Supplemental material

a)　　$\delta^{13}CH_4$ *analyses:*

$\delta^{13}CH_4$ measurements were performed using a purge and trap extraction coupled to a gas chromatography - isotope ratio mass spectrometer (GC-IRMS)[1]. Using this technique sample sizes of only 150-200 g of ice, equivalent to 15-20 ml of air at standard pressure (STP), are required for low CH_4 concentration samples during the glacial. Ice samples were melted in an ultrahigh vacuum glass vessel and the air was stripped from the molten sample with He carrier gas. Water is removed from the carrier gas stream by a cooled Nafion membrane and easily condensable gases (e.g. CO_2, N_2O) were largely removed in a consecutive cold trap. Subsequently, CH_4 was separated form the bulk of N_2 and O_2 on a preconcentration column (Hayesep D). After cryofocusing, these gases were separated on a GC column (Carbon PLOT, 30°C) and CH_4 quantitatively combusted to CO_2 in a microoxidation oven filled with Cu, Ni and Pt wires. The CO_2 peak produced was then admitted to the MS via an open split.

Absolute standardization is achieved in every run using (i) a pure CO_2 standard ($\delta^{13}CO_2$=-49.35±0.013 ‰) admitted via an open split, (ii) a pure CH_4 standard admitted to the GC He stream to constrain changes in the fractionation in the GC and the combustion oven (long-term average $\delta^{13}CH_4$=-40.27±0.07 ‰ after correction for systematic trends) and (iii) 10 ml STP of a synthetic atmospheric lab air standard admitted into the extraction vessel to correct for potential fractionation during the complete extraction process. All $\delta^{13}CH_4$ values are referenced against VPDB. To check the absolute accuracy of the overall extraction and combustion process a referenced modern air sample has been introduced five times. This showed

0.29±0.1 ‰ more enriched values than the reference value ($\delta^{13}CH_4$=-47.07±0.04 ‰).

Accordingly we corrected all our samples for this offset.

Extraction of our lab air standard (1000 ppbv CH_4, $\delta^{13}CH_4$=-40.85 ‰ after correction

for the 0.29 ‰ offset) through melt water directly after sample extraction showed on

average 0.18 ‰ more depleted $\delta^{13}CH_4$ than without melt water due to a memory

effect of the preceding ice sample. Using an isotope balance between ice sample and

consecutive air standard we can quantify our extraction efficiency to 90±2 %. Outliers

in the ice samples, where also the consecutive standard air samples deviated

significantly, were excluded from the data set and remeasured. Extraction of the same

air standard from totally degassed water showed no systematic fractionation during

the extraction process and a $\delta^{13}CH_4$ reproducibility of ±0.09 ‰. Accordingly, we

conclude that no systematic fractionation occurs during purging of air from molten ice

samples but that the small systematic fractionation of +0.29 ‰ occurs either during

preconcentration or combustion. Replicate samples from the EDML ice core have

been measured on 5 depth intervals, showing also a mean standard deviation of ±0.09

‰, with somewhat larger uncertainties for glacial samples with low CH_4

concentration. $\delta^{13}CH_4$ values given in this study were corrected for gravitational

enrichment in the firn column using $\delta^{15}N_2$ data[2]. This correction leads to 0.4-0.47 ‰

more depleted values for the LGM and Holocene. An 0.4-0.45 ‰ correction is also in

line with modelling of the firn column[3], however with a tendency to smaller

corrections for warm periods. In summary, we estimate the reproducibility of our

measurements to be better than 0.15 ‰ and the accuracy to be better than 0.3 ‰. The

latter value derives essentially from the systematic fractionation during our total

sample preparation and this offset is the same for all samples. Accordingly, it does not

influence the change in the isotopic signature between different time periods. Note that the uncertainty is more than one order of magnitude lower than the long-term changes in our $\delta^{13}CH_4$ ice core record over the last glacial/interglacial transition.

b)   Monte Carlo box model

Potential source emission mixtures have been determined for the different climatic stages in steady state using a box model of the atmospheric CH_4 cycle for time intervals where CH_4 and its isotopic signature were relatively constant (see supplemental table 2). Note, that this approach does not apply for times of rapid CH_4 variations (such as the transition from the YD to the PB), where both disequilibrium terms in the atmospheric isotope balance[4] as well as concentration gradient driven diffusion of CH_4 into the firn column[5] would lead to excursions in $\delta^{13}CH_4$ and $\delta D(CH_4)$. It should also been pointed out, that our model is intended as a first order approach and does not include temperature and water table dependencies of fractionation factors during CH_4 production or a temporal change e.g. in the partitioning between C3 and C4 plants which may change the effective isotope signature of the wetland and biomass burning sources.

The atmosphere in our model is divided into northern and southern hemisphere tropospheric and stratospheric boxes with prescribed air mass exchange[6]. CH_4 emissions into the northern and southern troposphere are prescribed with fixed isotopic signatures ([7, 8] and references therein) as summarized in Table S1. The model takes oxidation in the troposphere, stratosphere and uptake by aerated soils into account with prescribed fractionation factors[7] as given in Table S1. A secondary tropospheric sink by reaction with atomic Cl in the marine boundary layer as currently

discussed[9] has not been explicitly included in the model. To parameterize sink processes the total lifetime was specified as well as the relative contribution of the three sinks to the overall CH_4 loss. For validation, the model was forced with emissions from wetlands, ruminants, biomass burning, rice paddies, landfills, natural gas and coal emissions for the 1990s[7], where boreal wetlands are the only sources that emit CH_4 entirely into the northern troposphere. In this configuration the model reproduced the tropospheric CH_4 concentration, $\delta^{13}CH_4$, $\delta D(CH_4)$ and the interhemispheric gradients of all three parameters very well and lead to an atmospheric lifetime of 8.4 years in line with literature values[7]. The model was then expanded by allowing for potential additional emissions by plants under aerobic conditions[10, 11] and marine gas hydrate dissociation. So far no hydrogen isotopic signature for aerobic plant emissions has been reported in the literature. We used a $\delta D(CH_4)$ of plant emissions of -290 ‰ which is very close to the total emission weighted average of all sources. This means that we choose the plant source to be isotopically neutral with respect to hydrogen and that it does not influence the model outcome. In particular, this assumption does not affect our conclusions with respect to lifetime, biomass burning and boreal wetland emissions in the past, which are essentially determined by the total CH_4 emission, $\delta^{13}CH_4$ and the interhemispheric concentration gradient but not strongly by $\delta D(CH_4)$. Because the total plant emission is only weakly constrained by the model and data, we refrain from making any inferences on this source. Inclusion of aerobic plant and gas hydrate emissions for conditions during the 1990 lead only to minor adjustments of the emissions by the other sources as given in table S2.

To constrain CH_4 emissions in the past the model was first run in a Monte Carlo mode, where emissions of each individual source and the lifetime were randomly picked within reasonable limits. The atmospheric CH_4 model was then run forward in time to achieve equilibrium with the new emission values. The resulting atmospheric CH_4 concentrations in the northern and southern hemisphere, $\delta^{13}CH_4$ in the south and $\delta D(CH_4)$ in the north were then compared with our $\delta^{13}CH_4$ and literature data[3, 12-14]. If they agreed within ± 10 ppbv for concentrations, ± 0.4 ‰ for $\delta^{13}CH_4$ and ± 10 ‰ for $\delta D(CH_4)$ the model run was accepted as a possible realization and the Monte Carlo procedure was repeated until 10,000 possible realizations were found, defining a probability distribution of possible values. Because the range of allowed values changed for different time periods we normalized the probability functions of the Monte Carlo method to the most likely result to make the probability distributions comparable. Based on these normalized probability functions (NPF) we picked a realization close to the most likely result for each individual source and sink. Interestingly, the most likely results in each species reasonably fulfilled also the data constraints so only minor manual optimization was necessary to optimize the agreement between model and data constraint and to come up with an initial, only data constrained emission estimate. This implies that there are no other completely different realizations in the joint parameter space which fulfill the data constraints with equally high likelihood. However, also less likely realizations fulfill the data constraints. This becomes especially important for the atmospheric lifetime, where the NPF shows a strong tailing for higher lifetimes, which are more in line with atmospheric chemistry models[15, 16]. Accordingly, in a second step we constrained the results of our Monte Carlo model in line with such chemistry models to lifetimes longer than 5 yr to obtain our best guess estimates in Table S2. Note, that only bold

numbers represent emissions sufficiently constrained by a clear peak in the NPF. Other estimates (given in italic) show only weak or no peaks in the NPFs and can not be regarded as robust emission estimates.

Due to the close agreement of recent CH_4 data and emission estimates[7] with our model result the model configuration is unlikely to have a strong influence on the outcome in the past. However, larger uncertainties arise from the specification of isotopic source signatures for the individual CH_4 sources. In a sensitivity test, we changed the isotopic signature for biomass burning from our standard value of -23 ‰ to -20 ‰ to account for a possible extension of C4 grasses in the LGM. In line with the isotopic mass balance this led to a 10 % smaller estimate of biomass burning emissions. More problematic is the uncertainty in the isotopic signature of marine gas hydrates which span a wide $\delta^{13}CH_4$ range from -40 to -80 ‰ dependent on their thermogenic or biogenic origin, respectively. Even less is known for $\delta D(CH_4)$ emitted from marine gas hydrates, however the carbonate reduction pathway of CH_4 formation requires a source isotopically more enriched than for wetlands where acetate fermentation prevails[8]. In principle gas hydrates from both biogenic and thermogenic origin may have contributed to a release in the past, although isotopically depleted biogenic gas hydrates are ubiquitous in high productivity shelf areas around the continental margins and appear to be prime candidates. In our standard run we used an average $\delta^{13}CH_4$ signature for gas hydrate emissions of -60 ‰[8] and a $\delta D(CH_4)$ of -190 ‰[14]. In a sensitivity test we also used $\delta^{13}CH_4$= -80 ‰ and -40 ‰, which did not affect our conclusions on the shut off of boreal wetlands and on the temporal evolution of biomass burning over the transition. However, changing $\delta^{13}CH_4$ of gas hydrates changes the total amount of biomass burning emissions needed to fulfill the

ice core $\delta^{13}CH_4$ constraint, with biomass burning emissions being smaller the more isotopically enriched the gas hydrate source is assumed. In view of the good agreement of biomass burning estimates with literature values for the 1990s we picked a $\delta^{13}CH_4$ signature of marine gas hydrate emissions of -60 ‰ in our standard run. Changing the contribution of tropospheric OH oxidation relative to the other sinks has a strong influence on the hydrogen isotopic signature of atmospheric CH_4 but only a small effect on $\delta^{13}CH_4$. Thus, the total gas hydrate emission is not well constrained. However, the higher $\delta D(CH_4)$ value during cold conditions[14] contradicts a strong increase in the release of CH_4 from marine gas hydrates during rapid climate warmings as already pointed out by Sowers[14].   (Word count: 1921)

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Table S1: Isotopic signature of CH_4 sources (bold mainly natural, italic anthropogenic) and isotopic fractionation ε for CH_4 sinks ([7, 8] and references therein) as used in the 4 box model. For 1990 conditions the carbon isotopic signatures for natural sources were lowered by 1 ‰ to account for the uptake of light fossil fuel carbon in the substrate of CH_4 production. Values in parentheses refer to alternative runs for sensitivity studies. All values are given in ‰ against VPDB for $\delta^{13}CH_4$ and against SMOW for $\delta D(CH_4)$.

	$\delta^{13}CH_4$	$\delta D(CH_4)$	$\varepsilon(^{13}C)$	$\varepsilon(D)$
Tropical wetlands	**-58**	**-320**	-	-
Boreal wetlands	**-64**	**-327**	-	-
Plants	**-46**	**-290**	-	-
biomass burning	**-23 (-20)**	**-225**	-	-
marine gas hydrates	**(-40) -60 (-80)**	**-190**	-	-
Ruminants	**-59**	**-300**	-	-
rice paddies	*-63*	*-320*	-	-
Landfills	*-50*	*-310*	-	-
Gas	*-43*	*-185*	-	-
Coal	*-36*	*-140*	-	-
tropospheric oxidation	-	-	-5.4	-231
stratospheric oxidation	-	-	-12	-160
Soil Uptake	-	-	-22	-80

Table S2: Estimates of atmospheric lifetime (in years) and CH_4 emissions (in Tg CH_4/year) by individual sources for different time periods. Values in the upper line for each source represent initial, only data constrained estimates which cover the whole range of atmospheric lifetimes. The lower line represents data and chemistry model constrained best guess estimates, where atmospheric lifetimes were limited to values larger than 5 yr. Bold letters indicate estimates derived from clear peaks in the normalized probability functions (NPF), bold numbers in parentheses refer to emissions with 50 % probability of the peak in the NPF for the entire range of lifetimes. Note, that also values outside of this interval fulfill the data constraint but are less likely. Values given in italic refer to estimates not well constrained by the NPF and may vary largely. Therefore, italic numbers in parentheses give the whole range, in which emission were varied in the Monte Carlo model.

	preboreal Holocene 10-11 ka BP	Younger Dryas 11.7-12.6 ka BP	Bølling/ Allerød 13-14.5 ka BP	Last Glacial Maximum 19-22 ka BP
tropical wetlands	*170 (60-220)* *130*	*140 (60-180)* *75*	*140 (60-180)* *120*	*130(60-180)* *75*
boreal wetlands	**54 (35-73)** **54**	**20 (4-38)** **20**	**36 (18-56)** **36**	**3 (0-10)** **4**
plants	*30 (0-60)* *30*	*30 (0-60)* *25*	*30 (0-60)* *30*	*20 (0-60)* *20*
biomass burning	**55 (36-68)** **47**	**52 (32-68)** **36**	**46 (32-59)** **44**	**65 (41-90)** **41**
ruminants	*30 (0-70)* *30*	*30 (0-70)* *30*	*30 (0-70)* *30*	*20 (0-70)* *20*
marine gas hydrate	*20 (0-60)* *15*	*25 (0-60)* *18*	*30 (0-60)* *30*	*35 (0-60)* *20*
atmospheric lifetime	**5.4 (4.4-6.8)** *6.3*	**4.4 (3.3-5.4)** *6.5*	**5.8 (4.5-7.3)** *6.2*	**3.7 (2.7-4.2)** *5.6*