Development and evaluation of a suite of isotope reference gases for methane in air

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Abstract. Measurements made by multiple analytical facilities can only be comparable if they are related to a unifying and traceable reference. However, reference materials that fulfil these fundamental requirements are unavailable for the analysis of isotope ratios in atmospheric methane, which led to misinterpretations of combined data sets in the past. We developed a method to produce a suite of standard gases that can be used to unify methane isotope ratio measurements of laboratories in the atmospheric monitoring community. We calibrated a suite of pure methane gases of different methanogenic origin against international referencing materials that define the VSMOW and VPDB isotope scales. The isotope ratios of our pure methane gases range between −320 and +40 ‰ for δ2H-CH4 and between −70 and −40 ‰ for δ13C-CH4, enveloping the isotope ratios of tropospheric methane (about −90 ‰ and −47 ‰ for δ2H-CH4 and δ13C-CH4, respectively). We estimate combined uncertainties for our δ2H and δ13C calibrations of <1.5 ‰ and <0.2 ‰, respectively. Aliquots of the calibrated pure methane gases have been diluted with methane-free air to atmospheric methane levels and filled into 5-L glass flasks. These synthetic gas mixtures comprise atmospheric oxygen/nitrogen ratios as well as appropriate argon, krypton and nitrous oxide mole fractions to prevent gas-specific measurement artefacts. The resulting synthetic atmospheric reference gases will be available to the atmospheric monitoring community. This will provide unifying isotope scale anchors for isotope ratio measurements of atmospheric methane so that data sets can be merged into a consistent global data frame.
1 Introduction

Isotope ratios of trace gases in the present and the past atmosphere (e.g. from ice cores) are an emerging tool to study the biogeochemical processes that cause the variation of CH₄ in the atmosphere (Stevens and Rust, (1982), Lowe et al., (1994), Sapart et al., (2012), Sperlich et al., (2015)). Recently, two conflicting publications highlighted i) the interpretative power when data sets from multiple laboratories are combined for spatio-temporal analysis of CH₄ isotope ratios (Kai et al., 2011) and ii) the pitfalls when differences due to laboratory offsets are mis-interpreted as spatial variability of CH₄ sources (Levin et al., 2012). Levin et al., (2012) identified calibration offsets between three laboratories by comparing their long term observations in Antarctica where the carbon isotopic composition of CH₄ is assumed to be free of spatial gradients. However, this technique is a temporary work-around that excludes the use of data sets from laboratories without a history of observations in Antarctica or a traceable link to Antarctic observations. If a unique set of reference material were available to all laboratories that measure isotope ratios of atmospheric CH₄, the science community would be able to combine the available measured data sets to investigate spatio-temporal variations. However, such a sustainable solution that unifies the measurements of all laboratories has not been established.

The lack of unique reference gases has long been recognised in the literature on CH₄ isotope ratios, ranging from pioneering papers (e.g. Craig (1953), Schiegl and Vogel, (1970)) to recent technical publications on isotope ratios in atmospheric CH₄ (e.g. Sperlich et al., (2013), Tokida et al., (2014), Eyer et al., (2015)) as well as papers that present and interpret such data (Levin et al., 2012). So far, laboratories have either developed methods to calibrate purified CH₄ against international reference material of different physico-chemical properties (e.g. Schiegl and Vogel, (1970), Stevens and Rust, (1982), Dumke et al., (1989), Levin et al., (1993), Lowe et al., (1994), Quay et al., (1999), Sperlich et al., (2012)) or they reference their CH₄ samples to standards that were propagated from calibrations elsewhere (e.g. Bergamaschi et al., (1994), Brass and Röckmann, (2010), Bock et al., (2014), Schmitt et al., (2014), Rella et al., (2015), W.A. Brand 2015 pers. comm.). The diversity of referencing trajectories can lead to significant referencing offsets between the laboratories as shown by Levin et al., (2012).

Ghosh et al., (2005) established a method to harmonise isotope ratio measurements of atmospheric CO₂. Based on this method, the ISOLAB of the Max-Planck-Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, distributes a suite of reference gases, known as the “JRAS air set”, which is accepted as an isotope scale anchor by the community (WMO, 2012). Calibrating against the “JRAS air set” reduces laboratory offsets and helps reaching and maintaining the compatibility goal (Wendeberg et al., 2013).

This paper describes a method to produce isotope reference gases for atmospheric CH₄. The reference gases we produced bracket the isotopic ratios of tropospheric CH₄ and span over a large isotopic abundance range, which enables a two-point calibration to account for scale compression effects, thereby reducing the referencing uncertainty (Coplen et al., 2006). These isotope reference gases are produced from a well calibrated suite of CH₄ gases and will be made available from MPI-BGC. Our reference gases for CH₄ isotope ratios may help the community to reach the compatibility goals of 1 ‰ and 0.02 ‰ for δ²H-CH₄ and δ¹³C-CH₄, respectively (WMO, 2014).
2 Materials and Methods

The aim of this paper is to present the method that we use to calibrate and prepare isotope reference gases for CH₄ in air samples, as outlined in the flow diagram of Fig. 1. Our method is based on the initial calibration of two pure Master-CH₄ gases for their δ²H-CH₄ and δ¹³C-CH₄ isotope ratios against international isotope reference materials. The two Master-CH₄ gases are then used to calibrate a suite of further CH₄ gases. Once calibrated, aliquots of the pure CH₄ gases are diluted with CH₄-free air to atmospheric CH₄ mixing ratios. The resulting synthetic air standard can be distributed and analysed in a similar fashion as atmospheric samples by collaborating laboratories, following the Principle of Identical Treatment, PIT, (Werner and Brand, 2001).

Figure 1: Flow diagram of methodological steps to produce synthetic isotope reference gases for CH₄ in air. RM is the abbreviation for established international Reference Materials.

2.1 Gases and reference materials used in this study

Our study is based on a suite of CH₄ gases that differ in their commercial provider, methanogenic origin and isotopic composition. We identify our CH₄ gases by names as shown in Table 1. “Biogenic” and “Fossil” have been calibrated in a previous CH₄ referencing study (Sperlich et al., 2012) and are therefore of known isotopic composition. Treating these gases as unknowns in this study allows testing and evaluating the performance of the presented methods. Six other CH₄ gases were purchased from suppliers of commercial gases or laboratory equipment (Air-Liquide, Westfalen AG, Linde, Messer, Campro Scientific) and were used as purchased or as mixtures thereof. The purity level of all our CH₄ gases is 99.995% or higher.
Table 1: Gases used for this study. Note that Mike-1 and Martha-1 were created as gas mixtures but were topped up with further gases to create Mike-2 and Martha-2, respectively. Thus, Mike-1 and Martha-1 do not exist anymore.

<table>
<thead>
<tr>
<th>Gas name</th>
<th>Cylinder volume [L]</th>
<th>pressure [bar]</th>
<th>function in study</th>
<th>CH₄ source</th>
<th>gas supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Megan</td>
<td>10</td>
<td>lost</td>
<td>1st Master CH₄</td>
<td>fossil CH₄</td>
<td>Air Liquide</td>
</tr>
<tr>
<td>Merlin</td>
<td>10</td>
<td>190</td>
<td>2nd Master CH₄</td>
<td>fossil CH₄</td>
<td>Air Liquide</td>
</tr>
<tr>
<td>Mike-1</td>
<td>-</td>
<td>-</td>
<td>calibration CH₄</td>
<td>MPI mixture</td>
<td>MPI mixture</td>
</tr>
<tr>
<td>Mike-2</td>
<td>5</td>
<td>45</td>
<td>calibration CH₄</td>
<td>MPI mixture</td>
<td>Messer Griesheim</td>
</tr>
<tr>
<td>Merida</td>
<td>10</td>
<td>175</td>
<td>calibration CH₄</td>
<td>Unknown</td>
<td>Westfalen AG</td>
</tr>
<tr>
<td>Martha-1</td>
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<td>-</td>
<td>calibration CH₄</td>
<td>MPI mixture</td>
<td>MPI mixture</td>
</tr>
<tr>
<td>Martha-2</td>
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<td>165</td>
<td>calibration CH₄</td>
<td>MPI mixture</td>
<td>MPI mixture</td>
</tr>
<tr>
<td>Minion</td>
<td>3</td>
<td>150</td>
<td>calibration CH₄</td>
<td>Unknown</td>
<td>Messer Griesheim</td>
</tr>
<tr>
<td>Melly</td>
<td>50</td>
<td>193</td>
<td>calibration CH₄</td>
<td>Unknown</td>
<td>Westfalen AG</td>
</tr>
<tr>
<td>δ²H-Spike gas</td>
<td>0.4</td>
<td>2.5</td>
<td>spiking gas CH₃D</td>
<td>Campro Scientific</td>
<td></td>
</tr>
<tr>
<td>Fossil</td>
<td>30</td>
<td>2</td>
<td>calibration control</td>
<td>fossil CH₄</td>
<td>Air Liquide Denmark</td>
</tr>
<tr>
<td>Biogenic</td>
<td>30</td>
<td>2</td>
<td>calibration control</td>
<td>biogas plant</td>
<td>Biogas Plant</td>
</tr>
<tr>
<td>synthetic air</td>
<td>50</td>
<td>200</td>
<td>synthetic air matrix</td>
<td>Linde</td>
<td>Linde</td>
</tr>
<tr>
<td>Krypton</td>
<td>2</td>
<td>200</td>
<td>synthetic air matrix</td>
<td>Westfalen AG</td>
<td>Westfalen AG</td>
</tr>
<tr>
<td>Carina-1</td>
<td>50</td>
<td>200</td>
<td>isotope scale</td>
<td>Jena air</td>
<td>MPI-BGC</td>
</tr>
<tr>
<td>Carina-2</td>
<td>50</td>
<td>200</td>
<td>isotope scale</td>
<td>Jena air</td>
<td>MPI-BGC</td>
</tr>
</tbody>
</table>

“Megan” and “Merlin” were used as Master-CH₄ gases that were calibrated against international reference materials for their hydrogen and carbon isotopic composition. Table 2 summarises information on the applied reference materials.

Table 2: Reference materials used in this study. Column 1 and 2 show name and chemical formula, respectively. “RM” in column 3 indicates an international reference material while “ws” identifies local working standards. The δ²H and δ¹³C isotope ratios are shown in column 4 and 5, respectively, while column 6 and 7 list the sources and related publications of reference materials we used. We show the most recent values of reference materials as summarized by Brand et al., (2014). For MPI-BGC data the uncertainties correspond to the 95 % confidence limit of the error of the mean, i.e. the standard error of the mean, multiplied by Student’s t-factor. The * indicates an uncertainty estimate that is currently under investigation as explained in the main text.
2.2 Referencing CH₄ for δ²H against VSMOW/SLAP and against other CH₄ gases

We use a high temperature conversion elemental analyser (TC/EA) coupled to an IRMS (Delta Plus XL, Thermo Finnigan, Bremen, Germany) via an open split (ConFlo III, Thermo Finnigan, Bremen, Germany) to convert CH₄ to H₂ (+ carbon) and measure δ²H-CH₄ in pure CH₄ gases after the conversion to H₂ (Werner et al., 1999). This system is routinely used for the analysis of hydrogen and oxygen isotope ratios in water samples that are injected through a heated septum at (130°C) into a glassy carbon reactor where the H₂O is converted to CO and H₂ at temperatures above 1400°C (Gehre et al., 2004, Hilkert et al., 1999). In order to reference the hydrogen isotopic composition of pure CH₄ against international reference waters (VSMOW-SLAP scale), we inject pure CH₄ into the TC/EA using a two position 10-port valve (VICI, USA) that is configured as shown in Fig. 2. The outlet flow of this valve is routed through the septum also used for water injection so that the helium gas stream of 15 mL/min carries the CH₄ from the 1 mL sample loops into the TC/EA reactor. Typical CH₄ feed flow rates range between 2-3 mL/minute. The upstream plumbing can be configured so that every valve switch injects an aliquot of the same or of two alternating CH₄ gases into the reactor. Measurement sequences can now be created by injecting CH₄ gases manually and reference waters automatically (via injections through the septum from an autosampler) into the reactor, where both CH₄ and H₂O are converted to molecular hydrogen. Apart from the injection procedure itself, the generated H₂ of both CH₄ and international reference waters conforms with the Principle of Identical analytical Treatment (PIT) (Werner and Brand, 2001). The amounts of injected CH₄ and H₂O are adjusted in our experiments to achieve matching peak shapes and amplitudes during IRMS analysis in order to minimize H₂-factor variations between CH₄ and H₂O samples. The resulting peaks for CH₄ samples and reference waters are shown in Fig. 4. Following this method, we calibrated “Megan” and “Merlin” (Table 1) in three independent repetitions during three days against the in house standards “www-j1” and “BGP-j1”, which were independently calibrated against international reference waters VSMOW2 and SLAP2 (Table 2).
Figure 2: Configuration of two-position 10-port valve with plumbing for helium carrier gas, two ports to introduce the CH₄ sample and two 1-mL sample loops as indicated by thick blue lines. Note that vent 1 can be connected to CH₄ port 2 in order to introduce the same CH₄ gas with every injection. Sample loop 1 is vented through vent 1 for the injection of two alternating CH₄ gases.

The two sample loops attached to the 10-port valve (Fig. 2) can be fed by two different CH₄ gases. This configuration enables alternating measurements of unknown CH₄ against known CH₄ in an identical fashion. When used in this configuration, the previously calibrated “Megan” and “Merlin” served as known reference gases to calibrate the other CH₄ gases (Table 1) to the respective isotope scales. Additional injections of H₂O standards were used to control isotope scale contraction during δ²H-CH₄ analysis.

Because the δ²H-CH₄ range in our samples is very large (∼350 ‰, Table 3), sufficient control of potential scale compression effects is imperative (Renpenning et al., 2015). We achieve this by applying reference waters that span the full VSMOW2 to SLAP2 isotopic range from 0 to −427.5 ‰. The daily working reference waters (www-J1 and BGP-J1) cover a δ²H range of −67.0 to −187.1 ‰ (Table 2). Our suite of reference waters enables a multi-point calibration that largely envelopes the δ²H range of the CH₄ samples (Table 2 and 3).

In most routine isotope ratio measurements, samples are referenced against a standard of identical composition, following the principle of identical treatment (Werner and Brand, 2001). For example, measurement artefacts cancel when water samples are calibrated against reference waters. However, great care has to be taken when comparing two different materials, as is the case when calibrating CH₄ against reference waters. This is because standard and sample require material-specific attention to prevent isotope fractionation during analysis. Calibration errors may occur when i) only one of the two materials or ii) both...
materials are incompletely transported or converted, or when memory effects inside the sample conversion system are different for the respective materials. In order to rule out calibration artefacts due to the analysis of two chemically very different materials and in order to ensure that our method is suitable for quantitative analysis of both CH$_4$ and H$_2$O without isotope fractionation, we performed several series of experiments to optimise the reactor and septum temperatures, the compound-specific memory effects and the applied sample size as described in detail in Appendix 1.

The introduction of H$_2$ samples into the ion source of an IRMS leads to the formation of H$_3^+$ ions that are registered on the HD$^+$ detector, which is accounted for by the so called “H$_3$-factor correction” (Friedman, 1953), Sessions et al., (2001)). While the H$_3$-factor correction is experimentally determined and kept constant throughout a series of measurements, the H$_3^+$ formation may be dynamic over time. In order to minimise the impact of inaccurate H$_3$-correction between CH$_4$ and H$_2$O analysis, we matched the H$_2$ peak heights resulting from both CH$_4$ and H$_2$O injections around 5.5 ± 0.5 V. Typical peak widths were around 45 s and 60 s for H$_2$O- and CH$_4$-derived H$_2$ peaks, respectively. A typical chromatogram of the $\delta^2$H-CH$_4$ calibration including details on peak shape and background is shown in Fig. 3. This figure shows that both the CH$_4$-derived and the H$_2$O-derived H$_2$ peaks are of comparable height and width, which justifies the analysis of sample and reference material using the standard integration software (ISODAT, Thermo). We performed a range of experiments to test for systematic analytical effects that could impact on the isotope analysis of CH$_4$ and/or H$_2$O and used the results of these experiments to optimize the analysis. These experiments are described in detail in Appendix 1. The good control of peak shapes and the elimination of analytical artefacts allow for the conclusion that our method is suitable to calibrate CH$_4$ against reference H$_2$O with high precision and accuracy.
Figure 3: Chromatograms of δ²H-CH₄ calibration sequences using TC/EA-IRMS with traces of m/z 2 and m/z 3 shown in black and blue, respectively. The bottom panel shows an example of an entire calibration sequence which begins with 3 square-shaped peaks of pure H₂, followed by alternations of 3 to 4 H₂O- and 3 to 4 CH₄-derived H₂ peaks before the sequence ends with another 3 square shaped peaks of pure H₂. The top left panel enlarges 4 peaks that are derived from H₂O (peak # 6-7) and CH₄ (peak # 8-9), respectively. A zoom into baseline details of H₂O-derived peak # 7 and CH₄-derived peak # 8 is shown in the top right panel. Red lines indicate the sections used for peak integration (weak widths are 43 s and 59 s for H₂O- and CH₄-derived H₂ peaks) by the IRMS software.
2.3 Referencing CH₄ against LSVEC / NBS 19

We calibrated δ¹³C-CH₄ in pure CH₄ gases after conversion to CO₂ using an elemental analyser (EA 1100, CE, Rodano, Italy) coupled to an IRMS (Delta Plus, Thermo Finnigan, Bremen, Germany) through an open split (ConFlo III, Thermo Finnigan, Bremen, Germany). This system is routinely used for the analysis of ¹³C and ¹⁵N in samples with solid or liquid matrices (Werner et al., 1999, Brooks et al., 2003). For the CH₄ calibrations, we used the same 10-port valve assembly as described above (Fig. 2). We modified the EA autosampler to inject the CH₄ gas with a helium carrier gas stream of 10 mL/min through an extra 1/16” tube of 70/30 % Cu/Ni alloy into the oxygen plume region inside the combustion chamber of the EA (Fig. 4).

Figure 4: EA-IRMS system with additional inlet for gas injection into the combustion unit.

The plumbing of the system is designed so that gaseous and solid samples can be supplied to the same location inside the combustion reactor of the EA. All samples are oxidised at 1020°C (Werner et al., 1999) and experience identical analytical treatment after the combustion. After oxidation, the sample passes through a reduction reactor filled with elemental copper at 650°C to remove excess O₂ and to reduce NOₓ if present. The sample is dried using a combination of a Nafton™ dryer (Perma Pure LLC, Toms River, NJ, USA, not shown in Fig 4) and Mg(ClO₄)₂ before it is routed through a GC column that is held at 80°C (3m, 1/4”, Porapak PQS, CE instruments). The sample is then transferred into the IRMS through an open split.
Alternating CH$_4$ injections and applications of reference materials such as LSVEC, Mar-j1 and ali-j3 (Table 2) via an autosampler enable direct referencing of CH$_4$ gas to the VPDB isotope scale. We used this method to calibrate “Megan” and “Merlin” as Master-CH$_4$ gases (Table 1) over three independent measurement periods each. Alternating injections of a Master-CH$_4$ and unknown CH$_4$ gases were then used to calibrate all other CH$_4$ gases (Table 1) for $\delta^{13}$C. Two chromatograms resulting from both CH$_4$ and carbonate analysis using EA-IRMS are displayed in Fig. 5 and show very similar peak shapes for the analysis of both materials. Typical $m/z$ 44 amplitudes and peak widths were $\approx 7.4 \pm 0.2$ V and $101 \pm 1$ s for both materials, respectively.

Figure 5: Chromatograms of $\delta^{13}$C-CH$_4$ calibrations using EA-IRMS with traces for $m/z$ 44, 45 and 46 represented by green, brown and black lines, respectively. Analysis of CH$_4$ (Merlin) and Li$_2$CO$_3$ (LSVEC) are shown in the left and right-hand panels, respectively. Bottom panels show the entire chromatogram while the two top panels zoom into the baseline of the traces. The first three square-shaped CO$_2$ peaks stem from injections of pure CO$_2$ working gas while the tailing peaks result
from CH₄- and Li₂CO₃-derived CO₂ analysis. The two red lines in the top panel indicate the sections that the IRMS software uses for peak integration (101 s and 100 s for CH₄- and Li₂CO₃-derived CO₂ peaks, respectively).

5.2.4 Measurement uncertainty and error propagation

With the two-step calibration strategy approach the error treatment also has two major components. For the δ¹³C_VPDB calibration of the two Master-CH₄ gases Megan and Merlin we used the international reference materials NBS 19 and LSVEC with assigned δ¹³C_VPDB values +1.95 and −46.6 ‰, respectively (Coplen et al., (2006), Brand et al., (2014)). These were analysed within the same analytical sequences as the Master-CH₄ gases and used to position the δ¹³C-CH₄ values onto the international VPDB scale within every sequence by relating the δ¹³C-CH₄ value of each CH₄ peak to the known δ¹³C values of the reference materials. The final uncertainty for the Master-CH₄ gases is given as the standard error of the mean of each sequence, multiplied by t, Student’s factor for a 95 % confidence limit.

More recently, a variability between different LSVEC aliquots at the IAEA premises has been found which has been attributed to interaction with atmospheric CO₂ and water, leading to a small increase in δ¹³C_VPDB (S. Assonov, pers. comm.). The final δ¹³C_VPDB value assigned to the specimen used in our laboratory might therefore be subject to a (small) adjustment, which will directly affect the calibrated methane values. We have tentatively made allowance for the effect by including an estimated uncertainty of ±0.03 ‰ for the LSVEC specimen used in the BGC ISOLAB experiments (Table 2). A final adjustment can only be made when a suitable solution to this issue has been found, agreed upon and published.

Similar to the δ¹³C_VPDB calibration, the methane hydrogen isotopes have been calibrated using the international reference water samples VSMOW2 and SLAP2 with δ²H_VSMOW of 0.0 and −427.5 ‰, respectively. Both of these reference materials have small uncertainties of ±0.3 ‰ for δ²H_VSMOW (IAEA, (2009), Brand et al., (2014)). The uncertainties are included in the error values for the Master-CH₄ gases Megan and Merlin, which are otherwise obtained in an analogous fashion as described above: CH₄ and H₂O sample injections are made within the same sequence. The observed water δ²H values are then used to fix the δ²H-CH₄ results to the VSMOW/SLAP scale. Again, the final δ²H-CH₄ values for the Master-CH₄ gases are presented as the standard error of the sequence means, multiplied by t, Student’s factor for a 95 % confidence limit.

The secondary or “calibration” CH₄ gases have been directly analysed against the Master-CH₄ gases using identical procedures and equipment, switching the 10-port valve depicted in Fig. 2. The final errors evaluated for the gas-to-gas comparisons are obtained by the standard error of the calculated mean delta values, multiplied again by t, Student’s factor for a 95 % confidence interval. The uncertainty of the respective master methane gas is included in the combined error using standard error propagation. Possible scale contraction effects were treated routinely by measuring against a pair of reference water samples and applying a scale adjustment. This effect is part of the measurement uncertainty.
2.5 Producing synthetic isotope reference standards from pure CH$_4$ and CH$_4$-free air

The ISOLAB at the Max-Planck-Institute for Biogeochemistry operates a system to dilute pure CO$_2$ with CO$_2$-free air to atmospheric CO$_2$ mole fraction without isotopic fractionation (Ghosh et al., 2005). This system is referred to as ARAMIS and is used in this study to prepare atmospheric reference gases for CH$_4$. We dilute an aliquot of calibrated CH$_4$ with CH$_4$-free air to atmospheric CH$_4$ mole fractions (~2 ppm) in 5-L glass flasks with a final filling pressure of 1.8 bar absolute. The CH$_4$-free matrix air has been target-mixed from ultra-pure constituents. It contains N$_2$, O$_2$, N$_2$O and Kr at atmospheric mixing ratios. Krypton was added to this matrix air to account for the measurement artefact during GC-IRMS analysis of CH$_4$ for $\delta^{13}$C (Schmitt et al., 2013), so that the produced isotope reference gases reflect a natural air sample as closely as possible. A sensitive analysis using high-precision gas-chromatography yielded an upper limit for the CH$_4$ mixing ratio of 0.5 ppb. Further details on the matrix air and the krypton added are provided in Table 1. The $\delta^2$H and $\delta^{13}$C isotope ratios of CH$_4$ in the reference gases produced in the dilution experiments are measured with an average standard deviation (1σ) of 1.2 ‰ and 0.14 ‰, respectively, which is similar to the precision of the analytical system (1.0 ‰ and 0.12 ‰ for $\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$, respectively (W.A. Brand, 2015, pers. comm.) and suggests reproducible dilution of CH$_4$.

2.6 Comparison of isotope scales at MPI-BGI and IMAU

A new system to measure both carbon and hydrogen isotope ratios in atmospheric methane has recently been built at MPI-BGC, (W.A. Brand, pers. comm.). This system is referred to as iSAAC, in abbreviation for Isotope System for Analysing Atmospheric Constituents. iSAAC has been operational since 2012 with an external precision of 1.0 ‰ and 0.12 ‰ for $\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$, respectively, as determined using the performance chart technique (Werner and Brand, 2001) over a period of 3 years. We calibrated our measurements using atmospheric working standards referred to as “Carina-1” and “Carina-2” (Table 1). The “Carina” gases have been calibrated at the Institute for Marine and Atmospheric Research in Utrecht (IMAU), using the analytical setup described by Brass and Röckmann, (2010) and Sapart et al., (2011). The history of the isotope scale at IMAU is described in detail by Brass and Röckmann (2010). We arbitrarily chose “Carina-1” as master reference gas for the iSAAC system. While “Carina-1” and “Carina-2” agree well in $\delta^{13}$C-CH$_4$, their previously calibrated $\delta^2$H-CH$_4$ value differs by ~4 ‰. This offset has been confirmed as an artefact of the calibration at IMAU.

The synthetic isotope reference gases that were produced from previously calibrated CH$_4$ gases were analysed on iSAAC against “Carina-1”. The results of these measurements are compared to the calibration results of the pure CH$_4$ gases so that the differences between the calibrated isotope ratios and the measurements against “Carina-1” indicate the offset between the new and the previous isotope scales in Jena (Sect. 3.3).
3 Results

3.1 Results for Master-CH$_4$ gas calibrations on the international VSMOW and VPDB isotope scales

Our Master-CH$_4$ gases “Megan” and “Merlin” have been calibrated for their carbon and hydrogen isotope ratios against international reference material and in house working standards (Table 2). The results are shown in Table 3. “Megan” was used as Master-CH$_4$ gas for all initial experiments and calibrations until it was accidentally vented to ambient in May 2015. In order to compensate the loss, “Merlin” was lifted in reference hierarchy from calibration CH$_4$ gas to Master-CH$_4$ gas as successor of “Megan”. Therefore, Merlin was calibrated using two different methods, once against primary reference materials and once against a Master-CH$_4$ gas. Therefore, “Merlin” is listed twice in Table 3 with results that agree within the combined uncertainty.

Both “Megan” and “Merlin” are fossil CH$_4$ gases with typical dual isotope ratios for this source category (e.g. Quay et al., (1999), Mikaloff Fletcher et al., (2004)). The two Master-CH$_4$ gases are similar in $\delta^2$H-CH$_4$ with isotope ratios of $-168.0 \pm 0.6$ ‰ and $-165.7 \pm 0.6$ ‰, respectively. The calibrated $\delta^{13}$C-CH$_4$ isotope ratios of “Megan” and “Merlin” are $-40.75 \pm 0.07$ ‰ and $-39.07 \pm 0.07$ ‰, respectively.
Table 3: Results of CH$_4$ isotope calibrations. Each CH$_4$ gas is named in column 1 while its function is defined in column 2. Calibrated $\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$ values including combined uncertainties are listed in column 3 and 4, respectively. Note that results for “Merlin” are listed twice, once from its calibration against primary reference materials and once from calibration against Megan, the 1st calibrated Master-CH$_4$ gas. “Fossil” and “Biogenic” have previously been calibrated elsewhere (Sperlich et al., 2012). The results of the previous calibration are marked with (*) and are compared to the results of this method as discussed in the main text. Martha-1 and Mike-1 were intermittent gases used in the calibration comparison (Table 4) but were then mixed to be similar or more enriched in $\delta^2$H than tropospheric CH$_4$.

<table>
<thead>
<tr>
<th>Gas name</th>
<th>Function</th>
<th>$\delta^2$H-CH$_4$ [‰]</th>
<th>$\delta^{13}$C-CH$_4$ [‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Megan</td>
<td>Master</td>
<td>$-168.1 \pm 0.6$</td>
<td>$-40.75 \pm 0.07$</td>
</tr>
<tr>
<td>Merlin</td>
<td>Master</td>
<td>$-165.7 \pm 0.6$</td>
<td>$-39.07 \pm 0.07$</td>
</tr>
<tr>
<td>Merlin</td>
<td>Calibration</td>
<td>$-164.1 \pm 1.2$</td>
<td>$-39.14 \pm 0.19$</td>
</tr>
<tr>
<td>Martha-1</td>
<td>Calibration</td>
<td>$-176.6 \pm 1.3$</td>
<td>$-48.79 \pm 0.06$</td>
</tr>
<tr>
<td>Martha-2</td>
<td>Calibration</td>
<td>$+36.2 \pm 1.2$</td>
<td>$-48.87 \pm 0.15$</td>
</tr>
<tr>
<td>Mike-1</td>
<td>Calibration</td>
<td>$+44.5 \pm 1.1$</td>
<td>$-40.79 \pm 0.08$</td>
</tr>
<tr>
<td>Mike-2</td>
<td>Calibration</td>
<td>$-80.3 \pm 0.7$</td>
<td>$-42.74 \pm 0.10$</td>
</tr>
<tr>
<td>Merida</td>
<td>Calibration</td>
<td>$-171.7 \pm 1.1$</td>
<td>$-60.28 \pm 0.13$</td>
</tr>
<tr>
<td>Fossil</td>
<td>Calibration</td>
<td>$-171.9 \pm 1.6$</td>
<td>$-39.72 \pm 0.18$</td>
</tr>
<tr>
<td>Fossil</td>
<td>Comparison</td>
<td>$-170.1 \pm 0.7$ (*)</td>
<td>$-39.56 \pm 0.04$ (*)</td>
</tr>
<tr>
<td>Melly</td>
<td>Calibration</td>
<td>$-177.5 \pm 1.4$</td>
<td>$-69.87 \pm 0.11$</td>
</tr>
<tr>
<td>Minion</td>
<td>Calibration</td>
<td>$-182.7 \pm 1.2$</td>
<td>$-58.06 \pm 0.11$</td>
</tr>
<tr>
<td>Merkur</td>
<td>Calibration</td>
<td>$-195.8 \pm 1.2$</td>
<td>$-43.03 \pm 0.10$</td>
</tr>
<tr>
<td>Biogenic</td>
<td>Calibration</td>
<td>$-319.8 \pm 1.4$</td>
<td>$-56.55 \pm 0.11$</td>
</tr>
<tr>
<td>Biogenic</td>
<td>Comparison</td>
<td>$-317.4 \pm 0.7$ (*)</td>
<td>$-56.37 \pm 0.04$ (*)</td>
</tr>
</tbody>
</table>

3.2 Results for CH$_4$ gas calibrations against Master-CH$_4$ gases

The calibration results of all secondary CH$_4$ gases are shown in Table 3. Our gases include gases from natural and commercial gas sources as well as isotopically spiked CH$_4$ mixtures. The gases cover large ranges in carbon ($-70$ to $-39$‰) and hydrogen isotope ratios ($-320$ to $+36$‰), which include the isotopic composition of tropospheric CH$_4$. For $\delta^2$H-CH$_4$ this was achieved by spiking fossil CH$_4$ gases with pure CH$_3$D to yield “Martha-2” and “Mike-1”. In order to create a CH$_4$ gas with tropospheric $\delta^2$H-CH$_4$, “Mike-1” was diluted with a fossil CH$_4$ gas to produce “Mike-2”, thereby using up “Mike-1”.

14
3.3 Results for isotopic measurements of CH₄ in synthetic air standards

Aliquots of the previously calibrated CH₄ gases were diluted with CH₄-free air (Sect. 2.4) for analysis on a setup named “iSAAC” that has recently been developed at MPI-BGC for the analysis of dual isotope ratios of CH₄ in air samples (Sect. 2.5). In iSAAC, the diluted CH₄ reference gases are treated as unknown samples and referenced against “Carina-1”. The difference between the calibration results of the pure CH₄ gases and the diluted CH₄ gases is calculated by δᵢSAAC – δpure, which shows the calibration difference between the two different isotope reference materials. Table 4 displays the observed differences between the two calibration methods.

Our experiments show good agreement between the δ¹³C-CH₄ calibrations, but a systematic offset in the calibrations of δ²H-CH₄. While the average offset in δ¹³C-CH₄ of +0.02 ± 0.08 ‰ is smaller than the measurement uncertainty, the average offset in δ²H-CH₄ accounts for +4.0 ± 1.1 ‰, which is significant.

The measurements of “Biogenic” for δ¹³C-CH₄ showed a larger discrepancy between the two methods. The cause of this discrepancy could not be resolved. It may be due to an unknown impurity in the bulk CH₄ gas that only impacts on the analysis of the pure CH₄ gas as iSAAC separates CH₄ chromatographically. A sudden drift in the “Biogenic” cylinder could be another reason for this discrepancy, however, this is not reflected in the analysis of “Biogenic” as pure CH₄ gas over time. A pressure drop in the cylinder that is independent of CH₄ consumption during analysis is not detected. Because the discrepancy exceeds the measurement uncertainty by a factor of 4, we consider this result as an outlier and refrained from using it in further calculations.

Table 4: Comparison of the previous isotope scale for CH₄ in air of the iSAAC system as defined by “Carina-1”, which was calibrated by IMAU (Brass and Röckmann) and the new scale as based on the CH₄ calibrations presented in this study. The first column shows the name of the pure CH₄ gas that has been diluted with CH₄-free air for analysis as atmospheric sample (see Table 3). Columns 2 and 3 show the difference δᵢSAAC – δpure for δ²H-CH₄ and δ¹³C-CH₄, respectively. The bottom line shows the mean difference with 1σ uncertainty. The cause for the larger value in δ¹³C-CH₄ of “Biogenic” is unknown. Therefore, this value is marked with (*) and is not considered for the determination of the scale difference.

<table>
<thead>
<tr>
<th>Gas name</th>
<th>δ²H-CH₄ [%‰]</th>
<th>δ¹³C-CH₄ [%‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Megan</td>
<td>3.8</td>
<td>0.00</td>
</tr>
<tr>
<td>Merlin</td>
<td>4.0</td>
<td>–0.01</td>
</tr>
<tr>
<td>Minion</td>
<td>2.7</td>
<td>–0.03</td>
</tr>
<tr>
<td>Melly</td>
<td>4.3</td>
<td>0.13</td>
</tr>
<tr>
<td>Mike-1</td>
<td>5.7</td>
<td>–0.06</td>
</tr>
<tr>
<td>Martha-1</td>
<td>3.2</td>
<td>–0.05</td>
</tr>
<tr>
<td>Fossil</td>
<td>5.1</td>
<td>0.14</td>
</tr>
<tr>
<td>Biogenic</td>
<td>3.0</td>
<td>0.40 (*)</td>
</tr>
<tr>
<td>Average</td>
<td>+4.0 ± 1.1</td>
<td>+0.02 ± 0.08</td>
</tr>
</tbody>
</table>
4 Discussion

We have used standard on-line IRMS techniques to calibrate pure CH\textsubscript{4} for \(\delta^2\)H and \(\delta^{13}\)C on international isotope reference scales. The pure methane gases were injected into the same isotope analysis system as water and carbonate reference materials and, thus, subjected to the same analytical conditions.

The oxidation of CH\textsubscript{4} to CO\textsubscript{2} (and H\textsubscript{2}O) is usually accepted to produce no artefact. However, chemically CH\textsubscript{4} is rather stable; it requires high temperatures and a surplus of oxygen in order to drive the combustion reaction to completion. A major complication arises when yields are lower than 100 \% (Merritt et al., 1995). This would allow for unreacted CH\textsubscript{4}, which is a potent source of protonation in the IRMS ion source (Anicich, 1993). With CO\textsubscript{2} present, this results in the formation of CO\textsubscript{2}H\textsuperscript{+}, an important isobaric interference on the \(m/z\) 45 mass position, where \(\delta^{13}\)C is measured. This source of analytical error is important especially for analytical systems that don’t separate CO\textsubscript{2} and CH\textsubscript{4} after the combustion on a chromatographic column or by cryogenic means. In the MPI-BGC systems, we use post-combustion chromatographic column to separate N\textsubscript{2} and CO\textsubscript{2} peaks, which also separates any residual methane from CO\textsubscript{2}. In addition, we carefully checked for traces of methane left over from the reaction by monitoring the \(m/z\) 15 ion current carefully for un-converted CH\textsubscript{4} and found the combustion to be quantitative.

The introduction of carbonates to quantitatively release the CO\textsubscript{2} at high temperatures has been demonstrated to yield high precision results (Coplen et al., 2006). A considerable advantage is that the oxygen isotopic composition is altered completely. By “roasting”, it is forced to be very similar for all samples introduced into the combustion furnace, thus making the \(^{17}\)O correction identical as well. Hence, any ambiguity arising from the necessary correction for extracting \(\delta^{13}\)C values from the \(m/z\) 45 ion current tends to cancel. The technique has been used to revise the VPDB scale by adding LSVEC as a second scaling point (Coplen et al., 2006).

For hydrogen, we chose an analogue approach to process H\textsubscript{2}O and CH\textsubscript{4} through the high-temperature reactor of the TC/EA-IRMS system. This technique has been investigated earlier in detail and shown to result in quantitative conversion of H\textsubscript{2}O and methane at reactor temperatures above 1350 °C (Gehre et al., 2004). Possible artefacts can arise mainly from the different surface activities of H\textsubscript{2}O versus CH\textsubscript{4} before the conversion to H\textsubscript{2} (and CO or carbon) occurs. For water, this can lead to memory effects, which needs to be taken into account quantitatively either by correcting for it or by discarding initial injections (Werner and Brand, 2001). We found a further, minor dependence of \(\delta^2\)H-H\textsubscript{2}O to the septum temperature. In the appendix we describe experimental details to ensure optimal conditions for making the H\textsubscript{2}O and CH\textsubscript{4} high temperature reactions directly compatible for quantitative \(\delta^2\)H assessment and calibration.

We achieved the results presented in Table 3 for “Fossil” and “Biogenic” with a large number of analyses. Both gases had already been calibrated by one of the authors in an earlier study using the more classical approach, i.e. combusting pure methane quantitatively off line and sampling the resulting CO\textsubscript{2} and H\textsubscript{2}O for consecutive isotope analysis (Sperlich 2012). In this study, the CH\textsubscript{4} derived CO\textsubscript{2} was analysed by dual inlet IRMS while the H\textsubscript{2}O was analysed by either TC/EA-IRMS or cavity-ring-down spectroscopy. The results of both calibration methods agree in the order of the combined uncertainty of both
methods for $\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$ (Table 3). The values from our new calibration for “Biogenic” and “Fossil” appear to be slightly more depleted in $\delta^2$H-CH$_4$ (average difference of 2.1 ‰) and in $\delta^{13}$C-CH$_4$ (average difference of 0.17 ‰), suggesting that the discrepancy could be systematic. We conclude from the broad agreement with the previously published results on “Fossil” and “Biogenic” that our new method is capable to calibrate CH$_4$ gases accurately to the international isotope scales.

Our new results are based on a large number of individual CH$_4$ conversions and measurements, using GC-IRMS methods that are used for routine analysis since more than a decade. In comparison, the previously published values of Sperlich et al., (2012) were derived from only four analyses per gas, converted in an off-line reactor. We suggest that the method presented here is more accurate and robust compared to the method of Sperlich et al., (2012).

The calibration of “Merlin” against “Megan” as Master-CH$_4$ as well as against primary reference standards provides another indication of the accuracy of our analytical methods. The difference between the two calibrations of “Merlin” accounts for 1.6 ‰ in $\delta^2$H-CH$_4$ and for 0.07 ‰ in $\delta^{13}$C-CH$_4$, which is of the order of the analytical uncertainty. We interpret the good agreement as indicator that the presented methods for CH$_4$, H$_2$O and carbonate analysis do not create any significant isotope fractionation and suggest that our CH$_4$ gases are accurately calibrated. Note that this conclusion is a best estimation scenario that cannot be tested further without CH$_4$ reference material.

The total propagated uncertainty of the isotope calibration is smaller than or similar to the uncertainty of most analytical systems to measure CH$_4$ isotope ratios in air or ice core samples and can therefore help to increase the compatibility between international laboratories.

5 Conclusions

The number of laboratories that measure isotope ratios of atmospheric CH$_4$ is growing and combining data from multiple laboratories could lead to more powerful interpretative approaches of the combined data sets. However, the analysis of data from multiple laboratories is currently hampered by the lack of reference materials that enable the community to produce a unified data set.

To solve this problem, we accurately referenced twelve pure CH$_4$ gases to the international isotope scales for carbon and hydrogen and diluted aliquots of eight calibrated CH$_4$ gases with CH$_4$-free air in 5-L glass flasks. These synthetic gas mixtures were tested for their use as standards for CH$_4$ isotope ratios by comparing separately established isotope scales. From the combined results, the inter-laboratory calibration offsets of the two scales could be established reliably.

Our synthetic atmospheric reference gases for the isotopic composition of CH$_4$ will be made available to the atmospheric monitoring community upon request. Using these reference gases in multiple laboratories will help unifying the data sets of the atmospheric monitoring community, thus enabling compatible isotope ratio data sets of atmospheric methane on a global scale over time.
Acknowledgements

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Appendix A: Preliminary experiments for calibration of CH₄ with H₂O for δ²H

The injection of H₂O samples into the reactor is critical because it is prone to isotope fractionation (Werner and Brand, 2001). This isotope fractionation is caused by system memory due to adhesion of injected H₂O to the reactor walls. The isotope fractionation can be overcome by repetitive injections of H₂O samples with identical isotopic composition, thereby overwriting the memory effect until it reaches a marginal level. For H₂O analyses under constant analytical conditions (e.g. constant reactor temperature), the adhesion effect is a function mainly of the amount of injected H₂O sample. However, the effect on the isotopic composition furthermore scales with the isotopic difference between two consecutive samples (Gehre et al., 2004). Because there is no adhesion of the sample during CH₄ analysis, this memory effect is specific only to the analysis of H₂O in our study. Therefore, system memory of H₂O could propagate into the CH₄ calibrations. Memory effects are identified in a series of replicate H₂O measurements and are corrected for by modelling the memory function as described in Gehre et al., (2004) and Brand et al., (2009a) on a routine basis, as our system has been used for isotope analysis of H₂O samples for more than a decade. We conclude that our results are free of artefacts from memory effects.

Isotope fractionation during the analysis of the reference waters can also be caused by insufficiently heated septa (Gehre et al., 2004). We injected 106 H₂O samples while we increased the septum temperatures in 9 steps from 76°C to 137°C. In general, we observed a δ²H enrichment with increasing Septum temperature, however, there seems to be a second effect in the course of increasing temperature. A systematic variation is apparent at temperatures above 90°C with stabilising δ²H-H₂O values at septum temperatures around 130°C (Fig. A1, blue circles). At the three highest temperatures, δ²H-H₂O averages at -62.6 ± 0.5 ‰. The stabilising δ²H-H₂O at high temperatures suggests quantitative H₂O processing without significant isotope fractionation, in line with (Gehre et al., 2004). Note the disagreement with the three δ²H-H₂O values at the lower temperature range (red diamonds) that show a matching slope but an offset that does not align with the δ²H-H₂O pattern observed at temperatures above 90°C. We cannot explain this offset but can only speculate that the first experiments with a heated septum had a stronger initial impact on the measured isotopic composition. Note that the total septum temperature effect is in the order of twice the typical measurement uncertainty and is thus difficult to observe.
Figure A1: The $\delta^{2}H$ variation of $H_2O$ injections with septum temperatures. Blue circles show average values that fall onto a polynomial fit while red diamonds indicate the three values at low septum temperatures that include the offset. The error bars show $1\sigma$ standard deviations and the grey-dashed lines indicate the typical precision limit of $1\%$ for $\delta^{2}H$-$H_2O$ analysis (Gehre et al., 2004) around the $\delta^{2}H$-$H_2O$ of $-62.45\%$ as estimated by the polynomial fit for the operating septum temperature of $130°C$.

Quantitative conversion of both CH$_4$ and H$_2$O in the high temperature reactor is of utmost importance for our study, because incomplete conversion causes isotopic fractionation in the reaction products (e.g. Burgoyne and Hayes (1998), Hilkert et al., (1999) Gehre et al., (2004)). The temperature of the reactor is critical for the efficiency of the conversion process. We performed an experiment with CH$_4$ and H$_2$O injections at different reaction temperatures and show the results in Fig. A2. For water injections we observe a pronounced, non-linear $\delta^{2}H$-$H_2O$ change of $\sim15\%$ with reactor temperature increase from $1300°C$ to $1450°C$, reaching a plateau above $1400°C$. This pattern is consistent with previous observations in both trend and magnitude (Gehre et al., 2004). In contrast, the linear fit for $\delta^{2}H$-CH$_4$ increases by only about $1\%$ over the $150 K$ temperature range. However, the slope is statistically insignificant as shown by the $95 \%$ confidence interval of the linear fit (Fig. A2). This analyte-specific isotope variation is also reflected in the area of the H$_2$O and CH$_4$ derived H$_2$ peaks (Fig. A2). While the H$_2$O-derived H$_2$ peak areas increase with increasing reactor temperature, the CH$_4$-derived H$_2$ peak areas remain constant within the error bars throughout the experiments. For an unknown reason, three out of six H$_2$ peaks that resulted from H$_2$O injections at $1400°C$ were by 10-15 standard deviations smaller than the remaining three peaks. We present the averages and $1\sigma$ standard deviations of the H$_2$ peaks with and without removal of these outliers in Fig. A2, which shows the exceptional pattern at $1400°C$. Despite of this peak size variability, the isotopic composition of all H$_2$O injections at $1400°C$ is in good agreement. Our experiments indicate that high reactor temperatures of $1450°C$ are required especially for quantitative conversion of H$_2$O, while the effects of reactor temperature on both yield and the isotopic composition of CH$_4$-derived H$_2$ are comparably small. Therefore, we
operate the reactor at a temperature of 1450°C to guarantee quantitative conversion without isotope fractionation of both, H_2O (Gehre et al., 2004) and CH_4 (Burgoyne and Hayes, (1998), Hilkert et al., (1999)).

Figure A2: The variation in isotopic composition and peak area of H_2 derived from H_2O and CH_4 injections at reactor temperatures between 1300-1450°C. Top and bottom panels show experiments for H_2O and CH_4, respectively. Isotope ratios are shown in blue for H_2O and green for CH_4 and refer to the left hand axes. Average H_2 peak areas are indicated by grey crosses and refer to the right hand axes. All error bars indicate the 1σ standard deviation. The red diamond shows the average peak area and respective 1σ standard deviation when the three outliers are included (see Appendix text). Y-axes ranges are matched between top and bottom panels to enable direct comparison of the temperature effect for H_2O and CH_4. Equations describe the fits in both panels, displayed by dashed lines. The continuous lines in the bottom panel indicate the 95 % confidence interval of the linear fit.

Appendix B: Experiments for calibration of CH_4 with CaCO_3 and Li_2CO_3

Incomplete CH_4 combustion results in measurement artefacts, because CH_4-derived CO_2 and unconverted CH_4 enter the IRMS simultaneously, enabling the formation of CO_2H^+ fragments that contribute to the signal on the m/z 45 detector (Werner and...
Brand, 2001). In order to test the completeness of CH\textsubscript{4} combustion, we set the IRMS to monitor m/z 15 during the analysis of a CH\textsubscript{4} sample. We estimate that <0.1 % of an injected CH\textsubscript{4} sample reaches the IRMS unconverted, suggesting quantitative combustion of CH\textsubscript{4}.

The analysis of carbonates can suffer from a well characterised blank contribution that is due to the carbon impurities within the tin capsules that are used for the aliquotation of the carbonates (Werner et al., 1999). In contrast, no such blank is expected when samples are analysed without tin capsules, as would be the case for gaseous CH\textsubscript{4} samples. In order to fulfil the principle of identical treatment between analyses of carbonate reference materials and CH\textsubscript{4} samples, we added empty tin capsules to each CH\textsubscript{4} analysis and applied the routine blank correction to all measurements.

To test for the completeness of carbonate digestion, we added small amounts of tungsten trioxide (WO\textsubscript{3}) to the carbonate samples during weighing (about 1:1 by weight) to increase the instantaneous reaction temperature and to provide additional oxygen during the liberation of CO\textsubscript{2} from different carbonates. The addition of WO\textsubscript{3} did improve the peak shape for the analysis of BaCO\textsubscript{3} (Table 2) but had no effect on the results of our isotope ratio measurements. Other carbonates (CaCO\textsubscript{3} and Li\textsubscript{2}CO\textsubscript{3}) did not suffer from a broadened peak shape. This suggests that the carbonate digestion is not limited by either temperature or oxygen availability. Therefore, we conclude that the digestion of carbonate samples is quantitative and we refrained from adding WO\textsubscript{3} during the CH\textsubscript{4} calibration measurements.

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