Review of Bereiter et al… "Oldest Ice core gas signal diffusion…"

This is an excellent paper and should be published with only minor revisions. It is of high relevance to the IPICS goal of finding 1.5 Ma ice and a record of gases and climate over the time since then. It is of wide interest to the community and meshes well with the theme of the IPICS volume.

The one substantive comment I have concerns the 2-order-of magnitude disagreement on permeabilities. I wonder if this is the result of a confusion between two different ways of treating multiphase diffusion. Ice is a multi phase material, containing both gas inclusions and an ice matrix. As such, modeling the transport of gases through the ice is fundamentally a two-phase modeling problem. The unique thing about the ice phase is that it is the only phase in which transport can significantly occur. So the clathrates or inclusions must be viewed as non-transporting reservoirs, which nonetheless are measured in a bulk ice core gas measurement (it is impractical at present to measure the dissolved gas fraction separately).

Importantly, the Ikeda-Fukazawa results did not apply to this two-phase medium. They were for diffusion in the ice only. So modeling the two-phase medium using only their coefficients would be inappropriate. As an example, consider the following thought experiment:

A series of well-stirred 1-liter buckets containing water are connected by small pipes 1 square cm in cross sectional area and 10 cm long. The pipes have stagnant water so that transport within them is only by diffusion. An experimenter wishes to calculate the expected rate of bulk transport of salt by diffusion, through the entire series. To do this he uses the literature value for salt diffusion in water. His calculated value turns out to be more than two orders of magnitude larger than the observed value for the actual experiment. Why? Because the buckets are acting as reservoirs, and the salt that is being transported by diffusion in the pipes must fill the reservoirs before the concentration gradient can be propagated to the next pipe, and of course the gradient is what drives the transport, so the total transport is much less than would occur in a simple pipe of constant cross section.

At steady state, with a constant gradient through the series of buckets, he finds that his calculation does a good job, though. So Fick's first law is obeyed, it seems, in that the flux of salt is indeed given by the diffusivity of salt in water. Actually the salt seems to be transported slightly faster than predicted (because the stirring in the buckets helps to short-circuit that part of the linear path).

So the problem comes in the model architecture. The bucket volume must be included as a term that multiplies the time derivative, because the time rate of change of salt concentration for a given salt flux in a transient is much, much slower than would be the case in a simple pipe of constant cross section. To a good approximation this reservoir volume effect can be quantified by simply multiplying

the derivative by the ratio of the volume of the bucket to the volume of the adjoining pipe, or about 1000 cc/10 cc = 100.

To extend the thought experiment to the ice core situation, the abundance of gas molecules in the clathrate phase can be about two orders of magnitude more than the abundance of gas molecules in the dissolved phase in the ice. Yet diffusive transport of gas can only occur through the dissolved gas phase in the ice, because the clathrates are so small compared to the ice. So the Ikeda-Fukazawa diffusivites should be used in conjunction with this clathrate reservoir term. If the spatial derivative of the reservoir term can be assumed zero (a reasonable assumption), then the reservoir term can be incorporated into the spatial derivative as a constant that is dividing the Ikeda diffusivity. So the Ikeda diffusivity should be divided by a factor of about 100 (or more precisely, the ratio of gas molecules in clathrates to gas molecules dissolved). Of course, this ratio decreases as the dissociation pressure increases, so this will have to be done taking into account clathrate dissociation pressure and any temperature sensitivity it might have.

If this is indeed what is going on, then the authors should modify their model accordingly. If they have already taken this into account then my apologies are extended.

Minor comments:

Figure 1 shows Oldest Ice Core model results extending to a depth of 3100 m. Yet the text states that the depth of the Oldest Ice scenario was restricted to 2700 m (line 175). Please resolve this discrepancy.

Line 149 "In the case of the Vostok ice parameters…" could be rephrased as "In the case of Vostok, corresponding values for all ice parameters are not found in the literature, and if so, they are…."

Line 182 "The used experimental approaches…" could be "The experimental approaches that were used do not permit…."

Line 202 "parameters are based on a model…"

Line 256 "… is run with an O2/N2…"

Line 294 "…might enable us to derive reliable temperature sensitivities…"

Line 313 "…for most possible combinations…"

Line 315 I suggest rewording this sentence to "One simulation has been run for most possible combinations of the….. …resulting in 15 runs in total."

Line 336 It might be possible to identify dampening by comparing the Asian stalagmite d18O records with the oxygen-18 of O2 in the EDC core. The stalagmites should not be subject to dampening with time, so their frequency content can be used as a surrogate for the frequency content of the actual forcing on O-18 of air. (see Severinghaus et al. 2009 Science for the observed relationship between O-18 of air and the O-18 of the stalagmites) Stalagmite records now exist all the way back to 800 ka.

Line 341 "…in this ice core, we may safely conclude that vertical diffusion of gases…"

Line 345 "This is due to the strong thinning of the ice…."

Line 371 this use of the word "only" 55% might be confusing to the reader. I suggest that you strike out "only". The reader will probably be thinking that 55% is still a lot, and indeed you are making the point that it is still a lot, if I understand your point correctly.

Line 372 I suggest you strike out the word "also" – this is confusing and ungrammatical

Line 426 in place of "until now", I suggest "thus far"