Answers to comments by referee 1 on article "Improving accuracy and precision of ice core δD(CH_4) analyses using methane pre- and hydrogen post- pyrolysis trapping and subsequent chromatographic separation" by M. Bock et al.

Comments by referee 1 (R1) are reproduced in normal font, our answers appear *italic (A)*.

We kindly thank referee 1 for the comments which will lead to a clearer manuscript.

R1: Throughout the entire manuscript D or dD must be replaced by 2H and d2H since in its current form this manuscript does not meet IUPAC guidelines and recommendations with regards to nomenclature. According to IUPAC's recommendations (IUPAC: Nomenclature of Inorganic Chemistry. IUPAC Recommendations 2005, RSC Publishing, Cambridge, UK, 2005) heavy isotopes of hydrogen should be written as 2H (and 3H) rather than as D (and T).

A: We chose to write D as we feel that most of our readers are used to this. As Todd Sowers (referee 3) also prefers usage of D we would like to leave the decision to the editor.

R1: Page 11285, lines 22-25: (1) Which advantage holds this method of peak detection over peak detection based on start and end slope thresholds? (2) Has this fixed peak width method been validated (= proven to yield accurate results) and, if so, how? Please, provide supporting information.

A: (1) For normal peak shapes there is no advantage (besides a small gain in processing speed, as no derivative of the time series has to be calculated).
(2) We thought that through Table 1 and Fig. 6 enough information is presented to support the view that the system did not change in a measurable way concerning accuracy. However, we did now evaluate all data of 2013 again using slope thresholds for peak integration limits (e.g. Ricci et al. 1994). Using the same calibration procedure and parameters as presented in the discussion paper the values for Boulder (recent air) and for Saphir (reduced CH4) are heavier by 0.2 permil and 0.2 permil, respectively. Saphir measured via the melt water filled sample cylinder was lighter by 0.1 permil when using the slope criteria. Note that these differences are insignificant and much smaller than our reported numbers concerning precision and accuracy. Precision of samples and references did not show systematic effects comparing slope versus fixed peak width methods and was the same for all evaluations within 0.1 permil. We will add a sentence on the outcome of these re-evaluations:

"This choice is not critical as an alternative peak evaluation using the often used start and end slope criteria lead to the same results within the given error limits."

R1: Page 11286, lines 9-10: The authors ought to discuss the causes for the observed signal (=sample amount) dependency of measured 2H abundance values. Assuming the IRMS instrument used in this study is isotopically linear when tested with e.g. varying amounts of pure H2 gas or water (such as VSMOW) the cause for this observed non-linearity must be related to a process or combination of processes up-stream of the IRMS.

A: Yes, this is indeed the case and we will add this clarifying information at the respective sections: The H3+ factor did not change considerably compared to Bock 2010 RCM. During processing of chromatograms the H3+ correction is performed. So the signal dependency due to the mass spectrometer is factored out before the calibration routine. Observed signal dependency at this stage is due to any process before the mass spectrometer, e.g. pyrolysis conditions, time shift....
We add:

“We note that the H3+ factor did not change compared to Bock et al. 2010 and is accounted for during evaluation of chromatograms. Hence, residual signal dependency is due to processes up-stream of the mass spectrometer (e.g. pyrolysis conditions).”

R1: Page 11287, lines 5-10: While articles are cited with regards to how "Air Controle" was cross-referenced to VSMOW, a brief statement should be included confirming that scale calibration of its stated d2H value to the VSMPW/SLAP scale was indeed based on a 2-point calibration using e.g. VSMOW and SLAP.

A: We can confirm that “Alert”, our primary standard, was calibrated at IUP in Heidelberg based on a 2-point calibration. This is stated in the Poss 2003 reference, however, as this is in German we add another reference, Marik 1998, who is explaining (in English) the used 2-point calibration routine. We add this information in the revised text. Please see also the comment by referee 3 and our answers there.
(Ref: Marik, T., Atmospheric d13C and dD Measurements to Balance the Global Methane Budget, PhD thesis, University of Heidelberg, 1998).

R1: Page 11290, lines 15-17: Why speculate? Ion traces presented in all panels of Fig. 3 show quite clearly the detrimental effect any presence of CH4 or Kr in the ion source would have on isotope ratio measurement of m/z 3 / 2 and thus on d2H values.

A: This is true for our system. However, we refrain from transferring the effect observed with our set-up (Isoprime 100, Elementar, standard edition for CO2 and H2 (additional m/z 3 cup behind electrostatic filter)) to any other mass spectrometer. However, we changed the wording in line with the reviewer comment to:

”While we stress that this effect does not have an influence on our δD(CH4) analyses due to the post pyrolysis gas chromatographic separation, we speculate that the observed effects may also occur in a system where H2 and other species are simultaneously present in the mass spectrometer, potentially leading to biases in δD(CH4) as a function of the pyrolysis conditions and/or e.g. the CH4/Kr ratio as is the case for δ13CH4 (Schmitt et al., 2013a).“