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*Interactive comment on* "Real-time analysis of $\delta$<sup>13</sup>C- and $\delta$D-CH<sub>4</sub> in ambient air with laser spectroscopy: method development and first intercomparison results" *by* S. Eyer et al.

**S. Eyer et al.**

simon.eyer@empa.ch

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We would like to thank the two Referees, Hinrich Schäfer and Murray Hamilton for taking the time to read our manuscript and for their helpful comments and suggestions. These have been addressed individually. Each reviewer comment is followed by the replies and the proposed changes in the text are indicated with "".

Referee #1 (Hinrich Schaefer)

Specific comments: 1) Abstract (8927; 19-23): I find the current wording confusing

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as the reader is not yet familiar with the details of the remaining offset between various examined techniques after correcting to a standard measurement. I suggest replacing "Thus, the intercomparison also reveals ..:" with "Remaining inter-laboratory differences reveal . . ." or similar wording.

The authors agree that the current wording might be misleading and replaced the sentence by: "This also displays the potential to improve the interlaboratory compatibility based on the analysis of a reference air sample with accurately determined isotopic composition."

2) Introduction: (8927; 26 – 8928; 2): The WMO/GAW newsletter is arguably not the best reference here as it does not provide citations for individual findings. For example, an appropriate citation for the pre-industrial CH4 concentration could be C. MacFarling Meure, et al., Law Dome CO2, CH4 and N2O ice core records extended to 2000 years BP. Geophysical Research Letters 33 (2006).

The authors agree that the referenced WMO/GAW GREENHOUSE GAS BULLETIN does not present indi-vidual findings, but globally averaged mole fractions of greenhouse gases. To highlight this fact the wording "globally averaged" was added to the sentence: "Its globally averaged mole fraction has increased from around 722 ppb . . ."

In addition the suggested citation was added to the reference list: C. MacFarling Meure et al. Law Dome CO2, CH4 and N2O ice core records extended to 2000 years BP. Geophysical Research Letters, 33, L14810, doi:10.1029/2006GL026152, 2006.

3) 2.1.2.: (8931; 28) (also 8932; 12-13 and 8933; 24-25): please provide additional information on the geom-etry of the stand-off so that the reader can fully understand its function. From Fig. 1 it seems to be cylindrical. However, it is not clear whether it has a flat "bottom" surface that is pressed against the copper heat sink for better thermal contact. Also, the attachment of the spring and the position of the heat foil are unclear. A specific figure may be helpful; if the reader is referred to earlier methods papers for these details please do so explicitly.

The authors agree that the detailed geometry of the stand-off, including positioning of the spring is not given in the manuscript. Therefore a number of technical details were added to the following sentences:

Page 8931 Line 27 ff: "The tubing is curled around a custom-made cylindrical aluminium standoff (outer di-ameter 70 mm, height 28 mm) with an optimized wall thickness of 0.5 mm. "

Page 8932 Line 12 ff: "The contact pressure is adjusted to 100 N using a chromium-steel corrugated spring (WF-8941-SS, Durovis AG, Switzerland) placed centrically between actuator and standoff."

Page 8932 Line 14 ff: "The flat bottom surface of the aluminium standoff and the copper cold-plate were pol-ished and coated with a thin layer of . . .."

Page 8933 Line 23 ff: "Then, the trap temperature is stepwise raised to 145 K and 175 K by heating with a round flexible polyimide heat foil (diameter 62.2 mm, 100 W, HK5549, Minco Products Inc., USA) placed centrically at the bottom of the aluminum standoff and controlled by a PID temperature controller (cTron, Ju-mo Mess- und Regeltechnik AG, Switzerland)."

4) (8932; 3): the trap temperature is considerably lower than Cryo-traps with the same absorbent (Hayesep D) that are used in pre-concentration units for IRMS measurements of $CH_4$ isotopes (typically 130 – 150 K). The issue comes up again later when the co-desorption of $O_2$ with $CH_4$ is discussed. The wording in the paragraph here suggests that (break-through?) tests established the necessity for 100 K. It may be of inter-est to the reader to see details of such tests, given the fine balance between quantitative trapping of $CH_4$ and avoidance of co-trapping of interfering gases, in this case particularly $O_2$.

The authors agree that the balance between quantitative trapping of $CH_4$ and co-adsorption of $O_2$ is an important consideration. However, the optimum trap temper-

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ature for which quantitative adsorption is assured strongly depends on the given experimental parameters, e.g. trap and standoff geometry, cold plate temperature, and gas flow. Therefore, we consider more useful to mention the range of operating conditions, rather than give lengthy details about tests, which would be very specific to our experimental configuration. Regarding the considerably lower trap temperature compared to IRMS measurements, it is easily explained by the much higher flow rate of ambient air in the presented experimental setup of 900 ml min-1. The breakthrough volume at 101 K trap temperature was already mentioned on page 8943 Line 7 – 8. To highlight the fact that higher trap temperatures are not sufficient for quantitative CH4 adsorption at high flow rates the following sentence was added to the manuscript: page 8943 Line 10 ff:

". . ., was below 0.5 ppb (G1301, Picarro Inc., USA). Tests with higher trap temperatures (111 K) indicated de-tectable CH4 breakthrough at much lower adsorption volumes of 6.1 L at a flow rate of 900 mL min-1."

5) 2.1.3.: What is the minimum duration of a trapping-desorption-conditioning cycle? I understand that an analytical cycle will take longer and include the measurements of standards as discussed later, but the length of the trapping cycle itself is still of interest.

The authors agree that it would be interesting for the reader to know the length of the trapping cycle and added the respective information together with a new Figure describing the workflow during preconcentration on page 8933 Line 1 – 3:

". . . into three main phases as depicted in Fig. 1: CH4-adsorption (phase I, 27 min), CH4-desorption (phase II, 13.5 min) and trap conditioning (phase III, 5 min)."

6) 2.1.4.: Are the described changes to the laser instrument made only to one custom-made instrument used in this study or did the development feed back to the manufacturer of the precursor model (Aerodyne Re-search Inc.)? That is, is an instrument as described commercially available (or will it be)?

The hardware modifications and improvements were applied to an existing commercial spectrometer (QCL-76-D, Aerodyne Research Inc., USA) and were accomplished at Empa independently from the manufacturer. Instrumental developments at Aerodyne Research Inc. are independent from research going on at Empa; therefore it seems inappropriate to comment on activities within this company.

7) 2.2.1.: The first paragraph (8936; 9-13) is hard to follow because technical details on CG1 and CG2 are provided later. For example, it is not yet clear how two different tanks can yield "three different types of cali-bration gases" because the dilution system has not yet been introduced. The description of the calibration and target gases so far provided in 2.3. should be moved ahead of this paragraph because the reader needs that information to understand the design of the measurement cycle.

The authors agreed and moved the previous section 2.3 (now 2.2.1) "Calibration gases and target gas" ahead of the previous section 2.2.1 (now 2.2.2) ""TREX-QCLAS".

8) (8936; 10): Fig. 4 shows triplicate measurement of the analysed sample gas in one measurement cycle. Are the three individual results averaged?

No, the individual ambient air samples are preconcentrated and analysed. To under-line this fact the following text was added to the legend of Figure 4: ". . . (A) three measurements of consecutively preconcentrated dis-crete ambient air samples, . . ."

9) 2.2.5.: (8939; 21): Sperlich et al. (2013) describe an analytical set-up developed and used at the University of Copenhagen. That system differs markedly from the one described here for MPI. The reference therefore does not seem correct.

The authors agree and deleted the reference of Sperlich et al. (2013). The reference "(Brand et al., in prepa-ration)" was added instead on page 8939 Line 21.

10) (8940; 16-20): Is it possible to provide a precision measured for 10 repeats of standard air? That way, the stated precision would be directly comparable to UU and RHUL.

Authors: Calibrated data over years (as given by MPI-BGC) is a much more meaningful measure of system perfor-mance. Nevertheless, in the context of the data provided by UU and RHUL, the corresponding values for MPI-BGC was added on 8940 Line 20 ff: "The precision for 10 repeated measurements of standard air is typ-ically 0.07 ‰ (d13C) and 0.7 ‰ (dD)."

11) 2.2.6. (8941; 3): Can you provide either the volume of the container/bag that the sample is expanded from or the typical resulting pressure in the 75 cc sample loop? That would give a better estimate of the ac-tually analysed sample volume.

The authors added the required information to page 8941 Line 3 ff: "The 75 cm3 sam-ple volume is evacuated up to the solenoid valve directly before the bag valve, then the air flows from the bag into the sample volume maintaining ambient atmospheric pressure. This air is then pushed through the preparation system with a flow of helium gas set to a pressure of 758 hPa."

12) 2.3. As mentioned before, I recommend moving this paragraph ahead of 2.2.1. so that the reader can follow the design of the TREX-QCLAS cycles right away. Please also provide details on the dilution system for CG1 and CG2.

Authors: See our reply on comment 7 of reviewer #1. In addition one sentence was reformulated and one sentence added:

"The calibration gases CG 1 and CG 2 were prepared at Empa from pure fossil (99.9995 %, Messer, Switzerland) and biogenic CH4 (> 96 %, biogas plant Volketswil, Switzerland), diluted with high-purity syn-thetic air. The exact amounts of added CH4 were determined using a high precision flow measurement de-vice (molbox1, DH In-struments Inc., USA), and the dilution with synthetic air was controlled gravimetrically (ID 3, Mettler Toledo GmbH, Switzerland)."

13) (8941; 10-13): The fact that CG1 is a mixture of fossil and biogenic gas becomes clear only from Table 1. The resulting d13C-CH4 value of the mix for CG1 is not ideal

because it is more 13C-enriched than ambient air, i.e. CG1 and CG2 don't cover the range of measured d13C-values (Fig. 9). Given that CG1 is very close in d13C-CH4 to ambient air possible non-linearity problems are likely small or non-existent but the possibility of impacts on the results should be discussed. The same is true for dD (although in that case the atmospheric value cannot be achieved by mixing of fossil and biospheric sources).

The authors agree that it is not ideal that the CH4 isotopic composition of CG1 and CG2 do not cover the range of measured isotopic values (d13C, dD-CH4). For d13C-CH4, the difference between CG1 and the target gas (TG) is small around 1.4 ‰ while for dD it is considerably larger with around 60 ‰ (between CG2 and TG). This was optimized in a recent follow-up study by the addition of isotopically pure CH3D (T. Röckmann et al., manuscript in preparation). In addition, isotope ratios of CH4, and also CO2 and N2O analysed by QCLAS were found to be linearly dependent on delta values (Wächter et al., Optics Express, 2008; Tuzson et al., Applied Physics, 2008). Nonetheless, a sentence was added to page 8941 Line 18 ff:

"It should be noted that the isotopic composition of the measuring gas is outside the range covered by the calibration gases CG1 and CG2 for d13C and dD-CH4, which may create problems for analytical techniques with a non-linear response to isotope ratios. This, however, is assumed to be compensated by a correction of results of all analytical techniques/laboratories for the offset in the target gas between assigned value determined by MPI and respective measured values."

14) (8941; 18): Sperlich et al. (2012) describe a method for producing exactly quanti-fied CH4 isotope stand-ards and Sperlich et al. (2013) describe an analytical set-up for d13C-CH4 analysis. Both studies were con-ducted at the University of Copenhagen. Can you please clarify how the work described in these publications relates to the MPI isotope calibration scale? Are the very tanks produced by Sperlich et al. (2012) used at MPI or how is the MPI scale traced back to primary standards?

Authors: The primary calibration performed by Peter Sperlich in Copenhagen was a first attempt to establish a primary calibration for methane in air isotope measurements. The preparation technique was a classical combustion procedure followed by dual-inlet measurements. The work was continued by Peter Sperlich at MPI-BGC in Jena using a completely different approach with a closer link to the primary standards NBS 19/LSVEC and VSMOW/SLAP. In this case, measurements were made in single-step on-line systems, allowing a much larger number of high precision measurements to be made. The Copenhagen gases were included in this effort. The final manuscript of this work will be submitted in January 2016 (Sperlich et al, in preparation). Therefore the following reference was added to page 8941 Line 18:

". . . Jena, Germany (Sperlich et al. 2012, 2013, Sperlich et al, in preparation)."

15) 3.2. (8945; 20): the offset of the UU IRMS data is still within combined uncertainties, so arguably no more significant than differences between TREX-QCLAS and MPI IRMS. Is the purpose of this sentence (and of the preceding one) to present the applied offset? If so, were data sets with "insignificant differences" still offset corrected? Offset corrections for differences within combined uncertainties have the potential to create, or contribute to, offsets in the results discussed in Sect. 3.4. This is a minor point given that all offsets (except OA-ICOS) are small, but the authors may choose to clarify this issue.

The authors agree that the correction for an "insignificant difference" in dD-CH4 for the target gas between UU and MPI may have created the offset between TREX-QCLAS (Empa) and IRMS (UU) results in dD-CH4 for ambient air displayed in section 3.4. To clarify this issue a sub-sentence was added to page 8947 Line 15 ff:

". . . the applied analytical techniques. These differences in IRMS results of Utrecht University have been introduced by a -2.3 ‰ offset correction based on analysis of the target gas. In summary, the applied offset correction based on the pressurized air target gas ..."

16) (8947; 4-8): the sentence understates the discrepancy between CRDS and other measurements. The following sentence mentions specific times of CRDS drift relative to other values but no further comments are made. Even if the authors cannot provide further insight as to the reasons, this is not a trivial finding given that CRDS instruments are relatively cheap and easily deployed. The potential for erroneous results from more widely used CRDS analyses is something the community should be aware of.

Authors: As the main focus of the presented manuscript was on the development and validation of the TREX-QCLAS technique no further tests were conducted to investigate CRDS drift effects.

17) (8947; 20-24): to verify if differences in sampling time affect the comparability of the various data sets it would be instructive to provide cross-plots or simply correlation coefficients between isotopic differences on one hand and sampling time or CH4 mole fraction on the other.

The authors checked for the suggested correlations, but given their low R2 values (0.2 – 0.3), we decided to remove the respective statement regarding the assumed bias due to temporal changes in the CH4 isotopic composition of the analyte gas.

18) 3.5. (8948; 12-20): this paragraph would benefit from some more detail, as it is the section that demonstrates the suitability of the new technique to capture emission events. I recommend labeling the CH4 mole fraction, d13C-CH4 and dD-CH4 data points associated with the 19th-20th June emission event in Fig. 9. From the presented material it is not clear if the emission event (a single datum) is marked by extraordinary isotope values as well as high mole fraction. The datum in question should also be identified in Fig. 12. Assuming that this point is the one that falls within the isotopic range typical for landfills, a short discussion how that value may also be derived by mixing of biogenic and fossil fuel CH4 and why this is a more plausible scenario than pure landfill emissions is needed. It is also true that the source attribution for the 19th-20th June without the event data is distinct in d13C-CH4 (more13C-depleted) from the

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other biogenic sources, which is not discussed. Finally, how do source reconstructions from CRDS data compare? Do they provide similar estimates as the other instruments for the periods when CRDS doesn't drift (e.g., 8th-9th June) and how far off are the results during drift periods? While the focus of this study is the new TREX-QCLAS technique, CRDS instruments are much more readily available and insights into their capabilities are therefore important.

The authors agree to improve the visibility of the short emission event (captured by only one measurement point) on 19th to 20th June and label the respective data point in Figure 9 (Figure 2 in this response). Additionally a sentence is added in the respective caption:

"The data points capturing a distinct pollution event with a short duration on 20 June are marked with red circles (see text for more details)."

Following the reviewer suggestion, we estimated the source contributions to this singular pollution event by using a simple mass balance calculation. The measured values are best described by assuming a source mixture containing $\sim$ 40% microbial, i.e. 276 ppb CH4 (-61.5‰ d13C and -372‰ dD, derived by Keeling analysis) and $\sim$60% fossil, i.e. 423 ppb CH4 (-37.2 $\pm$1.5‰ d13C and -152 $\pm$11‰ dD) origin diluted in clean background air with 1900 ppb CH4 (-47.5‰ d13C and -81‰ dD). For a short discussion an additional text was added to page 8948 Line 18 ff:

". . . suggesting significant contributions of CH4 emissions from a local fossil gas source process. This short lasting (10-20 min) CH4 emission event was also confirmed by measurements at the nearby monitoring station of the Swiss Air Pollution Monitoring Network (NABEL), showing a sudden increase in CH4 mole frac-tions above 3000 ppb. Using a simple mass balance calculation and clean background air with 1900 $\pm$ 15 ppb CH4 with isotopic composition of -47.5‰ for $\delta$13C and -81‰ for $\delta$D-CH4 as reported by Bergamaschi et al. (Bergamaschi et al., JGR, 105, 2000), it is rather straightforward to estimate the isotopic signature of this singular event. Thus, the measured values are

best explained by an emission source enriched in 13CH4 and DCH3 ($\sim$-37.2 $\pm$ 1.5‰ for $\delta$13C and $\sim$-152 $\pm$ 11 ‰ for $\delta$D) contributing up to 60% to the observed increase in the CH4 mole fraction. The remaining 40% is attributed to microbial sources with isotopic signatures repeatedly determined during the campaign, i.e. -61.5‰ for $\delta$13C and -372‰ for $\delta$D-CH4 (see also Table 3). Alt-hough, the estimated source signature values agree with fossil origin, it should be noted that the analysis relies only on a single data point. This result, however, is plausible, as no landfill site is situated in the vicinity of the sampling location."

The authors agree and have derived source signatures from the CRDS data by Keeling analysis. The values are given in Fig 3 of this response. We will, however, only include the rows with an X in the first column to Table 3 of the manuscript (the first column with the X will be deleted).

In addition the authors added a few sentences on page 8948 Line 25 ff to discuss source signatures derived from CRDS data:

". . . of the linear regression (Table 3). Source signatures derived from the CRDS data display a high temporal coverage, but only in four cases the Keeling plot regression analysis lead to reasonable correlations (R2 >0.5) and thus meaningful source esti-mates. For all other cases with R2 below 0.5, the CRDS based signatures deviate significantly from the TREX-QCLAS and IRMS results. In the context of the present study, the increased temporal coverage alone does not provide any additional informa-tion, while the unavailability of $\delta$D information is a serious limitation with respect to the interpretation of the data."

Technical comments:

19) - 25): Done

26) (8943; 17-20): Please check style/grammar of this sentence, i.e.: ". . . a fraction of O2 remained on the trap is desorbed. . ."

The authors changed the sentence to: "In parallel to CH4, also bulk air components such as O2 and N2 are co-desorbed from the trap. Due to the much lower boiling point of oxygen (90 K) relative to nitrogen (77 K), the O2 mixing ratio in the absorption cell after preconcentration is increased to 40$\pm$2%."

27) - 29): Done

30) Fig. 1: please provide a legend; symbols for different types of valves and others (circled crosses or triangles) are not self-explanatory.

The authors agree and added a legend to figure 1 (See figure 4 of this response).

31) Fig. 6: typo in caption: remainder (or residual), not "reminder".

Done

32) Fig.12: the green field should be labelled "Biomass burning", not just "Biomass". Arguably, introducing the term "thermogenic" would be more specific than "fossil" as well, given that biogenic CH4 can be emitted from natural gas sources or ancient reservoirs like methane hydrates or permafrost (admittedly the latter are not of concern for this study). Indicating a mixing path between microbial and thermogenic emissions would illustrate the argument that the event datum is the result of simultaneous emissions.

The authors agree and replace "Biomass" by "Biomass burning" and "Fossil" by "Thermogenic".

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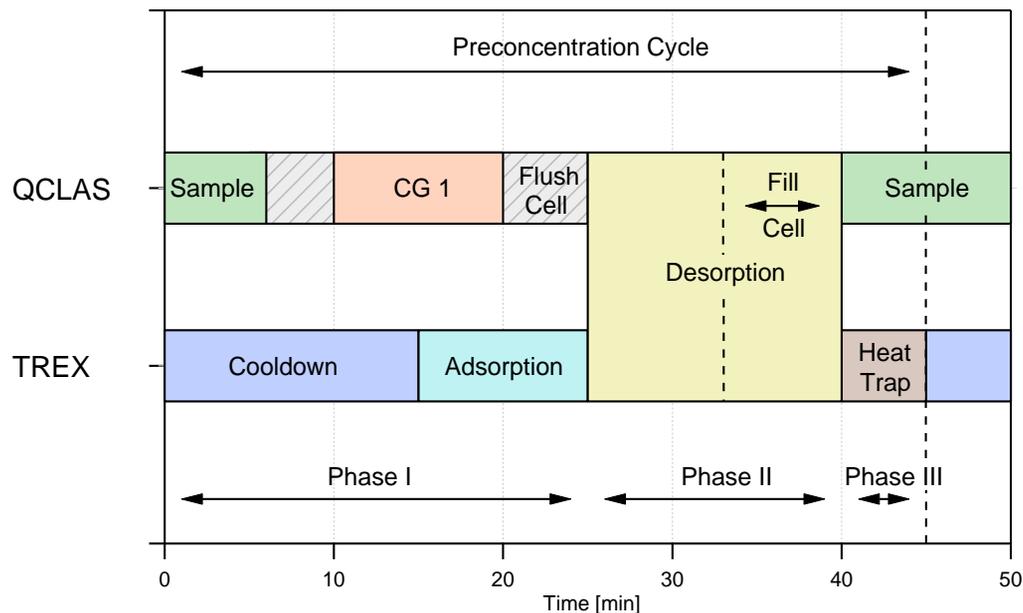**Fig. 1.** Workflow of QCLAS (top) and TREX (bottom) during a complete measurement cycle consisting of three phases: CH4-adsorption (phase I), CH4-desorption (phase II) and trap conditioning (phase III). ...

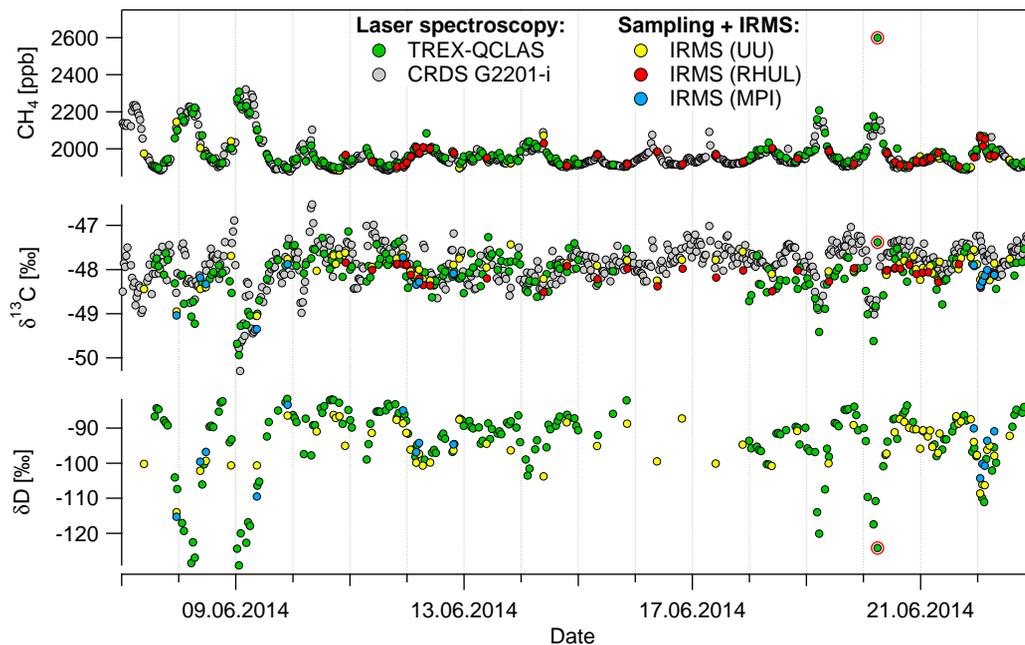**Fig. 2.** CH 4 mole fractions and isotopic composition analyzed during the interlaboratory comparison campaign in real-time by the laser spectroscopic techniques: TREX-QCLAS (CH 4 , d 13 C, d D), CRDS G2...

| Included in Publication | System | Time period (12:00 – 12:00) | #Points | $CH_4^{Max}$ ppb | $\delta^{13}C$-$CH_4$ [‰] | $\delta D$-$CH_4$ [‰] | $R^2$-$\delta^{13}C$ | $R^2$-$\delta D$ |
|---|---|---|---|---|---|---|---|---|
|  | CRDS | 05.-06.06.2014 | 22 | 2158 | -50.2 ±2.5 |  | 0.05 |  |
|  | CRDS | 06.-07.06.2014 | 41 | 2236 | -52.4 ±1.1 |  | 0.30 |  |
| X | TREX-QCLAS | 07.-08.06.2014 | 18 | 2222 | -55.1 ± 1.2 | -368 ± 13 | 0.72 | 0.97 |
| X | CRDS | 07.-08.06.2014 | 35 | 2228 | -50.2 ±0.9 |  | 0.16 |  |
| X | TREX-QCLAS | 08.-09.06.2014 | 18 | 2308 | -57.9 ± 0.6 | -351 ± 7 | 0.95 | 0.99 |
| X | CRDS | 08.-09.06.2014 | 35 | 2321 | -58.8 ±1.3 |  | 0.64 |  |
|  | CRDS | 09.-10.06.2014 | 36 | 2103 | -46.0 ±3.3 |  | 0.01 |  |
|  | CRDS | 13.-14.06.2014 | 31 | 2089 | -50.0 ±2.2 |  | 0.03 |  |
|  | CRDS | 15.-16.06.2014 | 36 | 2076 | -46.5 ±1.8 |  | 0.02 |  |
|  | CRDS | 16.-17.06.2014 | 35 | 2091 | -40.7 ±2.0 |  | 0.25 |  |
| X | TREX-QCLAS | 18.-19.06.2014 | 18 | 2208 | -57.2 ± 1.3 | -344 ± 12 | 0.78 | 0.97 |
| X | CRDS | 18.-19.06.2014 | 35 | 2147 | -58.7 ±1.0 |  | 0.78 |  |
| X | TREX-QCLAS | 19.-20.06.2014 [a)] | 17 | 2599 | -49.7 ± 2.1 | -264 ± 18 | 0.02 | 0.85 |
| X | TREX-QCLAS | 19.-20.06.2014 [b)] | 16 | 2176 | -61.5 ± 1.3 | -372 ± 12 | 0.89 | 0.97 |
| X | CRDS | 19.-20.06.2014 | 35 | 2151 | -60.2 ±1.3 |  | 0.74 |  |
| X | TREX-QCLAS | 21.-22.06.2014 | 15 | 2067 | -55.4 ± 1.7 | -374 ± 12 | 0.63 | 0.98 |
| X | IRMS UU | 21.-22.06.2014 | 10 | 2072 | -52.4 ± 1.9 | -351 ± 19 | 0.34 | 0.94 |
| X | IRMS MPI | 21.-22.06.2014 | 6 | 2072 | -54.7 ± 1.9 | -356 ± 20 | 0.74 | 0.98 |
| X | CRDS | 22.-23.06.2014 | 37 | 2092 | -55.5 ±0.8 |  | 0.71 |  |

**Fig. 3.** Overview of all the d 13 C-CH 4 and d D-CH 4 source signatures derived using the Keeling plot approach for the given time periods.
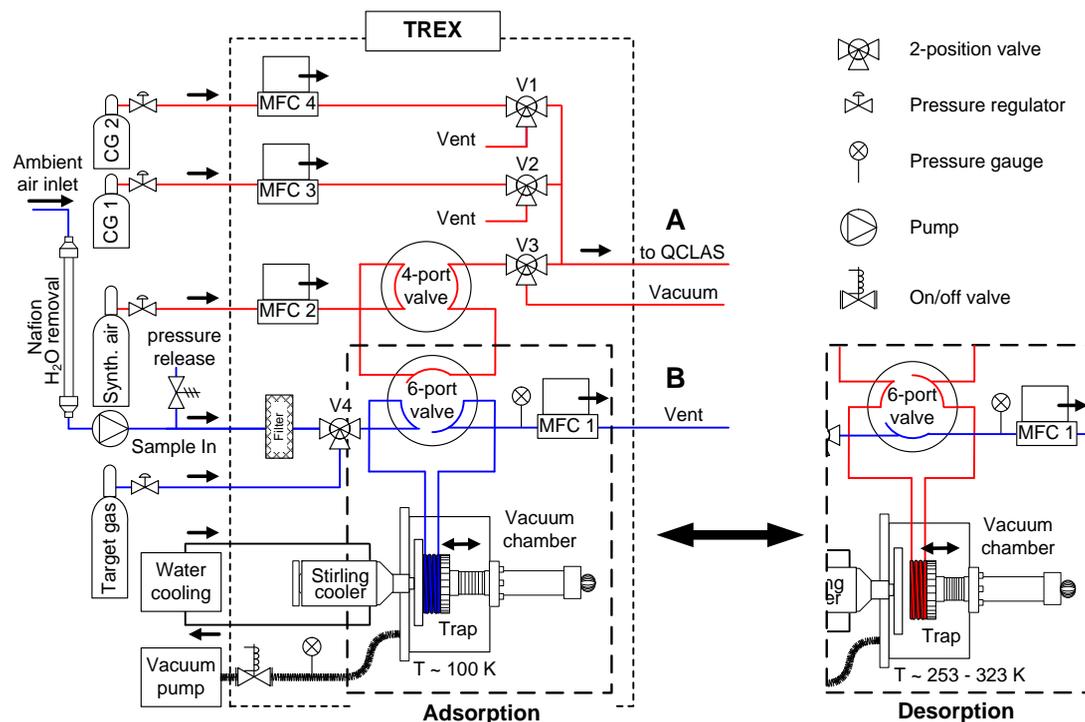
**Fig. 4.** Schematics of the preconcentration unit (TREX). The blue lines indicate the flow of sample air and TG, i.e. ambient air $CH_4$-mole fractions, while red lines represent the flow of calibration gases an