



**Kinetic fractionation
of gases**

K. Kawamura et al.

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Kinetic fractionation of gases by deep air convection in polar firn

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Abstract

A previously unrecognized type of gas fractionation occurs in firn air columns subjected to intense convection. It is a form of kinetic fractionation that depends on the fact that different gases have different molecular diffusivities. Convective mixing continually disturbs diffusive equilibrium, and gases diffuse back toward diffusive equilibrium under the influence of gravity and thermal gradients. In near-surface firn where convection and diffusion compete as gas transport mechanisms, slow-diffusing gases such as krypton and xenon are more heavily impacted by convection than fast diffusing gases such as nitrogen and argon, and the signals are preserved in deep firn and ice. We show a simple theory that predicts this kinetic effect, and the theory is confirmed by observations of stable gas isotopes from the Megadunes field site on the East Antarctic plateau. Numerical simulations confirm the effect's magnitude at this site. A main purpose of this work is to support the development of a proxy indicator of past convection in firn, for use in ice-core gas records. To this aim, we also show with the simulations that the magnitude of kinetic effect is fairly insensitive to the exact profile of convective strength, if the overall thickness of convective zone is kept constant.

1 Introduction

Trapped air in polar ice cores provides a unique archive of past atmospheric composition, and permits comparison of the past burden of greenhouse gases and associated climatic variations. Interpreting the gas records requires understanding the processes that modify the gas composition in the ~ 100 -m-thick permeable firn layer on top of polar ice sheets, because the gas trapped in bubbles originates as air in the base of the firn (Schwander, 1989). These processes include gravitational fractionation of heavy isotopes and gases, due to settling of the heavier components under the influence of molecular diffusion in the stagnant portion of the firn (Schwander et al., 1989; Sowers et al., 1989). A second diffusive process is thermal fractionation, in which gases

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separate due to temperature gradients in the stagnant air column (Severinghaus et al., 1998; Lang et al., 1999; Landais et al., 2004; Grachev and Severinghaus, 2005). This portion of the firn is known as the “diffusive column” (Sowers et al., 1992).

Near the surface, the air is not stagnant and is convectively mixed, due primarily to flow driven by local pressure gradients arising from interaction of the wind with small topographic irregularities, a process known as “windpumping” (Colbeck, 1989; Clarke and Waddington, 1991). Buoyancy-driven convection may also occur in winter, when dense cold air overlies the warmer firn (Powers et al., 1985; Severinghaus et al., 2001). This convective mixing reduces gravitational and thermal gas isotope fractionation, and tends to homogenize the gases with the free atmosphere. The layer in which isotope fractionation is inhibited is known as the “convective zone” (Sowers et al., 1992). The thickness of this convective zone varies from nearly zero to 23 m at those sites in modern firn that have been studied by withdrawing a depth profile of air samples from the firn and analyzing the gas composition (Schwander et al., 1993; Bender et al., 1994a; Battle et al., 1996; Severinghaus et al., 2001, 2010; Kawamura et al., 2006). Past variations in the thickness of the convective zone remain enigmatic and poorly understood, motivating the present study.

A search for a modern example of deep convection in firn was undertaken in an attempt to understand observations of lower-than-expected $\delta^{15}\text{N}$ values in ice core trapped air records from Antarctic sites such as Vostok (Sowers et al., 1992; Caillon et al., 2003; Bender et al., 2007) and Dome Fuji (Kawamura, 2000; Landais et al., 2006). Deep convection is one hypothesis to explain the low $\delta^{15}\text{N}$; the alternative hypothesis is that past firn thickness and hence gas age-ice age differences are overestimated, with implications for the relative timing of atmospheric CO_2 increases and temperature increases at the ends of glacial periods (Bender et al., 2007; Parrenin et al., 2012).

An obvious candidate for deep convection is the Megadunes site on the East Antarctic plateau (80.77914° S, 124.488° E; Fahnestock et al., 2002; Severinghaus et al., 2010), located southeast of Vostok station, where near-zero snow accumulation rate occurs on the lee slopes of large-scale snow antidunes in a strong katabatic wind

regime (Courville et al., 2007). Low accumulation rate is expected to enhance permeability and thus air flow through firn, due to large grain size resulting from extended exposure to seasonal temperature fluctuations and extreme firn metamorphism (Albert et al., 2004; Severinghaus et al., 2010).

Here we show that a previously unrecognized type of gas fractionation occurs in firn air columns subjected to intense convection. In contrast to gravitational and thermal fractionation, which are equilibrium processes, this third process arises from the disequilibrium caused by turbulent mixing. It is a form of kinetic fractionation that depends on the fact that different gases have different molecular diffusivities. In essence, convective mixing continually disturbs diffusive equilibrium, and gases diffuse back toward equilibrium. Heavy gases and isotopes tend to diffuse more slowly than other gases, leading to their steady-state depletion in the firn interior relative to fast-diffusing gases. In a regime where convection and diffusion compete strongly as transport mechanisms, slow-diffusing gases are more heavily impacted by convection. In other words, the convective zone is thicker for slow-diffusing gases such as Xe than for fast-diffusing gases such as N₂.

In the present work we show that a simple theory predicts this kinetic effect from first principles, and that the theory is confirmed by observations of heavy noble gas isotopes from the Megadunes site sampled in 2004 (Severinghaus et al., 2010). Numerical simulations confirm the effect's magnitude in the field with a more realistic mixing and gas transport parameterization than is possible from simple theory.

The ultimate aim of this work is to support the development of a proxy indicator of past convection in firn, for use in ice-core gas records. This indicator exploits the kinetic effect on the isotopes of Xe and Kr, which diffuse more slowly than Ar and N₂.

2 Simple theory of kinetic fractionation

Kinetic fractionation by convection can be predicted from first principles. Gas transport in a porous medium such as firn may be described by the 1-dimensional diffusion

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equation (e.g. Schwander et al., 1993), with an additional “eddy diffusion” term to represent the effect of turbulent mixing (Kawamura et al., 2006; Severinghaus et al., 2001, 2010; Buizert et al., 2012; Witrant et al., 2012):

$$s \frac{\partial \delta}{\partial t} = \frac{\partial}{\partial z} \left[s D_{\text{mol}}(z, T, p) \left(\frac{\partial \delta}{\partial z} - \frac{\partial \delta}{\partial z} \text{eq} \right) + s D_{\text{eddy}}(z) \frac{\partial \delta}{\partial z} \right] - s w(z) \frac{\partial \delta}{\partial z} \quad (1)$$

5 where δ is $\delta^{15}\text{N}$ (or δ for other gas pair), t is time, s is open porosity, z is depth, p is barometric pressure, T is temperature (K), and w is downward velocity of air due to bubble trapping, D_{mol} is effective molecular diffusivity, D_{eddy} is eddy diffusivity to represent turbulent mixing. This equation treats molecular diffusion as arising from the difference between the actual gradient and the equilibrium gradient (Bender et al.,
10 1994a; Severinghaus et al., 2001), where the equilibrium gradient contains terms for gravitational and thermal fractionation, and is given by:

$$\frac{\partial \delta}{\partial z} \text{eq} \cong \frac{\Delta m g q}{R T} - \Omega \frac{\partial T}{\partial z} \quad (2)$$

where Δm is mass difference ($0.001 \text{ kg mol}^{-1}$ for $\delta^{15}\text{N}$), g is gravitational acceleration, R is the gas constant, q is $(\delta/1000+1)$ and Ω is thermal diffusion sensitivity. At steady state, Eq. (1) simplifies to (Severinghaus et al., 2010):
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$$\frac{\partial \delta}{\partial z} = \frac{D_{\text{mol}}}{D_{\text{mol}} + D_{\text{eddy}}} \frac{\partial \delta}{\partial z} \text{eq} \quad (3)$$

This ratio of diffusivities is closely related to the Péclet number, a non-dimensional number that describes the ratio of advective transport to diffusive transport. Advective transport is typically given by a velocity w times a length scale L . Eddy diffusivity may be thought of as a velocity times a characteristic length traveled before the fluid motion changes to a new (random) direction. Péclet number is given by
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$$Pe \equiv \frac{wL}{D_{\text{mol}}} = \frac{D_{\text{eddy}}}{D_{\text{mol}}} \quad (4)$$

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This allows Eq. (2) to be written as:

$$\frac{\partial \delta}{\partial z} = \frac{1}{1 + Pe} \frac{\partial \delta}{\partial z} \text{eq} \quad (5)$$

For example, when turbulent mixing and molecular diffusion have the same magnitude, and are in direct competition with each other, the actual concentration gradient is only half the equilibrium gradient:

$$\text{if } D_{\text{mol}} = D_{\text{eddy}} \text{ then } Pe = 1 \text{ and } \frac{\partial \delta}{\partial z} = 0.5 \frac{\partial \delta}{\partial z} \text{eq} \quad (6)$$

The integral of the gradient over the firm depth interval, plus $\delta(0)$, gives δ at depth z :

$$\delta(z) = \int_0^{z'} \frac{\partial \delta}{\partial z} dz + \delta(0) = \int_0^{z'} \frac{1}{1 + Pe(z)} \left(\frac{\partial \delta}{\partial z} \text{eq} \right) dz + \delta(0) \quad (7)$$

Surface δ is zero for the purposes of this work and is neglected, as we study inert gases that are nearly constant in the atmosphere and we use the atmosphere as our reference gas.

A key point is that eddy diffusivity is nearly the same for all gases, because of the macroscopic nature of turbulent mixing, but molecular diffusivities vary among gases, typically decreasing with mass. Heavier gases with lower molecular diffusivities will therefore be affected more by turbulent mixing and will deviate more from the equilibrium gradient (Fig. 1).

This difference in gas behavior is a form of kinetic fractionation, analogous to the familiar kinetic fractionation in irreversible gas fluxes, because it depends on differences in molecular diffusivities. In concept, a disequilibrium situation is set up by convective mixing, and gases diffuse back toward equilibrium, with heavier gases diffusing more slowly. This leads to a steady state depletion of heavy gases. This type of kinetic fractionation has much in common with diffusive fractionation in the firm in response to

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recent strong increases in atmospheric mixing ratios of CO₂ and methane, which have created disequilibrium of the firm air with the overlying atmosphere (Trudinger et al., 1997). Both are essentially a response to disequilibrium.

The magnitude of the kinetic fractionation can be calculated from the difference of gas concentrations, normalized by the mass difference Δm (for simplicity we neglect thermal diffusion). For gas 1 with δ_1 having molecular diffusivity D_{mol_1} , and gas 2 with δ_2 having molecular diffusivity D_{mol_2} , the kinetic fractionation ε_k will be:

$$\varepsilon_k = \frac{\delta_1}{\Delta m_1} - \frac{\delta_2}{\Delta m_2} = \int_0^z \frac{D_{\text{mol}_1}}{D_{\text{mol}_1} + D_{\text{eddy}}} \frac{\partial \delta_1}{\partial z} \text{eqn} - \frac{D_{\text{mol}_2}}{D_{\text{mol}_2} + D_{\text{eddy}}} \frac{\partial \delta_2}{\partial z} \text{eqndz} \quad (8)$$

where the normalized gradient is given as:

$$\frac{\partial \delta}{\partial z} \text{eqn} = \frac{\partial \delta}{\partial z} \text{eq} \frac{1}{\Delta m} \quad (9)$$

In the limit $D_{\text{eddy}} \gg D_{\text{mol}}$, there is no fractionation at all, and in the limit $D_{\text{eddy}} \ll D_{\text{mol}}$, the equilibrium gradient holds for both gases so there is no kinetic fractionation. Only when D_{eddy} roughly equals D_{mol} will there be kinetic fractionation. Some simplification is possible by noting that the equilibrium gradient depends on Δm , which then cancels out:

$$\varepsilon_k \cong \frac{g}{RT} \int_0^z \frac{1}{1 + Pe_1(z)} - \frac{1}{1 + Pe_2(z)} dz \quad (10)$$

This expression is approximate because it uses the approximation for gravitational fractionation given above, which is good to 1 part in 10³ for typical isotope pairs. It is helpful to express the Péclet numbers in terms of the ratio of the molecular diffusivities, as that

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is the key physical parameter that causes the effect:

$$\varepsilon_k \cong \frac{g}{RT} \int_0^z \frac{1}{1 + Pe_2(z) \frac{D_{\text{mol}_2}}{D_{\text{mol}_1}}} - \frac{1}{1 + Pe_2(z)} dz \quad (11)$$

An important point is that this equation is valid only for trace gases diffusing into the major gas that is present. In other words, both molecular diffusivities given here are the binary diffusivities of trace gases with the major gas. In the case of air, which is our primary interest, the major gas is mass 28 dinitrogen, $^{28}\text{N}_2$. For practical reasons the natural choice for gas 2 is the gas pair $^{15}\text{N}^{14}\text{N}-^{28}\text{N}_2$, denoted $\delta^{15}\text{N}$, because it is easily measured and has a relatively large diffusivity compared to most trace gases in air. Thus it is convenient to consider the Péclet number as that of $^{15}\text{N}^{14}\text{N}-^{28}\text{N}_2$, written Pe_{15} for brevity. The fractionation in this case is therefore the fractionation of a trace gas y expressed as the gas pair $y-^{28}\text{N}_2$ relative to the $^{15}\text{N}^{14}\text{N}-^{28}\text{N}_2$ pair:

$$\varepsilon_k \cong \frac{g}{RT} \int_0^z \frac{1}{1 + Pe_{15}(z) \frac{D_{15}}{D_y}} - \frac{1}{1 + Pe_{15}(z)} dz \quad (12)$$

For example, if gas y is ^{136}Xe , Eq. (14) applies to the fractionation of the pair $^{136}\text{Xe}-^{28}\text{N}_2$. If it is desired to compute the fractionation of a ratio of trace gases, for example the $^{136}\text{Xe}-^{129}\text{Xe}$ ratio, Eq. (12) is not valid. The reason for this is essentially that molecular collisions between the two trace gases are rare, and instead the collisions are typically between a trace gas and $^{28}\text{N}_2$. Thus, the binary diffusivity of ^{136}Xe into ^{129}Xe is not physically relevant. Instead, the concentrations with $^{28}\text{N}_2$ must be separately computed, and then combined afterwards:

$$\varepsilon_{136-129} = \frac{\delta_{136-129}}{\Delta m_{136-129}} - \frac{\delta_{15}}{\Delta m_{15}} \cong (\delta_{136-28} - \delta_{129-28}) \frac{1}{\Delta m_{136-129}} - \frac{\delta_{15}}{\Delta m_{15}}$$

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$$\cong \frac{g}{RT} \int_0^{z'} \left(\frac{\Delta m_{136-28}}{1 + Pe_{15}(z) \frac{D_{15}}{D_{136-28}}} - \frac{\Delta m_{129-28}}{1 + Pe_{15}(z) \frac{D_{15}}{D_{129-28}}} \right) \frac{1}{\Delta m_{136-129}} - \frac{\Delta m_{15}}{1 + Pe_{15}(z)} dz \quad (13)$$

For example, if Pe_{15} is 1 (for simplicity), z is 30 m, the temperature is 224 K, and the molecular diffusivities are as in Table 1, Eq. (13) becomes:

$$\varepsilon_{136-129} \cong \frac{gz}{RT_K} \left[\left(\frac{108}{1 + \frac{D_{15}}{D_{136-28}}} - \frac{101}{1 + \frac{D_{15}}{D_{129-28}}} \right) \frac{1}{7} - \frac{1}{2} \right] = -0.020\% \quad (14)$$

In other words, the ^{136}Xe - ^{129}Xe ratio (when normalized by dividing δ by the mass difference of 7) will be 0.02 ‰ less than expected from the observed $\delta^{15}\text{N}$. This corresponds to a 4 m deeper convective zone for xenon isotopes than for nitrogen isotopes. Although this is small, it is a measurable signal in practice as will be shown below.

Many approximations are made above. An exact treatment is useful for checking the validity of these approximations, and is given in Appendix A. In summary, the approximations given here appear to be valid at the level of 1 part in 10^3 for typical polar conditions.

It is interesting to consider the behavior of the fractionation under widely varying Péclet number, as is likely to occur in Nature. It can be shown algebraically that the maximum fractionation occurs when the eddy diffusivity is equal to the geometric mean of the two molecular diffusivities, or when the product of the two Péclet numbers is 1. The fractionation falls off by factors of 2 to 4 at Péclet numbers of 0.1 to 10, respectively (Fig. 2). For comparison, Kawamura et al. (2006) found near-surface eddy diffusivities and Péclet numbers at four polar firn sites that were roughly in this range. These results suggest that at least some fractionation will occur in most naturally occurring convection regimes, even if the optimum conditions ($Pe_1 \times Pe_2 = 1$) are not exactly met.

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3 Experimental procedure

Air samples were withdrawn from the Megadunes firn in January 2004 as part of a multi-investigator, multidisciplinary field campaign to better understand the genesis of megadunes and their possible implications for ice core paleorecords. Detailed air sampling procedures were explained elsewhere (Severinghaus et al., 2010), thus only a brief description is given here. Air was sampled from a borehole made with a 3" Eclipse ice core drill, using an inflatable rubber packer to seal the borehole. Firn air was withdrawn from the bottom of the borehole through a 1/4" Synflex[®] tubing that penetrates the packer, and filled in two-liter glass flasks by flushing for the inert gas measurements. In addition, a number of other air samples were taken for halocarbons, CO₂ and methane concentrations and their isotopes (Severinghaus et al., 2010).

Flasks were analyzed at Princeton University for $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ of O₂, $\delta\text{O}_2/\text{N}_2$, and $\delta\text{Ar}/\text{N}_2$, following standard procedures (Bender et al., 1994b, 2005), with extra integration to increase precision (Table 2). Flasks were shipped to SIO, and then analyzed for $^{40}\text{Ar}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$, $^{132}\text{Xe}/^{36}\text{Ar}$, and $^{22}\text{Ne}/^{36}\text{Ar}$ following the procedures of Severinghaus and Battle (2006) with increased sample size to 80 ml STP, gettering time to 20 min, and homogenization time to more than 2 h. Duplicate or triplicate measurements were made for each flask. Pooled standard deviations of flask replicates from the mean for that sampling depth were $\pm 0.002\text{‰}$ for $\delta^{15}\text{N}$ and $\pm 0.006\text{‰}$ for $\delta^{40}\text{Ar}$. The $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$ data were published by Severinghaus et al. (2010).

A subset of the flasks ($n = 23$ out of 42 total) was then analyzed for isotopic ratios of krypton and xenon, $^{86}\text{Kr}/^{82}\text{Kr}$ and $^{136}\text{Xe}/^{129}\text{Xe}$, using the same general procedures of Severinghaus and Battle (2006) with modifications. Noble gases were extracted from ~350 ml STP air sample as follows (the sample size was reduced to ~80 ml STP if only Kr isotopes were measured). An aliquot of the flask air was taken by expansion into an evacuated 178-ml glass volume, and reactive gases in the aliquot were destroyed by an established gettering procedure (Severinghaus and Battle, 2006). Dual getter ovens were employed to accommodate enough getter sheets (56 strips of 8 × 5.5 mm SAES

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ST-101 getter sheets) for the large sample size. Typical gettering time was 60 min at 900 °C, with prior activation for 10 min, followed by H₂ absorption at 300 °C for 5 min. The noble gases were then cryogenically collected in a stainless steel dip tube immersed in liquid He. The valve on the dip tube was then closed and the above procedures were repeated once more. The noble gases from the second aliquot were collected in the same sample tube. After leaving the sample tube for more than 2 h at room temperature, the sample gas (~ 3.5 ml STP noble gases) was then admitted into a mass spectrometer (Finnigan MAT 252), and dual-collector measurements were made for ⁸⁶Kr/⁸²Kr and ¹³⁶Xe/¹²⁹Xe. Typical parameters for the measurements are detailed in Table 2. The ratios were measured against our reference gas, which is artificial mixture of pure Ar, Kr, Xe and Ne with ratios similar to the atmosphere (Severinghaus and Battle, 2006). Corrections were made for all data to account for small biases due to pressure imbalance between sample and reference gases and due to the variation in Kr/Ar and Xe/Ar ratios (the so-called “pressure imbalance correction” and “chemical slope correction”, respectively; Severinghaus et al., 2003).

Atmospheric samples collected in three flasks at the pier of SIO were measured with the same procedures ($n = 7$) before the sample measurements, and their mean value was used for standardizing the firn air data. The same samples were measured ($n = 3$) after the period of the firn air measurements (15 days) to confirm insignificant drift of the reference gas during the period. Pooled standard deviations of flask replicates from the mean for that sampling depth were $\pm 0.016\text{‰}$ for ⁸⁶Kr/⁸²Kr and $\pm 0.028\text{‰}$ for ¹³⁶Xe/¹²⁹Xe (one standard deviation), which are regarded as overall uncertainties of our measurements including those from sampling, storing and analyses. The average value of three Megadunes surface samples (i.e. atmosphere) agreed with the SIO atmospheric value within uncertainty (-0.014‰ for $\delta^{86}\text{Kr}$ and -0.010‰ for $\delta^{136}\text{Xe}$). We report the Megadunes firn air isotopic ratios as the deviations from the surface values to account for possible (although small) drift of the firn air composition during the flask storage for ~ 2 yr.

4 Numerical model of firn air profiles

To better understand the firn air data, finite-difference numerical simulations based on Eq. (1) are run that incorporate gravitational and thermal fractionation, with arbitrary parameters for eddy diffusivity and empirical estimates of effective molecular diffusivity found in an iterative procedure (Severinghaus et al., 2010). The advantage of this numerical approach is that it allows a more realistic representation of the actual diffusivities at the Megadunes site than would be possible with the simple theory, and allows us to test the hypothesis that kinetic fractionation occurs at the Megadunes site. The numerical model also contains a heat transport model that simulates temperature and thus thermal fractionation.

The effective molecular diffusivities were obtained in our previous work (Severinghaus et al., 2010) by trial-and-error fits of the forward model, forced with known atmospheric histories of CO₂, methane, and halocarbon. The diffusivities of CO₂ so derived are multiplied by the ratio of free-air diffusivities of each gas to CO₂ (Table 3) to derive molecular diffusivities of each gas. Pressure and temperature effects on molecular diffusivity are treated as in Severinghaus and Battle (2006).

The model is forced at the surface with measured temperature from Automatic Weather Station data (Appendix B). The arbitrary eddy diffusivity is parameterized as an exponential in the top 24 m, following Kawamura et al. (2006), with a linear taper to zero between 24 and 34 m (to avoid an artificial “step” at the bottom of the convection):

$$\begin{aligned} D_{\text{eddy}} &= D_{\text{eddy},0} \exp\left(-\frac{z}{H}\right) & 0 \leq z \leq 24 \text{ m} \\ D_{\text{eddy}} &= D_{\text{eddy},24} \frac{34-z}{10} & 24 \leq z \leq 34 \text{ m} \\ D_{\text{eddy}} &= 0 & z \geq 34 \text{ m} \end{aligned} \quad (15)$$

The arbitrary eddy diffusivity parameters are the surface value $D_{\text{eddy},0}$ and the scale depth H , and they are taken from our previous work (Severinghaus et al., 2010). As pointed out by Kawamura et al. (2006), these parameters are nonunique; different

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combinations of the two satisfy the deep profile data (see below). The near-surface data (top 15 m) may constrain the solution further, because the amplitude of the seasonal thermal fractionation pulse (Fig. 3; Severinghaus et al., 2001) is sensitive to the value of $D_{\text{eddy},0}$. However, these near-surface data may reflect transient convective events in the previous few months prior to sampling, rather than long-term average conditions. Thus any particular value of H or $D_{\text{eddy},0}$ found by this method should be viewed as one of a range of possible values for the long-term (multi-year) average eddy diffusivity.

Furthermore, the exponential form of the eddy diffusivity is likely to be incorrect (Severinghaus et al., 2010), and a more accurate form of the eddy diffusivity would take into account permeability variations. At the present time we lack sufficient knowledge of the effective bulk permeability of the firn at the Megadunes site, due to the presence of large (multi-cm diameter) vertical cracks that greatly enhance air flow (Courville et al., 2007; Severinghaus et al., 2010). Thus further refinement of the eddy diffusivity beyond the provisional estimates given here seems at present unjustified.

Thermal fractionation may contribute to the gas data (Fig. 3; see next chapter for discussion), masking part of the effect of convection. To compute the eddy diffusivities accurately, therefore, Severinghaus et al. (2010) fitted the $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}/4$ data simultaneously, which requires introduction of an arbitrary temperature gradient into the model (gravitational settling and convective mixing alone cannot reproduce the magnitude of the offset between the argon and nitrogen data, as they have similar molecular diffusivities). The eddy and molecular diffusivity profiles so found are given in Fig. 4, along with the Péclet number for $\delta^{15}\text{N}$.

In order to produce model estimates of krypton and xenon isotopes, the thermal diffusion sensitivities of these pairs are needed. Prior to this work, these had never been measured in air, and air coefficients are different from those in pure gases due to the fact that collisions in air are mostly with $^{28}\text{N}_2$ (Grachev and Severinghaus, 2003a). For this reason we measured them by equilibrating air in a known temperature gradient in the laboratory, following established procedures (Grachev and Severinghaus, 2003b).

Details are given in Appendix C. The resulting Ω values are shown in Table 3, and the following parameterizations are obtained.

$${}^{86}\text{Kr}/{}^{82}\text{Kr} \quad \Omega = 5.05/T_K - 580/(T_K)^2 \quad \text{‰K}^{-1}$$

$${}^{136}\text{Xe}/{}^{129}\text{Xe} \quad \Omega = 11.07/T_K - 2000/(T_K)^2 \quad \text{‰K}^{-1}$$

As discussed above, the trace gas is run against ${}^{28}\text{N}_2$, so the appropriate coefficient should be the Ω value for ${}^{86}\text{Kr}/{}^{28}\text{N}_2$. For simplicity, however, this value of Ω was not computed; instead an approximation was made in which Ω for ${}^{86}\text{Kr}/{}^{82}\text{Kr}$ was assigned to the ${}^{86}\text{Kr}/{}^{28}\text{N}_2$ run, and a value of zero was assigned to the ${}^{82}\text{Kr}/{}^{28}\text{N}_2$ run, following Severinghaus et al. (2010). Because the temperature signals are small, this approximation introduced negligible error.

5 Results and discussion

5.1 Theoretical values of kinetic fractionation

Numerical integration of the Péclet number profile (Fig. 4) allows computation of the expected kinetic fractionation at the Megadunes site using the simple theory (Eqs. 12 and 13). In this exercise, we slightly modified the eddy diffusivity profile of Severinghaus et al. (2010) to made it steady in time (H and $D_{\text{eddy},0}$ are 11.5 m and $1.6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, respectively). The value obtained for the xenon-nitrogen fractionation ($\varepsilon_{136-129}$) is -0.013 ‰ . In other words, the expected value for $\delta^{136}\text{Xe}/{}^{129}\text{Xe}$ would be $7 \times 0.013 = 0.093 \text{ ‰}$ less than $7 \times \delta^{15}\text{N}$. Likewise, the krypton-nitrogen fractionation (ε_{86-82}) is -0.011 ‰ . For argon-nitrogen (ε_{40-36}) the value is much smaller, -0.002 ‰ , as expected due to the similar diffusivities of Ar and N_2 . These values apply to the depth interval between 34 and 64 m (pure “diffusive zone”), due to the fact that the eddy diffusivity is set to zero in this interval.

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These values can be directly compared with the modeled difference between xenon and nitrogen isotopes, run with thermal fractionation set to zero, which is -0.015% (-0.012 for Kr, and -0.002 for Ar). This good agreement confirms that the simple theory and numerical simulation reproduce the same essential physics by very different means and are consistent. Note that the method for finding eddy diffusivities does not make use of Kr or Xe data. Thus, the fit of model and data for Kr and Xe can now be used to independently test the hypothesis that kinetic fractionation occurs at the Megadunes site.

5.2 Megadunes isotopic data and simulation

Results of the isotopic ratios are averaged for each depth and presented versus depth, normalized by the mass difference Δm for visual comparison (Fig. 3). As expected from theory, normalized Kr and Xe isotopes are less enriched in the firn air column than N_2 and Ar isotopes, and these differences extend throughout the column indicating that it is not a temporary phenomenon (because the mixing time for air in the deep firn is order 5 yr). This finding generally confirms the theory, and is the main result of this work.

A numerical simulation aids in the interpretation of the data, and the results are also shown in Fig. 3. We first simulate the firn air isotopic profiles using the model setup employed by Severinghaus et al. (2010). In that work, the surface eddy diffusivity was $D_{\text{eddy},0} = 1.6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ at all times, and the scale depth H increased with time from a value of 5.9 m prior to 1934 to 12 m at the time of sampling, to simulate gradual deepening of convection and to adequately reproduce the data in the lock-in zone. Note that the N_2 and Ar isotopes slightly disagree (Fig. 3) probably because a small amount of thermal fractionation has affected the gases (Severinghaus et al., 2010). This thermal fractionation effect must be taken into account in model simulations or data analyses to quantify kinetic effects, because Kr and Xe are less sensitive to thermal effects than N_2 (Grew and Ibbs, 1954). The temperature gradient is assumed to be $0.0028 \text{ }^\circ\text{C m}^{-1}$

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($\sim 1^\circ\text{C}$ between top and bottom of diffusive zone) to represent the thermal effects (see Severinghaus et al., 2010 for further discussion).

Using the molecular diffusivities and thermal diffusion sensitivities for Kr and Xe (Table 3), the modeled $\delta^{86}\text{Kr}$ and $\delta^{136}\text{Xe}$ agree with the data fairly well. The average differences between data and model over three depths at 50.24, 55.17 and 60.61 m are +0.002, 0.000, -0.001 and -0.003‰ for $\delta^{15}\text{N}$, $\delta^{40}\text{Ar}$, $\delta^{86}\text{Kr}$ and $\delta^{136}\text{Xe}$, respectively, and they are within the measurement uncertainties. We limit the data-model comparison for these three depths because the shallower data may contain thermal signals from seasonal temperature variations at surface and the deeper data may contain signals of the transient change in the convective zone. We also omit the data at 57.83 m from this and following analyses because $\delta^{15}\text{N}$, $\delta^{86}\text{Kr}$ and $\delta^{136}\text{Xe}$ at this depth are largely deviate with different signs from those expected from the adjacent data, suggesting errors during sampling or measurements.

The N_2 and Ar isotopes are useful for constraining the thermal effects, because they have very similar molecular diffusivities but different thermal diffusion sensitivities. We corrected the data for thermal effects using the following equation:

$$\delta_{\text{grav}} = \delta_{\text{obs}} - [\delta^{15}\text{N}_{\text{obs}} - (\delta^{40}\text{Ar}_{\text{obs}}/4 - \varepsilon_{40-36})]/(\Omega^{15} - \Omega^{40}/4) \times \Omega \quad (16)$$

where δ_{grav} is the pure gravitational component, δ_{obs} is the measured value, ε_{40-36} is -0.002‰ (see above), $(\Omega^{15} - \Omega^{40}/4)$ is +0.0047‰ K^{-1} (Grachev and Severinghaus, 2003a, b) and Ω is thermal diffusion sensitivity (Table 3). The kinetic fractionations ε_{86-82} and $\varepsilon_{136-129}$ thus estimated are 0.010 and 0.015‰, respectively. Model-based estimates of ε_{86-82} and $\varepsilon_{136-129}$ are obtained by running the model without thermal diffusion, and they are 0.012 and 0.015‰, respectively, in excellent agreement with the data-based values. The fit of the model and data demonstrate that kinetic fractionation occurs at the Megadunes site and that they are measurable with our precision.

Near-surface isotopic values give some constraint on the convection parameters $D_{\text{eddy},0}$ (and H) for modern firn air sites, as discussed above. However, no data is available in ice core gases to directly constrain these parameters in the past firn. Thus,

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the success of an ice-core proxy of the convective zone partly depends on the insensitivity of kinetic fractionation in deep firn to different combinations of $D_{\text{eddy},0}$ and H . In order to investigate this, we ran the model with several values of $D_{\text{eddy},0}$ (0.6, 1.0, 1.6 and $4.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$), while adjusting H to match $\delta^{15}\text{N}$ in deep firn within 0.001 ‰ (following Kawamura et al., 2006). Thermal effects are included as in the standard model runs. Unlike the standard runs, the values of $D_{\text{eddy},0}$ and H are kept constant in time. The results are shown in Fig. 5 and compared with the firn air data. The values of $\delta^{15}\text{N}$ - $\delta^{86}\text{Kr}$ (0.024, 0.023, 0.022 and 0.020 ‰) and $\delta^{15}\text{N}$ - $\delta^{136}\text{Xe}$ (0.030, 0.028, 0.027 and 0.024 ‰) for different combinations are similar to each other, and thus show that the kinetic fractionation is rather insensitive to the (poorly known) exact values of $D_{\text{eddy},0}$ and H . Improved constraints on the near-surface eddy diffusivity would reduce uncertainty associated with the calibration especially for Xe. The standard value of $D_{\text{eddy},0}$ ($1.6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$) that best reproduces the near-surface gas profiles at the Megadunes site (convective zone $\sim 23 \text{ m}$) is larger than those ($4\text{--}6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$) at Dome Fuji (convective zone $\sim 9 \text{ m}$) and YM85 (convective zone $\sim 14 \text{ m}$) (Kawamura et al., 2006; Severinghaus et al., 2010). With more data from different sites, it might be possible in the future to parameterize the near-surface eddy diffusivity with climatic parameters such as accumulation rate, which can be estimated from ice cores.

6 Conclusions

First principles predict that kinetic fractionation of gas isotopes occurs in firn when convection is intense near the surface. By establishing high-precision analytical methods of isotopic ratios of the heavy noble gases Kr and Xe, we have demonstrated that kinetic fractionation does occur in Nature. Further, the observed amounts of kinetic fractionation for Kr and Xe isotopes are consistent with numerical model predictions. Different eddy diffusion parameterizations yield similar kinetic fractionations, which is encouraging for the prospects of developing proxy indicators of past convective zone thickness.

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To evaluate the hypothesis that very deep convection (up to ~ 40 m) occurred preferentially during the glacial periods, further work is needed to establish methods and conduct high-precision ice-core measurements of Kr and/or Xe isotopes, as well as modeling exercises for calibrating the gas records to the depth of convection.

Using this convection indicator, it should be possible to also correct for the effect of convection on the ice core Xe/N₂ and Kr/N₂ ratios, which are being developed as indicators of past mean ocean temperature based on solubility effects (Headly and Severinghaus, 2007; Ritz et al., 2011). Quantifying past convection will also strengthen estimates of past temperature change in Antarctic records and associated phasing of greenhouse gas variations with climate (Caillon et al., 2003; Landais et al., 2006; Parrenin et al., 2012). Finally, enigmatic intervals of near-zero gravitational fractionation, seen in several Antarctic ice core Ar and N₂ isotope records (Severinghaus et al., 2003), may be due to deep convection enabled by mechanical disruption (crevassing or cracking) of the firn. A paleo-convection proxy would allow a decisive test of this hypothesis.

Appendix A

Exact treatment of simple theory

The commonly used δ parameter is cumbersome to treat exactly, so here we use the sample-to-standard ratio of gas ratios, also known as the separation factor q :

$$q \equiv \frac{R_{\text{sample}}}{R_{\text{standard}}} = \delta/1000 + 1 \quad (\text{A1})$$

A kinetic fractionation factor α_k is defined as the ratio of an actual isotope pair x , in a convecting system, to the expected value of the isotope pair. The expected value means the value that would occur in the absence of any kinetic fractionation. Thus for the case of no kinetic fractionation, $\alpha = 1$. The separation factor q of the ¹⁵N/¹⁴N

isotope pair can be used as a close proxy for this expected value (although it will have slight fractionation):

$$\alpha_k \equiv \frac{q_x}{q_{^{15}\text{N}/^{14}\text{N}}} \quad (\text{A2})$$

For simplicity, this equation only describes an isotope pair x having a one mass-unit difference, the same as the $^{15}\text{N}/^{14}\text{N}$ isotope pair. The equation can be generalized to any mass difference by noting that gravitational fractionation increases in proportion to the mass difference Δm :

$$q_x = e^{\Delta m_x g z / RT} \quad (\text{A3})$$

For a gas pair y having a larger mass difference:

$$\frac{\ln(q_x)}{\ln(q_y)} = \frac{\Delta m_x}{\Delta m_y} \equiv R_{\Delta m} \quad (\text{A4})$$

This allows us to normalize the separation of an isotope pair y to the value for a onemass-unit difference, using the ratio of the mass differences $R_{\Delta m}$:

$$q_x = q_y^{R_{\Delta m}} \quad (\text{A5})$$

$$\alpha_y \equiv \frac{q_y^{R_{\Delta m}}}{q_{^{15}\text{N}/^{14}\text{N}}} \quad (\text{A6})$$

Or, for convenience, the log of α can be used to describe the fractionation, which we call epsilon' to distinguish it from the epsilon used above in the approximate theory:

$$\varepsilon'_y \equiv \ln \alpha_y = R_{\Delta m} \ln q_y - \ln q_{^{15}\text{N}/^{14}\text{N}} \quad (\text{A7})$$

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The exact separation in a situation where thermal diffusion is neglected would be:

$$q_y(z) = \int_0^{z'} \frac{\Delta m_y g / (RT) q_y}{1 + Pe_y(z)} dz + q(0) \quad (\text{A8})$$

The q term in the integrand makes this an ordinary differential equation (ODE). This term was neglected in the prior approximation, but can have values as large as 1.06 for the Xe-N₂ pair in a 100-m deep firn column. The value of q at the surface, $q(0)$, is 1 because of our definition of q . The predicted fractionation factor α of a gas pair y may now be written exactly as:

$$\alpha_y = \frac{\left(\int_0^{z'} \frac{\Delta m_y g / (RT) q_y}{1 + Pe_{15}(z) \frac{D_{15}}{D_y}} dz + 1 \right)^{R_{\Delta m}}}{\int_0^{z'} \frac{\Delta m_{15} g / (RT) q_{15}}{1 + Pe_{15}(z)} dz + 1} \quad (\text{A9})$$

Here the D_{15} refers to the binary molecular diffusivity of ¹⁵N¹⁴N into air, and the Pe_{15} is the ratio of the eddy diffusivity to the molecular diffusivity of ¹⁵N¹⁴N into air in the porous medium (the Péclet number). In natural systems the Péclet number is typically a complicated function of depth, and so the expression is not easily integrated, and must be numerically approximated.

In the special case where the Péclet number is constant with depth (clearly not very realistic), the ODE is easily solved:

$$q_y(z) = \exp\left(\frac{\Delta m_y g / (RT)}{1 + Pe_y} z\right) \quad (\text{A10})$$

and the expression for the fractionation simplifies to:

$$\alpha_y = \frac{\left(\exp \left(\frac{\Delta m_y g z / RT}{1 + P e_{15} \frac{D_{15}}{D_y}} \right) \right)^{R_{\Delta m}}}{\exp \left(\frac{\Delta m_{15} g z / RT}{1 + P e_{15}} \right)} = \exp \left(\frac{\Delta m_{15} g z}{RT} \left[\frac{1}{1 + P e_{15} \frac{D_{15}}{D_y}} - \frac{1}{1 + P e_{15}} \right] \right) \quad (\text{A11})$$

$$\varepsilon'_y = \ln \alpha_y = \frac{\Delta m_{15} g z}{RT} \left[\frac{1}{1 + P e_{15} \frac{D_{15}}{D_y}} - \frac{1}{1 + P e_{15}} \right] \quad (\text{A12})$$

- 5 Note the similarity of Eq. (A12), which is exact, with Eq. (14). This similarity suggests that Eq. (14) is an excellent approximation for most practical circumstances (i.e. where ε' is order 10^{-4} or less).

Appendix B

Surface temperature observations used to force model

- 10 Automatic weather station (AWS) data are available for part of the year prior to sampling at the Megadunes site, from a station deployed by M. Fahnestock and T. Scambos in November 2002 (Fig. A1; denoted MGD). This station measured firn temperatures at several depths in addition to surface temperature, wind speed, barometric pressure, and other meteorological variables. In the extreme cold of late winter 2003, the AWS
 15 failed intermittently so no data are available for some intervals. During these intervals, a composite Megadunes surface temperature record was created using AWS air temperature data from a site near South Pole (Henry AWS, 89.01° S 1.03 ° W, 2755 m elevation a.s.l.), which empirically tracked Megadunes temperature very closely in the periods in which both stations were functioning. Firn temperature at Megadunes from

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1, 2, and 3 m depth was used to verify the composite record, taking advantage of the fact that diffusive propagation of heat through firn causes characteristic time lags that increase with depth. The numerical heat diffusion model was used to predict temperature at these three depths, for comparison with the data (Fig. A1). In several intervals the model run with Henry data produced mismatches with the Megadunes data, and in these intervals the composite record was manually adjusted to produce a match with the Megadunes subsurface data. After sampling firn air, a second AWS was deployed (denoted MAC) and this data record was used to further verify the method used to create the composite record. As can be seen, the model is about 1 deg too warm at the 7 m depth of the MAC data. This might be due to the existence of a negative temperature gradient in the firn, which was not in the model (the model assumed constant mean annual temperature for the two centuries prior to 2003 CE, making the firn essentially isothermal except for a small geothermal gradient). To mimic the seasonal cycle prior to the availability of data in 2002, an idealized seasonal temperature history (Severinghaus et al., 2001) with mean annual temperature of -49°C was used to force the gas model.

Appendix C

Laboratory measurement of thermal diffusion coefficients for Kr and Xe

Standard procedures (Grachev and Severinghaus, 2003a, b) were used with the following modifications. Ambient air was sampled in a 2-L glass flask at ~ 1 atm and then doped with pure Kr and Xe so that their concentrations became ~ 15 times the atmospheric values. This was necessary to obtain sufficient Kr and Xe signals for mass spectrometer measurements using small volumes for the thermal fractionation experiments (having two chambers of ~ 26 mL each in series). The doping is not expected to influence the results because Kr and Xe concentrations are so low that they still collide dominantly with major gases (N_2 , O_2 and Ar). The air was subsampled into the two

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volumes at ~ 1 atm, and then equilibrated under large temperature difference for 4 h (Table A1), with a valve between the two chambers open to allow diffusive transport. The temperature of each volume was controlled within 0.3°C (one standard deviation). After the equilibration, the valve between the two chambers was closed to separate them. Noble gases in each chamber were extracted with the standard procedure as used for the firn air samples, and then pure Ar was added to increase the total gas amount similar to that of typical firn air measurements. The isotopic ratios $^{86}\text{Kr}/^{82}\text{Kr}$ and $^{136}\text{Xe}/^{129}\text{Xe}$ from the “cold” chamber were measured against those from the “warm” chamber. Four control runs were made with the same procedures but using isothermal water bath at room temperature (Grachev and Severinghaus, 2003a, b). Results (Table A1 and Fig. A2) were fitted with quadratic function (Grachev and Severinghaus, 2003a, b).

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**Table 1.** Molecular diffusivity ratios used in this work.

Gas	Ratio
D_{15}/D_{36}	1.0076
D_{15}/D_{40}	1.0308
D_{15}/D_{82}	1.3360
D_{15}/D_{84}	1.3401
D_{15}/D_{86}	1.3442
D_{15}/D_{129}	1.5554
D_{15}/D_{132}	1.5586
D_{15}/D_{136}	1.5628

Ratios are calculated from free-air binary diffusivities of the specified gas into air, from the method of Fuller et al., as reported in Reid et al. (1987).

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**Table 2.** Typical measurement parameters for isotopes.

Gas	Sample size (mL _{STP} air)	Resistors (10 ⁻⁹ Ω)	Ion beam intensity (V)	Integration time (s)	Changeover cycles	1σ error (%)	Δ <i>m</i> (10 ⁻³ kg mol ⁻¹)	1σ error/ Δ <i>m</i>
²⁹ N ₂ / ²⁸ N ₂	2	0.3/300	4	16	128	0.003	1	0.003
⁴⁰ Ar/ ³⁶ Ar	80	0.3/100	7	16	80	0.008	4	0.002
⁸⁶ Kr/ ⁸² Kr	80	1000/1000	0.8	16	72–144	0.016	4	0.004
¹³⁶ Xe/ ¹²⁹ Xe	350	1000/1000	1	16	72–144	0.030	7	0.004

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Table 3. Gas parameters used in numerical model runs.

Gas pair	Binary molecular diffusivity ¹ (ratio to CO ₂)	Mass difference Δm (kg mol ⁻¹)	Thermal diffusion sensitivity ² Ω (% K ⁻¹)	
			<i>a</i>	<i>b</i>
¹⁵ N/ ¹⁴ N/ ²⁸ N ₂	1.247*	–	8.656	1232 ³
⁴⁰ Ar/ ³⁶ Ar	–	–	26.08	3952 ⁴
⁸⁶ Kr/ ⁸² Kr	–	–	5.05	580 ⁵
¹³⁶ Xe/ ¹²⁹ Xe	–	–	11.07	2000 ⁵
⁴⁰ Ar-air	1.210	0.011	26.08	3952
³⁶ Ar-air	1.238	0.007	0	
⁸⁶ Kr-air	0.9277	0.057	5.05	580
⁸² Kr-air	0.9334	0.053	0	
¹³⁶ Xe-air	0.7979	0.107	11.07	2000
¹²⁹ Xe-air	0.8017	0.100	0	
CO ₂ -air	1.0000	–	–	

¹ binary molecular diffusivities are for a trace gas into air, not into ²⁸N₂, and are from the method of Fuller et al. as described by Reid et al. (1987). Air is treated for this purpose as having a mass of 0.029 and an effective molecular volume equal to the weighted average of the N₂ and O₂ volumes.

² thermal diffusion sensitivity is given by $\Omega = a/T - b/T^2$, where *T* is effective average temperature in Kelvin.

³ Grachev and Severinghaus (2003b).

⁴ Grachev and Severinghaus (2003a).

⁵ this work (Appendix C).

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**Table A1.** Thermal diffusion coefficients for Kr and Xe.

T_{cold}	T_{hot}	T_{ave}	ΔT	$\delta^{86}\text{Kr}$	Ω_{Kr}	error	$\delta^{136}\text{Xe}$	Ω_{Xe}	error
-60.4	-20.2	-41.5	40.2	0.442	0.0110	0.0006	0.426	0.0106	0.0014
-66.5	-27.1	-47.9	39.4	0.438	0.0111	0.0006	0.382	0.0097	0.0015
-70.3	-30.4	-51.6	39.9	0.432	0.0108	0.0006	0.343	0.0086	0.0015
-73.8	-45.5	-60.3	28.3	0.311	0.0110	0.0009	0.211	0.0075	0.0021
-79.4	-39.5	-60.7	39.9	0.439	0.0110	0.0006	0.341	0.0086	0.0015

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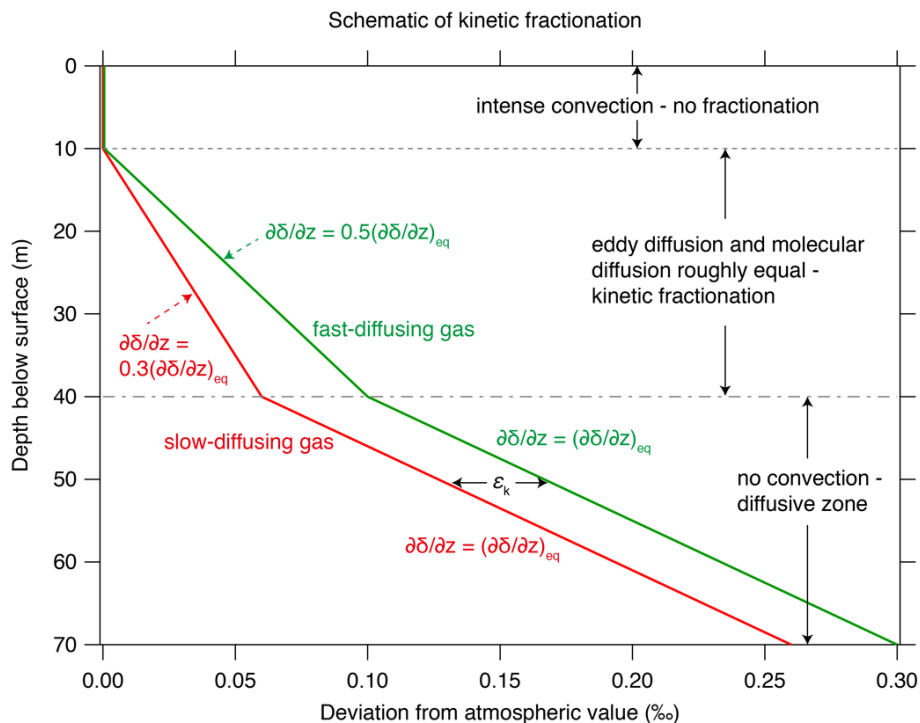


Fig. 1. Schematic illustrating the kinetic effect described here. Depth is plotted on the vertical axis, and the deviation of isotopic ratios (δ) from the atmospheric ratio is plotted on the horizontal axis. For clarity, the effects are exaggerated and an idealized convective zone is shown in which mixing is constant between 10 and 40 m and the Péclet number is 1 (for the fast-diffusing gas). Below 40 m, there is no convection and the δ values exhibit the full gravitational equilibrium slope. Note that the amount of kinetic fractionation, ϵ_k , does not increase in the diffusive zone.

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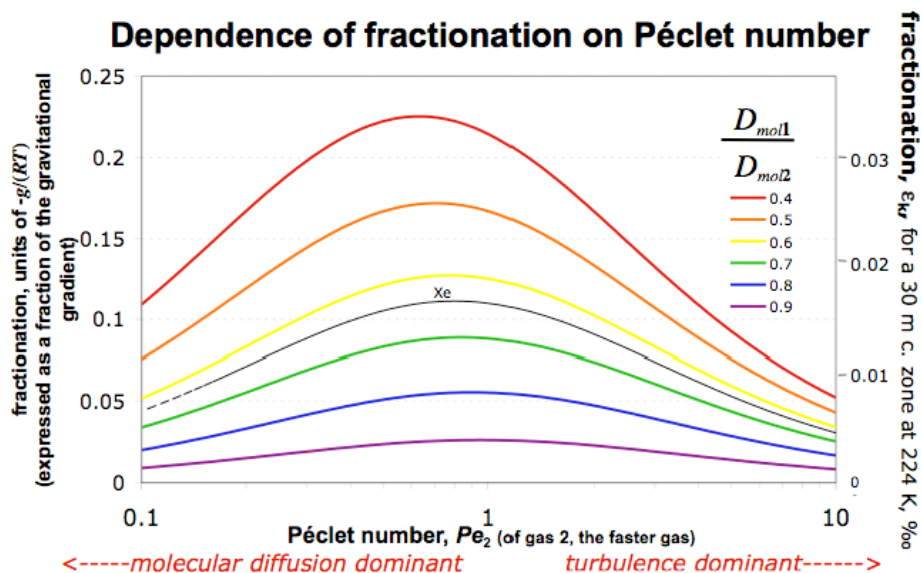


Fig. 2. Prediction of simple theory for dependence of fractionation on the Péclet number. The horizontal axis is the smaller of the two Péclet numbers, or that of the faster-diffusing gas. Different molecular diffusivity ratios are shown in different colors, as indicated by legend. For example, a diffusivity ratio of 0.65 would have a maximum fractionation equivalent to about 11 % of the equilibrium gradient. The values for ^{136}Xe - $^{28}\text{N}_2$ are shown in the dashed black line.

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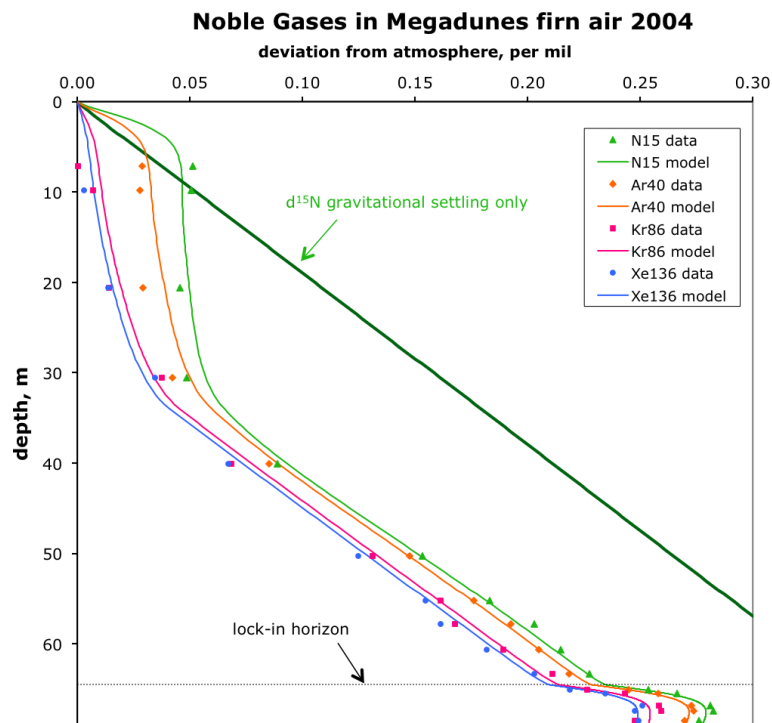


Fig. 3. Observed inert gas ratios in firn air at the Megadunes site, East Antarctica, January 2004. Values are averaged for each depth where replicate measurements are made. To facilitate comparison, δ values are normalized by dividing by the mass difference. The lock-in horizon depth of 64.5 m is found from measured CO_2 and CH_4 data. Model results are for a surface eddy diffusivity of $1.6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and scale depth H of 5.9 m in deep part of lock-in zone, increasing in upper part of lock-in zone in order to fit the data. This implies a deepening of convection through time, modeled as starting in 1920 CE and reaching the full depth of 12.2 m in 2004 CE.

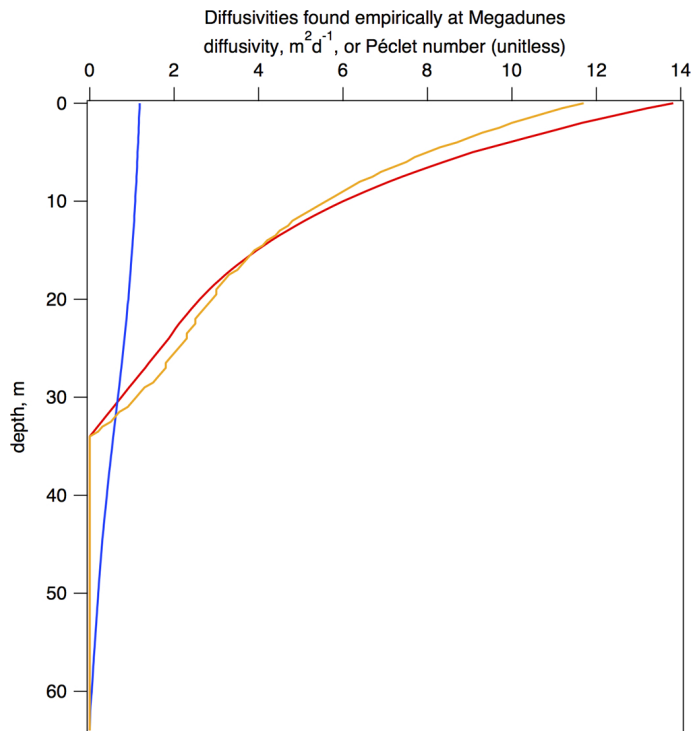


Fig. 4. Depth profiles of transport parameters found at Megadunes by fitting to data. Eddy diffusivities and molecular diffusivities are in units of $\text{m}^2 \text{day}^{-1}$ for ease of comparison with the Péclet number. Note that the crossover of the two diffusivities ($Pe = 1$) occurs around 25 m depth, and may be used as an alternative definition of the convective zone depth (Kawamura et al., 2006). Numerical integration of this Péclet number allows calculation of the kinetic fractionation via the simple theory.

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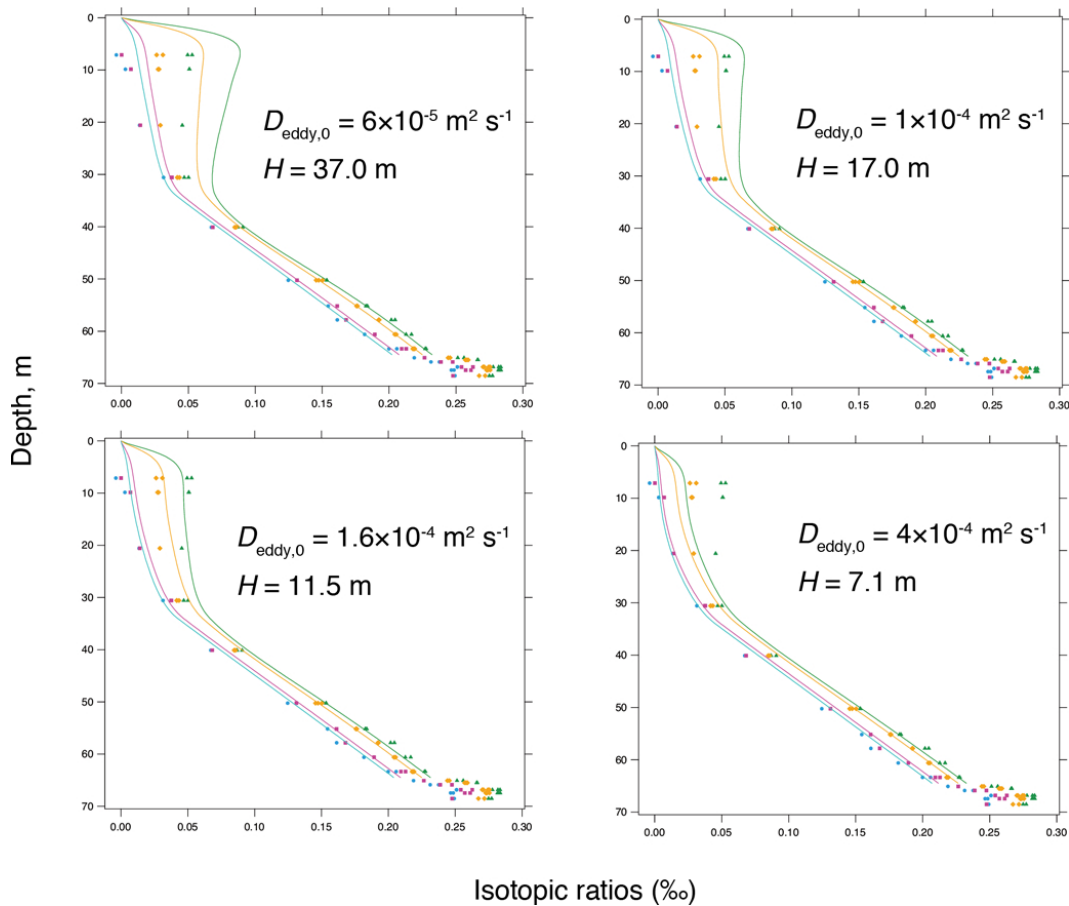


Fig. 5. Model results with different combinations of surface eddy diffusivity and scale depth.

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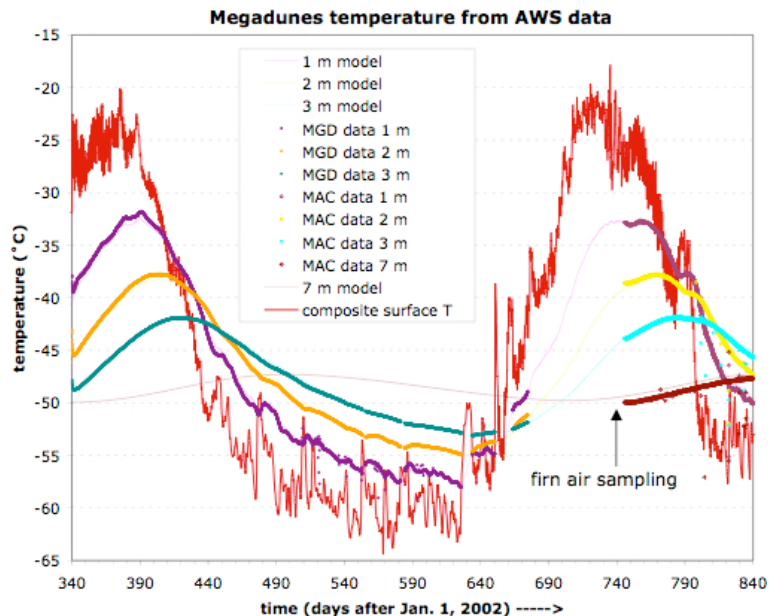


Fig. A1. Temperature observations and model results used to create composite surface temperature history for gas model forcing. Data from the first Megadunes AWS (MGD) has gaps around days 630, 660, and 680–740 due to instrument failure. Data from the Henry AWS was used to splice together a composite record, with small adjustments made to fit the subsurface temperature observations. After day 740 the MAC AWS data from Megadunes are shown.

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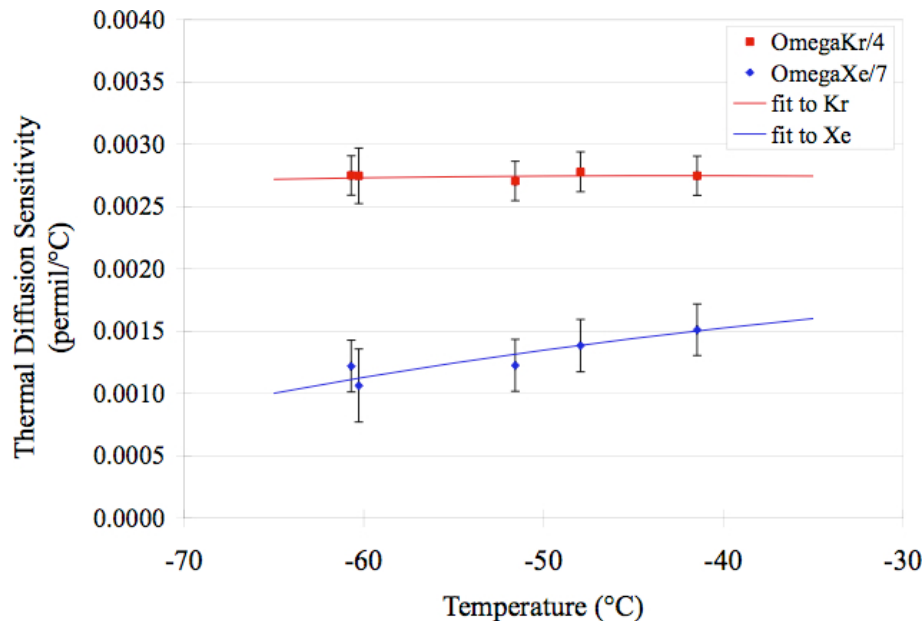


Fig. A2. Laboratory results of thermal diffusion coefficient measurements made in this study for the isotope pairs $^{86}\text{Kr}/^{82}\text{Kr}$ and $^{136}\text{Xe}/^{129}\text{Xe}$. Values are normalized by the mass difference for ease of comparison. Curve fits shown are $\Omega = 5.05/T_K - 580/(T_K)^2$ and $\Omega = 11.07/T_K - 2000/(T_K)^2$ ‰ K^{-1} for Kr and Xe, respectively (curve coefficients are actual values, not normalized).

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