation, from leaf water and seawater by photosynthesis on land and in the sea, respectively. This production is represented as a product of photosynthesis using "average water." Fractionation by respiration causes a mass-dependent (slope $\lambda = 0.513$) enrichment in the heavy isotopes. If photosynthesis and respiration were the only processes, then the system would have reached steady state at the point marked as "photosynthesis-respiration steady state." However, mass-independent (slope ≥ 1) photochemical reactions in the stratosphere deplete the heavy isotopes. As a results of this coupling of the isotopic composition of O_2 and water, the position of "average water" and "leaf water" can be calculated from the O_2 constrains. Known values are given in bold (and marked by closed circles), and calculated values are shown in italic (and marked by open circles). The $^{17}\Delta$ of the atmosphere relative to the water reference line (C = 0.525) is given by the vertical distance to it, and equals to -460 per meg. Since the magnitude of the effect of the mass-independent stratospheric processes is known (120 ± 10 per meg) as well as the slope of (weighted dark and light) respiration (0.513 ± 0.002), the position of the average water used for photosynthesis can be calculated. Assuming that the difference in $\delta'^{18}O$ between average water and the atmosphere is 20.9‰ (see text), the $^{17}\Delta$ of average water is calculated as -90 per meg (= $-460 + 120 + (0.525 - 0.513) \cdot 20.9$). From this value, the $^{17}\Delta$ of leaf water can be calculated as $-150 ± 50$ per meg (assuming that average water are 40‰ seawater and 60‰ leaf water). (b) The known values of seawater and atmospheric O_2, and the calculated values of average water and leaf water, on a $^{17}\Delta$ (for C = 0.525) versus $\delta'^{18}O$ plot.

equilibrium fractionation, where Eqn. 6 represents the relationship between λ and θ for the first extreme, and $\theta = \lambda$ gives the relationship for the second extreme. The numerical difference between θ calculated by Eqn. 6 and λ_R is on the order of 0.001–0.004.

3. θ VALUE FOR EQUILIBRIUM FRACTIONATION OF WATER ISOTOPOLOGUES

In equilibrium fractionation of water, the vapor and the liquid are let to react long enough so the evaporation and condensation fluxes are identical for any isotopologue. Hence, the fractionation is controlled by the different saturation vapor pressures of the isotopologues. The θ value associated with equilibrium fractionation of vapor and liquid water has not been measured directly. However, Jabeen and Kusakabe (1997), Meijer and Li (1998) and Miller (2002) have measured the slope (λ) of a linear regression line that passes through various natural and artificial water samples with similar results (0.527, 0.528 and 0.525 respectively). It has been argued that this slope defines a "global meteoric water line" (λ_{MWL}), which passes through all terrestrial waters. Although this conclusion is adequate at the level of precision of the currently available data, which is ± 60 per meg for individual measurements of ^{17}O/^{16}O, there may be small variations hidden within the analytical scatter of the measurements.

We assume that the "Meteoric Water Line" (MWL) for H$_2$^{18}O versus H$_2$^{17}O is predominately controlled by equilibrium fractionation, which is known to be true for the meteoric water line defined for HDO versus H$_2$^{18}O (Gat, 1996). This allows us to use the measured λ_{MWL} value as a good approximation to that characteristic of equilibrium evaporation and condensation. If kinetic fractionation produces a different λ value, it will differ only slightly from that of equilibrium fractionation, and hence should produce only a small effect on the measured λ_{MWL} value (however, as is the case for the HDO versus H$_2$^{18}O, kinetic effects may still be important for deviations from the MWL). We therefore choose to adopt the value of 0.525 (Miller, 2002) to represent equilibrium fractionation of liquid and vapor water in the atmosphere (we choose the lowest value from the three measured ones since it will give a minimum estimate of the deviation of the kinetic slope for the equilibrium one, as we will show later). This fractionation is governed primarily by Rayleigh type distillation processes, and thus the corresponding θ value (θ_{eq}) can be calculated from Eqn. 6 (with $^{18}\varepsilon \sim 10$‰) to be ~ 0.526.

The equilibrium fractionation factors (both for vapor-liquid—α_{vl}—and vapor-solid—α_{vs}) of H$_2$^{17}O and H$_2$^{18}O and their dependence of temperature were calculated by Van Hook (1968), based on theoretical considerations. The value for both θ_{vl} and θ_{vs} derived from these equations is ~ 0.529—very similar to the value of 0.526 we adopt from experimental results (see Young et al., 2002, and Matsuhisa et al., 1978, for a possible explanation for the slight deviation from theory). Moreover, these equations predict that the dependence of θ_{vl} and θ_{vs} on temperature is extremely small ($\sim 4 \cdot 10^{-6}$ K^{-1} for the temperature range -20°C to $+20$°C). As a result, we can rightly assume in the rest of this paper that $\theta_{vl} \cong \theta_{vs} \cong \theta_{eq} \cong 0.526$ with no dependence on temperature.

4. THE θ OF KINETIC FRACTIONATION OF WATER ISOTOPOLOGUES

The fractionation associated with diffusion of water vapor in air is known as "water kinetic fractionation." This fractionation becomes important when there is a net diffusive transport (the effective fractionation may be lower if part of the transport is due to turbulence). No measurements of the θ associated with kinetic fractionation of water vapor (θ_k) exist at this time. Therefore, we estimate this parameter by matching the $^{17}\Delta$ of leaf water ($^{17}\Delta_l$), calculated from the constraints of the global O$_2$ cycle, with that calculated from a model of the three water isotopologues in the hydrological cycle.

4.1. Estimating the $^{17}\Delta$ of Mean Global Leaf Water from O$_2$ Constrains

To estimate the ^{17}O excess of leaf water, we exploit the coupling of the isotopic composition of water and O$_2$ by photosynthesis. The isotopic composition of atmospheric O$_2$ is determined by the isotopic composition of the substrate water used for photosynthesis (there in no fractionation in O$_2$ production by photosynthesis; Guy et al., 1993) and subsequent fractionation is mainly by respiration. Another important process controlling the ^{17}O/^{18}O ratios of atmospheric O$_2$ is the mass-independent fractionation of O$_2$ in stratospheric processes (Luz et al., 1999). As a result of these mass-independent processes, the point that represents the isotopic composition of atmospheric oxygen on a triple isotope plot (Fig. 1) lies below the point that represents the isotopic composition of air in steady-state between photosynthesis and respiration. Since the contributions of the biosphere (Angert et al., 2003) and the stratosphere (Luz et al., 1999) to the atmospheric oxygen $^{17}\Delta$ are known, it is possible to calculate from the atmospheric composition of O$_2$ the composition of air in photosynthesis-respiration steady state. From this the isotopic composition of the average water used for photosynthesis can be calculated. This average water is composed of seawater (the substrate for photosynthesis in the ocean) and (average) leaf water (the substrate for photosynthesis on land). Since the isotopic composition of seawater is known from measurements (Luz and Barkan, 2000), that of leaf water can be calculated.

To this aim, we will first calculate the $^{17}\Delta$ value of atmospheric O$_2$ relative to the water reference line used in this study (a line with a slope of C = 0.525 passing through mean seawater). The $^{17}\Delta$ of seawater relative to the O$_2$ reference line, which is defined as a line with a slope of C = 0.516 passing through atmospheric O$_2$, is $+250$ per meg (Luz and Barkan, 2000). As shown in Figure 1, that makes the $^{17}\Delta$ of atmospheric O$_2$ -460 per meg relative to the water reference line ($-250 - [0.525 - 0.516] \cdot 1000 \cdot 23.5 = -460$, where 23.5 is the δ'^{18}O of atmospheric oxygen relative to seawater; Coplen et al., 2002).

In the second step we calculate the δ'^{18}O of average water used for photosynthesis, relative to atmospheric O$_2$. For this we use a value of δ'^{18}O = $+4.4$‰ for average leaf water, relative to SMOW (Farquhar et al., 1993), and assume that 40% of global O$_2$ production by photosynthesis take place in the oceans and 60% on land. These values are based on global Gross Primary Production estimates corrected for the flux of O$_2$

used by photorespiration (Bender et al., 1994; Field et al., 1998). The resulting $\delta'^{18}O$ of average water used for photosynthesis is $-20.9‰$ relative to atmospheric O_2 ($4.4‰ \cdot 0.6 + 0‰ \cdot 0.4 - 23.5‰ = -20.9‰$).

Using the above calculated $\delta'^{18}O$ value of average water, the value estimated for the $^{17}O/^{18}O$ slope of global respiration ($\lambda = \theta = 0.513 \pm 0.002$, including both dark respiration and photorespiration; Angert et al., 2003) and the magnitude of the effect of the mass-independent stratospheric processes (120 ± 10 per meg, Luz et al., 1999) the value of the ^{17}O excess of the average water used for photosynthesis is -90 per meg ($-460 + 120 + (0.525 - 0.513) \times 1000 \times 20.9 = -90$). Based on the 60%/40% partitioning of land and ocean photosynthesis the ^{17}O excess of leaf water ($^{17}\Delta_l$) can be then calculated as -150 ± 50 per meg relative to seawater (Fig. 1).

We find here that to close the gap between the $^{17}\Delta$ value of seawater and atmospheric O_2 we need a negative deviation of leaf water ^{17}O relative to the water reference line, in addition to the stratospheric mass-independent fractionation, and a slope of respiration that is lower than that of the water line. This result is in stark contrast to the conclusions of Young et al. (2002) who reported that the O_2 triple isotopic balance could be closed through consideration of only the difference between the slope of respiration and that of the equilibrium water line. The source for these different conclusions is probably due to two differences between this analysis and that of Young et al.: first, the $^{17}\Delta$ value of atmospheric O_2 (150 per meg) reported by Luz et al. (1999) was taken to represent deviations from the water line, while it actually represents deviation from the respiration line. Second, the ratio of global photosynthetic rate to global respiration rate was assumed to be 1.75 instead of ~1 (since atmospheric [O_2] is practically in steady state).

4.2. The Dependence of Modeled $^{17}\Delta$ of Leaf Water on θ_k

To estimate the effect of θ_k on the $^{17}\Delta$ of leaf water we use here a simple model of the hydrological cycle. The three essential steps in the hydrologic cycle, for our purposes, are evaporation of water from the oceans, transport and precipitation of this water over land and evapotranspiration at leaf surfaces (Fig. 2). Kinetic fractionation is involved in both evaporation from the oceans and in the evapotranspiration process. Precipitation of rain is generally considered to be well described as an equilibrium process whereas direct formation of ice may have a significant component of kinetic fractionation (Jouzel and Merlivat, 1984).

For the first step, evaporation from the ocean, we use the steady-state model of Merlivat and Jouzel (1979), which follows the Craig and Gordon (1965) formulation for evaporation. Under the steady-state assumption, the initial vapor formed above the ocean has the same isotopic composition as that of the net evaporative flux. As a result, there is no need to explicitly assume a value for the mean isotopic composition of vapor above the ocean—a value that is poorly known for ^{18}O and deuterium and has never been measured for ^{17}O. The isotopic ratio of the mean initial vapor (R_{V0}) in this model is given by:
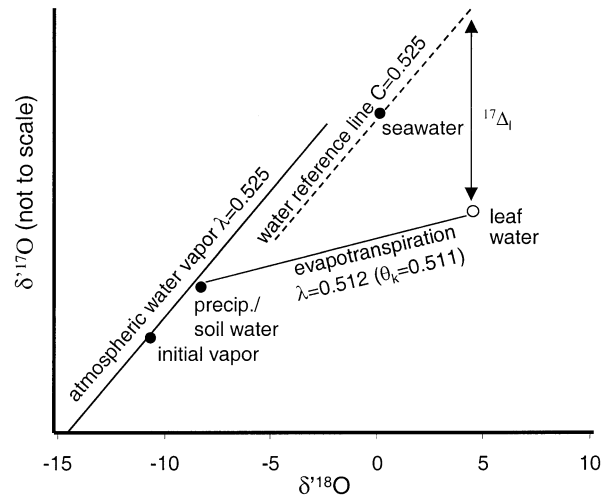

Fig. 2. Schematic plot ($\delta'^{17}O$ not to scale) showing the suggested triple isotope hydrological cycle. Kinetic effects in evaporation from the ocean cause the initial vapor to be off the water reference line (that goes through seawater). Subsequent fractionation of the water vapor follows a parallel line to that of the reference line ($\lambda = 0.525$). Precipitation is formed with a slight offset (see text) from the atmospheric vapor line. Strong kinetic effects that are associated with evapotranspiration cause a low slope ($\lambda = 0.512$) and as a result, leaf water has a negative ^{17}O excess ($^{17}\Delta_l$).

$$^{x}R_{V0} = \frac{^{x}\alpha_{ks} {}^{x}\alpha_{vl} {}^{x}R_{sea}}{1 - h_s + {}^{x}\alpha_{ks}h_s} \tag{7}$$

where x can be either 17 or 18, $^{x}\alpha_{ks}$ is the kinetic fractionation factor associated with evaporation from the ocean, $^{x}\alpha_{vl}$ is the equilibrium fractionation of vapor relative to liquid, $^{x}R_{sea}$ is the isotopic composition of seawater and h_s is the mean relative humidity over the ocean.

In the second step, the water vapor is transported over land and fractionated as precipitation is formed in clouds. The formation of precipitation can be described, to a first approximation, as an equilibrium process that follows the Rayleigh distillation curve (Dansgaard, 1964). Since the slope (C) of the reference line was chosen to represent this equilibrium process, $^{17}\Delta$ is conserved in it. Hence, the $^{17}\Delta$ of precipitation (and in the remaining vapor) is identical to that of the source vapor (V_0).

In the third step, the isotopic composition of leaf water is controlled by both the isotopic composition of water from the plant stem, which generally is the same as soil water (and hence local precipitation), and the outgoing flux of evaporation, which is controlled by equilibrium and kinetic fractionation. Assuming steady state, and again using the Craig and Gordon (1965) formulation for evaporation, the isotopic ratio of the leaf water at the site of evaporation (R_l) is described by White (1989) and Flanagan et al. (1991) as:

$$R_l = \left(\frac{^{x}R_s(1 - h_l)}{^{x}\alpha_{kl}} + {}^{x}R_v h_l \right) \frac{1}{^{x}\alpha_{vl}} \tag{8}$$

where x can be 17 or 18 and $^{x}R_s$ and $^{x}R_v$ are the isotopic composition of the soil water and the vapor at the leaf surface, respectively. The relative humidity at the leaf surface is given

by h_l, and $^x\alpha_{kl}$ is the kinetic fractionation specific to evaporation from leaves.

Kinetic fractionation for evaporation from leaves ($^x\alpha_{kl}$) and for evaporation from the ocean ($^x\alpha_{ks}$) are different because turbulent transfer plays an important role in the ocean (Merlivat and Jouzel, 1979) but only a minor role in leaves, where diffusion through the stomata is the major limitation for evaporation (Farquhar et al., 1982). Quantitatively, the value of α_k is approximated as the ratio of the effective diffusivities (including both molecular diffusion and turbulent transport effects) of the rare isotope to the common one (K_x/K_c) (Merlivat and Jouzel, 1979). We use a simple approximation to describe the relationship between molecular diffusivities and effective diffusivities where $K = D^n$ (Stewart, 1975). n is a term which describes the turbulent transport component of diffusion such that n = 1 for transport by pure molecular diffusion and n ≈ 0.5 for evaporation from the ocean. However, it can be shown that the θ_k is constant for any value of n, and therefore depends only on the ratio of the molecular diffusivities (^xD) of the different isotopologues (where "x" refers to the mass of the oxygen atom):

$$\theta_k = \frac{\ln(^{17}\alpha_k)}{\ln(^{18}\alpha_k)} = \frac{\ln((^{17}D/^{16}D)^n)}{\ln((^{18}D/^{16}D)^n)} = \frac{\ln(^{17}D/^{16}D)}{\ln(^{18}D/^{16}D)} \quad (9)$$

As a result, a single value of θ_k is used to calculate both $^{17}\alpha_{kl}$ and $^{17}\alpha_{ks}$ from Eqn. 5 ($^{17}\alpha = [^{18}\alpha]^\theta$).

For the first step of the model, i.e., evaporation from the oceans, we use $h_s = 0.8$, and $^{18}\varepsilon_{ks} = -7‰$ (Merlivat and Jouzel, 1979) and for $^{18}\alpha_{vl}$ we follow Horita and Wesolowski (1994) (for a sea surface temperature (T_s) of 25°C this gives $^{18}\varepsilon_{vl} = -9.26$). The value of $^{17}\alpha_{vl}$ is calculated from Eqn. 5 using $\theta_{eq} = 0.526$.

For the third step of the model, i.e., evaporation from leaves, we use the values of global average $\delta^{18}O$ of soil water and vapor at the leaf surface (averaged by Gross Primary Production) as estimated by Farquhar et al. (1993): $-7.9‰$ and $-18.2‰$ (versus SMOW), respectively. The relative humidity at the leaf surface is taken as 65% and the ^{18}O kinetic fractionation in leaves (including turbulent transport in the leaf boundary layer) as $^{18}\varepsilon_{kl} = -26‰$ Farquhar et al. (1993). Using these values along with the $^{17}\Delta$ of soil water and vapor at the leaf surface (assumed to be the same as precipitation and the initial vapor, respectively) the isotopic composition of global average leaf water is calculated from Eqn. 8. We find in this analysis that the calculated value of the ^{17}O excess in leaf water ($^{17}\Delta_l$) is strongly dependent on the value of θ_k.

The value of θ_k that allows the $^{17}\Delta_l$ of the model to match that calculated in section 4.1 from O_2 constraints ($^{17}\Delta_l = -150 \pm 50$ per meg) is 0.511 ± 0.005 (the uncertainty is based on that in $^{17}\Delta_l$ alone), and is considerably lower than that of equilibrium fractionation ($\theta_{vl} \sim 0.526$). The value used for θ_k affects the fractionation during both evaporation from ocean and leaves. However, molecular diffusion plays a more important role during evaporation from leaves and the associated kinetic effects are much larger than in evaporation from ocean. Therefore, θ_k has only a small impact (~8 per meg) on the calculated values of $^{17}\Delta$ for the initial vapor. The value we have calculated for θ_k falls in the range expected for mass-dependent processes and is similar to that found for consumption of O_2 by the biologic processes of dark respiration and photorespiration (0.516 ± 0.001 and 0.506 ± 0.005 respectively; Angert et al., 2003).

We have performed sensitivity analyses which demonstrate that using a value for $\delta^{18}O_v$ different by ±5‰, or $^{17}\Delta_v$ different by ±10 per meg, changes the calculated θ_k by only ±0.001. Changing the $\delta^{18}O_s$ value by ±5‰ changes the calculated θ_k by less than 0.001. Using a value for h_l that is lower by 0.05 increases the θ_k calculated by 0.004. However, such a change in h_l will cause also a 1.9‰ increase in the $\delta'^{18}O$ of the mean leaf water and, as a result, a change in ^{17}O excess of leaf water (calculated in section 4.1.). Hence, the net sensitivity of θ_k for such change in h_l is very low (~0.0002). Assuming that global productivity is 50% on land (instead of 60% as we have done) leads to a decrease in the calculated θ_k by 0.003.

The calculated large difference between θ_k (0.511) and θ_{eq} (0.526) is therefore observed to be quite robust. This conclusion is reinforced because we have chosen to use the λ_{MWL} from (Miller, 2002), which is slightly lower than that found in two other studies (Jabeen and Kusakabe, 1997; Meijer and Li, 1998). Thus, we present a minimum estimate for the difference between θ_k and θ_{eq}.

The value calculated for θ_k is related to the molecular diffusivities of the water isotopologues by Eqn. 9. The ratio of diffusivities can be expressed, according to the kinetic theory of gases, as (Merlivat, 1978):

$$\frac{D_x}{D_c} = \left(\frac{M_c}{M_x}\frac{M_x+M_G}{M_c+M_G}\right)^{1/2}\left(\frac{\Gamma_c+\Gamma_G}{\Gamma_x+\Gamma_G}\right)^2 \quad (10)$$

where M is the molecular mass, Γ is the molecular (collision) diameter, and the subscripts x, c, and G stand for the rare isotopologues ($H_2^{18}O$ or $H_2^{17}O$ in our case), the common one ($H_2^{16}O$ in our case), and the gas in which the diffusion occurs (assumed to be N_2).

If we assume that the molecular diameters of $H_2^{18}O$, $H_2^{17}O$, and $H_2^{16}O$ are identical (as indicated by the Born-Oppenheimer approximation) then the calculated $\theta_k = 0.520$, which is slightly higher than the value we estimated above, although still different from the equilibrium value. (When assuming equal molecular diameters Eqn. 10 corresponds to eqn. 25 of Young et al. (2002) only using the H_2O-N_2 reduced mass in place of the oxygen atomic masses, and hence the difference in the predicted θ_k for water diffusion.) This value of θ_k (0.520) yields $^{17}\Delta_l = -77$ per meg for the conditions stated above, clearly outside the range of $^{17}\Delta_l$ inferred from O_2 constraints (150 ± 50). However, our results presented above can be reconciled with the predictions from Eqn. 10 by allowing for extremely small differences in the molecular diameters of the water isotopologues. For example, we find excellent agreement assuming $\Gamma_{16} = 2.650 \cdot 10^{-10}$m, $\Gamma_{18} = 2.648 \cdot 10^{-10}$m and $\Gamma_{17} = 2.64825 \cdot 10^{-10}$m. Similarly good agreement can be found taking $\Gamma_{16} = 2.650 \cdot 10^{-10}$m, $\Gamma_{18} = 2.638 \cdot 10^{-10}$m after Merlivat (1978), and assuming $\Gamma_{17} = 2.643 \cdot 10^{-10}$m. Thus, we find the calculated θ_k is exceptionally sensitive to molecular scale details. The difference in the molecular diameters above is small (<0.05% in one case), and is impossible to explain from first principles. However, such small differences do not significantly effect the calculated value for $^{18}\alpha_k$ and therefore are not in disagreement with the recent study of

(Cappa et al., 2003) where no detectable differences between the molecular diameters of $H_2^{18}O$, $HD^{16}O$ and $H_2^{16}O$ were found. Similar need to assume very small variations in the molecular diameters of ^{18}O ^{17}O, and ^{16}O containing species, occurs for diffusion of O_2 in air. The measured θ value of this process (0.521, (Angert et al., 2003)) disagrees with that calculated from Eqn. 10 (0.512) if identical diameters are assumed for $^{16}O^{18}O$, $^{16}O^{17}O$, and $^{16}O^{16}O$, but can be explained if small variations in these diameters exist. For both water and O_2, the diameter of the ^{17}O containing species we estimated is slightly different than the average diameter of the ^{16}O and ^{18}O species.

Clearly, careful measurement of $^{17}\Delta_l$ in leaf water from a variety of regions as well as direct measurement of θ_k is desirable to accurately understand the influence of kinetic effects on $^{17}\Delta$ values in water. Regardless, the value of θ_k estimated in this section from O_2 constraints, and the values of θ_{vl} and θ_{vs} estimated in the previous section represent a reasonable first approximation for these values. In the following section we use these values to evaluate the usefulness of ^{17}O as an additional tracer within the hydrological cycle.

5. EVALUATING THE USEFULNESS OF WATER ^{17}O

The analysis described above suggests that small variations of $^{17}\Delta$ may be present in precipitation. The existence and size of these variations are controlled by kinetic effects in the hydrological cycle. There are three circumstances where kinetic effects are thought to be important—in evaporation from the oceans, in evapotranspiration and in the condensation of water vapor directly to ice. Another useful tracer, the deuterium excess, defined as $d = \delta D - 8 \cdot \delta^{18}O$, is also sensitive to kinetic effects associated with evaporation (Merlivat and Jouzel, 1979), and ice formation (Jouzel and Merlivat, 1984). To explore the usefulness of $^{17}\Delta$ as a tracer, we compare the relative effects of evaporation on d and $^{17}\Delta$.

5.1. Model Equations

To illustrate the behavior of $^{17}\Delta$ we use a simple model where the isotopic composition of the initial vapor evaporated from the ocean is given by Eqn. 7 (where x can now be 17, 18 or 2 for deuterium) and is subsequently modified through Rayleigh distillation. Three different variations on the Rayleigh distillation process are used to calculate the isotopic composition of precipitation. In a Rayleigh model, the vapor is increasingly depleted in the heavy water isotopologues as water is removed by precipitation. In the simplest type of such a model, only equilibrium fractionation is taken into account, and the fractionation factor is assumed to be constant (we will use $\alpha = \alpha(T = 5°C)$, and $\theta_{vl} = 0.526$) while the water vapor is cooled isobarically. The wringing out of moisture is controlled by temperature according to the Clausius-Clapeyron equation, and as a result the isotopic composition of the vapor (R_v) is given by:

$$\frac{R_v}{R_{v0}} = \exp\left(-B\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)^{\alpha_{lv}} \quad (11)$$

(Dansgaard, 1964; Gat et al., 2000) where B is a constant (B = 5349 K), T_0 is the initial temperature of the vapor, and α_{lv} is the fractionation of liquid versus vapor water ($1/\alpha_{vl}$). The

precipitation is assumed to be in isotopic equilibrium with the vapor such that:

$$R_p = \alpha_{lv}R_v \quad (12)$$

where R_p is the isotopic composition of the precipitation. A more accurate model will include the dependence of the equilibrium fractionation factor on temperature, and Eqn. 11 should be integrated accordingly. When temperature is taken into account, the values for α_{vl} are after Horita and Wesolowski (1994). We will refer to the first approach as the $\alpha = $ const model, and the second one as the $\alpha = f(T)$ model.

At low temperatures (below $\sim -20°C$), the fractionation associated with ice formation in clouds should be taken into account. Jouzel and Merlivat (1984) included fractionation associated with ice formation, in the model referred to as RMK, by replacing α_{lv} (the liquid-vapor fractionation) in Eqn. 11 and 12, by $\alpha_{sv} \cdot \alpha_{kin}$ (the solid-vapor equilibrium fractionation times the appropriate kinetic fractionation factor), for temperatures below $-20°C$. The kinetic fractionation factor (α_{kin}) is given by:

$$\alpha_{kin} = \frac{S}{\alpha_{sv}\frac{D}{^xD}(S-1)+1} \quad (13)$$

where $(D/^xD)$ is the relation of the diffusivities between $H_2^{16}O$ and the heavier isotopes. S is the dimensionless supersaturation function for which we choose to use the parameterization $S = 1 - 0.003T$ (where T is in °C) (Hoffmann et al., 1998). The ratios $^{18}D/D$ and $^2D/D$ were taken as 0.9691 and 0.9839 (Cappa et al., 2003), respectively (use of the older values reported by Merlivat (1978) will have no implication for demonstrating the usefulness of $^{17}\Delta$). The ratio $^{17}D/D$ was calculated by Eqn. 9 from the ratio $^{18}D/D$ and θ_k (0.511).

5.2. Model Results and Implications

The first step, evaporation from the ocean, is identical in the three models. In this step, kinetic effects in evaporation shift the ^{17}O excess of the initial vapor ($^{17}\Delta_{vo}$) to low positive values (for example for $T_s = 25°C$ and $h_s = 0.8$ we get $^{17}\Delta_{vo} = 8$ per meg). In the three models, there is a small difference (~10 per meg) between the initial vapor and the first precipitation, caused by using a reference slope (C = 0.525) which is slightly different than the slope of equilibrium condensation ($\theta_{lv} = \theta_{vl} = 0.526$). Subsequent changes in the isotopic composition differ between models. In the $\alpha = $ const model, $^{17}\Delta$ is not affected by the wringing out of the water mass by precipitation. This is expected, because we chose C = 0.525, and $\theta_{vl} = 0.526$ such that $\lambda_R = 0.525$ and therefore $^{17}\Delta$ is conserved in such a Rayleigh process. In contrast, the value of $^{17}\Delta$ is slightly temperature dependent (only 10 per meg over a range of 40°C) in the more realistic $\alpha = f(T)$ model (Fig. 3). These changes appear even though θ is temperature-independent because the associated $^{18}\alpha$ is not, and the governing equations are nonlinear. The predicted difference in $^{17}\Delta$ between seawater and v_0, as well as subsequent changes in $^{17}\Delta$ of precipitation, are small relative to the uncertainty in current measurements of water $^{17}\Delta$. Hence, real differences could easily have gone undetected in previous studies, as we proposed above (section 3). These
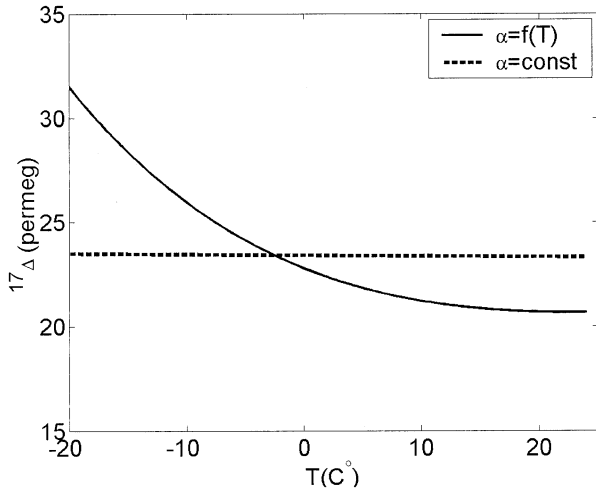
Fig. 3. Comparison of $^{17}\Delta$ produced in precipitation (as a function of the temperature at which precipitation forms) in two models. In the first (α = const) the fractionation ($^x\alpha$) is assumed to be independent of temperature, while in the second the temperature effect on $^x\alpha$ is taken into account. This effect causes a slight increase in the precipitation $^{17}\Delta$ with lower temperatures.

small changes also imply that uncertainty in the isotopic changes in evaporation and precipitation has negligible effect on the assessment of θ_k in section 4.

To investigate if $^{17}\Delta$ contains additional information to d, we will compare these two variables in the α = f(T) model, under three scenarios. In the "base" scenario we will use for the evaporation from the ocean T_S = 25, h_s = 0.8. In the "high h" scenario T_S = 25, h_s = 0.85, and in the "low T" scenario T_s = 20, h_s = 0.8.

The results of these three scenarios are presented in Figure 4. Both the "high h" and the "low T" scenarios produced precipitation with lower d than that of the base scenario. The lower d in the "high h" scenario results from diffusive fractionation playing a less important role in evaporation whereas the lower d in the low T scenario is due to a temperature dependent shift of the equilibrium D/H and ^{18}O/^{16}O ratios, and the much stronger temperature dependence of the D/H fractionation factor. As a result, it is impossible to directly infer changes in the source region humidity or temperature from the d value of precipitation alone. In contrast, while $^{17}\Delta$ of the "low T" precipitation is identical to that of the base line, the "high h" precipitation has lower $^{17}\Delta$ by ~7 per meg. Hence, a change in d that is not accompanied by a change in $^{17}\Delta$ can be interpreted as a change in the temperature of the source ocean, while cooccurring changes of the two indicate changes in the relative humidity at the ocean surface. This finding suggests that measurements of d and $^{17}\Delta$ in ice cores, could be used to quantitively assess past changes in the temperature of the source ocean and the relative humidity above it. The expected variations of $^{17}\Delta$ in the three scenarios are only ~5 per meg. This is a small signal, but similar in magnitude to the measured signal in the $^{17}\Delta$ of O$_2$ caused by changes in global productivity (Luz et al., 1999; Blunier et al., 2002). Hence, improving the accuracy of water $^{17}\Delta$ measurements to the same level as that of O$_2$ measurements, will enable the use of water $^{17}\Delta$ as a valuable tracer for past conditions at the source of the vapor.

The results of the RMK model demonstrate that an additional type of information can be gained from the measurement of water $^{17}\Delta$. In Figure 5, we compare the $^{17}\Delta$ of precipitation with the inclusion of kinetic fractionation (RMK model) and without it (α = f(T) model). The two models are identical at temperatures above $-20°C$, but below this temperature they diverge. Without the kinetic fractionation in ice formation there is a small increase of $^{17}\Delta$ with decreasing temperature due to the changes in $^{18}\alpha$ (θ is fixed) and the nonlinearity of the governing equations. However, the RMK model predicts a substantial decrease in $^{17}\Delta$ that reaches -125 per meg at $-50°C$. The discontinuity observed at $-20°C$ in the RMK model results from our particular formulation, where we switch from liquid-vapor to ice-vapor fractionation (including kinetic effects) in a single step. However, this limitation does not affect the general conclusions presented here. In an additional run of the RMK model (named "low S") we parameterized the supersaturation function as S = 1 − 0.002T (instead of S = 1 −
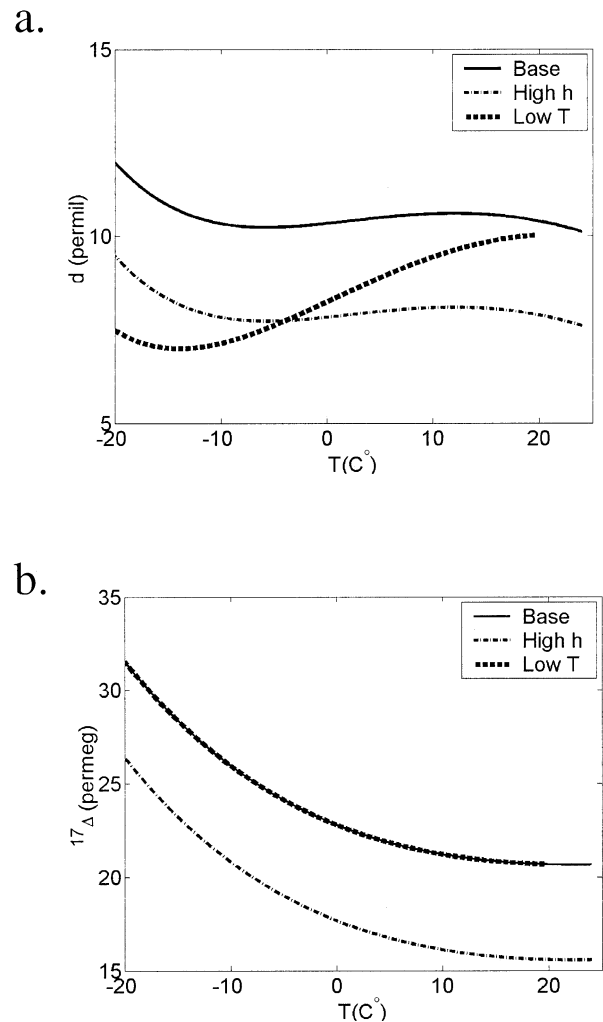
a.

b.

Fig. 4. Comparison of (a) deuterium excess (d) and (b) ^{17}O excess ($^{17}\Delta$) produced in precipitation (as a function of the temperature at which precipitation forms) in response to different temperature and relative humidity in the ocean that serve as the vapor source. Base: T_S = 25, h_s = 0.8. High h: T_S = 25, h_s = 0.85. Low T: T_S = 20, h_s = 0.8.
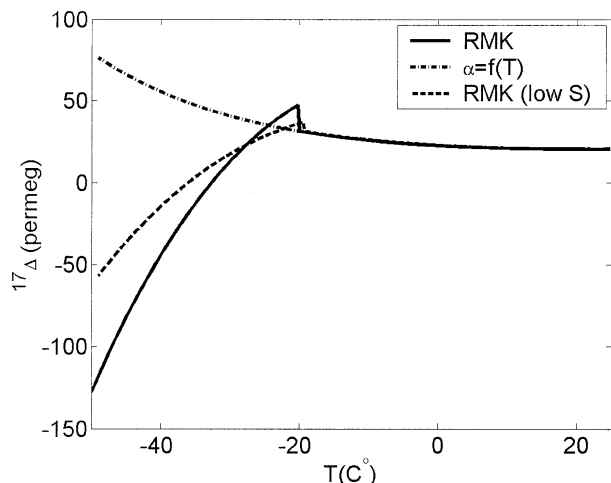
Fig. 5. Comparison of $^{17}\Delta$ produced in precipitation (as a function of the temperature at which precipitation forms) in three different models. The first (RMK) includes the Jouzel and Merlivat (1984) formulation for kinetic effects in ice formations. The second model ($\alpha = f(T)$) ignores processes of ice formation, while the third one (RMK, low S) includes the Jouzel and Merlivat formulation with different S function.

0.003T). This change results in $^{17}\Delta$ values 60 per meg higher than those of the standard RMK run at the coldest temperatures. This result demonstrates that the $^{17}\Delta$ of water is very sensitive to the formulation of the supersaturation (which is also true for deuterium excess) because S determines the relative contribution of diffusion effects in snow formation. The current formulation of S was chosen by Jouzel and Merlivat (1984) and Hoffmann et al. (1998) because it gives a reasonable fit between the RMK model and the observed deuterium excess measured in Antarctic snow (although it should be pointed out that other formulations for S yielded similarly acceptable results).

Hendricks et al. (2000) showed that a model that includes mixing in the atmosphere can explain the observed data, even when no kinetic effects in ice formation are considered, suggesting that kinetic effects during ice formation may not be important. (In a later version of the model, Kavanaugh and Cuffey (2003) included both mixing and kinetic effects). In addition, the prediction of very low $^{17}\Delta$ in snow at low temperatures by the RMK model is inconsistent with experimental findings where it was found that $^{17}\Delta$ of Antarctic ice standard (SLAP) is similar to that of other water samples (Jabeen and Kusakabe, 1997; Miller, 2002). This inconsistency taken together with the sensitivity of $^{17}\Delta$ to the formulation of S suggests that direct measurements of θ_k and θ_{vs}, and additional measurement of $^{17}\Delta$ in ice caps could help improve the parameterization of kinetic effects in ice formation.

The simple models described above demonstrate that different formulations of the kinetic effects yield changes in $^{17}\Delta$ in the order of tens of per meg. We believe that signals of such an order of magnitude could be measured by coupling existing fluorination systems to mass-spectrometers dedicated for the measurement of $^{17}\Delta$ of oxygen that currently reach an accuracy of ± 7 per meg (Luz et al., 1999; Blunier et al., 2002). Although the fluorination may cause a slight offset in the measured $\delta'^{18}O$ and $\delta'^{17}O$, this offset is expected to be mass-dependent. Hence,

the correction for $^{17}\Delta$ is expected to be small, and could be easily achieved by additional measurement of $\delta'^{18}O$ by standard techniques. As a result, practical use of $^{17}\Delta$ to constrain kinetic effects in ice formation is feasible with current technology.

6. CONCLUSIONS

Model calculations based on O_2 data indicate that the θ value associated with kinetic effects (i.e., vapor phase diffusion) is 0.511 ± 0.005, which differs significantly from the inferred value for equilibrium evaporation and condensation (0.525). This difference is hypothesized to arise from the difference in the governing equations of the two processes.

If the proposed difference in θ values is true, kinetic fractionation during evaporation will have an effect on the $^{17}\Delta$ of precipitation. This $^{17}\Delta$ value, however, is not affected by the temperature of evaporation. This would make $^{17}\Delta$ of water a unique tracer that complements ^{18}O and deuterium (in particular, the deuterium excess), and should enable one to distinguish between changes in the temperature of the ocean that serves as the vapor source and changes in the relative humidity above the ocean. As $^{17}\Delta$ will also be affected by kinetic fractionation during condensation of water vapor directly to ice, use of this variable as an additional constraint should lead to better parameterization of the isotopic fractionation effects for high latitude precipitation for all water isotopologues.

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