**Atmospheric
Measurement
Techniques
Discussions**

A combustion setup to precisely reference δ^{13}C and δ^2H isotope ratios of pure CH$_4$ to produce isotope reference gases of δ^{13}C-CH$_4$ in synthetic air

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Abstract

Isotope records of atmospheric CH_4 can be used to infer changes in the biochemistry of CH_4. One factor limiting quantitative estimates of changes in the biogeochemistry of CH_4 are the uncertainties of the isotope measurements due to the lack of a unique
⁵ isotope reference gas, certified for $\delta^{13}C$-CH_4 or δ^2H-CH_4. We present a method to produce isotope reference gases for CH_4 in synthetic airs that are precisely anchored to the VPDB and VSMOW scale and contain $\delta^{13}C$-CH_4 values typical for the modern and glacial atmosphere. We quantitatively combusted two pure CH_4 gases from fossil and biogenic sources and determined the $\delta^{13}C$ and δ^2H values of the produced CO_2
¹⁰ and H_2O relative to the VPDB and VSMOW scale within a very small analytical uncertainty of 0.04‰ and 0.7‰, respectively. We found isotope ratios of −39.56‰ and −56.37‰ for $\delta^{13}C$ and −170.1‰ and −317.4‰ for δ^2H in the fossil and biogenic CH_4, respectively. We used both CH_4 types as parental gases from which we mixed two filial CH_4 gases. Their $\delta^{13}C$ was determined to be −42.21‰ and −47.25‰, representing
¹⁵ glacial and present atmospheric $\delta^{13}C$-CH_4. The δ^2H isotope ratios of the filial CH_4 gases were found with −193.1‰ and −237.1‰, respectively. Next, we mixed aliquots of the filial CH_4 gases with ultrapure N_2/O_2 ($CH_4 \leq 2\,ppb$) producing two isotope reference gases of synthetic air with CH_4 mixing ratios near atmospheric values. We show that our method is reproducible and does not introduce isotopic fractionation for $\delta^{13}C$
²⁰ within the uncertainties of our detection limit (we cannot conclude this for δ^2H because our system is currently not prepared for δ^2H-CH_4 measurements in air samples). The general principle of our method can be applied to produce synthetic isotope reference gases targeting δ^2H-CH_4 or other gas species.

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1 Introduction

Methane is a powerful greenhouse gas and therefore of major interest when studying the climate system. Records of CH_4 in the recent atmosphere exhibit small changes in seasonal and spatial patterns (e.g., Dlugokencky et al., 2009; Tyler et al., 2007).
In contrast, ice core records of CH_4 mixing and isotope ratios show much stronger variability on decadal to glacial time scales (e.g., Loulergue et al., 2008; Ferretti et al., 2005; Sowers, 2006; Bock et al., 2010). The isotopic composition of atmospheric CH_4 is a function of the relative strengths of its sinks and sources, which are themselves characterized by distinct signatures of the carbon and hydrogen isotope ratios (e.g., Quay et al., 1999), see Fig. 1. Therefore, changes in the biogeochemistry of CH_4 can be inferred by analyzing the CH_4 mixing ratio and isotope records. Isotope ratios are reported using the delta notation according to Eq. (1):

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \qquad (1)$$

where R denotes the ratio of the rare over the abundant isotope in the sample and the standard, respectively. Dual Inlet-Isotope ratio mass spectrometry (DI-IRMS) and gas-chromatography coupled isotope ratio mass spectrometry (GC-IRMS) are commonly applied to measure the isotope ratios of atmospheric CH_4 (Merritt et al., 1995b; Rice et al., 2001), following the identical treatment principle (IT-principle), (Werner and Brand, 2001). Isotope reference gases are used to anchor the sample to the international isotope scales, which is VPDB for δ^{13}C-CH_4 and VSMOW for δ^2H-CH_4. Ideally, the isotope reference gas is similar in mixing ratio and the isotopic composition to the measurand (Werner and Brand, 2001; Brand et al., 2009) to allow for the highest analytical precision and accuracy. Accurate referencing is vital which becomes particularly obvious when datasets from different laboratories are merged for the interpretation of spatial atmospheric processes. In this case, differences could be due to natural variability or analytical offsets. Even very small differences in isotope values can have a large

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impact on the quantification of sink and source budgets (Fletcher et al., 2004). One limitation to the accuracy of CH_4 isotope measurements is the accuracy to which the true isotope value of the isotope reference gas is known. Laboratories can increase their compatibility by circulating a suite of isotope reference gases in so called round-robins. Round-robins have been conducted for more than 14 yr and included several measurands e.g. CH_4 mixing ratios and CO_2 isotopes in air to highlight accuracy off-sets and to identify scale contraction effects (Brand, 2011). However, the comparison is limited as the flasks are not permanently available to each laboratory. To our current knowledge, round-robin results for CH_4 isotopes in air have not been published yet. The compatibility of measurements on CH_4 isotopes in air could be achieved by estab-lishing a suite of unique isotope reference gases that are available to all laboratories, as it is done for CH_4 mixing ratios (Dlugokencky et al., 2005) and CO_2 isotopes (Ghosh et al., 2005), respectively. An ideal suite of isotope reference gases would cover the isotope and mixing ratio variability of modern and glacial atmospheres. Despite the obvious demand, a suite of unique isotope reference gases is currently not available for CH_4 isotopes. Even pure CH_4 gases with certified isotope ratios are currently not available from recognized authorities (such as the International Atomic Energy Agency, IAEA, or the National Institute of Standards and Technology, NIST). Here, we present a method to produce large amounts of isotope reference gases for atmospheric CH_4 with targeted and precisely referenced isotope ratios.

2 Methods

2.1 Method overview

All standards and gases employed in the method are listed in Table 1, using the termi-nology according to Coplen (2011). We prepared two pure CH_4 gases that are referred to as fossil and biogenic CH_4, respectively, with regards to their origin. Next, we de-termined the isotopic composition of the fossil and biogenic CH_4 versus VPDB and

VSMOW for δ^{13}C and δ^2H, respectively. This was achieved with a referenced CO$_2$ gas (referred to as CO$_2$-40 339) and three isotope reference waters (named DC′02, NM′09 and −15). The mentioned isotope reference materials are calibrated versus international measurement standards, specified by Verkouteren (1999) and IAEA (2009).

5 From the parental fossil and biogenic CH$_4$, we mixed two filial CH$_4$ gases. We matched the δ^{13}C value of the filial mixtures to atmospheric values reported for the present day and the last glacial maximum (Quay et al., 1999; Fischer et al., 2008). The filial CH$_4$ mixtures will hereafter be referred to as the glacial isotope standard (GIS$_p$) and the modern isotope standard (MIS$_p$), respectively, where the index p specifies a pure CH$_4$

10 gas. Both δ^{13}C-CH$_4$ and δ^2H-CH$_4$ isotope ratios of GIS$_p$ and MIS$_p$ were precisely referenced versus CO$_2$-40 339 and the isotope reference waters, see Fig. 1. Next, aliquots of GIS$_p$ and MIS$_p$ were blended with CH$_4$-free air, until atmospheric mixing ratios of CH$_4$ were reached. This resulted in two synthetic isotope reference gases containing CH$_4$ with δ^{13}C values akin to the glacial and modern atmosphere which will be referred

15 to as GIS and MIS, respectively. We then used GIS and MIS as isotope reference gas to reference a tank of atmospheric air (taken at a clean air site in North-West Greenland (77.45° N, 51.06° W) in July 2008, hereafter referred to as NEEM) according to the IT-principle (Werner and Brand, 2001). Finally, our results for δ^{13}C-CH$_4$ of NEEM were compared to the results of two external laboratories (not for δ^2H-CH$_4$ because

20 our setup is currently not equipped for such measurement).

2.2 Calibration of pure CH$_4$

Figure 2a shows the setup used to quantitatively combust pure CH$_4$ to CO$_2$ and H$_2$O, which were subsequently trapped for consecutive isotope analysis. This procedure will hereafter be referred to as offline combustion method. The combustion unit is a vacuum

25 system consisting of two quartz glass tubes of 10 and 12 mm inner diameter (ID) and 350 mm in length. Both are routed through a tube furnace (300 mm heated length, 60 mm ID) and are filled with copper oxide (61205-100G, Sigma-Aldrich, Denmark)

throughout the heated zone. The copper oxide is held in place by quartz glass frits to one side and with quartz wool to the other side. Tubes outside the furnace are made of borosilicate glass. Figure 2a shows the H$_2$O section to the right side and the CO$_2$ section with the gas inlet to the left side of the furnace. The H$_2$O section is made of a glass tube with 10 mm outer diameter (OD). It consists of a double loop used as continuous H$_2$O trap which leads into a 250 ml bottle trap. The tear shaped bottle bottom enables to focus the H$_2$O in a narrow, well defined spot for easy pipetting of the sample into a sample vial for subsequent δ^2H analysis. The tubes in the CO$_2$ section are of 12 mm OD, only the branch to the gas inlet is of 6 mm OD so it can be connected to a 1/4″ stainless steel T-piece. A 250 ml cylindrical trap with a stopcock is connected with a 1/2″ Ultra-Torr connector. It can be removed to transfer the CH$_4$-derived CO$_2$ for subsequent analysis. Figure 2b displays the gas manifold, which represents the interface between the combustion unit and all peripheral units such as the pump, gas tanks and sample cylinders. Manifold and combustion unit are connected via a flexible stainless steel tube that prevents the propagation of vibration from the pump to the glass system. A pressure gauge (2 bar max) between combustion unit and flexible tube is used to quantify the amount of introduced sample gas and to indicate pressure changes inside the combustion unit. The pressure in the mixing part of the manifold is measured by a second pressure gauge (60 bar max). Two 1 l sample cylinders in the high pressure part of the manifold are used as reservoirs to mix and store pure CH$_4$ gases. The copper inside the combustion unit is oxidized with O$_2$ (Table 1) at temperatures of 600 °C according to Reaction (R1):

$$2Cu + O_2 \rightleftharpoons 2CuO \tag{R1}$$

O$_2$ is released during the combustion by the reverse reaction of R1 when the furnace is heated to 850 °C. The copper serves as either reducing or oxidizing agent (O$_2$ acceptor or donor) depending on the furnace temperature setting (Merritt et al., 1995a). At the beginning of a combustion process, the continuous H$_2$O trap was cooled to −78 °C. Aliquots of 120–160 ml CH$_4$ were injected into the evacuated combustion reactor at ambient temperatures. Subsequently, the oven was heated to 850 °C so that the copper

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oxide of the combustion unit released the oxygen for the CH$_4$ oxidation (Merritt et al., 1995a). The CO$_2$ and the H$_2$O trap were alternately submerged in liquid nitrogen to transfer CO$_2$ and H$_2$O through the system resulting in convection that forced the CH$_4$ through the combustion reactor. This process is hereafter referred to as cryo-transfer.
The cryo-transfers generate CO$_2$ and H$_2$O until the CH$_4$ is quantitatively combusted. This step is critical as isotope fractionation occurs in the combustion process so that incomplete oxidization leads to an offset between the δ^{13}C of the initial CH$_4$ and the δ^{13}C of the CO$_2$ derived from it (Merritt et al., 1995a). Tests showed reproducible δ^{13}C values when the samples were quantitatively combusted (Fig. 3), which was the case after 25 cryo-transfer cycles.

N$_2$O might form from traces of N$_2$ and O$_2$ in the oxidation reactor (Vaughn et al., 2004) and must be eliminated to avoid mass interferences with CO$_2$ in the DI-IRMS (Ghosh and Brand, 2004). Therefore, we reduced N$_2$O to N$_2$ and O$_2$ in the reduction reactor (Fig. 2a) according to the following Reaction (R2):

$$N_2O + Cu \rightarrow N_2 + CuO \tag{R2}$$
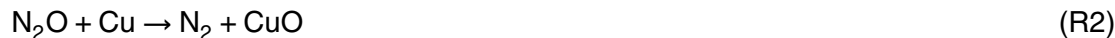
First, we cryo-focus the sample gas in the traps and close the trap valves. Next, the reduction unit is evacuated while held at a constant temperature of 850 °C. This step liberates any O$_2$ in the reduction unit according to Reaction (R1), thereby increasing the reduction capacity of the copper in preparation for the following reduction process (Kapteijn et al., 1996). Afterwards, the oven temperature is decreased to 600 °C and we cryo-transfer the sample gas 10 times through the reduction unit, where N$_2$O is reduced according to Reaction (R2). While O$_2$ is absorbed by the copper, N$_2$ remains in the sample gas (Kapteijn et al., 1996). The CO$_2$ does not react with the copper at 600 °C. This way, N$_2$O is quantitatively eliminated from the sample gas. Subsequently, the CO$_2$ trap is submerged in liquid nitrogen for four minutes until all CO$_2$ is trapped. Extending the CO$_2$ trapping time to 20 min showed no effect on the δ^{13}C values. The CO$_2$ trap is closed and disconnected for subsequent analysis. The continuous H$_2$O trap is heated and all H$_2$O focussed in the tear of the bottle shaped H$_2$O trap by submerging it in

liquid nitrogen. From there the water is transferred into a 1 ml glass vial for subsequent analysis. The combustion unit gets re-oxidized with pure O_2 at 600 °C in preparation of the consecutive sample. We measured the $\delta^{13}C$ of CO_2 produced from the CH_4 combustion by DI-IRMS (Delta V Plus, Thermo Finnigan, Germany). For δ^2H in H_2O we used either GC-IRMS coupled to an Elemental Analyzer (Thermo Finnigan, Delta V Advantage) or laser spectroscopy (Picarro Inc., USA).

2.3 Preparation of pure CH_4 gases and mixing of GIS_p and MIS_p

We mixed fossil and biogenic CH_4 to obtain GIS_p and MIS_p (Fig. (1). The fossil CH_4 was commercially purchased and has a high purity level of 99.995%. The biogenic CH_4 was taken from a biogas reactor (Table 1) and needed purification prior to its use. Biogenic CH_4 is produced when methanogenic bacteria ferment organic material in anaerobic conditions. This process is commercially used to generate biogenic CH_4 as a green fuel from agricultural products with CH_4 concentrations of $\sim 95\%$, where the remaining 5 % are mostly N_2/O_2 but also traces of CO_2, H_2O and H_2S. We received a 50 l tank of biogenic CH_4 and removed the CO_2, H_2O and H_2S while a CH_4 aliquot was transferred from the source tank to a 1 l sample cylinder at the manifold (Fig. 2b). A 1.5 m long, 1/4″ OD tube was filled with sodium hydroxide and magnesium perchlorate hydrate to absorb CO_2 and H_2O, respectively. Subsequently, a coiled 1/8″ tube (2 m long) submerged in a liquid nitrogen/n-Pentane slush froze out H_2S and residual H_2O at −131 °C. Aliquots of purified biogenic CH_4 could then be introduced into the combustion unit from the 1 l sample cylinder for analysis as described in Sect. 2.2. We introduced biogenic CH_4 into both 1 l sample cylinders shown in Fig. 2b. Afterwards, we added fossil CH_4 and barometrically controlled the mixing ratio between biogenic and fossil CH_4 in each mixture. We produced GIS_p and MIS_p with 15 % and 52 % of biogenic CH_4, respectively, and analyzed their isotopic composition using the offline combustion method (Sect. 2.2).

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2.4 Producing and measuring synthetic isotope reference gases GIS and MIS

The N_2/O_2 mixture that we used for mixing the synthetic isotope reference gases consisted of N_2 and O_2 in atmospheric mixing ratios but additionally contained 2 ppm of CH_4 which needed to be removed prior to blending. Therefore, the N_2/O_2 mixture was routed through a combustion furnace built from a 60 cm long piece of 1/2″ OD seamless stainless steel tube. The central 20 cm of this tube is filled with a catalyst (SF-PH-102S-1008201, PureSphere, South Korea) and heated to 520 ± 1 ˚C. Downstream of the oven, two traps in series retained H_2O in the air flow. The first trap is a 1 m long, 1/4″ OD line filled with magnesium perchlorate, which is followed by a 2 m coil of 1/8″ OD tube submerged in ethanol-dry ice (-78 ˚C). The furnace is efficiently removing CH_4 from the N_2/O_2 mixture to ≤ 2 ppb, i.e., the detection limit of the laser spectrometer (Picarro Inc, USA). The purified N_2/O_2 mixture is hereafter referred to as CH_4-free air (Table 1).

The produced isotope reference gases based on GIS_p and MIS_p will be referred to as GIS and MIS, respectively. We started preparing the mixing of the synthetic isotope reference gas by transferring an aliquot of GIS_p or MIS_p to the designated aliquot volume of 280 ± 3 µl (Fig. 2b) while measuring the pressure within this section. We used two 6 l air sample flasks (SilcoCan, Restek, USA) to mix and store the synthetic isotope reference gases. Each flask was flushed with CH_4-free air and evacuated 3 times prior to the mixing to remove residual air. We first filled the evacuated target flask with CH_4-free air through a line bypassing the aliquot (Fig. 2b). At a pressure of 1 bar, the CH_4-free air flow was re-routed through the aliquot volume to inject the CH_4 into the flask. We continued filling the flask with CH_4-free air until the calculated pressure to obtain the desired CH_4 mixing ratio was reached. For MIS, the final mixing ratio was 1800 ± 20 ppb. The CH_4 mixing ratio of GIS was 1420 ± 20 ppb. GIS exceeded the CH_4 mixing ratio reported for the glacial atmosphere by a factor of ~ 4, which is due our limitation to further dilute GIS_p, given by the maximum pressure of the sample flask. A larger mixing reservoir would obviate this limitation.

We used GIS and MIS to reference the δ^{13}C-CH$_4$ in NEEM according to the IT-principle, using a GC-IRMS setup designed for measurements of atmospheric samples. In this setup, CH$_4$ is chromatographically separated from the main air components before it is combusted to CO$_2$ and H$_2$O within a He carrier gas flow. The CH$_4$ derived CO$_2$ is then analyzed for δ^{13}C. All measurements are referenced to the VPDB scale via the square peaks of CO$_2$-40 339, which is injected into the IRMS via the reference open split. In the following, we assume that the δ^{13}C values of GIS and MIS are identical to those of GIS$_p$ and MIS$_p$ i.e., our mixing method does not cause isotopic fractionation. The deviation between GC-IRMS measurements of GIS or MIS and the respective DI-IRMS measurements of GIS$_p$ or MIS$_p$ defines the system offset of the GC-IRMS setup due to fractionation effects, occurring in the cryo-trapping, chromatography and online combustion steps. We correct our measurements of NEEM for this offset. In order to validate our method to produce isotope reference gases, we compare our final results for NEEM to the δ^{13}C-CH$_4$ values that two external laboratories have reported for NEEM. These are the Institute of Marine and Atmospheric Research in Utrecht (IMAU), University of Utrecht, The Netherlands, using the system described by Sapart et al. (2011) and the Institute for Climate and Environmental Physics (Bern), University of Bern, Switzerland. IMAU measured NEEM with -47.31 ± 0.05‰ (C. J. Sapart, personal communication, 2011) and Bern with -47.30 ± 0.11‰ (J. Schmitt, personal communication, 2011), respectively.

3 Results and discussion

All results of CH$_4$ isotope ratios measured by DI-IRMS, laser spectroscopy and GC-IRMS, respectively, are shown in Table 2. Based on the pooled standard deviation of 13 samples (fossil and biogenic CH$_4$, GIS$_p$ and MIS$_p$) the precision of the offline combustion method for pure CH$_4$ gases is 0.04‰ for δ^{13}C and 0.7‰ for δ^2H. Two of those samples were measured for δ^2H using laser spectroscopy as part of

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a larger batch of measurements which needed correction for a 4.4‰ instrument offset of unknown origin. We found δ^{13}C and δ^{2}H values of -39.56 ± 0.04‰ and -170.1 ± 0.7‰ in our fossil CH$_4$ and -56.37 ± 0.04‰ and -317.4 ± 0.7‰ in our biogenic CH$_4$ in line with values reported by Quay et al. (1999) for those sources. We

5 mixed these CH$_4$ gases and matched the δ^{13}C values in the filial mixtures to glacial and present atmospheric values. GIS$_p$ and MIS$_p$ show δ^{13}C values of -42.21 ± 0.04‰ and -47.25 ± 0.04‰, respectively. Resulting δ^{2}H values for GIS$_p$ and MIS$_p$ are -193.1 ± 0.7‰ and -237.1 ± 0.7‰, respectively. The δ^{2}H values do not correspond to atmospheric values. Atmospheric δ^{2}H-CH$_4$ is so strongly enriched in ^{2}H due to

10 sink fractionation Quay et al. (1999) that it cannot be realized by mixing of CH$_4$ from commonly available sources (Fig. 1). Repeated referencing of the produced isotope reference gases GIS and MIS versus CO$_2$-40 339 in our GC-IRMS system revealed (i) an offset of the measured versus the true value and (ii) a day to day variability of the offset. This demonstrates the importance of the IT-principle in combination with the

15 availability of atmospheric isotope reference gases. The day to day offset we observe in our GC-IRMS system has typical values of -0.3‰ and propagated uncertainties between 0.04‰ and 0.07‰. We repeatedly measured NEEM against GIS and MIS, applied the offset corrections and obtained -47.29 ± 0.05‰ and -47.32 ± 0.08‰, respectively. The NEEM air was also measured at IMAU and Bern, both partners in the

20 NEEM project. We found a difference of 0.02‰ and -0.01‰ for our referencing of NEEM versus GIS and MIS, respectively, compared to the mean of IMAU and Bern. The results agree well within the uncertainty of the measurements. All uncertainties of the GC-IRMS measurements on atmospheric samples are shown in Table 2 and are determined by the propagated standard error of the mean. Our results show that our

25 method is reproducible and does not introduce significant isotopic fractionation.

4 Conclusions

We developed a high precision method to reference the δ^{13}C and δ^2H isotopic composition of pure CH_4 samples on the VPDB or VSMOW scale, respectively. Based on the pooled standard deviation, we estimate the reproducibility of our offline combustion method to 0.04‰ and 0.7‰ for δ^{13}C and δ^2H. Referenced parental CH_4 gases were mixed to obtain pure CH_4 gases with precisely referenced isotopic composition of δ^{13}C near atmospheric values. Based on these CH_4 mixtures, we created synthetic isotope reference gases with atmospheric CH_4 concentrations and δ^{13}C-CH_4 isotope values. The synthetic reference gases allow us to detect and correct for system drifts and offsets in our GC-IRMS setup for atmospheric samples. The effects we see demonstrate the importance of our effort to produce atmospheric reference gases. We measured an air sample from a Greenland clean air site and found our results to be in excellent agreement with the results from partner laboratories. Isotope measurements become increasingly precise. Therefore it is important to establish a suite of isotope reference gases for δ^{13}C in CH_4 covering the whole range of investigated δ^{13}C and CH_4 mixing ratios, as was done for CH_4 mixing ratios (Dlugokencky et al., 2005) and for CO_2 isotope ratios Ghosh et al. (2005). Our method can be used to produce synthetic isotope reference gases for δ^{13}C-CH_4 in air at various mixing ratios. With a heavily fractionated source gas the suite could be extended to atmospheric values of δ^2H-CH_4. Further, additional components (e.g. N_2O, CO_2, CO) can potentially be added which would be beneficial for new analytical systems which are measuring multiple components in one sample.

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Table 1. Overview of gases and waters. All gases used for measuring, mixing and referencing are mentioned in the top panel, the bottom panel displays all waters that were used to reference the δ^2H-CH$_4$. The application and reference path of each measure are described in the second column while the third column informs on material type and purity level if applicable. The fourth column identifies the distributor of materials or specifies the origin of the measure if not commercially purchased.

Gas name	Application	Gas type	Origin
Fossil CH$_4$	parental gas, CH$_4$ mixing	CH$_4$, N45	Air Liquide, Denmark
Biogenic CH$_4$	parental gas, CH$_4$ mixing	CH$_4$	biogas plant
GIS$_p$	pure CH$_4$, glacial δ^{13}C	mixed CH$_4$	fossil and biogenic CH$_4$
MIS$_p$	pure CH$_4$, modern δ^{13}C	mixed CH$_4$	fossil and biogenic CH$_4$
GIS	synthetic isotope reference gas, glacial δ^{13}C	CH$_4$ in air	GIS$_p$ with CH$_4$ free air
MIS	synthetic isotope reference gas, modern δ^{13}C	CH$_4$ in air	MIS$_p$ with CH$_4$ free air
NEEM	sample, referenced with GIS and MIS	atmospheric air	NEEM camp, Greenland
RM 8563	international measurement standard	CO$_2$	IAEA
CO$_2$-40 339	isotope reference gas, RM 8563	CO$_2$, N48	Air Liquide, Denmark
CH$_4$-free air	matrix air for gas mixing	N$_2$/O$_2$, labline 5.0	Strandmøllen, Denmark
O$_2$	oxidation combustion ractor	O$_2$, Alphagaz 1	Air Liquide, Denmark
Water name	Application, reference path	Type	Origin
DC$'$02	isotope reference material, VSMOW-2, SLAP-2	H$_2$O	Dome C, Antarctica
NM$'$09	isotope reference material, VSMOW-2, SLAP-2	H$_2$O	NEEM camp, Greenland
−15	isotope reference material, VSMOW-2, SLAP-2	H$_2$O	internally produced
VSMOW-2	international measurement standard	H$_2$O	IAEA
SLAP-2	international measurement standard	H$_2$O	IAEA

Table 2. Mean δ^{13}C and δ^2H isotope values of pure CH$_4$ gases (top panel) and of NEEM, measured with the produced isotope reference gases (bottom panel). The calculations of the uncertainties are explained in Sect. 3 and are based on n repetitive measurements. "oc" denotes the offline combustion method, DI-IRMS refers to Dual Inlet IRMS and laser spec. indicates δ^2H measurements by laser spectroscopy. The * indicates the δ^2H measurements that needed correction for a 4.4‰ system offset (Sect. 3). The indices GIS and MIS indicate the applied isotope reference gas for the measurement of NEEM. The laboratory agreement shows the difference between the referencing of NEEM with our GC-IRMS setup and our produced isotope reference gases compared to the mean value of the two external laboratories. Our GC-IRMS system can currently not measure δ^2H-CH$_4$.

Measurand	δ^{13}C (‰)	δ^{13}C method	δ^2H (‰)	δ^2H method	n
Fossil CH$_4$	-39.56 ± 0.04	oc, DI-IRMS	-170.1 ± 0.7	oc, GC-IRMS	4
Biogenic CH$_4$	-56.37 ± 0.04	oc, DI-IRMS	-317.4 ± 0.7	oc, GC-IRMS	4
GIS$_p$	-42.21 ± 0.04	oc, DI-IRMS	-193.1 ± 0.7	oc, GC-IRMS	3
MIS$_p$	-47.25 ± 0.04	oc, DI-IRMS	-237.1 ± 0.7	oc, laser spec.*	2
Measurand	δ^{13}C (‰)	δ^{13}C method	Daily system error (‰)	Laboratory agreement (‰)	n
NEEM$_{GIS}$	-47.29 ± 0.05	GC-IRMS	-0.29 ± 0.04	0.02	3
NEEM$_{MIS}$	-47.32 ± 0.08	GC-IRMS	-0.34 ± 0.07	-0.01	6

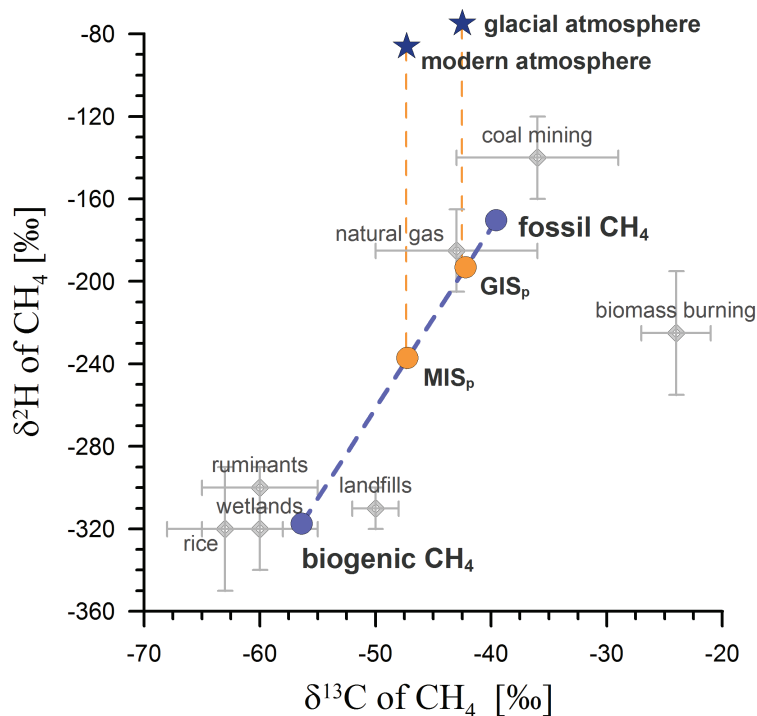**Fig. 1.** Dual isotope signatures of CH$_4$ for δ^{13}C and δ^2H. Grey diamonds mark the field of δ^{13}C and δ^2H isotopes of CH$_4$ according to its source (Quay et al., 1999). Blue circles indicate δ^{13}C and δ^2H pairs of the parental CH$_4$ gases (fossil and biogenic CH$_4$). Based on our fossil and biogenic CH$_4$, we can produce filial CH$_4$ mixtures with δ^{13}C and δ^2H isotope values that fall on the dashed blue mixing line. The two filial CH$_4$ gas mixtures are indicated by orange circles where GIS$_p$ and MIS$_p$ represent the δ^{13}C of glacial and modern atmospheric samples, respectively. Isotope signatures of glacial and modern atmospheric CH$_4$ are indicated by the dark blue stars.
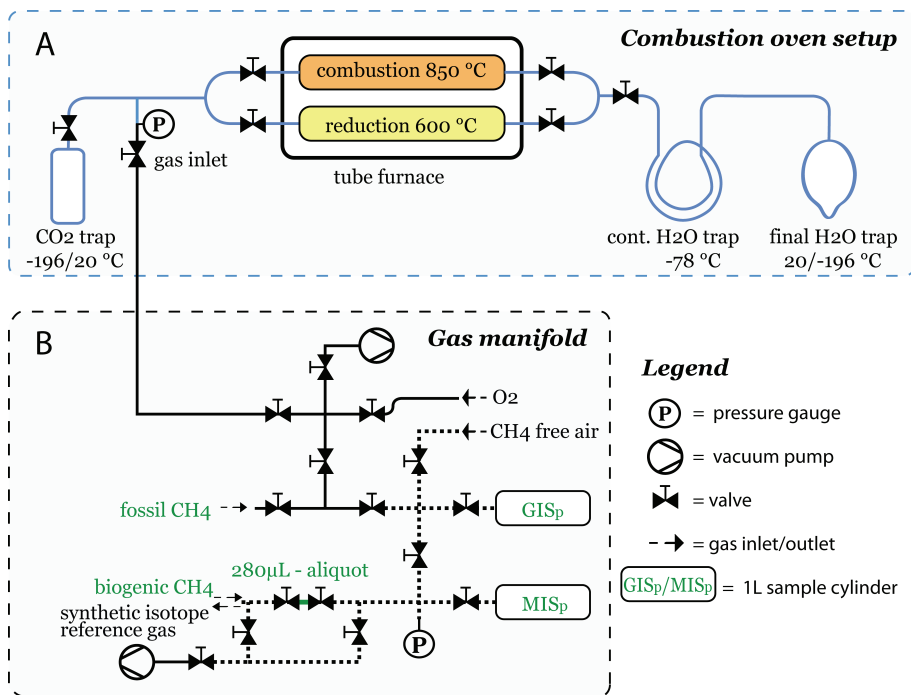
Fig. 2. Schematic figure of the setup. The top panel **(A)** illustrates the combustion and reduction reactors as well as the CO_2 and the two H_2O traps. The blue lines indicate the glass parts of this vacuum component. The bottom panel **(B)** shows the gas manifold that facilitates mixing and aliquoting the samples. Solid black lines represent the brass components used for gas introduction and evacuation. Dotted black lines indicate stainless steel components that take pressures of up to 60 bar.
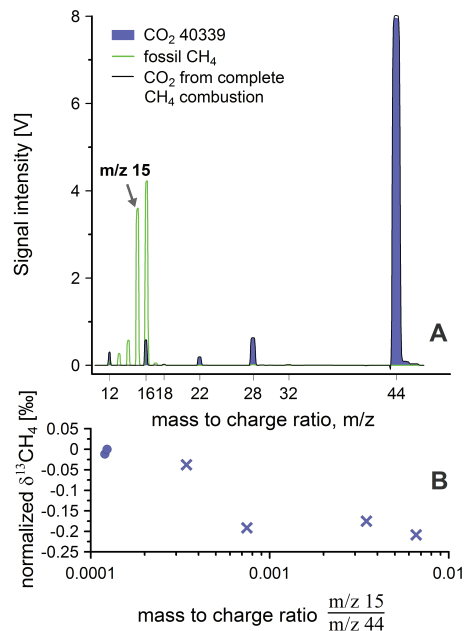
Fig. 3. Assessment of the completeness of the combustion of pure CH$_4$ gases. **(A)**: shown are three scans of mass abundances, resulting from fossil CH$_4$ (green line), CO$_2$-40 339 (blue filled line) and CH$_4$ derived CO$_2$ (black line). Both CH$_4$ and CO$_2$ fractionate in the source, but a signal on mass to charge ratio m/z 15 can only result from CH$_4$, while only CO$_2$ produces a signal on m/z 44. The ratio of m/z 15 over m/z 44 can therefore be used to quantify the abundance of CH$_4$ in a CO$_2$ gas. **(B)**: normalized δ^{13}C-CH$_4$ offsets with varying completeness of combustion. CO$_2$ from completely combusted CH$_4$ gas shows ratios of m/z 15 over m/z 44 of ≤0.0002 (blue circles), indicating absence of CH$_4$. Incomplete CH$_4$ combustion produces offsets in normalized δ^{13}C-CH$_4$ (blue crosses). Complete combustion is reached after 25 cryo-transfers when m/z 15 over m/z 44 in the CH$_4$ derived CO$_2$ is ≤ 0.0002 and the δ^{13}C-CH$_4$ offset becomes negligible.