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# Enrichment in $^{13}\text{C}$ of atmospheric $\text{CH}_4$ during the Younger Dryas termination

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## Abstract

The abrupt warming across the Younger Dryas termination (~11 600 yr before present) was marked by a large increase in the global atmospheric methane mixing ratio. The debate over sources responsible for the rise in methane centers on the roles of global wetlands, marine gas hydrates, and thermokarst lakes. We present a new, higher-precision methane stable carbon isotope ratio ( $\delta^{13}\text{CH}_4$ ) dataset from ice sampled at Pákitsoq, Greenland that shows distinct  $^{13}\text{C}$ -enrichment associated with this rise. We investigate the validity of this finding in face of known anomalous methane concentrations that occur at Pákitsoq. Comparison with previously published datasets to determine the robustness of our results indicates a similar trend in ice from both an Antarctic ice core and previously published Pákitsoq data measured using four different extraction and analytical techniques. The  $\delta^{13}\text{CH}_4$  trend suggests that  $^{13}\text{C}$ -enriched  $\text{CH}_4$  sources played an important role in the concentration increase. In a first attempt at quantifying the various contributions from our data, we apply a methane triple mass balance of stable carbon and hydrogen isotope ratios and radiocarbon. The mass balance results suggest biomass burning (42–66 % of total methane flux increase) and thermokarst lakes (27–59 %) as the dominant contributing sources. Our results do not suggest as large a role for tropical wetlands, boreal peatlands or marine gas hydrates as commonly proposed.

## 1 Introduction

Ice core records from both Antarctica and Greenland demonstrate numerous abrupt climate changes throughout the Quaternary (Brook et al., 2000). One such event, the Younger Dryas–Preboreal transition (YD-PB) (~ 11.6 kyr before 1950 AD; k.a. BP) saw a rapid climate change leading a large increase in the atmospheric methane mixing ratio ( $[\text{CH}_4]$ ) (Severinghaus et al., 1998). This increase could have been driven by changes in either the methane sources or sinks. However, modelling studies

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investigating interglacial-glacial changes in the predominant  $\text{CH}_4$  tropospheric sink, the OH radical, indicate only a small variability in sink strength (Thompson et al., 1993; Martinerie et al., 1995). Interpretation of the YD-PB  $\text{CH}_4$  record has thus focused on methane's natural sources with the debate centering on the roles of tropical wetlands (Chappellaz et al., 1990; Brook et al., 2000), marine gas hydrates (Kennett et al., 2003), and thermokarst lakes (Walter et al., 2007).

Wetlands are the most important natural methane source, accounting for approximately 75 % of global emissions in the Preindustrial Holocene (PIH) (Chappellaz et al., 1993; Wuebbles and Hayhoe, 2002), thus the wetland hypothesis purports that an invigorated hydrologic cycle with higher precipitation allows expansion of wetland area, and increased wetland methane emissions, particularly in the tropics (Brook et al., 1996).

The clathrate (methane hydrate) release hypothesis comprises several scenarios. One contends that marine clathrates situated on the continental margins are capable of episodic destabilization events triggered by the warming of the upper thermocline waters. This scenario assumes that the majority of released methane passes through the water column, without oxidation, to the atmosphere (Kennett et al., 2003). A recent update on this hypothesis, based upon preserved tar records in sediments from the Santa Barbara basin, proposes that methane hydrates may act as a “climate sensitive valve system for thermogenic hydrocarbons”, i.e. clathrate release allows for the increased release of methane from hydrocarbon seeps (Hill et al., 2006).

Thermokarst lakes have been shown to release very large amounts of methane from point-source locations with hotspots that produce up to  $50 \text{ g CH}_4 \text{ m}^2 \text{ yr}^{-1}$  (Walter et al., 2006). The large amount of available carbon (Zimov et al., 2006) and the high methane emission potential make thermokarst lakes a potential player in past abrupt climate changes (Walter et al., 2007).

The stable and radiogenic isotope ratios ( $^{13}\text{C}/^{12}\text{C}$ , D/H,  $^{14}\text{C}/^{12}\text{C}$ ) of atmospheric methane trapped in glacial ice can be used to probe the dynamics of methane's sources and sinks (Schaefer et al., 2006; Sowers, 2006; Fischer et al., 2008; Petrenko

et al., 2009) and distinguish between these competing hypotheses. Primary methane sources have characteristic isotope signatures, although in some cases with similar and/or broadly ranging values for a single isotope system (Whiticar, 1999). However, the combination of all three methane isotopes overcomes many of their individual limitations, and is used here to investigate the dynamics behind the CH<sub>4</sub> flux increase during the YD-PB.

## 2 Methods

### Sample collection and analysis

Ice samples were collected using un-lubricated chainsaws from the western margin of the Greenland ice sheet at Pákitsoq (69°825.830 N, 50°815.200 W) during the 2003–2005 sampling seasons. The start and end point of the Younger Dryas–Preboreal transition (YD-PB) in a sampling profile were determined in the field using gas chromatography (GC) analysis of [CH<sub>4</sub>]. This was later confirmed on parallel samples (collected along strike of the layers) by GC [CH<sub>4</sub>] analysis at Oregon State University (OSU), USA and δ<sup>15</sup>N and δ<sup>18</sup>O<sub>atm</sub> analysis at Scripps Institution of Oceanography, USA (Petrenko et al., 2006). The strike and dip of the ice was determined by visual cues as well as laboratory analysis (Petrenko et al., 2006). Ice from the actual YD-PB transition period is confined to 50 cm width and is directly accessible at the surface for precision sampling. Sample width was between 3 and 5 cm perpendicular to the strike of the profile. The YD-PB transition was resolved in great detail with ca. 6 to 8 age horizons, and 1 to 5 replicates sampled at each age horizon per field campaign. Replicate samples were taken along the strike of the layers. Samples were shipped frozen to the University of Victoria (UVic), Canada, or OSU.

In the laboratory we measured the methane stable carbon isotope ratio (δ<sup>13</sup>CH<sub>4</sub>; referenced to Vienna Pee Dee Belemnite – VPDB) from occluded gas in 61 individual shaved ice samples (ca. 100–200 g). Measurements were made via an improved

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wet-extraction, isotope ratio mass spectrometer (IRMS) method with analytical precision  $<0.3\text{‰}$  and no introduced error or offset due to the wet extraction procedure (Melton et al., 2011). The main improvements to the procedure of Schaefer et al. (2006) and Schaefer and Whiticar (2007) include (i) a He carrier gas pre-scrubbing trap, (ii) introduction of two carbon monoxide (CO) traps, and (iii) post-combustion trapping of the methane to produce a high amplitude sample peak, increasing the signal to noise ratio of the sample. The maximum blank contribution was  $\sim 5\%$  of the sample signal, while more commonly  $<3\%$ . Samples were corrected for the blank as per Schaefer and Whiticar (2007).

Atmospheric air tests were routinely measured at the start and end of an ice sample measurement day, as well as regularly between ice samples across a period of three years (2006, 2007, and 2009). These atmospheric air tests showed a mean  $\delta^{13}\text{CH}_4$  value of  $-47.51 \pm 0.29\text{‰}$  ( $1\sigma$ ;  $n = 48$ ; methane content varying between  $\sim 160\text{--}830\text{ pmol}$ ). The smallest atmospheric air samples measured ( $\sim 160\text{ pmol}$ ) did not show significantly different values and no loss in precision compared to the total dataset ( $-47.50 \pm 0.18\text{‰}$ ;  $1\sigma$ ;  $n = 5$ ) (Melton et al., 2011). The Pákitsoq sample with the lowest  $\text{CH}_4$  content measured contained  $\sim 240\text{ pmol CH}_4$ , which is well within the range measured by the atmospheric air samples. Additionally, samples of artificial reference ice were measured on most sample measurement days with a mean  $\delta^{13}\text{CH}_4$  value of  $-47.51 \pm 0.29\text{‰}$  ( $1\sigma$ ;  $n = 32$ ; methane content varying between  $\sim 415$  to  $1080\text{ pmol}$ ). These artificial reference ice measurements (see Supplement, Fig. S1) and the atmospheric air samples (Melton et al., 2011) show good linearity over the range in  $\text{CH}_4$  content found in Pákitsoq samples, as well as over the range in sample mass for reference ice samples. The precision of our method is a significant improvement from Schaefer and Whiticar (2007) as these same tests yielded reported standard deviations of  $\pm 0.47\text{‰}$  and  $\pm 0.52\text{‰}$  for atmospheric air and artificial reference ice, respectively. As well, the calculated standard deviation across our three-year atmospheric air and artificial ice sample dataset is slightly greater than the true analytical standard deviation because of seasonal changes of the local atmospheric  $\delta^{13}\text{CH}_4$

used as the reference air. The seasonal change in  $\delta^{13}\text{CH}_4$  is  $\pm 0.11\text{‰}$  on the nearby Olympic Peninsula during the period from 1988 to 1995 (Quay et al., 1999). However, due to the uncertainty of the seasonal change in  $\delta^{13}\text{CH}_4$  in Victoria air, we do not correct for intra-annual variability.

Tests were also performed on the remaining pieces of a shallow section of the Greenland Ice Sheet Project II (GISP2) Core #139 used in Schaefer and Whiticar (2007) and discussed in Melton et al. (2011). The quality of these samples is poor, with much of the ice highly fractured. The mean  $\delta^{13}\text{CH}_4$  of the GISP2 ice is  $-49.37 \pm 0.58\text{‰}$  ( $1\sigma$ ;  $n = 5$ , corrected for gravitational fractionation) for a gas age of  $\sim 225 \pm 20$  yr BP. Recently, Sowers (2010) published a  $\delta^{13}\text{CH}_4$  record using GISP2 ice, reporting a  $\delta^{13}\text{CH}_4$  of  $-49.24 \pm 0.17\text{‰}$  ( $1\sigma$ ;  $n = 3$ ) for ice with a gas age of  $\sim 200$  yr BP. The good agreement of mean values is an indicator of our accuracy, although our standard deviation is much higher than Sowers (2010). However, as fractured ice has been reported by multiple investigators to lead to spurious values (Craig et al., 1988; Schaefer and Whiticar, 2007; Behrens et al., 2008), we view our artificial ice results as more indicative of our analytical method precision than those of the GISP2 ice. Additionally, there is no indication that the artificial ice samples would somehow lead to better precision than natural ice samples given that Schaefer and Whiticar (2007) reported poorer standard deviation for their artificial ice samples ( $\pm 0.52\text{‰}$ ) than for their GISP2 samples ( $\pm 0.32\text{‰}$ ). We note that Schaefer and Whiticar (2007) used higher quality parts of the GISP2 core section, so that the difference in precision to our study does not necessarily reflect on the quality of the new technique.

The mean CF-IRMS measured methane concentration for the GISP2 Core #139 samples is  $703 \pm 43$  ppb ( $1\sigma$ ;  $n = 5$ ). This  $\text{CH}_4$  concentration agrees reasonably well with measurements made with a conventional GC flame ionization detector from the GISP2 Eurocore 235 ( $724 \pm 5$  ppbv) for  $\sim 217$  yr BP (Etheridge et al., 1998).

As Pákitsoq ice can contain anomalous  $[\text{CH}_4]$  (Schaefer et al., 2009), samples were filtered for anomalous methane concentrations. The assessment uses two criteria for exclusion: (i) samples that showed visible post-depositional features in the ice, such

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as fractures; layers or occlusions of dust; or samples with bubble-free bands in the ice (Petrenko et al., 2006), and (ii) samples that had IRMS-measured  $[\text{CH}_4]$  values more than 100 ppb different from the contemporaneous GISP2  $[\text{CH}_4]$  (Brook et al., 2000). Sample  $[\text{CH}_4]$  for this data filter are derived by calculation against calibration curves from reference gases and air standards using the IRMS  $m/z$  44 ion peak height (derived from the ice sample  $^{12}\text{CH}_4$ ) and air content of the ice. The air content of the  $\delta^{13}\text{CH}_4$  ice samples is determined via parallel samples that were measured with GC at OSU. The standard deviation for  $[\text{CH}_4]$  measured with the IRMS is taken as the value determined using GISP2 section #139 in our lab. Due to the poor quality of the latter, this is a conservative estimate. The 100 ppb limit for inclusion of samples was selected by summing the magnitude of analytical standard deviation and uncertainty in the reference GISP2  $[\text{CH}_4]$  ( $\sim \pm 10$  ppb) (Brook et al., 2000). This led to the removal of 21 unsuitable samples of the 61 total. For the actual  $\sim 150$  yr YD-PB transition, only 3 anomalous samples were removed of the total 46 samples that fall within the gas age limits for inclusion in the weighted linear regression (see Fig. 1). The three suspicious samples were not considered in our subsequent source analysis (Sect. 3.3). However, the removal of those samples has no significant effect on the  $\delta^{13}\text{CH}_4$  trend across the YD-PB (see Supplement, Fig. S2).

For replicate measurements (multiple ice samples of equal age) median values with standard deviations are reported. For single measurements, analytical precision as derived from the artificial reference ice measurements is shown (Melton et al., 2011). All raw  $\delta^{13}\text{CH}_4$  values are presented in the Supplement (Table S1). The  $\delta^{13}\text{CH}_4$  data have been corrected for thermal, gravitational, and diffusion fractionation (see Supplement S1a–d, Table S2).

To establish the age of the air bubbles within the Pâkitsoq ice, we match high-precision  $[\text{CH}_4]$  records using gas chromatography at OSU and other geochemical records ( $\delta^{15}\text{N}$  of atmospheric  $\text{N}_2$ ,  $\delta^{18}\text{O}_{\text{ice}}$  from the ice matrix,  $\delta^{18}\text{O}_{\text{atm}}$  of atmospheric  $\text{O}_2$ ) measured in Pâkitsoq ice to those of GISP2 (Brook et al., 2000) and other suitable, well-dated ice cores (Petrenko et al., 2006) (see Supplement S2 and Table S3). The

inflection points in the  $[\text{CH}_4]$  record provide excellent tie-points for the onset and end of climatic transitions.

### 3 Results

The  $\delta^{13}\text{CH}_4$  data are plotted in Fig. 1 on a common age scale with previous Pákitsoq data (Schaefer et al., 2006) (which are adjusted to account for a small systematic offset; see Supplement S1d). The Schaefer et al. (2006) Pákitsoq dataset includes ice with an uneven distribution of gas age from each of the 2001–2003 sampling seasons (particularly at the start of the YD-PB) (Schaefer et al., 2006). In contrast, the combination of our dataset and the Schaefer et al. (2006) dataset now provides replicate samples over multiple field campaigns (2001–2005) for each part of the record to minimize sampling biases and analytical uncertainty. The combined record contains 43 individual samples with gas ages within the  $\sim 150$  yr YD-PB.

#### 3.1 Observed trend in $\delta^{13}\text{CH}_4$ values across the YD-PB

Throughout the late YD and early PB periods, while  $[\text{CH}_4]$  was stable, there is a trend of  $^{13}\text{CH}_4$  depletion (Fig. 1) that has been observed previously (Fischer et al., 2008). In contrast, the fast YD-PB  $[\text{CH}_4]$  rise coincides with strong enrichment in  $^{13}\text{CH}_4$  that reverses the long-term  $^{13}\text{CH}_4$  evolution. We use the  $\delta^{13}\text{CH}_4$  increase to delineate the driving processes of  $[\text{CH}_4]$  rise at the YD-PB. We focus on the methane budgets at the start and end of the  $[\text{CH}_4]$  rise to: i) minimize uncertainties due to fractionation that gases and their isotopologues undergo as they move through the unconsolidated snow (firn) prior to bubble close-off, and ii) avoid transient signals, such as diffusional smoothing (see Supplement S1b). The change in  $\delta^{13}\text{CH}_4$  across the YD-PB ( $\Delta\delta^{13}\text{CH}_4$ ) shows a mean  $^{13}\text{C}$ -enrichment of 1.5‰ for the combined dataset as determined by a weighted linear regression with a 99% confidence interval (CI) range of 1.0 to 1.9‰ (Fig. 2). This is a conservative estimate of  $\Delta\delta^{13}\text{CH}_4$  because gas diffusion in the firn dampens the

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excursions that form the beginning and end of the reversal in the ice record and therefore smoothes the signal of atmospheric changes. The measured Pákitsoq  $\Delta\delta^{13}\text{C}_{\text{CH}_4}$  over the  $\sim 150$  yr transition is similar in magnitude to the  $\sim 2\text{‰}$   $^{13}\text{C}$ -enrichment from 1850 to 2000 AD (Sowers, 2010), despite the absence of anthropogenic sources.

## 3.2 Robustness of the findings

Pakitsq ice is known to produce anomalously high results for  $[\text{CH}_4]$  as compared to contemporary GISP2 ice (Petrenko et al., 2006; Schaefer et al., 2009). It is therefore necessary to test whether the finding of the  $^{13}\text{C}$  enrichment trend is robust. It can be shown that, although excess  $[\text{CH}_4]$  may lead to lower precision and introduce uncertainty, it does not systematically affect  $\delta^{13}\text{C}_{\text{CH}_4}$  in the Pákitsoq ice (Schaefer et al., 2006). For the presented data, the maximal values of  $[\text{CH}_4]$  excess reach up to 480 ppb with two extreme values  $>1000$  ppb (defined as the difference between Pákitsoq IRMS-derived  $[\text{CH}_4]$  and GISP2 (Brook et al., 2000). This is clearly higher than the conservative estimate of our  $[\text{CH}_4]$  precision ( $\pm 43$  ppb) and excess values span three orders of magnitude, yet excess  $[\text{CH}_4]$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  are not correlated with  $r^2 = 0.092$  (see Supplement, Fig. S3). Even if there was a systematic effect of excess  $[\text{CH}_4]$  on  $\delta^{13}\text{C}_{\text{CH}_4}$ , the former would have to affect certain parts of the record more than others in order to create an artifactual trend. This is not evident with  $r^2$  values for age versus  $[\text{CH}_4]$  excess over the ca. 150 yr transition period of 0.02 and 0.01, with and without two major outliers ( $[\text{CH}_4]$  excess  $>1000$  ppb), respectively see Supplement (Fig. S3). We cannot rule out that the lower-than-standard precision of our method for  $[\text{CH}_4]$  masks a minor trend in  $[\text{CH}_4]$  excess. However, due to the lack of correlation between  $\delta^{13}\text{C}_{\text{CH}_4}$  and the large range of detected  $[\text{CH}_4]$  excess we consider it unlikely that such a masked trend in  $[\text{CH}_4]$  excess would cause the observed  $^{13}\text{C}$ -enrichment trend. We also note that in Pákitsoq ice  $[\text{CH}_4]$  excess is more prevalent in ice from warm periods than in cold ones (Schaefer et al., 2009). As in situ produced  $\text{CH}_4$  is expected to be  $^{13}\text{C}$ -depleted due to the metabolic fractionation during methanogenesis (Whiticar, 1999), we would

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anticipate lower  $\delta^{13}\text{CH}_4$  in the contamination prone PB ice compared to YD ice. The observed trend in our record is of opposite sign, so it is unlikely to be a natural artifact from in situ  $\text{CH}_4$  production in the ice.

We further note that the magnitude of the enrichment (1.5 ‰) clearly exceeds analytical precision ( $< \pm 0.3$  ‰) (Melton et al., 2011) and pooled standard deviation ( $\pm 0.56$  ‰) of our new data set (including points removed by the data filter). The 99% CI of the trend, which is weighted by data uncertainty, shows that the trend is statistically significant with a minimum enrichment of 1.0 ‰. The reversal to higher  $\delta^{13}\text{CH}_4$  is also not dependent on the applied data filter as it is evident in both the filtered and unfiltered data sets with almost identical magnitudes (see Supplement, Fig. S2). Additionally, the sum of all applied fractionation corrections (see Supplement S1a–c) takes the form of a flat-topped peak that is distinct from the near linear  $\delta^{13}\text{CH}_4$  trend across the YD-PB (see Supplement, Fig. S4), i.e. uncertainties in the applied corrections cannot account for the trend. We conclude that the enrichment is a statistically significant and robust feature of our data set.

Two previously published  $\delta^{13}\text{CH}_4$  studies covering the same time period have not reported an enrichment trend during the YD-PB. A closer look at the published data, however, reveals evidence for the enrichment in those records. The mean  $\delta^{13}\text{CH}_4$  values of the Schaefer et al. (2006) data set show a continuous development to more  $^{13}\text{C}$ -enriched values throughout the YD-PB, where the  $\delta^{13}\text{CH}_4$  values at the end of the  $[\text{CH}_4]$  rise exceed those at the start by a margin bigger than the combined uncertainties (Schaefer et al., 2006). The authors did not state a trend because the start of the transition was represented by samples from only one field season, introducing the possibility of a sampling bias. The combined Pákitsoq data set now shows that the feature is reproducible in sample sets from various campaigns. Schaefer et al. (2006) also presented high precision  $\delta^{13}\text{CH}_4$  measurements on large volume samples performed on a different experimental setup (Ferretti et al., 2005). These values integrate over long time spans and therefore present a strongly muted version of the atmospheric signal, but  $^{13}\text{C}$  enrichment is evident (Schaefer et al., 2006). The  $\delta^{13}\text{CH}_4$  record from EDML,

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Antarctica, shows a near continuous  $^{13}\text{C}$ -depletion trend from the start of the YD that persists far into the PB (Fischer et al., 2008). However, the record does not resolve the YD-PB in detail and presents only values before and after (but not during) the rapid  $[\text{CH}_4]$  increase. The two bracketing values show the only reversal of the long-term depletion trend with an enrichment of 0.5‰ (Fig. 1). This value is significant with respect to the stated data uncertainty ( $\pm 0.15\%$ ). The significance of the  $^{13}\text{C}$  reversal was not recognized due to the low temporal resolution of the record.

We conclude that a trend to higher  $\delta^{13}\text{CH}_4$  during the  $[\text{CH}_4]$  increase of the YD-PB is a statistically significant feature recorded in ice from two different locations and measured using four different extraction and analytical techniques. Thus while our record has higher uncertainty given the necessity of applying a contaminated samples filter, it appears that the observed  $^{13}\text{C}$ -enrichment trend is robust enough to allow further interpretation.

### 3.3 Triple isotope mass balance

From the weighted linear regression, the atmospheric  $\delta^{13}\text{CH}_4$  values at the start and end of the YD-PB are  $-46.9\%$  and  $-45.4\%$ , respectively. The  $\delta^{13}\text{CH}_4$  value of the total methane source can be derived from the atmospheric  $\delta^{13}\text{CH}_4$  by applying a weighted aggregate isotopic fractionation of total sink processes ( $\varepsilon = -6.72\%$ ), and correction for isotopic disequilibrium (Tans, 1997; Lassey et al., 2000) (Table 1 and Supplement S1c). Epsilon is calculated from the fractional proportion of each sink (including the highly fractionating atomic chlorine in the marine boundary layer (MBL) sink) and its ratio of the rate coefficients,  $\alpha$ , for each isotope as  $\varepsilon = 10^3(\alpha - 1)$ . Using the increase in atmospheric  $[\text{CH}_4]$  across the YD-PB (ca. 250 ppb; Brook et al. 2000), an isotope mass balance yields the stable carbon isotope ratio of the additional emissions ( $\delta^{13}\text{CH}_4 \uparrow_{\text{T}}$ ) to be  $-49.2 \pm 1.3\%$ .

To further narrow the possible source(s) of the increased methane flux during the YD-PB transition, we can use the other isotopes of methane ( $\delta D-CH_4$  and  $^{14}C-CH_4$ ).

The GISP2 stable hydrogen isotope ( $\delta D-CH_4$ ) record for the YD-PB (Sowers, 2006) shows no significant trend within the transition with a near constant approximate value of  $-90\text{‰}$ , although there are relatively few measurements and thus higher uncertainty. The mean  $\delta D-CH_4$  value of the additional emissions ( $\delta D-CH_4 \uparrow_T$ ) is  $-314 \pm 8\text{‰}$ , after correction for sink processes ( $\varepsilon = -223.9\text{‰}$ ) and isotopic disequilibrium (Table 1 and Supplement S1c). No primary  $CH_4$  source has this combined  $\delta^{13}CH_4$  and  $\delta D-CH_4$  signature (Fig. 3). Therefore, it is likely that the  $\Delta Q_T$  during the YD-PB cannot be attributed to variations of a single source and the observed  $\Delta Q_T$  likely results from increased flux of two (or more) sources.

The YD-PB  $^{14}C-CH_4$  record provides a third constraint (Petrenko et al., 2009), although this record has high uncertainty due to a correction for in-situ  $^{14}C$  production and because the necessarily large samples contain gas of ages beyond the actual transition (Fig. 1). The  $^{14}CH_4$  record shows a fossil methane contribution in the later stages of the YD-PB ( $^{14}CH_4 \uparrow_T = -138\text{‰}$ ; range of 1.5 to  $-276\text{‰}$ , Petrenko et al., 2009).

Using the isotope records of the YD-PB, three separate mass balances can be formulated for the sources of  $\Delta Q_T$  as:

$$\delta^{13}C \uparrow \cdot \Delta Q_C = \delta^{13}C_1 \cdot \Delta Q_1 + \delta^{13}C_2 \cdot \Delta Q_2 + \delta^{13}C_3 \cdot \Delta Q_3 \quad (1)$$

$$\delta D \uparrow \cdot \Delta Q_C = \delta D_1 \cdot \Delta Q_1 + \delta D_2 \cdot \Delta Q_2 + \delta D_3 \cdot \Delta Q_3 \quad (2)$$

$$\Delta^{14}C \uparrow \cdot \Delta Q_C = \Delta^{14}C_1 \cdot \Delta Q_1 + \Delta^{14}C_2 \cdot \Delta Q_2 + \Delta^{14}C_3 \cdot \Delta Q_3 \quad (3)$$

where  $\Delta Q_n$  and  $\delta(^{13}C, D, ^{14}C) \uparrow_n$  are the fractional mass flux change across the YD-PB and the field measurement-based characteristic isotope values ( $\delta^{13}CH_4$ ,  $\delta D-CH_4$ ,  $^{14}CH_4$ ) of the  $n$ -th source term, respectively (Table 2).  $\Delta Q_C$  is the calculated total fractional mass flux (set as 1).  $\delta(^{13}C, D, ^{14}C) \uparrow_C$  are the calculated cumulative isotope values of the mixed sources, which can be compared to those derived from the ice

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records ( $\delta(^{13}\text{C}, \text{D}, ^{14}\text{C}) \uparrow_{\text{T}}$ ). As we have three mass balances with three unknowns, the mass balances can be solved simultaneously for  $\Delta Q_1$ ,  $\Delta Q_2$ , and  $\Delta Q_3$  (Supplement S3). The results must account for the analytical uncertainties of the underlying isotope data. Therefore, error ranges have been conservatively selected for each of  $\delta^{13}\text{CH}_4 \uparrow_{\text{T}}$ ,  $\delta\text{D-CH}_4 \uparrow_{\text{T}}$ , and  $^{14}\text{CH}_4 \uparrow_{\text{T}}$ . The  $\delta^{13}\text{CH}_4 \uparrow_{\text{T}}$  range ( $\pm 1.3\%$ ) was determined from the standard error-weighted linear regression model's 99% confidence interval maximum range (Fig. 2). For  $\delta\text{D-CH}_4$ , as there is little or no trend across the YD-PB, the  $\delta\text{D-CH}_4 \uparrow_{\text{T}}$  range ( $\pm 8\%$ ) is taken as double the experimental external precision ( $\pm 4\%$ ) (Sowers, 2006) to accommodate any possible errors due to under-sampling. The available  $^{14}\text{CH}_4$  record agrees well for the two YD measurements while the two PB values differ substantially (Petrenko et al., 2009). The  $^{14}\text{CH}_4 \uparrow_{\text{T}}$  range is calculated from the mean YD  $^{14}\text{CH}_4$  value and each of the PB  $^{14}\text{CH}_4$  values as 1.5 to  $-276\%$ .

As no primary  $\text{CH}_4$  source has the observed  $\delta^{13}\text{CH}_4 \uparrow_{\text{T}}$  ( $-49.2 \pm 1.3\%$ ) and  $\delta\text{D-CH}_4 \uparrow_{\text{T}}$  ( $-314 \pm 8\%$ ) signature, matching calculated  $\delta^{13}\text{CH}_4 \uparrow_{\text{C}}$  values to the ice records requires a mix of  $^{13}\text{C}$ -enriched and  $^{13}\text{C}$ -depleted sources. Only biomass burning and geologic emissions of methane (GEM) have  $\delta^{13}\text{CH}_4$  that can serve as the  $^{13}\text{C}$ -enriched source. Six primary sources can supply sufficiently  $^{13}\text{C}$ -depleted methane: aerobic plant methane (APM), tropical and boreal wetlands, thermokarst lakes, ruminants, and termites. To satisfy the requirement for a fossil methane contribution, as shown by the  $^{14}\text{CH}_4$  record, three sources emit fossil or  $^{14}\text{C}$ -depleted methane: GEM, thermokarst lakes, and marine gas hydrates. There are then 29 possible three-source scenarios that include a  $^{13}\text{C}$ -enriched, a  $^{13}\text{C}$ -depleted and a fossil component, where the contribution from each source can be quantified from the triple mass balance (see Supplement, Table S4). We impose two criteria on the mass balance calculation's source combinations to identify valid scenarios. First, the calculated cumulative isotope values,  $\delta(^{13}\text{C}, \text{D}, ^{14}\text{C}) \uparrow_{\text{C}}$ , must reproduce the ice isotope records within their respective uncertainties, which are chosen to be the reported analytical precision for  $\delta^{13}\text{CH}_4$ ,  $\delta\text{D-CH}_4$  and  $^{14}\text{CH}_4$  i.e.,  $\pm 0.3\%$  of  $\delta^{13}\text{CH}_4 \uparrow_{\text{T}}$ ,  $\pm 4\%$  of  $\delta\text{D-CH}_4 \uparrow_{\text{T}}$ ,

and  $\pm 10\%$  of  $^{14}\text{CH}_4 \uparrow_{\text{T}}$ , the latter an approximate conversion of the reported value ( $\sim 1$  pMC; Petrenko et al., 2009) to  $\Delta$ -notation. Second, the fractional contribution from each source,  $\Delta Q_1$ ,  $\Delta Q_2$ , and  $\Delta Q_3$ , must sum to  $1.0 \pm 0.1$  (the closer to one, the more probable).

All valid scenarios derived from the triple isotope mass balances listed in Table 3 have in common that the increased  $\text{CH}_4$  flux across the YD-PB,  $\Delta Q_{\text{T}}$ , is predominantly sourced ( $>50\%$ ) from biomass burning with a strong contribution ( $\sim 43\%$ ) from thermokarst lakes. The remaining sources (global wetlands, APM, termites, and ruminants) appear equally likely to have contributed a minor amount ( $<10\%$ ). A previous ice core  $\delta^{13}\text{CH}_4$  study concluded that the biomass burning source flux remained stable between the YD and PB periods (Fischer et al., 2008). Their conclusion is based on the comparison of average YD and PB values using the long-term decreasing  $\delta^{13}\text{CH}_4$  trend. In contrast, the pronounced rise in pyrogenic  $\text{CH}_4$  reported here specifically applies to the short transition period while  $[\text{CH}_4]$  and  $\delta^{13}\text{CH}_4$  change.

Accounting for the uncertainties in the various isotope data from the ice records by investigating the minimum and maximum values of each isotope while holding the other two at their mean values (see Supplement, Table S5) produces ranges for the various sources as  $\sim 42\text{--}66\%$  for biomass burning,  $\sim 27\text{--}59\%$  for thermokarst lakes and  $\sim 0\text{--}29\%$  for the complementing third source. Given these probability ranges, the finding that  $\Delta Q_{\text{T}}$  is composed mainly from biomass burning and thermokarst lakes with some contribution from a third source (or several minor ones), seems robust. However, additional uncertainty is introduced by incomplete understanding of present and past methane isotope budgets, which are investigated in the following section's sensitivity tests.

From Supplement (Table S5), three scenarios deserve further comment. If the YD-PB methane isotope values are best represented by the minimum  $\delta\text{D-CH}_4 \uparrow$  value ( $-322\%$ ) or the maximum  $\delta^{13}\text{CH}_4 \uparrow$  value ( $-47.9\%$ ) then the triple mass balance calculates a two-source mix of biomass burning and thermokarst lakes. While these source scenarios exceed the  $\sum \Delta Q$  acceptance criteria (by 1 to 2%), they fit the

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atmospheric isotope constraints better than any other source combinations for the minimum  $\delta\text{D-CH}_4 \uparrow$  or maximum  $\delta^{13}\text{CH}_4 \uparrow$  values (including all other source combinations listed in the Supplement, Table S6). Also the minimum  $^{14}\text{CH}_4 \uparrow$  value ( $-276\text{‰}$ ) produces no valid scenarios. This implies that a fossil contribution over the YD-PB transition of this magnitude is unlikely. The source fractional contributions thus do not include this scenario in the calculation of their ranges.

### 3.4 Mass balance sensitivity tests

The source contributions quoted in Sect. 3.3 are based on a standard scenario that uses modern isotope values adapted for the Younger Dryas conditions (Schaefer and Whiticar, 2008) (Tables 1, 2). We varied these parameters to investigate the sensitivity of the triple mass balance results for (i) alternative source isotope values, proportional sink strengths, and sink fractionation factors, (ii) the impact of changing environmental and climatic conditions upon source isotope values, including changes in the distributions of, and methane produced by,  $\text{C}_3$  and  $\text{C}_4$  vegetation (Schaefer and Whiticar, 2008), and (iii) different strengths of the MBL atomic chlorine sink. All sensitivity tests using the mean ice core based  $\delta^{13}\text{CH}_4 \uparrow$ ,  $\delta\text{D-CH}_4 \uparrow$ , and  $^{14}\text{CH}_4 \uparrow$  values are described in detail below. The sensitivity tests produce different sets of source scenarios that are subjected to the same evaluation criteria as the standard scenario. Valid scenarios are shown in the Supplement (Table S6).

#### 3.4.1 Fen-dominated wetlands

At the YD-PB, boreal peatlands were in their early development stages, which are likely best characterized as fen-dominated wetlands (MacDonald et al., 2006), rather than ombrotrophic *Sphagnum*-dominated bogs that are extensive in the boreal region today with a  $\delta^{13}\text{CH}_4$  value of about  $-65\text{‰}$ , as used in the standard scenario. Fen-dominated wetlands are arguably better represented by a more  $^{13}\text{C}$ -enriched  $\delta^{13}\text{CH}_4$

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value of  $-60\text{‰}$  (MacDonald et al., 2006) (Table 2). We investigated the triple mass balance sensitivity to this selection of the  $\delta^{13}\text{CH}_4$  value and found the changes to be minor. None of the scenarios changed their status as valid or invalid. The maximum estimated fractional contribution from boreal wetlands increases from 0.07 to 0.10.

### 3.4.2 Changing environmental and climatic conditions

In our standard scenario, source isotope values are changed from present day literature values following Schaefer and Whiticar (2008) and Whiticar and Schaefer (2007) to reflect different environmental and climatic conditions during the YD period. For  $\delta^{13}\text{CH}_4$ , we account for changes between modern and Preboreal/YD environmental and climatic conditions including: (i) changes in atmospheric  $\delta^{13}\text{CO}_2$ , (ii) vegetation patterns, including  $\text{C}_3/\text{C}_4$  plant distribution patterns, which influence the  $\delta^{13}\text{C}$  of the organic  $\text{CH}_4$  precursor material, (iii) the impact of temperature change on  $\text{CH}_4$  production itself, particularly in wetlands, and (iv) partial oxidation before emission to the atmosphere. To test the triple mass balance model sensitivity to these changes, we investigated two scenarios using  $\delta^{13}\text{CH}_4$  values characteristic of (i) modern conditions and (ii) the Preboreal period (Table 2). All other model parameters are unchanged. These changes resulted in no significant changes to the results of the standard scenario (see Supplement, Table S6).

### 3.4.3 Atomic chlorine in the marine boundary layer sink

A recent modelling study suggests that  $\delta^{13}\text{CH}_4$  enrichment on the order of  $0.3\text{‰}$  can result from glacial to interglacial changes in the sink configuration, primarily due to changes in the highly fractionating MBL atomic chlorine sink (Levine et al., 2011). As our observed trend far exceeds the modelled value, this supports the view that the processes are primarily source driven, although a contribution from sink changes cannot be ruled out. The impact of the inferred atomic chlorine sink in the MBL (Allan et al., 2001) is thus investigated. The strength of the MBL sink is based upon the estimated

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modern strengths from Allan et al. (2007). The standard scenario assumes a MBL sink at the estimated minimum modern strength (Allan et al., 2007) (Table 1). Sensitivity tests explore the influence of assuming (i) no MBL sink, (ii) the mean, and (iii) the maximum sink strength from Allan et al. (2007). All other model parameters remain the same as the standard scenario, except the fractional contributions from the other sinks are adjusted to accommodate the changes in the MBL sink. The ranges used in the sensitivity tests are  $-5.39$  to  $-9.02\text{‰}$  for total  $\epsilon_{\text{C}}$  and  $-218.3$  to  $-233.6\text{‰}$  for total  $\epsilon_{\text{D}}$ . The results of these changes to the MBL sink are small. The most significant difference is that a scenario with biomass burning (contribution of 66 %), thermokarst lakes (40 %) and marine gas hydrates (4 %) is valid for a zero MBL sink, however, this scenario is on the limit of the acceptance criteria. We note that these tests, as well as all mass balance scenarios, assume that  $\epsilon$ -values do not change through the transition.

### 3.4.4 Alternative $\delta^{13}\text{CH}_4$ and $\delta\text{D-CH}_4$ characteristic budgets

Alternative characteristic primary isotope value estimates for methane source types are used in the literature. Here we test model sensitivity compared to our chosen primary  $\delta^{13}\text{CH}_4$  and  $\delta\text{D-CH}_4$  values (Tables 1, 2). The first alternative budget tested is that of Fischer et al. (2008). This budget does not include termites, GEM, thermokarst lakes or an MBL sink. Additionally, their APM characteristic isotope values are not supported by measurements (Keppler et al., 2006; Vigano et al., 2009). We thus do not investigate scenarios involving these sources/sink with the exception of thermokarst lakes where our standard value is used.

The second alternative budget is that of Lassey et al. (2007), which does not include source characteristic values for APM, marine gas hydrates, or thermokarst lakes. Additionally, they do not distinguish  $\delta^{13}\text{CH}_4$  values between tropical and boreal wetlands (Lassey et al., 2007). We do not investigate scenarios involving APM or marine gas hydrates with the Lassey et al. (2007) budget.

The mass balance results of the two alternative budgets by Fischer et al. (2008) and Lassey et al. (2007) do not produce additional valid scenarios compared to the standard scenario (see Supplement, Table S6). This further supports the conclusion that the additional YD-PB CH<sub>4</sub> emissions were predominantly caused by biomass burning and thermokarst lakes with only small contributions from other sources.

From the sensitivity tests, the mass balances are most sensitive to changes in the primary source isotope values (see Supplement, Table S6). However, these probable alternative isotope values result in valid scenarios with the same dominant sources as the standard scenario.

### 3.5 Dominant source contributions

The fractional source flux changes from the triple mass balance calculations can be converted to absolute fluxes (in units of Tg CH<sub>4</sub> yr<sup>-1</sup>) by assuming a total flux increase  $\Delta Q_T$  of 64 Tg CH<sub>4</sub> yr<sup>-1</sup> (Petrenko et al., 2009). Due to the uncertainties in the ice core data and the model assumptions, the derived absolute fluxes for individual sources should be regarded as a best estimate only. However, the exercise may be informative to assess if individual source changes are probable in light of total source strengths and their estimated variability.

We calculate  $\Delta Q$  for biomass burning to be 27–42 Tg yr<sup>-1</sup>. This indicates an increase of up to ~100% by the end of the YD-PB, compared to estimates of the YD biomass burning CH<sub>4</sub> flux (Fischer et al., 2008; Melton, 2010). For comparison, global methane budget modelling results covering the last two decades show modern pyrogenic emissions ranging almost 30 Tg yr<sup>-1</sup> interannually (Bousquet et al., 2006; Drevet, 2008). While these studies necessarily include anthropogenic influences, they still illustrate the recognized sensitivity of biomass burning to climate and vegetation (Westerling et al., 2006; Bowman et al., 2009) even in the absence of an event the scale of the YD-PB. Changes in fire regimes can be related to fuel accumulation and vegetation distribution, as well as ignition sources, i.e. lightning (Westerling, 2009). Evidence of enhanced burning close to the YD-PB is observed in global charcoal datasets (Power

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et al., 2008; Daniau et al., 2010) and a North American charcoal and pollen dataset (Marlon et al., 2009).

It is also worthwhile to investigate if  $\text{CH}_4$  isotopes can provide quantitative estimates of changes in global biomass burning. Carbon monoxide is a trace gas component that can be used to confirm estimates of biomass burning. CO is largely produced through biomass burning and oxidation of non-methane hydrocarbons, and the relative proportions of these sources can be distinguished using stable isotopes. Recent results from an Antarctic ice core record CO mixing ratio and isotopic ratios record spanning the last 650 yr (Wang et al., 2010) supports the biomass burning estimates from two Antarctic ice core  $[\text{CH}_4]$  and  $\delta^{13}\text{CH}_4$  records (Ferretti et al., 2005; Mischler et al., 2009) and is generally consistent with the tropical charcoal index (Daniau et al., 2010). The Wang et al. (2010) study thus supports the ability of  $\delta^{13}\text{CH}_4$  to estimate changes in global biomass burning fluxes.

We estimate thermokarst lake  $\Delta Q$  to be  $17\text{--}38 \text{ Tg yr}^{-1}$ , i.e., slightly higher than derived from thermokarst lake basal initiation dates ( $\sim 10\text{--}16 \text{ Tg yr}^{-1}$ ) (Walter et al., 2007). As well, a recent reanalysis of the thermokarst lakes basal initiation dataset using a different methodology finds that the main thermokarst lakes expansion occurred after the YD-PB (Reyes and Cooke, 2011), contrary to our results. We note that both of these studies using thermokarst lake basal  $^{14}\text{C}$  initiation dates are somewhat uncertain as the database contains only 66 dates. As well, the initiation dates don't necessarily capture lateral expansion caused by climate changes (similar to peatlands, Korhola et al., 2010), which may at least partially account for the discrepancy between our estimates and those based upon thermokarst basal initiation dates. Thermokarst lake emissions into the Northern Hemisphere are consistent with the increase in inter-hemispheric  $[\text{CH}_4]$  gradient between the averages of the YD and PB periods (Brook et al., 2000; Dällenbach et al., 2000), although the latter may not be indicative of the short term transition dynamics. In conclusion, there is no clear support for our estimated magnitude of increased thermokarst lake  $\text{CH}_4$  production during the YD-PB from field evidence indicating a possible overestimate.

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Reyes and Cooke (2011) also reanalyzed two large basal peatland  $^{14}\text{C}$  datasets, one for Alaska (Jones and Yu, 2010) and the other spanning all circumpolar regions (MacDonald et al., 2006). They conclude that northern peatlands could not have been the primary drivers of the rapid increases in  $[\text{CH}_4]$  observed during the deglaciation. Their analysis is consistent with our triple mass balance results that show a minimal contribution from boreal peatlands, even if we assume the newly formed peatlands to be more productive minerotrophic fens rather than the present day ombrotrophic *Sphagnum*-dominated bogs (MacDonald et al., 2006) (Table 2, Sect. 3.4.1). Both their and our studies do not support an earlier suggestion (Jones and Yu, 2010) that Alaskan peatlands, less encumbered by ice sheet dynamics and thermal inertia than other circumpolar peatlands, could have contributed strongly to the  $\text{CH}_4$  rise.

Scenarios with substantial contributions ( $>10\%$ ) from either GEM (including thermogenic clathrates) or biogenic marine clathrates overestimate  $\Delta Q_T$  by at least 22% and 45%, respectively (Table 3) and do not satisfy the isotope constraints. Thus our findings are not consistent with any significant clathrate release over hydrocarbon seeps (GEM) (Hill et al., 2006) during the YD-PB.

### 3.5.1 Tropical wetlands

Tropical wetlands have been discussed as the predominant driver of the atmospheric methane concentration increase over the YD-PB (Brook et al., 2000). These arguments are based on the size of this source at present day (Denman et al., 2007) and inferred changes to the low-latitude hydrologic cycle (Peterson et al., 2000). However, from the triple mass balance results (Table 3 and Supplement, Table S4), tropical wetlands do not appear likely to have greatly increased their  $\text{CH}_4$  flux over the YD-PB, while we note that stable isotope values of wetland sources are possibly sensitive to changes in the ratio of net to gross  $\text{CH}_4$  production (Sowers, 2006) and source water  $\delta\text{D-H}_2\text{O}$  values (Bock et al., 2010).

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The hydrogen isotope ratio of wetland methane is ultimately derived from the hydrogen isotope ratio of meteoric water and hence precipitation (Whiticar, 1993) (recirculation notwithstanding). The hydrogen isotope ratio of precipitation is not constant through time. It is influenced by several factors, including the isotopic composition of the ocean, which, in turn, is largely determined by the size of terrestrial ice sheets. For example, the  $\delta\text{D-H}_2\text{O}$  values of the ocean during the Last Glacial Maximum ( $\sim 21$  kyr BP, LGM) are reported to be 6.5 to 9‰ more  $^2\text{H}$ -enriched than at present (Schrag et al., 2002). In addition, the modulating Rayleigh distillation effect will be strengthened by a stronger pole-to-equator temperature gradient in cold climates. Modelling of the LGM suggests that  $\delta\text{D-H}_2\text{O}$  values were 15 to 30‰ more  $^2\text{H}$ -depleted in northern latitudes while values in low latitudes may have been 0 to 8‰ more  $^2\text{H}$ -enriched than at present (Jouzel et al., 2000). The rapid changes in the hydrologic cycle proxies are suggested to reflect movement of the Intertropical Convergence Zone (ITCZ). Close to the ITCZ, the changes are unlikely to have a major effect on the  $\delta\text{D-H}_2\text{O}$  as the water is rapidly recycled, however the changes should lead to a latitudinal relocation of tropical wetlands. This effect has been assumed to be relatively small (Bock et al., 2010). For the carbon system, the  $\delta^{13}\text{CH}_4$  changes due to environmental and climate changes of the YD have been estimated to be 1.7‰ (Schaefer and Whiticar, 2008). No similar estimate exists for the hydrogen system.

To test the mass balance results for tropical wetlands, the  $\delta\text{D-CH}_4$  and  $\delta^{13}\text{CH}_4$  characteristic values for tropical wetlands were changed to extreme values to test the maximum contribution from tropical wetlands. The tropical wetland  $\delta\text{D-CH}_4$  value was changed to range between  $-300$ ‰ and  $-330$ ‰ (from a standard value of  $-315$ ‰). Shifts of this magnitude are larger than present evidence indicates (Jouzel et al., 2000; Bock et al., 2010) and result in a maximum estimate of tropical wetland  $\text{CH}_4$  flux increase. The tropical wetland  $\delta^{13}\text{CH}_4$  value is changed by  $+8.9$ ‰ from the modern value, or  $+7.2$ ‰ from the estimated YD value, to  $-50$ ‰ (see Table 1 for standard values) in the direction of the mean  $\delta^{13}\text{CH}_4 \uparrow$  value. To achieve a  $\delta^{13}\text{CH}_4$  value this  $^{13}\text{C}$ -enriched would require a disproportionately large contribution from  $\text{C}_4$  organic matter

to tropical wetland emissions as compared to estimated  $C_4/C_3$  distributions (Collatz et al., 1998; Schaefer and Whiticar, 2008). However, even with these extreme characteristic values, the fractional contribution only increases from 0.08 (standard scenario with mean  $\delta^{13}CH_4 \uparrow$ ,  $\delta D-CH_4 \uparrow$ , and  $^{14}CH_4 \uparrow$  values) to 0.22. As well, no additional scenarios pass the acceptance criteria besides those including biomass burning and thermokarst lakes as the main sources, as is the case for the standard tropical wetlands isotope values. Therefore, within the tested uncertainty ranges, our isotope mass balance results are not consistent with the hypothesis that tropical wetlands were the major source of increased methane flux during the YD-PB transition.

## 4 Conclusions

We present a new  $\delta^{13}CH_4$  dataset measured from Pákitsoq ice covering the YD-PB transition. A  $^{13}C$ -enrichment trend across the transition is evident and well exceeds measurement uncertainty. The trend is also evident in previously published Pákitsoq measurements (Schaefer et al., 2006) using different experimental setups (Ferretti et al., 2005; Schaefer et al., 2006), and an independent ice core study from Antarctica (Fischer et al., 2008).

A triple mass balance has been used to determine the most plausible source combination for the rapid  $[CH_4]$  increase during the YD-PB transition. The mass balance results show a strong role for biomass burning with an additional significant contribution from thermokarst lakes. The dominance of these two sources seems robust in spite of analytical uncertainties of the ice isotope records they are based on, as well as assumptions on past methane budgets as confirmed by sensitivity tests. In contrast, the quantitative interpretation of the fluxes is subject to the uncertainties of analyses and assumptions. Our analysis agrees with an increase in thermokarst lake methane emissions as previously suggested (Walter et al., 2007; Petrenko et al., 2009), but does not find a dominant role for tropical or boreal wetlands. The suggestion of a strong role for biomass burning in the rapid methane mixing ratio increase during the YD-PB

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transition is novel. If our results can be confirmed, they would indicate that as climate warms into the future as projected, special attention should be paid to the dynamics of biomass burning and thermokarst lakes. Both of these methane sources appear capable of responding to a changing climate with substantial increases in methane flux producing a positive feedback on the climate system.

**Supplementary material related to this article is available online at:**  
<http://www.clim-past-discuss.net/7/3287/2011/cpd-7-3287-2011-supplement.pdf>.

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**Table 1.** Carbon and hydrogen isotope fractionation factors and proportional strength values for the  $\text{CH}_4$  sink terms used in the mass balance calculations. The standard scenario with a weak MBL is denoted in bold font. Alternative values tested are shown in parentheses.

Sink	$\varepsilon_{\text{C}}$ (‰ VPDB)	$\varepsilon_{\text{D}}$ (‰ VSMOW)	Sink Fractional Strength			
			No MBL <sup>j</sup>	Weak MBL <sup>l</sup>	Mean MBL <sup>l</sup>	Strong MBL <sup>l</sup>
OH oxidation	<b>-3.9<sup>a</sup></b> (-5.4 <sup>i</sup> ) (-4.65 <sup>k</sup> )	<b>-231<sup>b</sup></b>	0.879 (0.838 <sup>k</sup> )	<b>0.860</b>	0.843	0.827
Soil uptake	<b>-22<sup>c</sup></b> (-20 <sup>k</sup> )	<b>-80<sup>d</sup></b>	0.052 (0.051 <sup>k</sup> )	<b>0.051</b>	0.050	0.049
Stratospheric Loss	<b>-12<sup>e</sup></b> (-3 <sup>k</sup> )	<b>-160<sup>f</sup></b>	0.062 (0.068 <sup>k</sup> )	<b>0.067</b>	0.066	0.065
Atomic chlorine in the marine boundary layer	<b>-66<sup>g</sup></b> (-60 <sup>k</sup> )	<b>-474<sup>h</sup></b>	0 (0.042 <sup>k</sup> )	<b>0.022</b>	0.041	0.060

<sup>a</sup> Saueressig et al. (2001)

<sup>b</sup> Gierczak et al. (1997)

<sup>c</sup> King et al. (1989), Tyler et al. (1994), Reeburgh et al. (1997)

<sup>d</sup> Snover et al. (2000)

<sup>e</sup> Wahlen et al. (1989a), Brenninkmeijer et al. (1995)

<sup>f</sup> Irion et al. (1996)

<sup>g</sup> Saueressig et al. (1995)

<sup>h</sup> Tyler et al. (2000)

<sup>i</sup> Alternative value by Cantrell et al. (1990) used by Fischer et al. (2008).

<sup>j</sup> Proportional sink strengths are in line with estimates in Denman et al. (2007).

<sup>k</sup> Values from Lassey et al. (2007).

<sup>l</sup> Proportional sink strengths are adjusted to accommodate the modern estimated sink strength of Allan et al. (2007) mean, low and high estimates.



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**Table 2.** Characteristic isotope values for primary sources used in the triple mass balance calculations. Isotope values used in the standard scenario are denoted in bold font. Isotope  $\delta^{13}\text{CH}_4$  values that are assumed not to change with time are denoted by “–”.  $\delta\text{D-CH}_4$  and  $\Delta^{14}\text{CH}_4$  values are unchanged from modern isotope values. Alternative source values for the sensitivity tests are shown in parentheses.

Source	$\delta^{13}\text{CH}_4$ (‰ vs. VPDB)			$\delta\text{D-CH}_4$ (‰ vs. SMOW)	$\Delta^{14}\text{CH}_4$ (‰ vs. NBS OAS <sup>a</sup> )
	Modern	PB <sup>b</sup>	YD <sup>b</sup>		
Tropical wetlands	–58.9 <sup>c</sup> (–60 <sup>g</sup> ) (–58 <sup>l</sup> )	–57	<b>–57.2</b>	– <b>315</b> <sup>d</sup> (–320 <sup>f</sup> )	<b>130</b> <sup>h</sup>
Boreal wetlands	–64.5 (–64 <sup>f</sup> ) (–60) <sup>o</sup>	–64.2	<b>–64.4</b>	– <b>360</b> <sup>d</sup> (–327 <sup>f</sup> )	<b>130</b> <sup>h</sup>
Thermokarst Lakes	–70 <sup>e</sup>	–	–	– <b>380</b> <sup>e</sup>	– <b>738.5</b> <sup>i</sup>
APM	–61 <sup>f</sup>	–59.4	<b>–59.6</b>	– <b>348</b> <sup>g</sup>	<b>200</b> <sup>j</sup>
Biomass burning	–24.6 <sup>c</sup> (–23 <sup>f</sup> ) (–25 <sup>g</sup> )	–26	<b>–26.2</b>	– <b>225</b> <sup>c</sup>	<b>300</b> <sup>k</sup>
Marine Gas hydrates	–62.5 <sup>c</sup> (–60 <sup>f</sup> )	–	–	– <b>190</b> <sup>c</sup>	– <b>1000</b> <sup>l</sup>
Ruminants	–60.5 <sup>c</sup> (–59 <sup>f</sup> ) (–62 <sup>g</sup> )	–57.6	<b>–57.8</b>	– <b>330</b> <sup>c</sup> (–300 <sup>f</sup> )	<b>200</b> <sup>h</sup>
GEM	–41.8 <sup>c</sup> (–40 <sup>g</sup> )	–	–	– <b>200</b> <sup>c</sup>	– <b>1000</b> <sup>m</sup>
Termites	–65 <sup>c</sup> (–57 <sup>g</sup> )	–64.8	<b>–65</b>	– <b>390</b> <sup>c</sup>	<b>238</b> <sup>n</sup>

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## Table 2. Continued.

<sup>a</sup> NBS OAS: oxalic acid standard (Donahue et al., 1990)

<sup>b</sup> Modern values are adapted for the PB and YD as in Schaefer and Whiticar (2008) and Whiticar and Schaefer (2007). If the initial modern value chosen differs from those in Schaefer and Whiticar (2008), the absolute change between time periods is applied to the isotope value chosen. Source isotope values that are not expected to be sensitive to environmental and climatic changes are kept at their modern isotope values. Equivalent changes due to the palaeo-environment have not been quantified for  $\delta\text{D-CH}_4$  thus modern values are used throughout (with the exception of the tropical wetlands sensitivity test outlined in Sect. 3.5 and Appendix D).  $\Delta^{14}\text{CH}_4$  values are assumed to not systematically change across the time periods.

<sup>c</sup> Whiticar and Schaefer (2007)

<sup>d</sup> Based upon Nakagawa et al. (2002a), Nakagawa et al. (2002b), and Waldron et al. (1999)

<sup>e</sup> Walter et al. (2008)

<sup>f</sup> Value is an average based on Keppler et al. (2006) and Vigano et al. (2009) for detached plant material. Whole plant values are not used due to the non-biotic nature of the  $\text{CH}_4$  production (Nisbet et al., 2009). A weighted average between  $\text{C}_3$  and  $\text{C}_4$  plants was based upon 25 % global grassland coverage, 57 % of which are  $\text{C}_4$  plants (Collatz et al., 1998).

<sup>g</sup> The measurements of Vigano et al. (2009) are the only reported  $\delta\text{D-CH}_4$  values. Isotope value is a weighted average of  $\text{C}_3$  and  $\text{C}_4$  plants in same proportion as noted above.

<sup>h</sup> Lassey et al. (2007)

<sup>i</sup> Walter et al. (2008). Estimate has high uncertainty as it is based on data from only two thermokarst lakes. Thermokarst lakes have been shown to emit methane with  $\Delta^{14}\text{CH}_4$  values ranging from modern to  $-993\text{‰}$  thus we follow Petrenko et al. (2009) in assuming the  $^{14}\text{C}$  in thermokarst lakes is a mixing of two-end member organic substrate materials: one modern and the other  $^{14}\text{C}$ -free. We assume the fraction of these two end-members is the same during the YD and PB as present and use the same flux-weighted average (Walter et al., 2008; Petrenko et al., 2009).

<sup>j</sup> We are not aware of any measured APM  $^{14}\text{CH}_4$  values therefore we assign APM the  $^{14}\text{C}$  value of ruminant  $\text{CH}_4$ .

<sup>k</sup> Quay et al. (1999). We assume that natural biomass burning has the same  $\Delta^{14}\text{CH}_4$  values as anthropogenic biomass burning measured  $\Delta^{14}\text{CH}_4$  values.

<sup>l</sup> Winckler et al. (2002)

<sup>m</sup> Quay et al. (1999). We assume mined natural gas has the same  $\Delta^{14}\text{CH}_4$  value as GEM.

<sup>n</sup> Wahlen et al. (1989b)

<sup>o</sup> To test the suggestion of MacDonald et al. (2006) that boreal wetlands during the deglaciation would be likely characterized by minerotrophic fens (e.g.  $-60\text{‰}$  but ranging  $-50$  to  $-73\text{‰}$ , Bellisario et al., 1999) rather than the present *Sphagnum* bog complexes.

<sup>p</sup> Table 1 of Etiope et al. (2008) lists the range of values for the different geologic sources.

<sup>q</sup>  $\delta^{13}\text{CH}_4$  values from Lassey et al. (2007).

<sup>r</sup>  $\delta^{13}\text{CH}_4$  and  $\delta\text{D-CH}_4$  values from Fischer et al. (2008).

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**Table 3.** Triple isotope mass balance model results for YD-PB source scenarios. Fractional source contributions are calculated simultaneously via the triple isotope mass balance and compared to the mean ice record  $\delta^{13}\text{CH}_4 \uparrow_{\text{T}}$ ,  $\delta\text{D-CH}_4 \uparrow_{\text{T}}$  and  $^{14}\text{CH}_4 \uparrow_{\text{T}}$  values for scenario acceptance. All valid scenarios (bold font) pass the acceptance criteria outlined in the text. Solutions with negative emissions are physically meaningless and are listed in the Supplement (Table S4).

Scenario #	Source Fractional Contribution ( $\Delta Q$ )										$\Delta Q_{\text{C}}$	Satisfy acceptance criteria?
	Biomass burning	GEM	Thermokarst lakes	Biogenic marine gas hydrates	Aerobic plant methane	Ruminants	Tropical wetlands	Boreal wetlands	Termites			
1	<b>0.54</b>		<b>0.43</b>		<b>0.08</b>						<b>1.05</b>	<b>Y</b>
2	<b>0.55</b>		<b>0.43</b>			<b>0.08</b>					<b>1.06</b>	<b>Y</b>
3	<b>0.56</b>		<b>0.43</b>				<b>0.08</b>				<b>1.07</b>	<b>Y</b>
4	<b>0.56</b>		<b>0.43</b>					<b>0.07</b>			<b>1.06</b>	<b>Y</b>
5	<b>0.53</b>		<b>0.43</b>						<b>0.08</b>		<b>1.04</b>	<b>Y</b>
6	0.60	0.38			0.29						1.28	N
7	0.64	0.39				0.28					1.31	N
8	0.68	0.38					0.28				1.33	N
9	0.65	0.37						0.26			1.28	N
10	0.56	0.37							0.29		1.22	N
11	0.71		0.37	0.08							1.15	N
12	1.01	0.24		0.20							1.45	N

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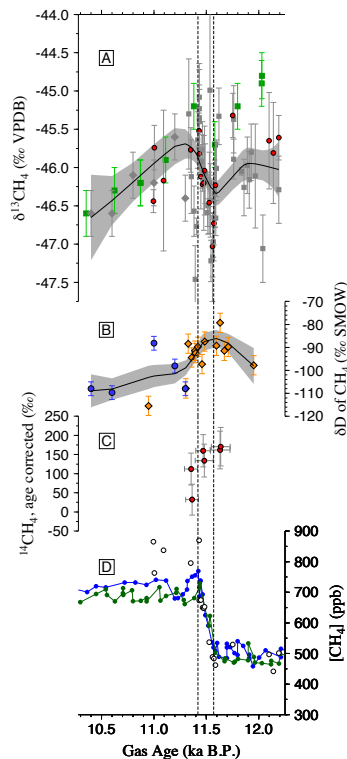
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**Fig. 1.** The Younger Dryas to Preboreal  $\delta^{13}\text{CH}_4$ ,  $\delta\text{D}-\text{CH}_4$ ,  $^{14}\text{CH}_4$ , and  $(\text{CH}_4)$  records. **(A)** Pákitsoq, Greenland  $\delta^{13}\text{CH}_4$  records from this study (circles) and Schaefer et al. (2006) (grey squares) (Schaefer et al., 2006), GISP2 (diamonds) (Sowers, 2010), and EPICA EDML (green squares) (Fischer et al., 2008). A weighted loess spline fit to the Greenland data (shaded region is a  $1\sigma$  standard error envelope, span 0.75) shows the general trends although it dampens the larger changes in the isotope record. **(B)** The  $\delta\text{D}-\text{CH}_4$  record from GISP2 (circles – Sowers, 2010 – and diamonds – Sowers, 2006) with a weighted loess spline (span 0.75). **(C)** The  $^{14}\text{CH}_4$  record from Pákitsoq, Greenland (cosmogenic  $^{14}\text{C}$ -corrected values) (Petrenko et al., 2009). **(D)**  $[\text{CH}_4]$  records from GISP2 (blue) (Brook et al., 2000), EDML (green) (EPICA Community Members, 2006), and Pakitsoq IRMS (open circles). The latter record has lower precision. All data are shown using the revised Pak06 age scale (see Supplement S2). The vertical dashed lines show the YD-PB limits.

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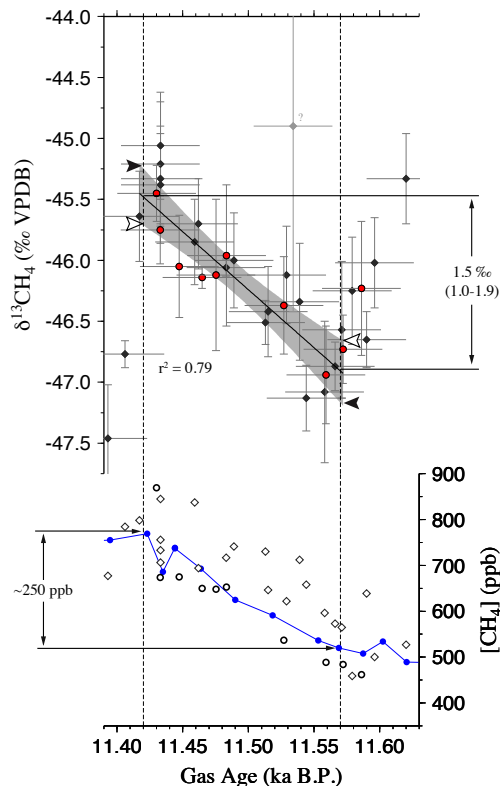
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**Fig. 2.** The YD-PB equilibrated atmospheric  $\delta^{13}\text{CH}_4$  and  $[\text{CH}_4]$  record from Pākitoq ice samples. The top panel shows the isotopic disequilibrium corrected  $\delta^{13}\text{CH}_4$  from this study (circles) and Schaefer et al. (2006) (diamonds). The data are fit with a weighted linear regression between the gas ages of the last low  $[\text{CH}_4]$  value and the peak  $[\text{CH}_4]$  value in the GISP2 record (shaded region is the 99% model fit confidence interval). The  $\delta^{13}\text{CH}_4$  value range is found from the model confidence interval's minimum (unfilled arrowheads) and maximum (filled arrowheads) differences. The estimated range in age per sample is ca. 25–35 yr (indicated as uncapped horizontal bars), which includes both sample thickness and gas age distribution due to diffusion and bubble enclosure (Schaefer et al., 2006). Bottom panel:  $[\text{CH}_4]$  records from GISP2 (blue line) (Brook et al., 2000) and Pākitoq (open circles (this study) and diamonds; Schaefer et al., 2006).

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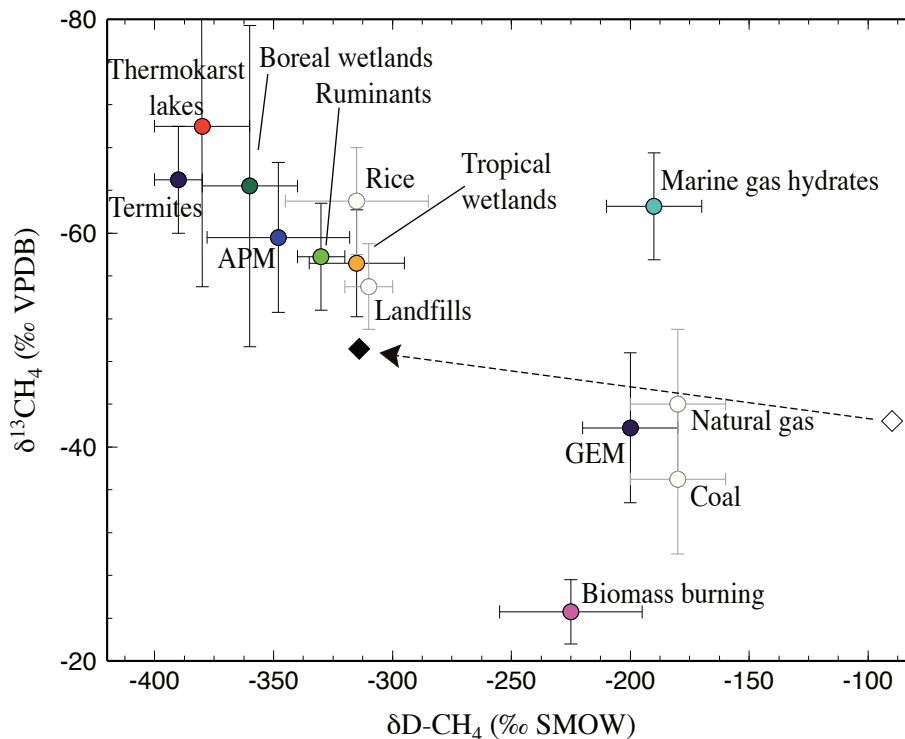
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**Fig. 3.** Combination of characteristic  $\delta^{13}\text{CH}_4$  and  $\delta\text{D-CH}_4$  signatures for the major primary sources of methane to the troposphere, together with the calculated mean source isotope values ( $\delta^{13}\text{CH}_4 \uparrow_T$ ,  $\delta\text{D-CH}_4 \uparrow_T$ ) (black diamond) as derived from the ice core signal (white diamond) (Tables 1, 2). Unfilled circles are anthropogenic sources.

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