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Interactive Comment

Interactive comment on "Kinetic fractionation of gases by deep air convection in polar firn" *by* K. Kawamura et al.

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article ifxetex

REPLY BEGINS HERE. Our responses are written in Bold Italic letters.

Anonymous Referee #1

The authors explain quantitatively a hitherto not described kinetic gas fractionation in the upper firn layers resulting from competing molecular and turbulent diffusion. Ice core records of this fractionation could soon become a proxy for convective mixing in firn. This work has therefore the potential to initiate solving the long existing problem of unknown importance of paleo-convection in polar firn. Reconstructing the size of past convective layers will lead to improved gas age chronologies and thus for example help constraining phase relations between greenhouse gases and temperature within and between hemispheres. Such records could also help to improve firn densification modelling during glacial conditions. The paper is well structured and the content very well presented. The experimental data appear of excellent quality. The only minus seem to be in some mathematical deductions and some slips, as pointed out below.

Specific comments.

p. 7028, eq. 8: It should be specified here that Delta_m is a normalized mass difference, i.e. dimensionless (in order to make epsilon_k dimensionless). Later, to cancel Delta_m in Eq. (10), you use Eq.(2) containing a real mass, dimension of a mass! The use of this variable should be made consistent.

We will change the $\triangle m$ in eqations 8 and 9 with $\triangle M$ representing difference in relative molecular masses of two isotopes (dimensionless).

We will modify the text accordingly.

p. 7028, l. 12: “Only when Deddy roughly equals Dmol will there be kinetic fractionation”. As there is fractionation also for Pe far away from 1 this statement is wrong (see Fig. 2). Use a more relative formulation.

We will change the text to:

“Only when D_{eddy} and D_{mol} are roughly on the same order of magnitude will there be measurable kinetic fractionation”.

p. 7028, l. 13: “Some simplification is possible by noting that the equilibrium gradient depends on Delta_m, which then cancels out". In addition it is assumed that q1=q2=1. Some short justification would be helpful for the reader.

Such explanation was indeed given just after the equation in the original manuscript. We will change the text to make the justification clearer.

"Some simplification is possible by noting that the equilibrium gradient depends on Δm, and by applying the approximation for gravitational fractionation (q1$\sim$q2$\sim$1) which is good to 10^{-3} per mil for typical isotope pairs:"

p. 7029, l. 13: Eq. (14) should be Eq. (12) (?)

We will correct it.

p. 7029, Appendix A: To derive Eq. (A12) you assume Pe to be constant with depth. If you assume the same for Eq. (12), then Eq (12) becomes identical with Eq. (A12) [modulo Delta_m, but this is due to the above mentioned dimension problem]. Then, if I didn't misunderstand, it seems that the exercise of Appendix A is in fact not to present the exact treatment, but rather the (exact) derivation of Eq. (12) under special conditions. (?)

The reviewer appears to have missed the fact that ε' in Eq. (A12) is not the same variable as the ε in Eq. (12). The former variable allows the derivation to be done exactly, whereas the latter necessitates an approximation. The main purpose of this appendix is to present the exact treatment of the simple theory under the most general conditions possible (at least until A9), so the title of the Appendix is appropriate, we believe. The reviewer is correct that Eq. A12 is nearly identical to Eq. 12 in the special case. We will point it out in the revision.

p. 7038: Insensitivity to choice of D_eddy,0 and H: If the method is to be applied as a proxy for the past convective zone, what would you suggest as meaningful parameter(s) to characterize this zone? A plot of H versus 1/(D_eddy,0)ËĘ2 shows a nearly linear relation (empirical), allowing to extrapolate to infinite D_eddy,0. Would the y-intercept be a useful value? (here about 6.6 m) - just a thought.

We thank the reviewer for this interesting suggestion. The value of 6.6 m is much too small, however. The convective zone at this site is 23 m thick (Severinghaus et al. 2010). For the future application of a paleoproxy for convective zone thickness, we will adopt the definition of convective zone thickness given in Severinghaus et al. (2010), which we believe is the most physically meaningful definition. This definition is the δ^{15}N-equivalent thickness obtained by running a model with the eddy diffusion term set to zero.

p. 7039, l. 22: "expected value". I think this term is not adequate. In the real kinetic world we do expect kinetic fractionation. So rather call it "value without kinetic fractionation". The following explanatory sentence is then not needed.

We will correct it.

p. 7042, l. 5+6: Eq. (14) => Eq. (12) (?)

We will correct it.

p. 7042, l. 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." A similar look does not infer similar results. This is not scientific. Please be more precise. (But see also above comments on Appendix A)

We will delete this sentence. (see also above reply)

ACPD

13, C4065–C4081, 2013

Interactive Comment

p. 7054, Fig. 2: In my PDF the dashed line is hardly recognized as dashed

We will correct the figure.

p. 7056, Fig. 4: Figure needs legend

We will add legends.

p. 7058, Fig. A1: What is the reason for some straying values in the temperature records?

We are not sure what the reviewer means by "straying" values. If the mismatch of data and model is what was intended, then the reason for this mismatch is likely to be the inherent limitations of a one-dimensional model in attempting to represent the 3-dimensional nature of a complex and laterally inhomogeneous snowpack. Another source of mismatch may be a small error in the depth of the thermistor. If on the other hand the reviewer intended to comment on the high frequency fluctuations in the surface temperature curve (red), then these fluctuations are real; climate in Antarctica is noisy on these timescales.

References: Bender et al, 2007 in text = Bender et al., 2006 in references?

We will correct it.

Fahnestock et al, 2002 in text = Fahnestock et al., 2000 in references?

We will correct it.

No citation in text found for:

Battle et al. 2011

ACPD

13, C4065–C4081, 2013

We will delete it.

Fabre et al. 2000

We will delete it.

Severinghaus and Brook, 1999

We will delete it.

Reference for Grew and Ibbs, 1954 is missing.

We will correct it.

ACPD

13, C4065–C4081, 2013

Interactive Comment

Anonymous Referee #2

This article presents an attempt to develop a proxy indicator of past convection in firn.

This manuscript in fact does not attempt to develop a proxy indicator of past convection in firn. It is rather the first step towards such a development, which is to identify the relevant physical process in a modern setting (kinetic fractionation). We only mention the plans for future proxy development to motivate the present study. The title of the manuscript succinctly communicates these facts, we believe (note that we put nothing in the title about proxies or past convection). The reviewer has apparently misunderstood our paper.

This issue is related to the definition of the difference in age between gases and the surrounding ice, it is thus of wide interest to the ice core, paleo environment and atmospheric sciences community. It likely involves an important experimental development to be able to precisely measure differences between isotopic ratios of several gases of about 0.03 ‰The results on Fig. 5 show that different values of convective transport intensity and depth in firn lead to the same model results below 40 meters depth. As ice core data only trace isotopic ratios in deep firn (where most of the air is trapped), I am not optimistic about the prospect of using Krypton and Xenon isotopes as indicators of paleo convection. The key missing element is a direct link between the measured _ values of isotopic tracers and convective zone thickness.

The reviewer perhaps misunderstands the Fig. 5 results and their implications. All of the results shown in Fig. 5 have vigorous convection, and all result in a reduced enrichment of isotopic ratios in the deep firn (which ultimately governs the contents of the ice core). The point of Fig. 5 is instead that the details of the two arbitrary parameters used to represent convection in the model (eddy

ACPD

13, C4065–C4081, 2013

diffusivity surface value and scale depth) do not matter to the signal of interest, the kinetic fractionation. It is this insensitivity of the modeled epsilon to exact eddy diffusivity profiles (chosen to match deep-firn d15N) that suggests the usefulness of Kr and Xe isotopes as paleo-convective indicators where the exact eddy diffusivity profile is unknown. Of course, this paleo-indicator will not be able to give us values for the two arbitrary parameters. Instead, it will give a lower bound on the thickness of the convective zone, and will thus be useful in identifying the presence of past convection. This thickness is defined not as the (arbitrary) scale depth of the eddy diffusivity (perhaps the source of the reviewer's confusion), but rather this thickness is the equivalent depth implied by the reduction in deep-firn d15N due to convection (Sowers et al., 1992; Severinghaus et al., 2010). We will, of course, investigate further the link between epsilon and convective zone for different surface conditions in future studies. As we wrote in the original manuscript, the investigation should include efforts to constrain near-surface eddy diffusivity under various climatic conditions, which is beyond the scope of the current manuscript.

Nevertheless, the initial idea of using inert gases having different physical properties (molecular and thermal diffusion coefficients in air) to better constrain past convection in firn is excellent and although deceiving, the results deserve to be published in the scope of Atmospheric Chemistry and Physics and its special issue on firn air.

General comments

The presentation of the theory (Section 2 and Appendix A) can be made clearer and shorter to be easier to understand for a wider audience than scientists trained in firn physics. Equation (12) can be easily derived from Equation (4) in Severinghaus et al. (2010) and two simple definitions. The basis of the simple theory is already presented

ACPD
13, C4065–C4081, 2013

Interactive Comment

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Interactive Discussion

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(more clearly in terms of underlying assumptions) in Severinghaus et al. (2010), thus Section 2 can be shortened and Appendix A suppressed. The first sentence of the abstract suggests that a new physical process in firn has been discovered whereas the unmodified model of Severinghaus et al. (2010) can simulate it. This is needlessly confusing.

It is true that this form of kinetic fractionation has been unrecognized until now, so we think the abstract is appropriate as it is. We will explain in the revised manuscript that the Severinghaus et al. (2010) model can simulate it by applying it for different gases, and the reasons why it has been unrecognized. The main reasons are that 1) gas transport has been considered mostly using nitrogen and argon (having similar diffusivities), 2) that there have been no techniques to precisely measure Kr and Xe isotopes, and 3) that most firn columns have too small a convective zone to validate the theory. We will be able to skip a few equations in Section 2 as suggested by the reviewer, but we think Appendix A should be kept because it is not described in previous publications.

Section 5.1: it should be stated that the simple theory as applied here (integrating Pe(z) from the Severinghaus et al. (2010) model) is not applicable to ice core data in paleo-climatic conditions as the vertical profile of Pe(z) is unknown.

This section is dedicated to the comparison between theoretical and numerical estimates for firn-air kinetic fractionation, as the Section title indicates. Therefore, it is not appropriate to discuss ice-core applications here. The discussion of ice-core applications is given in the latter part of section 5.2.

For the calculation in Section 5.1, it is explained that the Severinghaus et al. (2010) model is run with thermal fractionation set to zero. I presume that in Figures 3 and 5, _ - depth lines in the diffusive zone for the four gases are not parallel due to the non null thermal fractionation. This effect is significant and has important consequences for ice

ACPD
13, C4065–C4081, 2013

core applications, it should be discussed.

Note that the convection signals (kinetic fractionation) on isotopes of different gases are only discussed for deep firn data. The reviewer is correct that the slopes are different for different gases in the diffusive zones in Figs. 3 and 5 due to the thermal signal. However, it would be irrelevant to the estimation of past convective zones using ice core data in future studies, as long as the thermal signal in the data is appropriately considered and corrected using N2 and Ar isotopes (see original manuscript). We will spell out in the revised manuscript that the model curves for different gases in Fig. 3 and 5 have different slopes in the diffusive zone, and thus it is important to correct the thermal signal for ice-core applications (so one needs at least three gas species to characterize the convective zone, diffusive zone and thermal gradient in firn from the gas data). We will also point out that N_2-Kr and N_2-Xe isotope differences in the last part of section 5.2 are larger than the values of epsilon deduced in section 5.1 because of the thermal signal. In a first-order approximation where epsilon and convective zone thickness are linearly related, the spread of isotopic differences (mean +/- 0.002 and 0.003 per mil for N_2-Kr and N_2-Xe, respectively) from the uncertainty in exact shape of the eddy diffusivity profile would mean the uncertainty of our constraint on convective zone thickness is on the order of 4 m. Since we are aiming at detecting a $\sim$40-m convective zone (here Megadunes has only $\sim$23-m), this magnitude of uncertainty would be acceptable. A more significant source of uncertainty is the measurement precision of the Kr and Xe isotopes (currently 0.004 per mil when normalized), giving uncertainty in convective zone thickness on the order of 20 % for a 40-m convective zone as one standard deviation if we use single ice-core data. We will need to measure and average several data points from similar depth (age) to decrease the uncertainty. We will also add this discussion to the revision.

ACPD

13, C4065–C4081, 2013

Section 5.2: I disagree with the idea that the insensitivity of kinetic fractionation in deep firn to upper firn convection intensity and scale height (Deddy,0 and H) indicates that the measured isotopic ratios are efficient ice core proxies of the convective zone (p7038 l1-2). Which convection related physical parameter is traced by the data ?

Formulating the proxy indicator problem in the simplest way (ignoring the non steady state issue in the lock-in zone), the main question is: how can the diffusive zone and convective zone thicknesses (as defined for gas dating purposes) at the Megadunes site be reconstructed from isotopic measurements at the lock-in horizon ? This question is not answered or discussed.

Defining and developing the paleo proxy is beyond the scope of the present manuscript, as discussed above, so we give the explanation below only for this response. To deduce diffusive zone and convective zone thicknesses from the firn air or ice-core data, one needs the isotopic data of N2 and Ar and at least one of Kr or Xe, and calculate ε_{86-82} ***and/or*** $\varepsilon_{136-129}$ ***(in this study they are 0.010 and 0.015 per mil, respectively) taking advantage of*** $\delta^{15}N$ ***and*** $\delta^{40}Ar$***/4, which have very similar diffusivities as described in the original manuscript (see paragraph containing eq. 16). Since they are close to the model estimation, one can relate epsilon and convective zone thickness from the model runs under different convection strength. Uncertainty is discussed above. Diffusive zone can be estimated from*** $\delta^{15}N_{grav}$ ***as commonly done in the literature.***

The abstract and conclusion should provide a more precise statement about the feasibility of constraining the convective zone from ice core data.

We will add that there is the feasibility to identify a $\sim$***30 to 40-m convective zone which is required for the intense-glacial-convection hypothesis. We will avoid making a precise statement of uncertainty for ice-core applications, as it is strongly dependent on the actual ice-core measurement precision and number***

ACPD
13, C4065–C4081, 2013

of data points to be measured within a climatic stage.

Specific comments

Page 7023 line 25 - page 7024 line 4: the stagnant zone concept seems important for the authors (repeated three times) but is not mentioned in the references cited (Schwander et al., 1989; Sowers et al., 1989), an appropriate reference should be provided.

The stagnant portion of firn is known as the "diffusive column" (Sowers et al., 1992) as described in the original text. This usage is common in the firn air literature, and we thus do not believe that additional references are necessary here.

Page 7024 lines 4-15: in relation with Section 5.2, it should be mentioned that convection can be formulated in different ways in physical models. For example, references to Schwander (1989) and Powers et al. (1985), cited in the article, could be used in this aim.

We will mention this in the revision and cite the paper by Buizert et al. (2012, the same ACP special issue) which compares most firn air transport models with different treatments of the convective zone.

Page 7024 lines 22-25: a third hypothesis involving the impurity content of ice has been made recently and should be mentioned (Hörhold et al., 2012; Capron et al., 2013).

We will mention this and cite the paper as suggested.

Page 7026 Equation 4: the middle and right terms of Eq. 4 imply that a downward velocity term due to bubble trapping has to balance convection. This is not true. The middle term should be omitted and the text should explain that the Péclet number can be defined in different ways depending on the dominant physical processes at work (and the way they are formulated in models). At the Megadunes site, the near zero accumulation rate implies a near-zero downward velocity and bubble trapping, whereas the effect of convection is strong in the upper firn. The role of seasonally varying thermal convection on disequilibrium should be discussed.

We thank the reviewer for pointing out that we have created confusion by the use of the variable w for both downward flow due to bubble trapping and convective flow. This will be changed in the revision; we replace w in Equation 4 with u for the speed of the convective air flow driven by wind pumping.

Page 7028 Equations 8 and 9: I see only equilibrium terms in these equations aiming at representing disequilibrium. This is needlessly confusing.

The reviewer has apparently missed the eddy diffusivity, which is not an equilibrium term.

Page 7029 lines 3-5 and Table 1: This seemingly new presentation of molecular diffusion coefficient ratios raises a strong uncertainty issue: the precision of molecular diffusion coefficients is of the order of the percent (see e.g. references in Buizert et al. 2012, supplementary Table 4), whereas the ratio of diffusion coefficients between two isotopes of the same gas has to be known more precisely. Thus the presentation of diffusion coefficient ratios between isotopes of different gases is needlessly confusing.

The ratio of diffusion coefficients of two isotopes of the same gas is in fact given very precisely by the method used here, that of Fuller et al. as described in Reid et al. 1987. The reasons for presenting the ratios relative to nitrogen are explained in the text clearly, we believe (most collisions involving a trace gas are

ACPD
13, C4065–C4081, 2013

Interactive Comment

with nitrogen). Nonetheless, the underlying precise isotope coefficient ratios are preserved by this presentation. The exact ratios of coefficients of different gases do not need to be known very well because the effects of these collisions with nitrogen are second order. At present the major source of uncertainty is by far the measurement error .

The consistency between the diffusion coefficients used here and those in Buizert et al. (2012), supplementary Table 5 and its impact on the main results should be explained.

The present manuscript is intended to be a companion paper to Severinghaus et al. 2010, and therefore uses the methodology of that paper to calculate diffusion coefficients. There are subtle differences with the Buizert et al. (2012) paper's coefficients that do not materially affect the outcomes in any significant way.

Page 7030 lines 11-12: the precision of the approximation cannot be estimated before the comparison with a model involving less approximations is made (Section 5). The required level of precision for _k is rather <0.01 ‰1 ‰

We will add "(see Chapter 5)" to the text. The approximation appeared to be valid at the level of 0.002 per mil as examined later in the original text (section 5.1), so we will also correct the number.

Page 7032 lines 13-15: the magnitude of the pressure imbalance and chemical slope corrections should be provided.

The both corrections are typically in the range of 10-20 per mil. We will add the information to the revised manuscript.

Page 7033: the word "arbitrary" is used three times to characterize the eddy diffusivity parametrisation. As convection is the main topic of the article, this is confusing and

ACPD
13, C4065–C4081, 2013

should be reformulated.

The surface eddy diffusivity and scale depth are indeed arbitrary and we do not wish to obscure this fact in any way. These parameters are tuned to fit data. They thus contain useful information after the tuning procedure. It is common in physics to describe tuneable parameters as arbitrary, to highlight the difference from constants of Nature. As the journal is named Atmospheric Chemistry and Physics, it seems justified to use this wording.

Page 7037 line 24: replace “data-based values” with “simple theory values”

No. These values are estimated from the data (line 21 of the same page).

Page 7039 lines 5-15: these lines contain introducing rather than concluding statements.

These lines presents future, potential applications of the convective zone indicator if it is successfully developed, in addition to the chief motivation to solve the long-standing problem of deep convection in glacial periods. We thus do not wish to move it to introduction as it may distract readers' attention from the main problem.

Technical corrections

Page 7023 line 25: Schwander et al., 1989 - suppress "et al."

We will correct it.

Page 7027 line 12: explain what is meant by nearly in “eddy diffusivity is nearly the same for all gases”.

We will delete "nearly".

Page 7030 line 10: "Many approximations are made above". The main approximations should be clearly summarized.

Approximations include Eq. (2), the assumption of arithmetic additivity of epsilon in Eq. (8), and the neglect of the q term in Eq. (11). We will add this to the revised manuscript.

Table 1: Fuller et al. (year?) and Reid et al. (1987) are not provided in reference list.

Gas names should be really specified in the table.

We will add the reference and gas names.

Table A1: what is meant by Tave should be explained. Is it the classical arithmetic mean or the more complex mean in e.g. Eq. 4 of Grachev and Severinghaus (2003a) ?

We will explain that Tave here refers to Grachev and Severinghaus definition.

Caption of Figure 4 should define which colour shows which parameter.

We will add information.

Figure A1: thin and thick lines are not clearly defined. Dots are hard to see.

We will correct the figure.

Reference not cited in the reviewed article

ACPD

13, C4065–C4081, 2013

Hörhold et al., Earth and Planetary Science Letters 325-326, p93-99, 2012.

We will delete it.

Capron et al., Climate of the Past, 9, p983-999, 2013.

We will delete it.

ACPD

13, C4065–C4081, 2013

Interactive Comment