Lattice Boltzmann simulation of water isotope fractionation
during ice crystal growth in clouds

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Abstract

We describe a lattice Boltzmann (LB) method for simulating water isotope fractionation during diffusion-controlled ice crystal growth by vapor deposition from water-oversaturated air. These conditions apply to the growth of snow crystals in clouds where the vapor composition is controlled by the presence of both ice crystals and water droplets. Modeling of water condensation with the LB method has the advantage of allowing concentration fields to evolve based on local conditions so that the controls on grain shapes of the condensed phase can be studied simultaneously with the controls on isotopic composition and growth rate. Water isotope fractionation during snow crystal growth involves kinetic effects due to diffusion of water vapor in air, which requires careful consideration of the boundary conditions at the ice-vapor interface. The boundary condition is relatively simple for water isotopes because the molecular exchange rate for water at the interface is large compared to the crystal growth rate. Our results for the bulk crystal isotopic composition are consistent with simpler models using analytical solutions for radial geometry, confirming that the overall isotopic fractionation is mainly controlled by diffusive transport in the vapor phase on scales similar to the crystal dimension. The extent of vapor oversaturation plays a major role in determining the water isotope fractionation as well as the degree of dendritic growth. Departures from isotopic equilibrium increase at colder temperatures as diffusivity decreases. Dendritic crystals are isotopically heterogeneous. Isotopic variations within individual snow crystals could yield information on the microphysics of ice condensation as well as on the accommodation or sticking coefficient of water associated with vapor deposition. Our results are ultimately a first step in implementing LB models for kinetically controlled

condensation or precipitation reactions, but needs to be extended also to cases where the molecular exchange rate is comparable to the crystal growth rate, which is more challenging and has not yet been attempted. This work represents a first study on isotopic chemistry of snow crystals in the atmosphere, but could also be applicable to aerosol chemical evolution.

Key Words: lattice Boltzmann, snow crystal, kinetic, equilibrium, isotope fractionation

1. INTRODUCTION

Lattice Boltzmann (LB) methods have been developed in the last two decades for simulating complex fluid flows and physics. The fundamental idea of the LB methods is to construct simplified kinetic models that incorporate the essential physics of microscopic or mesoscopic processes so that the macroscopically averaged properties obey the desired macroscopic equations (Chen and Doolen, 1998). LB methods have been successfully applied to studying flow in porous media, turbulence, multiphase and multicomponent flows, particles suspended in fluids, heat transfer and reaction-diffusion (Chen and Doolen, 1998). Thermal LB methods have been used to study liquid-solid phase transitions, with enhanced collision schemes and coupled with the phase-field method (de Fabritiis et al., 1998; Miller et al., 2001). Studies have shown that the LB methods can provide detailed information in pore spaces regarding flow, chemical dissolution and precipitation in porous media (Kang et al., 2002, 2003). Nucleation and

crystal growth have been studied for the effects of diffusion and reaction (Kang et al., 2004; Chen et al., 2012) and vapor deposition (Lu et al., 2009).

There are few studies using the LB method to study isotope fractionation behavior during crystal growth, even though there are characteristics of LB that make it potentially useful for describing the more complex aspects of isotope fractionation associated with the growth of solids in fluid media. It is generally recognized that the rate of ice crystal growth in the atmosphere is controlled by water vapor diffusion to the crystal surface. Models for isotope fractionation in this regime are ultimately based on the theory of kinetic isotope fractionation (Bigeleisen and Wolfsberg, 1958; Melander and Saunders, 1980 and others). In a previous paper, we described the LB approach, the scaling needed to describe ice crystal growth by vapor deposition from supersaturated air, and the relationships between crystal morphology, oversaturation and growth rate (Lu et al., 2009).. This paper uses similar models, but modified to describe water isotope fractionation associated with ice crystal growth. The key challenge for this modeling is to implement appropriate boundary conditions at the surface of the growing crystal, and to maintain accurate mass conservation throughout the calculation. Our results exhibit the use of the LB approach to study microscopic aspects of isotopic fractionation during phase transitions, and allow us to evaluate the potential extent of solid phase heterogeneity caused by the interaction of complex dendritic growth patterns with vapor phase transport.

We have chosen to model the growth of ice crystals from vapor-oversaturated air partly because it is simpler than many other analogous condensation problems, and because of the significance of water isotope fractionation for the global water cycle (e.g.

Dansgaard, 1964; Jouzel et al., 1993). The simplicity stems from the fact that there is only one chemical component (H_2O), and also that the chemical reaction is just the vapor–solid conversion. Another important consideration is that the vapor deposition and exchange at the solid-vapor interface is extremely fast, which forces the vapor immediately above the solid surface to be close to isotopic equilibrium with the solid surface. The LB model is capable of simulating both diffusive flux and chemical reaction, hence allowing us to compare the LB model results to those of analytical solutions. This rapid-exchange condition is not generally applicable to other types of phase transitions, such as the precipitation of minerals from aqueous solution (DePaolo, 2011); in those cases the boundary condition at the crystal surface is more complicated and constitutes a future focus of our LB modeling studies. Our modeling also does not describe heat transport, although that is expected to be relatively unimportant for modeling ice crystal growth (Seinfeld and Pandis, 1998).

2. FRACTIONATION OF WATER ISOTOPES

2.1. Water isotopes in ice crystals condensed from supersaturated air

The primary isotopic species of water (H_2^{16}O , HD^{16}O , and H_2^{18}O) are widely used as tracers of atmospheric vapor transport (e.g. Merlivat and Jouzel, 1979; Rozanski et al., 1993; Gedzelman and Arnold, 1994; Schmidt et al., 2005) and proxies of paleoclimate (e.g. Jouzel et al., 1993; 2007; Hoffmann et al., 2005; Sturm et al. 2010). The three isotopic species, or isotopologues, are fractionated during phase changes. Equilibrium fractionation occurs due to differences in vapor pressures (Craig and Gordon, 1965; Jouzel and Merlivat, 1984), and so-called “kinetic” fractionation takes place due to

molecular diffusion to and from surfaces of evaporation or condensation (Cappa et al., 2003; Luz et al., 2009).

The growth of ice crystals in clouds occurs under both near-equilibrium and vapor-oversaturated conditions (Rogers et al., 2001; Pruppacher and Klett, 1997; Jouzel, 1986). At temperatures between about -5°C and -25°C , clouds typically are a mixture of water droplets, ice crystals, and water vapor. The water vapor pressure in equilibrium with liquid water is higher than that in equilibrium with ice, the difference increasing with decreasing temperature so that it is about 15% at -15°C and 62% at -50°C (Lu et al., 2009; Rogers et al., 2001). The water droplets can be unstable and evaporating while ice crystals are forming. Condensation, or vapor deposition, on ice crystals is slow enough that the vapor pressure is maintained well above the saturation value for ice; which is the so-called Wegener-Bergeron-Findeisen mechanism (Korolev, 2007). The ice crystals therefore grow in an environment of substantial water vapor oversaturation and hence far from equilibrium. There are qualitative correlations between ice crystal morphology and the extent of vapor oversaturation (e.g. Pruppacher and Klett, 1997), and some aspects of these correlations are captured in our previous LB modeling results (Lu et al., 2009).

Molecular exchange rates between the condensed and vapor phases are high relative to the growth rate of the crystals, which implies that there are near-equilibrium conditions at the surface of the crystals (cf. DePaolo, 2011). The growth of the crystals is limited by diffusion of water vapor to the crystal surface (Seinfeld and Pandis, 1998; Pruppacher and Klett, 1997). The diffusive water vapor flux is limiting because of the low vapor density, the low concentration of water vapor in cold air, and the relatively small diffusivities at low temperature. In addition, and also a function of density contrast

between phases, the time-scale for growth of crystals or droplets of dimension 10 μm or greater is roughly minutes, orders of magnitude longer than the characteristic diffusion time (microseconds) for water vapor over equivalent distances. This contrast allows the growth of a spherical solid by diffusion-limited vapor supply to be fairly accurately approximated with a *steady state* radial diffusion model (cf. Seinfeld and Pandis, 1998). The solution of the steady state radial diffusion equation with a central sink yields for the growth rate of crystals:

$$\frac{dm_c}{dt} = \rho_c \frac{dv_c}{dt} = 4\pi AD_f(\rho_\infty - \rho_{sat}) \quad (1)$$

where m_c is the mass, v_c is the volume, and ρ_c is the density of the crystal (condensed phase; hereafter the subscript c is used for the crystal). D_f is the diffusion coefficient of water vapor in air, ρ_∞ is the water vapor density (or concentration in mass/volume) far from the crystal, and ρ_{sat} is the water vapor saturation density. A is a shape factor that accounts for non-spherical crystal geometry; For spherical crystals or liquid droplets, $A = a$ (the crystal radius).

Equation 1 needs to be modified if the crystal dimension is the same order as the mean free path of water vapor in air (about 0.05 μm) because the rate of the molecular exchange at the crystal surface becomes slow enough that it begins to limit the growth rate (cf. Seinfeld and Pandis, 1998). For the case of ice crystal growth, equation 1 gives a value for the crystal growth rate as a function of crystal shape (through the parameter A), but contains no information about the relationship of crystal shape to growth rate. Use of an LB approach can simultaneously simulate growth rate, growth habit, and isotopic

composition, and can also indicate the extent of isotopic heterogeneity that can be expected in individual crystals.

Isotopologues of water fractionate during condensation due to their differences in mass, the collision diameters of the molecules (Merlivat, 1978; Cappa et al., 2003), and ρ_{sat} . To describe the isotopic effects, an equation can be derived that relates the condensation rate ratio of the isotopologues (r_c) to the isotopologue ratios in the vapor phase far from the crystal (r_∞). The value of r_c / r_∞ is referred to as the fractionation factor, α_c , which in general differs from the equilibrium fractionation factor, α_{eq} . Since water contains 3 isotopologues of interest here (H_2^{16}O , H_2^{18}O , HD^{16}O), a version of equation 1 can be written for each isotopologue ratio, although we treat only $\text{H}_2^{18}\text{O} / \text{H}_2^{16}\text{O}$ and $\text{HD}^{16}\text{O} / \text{H}_2^{16}\text{O}$. The resulting relationship is obtained after some manipulation (Jouzel and Merlivat, 1984):

$$\alpha_c = \frac{a_{eq} S}{a_{eq} (D_f / D'_f) (S - 1) + 1} \quad (2a)$$

where $S = \rho_\infty / \rho_{\text{sat}}$, D is the diffusion coefficient for the major water isotopologue (H_2^{16}O), and D'_f is the diffusion coefficient for the minor isotopologue (H_2^{18}O or HDO).

This equation can also be written in the form:

$$\frac{1}{\alpha_c} = \frac{1}{S} \left(\frac{S - 1}{D'_f / D_f} + \frac{1}{a_{eq}} \right) \quad (2b)$$

which shows that the effective fractionation factor is a blend of the equilibrium value, α_{eq} , and the diffusivity ratio D' / D , and depends only on the saturation of the vapor phase.

As S approaches unity, the fractionation factor α_c approaches the equilibrium fractionation factor α_{eq} . As S increases the fractionation factor α_c tends toward the ratio D'_f / D_f , although it can get close to this ratio only if $S \gg 1$, which does not apply for ice condensation in the atmosphere

As crystals or water vapor droplets grow in the atmosphere, they eventually reach a size where they fall through the atmosphere at a substantial rate, and then airflow around the crystal defines the thickness of the diffusive boundary layer around the crystal. This effect can be taken into account in both equations 1 and 2 with incorporation of ventilation coefficients (f and f') and the result is that the effects of diffusion on the isotopic fractionation are reduced (Ciais and Jouzel, 1994; Stewart, 1975). Flow can also be simulated with LB methods, but that aspect of the problem is not treated here.

2.2. Isotope fractionation for arbitrary crystal geometry

To develop a set of equations that can be treated with the LB method and that apply to arbitrary crystal geometry, we start with the isotope exchange reaction between solid and vapor, which for hydrogen and deuterium would be:

where subscript v indicates vapor phase and p precipitate. At a specific temperature the equilibrium fractionation factor (α_{eq}) is the equilibrium constant for the exchange reaction, which is expressed as

$$K = \frac{[H_2O]_v [HDO]_p}{[H_2O]_p [HDO]_v} = \frac{(D/H)_p}{(D/H)_v} = \frac{r_p}{r_v} = \alpha_{eq} \quad (4)$$

where the terms in parentheses are the molar ratios of D/H , also denoted as the isotopic ratios r_p and r_v . The exchange equation governs the partitioning of the minor isotope between the vapor and solid phase at equilibrium, and in turn affects the concentration gradient and the diffusive transport to the precipitate because the conditions are such that the vapor phase at the crystal surface is nearly in equilibrium with the crystal.

The approximate boundary condition for the minor isotope in the vapor at the crystal surface, which is used in deriving equation 2, can be determined from the above exchange equation. Writing the equilibrium or saturation concentration of the major (lower mass) isotope species as $C_{sat} = [H_2O]_{v,eq}$, and the equilibrium concentration of the minor isotope species as $C'_{sat} = [HDO]_{v,eq}$, we can derive from Equation 4 the following relationship:

$$\left(\frac{C'_{sat}}{C_{sat}} \right)_s = r_s = \frac{r_p}{\alpha_{eq}} \quad (5)$$

Where the subscript s denotes the location at the crystal surface. The value of r_s depends on the isotopic ratio of the surface of the solid, r_p , which in a growing crystal can vary spatially. This near-equilibrium condition is approximately maintained because the molecular exchange rate between vapor and the crystal surface is so large. To illustrate, the calculated exchange rate at -15°C is about $1.2 \text{ mol/m}^2/\text{sec}$, whereas the growth rate is only about $0.002 \text{ mol/m}^2/\text{sec}$ (DePaolo, 2011). Small departures from equation 5 are discussed below, and the fact that our LB model accounts for these small differences

makes it slightly different from the radial diffusion models (Eq. 1 and 2) that assume that equation 5 holds exactly.

To derive analytical expressions that more accurately describe the vapor isotopic composition at the crystal surface, we start with the flux balance at the crystal surface, where the concentration gradient for the major isotope at the interface is linked to the rate of precipitation. Assuming that the precipitation is first order we then have:

$$D_f \frac{\partial C}{\partial n} = k (C_s - C_{sat}) \quad (6)$$

where subscript s indicates concentration in the vapor at the solid surface, n is the direction normal to the crystal surface, and k is the kinetic rate coefficient.

The minor isotopologue has the analogous equation:

$$D'_f \frac{\partial C'}{\partial n} = k'(C'_s - C'_{sat}) = k'(C'_s - \frac{r_p}{\alpha_{eq}} C_{sat}) \quad (7)$$

The kinetic rate coefficients are assumed to be deducible from kinetic gas theory:

$$k = \chi \left(\frac{RT}{2\pi M} \right)^{1/2} \quad \text{and} \quad k' = \chi' \left(\frac{RT}{2\pi M'} \right)^{1/2} \quad (8)$$

where M is the molecular mass of the condensing species, and χ is the condensation coefficient or accommodation coefficient, which we take to be constant, equal to 0.1, and identical for both isotopic species. The condensation coefficient value chosen is in the range of probable values. Details are discussed in Lu et al. (2009). Based on Eq.8 and our assumption that $\chi = \chi'$, we have $k/k' = (M/M')^{-1/2}$. Table 2 also lists reaction rate

coefficients, based on kinetic theory and with the assumption that the condensation coefficient is 0.1 (Lu et al., 2009). More discussion is provided in Section 5.5.

To refine the relation represented by Eq. 5, we first note that new precipitate being added to the solid at any time t has isotopic ratio $r_p(t)$, defined as:

$$r_p(t) = \frac{D'_f \frac{\partial C'}{\partial n}}{D_f \frac{\partial C}{\partial n}} = \frac{k'(C'_s - \frac{r_p}{\alpha_{eq}} C_{sat})}{k(C_s - C_{sat})} \quad (9)$$

This equation yields the modeled, vapor saturation-dependent isotope fractionation factors and the modeled solid phase isotope ratios as a function of vapor isotope ratio and saturation state. As noted above, the isotopic composition of new precipitate on an existing snow crystal surface is affected by the isotopic composition of the existing solid surface. This is an issue for the modeling at the start of the simulation because the initial isotopic composition is unknown. However, because of the fast timescale associated with the large magnitude of k and k' , the value of r_p adjusts relatively rapidly until $r_p(t) = r_p$. Hence the initial value of r_p does not significantly affect the results. Rearranging the right side of Eq. 9 leads to an expression for the concentration of the minor isotopologue in the vapor at the crystal surface that accounts for the surface kinetics of vapor deposition:

$$\frac{r_s}{r_p} = \frac{1}{S_s} \left(\frac{S_s - 1}{k'/k} - \frac{1}{\alpha_{eq}} \right) \quad (10)$$

where S_s is relative saturation value at the crystal surface $S_s = C_s / C_{sat}$. This expression shows that as the vapor saturation at the crystal surface departs from equilibrium (Eq. 5;

$S_s = 1$), the vapor at the crystal surface becomes slightly different from the equilibrium value by an amount that is approximately proportional to $S_s - 1$. Equation 10 describes how the mass dependent rate constants affect the fractionation. Because k'/k is not too different from α_{eq} , and for the conditions of our simulations $S_s - 1 \approx 0.01$ to 0.001 , the rate constants have only a small effect on the computed fractionation factors.

There may be conditions where the surface reaction kinetics are more important. This possibility can be evaluated if we rewrite equation 6 in the approximate form:

$$\frac{2D_f}{a} (C_v - C_s) = k (C_s - C_{sat}) \quad (11a)$$

which can be rearranged to the form:

$$S_s - 1 = \frac{2D_f}{ka} (S_v - S_s) \quad (11b)$$

Where a is the crystal diameter and $a/2$ represents the approximate effective thickness of the diffusive boundary layer around the growing crystal. For the conditions of our simulations, with crystal diameter of order 0.1mm , $2D_f/ka \approx 0.028$, so for $S_v = 1.15$, then $S_s - 1 \approx 0.004$. For $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ the effect on the fractionation factor is only about 0.3% . For larger values of S_v , and smaller values of a , surface reaction kinetics could be more important. However, the values we are using for k are calculated assuming $\chi = 0.1$. If this coefficient is closer to unity, then it becomes less likely that surface kinetics will have much effect on the isotopic fractionation factors. For $\chi \ll 1$, it would be possible to use isotopic measurements on ice grown under appropriately controlled conditions to measure the value of χ .

2.3. Isotopic fractionation by diffusion

The previous section treats the effects of surface reaction kinetics on isotopic fractionation, and it is concluded that they are not likely to affect the fractionation behavior significantly under most conditions applicable to Earth's atmosphere. The kinetic isotope effects associated with ice crystal growth are therefore almost entirely due to differences in the diffusivities of the water isotopologues in air. The diffusivity values we use for the calculations are obtained from experimental data (Lu et al., 2009; Hall and Pruppacher, 1976), although we also report and experiment with values that are derived from kinetic theory.

The mass differences among the isotopologues affect both the equilibrium fractionation and the transport fractionation. The heavier isotopic species (H_2^{18}O and HDO) are preferentially incorporated into the stronger bonding environment of the solid, and consequently have a lower equilibrium vapor pressure than the lighter isotopic species (H_2^{16}O). This difference drives the enrichment of heavy isotopes in the solid phase, as represented by equilibrium fractionation factors greater than one. However, the light isotopic species has a larger diffusivity in the vapor phase due to its smaller mass and collision diameter (Cappa et al., 2003; Merlivat, 1978) and hence is preferentially transported to the solid surface by diffusion in the vapor. Hence, equilibrium favors preferential incorporation of the heavy isotopologues into the growing ice crystal but diffusion favors the incorporation of the light isotope. The larger the effect of diffusion, which corresponds to larger S_{v} , the larger the departure from equilibrium and the more the fractionation factor associated with condensation deviates from the equilibrium value and moves toward the ratio of the isotopologue diffusivities. Increasing S_{v} therefore causes α_p to decrease from the equilibrium value. The reaction rate constants,

diffusivities, and other key parameters for the modeling are tabulated in Tables 1 and 2.

3. MODELING METHODS

3.1. Lattice Boltzmann method

In this work, we treat the air-water vapor mixture as an isothermal and dilute-concentration system. We assume that the solute (i.e. H₂O) concentration does not affect the density and velocity of the solution. The solute transport in such a system can be described by the following lattice Bhatnagar-Gross-Krook (BGK) equation:

$$g_i^k(\mathbf{x} + \mathbf{e}_i \delta_t, t + \delta_t) = g_i^k(\mathbf{x}, t) - [g_i^k(\mathbf{x}, t) - g_i^{k(eq)}(C, \mathbf{u})] / \tau^k \quad (12)$$

where g_i is the distribution function of the solute concentration, $\mathbf{x}$ is the spatial coordinate, t is the time, δ_t is the time increment, τ^k is the relaxation time, C and $\mathbf{u}$ are the solute concentration and the fluid velocity, respectively, $\mathbf{e}_i$ is the discrete velocity, and g_i^{eq} is the corresponding equilibrium distribution function, and superscript k stands for the k -th solute species in a total of n solute species. In the most commonly used D2Q9 (two-dimensional, nine-speed) model, relaxation time τ^k is related to the diffusivity by $D = (\tau^k - 0.5\delta_x^2) / (3\delta_t)$ with δ_x being the spatial increment. Discrete velocity $\mathbf{e}_i$ is given by

$$\begin{aligned} e &= 0 & i &= 0 \\ &= (\cos[(i-1)\pi/2], \sin[(i-1)\pi/2]) & i &= 1-4 \\ &= \sqrt{2}(\cos[(i-5)\pi/2 + \pi/4], \sin[(i-5)\pi/2 + \pi/4]) & i &= 5-8 \end{aligned} \quad (13)$$

And g_i^{eq} has the following form

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$$g_i^{keq}(C, \mathbf{u}) = \omega_i C \left[1 + \frac{3\mathbf{e}_i \cdot \mathbf{u}}{c^2} + \frac{9(\mathbf{e}_i \cdot \mathbf{u})^2}{2c^4} - \frac{3\mathbf{u} \cdot \mathbf{u}}{2c^2} \right] \quad (14)$$

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335 where $c = \delta_x / \delta_t$. The ω_i 's are the associated weight coefficients, which are $\omega_0 = 4/9$, ω_i
 336 $= 1/9$ for $i = 1, 2, 3, 4$, and $\omega_i = 1/36$ for $i = 5, 6, 7, 8$ (Fig.1). The solute concentrations are
 337 calculated using

$$C^k(\mathbf{x}, t + \delta_t) = \sum_i g_i^k(\mathbf{x}, t + \delta_t) \quad (15)$$

338 It has been shown that, using the Chapman-Enskog expansion, the LB equation recovers
 339 the following convection-diffusion equation (Dawson et al., 1993).

340

$$\partial C^k / \partial t + (\mathbf{u} \cdot \nabla) C^k = \nabla \cdot (D^k \nabla C^k) \quad (16)$$

341

342

343 Since we have assumed that the solute concentration does not affect the density and
 344 velocity of the fluid, we can use the evolution equation of another distribution function to
 345 describe the fluid flow. It has been shown that the evolution equation recovers the correct
 346 continuity and momentum equations at the Navier-Stokes level (Qian et al., 1992; Chen
 347 et al., 1992).

348

349 **3.2. Modeling setup**

350 Nucleation of the “ice crystal” is initialized at the central point of the simulation
 351 domain. The deposition of water vapor at the crystal surface generates a concentration
 352 gradient, which drives a diffusive flux in the vapor phase toward the crystal. The water

vapor directly adjacent to the seed crystal is deposited onto the crystal surface according to the vapor phase saturation state and kinetic rate specified in Eq. (9). As the crystal grows, its surface area increases, the rate of removal of water vapor to the solid phase increases, and the crystal growth becomes more and more limited by diffusion to the crystal surface.

The vapor deposition is simulated with a two-dimensional 9-speed lattice Boltzmann model (D2Q9). The model domain is represented by a 202×202 grid. The four edges are treated as solid walls, where bounceback is used to remove the cyclic boundary condition. The model domain is set at 1.71×1.71 mm, which is deduced from the scaling relationships. The density of the crystal is set to 5 lattice units, five times higher than the density of the vapor phase. In reality, the density of the crystal is 10^6 times higher than the density of water vapor in air, but this change allows us to speed up the calculations by a large factor and does not affect the outcomes with regard to isotopic fractionation effects. Each simulation was run to 150,000 lattice time units, which corresponds to 40 seconds.

As the crystal starts to grow at the initial nucleation site, the deposited mass is accumulated into the central grid node until the integrated flux reaches the pre-set density of the ice crystal. When this threshold is reached, the central node becomes solid, and then the grid nodes next to this central node are the loci of vapor deposition. Once a node reaches the pre-set density, the crystal expands to an open (vapor phase) gridblock along the maximum concentration gradient. Then vapor deposition starts for the open nodes immediately around the just-filled node. The initial concentration of the heavier isotope is set to a small value that is close to the value of standard mean ocean water (see Section

5.3) in both the vapor phase and the seed crystal; this corresponds to an initial fractionation factor 1.0.

3.3. Boundary conditions and scaling analysis

The driving force in this model is the difference in concentration, i.e., the concentration gradient at the fluid-solid interfaces. At the macroscopic level, the first-order kinetic-reaction model at the interface (Lasaga, 1981) can be written as:

$$D'_f \partial C^k / \partial n = k_r^k (C^k - C_{sat}^k) \quad (17)$$

where D_f is the diffusivity, C is the solute concentration at the interface, C_{sat} is the saturated concentration, k_r is the local reaction-rate constant, and n is defined in Eq.6. Both the diffusivity and the kinetic rate constant for the major water isotope in the water vapor are well documented (Table 2). We implement the boundary condition for the vapor deposition reaction taking place at the solid-fluid interface with the volumetric mass balance approach detailed in Lu and DePaolo (2009).

4. RESULTS

4.1. Vapor saturation and crystal morphology

The level of vapor oversaturation has a strong effect on the geometry of the growing crystal, and this effect is produced by the model with no added perturbations needed to initialize it (Lu et al., 2009). The crystals shapes do not have the symmetry of real ice crystals because they tend to take the shape allowed by the square calculation grid. The significant aspect of the crystal shape is the extent of dendritic structure. Figure 2 shows

calculated crystal shapes for oversaturation from 1% to 15.1% at -15°C and for approximately constant simulated time. The maximum oversaturation yields a dendritic solid (Figure 2a), which is also larger due to the high growth rate. The simulated crystals become smaller as the oversaturation and growth rate drop. At the smallest oversaturation (1%) only a tiny crystal grows (Fig. 2d), but similar simulations carried out for longer times by Lu et al. (2009) show that at low oversaturation, the crystal remains compact and circular as it grows with no dendrite formation. The corresponding concentration fields at the end of the simulation show different responses depending on the degree of oversaturation (Figure 2) and the size of the crystal. In the case of the maximum oversaturation, the region of lowered concentration and significant concentration gradient has propagated out to the boundary of the simulation domain by the end of simulation (Figure 2a). At minimal oversaturation, the zone of depleted concentration is small compared to the simulation domain (Figure 2d); this latter situation also applies to the high oversaturation simulation at earlier stages of the simulation.

4.2. Deuterium fractionation

Deuterium (HDO/H₂O) has a larger equilibrium fractionation factor than oxygen-18 (H₂¹⁸O/H₂¹⁶O) (Merlivat and Nief, 1967). However, the diffusivity ratio, $\alpha_{kin,D} = D_{HDO}/D_{H2O}$ is closer to unity than that for O isotopes ($\alpha_{kin,O} = D_{H_2^{18}O}/D_{H_2^{16}O}$). The value of $\alpha_{kin,D}$ is somewhat problematical in that the experimental value of 0.977 determined by Merlivat (1978) is quite different from that predicted by kinetic theory 0.9836 (Table 1). We use the experimentally determined value, because that value has been used in previous studies and allows easier comparison with our results.

Deuterium fractionation was modeled for a series of oversaturation states from 1% to 15.1% at -15°C (Fig.3). The fractionation factor is set to 1.0 at the onset of the simulation and fluctuates greatly at the first few steps (the vertical lines for the initial few units of mass in Figure 3a). This instability arises from the dependence of the isotopic fractionation factor on the composition of the crystal (eqn. 9), which because of the small mass of the crystal, fluctuates by a large factor at the onset of the calculation. After these fluctuations subside, the fractionation factor initially, but then settles on a value much different from the initial value. As the crystal grows, the remaining vapor shows a steady decrease in D/H because the simulation domain is finite (Figure 3b). Because of this reservoir effect, the fractionation factor slowly drifts upward as the crystal accumulates mass, which is an artifact of the calculation. The fractionation factor is calculated by comparing the isotopic ratio in the crystal with that of the remaining vapor.

As expected from the simpler analytical model (Eq. 2) the degree of oversaturation in the vapor strongly affects the fractionation of deuterium (Figure 3). The fractionation is larger at lower oversaturation, approaching the equilibrium value as oversaturation goes to zero ($S \rightarrow 1$). Lower oversaturation also results in slower vapor deposition and thus slower crystal growth, and simpler crystal shape approaching circular. Higher supersaturation leads to a dendritic crystal shape (Lu et al., 2009) and a fractionation factor for HDO/H₂O that departs significantly from the equilibrium value.

4.3. Oxygen-18 fractionation

The equilibrium fractionation factor for H₂¹⁸O/ H₂¹⁶O is not as large as that for HDO/H₂O, and is affected by diffusion to a proportionally greater amount due the larger

mass difference between the isotopologues. At -15°C the equilibrium fractionation factor for H_2^{18}O is 1.0179. The diffusivity ratio of $\text{H}_2^{18}\text{O}/\text{H}_2\text{O}$ has been experimentally determined as 0.972 (Merlivat, 1978) and calculated using kinetic gas theory as 0.9687. These two values are close, but for our modeling, the diffusivity ratio is set to 0.972. The kinetic ratio $k'/k = 0.949$ (Table 1). The fact that these two values are significantly lower than those for HDO (Table 1), when combined with the smaller equilibrium fractionation factor for $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$, makes the $^{18}\text{O}/^{16}\text{O}$ fractionation proportionally much more sensitive to kinetic effects than D/H. The fractionation of oxygen-18 at -15°C was modeled using the same setup as that described in Section 4.2 above.

As is the case for HDO/ H_2O (or equivalently D/H) the fractionation for $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$, (or $^{18}\text{O}/^{16}\text{O}$) decreases in comparison to the equilibrium value as oversaturation increases (Fig. 4). The oversaturation is the primary control on the fractionation and on the departure from equilibrium. In contrast to the case for D/H, for O isotope fractionation at 15% oversaturation the model value of about 1.013 is significantly different from the value calculated with equation 2, which is 1.0116. This larger difference is partly due to the large difference between the equilibrium fractionation factor and the ratio of the kinetic rate constants (equation 10), and the variations in effective diffusive boundary layer thickness as the dendritic crystal grows (equation 11). As noted below, the differences in the modeled effects on HDO/ H_2O and $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ generate significant changes to the behavior of the d-excess value of precipitation at low temperatures. The simulated fractionation factor for $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ also drifts to slightly higher values as mass accumulates, which results from the effect of depletion of the simulation box, and

growth of the larger dendritic crystal to a size that is a large fraction of the simulation domain.

5. DISCUSSION AND IMPLICATIONS

5.1. Temperature dependence

Temperature affects snow crystal growth because of its effects on saturation, diffusivity, and the kinetics of water vapor deposition. In our simulations, the water vapor concentration is assumed to be at liquid water saturation (Table 2). The diffusivity values for water vapor decrease with decreasing temperature (Table 2; based on Lu et al., 2009; Hall and Pruppacher, 1976). Fractionation for both D and O¹⁸ deviate from equilibrium more and more as temperature decreases (Fig. 6). This trend results from increasing vapor saturation relative to ice, plus the temperature dependence of both vapor phase diffusivity and growth kinetics.

The absolute value of vapor saturation peaks at -12.5°C, and this favors the growth of a larger dendritic crystal, but the key factor for determining isotopic fractionation is relative oversaturation. The percentage oversaturation for ice increases from 1% at -1°C, to 55% at -50°C, to 66% at -100°C. The diffusivity and kinetic rate constants decrease with the drop in temperature with the former at lower pace than the latter, resulting in larger diffusion effects at lower temperature. However, Figure 6 carries the assumption that the water vapor is always in equilibrium with liquid water droplets, which is not accurate at the lowest temperatures.

5.2. Effect of domain size and initial isotope ratios

To evaluate the effect of the limited domain size of the simulations, we examined a case where the snow crystal grows in a substantially larger domain so that the water vapor depletion is negligible during the calculation. The large domain has dimensions of $87.5 \text{ mm} \times 87.5 \text{ mm}$ when scaled to physical length. The domain is still 200×200 nodes and deposition is initialized at the central node with a small seed crystal. The simulated time is 158,000 lattice units, which translates to a physical time of 2,000 seconds.

Figure 7 shows the fractionation for the crystal and the remaining vapor and comparison with the simulations in the small domain. Note that the crystal mass referred to in Figure 7 has been converted to μg based on the domain sizes. Results show that the deduced isotopic fractionation is independent of domain size, a conclusion that is evident in any case from Figures 3 and 4. It is shown that the drift of the observed fractionation factor due to vapor depletion is small and only significant when the crystal dimension is close to that of the calculation domain.

5.3. Intracrystal isotopic variations

The overall isotopic composition of the simulated ice crystals conforms approximately to the expectations for a sphere growing in a vapor, where the concentration field around the crystal has perfect radial symmetry. This correspondence is closer for $\text{HDO}/\text{H}_2\text{O}$ than for $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$, and implies that the dendritic shape has only a muted effect on the bulk isotopic compositions of the crystal, which is mainly affected by the large-scale diffusion field that still resembles a radially symmetric field. However, as the simulated crystals grow, and especially as the crystal shapes become dendritic, the diffusion length scale above the growing crystal surface varies around the crystal sufficiently that the local

isotopic fractionation varies and hence the crystals become substantially heterogeneous in isotopic composition.

The variability in fractionation is one of the potentially interesting outcomes from employing the LB approach. For example, in the simulation shown in Figure 5, the average value of α_D is close to 1.135 (Figure 4), but along the axis of the dendrites there are regions where the value is as high as 1.14. Similarly, with α_{18O} , the average value is 1.013, but along the axis of the dendrites the values are higher than 1.016 in many places. The high values along the dendrite axis are due to the distortion of the vapor phase concentration field at the dendrite tip, which causes the precipitate there to have a higher concentration of the minor (heavier) isotope. Continued condensation near the interior of the dendritic crystal, in contrast, is slower and from vapor that has the full diffusion-controlled depletion in the heavier isotope species. For $H_2^{18}O/H_2^{16}O$, this effect also significantly shifts the bulk isotopic composition of the simulated crystal so that it decreases the departure from equilibrium by about 20-25%.

A limitation of our model is that it is done in 2 dimensions. It is possible that if the third dimension were accounted for, there might be a larger deviation from the spherical model result because dendritic snowflakes have an overall 2-dimensional character. Three dimensional simulations are also needed to account for the varying habit of snow crystals under different conditions of temperature and saturation state. The 3D effects will be explored in a subsequent study. An additional issue is our failure to represent faceted crystals (cf. Libbrecht, 2005), which according to simple models of diffusion-controlled growth, imply that the accommodation coefficient can vary substantially across a facet. The effect of facets on crystal growth could be an interesting problem to be addressed

with LB simulations, since the simple models described in Libbrecht (2005) do not allow the crystal shape to respond to the vapor phase diffusion field as is done in our simulations. With regard to isotopic fractionation, the variations in accommodation coefficient are unlikely to be significant.

5.4. Application to Deuterium excess of precipitation

Deuterium excess of precipitation (defined as: $d = \delta D - 8 \times \delta^{18}O$) (Jouzel and Merlivat, 1984) has been interpreted as reflecting the relative humidity attending evaporation into air masses at their point of origin over the oceans. This view of the isotopic composition of high latitude snow carries the assumption that the main source of changes in d is the evaporation process, and that there is little additional contribution from subsequent transport of water vapor in the atmosphere and condensation. Indeed equation 2 predicts that there will be minimal change in d during precipitation at low temperatures (Figure 8). Hendricks et al. (2000) showed with simple models that transport effects can change this, but they assumed equilibrium condensation, which is probably not applicable.

Here we use the LB model to evaluate the potential changes in d that could be generated by condensation. For this calculation we modified the starting D/H and $^{18}O/^{16}O$ ratios for the calculations and made them equal to those of typical East Antarctic snow (155.76×10^{-6} and 2005.2×10^{-6} , respectively; Jouzel and Merlivat, 1984). The initial concentrations of the minor isotopes in the vapor phase are calculated using the snow values and the typical isotopic fractionation factor for the temperature range of interest. This yields a vapor phase isotopic composition that is similar to what is expected over Antarctica.

The other problematical issue with Antarctic precipitation is temperature, due to atmospheric inversions. For our models, the snow formation is assumed to occur in the inversion layer at the tropospheric temperature, which is obtained from ground level temperature T_g using $T = 0.67 T_g - 1.2$ (Lorius and Merlivat, 1977). The deuterium content is calculated from mean annual δD versus mean annual temperature at ground level T_g through the regression $\delta D = 6.04 T_g - 51$ (Phillpot and Zillman, 1970). $\delta^{18}O$ is calculated from meteoric water line $\delta D = 8\delta^{18}O + 10$.

The derived initial vapor has a D-excess of about 10, which is similar to what is generated by evapoarion over the oceans at low latitudes. The model generates an additional D-excess relative to this initial vapor. The results show that the deuterium excess expected for snow formed from water vapor that has $d = +10$ increases with decreasing temperature. Whereas equation 2 predicts that d should decrease slightly with decreasing temperature, the model shows d increasing with decreasing temperature.

Although there are a number of issues that can be raised, our model yields a good match to D-excess data of the snow from East Antarctica (Jouzel and Merlivat, 1984), which shows a significant increase in d with decreasing temperature (see also Figure 3 of Hendricks et al., 2000). This results suggest that the application of D-excess data from snow to determination of moisture sources could benefit from more realistic models of the effects of condensation on D-excess.

5.5. Modeling issues and implications

The modeling results we present are a first step in implementing LB models to better understand how isotopic fractionation during fluid-solid chemical reactions is influenced

by transport and surface kinetic effects. As noted above, water vapor-to-ice condensation is a good starting point because the chemistry is simple and the kinetics are relatively well known or at least relatable to the physics of gases. Nevertheless there are additional issues that we cannot resolve with the model. Ultimately, any model needs to be tested against experiments, and there is a paucity of experimental data available for evaluating the details of the isotopic effects associated with vapor deposition on ice.

One interesting issue is the condensation coefficient, χ , which is hard to measure but could possibly be constrained through isotopes. For our model, the exact value of this coefficient is not critical; it is mainly used for scaling the model to real world conditions. We use a value of 0.1, but there are observations and experimental data that indicate that the value can be as low as 0.001 and as high as 1.0. Of additional concern is whether there is an isotopic dependence to χ , or in other words whether the assumption $\chi = \chi'$ is reasonable, there are no strong arguments in favor of this assumption, but there are no data to suggest otherwise either.

The uncertainty about the isotopic dependence of χ does not matter for water vapor condensation because (at least theoretically) the molecular exchange between solid and vapor at the gas-solid interface is so fast that equilibrium is nearly maintained between the solid surface and the vapor immediately in contact with it.

The reason that the crystal/vapor isotopic fractionation deviates from the equilibrium value is solely because the vapor near the solid surface is different from the far field vapor due to the diffusion effects. Another way of describing this situation is that the growth rate of the solid (in units of mol/m²/sec) is small in comparison to molecular exchange rates (Libbrecht, 2005). For ice growing from water-saturated air at -15°C, and

for $\chi = 0.1$, the molecular exchange rate at the solid surface is about 2 mol/m²/sec, whereas the growth rate is of order 0.001 mol/m²/sec (DePaolo, 2011). An interesting implication, however, is that isotopes could be used to experimentally place constraints on the value of χ , because if χ were low enough (e.g. $\approx 10^{-4}$) the molecular exchange rate at the solid surface would be slow enough that k/k' would have an effect on the overall isotopic fractionation during vapor deposition.

Our model for water vapor deposition on ice crystals does not apply in general to condensation or crystallization processes. For the case of precipitation of calcite from aqueous solution, for example, the molecular exchange rate at the solid surface between the solid and the dissolved species in the aqueous fluid is similar in magnitude, or in some cases significantly slower, than the solid growth rate, and also small (order 10⁻⁶ mol/m²/sec) in comparison to the water exchange rate (DePaolo, 2011). In the case of aqueous precipitation, the kinetic rate constants are important in determining the isotopic fractionation and are also difficult to estimate based on theory or experiment (e.g. Nielsen et al., 2012).

Our results suggest that oxygen isotopic heterogeneity should be common in dendritic ice crystals and should contain information about growth rate and growth environment. The results also imply that for H₂¹⁸O/ H₂¹⁶O, the radial growth model may not be adequate for predicting the magnitude of kinetic isotope effects. Whether measurements of intra-crystalline isotopic variations could ever be made is unclear for natural samples, but if laboratory ice crystal growth experiments could be designed to allow for such measurements, the isotopic distributions could provide unique information on the physics of ice crystal growth.

6. CONCLUSIONS

We have developed a 2D LB model for isotope fractionation in solid ice crystallizing from a vapor phase of multiple water vapor components corresponding to the major isotopologues of water (H_2O , HDO , H_2O^{18}). The LB approach is useful in this case because it can accommodate complex solid phase geometries, and the crystal shape can be allowed to develop during the simulation rather than being specified from the onset. The boundary condition at the crystal surface, involving precipitation at the fluid-solid interface and the concomitant advance of the crystal surface into the vapor, is implemented with a volumetric approach with accurate mass balance. The scaling of the simulations to the physical problem of the growth of ice crystals in air by vapor deposition is aided by the availability of experimental values for the diffusivity of water vapor in air and the fact that the kinetics of vapor deposition can be related directly to the vapor phase temperature, pressure and concentration using kinetic gas theory.

The primary uncertainties in relating the calculations to the real world involve the 2D nature of the simulations, and the condensation coefficient, which may vary with temperature and position on a crystal surface. The calculations also do not account for surface energy effects. The 2D calculations can be considered as a description of the growth perpendicular to the crystal c axis under conditions where growth parallel to the c axis is slow.

Our work represents the first study with LB methods of water isotope fractionation. It provides a basis for further LB studies of crystal formation resulting from vapor-deposition, including isotope fractionation, airflow (ventilation), the effect of chemical

species, and surface melting. The results have implications for modeling of ice condensation in clouds and for interpretation of the isotopic composition of high latitude precipitation and glacial ice.

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edition). John Wiley and Sons, p.656.

796

797 Tables

798 Table 1. Diffusion and reaction properties of water vapors at -15°C

Parameters	Isotopes	Values
D (m ² /s) ^a	H ₂ O	0.1920e-4
k (m/s) ^b	H ₂ O	13.77
D'/D (kinetics) ^c	HDO	0.9836
	H ₂ O ¹⁸	0.9687
D'/D (Merlivat 1978) ^c	HDO	0.977
	H ₂ O ¹⁸	0.972
k'/k ^d	HDO	0.973
	H ₂ O ¹⁸	0.949

799 ^aDiffusivity for water vapor (Hall and Pruppacher, 1976; Lu et al., 2009).

800 ^bReaction rate constant calculated from kinetic theory of gases
801 with vapor deposition coefficient $\chi = 0.1$ for -15°C (Lu et al.,
802 2009). ^cData from kinetics are varied with temperature. Data from
803 Merlivat were experimentally determined and are used in our
804 calculations. ^dPrime indicates heavy isotopes. The values are
805 calculated as $k'/k = \sqrt{m/m'}$ based on kinetic gas theory (Eq.8).
806 And $D'/D = (m/m') (m' + m_{air}) / (m + m_{air})$ with m for the water
807 molecular weight, and m_{air} at 29 for the air mass.

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811 Table 2. Physical properties of water vapor for different temperatures

T (°C)	Water saturation ^a (g/cm ³)	Ice saturation ^a (g/cm ³)	D (m ² /s) ^b	k (m/s) ^c	α_{eq}^d HDO	α_{eq}^d H ₂ ¹⁸ O
-1	4.5157E-06	4.4730E-06	2.1228e-5	1.4137e+1	1.1319	1.0153
-5	3.3964E-06	3.2402E-06	2.0627e-5	1.4032e+1	1.1404	1.0160
-10	2.3442E-06	2.1341E-06	1.9887e-5	1.3901e+1	1.1511	1.0170
-15	1.5902E-06	1.3818E-06	1.9161e-5	1.3768e+1	1.1618	1.0179
-20	1.0588E-06	8.7869E-07	1.8447e-5	1.3634e+1	1.1758	1.0189
-25	6.9113E-07	5.4809E-07	1.7747e-5	1.3500e+1	1.1898	1.0198
-35	2.7571E-07	2.0027E-07	1.6386e-5	1.3224e+1	1.2178	1.0218
-50	5.7369E-08	3.6984E-08	1.4443e-5	1.2801e+1	1.2599	1.0247
-75	2.1423E-9	1.2113E-9	1.1470e-5	1.2062e+1	1.4057	1.0328
-100	2.3000E-11	1.3845E-11	8.8292e-6	1.1276e+1	1.5683	1.0409

812 Notes: a. Calculated from Mangus equation. Source: Pruppacher and Klett (1997, p. 854). b.
813 Experimental data from Hall and Pruppacher (1976) and cited in Lu et al. (2009). c. Calculated
814 from kinetic theory of gases equation in Lu et al. (2009, Eq. (32) with $\chi = 0.1$). d. Source from
815 Merlivat and Nief (1967) (HDO-H₂O) and by Majoube (1971) (H₂¹⁸O-H₂O).
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819 Table 3. Scaling of diffusion and reaction properties for H₂O at -15°C

LB model	Da	1260
	l_m	200
	D_m	5.5E-4
	k_m	3.46E-3
	t_m	158,000
Physical values	$D \text{ (m}^2\text{/sec)}^a$	0.19e-4
	$k \text{ (m/sec)}^b$	13.77
Scaling ^c	$l_r = D_p/k_p \cdot k_m/D_m$	8.75e-6
	$k_r = k_p/k_m$	3.98E+3
	$D_r = D_p/D_m$	3.48e-2
	$l_p \text{ (m)}$ (derived)	1.75e-3
	$t_r = m_r/(C_r l_r D_r)^d$	2.51e-4
	$t_p = t_m t_r \text{ (sec)}$	3.97E+1

820 ^aApproximated with atmosphere pressure at 1.0 bar from Hall and Pruppacher (1976) and Lu et al.
821 (2009). ^bCalculated from kinetic theory of gases with $\chi = 0.1$ for -15°C (Lu et al., 2009). ^cScaling
822 analyses detailed in Lu et al.(2009). ^d $m_r = C_r V_r = C_r l_r^2$. In the model, we set modeled density 1.0
823 (lattice unit) to physically represent vapor density 1.0E-06 (g/cm³). Subscript p indicates
824 physical value, and subscript m model value.

Figure 1. Schematic illustration of a wall node with the speed numbering.

Figure 2. Deuterium fractionation in simulated "snow crystals" grown at -15°C for different over-saturations of vapor: a. 15.1% (water saturation); b. 10%; c. 5%; and d. 1%. The maximum isotopic ratio $r \times 1000$ in d. is 1.1631. Diffusivity $0.19\text{e-}4 \text{ m}^2/\text{s}$, kinetic rate constant 13.77 m/s . Damkohler number $\text{Da } 1230$. Snow density set to 5.0 lattice units. The simulation time is $150,000$ lattice time units or 40 seconds. The dendritic structure centered in the plots delineates snow crystal. The square grid coupled with the stipulation that growth occurs preferentially in the direction of maximum vapor phase concentration gradient forces the simulated crystals to tend to grow along diagonals.

Figure 3. Deuterium fractionation versus deposited mass for various vapor saturations at -15°C: a. snow; b. remaining vapor. Ice saturated concentration $1.3818 \times 10^{-6} \text{ g/cm}^3$. Vapor diffusivity $0.19 \times 10^{-4} \text{ m}^2/\text{s}$, kinetic rate constant 13.77 m/s . Damkohler number Da 1230. The simulation time is 150,000 lattice time units. The simulation begins with a seed crystal of negligible mass having an isotopic ratio equal to that of the vapor ($\alpha_D = 1.000$), but the crystal isotopic ratio rapidly shifts to the steady state value determined by the diffusive isotope separation generated by diffusion-controlled growth. The remaining water vapor in the simulation domain gradually shifts to lower D/H, which is an artifact of the simulation setup that has a small effect on the resultant solid isotopic composition. For comparison, the fractionation factor calculated from equation 2 is 1.1337 at 15% oversaturation.

Figure 4. Oxygen isotope fractionation versus deposited mass for various vapor saturations at -15°C: a. solid; b. remaining vapor. Ice saturated concentration is $1.3818 \times 10^{-6} \text{ g/cm}^3$. Vapor diffusivity $0.19 \times 10^{-4} \text{ m}^2/\text{s}$, kinetic rate constant 13.77 m/s . Damkohler number Da 1230. The simulation time is 150,000 lattice time units. Other aspects of the calculation are similar those mentioned in the caption to Figure 3. For comparison, the fractionation factor calculated from equation 2 is 1.0116 at 15% oversaturation.

Figure 5. Deuterium and oxygen-18 isotopic fractionation and its relation to crystal morphology during crystal growth: Deuterium at 15.1% oversaturation (a) and 1.0% oversaturation (b); oxygen-18 at 15.1% oversaturation (c) and 1.0% oversaturation (d). The dendritic structure centered in the plots delineates the solid phase. The vapor concentration field is that for the end of the calculation and is contemporaneous with the solid as shown. Solid density is set at 5 lattice units, vapor concentration is 1. Simulation duration is 150,000 lattice times. Damkohler number for this calculation is 1,230. Other parameters are listed in Table 2. Simulated domain is 200×200 ; the figures show a closeup of the portion of the domain occupied by solid phase.

Figure 6. Water isotope fractionation during vapor deposition increasingly departs from equilibrium as the temperature of condensation is lowered: (a). Deuterium; (b). Oxygen-18. Red boxes are the equilibrium values, black circles are those calculated from Eq.2, blue circles are values calculated with the Lattice Boltzmann code. The vapor phase is assumed to be in equilibrium with liquid water, which may not be a good model below about -50C. For D isotopes, the LB model yields results that are nearly identical to those from equation 2, but for O isotopes the results are significantly different. Other parameters listed in Tables 1 and 2.

Figure 7. Deuterium fractionation in different-size calculation domains: (a). Crystal; and (b). Remaining vapor. Models run to 150,000 lattice steps. Parameters for the large domain, $D_m = 2.08\text{e-}3$, and $k_m = 0.65387$. Other parameters listed in Tables 1 and 2.

Figure 8. Deuterium excess calculated for snow crystal growth under atmospheric conditions applicable to East Antarctica. The condensation temperature assumed is the tropospheric temperature. Red boxes for equilibrium, black circles for Equation 2 in the paper, blue circles calculated from the code in this work. Diamonds are data for East Antarctic snow (from Fig. 6 in Jouzel and Merlivat, 1984).