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A New Method for High-Resolution Methane Measurements on Polar Ice Cores Using Continuous Flow Analysis

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Methane (CH_4) is the second most important anthropogenic greenhouse gas in the atmosphere. Rapid variations of the CH_4 concentration, as frequently registered, for example, during the last ice age, have been used as reliable time markers for the definition of a common time scale of polar ice cores. In addition, these variations indicate changes in the sources of methane primarily associated with the presence of wetlands. In order to determine the exact time evolution of such fast concentration changes, CH_4 measurements of the highest resolution in the ice core archive are required. Here, we present a new, semicontinuous and field-deployable CH_4 detection method, which was incorporated in a continuous flow analysis (CFA) system. In CFA, samples cut along the axis of an ice core are melted at a melt speed of typically 3.5 cm/min. The air from bubbles in the ice core is extracted continuously from the meltwater and forwarded to a gas chromatograph (GC) for high-resolution CH_4 measurements. The GC performs a measurement every 3.5 min, hence, a depth resolution of 15 cm is achieved at the chosen melt rate. An even higher resolution is not necessary due to the low pass filtering of air in ice cores caused by the slow bubble enclosure process and the diffusion of air in firn. Reproducibility of the new method is 3%, thus, for a typical CH_4 concentration of 500 ppb during an ice age, this corresponds to an absolute precision of 15 ppb, comparable to traditional analyses on discrete samples. Results of CFA-CH_4 measurements on the ice core from Talos Dome (Antarctica) illustrate the much higher temporal resolution of our method compared with established melt-refreeze CH_4 measurements and demonstrate the feasibility of the new method.

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Introduction

Polar ice cores have become a major climate archive in paleoclimatology, providing a wide spectrum of information about past climate as far back as 800 000 years (*1*). For a better interpretation of this valuable archive an exact synchronization of the time scales of different ice cores from various sites in Greenland and Antarctica is crucial.

Rapid variations of methane (CH_4) concentrations in the atmosphere are synchronous over the globe within its atmospheric mixing time of about one year, whereas the present atmospheric lifetime of CH_4 is on the order of 8 years (*2*). Accordingly, CH_4 concentration records, showing pronounced concentration variations during rapid climate changes, provide one of the best tools for an (interhemispheric) synchronization of ice core records (*3, 4*).

Established methods for measuring CH_4 concentrations in individual samples from the air bubbles enclosed in ice cores have provided reliable records of one of the most important greenhouse gases in the atmosphere (*5*−*7*). However, up to now the temporal resolution was mainly constrained by the time-consuming air extraction based on melting and refreezing of the ice.

Here we present a new method for quasi-continuous CH_4 measurements on ice cores. The gas measurement is coupled to an established continuous flow analysis (CFA) system (*8*), and permits high-resolution CH_4 measurements already in the field. For CFA, ice samples of typically 1 m length are continuously melted, and the melted sample, containing the air from bubbles in the ice, is pumped toward the analysis system. The air, which was previously discarded without scientific benefit, is now extracted continuously and analyzed by gas chromatography (GC).

Our novel method provides CH_4 records with a typical depth resolution of 15 cm with relatively little expenditure of time. Furthermore, the system is adapted for measurements in the field as part of a CFA system which enables dating of the ice core soon after a field campaign. A further advantage of the new system over the discrete CH_4 measurements in the lab is that no transport of the ice core samples is necessary, thereby expediting the analysis significantly and reducing the possibility of contamination or damage of the ice.

In this paper the new method is presented in detail. The melting device, gas extraction, and analysis by gas chromatography are described, and first measurements on a section of the Talos Dome ice core (East Antarctica) (*9*) covering the Antarctic Cold Reversal (ACR, approximately 13 ka BP) are compared with CH_4 measurements from the same section based on the established melt-refreeze gas extraction method.

Materials and Methods

Melting Device. For CFA, an ice sample (cross section of 3.2 × 3.2 cm^2) of a typical length of 1 m is continuously melted on a gold-coated melter head situated in a cold lab (typically −20 °C) or set up in the field on the Greenland or Antarctic ice sheets (*8*). The constant melt speed is achieved by keeping the melter head at constant temperature (about +20 °C) by controlled heating of the melter head body with an electrical heater cartridge placed in the center of the body. While melting, the sample is divided by a ring-shaped barrier (2.4 cm diameter) into an inner section providing the sample flow for analysis, and an outer section removing the meltwater of the potentially contaminated surface of the ice. By pumping off less sample from the inner section than available at a given melt speed of e.g. 3.5 cm/min (i.e., 15.8 mL/min) the

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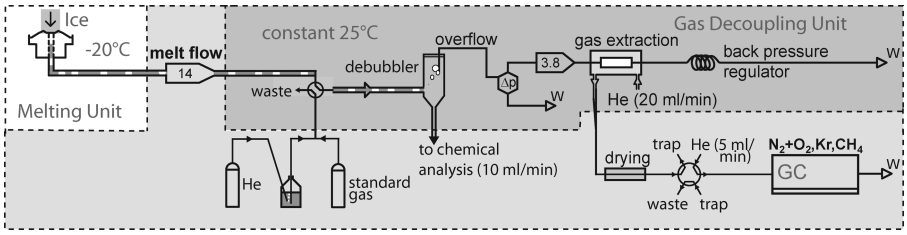

FIGURE 1. Setup of the CFA-CH_4 measuring method. After the melting of the ice the sample is pumped into the debubbler (pump tubes, flow directions and pump rates are indicated by arrow boxes). The overflow passes the open split (Δp) for the pressure decoupling and is further pumped to the gas extraction unit. The extracted gas in the He carrier flow is dried by a Nafion-dryer and then accumulated in a cryotrap. By switching the VICI 6-port valve, the sample is injected into the GC for analysis.

resulting small overflow toward the outer section efficiently prevents any ambient air from entering the sample flow as illustrated by the correct air content measurements of the ice (*8*) and (low) glacial CH_4 concentrations. Breaks and missing edges of the ice sample are logged in the processing journal in order to find and discard potentially contaminated data points afterward. No tracer for contamination is used since contamination with ambient air can clearly be detected by use of the processing journal and the larger amount of methane in the sample. However, contamination from ambient air has been detected only infrequently. From the inner section, a sequential sample flow of meltwater and gas bubbles from air enclosed in the ice (air content approximately 10% by volume STP) is pumped (peristaltic pump IPC12 with LFL-tubing, Ismatec) to the gas extraction unit and analysis system which are located in an adjacent warm lab.

Gas Extraction. The separation of air and water takes place in a temperature stabilized box (25 ± 0.02 °C) (Figure 1). Temperature control is essential in order to produce a constant fraction of air dissolved in the water for all the measurements and calibrations, because solubilities of gases in water strongly depend on temperature. Based on a two-box model we estimate a decrease of the CH_4-concentration by about 0.3% for a 1 °C increase in the sample air at room temperature.

First, the sample flow is pumped into a sealed debubbler volume (~300 μL). Most of the water is pumped from here to the chemical analysis units (*8*), whereas all the bubbles and some residual water pass through the overflow toward the gas extraction unit. The pressure in the sample flow before the debubbler is recorded continuously to correct for possible pressure fluctuations influencing the solubility. The rate of the overflow (typically 4 mL/min) is given by the difference between inflow and water consumption of the chemical analyses (Figure 1).

An open split between the debubbler and gas extraction unit decouples pressure changes caused by the gas extraction unit from the pressure sensitive chemical analysis system. Its sample consumption is slightly smaller than the overflow of the debubbler in order to prevent ambient air from entering the system and assuring all sample air is retained. A peristaltic pump (Reglo MS-2/12 with LFL-tubing, Ismatec) directs the remaining sequential sample flow (all air bubbles and some residual sample water) into the gas extraction unit. This unit consists of a 10 cm long glass tube (i.d. 4 mm) surrounding a gas-permeable hydrophobic membrane tube (Accurel, i.d. 1.5 mm/o.d. 2.5 mm, Microdyn). The Accurel and the glass tube are both fixed on aluminum bodies to seal them from ambient air (*10*). The pressure of the sample flow inside the Accurel is controlled by means of a subsequent back pressure regulator (Upchurch Scientific). Due to the partial pressure gradient across the membrane, the air passes through the membrane into a reverse helium (He) carrier flow (approximately 20 mL/min, purity ≥99.9999%) surrounding the membrane in the glass tube. Additionally, a fraction of the sample air which is dissolved in the remaining water diffuses through the membrane (18−25% of the dissolved air in a 10 cm long tube) (*10*). The water remains inside the membrane tube and passes through the back pressure regulator toward the waste.

Detection. At this stage a continuous sample gas flow of approximately 1 mL STP/min in a helium carrier flow (approximately 20 mL/min) is available. Thorough drying of the sample is crucial before entering the GC system because water vapor permeates through the Accurel membrane into the gas stream. Drying is achieved by the use of a custom-made Nafion membrane tubing drier (1 m, i.d. 0.3 mm) which is surrounded by a reverse He flow (*11*).

Subsequently the dry sample is accumulated in a cryotrap consisting of a stainless steel tube (15 cm, i.d. 0.76 mm) filled with Porapak Q (80−100 mesh, Supelco), cooled by liquid nitrogen (LN_2). Accumulation time is 30 s corresponding to about 0.5 mL of sample air. After lifting out of the LN_2 dewar, the trap is heated to about 50 °C within 5 s in order to achieve simultaneous release of all the sample components. Fast heating of the trap is possible by using the steel tube as a resistive heating element (approximately 0.4 Ω). Three V are applied between the ends of the steel tube, which is connected to PEEK connectors to avoid electrical charging of the whole system. Lifting, lowering, and heating of the trap are done automatically within a measurement cycle.

A six-port valve (VICI) in the GC is switched when the heating starts so that the He carrier (approximately 5 mL/min) from the GC is directed through the heated trap to inject the sample to the column (Figure 1). A PoraPLOT Q capillary column (25 m, i.d. 0.53 mm; Varian) is used for the separation of CH_4 from all other air components in the sample. The column is placed in a custom-made cooler kept at 4 °C (instead of an oven normally used for GC columns) as the separation characteristics of the column are enhanced at lower temperatures for our purposes. Active cooling is attained by thermoelectric coolers (Melcor) which are controlled by thermostats (JUMO) to ± 0.05 °C in a dynamic range of 2−30 °C. Operating the column at or above room temperature results in insufficient separation of CH_4 and krypton (Kr) from N_2+O_2 and superposition of the CH_4 and Kr signals disturbing proper evaluation.

The GC (CompactGC, Interscience) for the gas analysis is equipped with two detectors in series. The eluents first pass through a pulsed discharge detector (PDD, VICI) for the detection of CH_4 and Kr, and then through a thermal conductivity detector (micro-TCD, VICI) for the detection of nitrogen and oxygen (N_2+O_2). The PDD can be operated in three different modes resulting in either universal or selective response to chemical compounds. We use the nondestructive helium pulsed discharge photoionization mode (He-PDPID) with universal response. In this mode the PDD shows best sensitivities and a linear response over 5 orders of magnitude for most compounds (*12*).

Evaluation of the Chromatogram. The detectors deliver a chromatogram of the air components (ideally a series of distinct gas peaks), where the area under each peak is proportional to the specific amount of gas. To derive the

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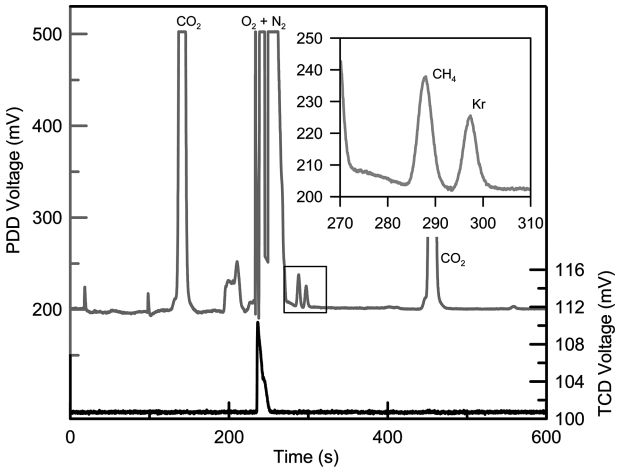

FIGURE 2. Typical responses of the PDD (gray) and the TCD (black) detectors to an ambient air sample. For N_2, O_2 and CO_2, the PDD is in saturation (500 mV). At the very end of the N_2+O_2 slope, CH_4 elutes followed by Kr (see inset). The large peak at 140s is the CO_2 peak of the previous injection. The N_2O peak at 560s in the PDD chromatogram is too small for a quantitative analysis and therefore ignored in our gas measurements.

concentration of a specific component (e.g., CH_4) in the sample air, the ratio of the peak areas of the trace gas and the main components (N_2, O_2), or a different constant air component, e.g. krypton (Kr), is evaluated. By performing calibration measurements with a standard gas of known concentrations of all relevant components (e.g., 500 ppbv CH_4 and 1.14 ppmv Kr in 20% O_2 and 80% N_2), peak area ratios can be assigned to the given trace gas concentrations. Due to the linearity of the detectors (see below), any peak area ratio can be evaluated after calibration as the calibration curve is forced through zero.

A distinct separation of CH_4 from all air components is crucial, as the PDD is sensitive to most gases in air, i.e., to krypton which elutes at about the same time as CH_4. The PDD response for a 250 μL air sample (approximately 1770 ppbv CH_4, 1140 ppbv Kr) is shown in Figure 2 along with an enlargement of the methane and krypton peaks. The retention times in the PoraPLOT Q column for the sample components in our setup are approximately 250s for N_2+O_2, 290s for CH_4, 300s for Kr, 460s for CO_2. Because the retention times for most air components are higher than the duration of one analysis cycle, it is crucial to avoid overlapping of peaks from subsequent injections. This is achieved by adjusting the injection frequency, helium carrier flow rate, and temperature of the column. A further challenge is the huge concentration difference between nitrogen and oxygen on the one side and CH_4 and Kr on the other. This results in CH_4 and Kr eluting at the very end of the nitrogen/oxygen tailing.

Krypton is a noble gas at a very constant mixing ratio (1.14 ppmv) in the atmosphere over the last millions of years with only slight variations (1−2‰) between glacials and interglacials (*13*). This minute effect is due to lower ocean water temperatures in glacials and hence increased gas solubility, leading to a slightly decreased Kr concentration due to higher solubility than N_2. In addition, gravitational separation in the firn column (*14*) leads to enrichment/depletion of Kr/CH_4 relative to N_2, depending on their mass difference. This effect enriches and depletes Kr and CH_4 typically by about 2% and −0.5%, respectively, in the air bubbles compared to the free troposphere for modern conditions. This gravitational enrichment is also subject to systematic glacial/interglacial changes due to the climatic change in the bubble close-off depth. Both the ocean solubility effect as well as the gravitational fractionation can be corrected for by using ocean temperature reconstructions as well as $\delta^{15}N_2$ measurements in ice cores, respectively. In this methodological paper we will not correct for these systematic but secondary effects, but we have to keep in mind that for the quantitative interpretation of an ice core CH_4 record in terms of the global methane cycle this becomes important. For the synchronization of ice cores, the rapid changes in CH_4 concentrations are much larger than this maximum 3% systematic error and, thus, can be ignored.

Calibration of the system is done by an artificially generated sequential flow of degassed water and standard gas. The Milli-Q water (Gradient A10, ≥18.2 MΩ/cm, Millipore) used for calibration is degassed by a vacuum pump and extensively flushed with helium to minimize residual gases dissolved in the water. An air and a water flow controller (F-200CV and L23 V02, Bronkhorst) are used to generate the sequential flow at a chosen air/water ratio of 0.09 (mL gas STP)/(mL water), which is in the range of the ratio typically found in polar ice samples. After the flow controllers, the gas-free water is merged with the standard gas by use of a T-fitting. The sequential flow is then directed through the system the same way as the sample, i.e., the tubing (adjusted in length to the tubing from the melter head to the debubbler) is connected before the debubbler (Figure 1). By the use of this procedure, solubility effects are effectively corrected for by the calibration because the same fraction of each air component is dissolved in the water during calibration and measurement. Calibration is done every 10−12 m of ice which corresponds to an analysis time of 5−6 h, to correct for potential variations of the system.

Performance of CFA−CH_4. Linearity and precision of the PDD and micro-TCD have been investigated. At first, direct injections of air by use of five different sample loops in a range between 0.1 and 0.45 mL were performed. Linearities (R^2) of 69 measurements between the volume of ambient air samples (1770 ppbv CH_4, 1140 ppbv Kr) and instrument responses are 0.992 for CH_4 and Kr, and 0.994 for N_2+O_2, respectively. All three linear regressions fit through the origin within the confidence interval of the regression. The relative reproducibilities (1σ/mean, where σ is the standard deviation) of the same measurements are 1.4% (CH_4), 1.9% (Kr), and 1.1% (N_2+O_2), respectively, with slightly better reproducibilities for larger amounts of CH_4. In order to compare these precision measurements with calibration measurements, the ratios CH_4/Kr and CH_4/(N_2+O_2) were considered as we only make relative measurements. The relative reproducibilities for these ratios of the above-described test measurements are 2% for CH_4/Kr and 2.3% for CH_4/(N_2+O_2). No systematic effect on CH_4 concentration is found when varying the gas amount. For the calibration measurements done with an artificial sequential flow (degassed mQ water and standard gas with 537 ppb CH_4, 1.14 ppm Kr and 20% O_2 in 80% N_2) the relative reproducibilities are 3.0% for CH_4/Kr and 3.1% for CH_4/(N_2+O_2), respectively. These values are higher than the direct gas measurements. Hence, additional variability is induced by producing the sequential flow air standard, and by the gas extraction. The precision of 3% corresponds to 10 ppbv and 20 ppbv for glacial and interglacial ice core samples, respectively. This is comparable to the reproducibility achieved using the traditional melt-refreeze extraction based CH_4 measurements in the range of 4−15 ppbv (*5, 15*). Note, that degassing of the standard mQ water may not have been complete leading to systematic shifts in the CH_4 concentration depending on the amount of residual gas in the water. This may at least partly explain the concentration offsets in Figure 3a (see Results and Discussion).

Results and Discussion

The new quasi-continuous CFA−CH_4 measurement method has been employed for the analysis of a section of the ice core from Talos Dome (Antarctica) (*9*). According to the

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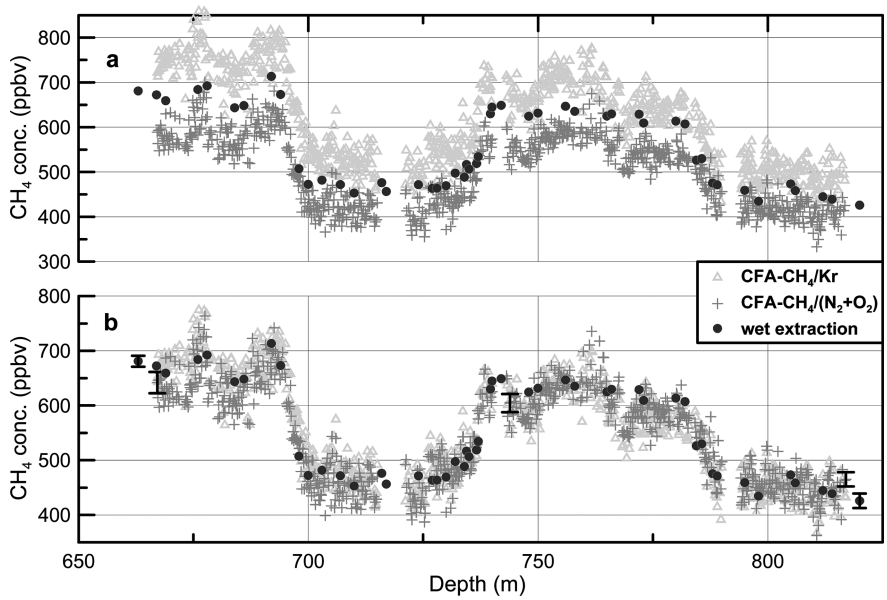

FIGURE 3. The raw data of the CFA-CH_4 record from the Talos Dome ice core in the depth interval of 667−817 m referenced to Kr measurements (light gray triangles) and to N_2+O_2 (dark gray crosses) are compared to individual measurements using wet extraction (black dots) (a). Calibrating the CFA−CH_4 data with one selected calibration results in the same absolute concentrations for both CFA-measurements (CH_4 referenced to Kr and to N_2+O_2, respectively) that are consistent with the wet extraction data (b). Error bars for both methods are indicated at the first and the last point only.

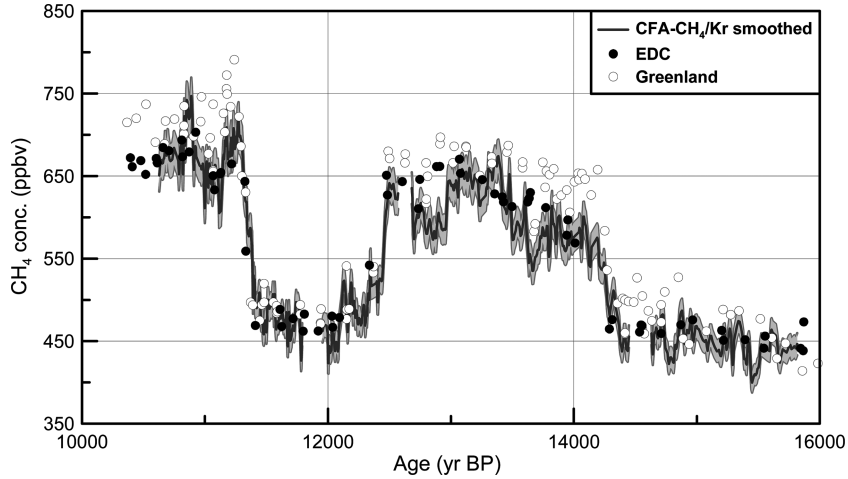

FIGURE 4. The CFA-CH_4 data, smoothed by a binomially weighted five-point running mean (dark gray line with a ±3% error band, light gray), are compared with the measurements on ice from Antarctica (*16*) (dots) and from Greenland (*3*) (circles). The CFA record is plotted on the *TD1alpha* age scale, which is fitted to the *EDC3* age scale (*20*). The Greenland record is shifted 250 years toward younger age to fit the other CH_4 variations on the EDC3 gas-age scale.

TD1alpha age scale, the measured depth range (667−817 m) corresponds to an age of the air in the ice of 10.5−16 kyr BP (before 1950), covering the Antarctic Cold Reversal (ACR) at the very beginning of the Holocene. In this time interval CH_4 concentrations between 400 and 700 ppbv are expected (*3, 16*), showing some distinct features reflecting the abrupt climate changes during the transition from the last ice age to the Holocene. During the melting of one meter of ice, 7−8 measurements of CH_4 could be obtained. This corresponds to a depth resolution of our CH_4 record of 12−15 cm. A few meters could not be measured in this interval due to completely broken ice samples or distinctive ash layers (these are cut from the sample to prevent damage of the chemical analysis systems).

Results of these measurements are presented in Figure 3. CFA-CH_4 raw data show pronounced CH_4 concentration variations in good agreement with the data points measured by the wet extraction method performed at the LGGE in Grenoble. The correlation between these 47 wet extraction data points and interpolated CFA-CH_4 data is $r^2 = 0.89$, which is highly significant ($r^2 > 0.138$ is significant at a two-tailed confidence interval of $\alpha = 0.99$ for 50 points). However, the absolute values differ from the wet extraction record (Figure 3a). The CFA−CH_4 data calibrated via Kr overestimate the CH_4 concentration, whereas the data calibrated via the main air components (N_2+O_2) underestimate the CH_4 concentration with respect to wet extraction CH_4 data. If we assume that the water for the standard measurements still contained a considerable amount of air, the higher solubility of Kr in water compared to CH_4 and of CH_4 compared to N_2 would favorably explain the overestimation of CH_4 concentration using Kr and the underestimation using N_2+O_2 in the sample measurements.

Calibration of the CFA-CH_4 method was done 13 times during all the measurements shown in Figure 3, and the mean value of these calibration factors was applied to the measured data. One calibration consists of 3−7 standard gas injections. The standard deviation for one calibration was

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<3% (1σ/mean). However, we observed large fluctuations (1σ/mean = 7.3%) of the calibration factor within the 13 calibration runs indicating difficulties providing a reproducible calibration setup. For every calibration, new degassed mQ water was used and several tube connections had to be reconnected which might be the origin of the additional variation. Clearly, this should be improved in the future by additional tests and a stringent degassing protocol of the mQ water. By applying the same degassing procedure for every calibration a similar low level of remaining gases in the water should be achieved, resulting in lower variability for the calibration runs.

Nevertheless, the new analysis system including the degassing unit exhibits high stability. This is shown when the whole CFA−CH_4 data set is shifted by a constant offset to match the concentration values of the wet extraction method (Figure 3b). Wet extraction and CFA−CH_4 data are then on the same levels throughout the whole interval. This also offers cross calibration of the CFA−CH_4 data via CH_4 records from other ice cores (from the same hemisphere given the small but significant interhemispheric gradient *7, 17*) or discrete wet extraction data points from the same ice core.

The short-term variations in the CH_4 record we derived with the new method (Figures 3 and 4) are larger (e.g., 6% for 150 subsequent measurements of approximately constant mean CH_4 concentration in the depth interval from 794 to 816 m) than the statistical error described above. Given that the uncertainty defined by our sequential flow standardization is reflecting the melt extraction of air from ice reasonably well, this would point to small scale variations of CH_4 concentrations in the ice. In the absence of comparable high-resolution measurements using classical discrete CH_4 extraction methods, the significance of such small-scale variations cannot be determined at this point but should be investigated in more detail in the future.

CFA−CH_4 data compared with other CH_4 records are shown in Figure 4. For clarity, only the CFA−CH_4 data calibrated by Kr is shown in this figure. The CFA data are the same as in Figure 3b but smoothed with a binomially weighted five-point running mean covering 20−45 years. Averaging of the high-resolution data is reasonable at this depth because of the diffusive smoothing of trapped gases in the ice due to pore close-off mechanisms which limit the maximum achievable temporal resolution (*18, 19*). The amplitude of the fast CH_4 concentration variations is strongly damped in the EPICA Dome C (EDC) record (*16*) due to the low accumulation rate and the related stronger smoothing (accumulation rate: 26 kg m^{-2} yr^{-1}) whereas the amplitude of the Greenland (accumulation rate: 240 kg m^{-2} yr^{-1}) (*3*) CH_4 variations is comparable or even larger than the amplitude of the Talos Dome (accumulation rate: 83 kg m^{-2} yr^{-1}) CH_4 variations, especially during warmer times. The CH_4 concentration of our new Talos Dome record is in good agreement with the EDC record, whereas the Greenland CH_4 concentrations are similar during cold times, but higher during warm times. This is consistent with earlier observations of the interhemispheric CH_4 gradient (*7, 17*) related to higher CH_4 emissions from boreal wetlands in the northern hemisphere.

In conclusion, a new quasi-continuous method for CH_4 measurements on polar ice cores was developed and successfully incorporated into an existing CFA system. A CH_4 record covering the ACR with a depth resolution of up to 12 cm was obtained from the Talos Dome ice core in a fraction of the measuring time discrete sampling methods would require. With the system being part of a CFA (*8*), which is suitable for field measurements, a high-resolution CH_4 record can now for the first time be generated during a field campaign. In the current status of this new CH_4 measurement system on polar ice cores, we still need some discrete classical CH_4 measurements for the absolute calibration of the system. However, the uncalibrated raw data provide a CH_4 record in unprecedented resolution which is suited for the synchronization of the cores and therefore for the dating of a new ice core. This provides an age scale for the air in a new core at a very early stage. After rigorous calibration the CH_4 data derived with our new system are comparable both in accuracy as well as in precision with classical methods and provide CH_4 records quickly in unprecedented resolution.

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