Review of Sapart et al., CH_4 isotopic studies from firn air at 11 sites

This manuscript presents a synthesis and analysis of a large body of data produced over many years, with the aim of providing the best possible estimate of the time history of atmospheric methane carbon-13 over the past century. It is an impressive body of work, on an important topic concerning global change and future greenhouse gas forcing. The writing is generally excellent and the modeling appears sound. However, I have some concerns about the fact that the model architecture that was used only contained molecular diffusion in the lock-in zone, and did not attempt to account for dispersive or non-fractionating transport within the deep layers of the lock-in zone (discussed in detail below). I also wonder about the effect of three-dimensional transport within the lock-in zone, in which gases could migrate horizontally by molecular diffusion but move vertically through small cracks (essentially capillaries from the standpoint of physics) via nonfractionating processes such as viscous flow. For all these reasons, I believe the manuscript should eventually be published, but only after a very thorough rethinking of the basic assumptions employed and a major revision that may well include changes to the model architecture including perhaps incorporation of new physics.

In a prior work that involved many of the same authors, Buizert et al. (2011) explored the rich data set of halocarbons and other trace gases obtained from the NEEM firn air experiments, to compare different firn gas transport models. One interesting new observation was that slow-diffusing gases such as CFC-113 were more enriched than expected based on models that only incorporated molecular diffusion in the deepest layers of the firn near the bubble close-off zone (known widely in the literature as the lock-in zone). These slow-diffusing gases have up to a factor of three lower diffusivity than methane, which immediately suggests that the sensitivity of transport to their diffusivity could in principle be quite substantial. Most of the models in the Buizert et al. study chose to alter their architecture to include a non-fractionating form of mixing or transport known as eddy diffusion or dispersion. This adjustment improved the fit of the model to the slow-diffusing gas data. The model used for the present manuscript, however, was not altered. Therefore it would be very relevant and helpful if the authors of the present manuscript would run a sensitivity test using a model that does include dispersion, to examine how important the neglect of dispersion is. Of course, diffusive fractionation is at the heart of the current manuscript, because of its profound influence on the isotope signals. The authors do mention at the end that their model may have produced a bias toward atmospheric histories with less change, due to this effect. But this is insufficient. Therefore I think it is fundamental and first-order to consider this issue before this manuscript can be considered for publication in ACP.

A less serious issue concerns the treatment of the two hemispheres in the global inversion, in which it was assumed that the Inter-Polar Gradient (IPG) in isotopes was unchanged with time. As detailed below, a more physically realistic approach would be to employ a simple two-box atmospheric model with mixing parameters derived from halocarbon and krypton-85 observations, so that northern and southern hemisphere sites could be inverted simultaneously. This seems like a way potentially to reduce the size of the error bars on the ultimate best-guess reconstruction of atmospheric $\delta^{13}C(CH_4)$.

One important point that is glossed over by the authors is that firn air studies do not sample the MEAN composition of air in the firn at any one particular depth. They sample only what is extracted from the open porosity, neglecting what resides in the bubbles and in macro-pores that are not necessarily bubbles but that have lost large-scale interconnectivity and so cannot be pumped in a firn air experiment. In this connection, it is relevant to reflect upon the fact that closed porosity is measured on hand samples of decimeter scale, which is small enough that many of these macro-pores may have been cut, such that they are recorded as "open porosity". In the deepest samples, the extractable air might only comprise 10% or less of the total air present at any one level. Thus it is important to consider the fact that the bubble records may be a better measure of the atmosphere, as bubbles sampled in aggregate by a typical large sample (such as used in the Law Dome studies, 500 g) indeed do closely represent the MEAN composition of firn air at any one particular depth. Also, Severinghaus and Battle (2006) have shown that close-off fractionation can severely alter the composition of this remaining residual of air that is extracted in a firn air experiment, to a much larger degree than the mean bubble composition. The composition of this residual air can evolve quite cumulatively and substantially in a sort of Rayleigh-distillation process.

It is also not inconceiveable that there is some isotopic fractionation of $^{13}C(CH_4)$ during this close-off process. Battle et al. (2011) have in fact identified isotope fractionation of epsilon = 5 per mil in ^{18}O of O_2 in WAIS Divide firn air, during the close-off fractionation process. Can the authors safely disregard such a fractionation process? To do so seems hazardous, absent better information. One consolation is that methane is a larger molecule than O_2 and as such might be expected to be immune to the isotopic effects of close-off fractionation, somewhat like argon appears to be (Battle et al., 2011, Controls on the movement and composition of firn air at the West Antarctic Ice Sheet Divide. *Atmos. Chem. Phys.* **11**, 18633-18675. doi:10.5194/acp-11-11007-2011).

Finally, this manuscript and the problem it treats has much in common with the study of ^{13}C in atmospheric CO_2. Similar problems have plagued this isotopologue in firn air studies. It seems important that the present authors read and incorporate any lessons learned from firn air studies of $13CO_2$. Specifically I recall that South Pole firn air $^{13}CO_2$ was never successfully reconciled with the bubble record from Law Dome and the Cape Grim archive record. It seems likely that there are fundamental problems with the treatment of diffusive fractionation in firn air, especially in the deep layers of the firn where only a small fraction of the total porosity is open porosity and the firn air that is extracted represents a small residual that is dwarfed by the amount of air contained in bubbles around it. The work of Francey, Trudinger, Bender, Etheridge and others comes to mind. It seems to me that a paper that only focuses on $^{13}C(CH_4)$ is missing part of the story. It is highly likely that the same model problems apply to both species.

I would like the authors to give serious thought to all of these issues, and I do need to see the manuscript again before it can be considered publishable. The authors should prepare a detailed response to this review, addressing each point in turn and justifying in a convincing way the choices made, including the editorial points raised below.

Other points to be addressed individually:

Pg 9589, Line 4 "…helps IN reconstructing…"

Pg 9590, line 15 "…REFERENCES therein)"

Pg 9590. Line 20 "…stable isotope RATIO measurements…"

Pg 9590, line 24 "…anthropogenic ^{13}C-enriched…"

Pg 9591, line 3 At some point in this discussion, it should be pointed out that the expectation is that all sites should agree, because the atmosphere is well-mixed on relevant timescales. This is an implicit assumption in this discussion, which should be made explicit. [Actually, the validity of this assumption is perhaps not immediately as clear as one would like. Is it really true that local CH4 sources upwind of Greenland do not affect the firn air record? I certainly would doubt it, but it perhaps needs some justification to disregard this possibility. You could cite the recent airborne trace gas sampling campaign HIPPO as justification, for example, that mid-troposphere air at 70 N is well-mixed and not sensitive to local sources.]

Pg 9591, line 4 "math/mismatch" seems a bit unclear. Perhaps you could find a better word? Perhaps "..mathematical aspects of the mismatch of these firn air results…"? I'm not sure exactly what you are trying to say here.

Pg 9592, line 3 "…trace GAS samples…"

Pg 9592, line 18 "…which STRONGLY reduce…"

Pg 9593, line 4 Witrant et al., (2011) is cited here. My understanding is that this is a Discussion paper, and did not pass peer review. Under present editorial policy of ACP, Discussion papers are fully citable. This is perhaps a philosophical question, but I wonder if these kind of citations, to literature that has not passed the peer review process, can be potentially misleading to readers? Isn't there a danger that the casual reader (which means most of us these days, in practice, since we are all so short of time) will misunderstand and come to view these papers as equivalent to published works? One possible remedy might be to include some sort of additional information, such as "Witrant et al. (Discussion, 2011)". This is stylistically somewhat analogous to the present use of "(E. Witrant, personal communication, 2011)", but of course with the vast advantage that readers can easily download the information in question. This situation has arisen because of the computer age, and perhaps our time-honored traditions of citation and scholarship have yet to fully catch up to the new technological situation and its wonderful advantages.

Pg 9593, line 11 "…is not ONLY affected by the micro-structure…but is ALSO related to…" Surely you do not believe that micro-structure has no impact on tortuosity? It is well known that clay particles (i.e. plate-like particles) create a porous media with very

much higher tortuosity than do spheres. In the particular case of firn, wind-packed snowflakes near the surface can have a much higher tortuosity than the porous medium containing rounded, quasi-spherical firn grains found at 5 meters depth. Furthermore, tortuosity is affected by the prevalence of "dead-end" or "cul-de-sac" pores, because these cause the average path length of molecule transport to increase due to "detours".

Pg 9593, line 24 "…Green's function…" for background see http://en.wikipedia.org/wiki/Green%27s_function

Pg 9593, line 26 "…to calculate the probability OF HAVING air of a certain age.."

Pg 9595, line 4 "THE DC and SPO-95 based SCENARIOS are flatter…"

Pg 9595, line 20 "…even in THE absence of A …trend…"

Pg 9595, line 23 "… using a firn model RUN IN A forward mode…"

Pg 9595, line 24 "…based on THE NOAA-ESRL…"

Pg 9595, lines 24-27 This sentence is too long and too confusing. Chop it in half perhaps? It seems that what you are trying to say is that the NOAA-ESRL methane concentration histories were used to isolate and model the effects of diffusion fractionation, with constant isotopic ratios in the atmosphere. As pointed out earlier, this calculation must be done separately for 12CH4 and 13CH4, and this was done in this case. It is not made clear in this sentence why Buizert et al 2011 is needed for the northern hemisphere, and Witrant et al., 2011 for the southern hemisphere. Are the concentration histories different in these works, from the NOAA-ESRL histories? Or did you just adopt the run results from these works, rather than running new experiments? Overall clarification is needed.

Pg 9597, line 6 "..only PROVIDED AN a posteriori CONSTRAINT ON THE DIFFUSIVITIES DERIVED FROM CO2."

Pg 9598, line 1 "…leads to a SMALLER fractionation…"

Pg 9598, line 2 Eliminate redundant parenthetical expression

Pg 9598, line 4 add a comma after "NM-09"

Pg 9598, line 10 high accumulation sites have thicker, not thinner diffusive column heights, all else being equal. Please revise this sentence. Perhaps the key point is the faster bubble trapping, which precludes an extended period of molecular diffusion in the highly tortuous lock-in zone, during which time the fractionation occurs.

Pg 9598, line 17 "…at DML, DESPITE THE FACT THAT it belongs to the…"

Pg 9599, line 10. You need to cite Buizert et al. 2011 in connection with this statement. Something like this would be appropriate: "…are strongly dependent on the diffusivity profile used, SIMILAR TO THE FINDING OF BUIZERT ET AL. (2011)."

Pg 9599, line 12 insert commas before and after the phrase "at least in the deep firn"

Pg 9599, line 16 "…leads SOMETIMES TO inconsistent…"

Pg 9601, line 3 "…no discrete age EXISTS for a given firn air sample."

Pg 9601, line 15 It is not very physically realistic for the two hemispheres to have independent atmospheric histories. Would it not be more physically realistic to use a simple two-box atmospheric model to perform your global multiple-site inversion? Because the methane residence time is roughly 8 times longer than the interhemispheric mixing time, it is very difficult for the two hemispheres to have radically different histories. Rather, the well-known atmospheric interhemispheric mixing parameters (based on halocarbon and krypton-85 observations) can be used with high confidence to force the two sets of results to be consistent with each other within the known constraints, taking advantage of the accurate methane concentration records that exist for the separate hemispheres. It seems likely that your ultimate error bars would be reduced by this approach because it brings additional constraints to bear.

Pg 9601, line 20 "…envelopes, the shape of the BEST ESTIMATE SCENARIO IS SLIGHTLY DIFFERENT for the two hemispheres…"

Pg 9602 line 1 It is not really clear from this discussion why it is a reasonable assumption that the IPG is fixed in time. Certainly, the fact that methane concentration trends flattened in the 1990s, suggests that one should not expect the IPG in isotopes to be constant in time. Perhaps the use of a two box model would be more appropriate?

Pg 9604 line 18 "…constrained by FEWER species."

Pg 9605 line 8 "…and in ice BUBBLES…"

Pg 9605 line 11 "…conclusions OBTAINABLE from the existing.."

Pg 9606 line 8 "…how WELL the diffusivity profiles…"

Pg 9606 line 17 "…models ARE important as well."

Pg 9607 line 1 "We THANK the team…"

Pg 9607 line 14 "…participants IN the field work.."

Pg 9612 line 7 "…depth at which the open/total porosity RATIO becomes…"

Pg 9615 line 1 (figure caption) "…separation ON 13CH4 fractionation."

Supplementary online information: 3. Sensitivity to the regularization term (page 3) The last word should be CONSTRAINED not constained.