This is a report of the 3rd round. In this report, my comments at the 1st, 2nd, 3rd round is shown as "R1", "R2", and "R3". Similarly, the authors' replies to my comments in the 1st and 2nd communications are shown as "A1" and "A2".

I checked the manuscript, but I still think of that the revision is not satisfactory. The main reasons are that the authors have not clearly explain how the predicted isotopic compositions of "gas phase products" and "aerosol products" were calculated using the results of PSIA and the simple assumptions the authors have made do not sound. In this paper, the calculation for the isotopic compositions of gas and condensed phase products using the results of PSIA for the unreacted alpha-pinene seems the novelty. The approach itself is interesting, if the calculation makes sense. Unfortunately, the current information given in the manuscript was insufficient for readers to evaluate and follow the method, thus, the reviewer still has a question how the results of PSIA are connected to the results of thermal-desorption/PTR-MS analysis. If the connection between those logically makes sense, the contents should be published in a paper, but the current version of manuscript and the replies from the authors did not convince me.

Before going into the third report in detail, I want to explain my thought on how KIEs at reactions influence the isotopic compositions of reactants and products.

It is generally known that a KIE is reaction-specific. A KIE for a unidirectional reaction of substance A (e.g., functionalization reactions by oxidants) can be determined experimentally, regardless of the intra-molecular 13C distribution in the reactant A.

$$A \xrightarrow[\text{Rate}]{\text{KIE}} B$$

Rxn1

The carbon isotopic composition of the reactant A and the single product B can be predicted using the Rayleigh function with the extent of reaction, the initial isotopic composition of A, and the carbon KIE for this reaction. This does not require the understanding the intra-13C distribution in the reactant A. It is, however, worthwhile to note that the magnitude of KIE will depend on the intra-molecular 13C distribution. This is because the KIE depends on the probability of primary 13C involvement in the reaction. For this reason, the understanding the reaction mechanism and intra-molecular position of 13C will be important upon the evaluation of KIE, but not the calculation of isotopic composition using the Rayleigh function.

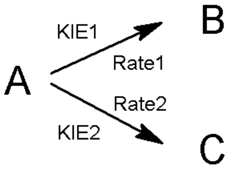
When the single unidirectional reaction produces multiple products (i.e., fragmentation likewise Rxn2 shown below), the story is different.

$$\mathrm{A} \xrightarrow[\text{Rate}]{\text{KIE}} \mathrm{B + C}$$

Rxn2

The Rayleigh function allows to calculate the isotopic compositions of A and B+C, but not of individual product. To predict the isotopic composition of individual product, the intra-molecular 13C distribution of A and the fragmentation mechanism are also needed in addition to the parameters and valuable referred earlier because the chance that bond-dissociation involves a 13C atom will depend on the intra-molecular distribution of 13C atoms, and this may cause the biased distribution of 13C between the product B and C, which cannot be determined by the Rayleigh function only.

The prediction would be complex in case of branching reactions. In the simple branching reaction shown in Rxn3, each pathway is assumed to produce a single product. Even for such a simple branching reaction the variations of isotopic compositions for A, B, and C can be complex because the KIEs and rates for the two pathways influence the isotopic composition of the parent reactant A, consequently the isotopic compositions of product B and C as well.



Rxn3

One can easily imagine that the prediction of isotopic composition will be more complex when each of the branching reactions produces multiple products. Furthermore, the prediction of isotopic composition for products is more difficult when oligomerization of these fragmented products takes place subsequently.

With consideration of these effects, I re-read the manuscript. The story does not seem to be so simple as the authors assume, but the attempt using the

combination of PTR-MS and isotope technique is interesting. The reviewer's third responses (R3) to the authors' second responses (A2) are written below.
R2: There were many sentences that it was hard to understand. For example, in the sentence in P4L29, "If…", I didn't know what "depletion of the gas phase" means, and I didn't get the logic why depletion of 13C at C9 position leads to it.
A2: We have rewritten the passage to be more clear: 'It is widely understood that the enrichment/depletion of a product depends on the enrichment of the starting material, the isotopic fractionation occurring in the mechanism of its formation, and the extent of reaction. Using PSIA we can take this analysis one step further: the enrichment of a product will depend on the positiondependent enrichments of the atoms from which it is formed. For example the ozonolysis mechanism transfers the C9-atom in a-pinene into several small, volatile products (see blue squares in Fig. 1). If the C9-position was depleted in 13C the gas phase products containing this atom would be depleted, and the SOA correspondingly enriched, if the position dependent effect was stronger than kinetic isotope effects.'
R3: This seems to explain the case of Rxn2 referred above, but what is not clear in the revised sentences is the statement, "if the position dependent effect was stronger than kinetic isotope effects." It is because the case the authors described (i.e., 13C depletion in one of the products and 13C enrichment in the other product) would be true regardless of the magnitude of position dependent (or kinetic isotope) effect. The authors need to rewrite this part.

R2: For the sentence in P7L26, I could not understand what kind of correction the authors have made. The authors should make a message in every sentence clear as writing.
A2: This passage describes the process of assigning chemical formulas and controlling / checking the assigned chemical formulas. No 'correction' was described or made in this passage. We are sorry to say that we are not sure how to rewrite the passage to improve clarity.
R3: I re-read the sentences there, and I likely misunderstood the explanation. I agree with this authors' response.

R2: There were also unnecessary sentences and paragraphs (I was impressed that those were unnecessary, but those may turn to be valuable, depending on for what the authors are going to explain using those sentences and paragraphs). For example, a paragraph in P3L9-18 defines a KIE and an epsilon value. However, any KIE and epsilon value for the pinene reaction never came out in the text. Those definitions may not be necessary, if the authors are not going to use the KIE in the interpretation.

A2: The passage in question was completely rewritten:

‘Isotopic substitution can cause reactions to be faster or slower than for the unsubstituted case, kinetically fractionating the isotopes and leading to isotopic enrichment or depletion in the products. This is known as the kinetic isotope effect (KIE). If a reaction leads to a single product, the product may initially have a different abundance, but due to the law of mass balance will achieve the same abundance as the reagent as the reaction goes to completion. If a reaction has multiple product channels, enrichment or depletion will occur if there are isotope dependent changes in the product branching ratios.’

R3: The described cases are Rxn1-2, but the actual case shown in Fig. 1 is likely the combination of Rxn 2 and 3. The authors should describe such possibility and their influence too. The revised sentences already described are also better spelled out. Feel free to use the reaction schemes likewise Rxn1-3 in their clearer explanation, if necessary.

R2: It is also not clear how the authors are going to discuss the observed isotope fractionation with functionalization, fragmentation, and oligomerization introduced in P3L27-P4L15. This paragraph impressed me at the beginning that the authors would discuss isotope fractionation at these reactions later to interpret the own data, but actually those were not discussed. If those are not available from own data or references, statements for combinational use of “isotope” and “functionalization (or oligomerization, fragmentation)” using one or two paragraphs may want to be avoided. Many of these things were piled up, and, at the end, I was not sure what I gained by reading the manuscript.

A2: We disagree. These terms are used extensively throughout the manuscript in discussing the origin of the observed results. In fact we refer back to these terms many times, be it when discussing O:C ratios or the isotope effects. We have revised the conclusions to be sure that we resolve questions raised earlier in the manuscript.

R3: If so, the authors should fairly evaluate the possible influence (how and how much) from the functionalization and fragmentations on the estimation of d13C shown in Table 5. By giving the range of d13C variations by these effects, readers will have an idea of the feasibility of this method. The current evaluation on "position dependent isotope effect" seems biased. Both are needed.

R2: The way to refer Supplementary Information, Tables, and Figures, also needs to be checked with the author's guide.

A2: Thank you, we have checked that our usage is consistent with the preparation guidelines. Specifically, the term 'in the SI' was omitted throughout the manuscript.

R3: Corrections were confirmed.

R2: Many figure captions and table headings also included unnecessary description, which can be inserted in the text.

A2: We have revised the figure captions and table headings in line with the preparation guidelines. However, please note that the author's guide asks for concise but descriptive captions. We tried our best to delete unnecessary content from the captions. In case abbreviations were included in the captions, doubles were deleted if they were introduced in the text before.

R3: The way the authors changed is not satisfactory, but the editor may accept this form. If not, the authors may consider the following suggestion.

Please check figure captions and table headings in other papers. Figure captions and table headings are sort of titles in general, but those in this manuscript are made of several sentences, which are unusual to me. The

following is just an example table heading for a Table 2. "*Table 2. Stable carbon isotope ratio of OC and TC ($\Delta(^{13}C)$), total mass loaded ($M^{PTR\text{-}MS}$), and O:C ratio for filter samples collected from smog chamber experiments.*"
Then provide some detail information in footnotes like
"^{a} $\Delta(^{13}C) = \delta(^{13}C) - \delta_{TC}(^{13}C)$", "^{b} Measured by Thermal-desorption isotope analysis.", "Measured by PTR-MS"

R2: For these reasons, I regret to say, but the manuscript does not seem to be ready to be published. Thorough revision is still needed. It may be the best to revise the manuscript with professional editors for expression in English, but this does not secure to turn the manuscript well organized. It is still the authors' responsibility that the order of explanations (sentence by sentence) and discussion (paragraph by paragraph and subsection by subsection) need to be well organized prior to the English check in order to make the flow of context smooth in the final form.
A2: Thank you for the opportunity to revise the manuscript to improve clarity, organization and readability.
R3: No problem.

R2: It is a minor thing, but the column containing "t/h" in Table 2 has also the information of "V/m^3". Those are different information and should be shown in different column.
A2: Since the sample flow was constant, these two values actually represent the same information. However, we follow your recommendation and separated them into two columns.
R3: Confirmed.

R2: I also recommend the authors to show units in brackets instead of slash in this table for consistency (i.e., the slash of "micro g / m^3" is meant a division, while the slash of "V/m^3" is meant for unit.

A2: In both cases, the slash is division. This is the method recommended by SI, NIST, IUPAC and others, see for example the IUPAC Green Book.
R3: The authors likely misunderstood my message. According to this explanation, “V/m^3” in Table 2 would mean volume per cubic meter. I suggested to change the “V/m^3” to V (m^3), the “$\mathrm{M}^{\mathrm{PTR\text{-}MS}}$ / μg/m^3” to $\mathrm{M}^{\mathrm{PTR\text{-}MS}}$ (μg/m^3), and all other column headings and units accordingly.

R2: Besides the writing issues, the followings are my responses (underlined) to the authors’ comments (Italic) to my previous comments (bold). Please note that I am responding to only the authors’ comments that I have opinions on. For those that I am not responding to, it is either of that I am satisfied with the changes or issues are overlapping with those I am already responding to.
A2: Thank you. We will add our response after your underlined comments. We omitted the quoted texts from the last revision for the sake of readability.
R3: Okay.

General comments
R1: After reading the manuscript, I had impression that points the authors argued were unclear: pieces of discussions seemed to be fragmented.
A1: The discussion was overhauled and there is now a separate section ’Discussion’ to allow a clearer distinction between results and discussion. Furthermore, a reaction scheme (new FIgure 1) was added as suggested and used to guide the reader through the paper.
R2: Thanks for attempting to revise along my advice, but this change is not satisfactory. I wanted the authors to focus on the important messages that the authors want to tell readers, and logically justify the arguments stepwise using own experimental results and references. The current form seems that the discussion section in the previous manuscript was just divided. The contents and arguments were still confusing. In addition, the “Results” section in the current manuscript substantially includes authors’ interpretation and discussion. It is okay to separate the “Results” and “Discussion” sections, but please give only the observed results in the *“Results”, and analyze and evaluate own data with references in “Discussion”.*
A2: We rearranged some of the content, but there is still some discussion left

in the 'Results' section, as this is very hard to be avoided in a paper like this. We have tried many different structures prior to submitting among the authors and in fact didn't want to have them divided until we go the reviewer's comments. Concerning the numbers in Table 5, they are still part of the 'Results' section as they are derived from basic algebra.

R3: The data given in Table 5 are the results of estimation, which include the authors' interpretation that others may not agree with. In general, a result section provides measurement results (like raw data in Table 1, 2, and 4, and Figure 2 - 7), which are independent of way to interpret. Then, data interpretation, likewise the information provided in Table 5, is shown in a discussion section. Similarly, the text in the result section should describe what we can see in the raw data, such as time series variation, magnitudes, etc. Keep it as simple, and analysis of data and its interpretation should be described in the discussion section. If you are going to discuss the interpretation right after presenting the raw data, then combine these sections as "results and discussion".

R1: I also had impression that some information and discussion (e.g., already studied C:O ratios and natural processes with isotope fractionations) were very detailed, and some (e.g., chemical reactions that lead to formation of low volatility products, calculation for predicted d13C in Table 5) were insufficient.

A1: We have shortened the former and expanded the latter. The calculations leading to the numbers shown in Table 5 are now illustrated with an example and Table 5 was overhauled. The new reaction scheme highlights the reaction pathways that lead to the calculations in Table 5.

R2: I was a bit confused to find "example" illustration for the calculation of position specific d13C of Dgas and Daerosol in Table 5, but the authors probably meant S5 in the Supplementary Information. I understood that the calculations were based on NMR data, which are for unreacted alpha-pinene. From the revised manuscript, however, I could not retrieve important information to explain the d13C of product Dgas and Daerosol in Table 5 using the position specific d13C of unreacted alpha-pinene.

A2: We have changed the text to make it clear that the values calculated in *table five are based on the MCM mechanism presented in Figure 1. Note that the precision of our argument is limited as the branching ratios are not known with certainty as is now pointed out even more clearly, and in any case, will change depending on temperature, pressure, humidity, OH, NOx and so on. We do not refer to S5 (or NMR data) but Table 5 and it is hard for us to explain the very basic algebra behind the numbers in Table 5 in more simple terms than we have done already. We have however, pointed out the assumptions very clearly at the beginning of the paragraph. The numbers in T5 are derived from the position-specific enrichment listed in Table 2 as described in the text. The beginning of the passage now reads:*

'Here a limiting case is presented for the isotopic difference of a number of plausible oxidation products. The underlying assumptions exclude isotope dependent changes in product branching ratios, as well as effects of temperature, relative humidity, pressure, ozone concentration, etc. This simplistic approach allows to estimate the maximum isotopic enrichment in a-pinene fragments using the Δi(13C) profiles obtained from PSIA.'

R3: It is not necessary to care parameters at different conditions, but please use parameters under own experimental condition in order to interpret own data. There will be readers who wonder how the calculation was done for the numbers in Table 5, so please clearly explain it. I tried to calculate the isotope ratios using the information given in Table 1 (not Table 2, I guess) by assuming that all KIEs were ignored and the pinene reaction with ozone completed, but I could not reach to the point that the isotopic compositions of gas and aerosol phase products were determined. It seemed that quantitative information of each product (specifically carbon fractions of each product relative to the total product carbon), which wasn't given, was needed to determine d13C of gas-phase and condensed-phase products, if the calculation was based on the isotopic composition of each product in either gas or aerosol phase, which was estimated based on the information in Table1. Did the author get this quantitative information from MCM? If so, I expect specific values of rates are supposed to be given for all the reaction pathways, which will give branching ratios at branching reactions and yields of each product. By the way, please state explicitly if only CO, formaldehyde, and acetone are treated as "the gas-phase products" and the rest of products in Fig. 1 are in aerosol phase products in the calculation.

There is another point I would like to make. Although the authors replied that they have pointed out the assumptions explicitly, those are still not clear in the text: that is, "The underlying assumptions exclude..." and "if a single carbon atom or reasonable combination..." are not clear enough to get what assumptions were actually used. Please describe them explicitly.

Given the reasonable assumptions and calculation for the isotopic compositions of products in gas and aerosol phases, it will be interesting to compare the determined values with the results from the simpler carbon mass balance calculation for the isotopic composition of gas and aerosol phase products (Irei et al., 2006).

R1: In addition, the authors may want to make more focus on what they can conclude from the data they gained. For example, the position-specific isotope analysis (PSIA) sounded a key achievement in the abstract. However, if my understanding is correct, the PSIA was performed only on the unreacted a-pinene. I did not get what conclusion the authors were going to draw from the comparison of this information with d13C of stepwisely evaporated OCs, each of which is still possibly a complex mixture of multiple substances as indicated by more than 400 of fragment ions in the table in S4 of SI. If the authors could identify a specific product possessing enriched/depleted 13C atom at a specific position, which may have originated from a specific position of a-pinene, they should make discussion with the observed evidence (e.g., the difference in d13C between the different samples).

A1: Thank you for your comment. It is correct that PSIA was performed on the unreacted a-pinene only. PSIA on single components of the SOA mixture is not possible at this moment. The argument is that if one dominant reaction channel prefers a certain reaction site on the alpha-pinene, then the position specific isotope distribution might govern the overall isotope signature. However, we cannot fully conclude that. PSIA on a-pinene was performed for the first time and we believe that this is an important result for future research and therefore chose to leave it in the abstract. Other parts of the abstract and large parts of the introduction were rewritten. A reaction scheme was added to better guide the reader in the introduction specifically when it comes to the idea that PSIA could play a role in the 'bulk' isotopic composition.

R2: Biased 13C distribution in intra molecular carbons of pinene is interesting, and I am not going to be offensive against this finding. However, again, my point is that it is not clear how this PSIA is related to the product analysis presented in this paper. It is reasonable that the authors will combine this result with results of future compoundspecific product study to explore isotope balance between the products, but those are not available at this moment. The presentation of the result here may be justified if Dgas and Daerosol in Table 5 were calculated based on the measurement results of PSIA with reasonable assumptions. However, the assumptions (i.e., "maximum expected enrichment" and "branching ratios do not influence the isotopic composition of products") do not sound. According to Hoefs (1997), the initial isotope ratio, the degree of processing, and the fractionation factor are needed to calculate the isotope ratio of a processing substance or product at any arbitrary time. Presumably, the authors assumed ~ 100% of degree of alpha-pinene oxidation ("completion" in the text probably suggests this), however, this does not secure that the complex subsequent reactions also completed, depending on relative reaction speeds (relative to the speed of ozonolysis of alpha-pinene) of subsequent reactions leading to the production of formaldehyde, acetone, CO, and other products. That is, branching reactions significantly influence product isotopic composition, unless otherwise there is no isotope fractionation (i.e., KIE = 0 permil) at all of these reactions. If even only one of these branching reactions had a significant KIE, which seems more reasonable assumption according to Fisseha et al. (2009), this KIE will significantly influence the isotopic composition of remaining alpha-pinene or intermediate(s) as reactions proceeded. This varying isotopic composition of precursors will then influence the isotopic composition of products from other branching reaction channels because all or a part of products originate from the same precursor. In the text, it is not clear what substances are defined as "aesosol" and "gasphase", what number of KIEs and branching ratios were used for the calculation. I am not sure what "the maximum expected enrichment" is, but if the authors assume zero of KIEs at all branching reactions and no branching reactions, I disagree with the assumptions. From the text I could not retrieve those information.

A2: It would be great data to analyse if one had the opportunity to perform PSIA on several of the product species, however, that was not possible in this experimental setup and has to be left for further studies. In the meantime we only have the starting picture (PSIA of a-pinene) and the end point (bulk δ *values of SOA). While maybe not 100 % satisfying, the best we can do with these fragments is to figure out the potential effect, or so to say how much of the starting picture is left at the end. The presented results demonstrate conclusively that both PSIA and isotope dependent product branching ratios must be considered in studies of isotopic fractionation in SOA formation reactions, especially for natural products. The assumptions made behind the numbers in Table 5 are of course not perfect, but our goal here was to get an estimate of the potential size of the effect. The branching ratios in the alpha pinene ozonolysis mechanism are unknown and very importantly, the branching ratios will depend on temperature, relative humidity, and the concentrations of ozone, OH, NOx and other species. We applied a simplification to a complex mechanism, and we did that for the first time with strong results. Concerning the product branching ratios anything is possible. We argue in the text one reaction having a very large KIE is not likely based on mechanistic considerations (standard addition reactions to a large molecule) and on e.g. the experimental results of e.g. Anderson at al 2004 and similar papers. The anomalously large KIE's seen in e.g. the ozone formation reaction are anomalies. In line with this, Fisseha et al.'s KIE is for the initial ozonation reaction, not for subsequent reactions, up to our understanding. The assumption to neglect the isotope effects of the branching ratios is not as far-fetched as it may seem at first.*

R3: I agree with that Fisseha et al. (2008) provide the carbon KIE at the first reaction step, and the reported KIE in their paper can be significantly different from the KIE at the initial step of alpha-pinene ozonolysis here due to possibly different intra-molecular 13C distribution. However, this does not necessarily mean that the KIEs in subsequent reactions shown in Fig. 1 are negligible. Rather, it is more likely that significant carbon KIEs exist in the mechanism in Fig. 1 because many primary carbon reactions are involved. In addition, the authors consider the production of CO, formaldehyde, acetone, pinoaldehyde, pinonic and pinic acids in the mechanism, and this indicates that the authors accept branching reactions. The assumptions sound contradictory to the mechanism. In my opinion, the calculation based on the combination case of Rxn 2 and 3 is feasible, but the authors should give scientific reasons (e.g., checking a trend for yields of products vs extent of the initial reaction) why their assumptions can be justified. With this dataset I could have seen the biased interpretation on isotopic compositions of specific products. For this reason, I referred in the previous reply that publishing the PSIA results here with results from future product-specific isotope analysis makes more sense.

R1: Lack of reaction mechanism for production of SOA from ozonolysis of pinene was also a problem to follow the discussions.
A1: Thank you for your comment. We made a new figure (Fig. 1) that identifies how the site-specific α-pinene d13C values propagate through the reaction mechanism highlighting some key arguments of our paper.
R2: Thanks for providing the reaction scheme. This will definitely make readers easier to follow the discussion. However, the scheme is incomplete and not reader-friendly to follow the reaction steps producing high and low volatility products. For example, taking a look at the production mechanism of pinonic acid and pinoaldehyde in Fig. 1, I don't know what was changed after the second processing step, "stabilization". I see that the red star mark on the carbon disappeared after the step, but what does this mean? I also don't get how "H2O" was involved in the subsequent reaction after the "stabilization". The same problem for the reaction with RO2 and HO2. The authors may want to check how other papers are presenting those reaction schemes. Second point is that the figure also does not show important elemental steps for the production of small products shown in the boxes in Fig. 1. The hidden reaction channels seem to involve reactions with C atoms, thus, must be key steps to explain the results of d13C calculations. Third point is that it is helpful for readers to see branching ratios in the figure.
A2: Considering point 1, the mechanism presented in Figure 1 is consistent with the best available understanding, as found in the Master chemical Mechanism and in the paper we reference (Camredon et al., 2010). By quoting these references, we also invite the reader (and reviewer) to read the literature on the known reactions in case theya re not presented in enough detail. The high complexity of the involved reactions disallows much more simplified representations. Points 2 and 3: Many people would like to know these branching ratios and the elementary steps of the reactions, but they are not known and might never be. Many experiments have only been able to detect products, and even with this information, it is ambiguous what the

exact contribution from each branch of the mechanism is. We would happily include this information if it was available to a level of detail that was helpful to interpreting our results, however, this is not the case, up to our knowledge.
R3: It is true that most of rates at each elemental step are not studied, but regardless of correctness MCM requires specific numbers for the calculation, as long as I understand. Please provide the used numbers in the kinetic calculation or state explicitly what the authors has done using MCM, if such a calculation was not made.

By the way, Fig. 1 seems to include the continuous errors from the paper by Camredon et al.: according to Fig. 1, Criegee intermediates are followed by fragmentation reactions, but the scheme labels some of those as "isomerization". The authors may want to correct those (check if there are such errors through the text, figures, and tables thoroughly), and to be consistent I suggest to label all reaction steps in Fig. 1 with "stabilization", "fragmentation", and "functionalizatoin". The current form shows some are labelled, some are not.

Specific comments
R1: P3l10: The authors may want to use a symbol of alpha instead of epsilon for the expression of fractionation factor.
A1: We rewrote the section in question and now describe the Kinetic Isotope Effect (KIE) using ε values, as is common practice. We believe this makes the explanation easier to follow and more clear. The replacement of ε by α does not change the manuscript as they are simply related by $\varepsilon=\alpha-1$ which is common knowledge within the field of isotope research (see for example Coplen, 2011).
R2: Regarding the definition of kinetic isotope effects, Colpen (2011) defines a kinetic isotope effect as 12k/13k, while Hoefs (1997) defines a fractionation factor as13k/12k. The authors may want to stick to either of these.
A2: The paragraph was completely rewritten, see above.
R3: Confirmed.

R1: Section 3.1.: The authors may want to present an example time series plot of ozone mixing ratios and pinene concentrations.

A1: Among authors we discussed providing a plot of the ozone mixing ratios but decided against it. The main reason against it being an interference of organic vapours on the ozone detection system yielding spikes of the ozone mixing ratios. This was tested and confirmed in extra experiments, but with no conclusion / suggestion on how to resolve the issue or how to correct our data for it. In order to avoid an extended discussion on operation and detection mechanisms of ozone monitors, we opted to leave the plot out. The pinene concentration was not measured.

R2: It is very important to have information of pinene concentration change over time at least. Is it possible to present such info based on MCM calculation with given experimental condition?

A2: Based on the ozone concentration, the reaction rate of a-pinene with ozone and the length of the experiment, we are confident that all of the alpha pinene has reacted, as we state in Section 2.3.

R3: Specific information will avoid unnecessary argument. This can be easily calculated with the initial pinene conc., minimal ozone conc., and the rate constant. It's up to the authors.

R1: In addition, according to Fig 7a, OC at 100 degree Celsius (7% of TC) has the largest difference of -3 permil in d13C. Any discussion for this difference? Does this difference attribute to different isotopic composition of different chemical species? This is the part the authors should make deeper discussion, I think.

A1: We suspect the reviewer was commenting on panel b of that Figure and will give our answer accordingly. The second last paragraph of section 3 discusses the strong enrichment observed at 100 C. However, the discussion has to stay vague as no clear conclusions can be drawn from the data. Unfortunately, no species or group of species could be assigned to this enrichment. We omitted the last part of the paragraph which dealt with the back filters and added another consideration based on oligomerisation. The *text was changed to:*

"The reason behind the enrichment in material desorbing from front filters at 100 °C cannot be unambiguously identified. The chemical analysis did not allow to identify single compounds or groups of compounds that contributed significantly more to the total aerosol concentration at 100 °C than at 150 °C and therefore could lead to the observed enrichment. Isotope effects associated with sampling artefacts, which are generally not well known, provide room for speculation on how to interpret the enrichment at 100 °C. During the negative sampling artefact, isotopically light isotopologues revolatilise from the ensemble of sampled compounds preferentially leading to an overall isotopic enrichment in compounds that are left on the filter. Revolatilisation should have it's largest effect at 100 °C. Another explanation can be based on oligomerisation. Hall and Johnston (2012) observed significant evaporation of oligomers in a thermodenuder already at desorption temperatures below 100 °C. The effect of oligomerisation on isotopes is not known, but if it leads to enrichment, the fragments of decomposed oligomers could be enriched and explain our observations."

R2: Sorry for confusion. It is correct that I was pointing on the panel b. I think it is not necessary to deeply argue with speculation, if there is no reasonable scientific explanation for the difference. However, it is important to point out the difference explicitly and briefly state possible reasons for the difference so that others can hint for future studies to progress the science.

A2: The section was removed.

R3; Okay.

R1: P16l20-33: There are papers discussing site specific isotope fractionations. Why do the authors argue with reactive isotope fractionations using the reference of sorption isotope fractionation of vanillin?

A1: There is not much literature available on the topic as the analysis technique is rather new. However, we now included the Botosoa et al., 2009b reference in the text and omitted speculations about bond length variations.

R2: I am not sure if we are misunderstanding our comments each other, but I can find references for position specific carbon isotope fractionation at different types of chemical reactions (not for physical phenomena), such as

Singleton and Szymanski (1999, JACS) and etc. Because the authors are discussing "carbon isotope fractionation" there, it is not necessary to compare only with the results obtained by NMR measurements. Carbon KIEs for elemental reactions obtained by different techniques have been studied for long, some of those may be comparable. Of course, the current reference is also okay, I think.

A2: Thank you, we agree that the reference we chose is appropriate.

R3: Okay.