

Interactive comment on “Improving accuracy and precision of ice core $\delta D(CH_4)$ analyses using methane pre- and hydrogen post-pyrolysis trapping and subsequent chromatographic separation” by M. Bock et al.

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Review of Bock et al.: “Improving accuracy and precision of ice core $\delta D(CH_4)$ analyses using methane pre- and hydrogen post-pyrolysis trapping and subsequent chromatographic separation”

Overall comments: The authors present an update on their analytical procedure for the measurement of hydrogen isotope ratios of methane. The previously described method is well established and has produced valuable time series. The additions and

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improvements reported here include more comprehensive purification of carrier gas, new post-analysis calibration routines and, most importantly, additional trapping steps of gas components before and after the pyrolysis step. The overall result is strongly improved precision of the analysis, which will increase the amount of environmental information that can be gained from the measurements. The results are compelling and presented clearly and in a well organised manuscript. I recommend the paper for publication in Atmospheric Measurement Techniques. Some minor comments and suggestions are listed below.

Specific comments:

Page 11281; lines 13 and following: It may be helpful to give examples of natural variability in $\delta 2H(CH_4)$ so that the reader can assess it with regards to analytical precision of previous measurements and the results presented in this study.

Page 11282, lines 21–27: It is not clear to me how the comparison of He-blanks run through the melt water versus the bypass quantifies the contamination of the carrier gas. If it did, one must invoke a process associated with the melt water to render the inherent contamination accessible to the subsequent trapping system. Is there a physical mechanism that could accomplish this? A simpler explanation is that the experiment shows residual CH_4 from the ice sample when the carrier gas is run through the melt water. In the initial methods paper (Bock et al., 2010) the authors report for equivalent test runs (“simple loop” and “loop after sample”) only that the $\delta 2H(CH_4)$ values are indistinguishable. No effect on peak area or height is documented and an elevation by 0.3% for minimum peak size may not be detectable. I can therefore not follow the argument that the experiment shows a blank reduction compared to the old set-up.

Page 11282, line 23: B34 has not been introduced yet, it would be easier to say “0.5% the area of a CH_4 peak characteristic for LGM measurements”.

Page 11283, lines 17–18: It would be convenient to provide details on traps T4 and T5,

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so that the reader doesn't have to go back to Bock et al. (2010) for this information.

Lines 18-19: Could you explain why the cold trap is preferable over the previously used Nafion trap?

Page 11284, lines 7-11: It may be necessary to spell out that CH₄ and C(2H)H₃ have different elution times from the GC.

Line 15: It is not clear to me what you mean by "time shift". Is it a shift in peak retention time between major and minor traces?

Page 11285, line 4: Please report what kind of gas you use for the conditioning.

Lines 11-12: It would be convenient if you reported the precision for the air content derived from Xe and consequently for the CH₄ and N₂O concentrations.

Page 11286, lines 5 and following: There is an additional calibration or correction that should be discussed. The described system uses a one-point calibration which means that samples with $\delta^2\text{H}(\text{CH}_4)$ that deviates more from the standard may be biased. This bias could be quantified if a second reference spanning the range of measured values was available. See, e.g., Ferretti et al. (2005), Supplementary Online Material, for an application of an "isotope ratio-linearity" correction. I understand that standards with calibrated isotope ratios are not available so that the authors are not able to implement this correction. Nevertheless, I think it is necessary to discuss this issue as a limitation for accuracy and a problem in inter-laboratory comparisons and the interpretation of the observed range of variability.

Section 3.1: The section on accuracy contains several paragraphs that would better be reported separately. The experiments using B34 deserve their own section as they demonstrate long-term stability of the analyses rather than accuracy in the strict sense. The paragraph on the inter-polar gradient (IPG) would fit a "first results" section and is, in my opinion, really misplaced in the treatment of accuracy. For a proper discussion of the IPG a plot of WAIS and B30 would be very helpful, if not necessary.

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Page 11288, lines 12-16: The depletion in deuterium would be of the right sign for preferential dissolution of the heavy isotope in the denser medium (melt water). If that is the case, then the fractionation could be larger for ice samples where the gas has more time for equilibration with the water during the melt process. The magnitude of this hypothetical process cannot be determined unless one had ice samples with known $\delta^2\text{H}(\text{CH}_4)$ occluded. In addition, a potential bias would only be a problem for intercomparisons with other labs but not the interpretation of time series from one analytical set-up. However, the problem has the potential to limit accuracy and should be discussed in more detail in the manuscript.

Page 11289, line 5: There is no further mention of N₂ interference in your set-up. Is the following analysis of the post-peaks sufficient to rule out an effect?

Lines 9 and following: It would be helpful to introduce the discussion of Kr and unpyrolysed CH₄ interference with an explanation how these large and heavy ions can cause interference with m/z 2 and 3.

Line 28: "Clean" CH₄ should maybe be better defined (e.g., pure CH₄ in He).

Page 11291, line 1: Just to be clear, is this offset compared to the set-up with neither pre nor post-trapping?

Page 11293, lines 12-14: Just out of curiosity, why does it take so much longer? The actual additional trapping steps add only about a minute per run, if I read the procedure correctly. How many samples could you process with the old system?

Page 11294, line 22: I was not able to follow Equation A4, probably because it was not clear to me how t is parameterised. I assumed that a morning run would produce a positive first argument for theta and a negative second one (or vice versa) and an afternoon run the opposite. However, I got the same signs for morning and afternoon runs (this is assuming that an analysis day is centred on noon). Is t a fraction of a day or a running value since an arbitrary start of a measurement period?

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Page 11295, lines 5-6: The statement is unclear. Is the preferred setting with or without the diurnal drift correction?

Table 1: It would be helpful to see the n for the references, maybe listed in parentheses after the sigma values? I assume that the value of "0.9" for Saphir 4, column 6, is actually the sigma value for the current study (and should be in column 5)?

Fig. 1: I find it hard to tell steel and silica tubing apart based on the line thickness. It would also be helpful to have their abbreviations spelled out in the caption (I missed the definition of FS in the text). It would also be convenient for the reader to have the absorbents for the various traps listed in the figure or its caption, so they don't have to flip back and forth for this information.

Fig. 2: The red crosses for the integration limits are hardly visible.

Fig. 3: I think it would be very informative to have the integration limits for the H₂-of-CH₄ peak indicated in the chromatograms. I would move the details describing B34 into the main text.

Fig. 4: I guess the symbol for the fitted air references in the legend should be a red dot, not a black one? A colour other than magenta for the correction would be better distinguished from the red fit curve.

Fig. 5: I would find it informative to see the raw data plotted in here to get a sense how large the corrections are (I understand that there is the caveat that this would be the total correction while the plots focus on the two individual corrections, but the plotted values include the total correction anyway).

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 11279, 2013.