First of all we would like to thank the referee, Hinrich Schaefer, for his comprehensive comments and suggestions. By incorporating his suggestions the paper considerably improved.

Note, the original reviewer text is in blue, our response is in black.

Schmitt et al. report on the problem of interference from Kr during measurements of stable carbon isotope ratios of methane ($\delta^{13}CH_4$). The study covers the complete process from detection of an interference to the identification of the "contaminant", and finally technical solutions to eliminate the problem during analysis and providing correction strategies for affected data series. The discovery of the problem has already sparked discussions in the atmospheric measurements community so that it is more than timely for this work to be published. Since my institute hosts an analytical system that is subject to the problem I have put the manuscript through its paces regarding the practical tests and solutions. I don't see reasons against publication of the manuscript as presented, as it provides a robust and comprehensive treatment of the issue. The manuscript is well structured and clearly written. I have noticed a few instances where I recommend clarification or minor corrections as detailed below. None of those concerns are of major importance. The only small point where I see room for improvement is to communicate the potential importance of the findings to other research fields. For instance, the list of affected studies could be moved from the conclusions section and discussed already in the introduction, which currently focuses only on ice core research. The implications for other mass spectrometry studies are discussed only briefly; it seems that the issue would be of interest to isotope chemists working in different fields as well. A list of good, relevant key words may be a way to bring the findings to their attention. However, I wonder if a more general title would be more effective. One suggestion would be to mention the low-energy tailing in the title. Overall, I recommend this manuscript for publication in Atmospheric Measurement Techniques.

Regarding your suggestion to widen the potential audience of this problem and to move the list of potentially affected research fields from the conclusions to the introduction. During the draft phase, we had a link to related fields in the introduction, but we removed it for clarity. To reach this audience we included also a link to other sample materials, i.e. to water samples, which could have situations where Kr is more abundant than CH_4. Additionally, a link to non-

CH$_4$ applications is given where triply charged Xe isotopes could potentially interfere with δ^{13}C analysis of trace gases.

You also raise a good point regarding the title: Both the title and the introduction is very specific to the field of atmospheric measurements and especially ice core measurements. One easy step is to remove "atmospheric" from the title to make clear that all sample types can be affected which contain both methane and Kr. We also collected a list of key words to allow scientists outside the "atmospheric measurement community" finding this paper

Note, the page and line numbers of the reviewer refers to the submitted word document. To allow the reader of the discussion paper pdf version to follow his comments and our reply we provided the page and line numbers of the pdf in brackets in black.

Specific comments:

Page 2; Line 8 (page 1411, line 21): Kai et al. and Levin et al. should be references for the preceding sentence (lines 3-5) as they don't report palaeo-data but modern atmospheric time series.

The two citations have been moved accordingly.

Page 3; Lines 18 & 19 (page 1413, line 11-12): quoting the actual deviation of 13CH4 values is helpful for the reader to understand the scale of the problem, yet such values are not provided in the manuscript except for a statement on page 6, lines 25 &26, and the AWI correction factors which amount to max. 1.3‰. A short report, maybe as a table, of the deviations observed during the round-robin exercise would be of interest to the reader.

We now added a new table, Table 2, to fulfil your request. The table shows the round robin results obtained from the labs of this paper as well as the results measured by Hinrich Schaefer at NIWA as for this lab both dual inlet (no Kr interference) and continuous flow data (with Kr interference) are available. Where a Kr-correction was possible, we also provide the respective values of the corrected data after correction.

Page 5; line 29 (page 1416, line 9): it may be preferable to introduce the abbreviations "PI", "GLA", and "PD" in this line, so that the reader easily sees what they stand for.

The abbreviations were introduced earlier as suggested.

Page 8; line 16 (page 1419, line 9): I think that the IMAU tests provide robust evidence for Kr as the interfering agent already at this point, so "believe" is very conservative wording.

Yes that's true, but at this stage there is still the possibility that a second compound caused anomalies as well.

Page 8; line 26 (page 1419, line 20): while using the manuscript as a manual to conduct the described test I got hung up on the magnitude of the accelerator voltage (AV) shift, here 55 V. This is less than the 85 V that are later quoted as needed to shift a given m/z beam to the next cup and the evidence for the Kr tailing across an AV range has not yet been mentioned or presented. Therefore, it is not clear at this point why the m/z 43 and 45 beams would be detectable in the major and minor 2 cups, respectively. It is true that lengthy explanations will distract from the simple and very useful test. Possibly, Section 4.1. should be moved to the end of Section 4. This would provide the reader with a better understanding how the test exploits the tailing and cup characteristics. The reader could be referred to Fig. 6, which illustrates the positioning of beams and cups very clearly. The one point that Section 4.1. currently provides in the logical flow of the argument is the demonstration of peak positions. These features can also be shown using Figs. 2 and 4 although I admit that peak overlap is not explicitly shown in those figures. Using the proposed order, readers would be armed with all information on the behaviour of Kr and CH_4-CO_2 before they explore their own set-up. This is a suggestion only.

You exactly point to the dilemma during preparation of the paper, when to provide which information and which figure. We decided to do it stepwise and let the facts evolve during the experiments. The simple tuning experiment leading to Fig. 3 immediately allows the leader to see that there is co-elution of CH_4 and Kr, thus a chromatographic problem which has to be fixed. Readers not interested in the complex details of the interference can bypass the rest of Section 4 and go directly to the solutions in Section 5. Since the other two reviewers did not

suggest changing the order of experiments, we keep the structure as it is. However, we include a link to Fig. 6 as it helps to understand why 55 V is sufficient for this experiment.

Page 9; lines 15 & 16 (page 1420, line 14): as m/z is defined as mass to charge ratio (page 2; line 22) it is unclear what is meant by "m/2z (for doubly charged ions)".

The sentence is rewritten.

Page 10; line 12 (page 1421, line 16-17): do you mean that the signal is 10x higher at the same run time (as opposed to the max. minor 2 signal of the air run with 350 mV)?

Yes, the comparison is meant for the same run time to illustrate that Kr peak cannot be seen on the shoulder of the CH_4-derived CO_2 peak. We rewrote the sentence to be clearer.

Page 11; line 6 (page 1422, line 16): What is the m/z 43 beam proximal to?

We rewrote this sentence to be clearer: "Because the m/z 43 beam produced by $^{86}Kr^{2+}$ is only a few m/z units away from the target signals at m/z 44, m/z 45 and m/z 46, we propose two hypotheses."

Page 12; line 27 (page 1424, line 19): should this be Fig. 6?

Actually, both figures are useful in this respect, therefore we changed it to Fig. 6 and 7.

Page 18; line 29 (page 1431, line 20): the wording "Kr now elutes 25 s before: : :" invokes the lead to be an inherent characteristic of the set-up. In contrast, using the trap one should be able to place the CH_4-CO_2 peak at any desired time in the window between Kr and N2O. Maybe this is worth clarifying?

Yes, in principle the user has free choice to place the CH_4-CO_2 in the chromatogram. However, the trapping time should not be unnecessary long, as CO_2 traces bleeding from the combustion oven adds to a blank contribution. We changed the wording accordingly.

Yes, typo corrected.

Yes, we did not explicitly point to this phenomenon to keep the paper as short as possible. We agree that this discrepancy is worth an explanation and added the following section as clarification:

Before continuing the calculation, we want to point to the counterintuitive temporal offset between the Kr peak maximum and the anomaly maximum of ion current ratio visible in Fig. 2, Fig. 4 and Fig. 11. The Kr peak maximum typically occurs a few seconds earlier than the maximum in the ion current ratio. Theoretically, if both the CH_4-derived CO_2 peak and the Kr peaks were ideally Gaussian, the background corrected ion current ratio on the right side of the Kr peak should asymptotically approach the ion current value of the Kr peak itself. However, the ion current ratio usually shows a maximum a few seconds after the maximum of the Kr peak and then declines towards the value of the CO_2. Our interpretation is that both peaks are non-Gaussian and CO_2 has a longer residence time in the source and in the capillaries due to adsorption effects compared to the noble gas krypton. For that reason we assume that the measured ion current signal in the region of the declining flank of the Kr peak becomes progressively dominated by a desorption tail of the CO_2 peak, thus also the ion current ratio.

We did not explain the details of this fitting step because it is not a problematic step of the entire procedure and the quality of this step can be easily checked visually. As mentioned in the text, the time series of $i^{45}_{Kr\text{-}excess}$ usually resembles a Gaussian-like peak. In fact the CH_4-

derived CO_2 sample peak and the Kr peak are almost congruent, thus, ideally the reconstructed $i^{45}_{Kr-excess}$ time series has the same shape as the preceding CH_4-derived CO_2 peak. Based on that, we use the peak shape of the CH_4-derived CO_2 peak as a template and scale it according to the peak height of the reconstructed Kr peak $i^{45}_{Kr-excess}$. We derive a robust peak height estimate of the $i^{45}_{Kr-excess}$ by subtracting a background value which is taken from a 1-s interval at a position of around 10 s after the CH_4 peak max. Clearly, this simple "fit" approach is less elegant than a least square approach, but it does not produce spurious results when the left side of the $i^{45}_{Kr-excess}$ time series markedly deviates from its ideal Gaussian shape. The latter happens sometimes in data sets where the ion current ratio of the CO_2 peak is not flat.

We added a short description on that in the updated text.

Page 22; line 4 (page 1435, line 18): what is the reported average standard deviation? Is it the pooled standard deviation of replicate measurements (n=?) for each tank? Or is this some measure of corrected versus measured values? Please provide more detail.

We added more detail to this sentence.

Page 23; lines 12 & 13 (page 1437, line 5): although the peak cut-off correction is close in magnitude to the algorithm, it is systematically higher. I wonder if this reflects the fact that the heavier isotopes tend to elute slightly later than the lighter ones (as the authors allude to in the previous paragraph), so the former would be more strongly affected by the peak cut-off. If this is the case the algorithm would not only provide more consistent but also more accurate results.

Yes, this is the case. However, this systematic bias from the early cut-off can be corrected when the principle of identical treatment is applied, i.e. when the effect of the cut-off from a CH_4 working standard or reference peak is processed in the same way as the sample. Both approaches have their inherent advantages and disadvantages and which of approach can be applied to correct a data set depends on many details, like peak separation, time shift and the investment to apply these routines.

If I am not mistaken Kr's higher solubility should lead to higher CH4/Kr ratios (not lower as currently stated) as proportionally more CH4 is extracted into the head space.

We rather meant the change in the CH_4/Kr mixing ratio of a natural water sample after equilibration with the atmosphere. We then assumed that during analysis all gases are extracted quantitatively. We changed the wording to be clearer on that.

it seems important to complete the argument and state that the Kr bias related to CH4 concentration will lead to erroneous assessments of alpha.

We made this point more clear.