



A combustion setup to precisely reference $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope ratios of pure CH_4 to produce isotope reference gases of $\delta^{13}\text{C}\text{-CH}_4$ in synthetic air

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Received: 17 March 2012 – Published in Atmos. Meas. Tech. Discuss.: 11 May 2012

Revised: 2 September 2012 – Accepted: 3 September 2012 – Published: 18 September 2012

Abstract. Isotope records of atmospheric CH_4 can be used to infer changes in the biogeochemistry of CH_4 . One factor currently limiting the quantitative interpretation of such changes are uncertainties in the isotope measurements stemming from the lack of a unique isotope reference gas, certified for $\delta^{13}\text{C}\text{-CH}_4$ or $\delta^2\text{H}\text{-CH}_4$. We present a method to produce isotope reference gases for CH_4 in synthetic air that are precisely anchored to the VPDB and VSMOW scales and have $\delta^{13}\text{C}\text{-CH}_4$ values typical for the modern and glacial atmosphere. We quantitatively combusted two pure CH_4 gases from fossil and biogenic sources and determined the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of the produced CO_2 and H_2O relative to the VPDB and VSMOW scales within a very small analytical uncertainty of 0.04 ‰ and 0.7 ‰, respectively. We found isotope ratios of -39.56 ‰ and -56.37 ‰ for $\delta^{13}\text{C}$ and -170.1 ‰ and -317.4 ‰ for $\delta^2\text{H}$ 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 $\delta^{13}\text{C}$ was determined to be -42.21 ‰ and -47.25 ‰ representing glacial and present atmospheric $\delta^{13}\text{C}\text{-CH}_4$. The $\delta^2\text{H}$ isotope ratios of the filial CH_4 gases were found to be -193.1 ‰ and -237.1 ‰, respectively. Next, we mixed aliquots of the filial CH_4 gases with ultrapure N_2/O_2 ($\text{CH}_4 \leq 2$ 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 $\delta^{13}\text{C}$ within

the uncertainties of our detection limit (we cannot conclude this for $\delta^2\text{H}$ because our system is currently not prepared for $\delta^2\text{H}\text{-CH}_4$ measurements in air samples). The general principle of our method can be applied to produce synthetic isotope reference gases targeting $\delta^2\text{H}\text{-CH}_4$ or other gas species.

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., Bock et al., 2010; Ferretti et al., 2005; Fischer et al., 2008; Loulergue et al., 2008; Sowers, 2006). 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):

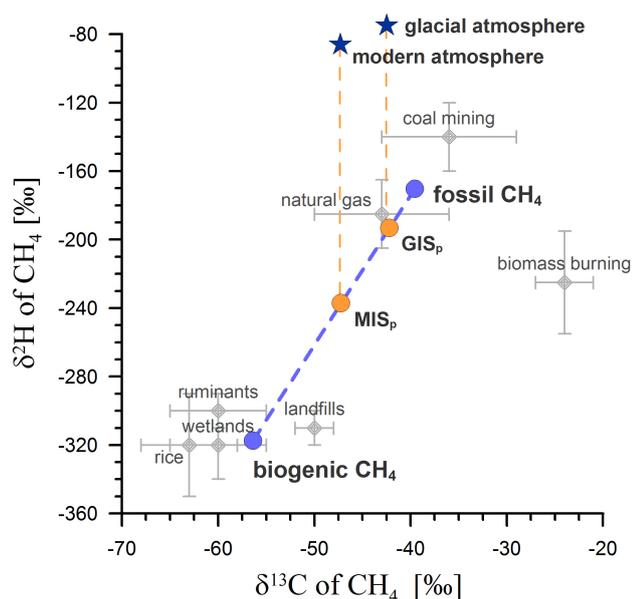


Fig. 1. Dual isotope signatures of CH₄ for $\delta^{13}\text{C}$ and $\delta^2\text{H}$. Grey diamonds mark the field of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotopes of CH₄ according to its source (Quay et al., 1999). Blue circles indicate $\delta^{13}\text{C}$ and $\delta^2\text{H}$ pairs of the parental CH₄ gases (fossil and biogenic CH₄). Based on our fossil and biogenic CH₄, we can produce filial CH₄ mixtures with $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope values that fall on the dashed blue mixing line. The two filial CH₄ gas mixtures are indicated by orange circles where GIS_p and MIS_p represent the $\delta^{13}\text{C}$ of glacial and modern atmospheric samples, respectively. Isotope signatures of glacial and modern atmospheric CH₄ are indicated by the dark blue stars.

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

where R denotes the ratio of the heavy over the light 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 CH₄ (Merritt et al., 1995b; Rice et al., 2001), following the principle of identical treatment (Werner and Brand, 2001). Isotope reference gases are used to anchor the sample to the international isotope scales, which is VPDB for $\delta^{13}\text{C}$ -CH₄ and VSMOW for $\delta^2\text{H}$ -CH₄. Ideally, the isotope reference gas is similar in mixing ratio and 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. This becomes particularly obvious when datasets from different laboratories are merged for the interpretation of spatial atmospheric processes (Levin et al., 2012). It is essential to unambiguously determine whether different observations are due to natural variability or analytical offsets. Even very small

offsets in isotope values can have a large impact on the quantification of sink and source budgets (Mikaloff Fletcher et al., 2004). One limitation to the accuracy of CH₄ 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. CH₄ mixing ratios and CO₂ isotopes in air to highlight accuracy offsets 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 knowledge, round-robin results for CH₄ isotopes in air have not been published yet. The compatibility of measurements on CH₄ isotopes in air could be achieved by establishing a suite of unique isotope reference gases that are available to all laboratories, as it is done for CH₄ mixing ratios (Dlugokencky et al., 2005) and CO₂ 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, such a suite of unique isotope reference gases is currently not available for isotopes of CH₄. Even pure CH₄ 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 that can potentially be used to produce large amounts of isotope reference gases for atmospheric CH₄ with targeted and precisely referenced isotope ratios.

2 Methods

2.1 Method overview

This method is designed to produce atmospheric isotope reference gases for CH₄, based on a suite of initial gases that are needed for the process. All standards and gases employed are listed in Table 1, using the terminology of Coplen (2011). Figure 2 illustrates the relationship of the measured gases to the VPDB and VSMOW isotope scales. We prepared two pure CH₄ gases that are referred to as fossil and biogenic CH₄, respectively, with regards to their origin. Next, we determined the isotopic composition of the fossil and biogenic CH₄ versus VPDB and VSMOW for $\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively. This was achieved with a pure, referenced CO₂ gas (referred to as CO₂-40339) 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) for CO₂ and IAEA (2009) for H₂O. From the parental fossil and biogenic CH₄, we mixed two filial CH₄ gases. We matched the $\delta^{13}\text{C}$ value of the filial mixtures to atmospheric values reported for the present day and the last glacial maximum

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 $\delta^2\text{H-CH}_4$. 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 shows the relevant isotope ratios of applied reference material, the fifth column identifies the distributor of materials or specifies the origin of the measure if not commercially purchased.

Gas name	Application	Gas type, purity	$\delta^{13}\text{C}$ [‰]	Origin
RM 8563	international measurement standard	CO ₂	−41.56	IAEA
CO ₂ -40339	isotope reference gas	CO ₂ , 99.998 Vol. %	−35.41	Air Liquide, Denmark
fossil CH ₄	parental gas, CH ₄ mixing	CH ₄ , 99.995 Vol. %		Air Liquide, Denmark
biogenic CH ₄	parental gas, CH ₄ mixing	CH ₄		biogas plant, northern Germany
GIS _p	pure CH ₄ , glacial $\delta^{13}\text{C}$	mixed CH ₄		fossil and biogenic CH ₄
MIS _p	pure CH ₄ , modern $\delta^{13}\text{C}$	mixed CH ₄		fossil and biogenic CH ₄
GIS	synthetic isotope reference gas, glacial $\delta^{13}\text{C}$	CH ₄ in air		GIS _p with CH ₄ -free air
MIS	synthetic isotope reference gas, modern $\delta^{13}\text{C}$	CH ₄ in air		MIS _p with CH ₄ -free air
NEEM	sample, referenced with GIS and MIS	atmospheric air		NEEM camp, Greenland
CH ₄ -free air	matrix air for gas mixing	N ₂ /O ₂ , labline 5.0		Strandmøllen, Denmark
O ₂	oxidation combustion reactor	O ₂ , 99.995 mol %		Air Liquide, Denmark
Water name	Application	Type	$\delta^2\text{H}$ [‰]	Origin
VSMOW-2	international measurement standard	H ₂ O	0.0	IAEA
SLAP-2	international measurement standard	H ₂ O	−427.5	IAEA
DC'02	isotope reference material	H ₂ O	−427.6	Dome C, Antarctica
NM'09	isotope reference material	H ₂ O	−257.3	NEEM camp, Greenland
−15	isotope reference material	H ₂ O	−111.1	internally produced

(Quay et al., 1999; Fischer et al., 2008). The filial CH₄ 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 CH₄ gas. Both $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ isotope ratios of GIS_p and MIS_p were precisely referenced versus CO₂-40339 and the isotope reference waters, see Fig. 1 and section 2.2. Next, aliquots of GIS_p and MIS_p were blended with CH₄-free air, until atmospheric mixing ratios of CH₄ were reached. This resulted in two synthetic isotope reference gases containing CH₄ with $\delta^{13}\text{C}$ values akin to the glacial and modern atmosphere which will be referred 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 principle of identical treatment (Werner and Brand, 2001). Finally, our results for $\delta^{13}\text{C-CH}_4$ of NEEM were compared to the results that two external laboratories found for NEEM (not for $\delta^2\text{H-CH}_4$ because our setup is currently not equipped for such measurement).

2.2 Calibration of pure CH₄

Figure 3a shows a schematic of the setup used to quantitatively combust pure CH₄ to CO₂ and H₂O, which were subsequently trapped for consecutive isotope analysis. This procedure will hereafter be referred to as the offline combustion method. The combustion unit is a vacuum 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 3a shows the H₂O section to the right side and the CO₂ section with the gas inlet to the left side of the furnace. The H₂O section is made of a glass tube with 10 mm outer diameter (OD). It consists of a double loop used as a continuous H₂O trap which leads into a 250 ml bottle trap. The tear-shaped bottle bottom enables focusing the H₂O in a narrow, well defined spot for easy pipetting of the sample into a septum-sealed sample vial for subsequent $\delta^2\text{H}$ analysis. The tubes in the CO₂ 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 CH₄-derived CO₂ for subsequent analysis. Figure 3b 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 vibrations 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

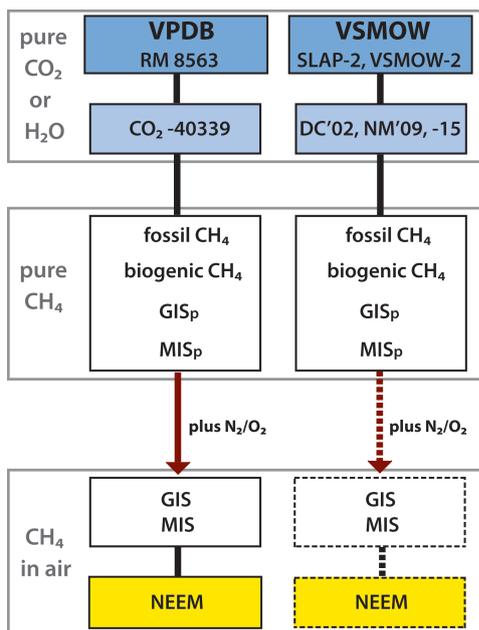
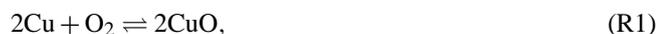


Fig. 2. Shown are the relations of measurements to the VPDB and VSMOW isotope scales in a top-down hierarchy. The dark blue boxes represent the isotope scales and name the international measurement standard used to reference our isotope reference materials, shown in light blue boxes. These isotope reference materials were used to reference the pure CH₄ gases to the respective isotope scale. The red arrows indicate the step where GIS and MIS are produced by diluting the referenced GIS_p and MIS_p with CH₄ free air, respectively. The yellow boxes in the bottom line represent the sample level. NEEM was referenced according to this reference scheme and is thus anchored to the isotope scales via the respective hierarchy of isotope reference materials. GIS, MIS and NEEM could not be referenced to the VSMOW scale because the GC-IRMS setup is not prepared for isotope measurements of δ²H on CH₄ in air (therefore indicated by arrows and boxes in dashed lines). Grey boxes group the type of measurement standards, isotope reference materials and gas mixtures.

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 11 sample cylinders in the high pressure part of the manifold are used as reservoirs to mix and store pure CH₄ gases. The copper inside the combustion unit is oxidized with O₂ (Table 1) at temperatures of 600 °C according to Reaction (R1):



O₂ is released during the combustion by the reverse reaction of (R1) when the furnace is heated to 850 °C. The copper either serves as a reducing or oxidizing agent (O₂ acceptor or donor) depending on the furnace temperature setting (Merritt et al., 1995a). In the beginning of a combustion process, the continuous H₂O trap was cooled to −78 °C. Aliquots of 120–160 ml CH₄ were injected into the evacuated combustion

reactor at ambient temperatures, resulting in pressures of about 200 mbar. Subsequently, the oven was heated to 850 °C so that the copper oxide in the combustion unit released the oxygen for the CH₄ oxidation (Merritt et al., 1995a).

The combustion process is accelerated by submerging either the CO₂ or the H₂O trap in liquid nitrogen (−196 °C), while the respective other trap is heated to room temperature. Alternately, cooling the CO₂ or the H₂O trap to liquid nitrogen temperatures forces the CO₂ and H₂O back and forth through the system and thereby transports the CH₄ through the combustion reactor. This process is hereafter referred to as cryo-transfer, where each cryo-transfer lasted approximately 10 min. Each cryo-transfer cycle generates more CO₂ and H₂O until the CH₄ is quantitatively combusted. While the CO₂ is driven back and forth through the combustion reactor, the H₂O accumulates in the continuous H₂O trap. Whenever the CO₂ trap is cooled for a cryo-transfer, the newly produced H₂O first freezes in the CO₂ trap along with the CO₂ and is then transferred to the continuous H₂O trap during the following cooling of the final H₂O trap with liquid nitrogen. The transfer of H₂O into the continuous H₂O trap was accelerated by heating the CO₂ trap and the glass lines with a heat gun.

The number of cryo-transfer cycles is critical as isotope fractionation occurs during the combustion process. Incomplete oxidation leads to an offset between the δ¹³C of the initial CH₄ and the δ¹³C of the CO₂ derived from it (described in detail by Merritt et al., 1995a, and Zeng et al., 1994). Tests showed reproduced δ¹³C values when the samples were quantitatively combusted. This was the case after 25 cryo-transfer cycles for test with sample sizes between 115 and 160 ml and combustion temperatures between 840 and 860 °C (Fig. 4). Higher temperatures in the combustion unit increase the equilibrium pressure of oxygen over the copper and thereby the oxidation rate, thus, requiring less cryo-transfers for a complete combustion. However, we chose to limit the oxidation temperature to 850 °C in order to increase the life-time of the combustion reactor, following Merritt et al. (1995a) and Zeng et al. (1994).

N₂O might form from traces of N₂ and O₂ in the oxidation reactor (Vaughn et al., 2004) and must be eliminated to avoid mass interferences with CO₂ in the DI-IRMS (Ghosh and Brand, 2004). Therefore, we reduced N₂O to N₂ and O₂ in the reduction reactor (Fig. 3a) according to the following Reaction (R2):



First, we freeze all sample gas by cooling the traps to liquid nitrogen temperatures and thereby cryo-focus the samples in the traps before we close the trap valves. Next, the reduction unit is evacuated while held at a constant temperature of 850 °C. This step liberates any O₂ 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

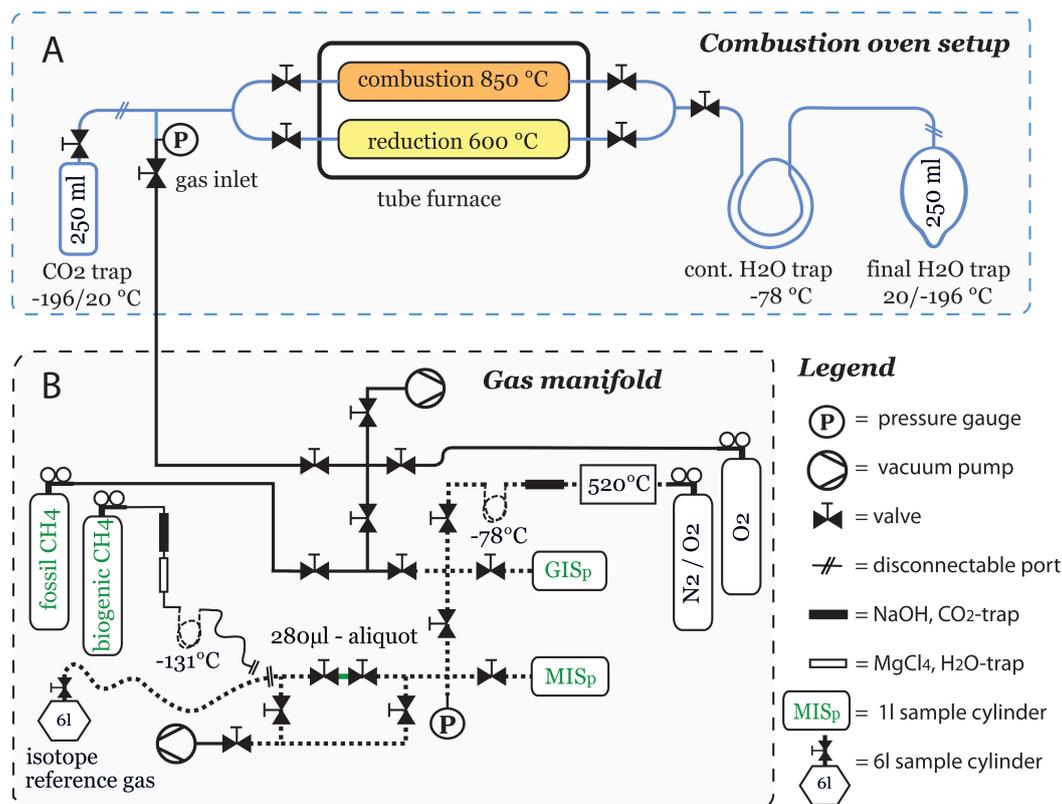


Fig. 3. Schematic figure of the setup. The top panel (A) illustrates the combustion and reduction reactors as well as the CO₂ and the two H₂O traps. The blue lines indicate the glass parts of this vacuum component. The diagonal parallel lines indicate the disconnection ports, where the CO₂ trap and the H₂O trap can be removed to transfer the sample. 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 bars. Diagonal parallel lines show the disconnection port that either connects the tank of biogenic CH₄ or the reservoir for the isotope reference gas. The aliquot volume of 280 μl is indicated by the green line between the valves

temperature is decreased to 600 °C and we cryo-transfer the sample gas 10 times through the reduction unit, where N₂O is reduced according to Reaction (R2). While O₂ is absorbed by the copper, N₂ remains in the sample gas (Kapteijn et al., 1996). The CO₂ does not react with the copper at 600 °C. This way, N₂O is quantitatively eliminated from the sample gas. Subsequently, the CO₂ trap is submerged in liquid nitrogen for four minutes until all CO₂ is trapped. Extending the CO₂ trapping time to 20 min showed no effect on the δ¹³C values. The CO₂ trap is closed and disconnected for subsequent analysis. The continuous H₂O trap is heated and all H₂O focussed in the bottom of the tear-drop-shaped H₂O trap by submerging the latter in liquid nitrogen. Afterwards, the H₂O is melted within the small tear and the H₂O trap is disconnected to transfer the H₂O with a pipette into a 0.7 ml glass vial (548-0036, VWR International, Denmark) for subsequent δ²H analysis. The glass vial is crimp-sealed with a septum to prevent loss through evaporation.

The combustion unit gets re-oxidized with pure O₂ at 600 °C in preparation for the consecutive sample. The O₂

absorption time depends on the oxidation level of the copper. We re-oxidized the combustion reactor after each sample by maintaining a constant O₂ pressure of 900 mbar for 10 min. It takes one day to prepare and combust one sample including the time to prepare the setup for the consecutive experiment.

We measured the δ¹³C of CO₂ produced from the CH₄ combustion by DI-IRMS (Delta V Plus, Thermo Finnigan, Germany). For δ²H in H₂O, we used commercial instruments, either a high Temperature Conversion/Elemental Analyser coupled to an IRMS (TC/EA-IRMS, Thermo Finnigan, Delta V Advantage) or laser spectroscopy (Picarro Inc. USA) as described by Gkinis et al. (2010).

We performed a sensitivity test for the effect of laboratory air leakage on the measured δ¹³C-CH₄ and monitored the variability of laboratory air in all combusted samples. We conclude that leakage or system blanks have no significant effect on our results (detailed information in the Supplement).

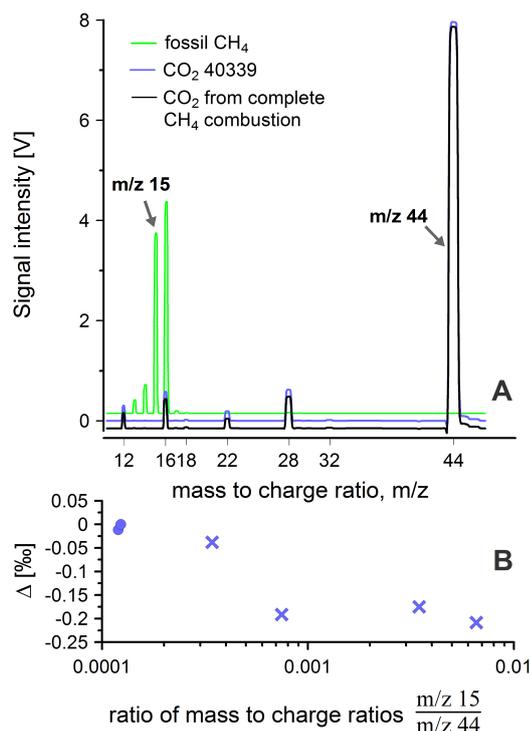


Fig. 4. Assessment of the completeness of the combustion of pure CH₄ gases. **(A)** Shown are three scans of mass abundances, each resulting from the injection of one gas into the ion source of the dual inlet IRMS. The lines result from pure CH₄ (green line), the pure CO₂-40339 (blue line) and CO₂ derived from a completely combusted CH₄ sample (black line). Because all measurements have the same background signal and would overlap, the green and the black line are artificially offset by 0.15 V and -0.15 V, respectively, to highlight the details. Both CH₄⁺ and CO₂⁺ decompose in the source, but a signal on mass to charge ratio m/z 15 can only result from injection of CH₄, while only injected CO₂ produces a signal on m/z 44. The ratio of m/z 15 over m/z 44 can therefore be used to quantify the remaining fraction of CH₄ within the CO₂ of a combusted sample. A high ratio of m/z 15 over m/z 44 indicates a large fraction of CH₄ in the CO₂ gas, hence an incomplete combustion. **(B)** The difference between measured and expected $\delta^{13}\text{C-CH}_4$ (Δ) in dependence on the completeness of combustion. CO₂ from completely combusted CH₄ gas shows ratios of m/z 15 over m/z 44 of ≤ 0.0002 (blue circles), indicating absence of CH₄. Incomplete CH₄ combustion produces offsets in normalised $\delta^{13}\text{C-CH}_4$ (blue crosses). Complete combustion is reached after 25 cryo-transfers when m/z 15 over m/z 44 in the CH₄ derived CO₂ is ≤ 0.0002 and the $\delta^{13}\text{C-CH}_4$ offset becomes negligible.

2.3 Preparation of pure CH₄ gases and mixing of GIS_p and MIS_p

We mixed fossil and biogenic CH₄ to obtain GIS_p and MIS_p (Fig. 1). The fossil CH₄ was commercially purchased and has a high purity level of 99.995 %. The biogenic CH₄ was taken from a biogas reactor in northern Germany (Table 1) and needed purification prior to its use. Biogenic CH₄ is

produced when methanogenic bacteria ferment organic material in anaerobic conditions. This process is commercially used to generate biogenic CH₄ as a green fuel from agricultural products with CH₄ contents of up to ~ 95 %. The remaining 5 % mostly consist of atmospheric air but also of traces of CO₂, H₂O and H₂S that are also generated during the biogas production. We received a 50 l tank of biogenic CH₄ and removed CO₂, H₂O and H₂S while a CH₄ aliquot was transferred from the source tank to a 1 l sample cylinder at the manifold (Fig. 3b). A 1.5 m long, 1/4" OD tube was filled with sodium hydroxide and magnesium perchlorate hydrate to absorb CO₂ and H₂O, respectively. Subsequently, a coiled 1/8" tube (2 m long) submerged in a liquid nitrogen/n-Pentane slush froze out H₂S and residual H₂O at -131 °C. Aliquots of purified biogenic CH₄ 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 CH₄ into both 1 l sample cylinders shown in Fig. 3b. Afterwards, we added fossil CH₄ and controlled the mixing ratio between biogenic and fossil CH₄ in each mixture by terminating the flow of fossil CH₄ when the pressure indicated that the desired mixing ratio was reached. We produced GIS_p and MIS_p with biogenic CH₄ contents of 15 % and 52 %, respectively, and analysed their isotopic composition using the offline combustion method (Sect. 2.2). Detailed information on the determination of the purity level of the purified biogenic CH₄ is available in the Supplement.

2.4 Producing and measuring synthetic isotope reference gases GIS and MIS

The N₂/O₂ mixture that we used for mixing the synthetic isotope reference gases consisted of N₂ and O₂ in atmospheric mixing ratios but additionally contained 2 ppmv of CH₄. This CH₄ fraction needed to be removed prior to blending. Therefore, the N₂/O₂ 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 removed H₂O from 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 CH₄ from the N₂/O₂ mixture to ≤ 2 ppbv, i.e. the detection limit of the laser spectrometer used to monitor the CH₄ fraction (Picarro Inc, USA). The process steps applied for the purification are shown in Fig. 3b. The purified N₂/O₂ mixture is hereafter referred to as CH₄-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 ± 1 μl (Fig. 3b) while

Table 2. Mean $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope values of pure CH₄ 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 $\delta^2\text{H}$ measurements by laser spectroscopy. The * indicates the $\delta^2\text{H}$ 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 $\delta^2\text{H}\text{-CH}_4$.

Measurand	$\delta^{13}\text{C}$ [‰]	$\delta^{13}\text{C}$ method	$\delta^2\text{H}$ [‰]	$\delta^2\text{H}$ method	<i>n</i>
fossil CH ₄	-39.56 ± 0.04	oc, DI-IRMS	-170.1 ± 0.7	oc, TC/EA-IRMS	4
biogenic CH ₄	-56.37 ± 0.04	oc, DI-IRMS	-317.4 ± 0.7	oc, TC/EA-IRMS	4
GIS _p	-42.21 ± 0.04	oc, DI-IRMS	-193.1 ± 0.7	oc, TC/EA-IRMS	3
MIS _p	-47.25 ± 0.04	oc, DI-IRMS	-237.1 ± 0.7	oc, laser spec.*	2
Measurand	$\delta^{13}\text{C}$ [‰]	$\delta^{13}\text{C}$ method	Daily system error [‰]	Laboratory agreement [‰]	<i>n</i>
NEEM _{GIS}	-47.29 ± 0.06	GC-IRMS	-0.29 ± 0.04	0.02	3
NEEM _{MIS}	-47.32 ± 0.06	GC-IRMS	-0.34 ± 0.06	-0.01	6

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 CH₄-free air and evacuated 3 times prior to the mixing to remove residual air. We first filled the evacuated target flask with CH₄-free air through a line bypassing the aliquot (Fig. 3b). This was to introduce CH₄-free air into the target flask so potential adsorption effects between gas and flask-wall could take place with CH₄-free air rather than with CH₄ to minimise potential isotope fractionation of CH₄. At a pressure of 1 bar, the CH₄-free air flow was re-routed through the aliquot volume to inject the CH₄ into the flask. We continued filling the flask with CH₄-free air until we reached the calculated pressure to obtain the desired CH₄ mixing ratio. We produced one mixture of MIS and one of GIS. The determined CH₄ mixing ratio for MIS was 1800 ± 20 ppb and for GIS 1420 ± 20 ppb (the large error bars result from the GC-IRMS system that is not optimised for high precision measurements of CH₄ mixing ratios). GIS exceeded the CH₄ mixing ratio reported for the glacial atmosphere by a factor of ~ 4 , which is due to our limitation to further dilute GIS_p, given the maximum pressure of the sample flask of 2.8 bar. A larger mixing reservoir would avoid this limitation.

We used a GC-IRMS setup designed for measurements of atmospheric samples to test the produced isotope reference gases. Our GC-IRMS system and data analysis is similar to the method described by Sapart et al. (2011) where CH₄ is pre-concentrated, cryo-focussed and chromatographically separated from other sample components before it is combusted to CO₂ and H₂O within a He carrier gas flow. In a first step, the isotope ratios of the CH₄ derived CO₂ of standards and samples are referenced via the flat-topped peaks of our pure, referenced CO₂-40339, which is injected into the IRMS through the reference open split. In the consecutive data processing, the measurements of the samples are referenced to the VPDB scale by applying a simple correction

algorithm that accounts for the systematic errors as determined by blocks of 3 standard measurements that bracket blocks of 3 sample measurements according to Werner and Brand (2001).

For the following tests, we assumed that the $\delta^{13}\text{C}$ values of GIS and MIS are identical to those of GIS_p and MIS_p and that our gas-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 then represents the quantity of the daily system offset of the GC-IRMS setup and could then be used in the data correction algorithm. Thereby, GIS and MIS serve as standards to anchor the $\delta^{13}\text{C}\text{-CH}_4$ in NEEM to the VPDB isotope scale. In order to validate our method to produce isotope reference gases, we compare our final results for NEEM to the $\delta^{13}\text{C}\text{-CH}_4$ values that two external laboratories have reported for NEEM. These are the Institute for 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 ‰ (Sapart et al., 2012) and Bern with -47.30 ± 0.11 ‰ (J. Schmitt, personal communication, 2011), respectively.

3 Results and discussion

All results of CH₄ isotope ratios measured by DI-IRMS, TC/EA-IRMS, laser spectroscopy and GC-IRMS, respectively, are summarized in Table 2. Based on the pooled standard deviation of 13 samples (fossil and biogenic CH₄, GIS_p and MIS_p) the precision of the offline combustion method for pure CH₄ gases is 0.04 ‰ for $\delta^{13}\text{C}$ and 0.7 ‰ for $\delta^2\text{H}$. Two of those samples were measured for $\delta^2\text{H}$ using laser spectroscopy as part of a larger batch of measurements which

needed correction for a 4.4‰ offset of unknown origin. We speculate this offset resulted from isotope fractionation due to evaporation/condensation processes within the sample vials when an autosampler failure caused a significantly longer storage time at room temperature.

We found $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of -39.56 ± 0.04 ‰ and -170.1 ± 0.7 ‰ in our fossil CH₄ and -56.37 ± 0.04 ‰ and -317.4 ± 0.7 ‰ in our biogenic CH₄ in line with values reported by Quay et al. (1999) for those sources. We mixed these CH₄ gases and matched the $\delta^{13}\text{C}$ values in the filial mixtures to glacial and present atmospheric values. GIS_p and MIS_p show $\delta^{13}\text{C}$ values of -42.21 ± 0.04 ‰ and -47.25 ± 0.04 ‰, respectively. Resulting $\delta^2\text{H}$ values for GIS_p and MIS_p are -193.1 ± 0.7 ‰ and -237.1 ± 0.7 ‰, respectively. The $\delta^2\text{H}$ values do not correspond to atmospheric values. Atmospheric $\delta^2\text{H}$ -CH₄ is so strongly enriched in ²H due to sink fractionation (Quay et al., 1999) that it cannot be realised by mixing of CH₄ from commonly available sources (Fig. 1). Repeated referencing of the produced isotope reference gases GIS and MIS versus CO₂-40339 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. The observed systematic offset in our GC-IRMS system shows a typical variability between 0 and 0.05‰ throughout one day and a maximum variability of 0.4‰ between different days. The propagated uncertainties of the day to day variability ranges between 0.04‰ and 0.06‰. The variation of the uncertainty demonstrates the importance of measuring isotope reference gases and samples following the principle of identical treatment. We repeatedly measured NEEM against GIS and MIS, applied the offset corrections and obtained -47.29 ± 0.06 ‰ and -47.32 ± 0.06 ‰, respectively. All uncertainties of the GC-IRMS measurements on atmospheric samples shown in Table 2 are independently calculated by propagating the standard errors of the mean (because we produced one mixture of each GIS and MIS, uncertainties based on the gas mixing are not included). The NEEM air was also measured at IMAU and Bern, both partners in the NEEM project. We found a difference of 0.02‰ and -0.01 ‰ between our NEEM results being referenced versus GIS and MIS, respectively, and the mean of IMAU and Bern. The results agree well within the uncertainty of the measurements. Our results show that our method to produce isotope reference gases is reproducible and does not introduce significant isotopic fractionation.

4 Conclusions

We developed a high precision method to reference the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotopic composition of pure CH₄ 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 $\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively. Referenced parental CH₄ gases were

mixed to obtain pure CH₄ gases with precisely referenced isotopic composition of $\delta^{13}\text{C}$ near atmospheric values. Based on these CH₄ mixtures, we created synthetic isotope reference gases with atmospheric CH₄ concentrations and $\delta^{13}\text{C}$ -CH₄ 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 demonstrating 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 as determined with our produced isotope reference gases to be in excellent agreement with the results from partner laboratories. Isotope measurements are becoming increasingly precise. Therefore, it is important to establish a suite of isotope reference gases for $\delta^{13}\text{C}$ in CH₄ covering the whole range of investigated $\delta^{13}\text{C}$ and CH₄ mixing ratios, as was done for CH₄ mixing ratios (Dlugokencky et al., 2005) and for CO₂ isotope ratios (Ghosh et al., 2005). Our method can be used to produce synthetic isotope reference gases for $\delta^{13}\text{C}$ -CH₄ in air at various mixing ratios. The system can be adapted for mixing isotope reference gases in large tanks with pressures of up to 60 bar, requiring additional tests on the stability of large volume mixtures. With a source gas that is more enriched in $\delta^2\text{H}$, the suite could be extended to atmospheric values of $\delta^2\text{H}$ -CH₄. Further, additional components (e.g. N₂O, CO₂, CO) can potentially be added, which would be beneficial for new analytical systems, which are measuring multiple components in one sample. However, we feel that it is important to complement multi-component isotope reference gas mixtures with single-component isotope reference gases because the combination of the two enables to identify analytical interferences with other trace gases present. Most important for the future would be to initialise a program to produce and maintain such isotope reference gases in order to provide them to the community in a long term perspective, thereby fulfilling the requirements of the WMO-GAW.

Supplementary material related to this article is available online at: <http://www.atmos-meas-tech.net/5/2227/2012/amt-5-2227-2012-supplement.pdf>.

Acknowledgements. We would like to thank the field team that took the gas samples during the field season 2008 at NEEM. NEEM is directed and organized by the Center for Ice and Climate at the Niels Bohr Institute and US NSF, Office of Polar Programs. It is supported by funding agencies and institutions in Belgium (FNRS-CFB and FWO), Canada (GSC), China (CAS), Denmark (FIST), France (IPEV, CNRS/INSU, CEA and ANR), Germany (AWI), Iceland (RannIs), Japan (NIPR), Korea (KOPRI), The Netherlands (NWO/ALW), Sweden (VR), Switzerland (SNF), United Kingdom (NERC) and the USA (US NSF, Office of Polar Programs). Furthermore, we would like to thank Jörg Polzer and HAASE Energietechnik AG for kindly providing the biogenic

CH₄ as well as Michael Bock, Barbara Seth and Jochen Schmitt for measuring $\delta^{13}\text{C}\text{-CH}_4$ in "NEEM" air. Many thanks also to Mads Dam Ellehøj, Henriette Lerche and Bo Vinther for the $\delta^2\text{H}$ measurements, to Colleen Templeton and furthermore to Pantmann Labglass for Danish Design glass-blowing. Furthermore, we would like to thank the three anonymous reviewers for their constructive comments that helped improve the manuscript.

Edited by: A. C. Manning

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