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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Post bubble-closeoff fractionation of gases in polar firn and ice cores: effects of accumulation rate on permeation through overloading pressure" *by* T. Kobashi et al.

Anonymous Referee #1

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In this paper, Kobashi et al. tackle the difficult question: What controls the Ar/N2 and O2/N2 ratios in ice cores? Ar/N2 is a particularly useful tool for investigation because the ratio is essentially constant in the atmosphere (on the relevant timescales and with attainable precision).

The authors take two approaches: Using Holocene data from GISP2 and GRIP, they look for correlations between variations in Ar/N2 and temperature and/or accumulation rate. They also develop a model of size-dependent permeation that they apply to a) post-coring gas evasion and b) gas losses during bubble formation and air enclosure.

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Overall, I find this work is interesting, important, thoughtfully conceived and carefully executed. I have few suggestions or comments on the scientific content of the manuscript and none are major. However, primarily because the authors are not writing in their native languages, there is a definite need for correction and clarification in the writing. I have been extremely detailed in my comments below because these apparently minor grammatical errors and ambiguities made it much harder for me to absorb the substance of the work upon first reading.

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First, my more substantive questions/comments:

Overall: When considering post-coring artifacts, you should acknowledge the possibility that, not only does there appear to be gas leaking out of recently closed pores, but there is also the possibility of open bubbles closing off and trapping ambient air. Compelling evidence of this was seen by Aydin et al (Atmos. Chem. Phys., 10, 5135–5144, 2010). Have you considered this in your analysis?

P15714 Lines 25-26: When you say "between the bubbles and the atmosphere", you're limiting yourself to either post-coring losses or permeation between very recently closed bubbles and the open porosity. However, you suggest the same process is responsible for smoothing records deep in ice cores. Please clarify.

P15716 Line 13 (and later in the manuscript): This phrase "a firn densification-heat diffusion model" doesn't really describe these models correctly. They are primarily models of gas transport, influenced by firn densification and thermal gradients (due to heat diffusing through the system). Line 20: How did you arrive at the number 21? You should explain where it comes from.

P15718 First paragraph: It seems to me that you're claiming that Ar/N2 rises in the brittle ice zone because N2 is reluctant to go into clathrates so it escapes and Ar is left behind. Fair enough. But to where does the N2 escape? Presumably this is an

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example of post-coring loss so the N2 just enters the atmosphere at large. Also, if this picture is correct, shouldn't the problem persist at all depths below the onset of clathrates? Or is it only the fractures that allow the N2 to escape? Please clarify!

P15724 Line 10: Is the diffusion coefficient for Argon from experiment? If so, cite the source. If not, change the sentence so it clearly states that the Argon value comes from the dynamics simulation too.

P15727 Line 1 The value of 0.375MPa seems arbitrary. How did you choose this value? Line 6 You say earlier that Vostok only has 0.3% of the air in microbubbles, yet you are exploring the range 1% -3%. Why? You should explain this choice.

Figure 9 is essentially incomprehensible. It is too small to read without 300% enlargement, but more importantly, the content is inadequately explained. For example, despite the statement on line 19, it's not at all clear that Fig. 9a is showing us that 99% of the air is trapped as normal bubbles near the lock-in zone. Is this statement based on output from the model (somehow derived from the multitude of curves shown in Fig 9a)? Or does Fig. 9a show (somehow) that the model successfully reproduces a set of independent observations? The other panels are similarly cryptic: Which are the 3 bottom layers in 9b and 9c and why don't they show the same shape as the three bottom layers in 9a? Why does dAr/N2 in 9e look so different from every layer in 9d? I'm sure this is a useful and potentially informative figure, but in its present form, it's merely confusing.

P15728 Lines 9-11: I can't really assess the statement beginning "The difference. . ." because I can't fully understand Fig. 9. However, the idea microbubbles would not be subject to the same compression and volume change that normal bubbles experience certainly begs for a sentence or two of explanation. Perhaps you mentioned this earlier in the paper and I missed it.

P15729 This paragraph lays out an important result from this work. According to the model presented here, the behavior of Ar/N2 in microbubbles under cold conditions is

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the same as was anticipated by Severinghaus and Battle (2006). That is to say, longer bubble residence time in the firn leads to greater permeation and fractionation. On the other hand, the normal bubbles don't show much of any effect. Furthermore, higher accumulation rate leads to the more fractionation in the microbubbles (presumably again due to the longer residence time), but to less fractionation in the normal bubbles. Why is this? The fact that the model reproduces the results of the multiple linear regression doesn't do much good unless we can learn from the model which processes are causing this counterintuitive behavior. Figure 8c: Do you really mean to plot air content change? I would think you're actually plotting the percentage of original air remaining, but I'm not certain. As it stands I can't make sense of a 99% air content change that then falls with depth.

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Second, a long list of grammatical corrections/clarifications.

P15713 Line 8: change to "we find" Line 10-11 should read "...the precise records spanning the last 4000 years show temperature and accumulation rate have nearly equal effects..." Line 14: put the quotes around "microbubbles" only (not the parenthetical statement). Lines 16-17 should read "...the accumulation rate due to changes in overloading pressure, as seen in the observations. Colder (warmer) temperatures in the firn induce more (less) depletion in..." Lines 25 and following: The studies cited are not really firn studies. Instead, they are about much longer ice-core histories. My guess is that you really are trying to say is "...trapped in the firn layer (unconsolidated snow; ~70m at the Greenland Summit) and preserved in the underlying ice sheets provide precious..."

P15714 Line 10 should read "we investigate a third process" Line 16 should read "the process continues during/after coring" Line 20 remove the word "rapid" Lines 21-22 should read "Depletion of the total air content by..." Line 25 should read "and is induced"

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P15715 Line 5: Should read “Variations in dO2/N2 on orbital timescales closely follow. . .” Lines 5-16: This section is a bit confusing in its order. In the previous paragraph (on p15714), you should explicitly state the situations in which this single process operates: As bubbles close at the firn-ice transition, deep within the ice sheet, after coring. Then address these in the same order on p15715.

Lines 17-19 should read “. . .using records from GISP2 for the entire Holocene and NGRIP for the past 2100 years, we investigate the multi-decadal to centennial variability of Ar/N2, as well as gas loss processes during storage.” Line 22: should read “over the relevant period” Line 25: remove the comma after “data” Line 29: should read “drawing conclusions”

P15716 Line 2: should read “measured in the” Line 10: should read “obtain high analytic precision (Kobashi. . .” Line 14: “uncertainties” in what are ∼10%? Gas ages? Or the gas-age/ice-age difference? Please clarify. Line 15 -20 should read “To investigate the Ar/N2 fractionation, we used. . . . . .Gkinis et al., 2014). The annual resolution. . . . . .with 21-year running means. . .” Line 22-23: Should read “We also used new dAr/N2 data for the past 2100 years from the NGRIP ice core, providing a good . . .”

P15717 Line 10 should read “The coefficient 11 arises because the. . .” Lines 13-14 should read “. . .temperature sentivities of d15N and dAr/N2 are slightly. . .” Line 16 Remove the whole sentence beginning “Therefore, these corrections. . .” Line 17-18 should read “attributed only to gas loss. Line 18-20: The sentence beginning “It is also noted. . .” is very unclear to me. You appear to say above that GISP2 only had data with mass 29. Last paragraph: Where does the number “21” come from? It appears to be a completely arbitrary choice, but I imagine it’s not.

P15718 Line 8 should read “. . .preferential leakage of nitrogen, and thus argon. . .” Line 19 should read “. . .variations. We found a significant. . .” Lines 20-21 should read “. . .accumulation rate for the past 6000 years, a time interval in which the abnormal dAr/N2. . .”

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P15719 Line 2 should read "...variations because precise..." Line 9: Shouldn't the last r value (0.26) actually be negative? Line 10 should read "with a 38-year lag" Line 11: should read "We note that the surface..." Line 12 should read "rate have a negative..."

P15720 Line 1: It would be very nice to see a figure of the centennial variations in model and data. Also, how are centennial variations determined? Is it a 100-year running mean or a spline or some other technique? Lines 8-9 should read "do not have Ar-isotope based temperature information before 4000 year BP. " Line 10 should read "...contains substantial noise" Line 21 Remove the comma after "rate" Line 22 should read "with the d18O_ice-based temperature proxy and... Lines 24-25 should read "...discussed earlier. Except for the time interval around ~7000 BP, the model and observed dAr/N2 exhibit rather constant..."

P15721 Line 13 should read "...better precision on dAr/N2 than the one used for GISP2" Line 19 should read "...detrending) and were uncorrelated in the shallower part." Line 22 should read "dAr/N2 data from the depth range 64.6-80m exhibit some..."

P15722 Line 1 should read "...of contamination, and" Line 3 should read "uncertainties using ice samples" and "...we interpret the" Line 4: In what sense do things "decrease"? With greater depth? As you approach the surface? As written, it's not clear. Line 5 should read "Fig 6). Based on isotope mass balance..." Line 7 should read "a clue to the processes" Lines 9-10 should read "and application to post-coring fractionation." Line 11 should read "after coring" Line 13 should read "depletions of" Line 18 (and subsequent occurrences) should have "species m" instead of "m molecule". Line 25 ibid.

P15723 Line 2 should read "are mole fractions of species m" Line 8 should read "during storage" Line 9 should read "14 years after coring, but with different temperature histories. GISP2..." Line 10 should read "After shipment," Line 13 should read "2015). The ice samples were then cut..." Line 24 Remove the comma before "and". Also,

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latter part should read "...to 1MPa; a normal bubble..."

P15724 Line 4 should read "storage often have" Line 6 should read "surface areas imply the" Line 27 should read "respectively. We note that"

P15725 Line 1 should read "that our estimated" Line 2 should read "several times larger than" Line 3 should read "introduced noise into" Line 9 should read "introduce more noise if the gas loss is greater" Lines 11-12 should read "2000): normal bubbles and so-called microbubbles" Line 16 should read "depth. Most of the air in cores is captured as normal bubbles"

P15726 Line 6 should read "to the total air content" Line 8 should read "can approach ice load pressure at the bubble closeoff" Line 20 remove the word "concerned" Lines 21-22 should read "With I increasing in one-year steps, the microbubbles" Line 23 remove the words "a concerned" Line 25 should read "starts increasing"

P15727 Line 16 should read "which corresponds to 5%" Line 27 should read "how much bubble volume is generated"

P15728 Line 4 should read "newly trapped air" Line 20 should read "we assume the gas" Line 23 should read "O2/N2) within the bubbles decreases with" Lines 24-25 should read "However, the amount of air contained in these bubbles is so small that the influence on the total"

P15729 Fig. 10: Change the color scheme so that cold temperatures are blue and warmer temperatures are red. In the paragraph beginning "The permeation..." please removal all of the parenthetical terms in the more/less, higher/lower, warmer/colder pairings. They're just distracting, and the converse of each term is clear.

P15730 Line 12 should read "may indicate even larger" Line 25 should read "GISP2. We found that" Line 28 should read "with an 11-year lag"

P15731 Line 3 remove the word "time" Line 18 should read "2002). Our work demonstrates that the"

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P15732 Line 5 should read “there is some evidence of” Line 7 should read “2011). In particular, poor quality” Lines 12-13 should read “appear to have small or non-existent effects on isotopes (Kobashi” Line 19 should read “Another sign of isotope fractionation” Line 20 should read “enrichment in ice cores” Line 22 should read “caused by processes” Line 23 should read “evidence has been found in firn air studies” Line 25 should read “it should be correlated with” Lines 27-28 should read “2015), dKr/Ar (Severinghaus et al., 2003), or a constant value (Orsi, 2013; Kobashi et al., 2015). All these methods of correction generate”

P15733 Line 9 should read “stronger constraints” Line 11 should read “that ice core” Line 15 should read “use of large ice samples” Line 16 should read “the noise in” Line 21 should read “of permeation” Line 26 should read “after bubble closeoff” Line 27 should read “especially in ice cores. In this study, we investigated gas”

P15734 Line 25 should read “surface temperature. It is also” Figure 2 caption: Was the spline really set to a 31 year cut-off period, or a 21 year? Similarly for the length of the RMs. Figure 11 caption: The 4th line should read “Settings for”

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