Reply to the comments of referee 1:

We thank the referee for the thorough and supportive review of our paper. We acknowledge that improvements in the presentation and clarity are required. As the referee states, our semi-quantitative analysis of the dataset goes further than what previous papers have attempted. In the end, our conclusion is somewhat negative because we identify previously unnoted issues with this semi-quantitative approach. The difficult decision is in how much detail this should be presented in a scientific paper. We thin that it is important to show the in-depth analysis of the most important aspects to the community, but apparently we were not successful in doing this cclearly. We are grateful for the referee for actually making constructive suggestions, and we will incorporate them in the thoroughly revised version as outlined below. The referee comments are given in italics, the answers in normal font.

The paper presents and discusses in detail the isotopic composition of methane measured in balloon-borne air samples collected between □6 and □35 km, i.e. largely in the stratosphere. Indeed, the dataset originating from very different latitudes and seasons and encom-passing a time period of 16 years is impressive and by far tops the few data points published so far. Moreover, the analysis goes in depth and the first author is a well-recognized expert in atmospheric isotope studies. However, I have two major concerns and many minor ones (see below) and thus cannot support publication in the present form, yet.

Major concerns
(1) Poor presentation and clarity
I have to admit that I never spent more time to review a manuscript than with this one. And indeed this is only partially due to the complexity of the topic! Often I could not follow how or based on what equations, resp., certain findings or numbers have been inferred. Frequently and I would even say mostly, the actual (mathematical) analysis of the data starting from the raw data to a certain result is not given. In the first sections (primarily in section 5) many equations are given and this is fine. However, later in the discussion, simply the results are shown and mostly I could not decipher what equations were used and how they were combined for the interference of the results. Almost ever, sentences such as "Based on equation X and Y and inserting the data Z shown in . . ." are missing. This makes the reading and understanding of the manuscript and most importantly the assessment extremely difficult.
Reply: We thank the referee for this constructive comment and in the revised manuscript we will clearly link our interpretation throughout the entire analysis section to the respective equations.

This lax presentation already starts in section 5 where the theoretical basis for interpreting the data is given. Often the equations are simply given. Either the derivation of the equations or the relevant citations where the derivation is given are missing. In section 5, altogether four different epsilons are introduced, i.e. εapp, εmix, εeff, and εRayleigh. The definition of these epsilons is missing, and is εapp not identical with εmix? I ever understood more or less what is meant, but this "more or less" is too little for a scientific paper.
Reply: We are sorry for the confusion. The referee is correct that they are "more or less" the same, but formally not. εapp and εeff are the ATMOSPHERIC quantities, resulting from a mixture of different chemical and physical processes. εmix and εRayleigh are the corresponding quantities in an idealized model where the processes are parameterized by one representative chemical sink, and one physical mixing process. For the interpretation εeff is identified with εRayleigh, and εapp with εmix). We will clarify this in the revised version

The same shortcomings apply to the table and figure captions. Often I understood what is displayed in a figure only when I have read the relevant text which ever took another 30 seconds to find it. The captions should at least be so complete that a reader can immediately understand what is plotted

and what the lines and dots are. In conclusion, all this makes it very difficult and I would even say almost impossible to fully understand the paper and (important for the authors) to appreciate the work. I estimate that no more than 15-20 experts worldwide are more familiar with this isotope stuff than I am. If already I have so many problems what is with all the other potential readers? Please, dear authors, make the paper more digestible!
Reply: Understood, and we are grateful for the constructive suggestions, which will be all incorporated.

(2) Data interpretation
I strongly question the derivative of the relative sink fractions a. There are a very important point which is in my opinion not adequately considered. The major decomposition of CH4 molecules in terms of molecules s-1 cm-3 occurs above 30 km. That is, the CH4 loss rate in terms of ppmv s-1 cm-3 will peak in the upper stratosphere (>40 km) and is very small and even almost negligible below 30 km. This means in turn that the CH4 oxidation below 30 km, although it is not negligible (i.e. a<30 km »0), cannot be seen in the data collected below 30 km. As the transport (or turnover) time at 30 km is still a factor of ~5 shorter than the chemical lifetime of CH4, below 30 km the CH4 concentration and isotope composition is almost exclusively determined by transport, namely by the mixing of CH4 imported from the troposphere and CH4 isotopically modified above 30 km. Between the tropopause and ~30 km we will thus largely see a slope equilibrium between two mixing reservoirs, which explains the very uniform and compact 13C-D plot (Figure 3). The upper reservoir strongly changes with latitude and in case of the polar latitudes with season. This change is nicely visible e.g. in Figure 1. Dear authors, I absolutely appreciate your efforts to retrieve meaningful results (and >50% of the paper deal with this endeavor), but in my opinion a significant fraction of these efforts goes in a wrong direction. Consider that more than 90% of the data originate from below 30 km, i.e. from the two-member controlled mixing region or slope equilibrium region, respectively.
Reply: We thank the referee for making this point clear, because in essence this is what we find from the semi-quantitative data analysis as well. We note that the idea of deriving the relative sink fractions has been around in our community for some time. We find that this this not possible, because of the important role of mixing processes, and the referee comment, arguing from the dynamical perspective, will be incorporated (acknowledging this referee comment).

I certainly realized that you are aware of the mixing controlled layer (section 2 and 5.2.2), but in my opinion you largely did not consider it in the interpretation of the data. Indeed, many approaches for the data interpretation are fine, but the interference of the a's is in my opinion not allowed in the present form, namely that you try to interpret a mixing line/curve as it would be due to chemistry (although I agree that the upper end member is – besides dynamics/mixing – strongly affected by chemistry).
Reply: This goes in the same direction. The dynamical aspects will be stated in the revised version as a starting point, not only as a result of isotope interpretations.

Minor concerns

p.12040, l.14 and p.12041, l.14. You should at least mention that CH4 photolysis is a further loss channel which is in the mesosphere even very important.
Reply: Will be added

Section 2. The first paragraph is not state-of-the-art. There a many newer publications e.g. by K. Rosenlof or just check the paper by H. Bönisch (Atmos. Chem. Phys., 11, 3937–3948, 2011). Distinguish between STE <380 K (with TTL) and above.
Reply: We will update this, but note that the senior author of the Bönisch paper is also coauthor of our paper.

Isentropic mixing is physically impossible. Thus, write e.g. "mixing along isentropes" in the entire paper.
Reply: Agreed, although this term is widely used (was taken from Waugh and Hall, Age Of Stratopheric Air, [24],[38]. It will be replaced.

l.15. Define TLL
OK

Is the entire last paragraph (l.7-l.29) necessary? In my opinion not!
Reply: It is not strictly necessary, but was deemed useful as an introduction for the isotope community.

p.12044, l.23. ". . . relative to a laboratory standard". What is the total uncertainty of the data?
Reply: Most of the technical information is included in the technical paper that is referred to, but the key numbers will be given in the revised version.

p.12046, l.13. You cannot write "STE is minimal in autumn". First T-to-S transport is even maximal in late summer and autumn and as the PV-gradient across the tropopause is minimal in late summer and autumn, also the transport from the LMS into the tropopause is significant. Only the transport "overworld air" into the troposphere is weak in autumn.
Reply: Yes, this wording was not clear, and we will update it accordingly

p.12047/12048. Once you write δ13C(c), in equation 1 only δ13C. Make it uniform!
Reply: Our incentive was to keep the equations as simple as possible (thus leaving out variables if not needed), but we will also keep a close eye on clarity and uniformity.

p.12049, l.4. "Pure Raleigh fractionation would show a slightly increasing . . .". I don't understand this. As D is associated with much stronger fractionation, continuous fractionation would lead to successively smaller changes in δD than in δ13C which results in decreasing slopes, as observed.
Reply: NO, this is a straightforward and inherent property that arises from the non-linearity of the definition of the δ value. If CH4 is removed with a far larger fractionation for H than C (, the isotope-isotope plot (δD versus δ13C), will show a slightly positive curvature, thus become steeper. This fact, that will be easy to follow again for isotope specialists, follows from equation 2 for D and ^{13}C

$$\frac{\ln\left(\delta^{13}C+1\right)}{\left(\frac{1}{^{13}KIE}-1\right)}=\ln\left(\frac{c}{c_0}\right)=\frac{\ln\left(\delta D+1\right)}{\left(\frac{1}{^{2}KIE}-1\right)}$$

$$\ln\left(\delta D+1\right)=\frac{\left(\frac{1}{^{2}KIE}-1\right)}{\left(\frac{1}{^{13}KIE}-1\right)}\ln\left(\delta^{13}C+1\right)=c\ln\left(\delta^{13}C+1\right)$$

$$\delta D=\left(\delta^{13}C+1\right)^{c}-1$$

and c~10.

p.12050, equation 2. As in case of almost each equation in section 5 and mentioned above, either citations or the derivative of the equation is missing.
Reply: But this is the central text-book equation for isotope fractionation, the Rayleigh fractionation equation, which is never derived in any isotope publication.

p.12052, l.9. Is "Rayleigh plot" a well-known expression? I know the Keeling plot, but you mean simply δ-value vs. concentration, right? Please clarify this that everyone can understand what is meant.
Reply: This is a common expression in isotope research, but it will be clarified. It is basically ln(δ+1) versus ln(f) where f is the remaining fraction ad δ the delta value.

p.12052, equation 8. That's a strange equation. What is the "i" for?
Reply: this was meant as mathematical expression of what can probably said more easily in words, so we will remove this equation

Section 5.2.1. and 5.2.2. These two sections are not felicitous. The headers say more than the text, i.e. the text and the equations do not well describe the different influences of "diffusive mixing" and "two-end-mixing" on the isotopologues. I have also general problems with these two types of mixing processes, see my comment to section 6.3. below. Also the altogether four used ε's (εeff, εapp, εmix, εRayleigh) are badly defined, i.e. what fractionation they describe and their relation gets not clear.
Reply: We agree, after all mixing is mixing (see your comment to 6.3). Our intention was to distinguish the "continuous mixing" that is present everywhere in the atmosphere from mixing across transport barriers, where chemically distinct air masses (both subject to the "continuous" mixing) mix again. The classification into diffusive mixing and two-end-member mixing has been around in the isotope community for some time, but we will rewrite this in view of the general comment to 6.3 (below).

Fig. 4 I don't understand, at all. Where are the end-members (p.12054, l.23)? Fig. 4 is badly explained, also the figure caption is pure.
Reply: This figure will be imbedded better in the revised text of sections 5.2.1 and 5.2.2 (see last point), as an example of mixing two distinctly different air masses, e.g. across transport barriers.

p.12055, l.17. ".. decrease linearly" add "as observed (Figure 1)".
OK

p.12055, l.18. "is then mixed" exchange with "should mix"
Reply: No, this is a misunderstanding. This is the mixing in the hypothetical example. We describe what is done in this example.

Section 5.2.3. In this section the theoretical framework introduced before should be explained based on an example, right? . . . and indeed this is mandatory! Please also conclude that fdiffusion,min = 0.5 and that additional large-scale mixing can lead to f <0.5 (which is somehow written before, but as criticized before can hardly be understood by non-experts).
Reply: Yes, this is exactly the intention, but it is still a hypothetical example since the balloon samples miss the spatial and temporal situation to follow such a mixing event directly in the atmosphere. So here we show what happens when you mix two distinct reservoirs with different isotope composition (similar to shat we expect across the polar vortex). As the referee points out, it follows that this mixing can lead to *f*<0.5, and this will be stressed again in the revised version

Section 6.2, Fig.10. I don't see a significant correlation for εD. Give the slopes and the correlation factors.
Reply: Indeed there is not a significant correlation for εD, will be updated.

Section 6.2, Fig.11. Is it true, that you calculated the ε's by successively omitting data points, starting with the highest CH4 mixing ratios? A point in Fig. 11 plotted at CH4 = 1000 ppbv symbolize a calculation where all data points below 1000 ppbv have been considered? Please

explain it more clearly. Again I don't see a significant correlation for εD.
Reply: The interpretation is correct, and . Explain once more explicitly. Review correlation eD

Section 6.3. As mentioned before (major concern 2) the entire discussion of the observed KIE or ε, respectively, is in my opinion wrong. For instance, sentences like ". . .correlations result from a balance between fractionation due to chemical loss and mixing processes, primarily eddy-diffusion" (p.12061, l.20) are only half-true. Indeed the major process that causes the mixing line is "two-member-mixing". You cannot simply distinguish between this two-member-mixing and diffusive mixing. One property of two-member-mixing is that the two reservoirs mix down to very small, i.e. Fially molecular scales. This final mixing step where all spatial structures disappeared, you call "diffusive mixing". I don't like this differentiation.
This two-member-mixing is simply a successive mixing where the spatial scales get smaller and smaller, see e.g. Lovejoy et al. Atmos. Chem. Phys., 9, 5007–5025, 2009.
Reply: As mentioned above, we agree that mixing is mixing. This will be rewritten accordingly.

Equation 21. You mean ε, not KIE. You have at least shortly to explain why these modelled ε's are much larger than the observed ones and have to refer to the relevant parts in chapter 5.
Reply: Agreed, this will be done.

p.12064 and Table 7. As criticized in major concern 1 and which applies to many tables and figures, I don't see how the calculation is done for Table 7.
Reply: This is actually a point that comes from our "isotope perspective" directly to the conclusion of the referee. We want to keep it in, for people that think from our perspective. The derivation of the numbers will be clarified.

p.12064, l.27 ff. As written before, you cannot expect a "fairly realistic sink partitioning". The entire discussion from here on is in my opinion wrong. In this respect, I don't understand section 7.3, at all. More than 90% of your data are from below 30km and you write ". . . the lower stratosphere, which is not accessible from the stratospheric measurements" (p.12065, l.24)???
Reply: We acknowledge that our presentation is not fortuitous, but point out that the argumentation can be related to the "end member" from above 30 km that mixes down. This end member must have been produced by chemical reactions after all, as the referee acknowledges, and it appears that we cannot realistically partition the sinks. We think that this is an important conclusion for the isotope community. We will leave out section 7.3, since this is a too specialized elaboration of a concept that is itself questionable.

Please, reassess your entire interpretation of the "global KIEs"!! You have to give really good arguments for your analysis; otherwise I get strong problems to support your paper.
Reply: We point out that our section & is actually titled: LIMITATIONS of global mean sink partitioning, so we think that we arrive from our perspective at the conclusions that this interpretation is indeed limited. Maybe we were not clear in phrasing this behind (too) much text.

Appendix A. The paper is in any case very long, complicated and hard to read. In this respect, is this appendix really necessary? I haven't learnt much and the information you can also purchase in two sentences where you explain what approach leads to a lower limit of aOH.
Reply: As we will leave out section 7.3, also the appendix will be removed