

Independent variations of CH₄ emissions and isotopic composition over the past 160,000 years

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During the last glacial cycle, greenhouse gas concentrations fluctuated on decadal and longer timescales. Concentrations of methane, as measured in polar ice cores, show a close connection with Northern Hemisphere temperature variability, but the contribution of the various methane sources and sinks to changes in concentration is still a matter of debate. Here we assess changes in methane cycling over the past 160,000 years by measurements of the carbon isotopic composition $\delta^{13}\text{C}$ of methane in Antarctic ice cores from Dronning Maud Land and Vostok. We find that variations in the $\delta^{13}\text{C}$ of methane are not generally correlated with changes in atmospheric methane concentration, but instead more closely correlated to atmospheric CO₂ concentrations. We interpret this to reflect a climatic and CO₂-related control on the isotopic signature of methane source material, such as ecosystem shifts in the seasonally inundated tropical wetlands that produce methane. In contrast, relatively stable $\delta^{13}\text{C}$ values occurred during intervals of large changes in the atmospheric loading of methane. We suggest that most methane sources—most notably tropical wetlands—must have responded simultaneously to climate changes across these periods.

Climate variations over the past glacial cycle are characterized by global temperature changes^{1,2}, sea-level fluctuations^{3,4} and substantial changes in atmospheric greenhouse gas concentrations⁵. Abrupt climate shifts, for example Dansgaard–Oeschger events, characterize much of the glacial records in the Northern Hemisphere and are mirrored in the ice-core CH₄ record^{6,7}.

The nature of the CH₄–climate coupling on glacial–interglacial and millennial timescales is still a matter of debate^{7,8}. Studies of the inter-polar CH₄ concentration difference using ice cores from both polar regions are interpreted as a constraint of the latitudinal distribution of CH₄ emission sources^{9,10}. Furthermore, most CH₄ sources/sinks have characteristic isotope signatures. Accordingly, atmospheric CH₄ isotope records provide refined boundary conditions to constrain changes in individual sources or sinks over time^{11–13}. Here we present CH₄ isotope data from ice cores covering the past 160,000 years (160 kyr; Fig. 1), thereby extending the atmospheric $\delta^{13}\text{CH}_4$ record to a full glacial–interglacial cycle.

Generally, our record confirms increased $\delta^{13}\text{CH}_4$ values under full glacial conditions¹¹, decreasing $\delta^{13}\text{CH}_4$ during terminations (except during the unique Younger Dryas cold reversal) and the continuation of this declining trend over the following interglacial¹³, irrespective of the CH₄ evolution. Although an unambiguous alignment of termination I and II is not possible owing to the Younger Dryas event, $\delta^{13}\text{CH}_4$ values of the two deglaciations seem to be offset by $\sim 2\%$ (Fig. 2). Minimum $\delta^{13}\text{CH}_4$ values are found during marine isotope stage (MIS) 5d–e. $\delta^{13}\text{CH}_4$ increases over the past glaciation, superimposed by variability largely in parallel to millennial CO₂ changes. Most importantly, this new $\delta^{13}\text{CH}_4$ record does not share common features with the CH₄ record over the same interval. The most striking of these dissimilarities is found during the MIS 5–4 transition (between 70

and 64 kyr before present (BP), where present is defined as 1950), when $\delta^{13}\text{CH}_4$ rises by $\sim 4\%$, whereas CH₄ fluctuations are smaller than 50 parts per 10⁹ (ppb; Fig. 3). In stark contrast to the MIS 5–4 transition, rapid CH₄ changes during Dansgaard–Oeschger events are not imprinted in the $\delta^{13}\text{CH}_4$ record.

Comparing the full $\delta^{13}\text{CH}_4$ record with other global climate records provides some surprising insights into the CH₄/ $\delta^{13}\text{CH}_4$ system (Fig. 1): correlations of our $\delta^{13}\text{CH}_4$ record with CH₄, sea level and CO₂ data lead to correlation coefficients (R^2) of 0.29, 0.47 and 0.74, respectively. Moreover, $\delta^{13}\text{CH}_4$ and CO₂ are not only correlated on the glacial–interglacial timescale, but also over millennial scale variations associated with the Antarctic Isotope Maxima^{2,14}.

In summary, the decoupling of CH₄ loading and $\delta^{13}\text{CH}_4$ can be separated into two general phenomena: times when CH₄ source/sink variations change the atmospheric loading with little or no imprint in $\delta^{13}\text{CH}_4$; and times when $\delta^{13}\text{CH}_4$ varies substantially but the balance of sources and sinks, thus CH₄ concentration, seems to be rather constant. We will discuss the $\delta^{13}\text{CH}_4$ record in two parts, based on these two surprising observations.

Rapid CH₄ concentration changes

The mean carbon isotopic signature of atmospheric CH₄ represents a flux weighted mean of all source emissions shifted by the isotopic fractionation induced by its sinks¹⁵. We can think of several explanations for periods where CH₄ loading changed, but $\delta^{13}\text{CH}_4$ remained effectively constant. Given that the primary sink for atmospheric CH₄ is OH oxidation (>85%), changes in the palaeo OH reaction rates would influence the loading through changes in lifetime, but leave $\delta^{13}\text{CH}_4$ unchanged. We discount this possibility based on atmospheric chemical modelling studies that show only subtle changes (<20%) in OH sink strength during glacial

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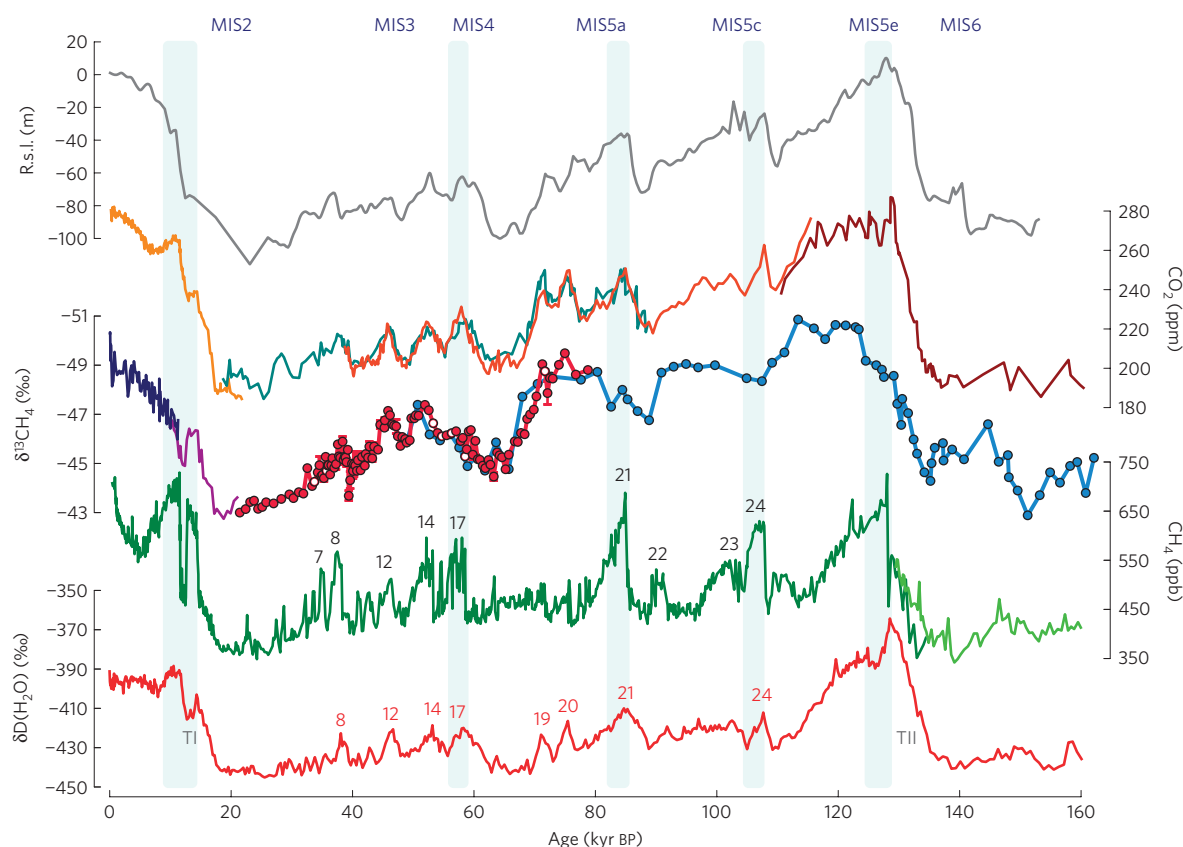


Figure 1 | Methane carbon isotope and other climate records. From top: relative sea-level (r.s.l.) reconstruction^{3,4}. Atmospheric CO₂ from Vostok⁴⁷ (brown), EDML and Talos Dome⁴⁸ (orange), Byrd¹⁴ (turquoise) and EPICA Dome C (EDC; ref. 49; yellow), in parts per million (ppm). $\delta^{13}\text{CH}_4$ from Vostok (light blue) and EDML (dark red). Records for termination 1 (TI; ref. 11; EDML, purple) and the Holocene (Greenland Ice Sheet Project Two (GISP2), dark blue). Note the inverted y axis for the $\delta^{13}\text{CH}_4$ records. Samples potentially affected by diffusive fractionation are marked by white circle fillings. Atmospheric CH₄ from EDC (ref. 7; light green) and EDML (ref. 5; dark green). δD in precipitation at Dome C (ref. 50; red). Arabic numbers indicate the timing of Dansgaard-Oeschger events and their respective Antarctic counterparts^{1,2}. All records, except GISP2 $\delta^{13}\text{CH}_4$ and r.s.l., are given on the unified ice-core chronology⁴⁶. Vertical bars indicate periods when the correlation between CO₂ and CH₄ breaks down. TII, termination 2.

periods^{16,17}. We note however that the lifetime estimate is somewhat uncertain owing to the lack of accurate reconstructions for glacial NO_x and volatile organic carbon concentrations, which influence tropospheric OH levels.

Alternatively, rapid Dansgaard-Oeschger CH₄ variability without a corresponding imprint in $\delta^{13}\text{CH}_4$ could imply an almost proportional scaling of the main sources, causing the atmospheric $\delta^{13}\text{CH}_4$ signature to remain relatively stable. Several lines of evidence suggest that this was the case. The latitudinal position of the intertropical convergence zone and the associated main monsoon systems are intimately coupled to Dansgaard-Oeschger climate variability^{6,18–21}. Hydrological changes in low latitudes and their primary control on waxing and waning of tropical wetland emissions are arguably the most important factors driving glacial CH₄ emissions^{6,18}. As the isotopic signature of tropical wetland emissions is closest to the mean $\delta^{13}\text{CH}_4$ signature of all sources, changes in their emissions have only little impact on atmospheric $\delta^{13}\text{CH}_4$.

Palaeofire reconstructions inferred from charcoal records suggest increasing wildfire activity during interstadial periods²², although they do not allow for a quantitative estimate of wildfire CH₄ emissions. Wildfire emissions have the strongest leverage on the atmospheric $\delta^{13}\text{CH}_4$ value, as its carbon isotopic signature is strongly enriched. Accordingly, the lack of considerable $\delta^{13}\text{CH}_4$ shifts during Dansgaard-Oeschger events implies that increased wildfire emissions had to be compensated by another, isotopically light source. Combinations including additional ¹³C-enriched wildfire emis-

sions during interstadials²² and ¹³C-depleted boreal permafrost emissions^{12,23,24} could explain the observations, although it seems fortuitous that such relative changes would perfectly balance each other in all investigated events.

Enhanced emissions from high-latitude Northern Hemisphere CH₄ wetland sources (such as thermokarst lakes²⁴, peatlands and permafrost thaw²³, further denoted as boreal wetlands) have been suggested to explain increased inter-polar CH₄ gradients during interstadial periods^{9,10}. Increased Northern Hemisphere CH₄ levels during interstadials, however, could also be caused by increased emissions from mid-to-low latitude wetland sources, for example, seasonally inundated floodplains in the Chinese lowlands, which are affected by expansive Asian summer monsoon rainfall²¹.

Finally, although geological CH₄ sources are thought to be slightly increased during glacial times owing to lowered sea levels^{25,26}, they should be unaffected by Dansgaard-Oeschger events. Furthermore, large emissions from marine hydrates²⁷ during abrupt CH₄ episodes have been ruled out based on our recent $\delta\text{D}(\text{CH}_4)$ ice-core studies^{12,28}.

Possible sink configuration changes that could induce an equivalent enrichment in $\delta^{13}\text{CH}_4$ to compensate for potential boreal CH₄ emissions would have to reduce the relative importance of the OH sink in the troposphere. However, owing to the expected reduction of volatile organic carbons during the glacial^{29,30} and the feedback of lower CH₄ concentrations on the atmospheric OH concentration itself, the OH sink was probably even more important during cold conditions. In summary, a strong feedback of the main monsoon

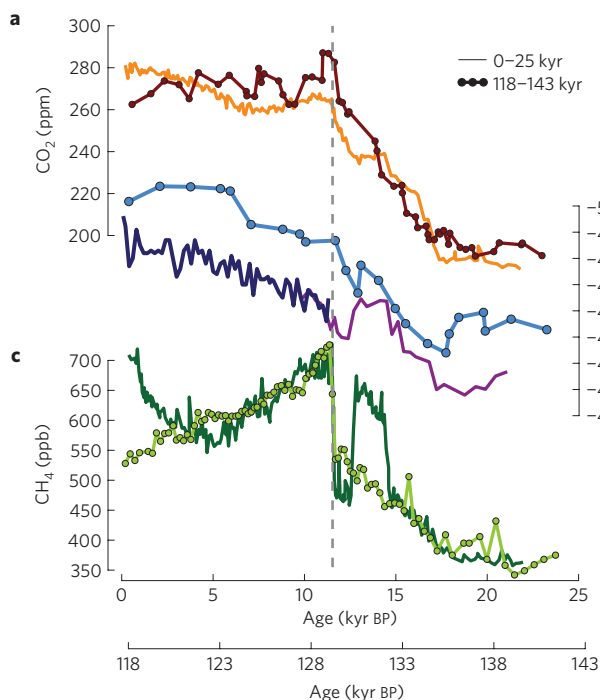


Figure 2 | Climate conditions during the ultimate and penultimate glacial terminations. **a**, CO₂ from Vostok⁴⁷ (TII, brown) and EDC (ref. 49; TI, orange). **b**, δ¹³CH₄ from Vostok (TII, light blue), EDML (ref. 11; TI, purple, reprocessed and corrected for Kr effect) and GISP2 (ref. 13; TI, dark blue, original timescale, corrected for Kr effect), all with inverted y axis. **c**, CH₄ from EDC (ref. 7; TII, light green) and EDML (ref. 5; TI, dark green). Except for GISP2 δ¹³CH₄, all records are given on the unified ice-core chronology⁴⁶. Upper x axis refers to TI (0–25 kyr BP), lower x axis to TII (118–143 kyr BP), aligned at the major CH₄ rises (grey dotted line).

systems on tropical wetland emissions, fostered by a proportional scaling of emissions from the remaining non-geological CH₄ sources (mainly boreal wetlands and biomass burning), combined with a slight change in CH₄ lifetime during rapid climate change, represent the most likely explanation for strong CH₄ variability that is not accompanied by synchronous δ¹³CH₄ changes.

Climate and CO₂-induced changes in wetland ecosystems

The time interval between 71 and 65 kyr BP in our δ¹³CH₄ record (the MIS 5–4 transition), particularly, demonstrates the decoupling of changes in δ¹³CH₄ from atmospheric CH₄ mixing ratios, which were rather stable at that time (~450 ppb). CH₄ variations did not exceed 50 ppb, whereas δ¹³CH₄ shifted strongly (~4‰) towards higher values. At the same time sea level dropped by 30–40 m and CO₂ levels decreased by 35 ppm leading to boundary conditions comparable to glacial maxima.

We can think of two plausible explanations that would account for δ¹³CH₄ variations during periods of relatively constant CH₄ concentrations. First, there could be periods when one source with low δ¹³CH₄ was replaced by an equivalent increase in a source with an increased δ¹³CH₄ signature, causing a net shift in the mean isotopic composition, while keeping the overall CH₄ loading constant. For example, the progressive glaciation of high-latitude Northern Hemisphere land masses was probably accompanied by a significant reduction of ¹³C-depleted boreal methane sources^{6,18,31}. The CH₄ load could be maintained by the increase of tropical emissions, for example, related to the expansion of tropical wetland sources on newly exposed shelf areas such as the Sunda shelf³¹. Assuming a 10‰ difference in their δ¹³CH₄ signature, shifting 30 Tg CH₄ yr⁻¹ from boreal to tropical wetland emissions could explain

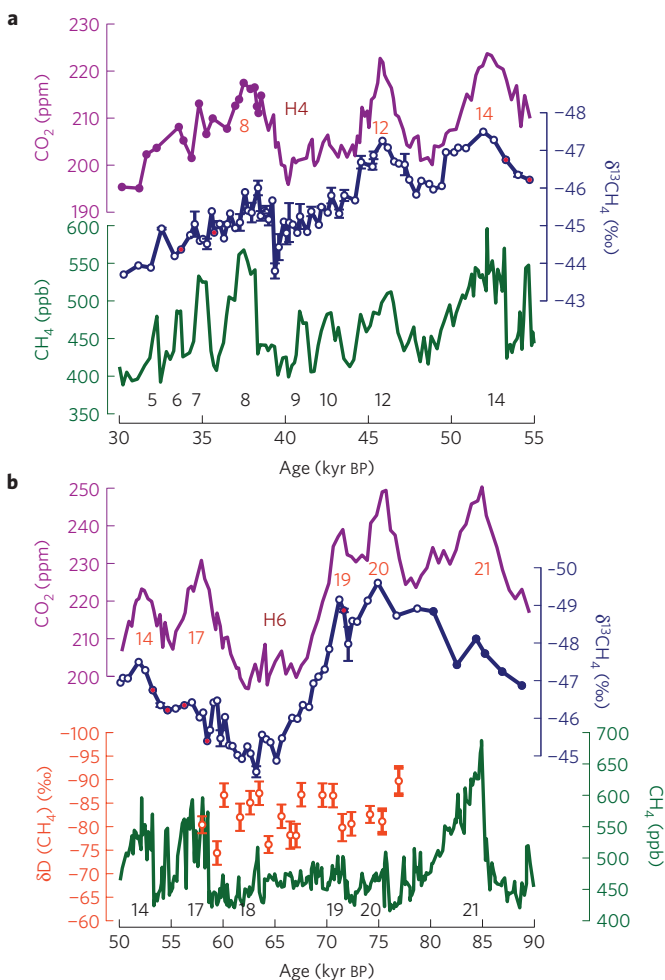


Figure 3 | Zoom into MIS 3 and the MIS 5–4 boundary. **a**, CO₂ between 30 and 55 kyr BP from EDML and Talos Dome⁴⁸ (purple), after 38.5 kyr BP from Byrd¹⁴ (filled circles). δ¹³CH₄ from EDML (blue) and CH₄ from EDML (ref. 5; green). **b**, CO₂ from EDML and Talos Dome⁴⁸ (purple) between 50 and 90 kyr BP. Composite δ¹³CH₄ (blue) (80–90 kyr BP from Vostok (filled circles), all others from EDML (open circles), y axis inverted). Samples potentially subject to diffusive fractionation marked by red circle fillings. δD(CH₄) from EDML (orange), CH₄ from EDML (ref. 5; green). H numbers indicate the timing of Heinrich events in the North Atlantic. Arabic numbers indicate the timing of Dansgaard–Oeschger events and their respective Antarctic counterparts¹². All data sets are reported on the unified ice-core chronology⁴⁶. Standard deviations of replicate measurements illustrated by error bars.

an atmospheric increase of 2‰ in δ¹³CH₄. Note that this would also imply a near shutdown of all boreal sources.

To investigate whether such a shift occurred during the MIS 5–4 transition, we also measured δD(CH₄) over this interval (Fig. 3b). At first order, δD(CH₄) is a function of the hydrogen isotopic signature of the precipitation in wetland areas^{12,28}. Accordingly, we would expect a general increase in δD(CH₄) values to accompany the observed δ¹³CH₄ shift, if boreal CH₄ sources were exchanged with tropical sources, which are more enriched in deuterium. However, our complementary δD(CH₄) data do not show such a covariation, indicating that a simple exchange of one source for another cannot satisfactorily explain the observed δ¹³CH₄ enrichment. Note that a large change in the hydrogen isotopic signature of boreal wetlands expected for cold conditions³² would not have had a strong influence on the atmospheric composition if boreal wetland emissions were already low before the MIS 5–4

transition³¹. This hypothesis would lend support to the idea that $\delta^{13}\text{CH}_4$ is governed mainly by processes taking place in the tropics at that time.

Another, more likely, explanation for the $\delta^{13}\text{CH}_4$ shift during the MIS 5–4 transition involves changes in the characteristic isotope values of individual sources themselves³³, controlled by climate and CO_2 -induced changes in ecosystem composition. As the primary process of CH_4 production is the anaerobic decomposition of plant material, atmospheric CO_2 affects $\delta^{13}\text{CH}_4$ in many ways. Changes in the carbon isotopic signature of CO_2 ($\delta^{13}\text{CO}_2$) are directly imprinted in $\delta^{13}\text{CH}_4$ through incorporation into the plant precursor material during photosynthesis. However, the $\delta^{13}\text{CO}_2$ variations over glacial–interglacial cycles (0.2–0.5‰) are small³⁴ compared with those in $\delta^{13}\text{CH}_4$. More notably, the CO_2 concentration itself may have an impact on $\delta^{13}\text{CH}_4$ in two ways.

First, CO_2 influences the C3/C4 plant ratio, with the relatively ^{13}C -enriched C4 large subscript for all mentions of C3 and C4 plants as in <http://www.nature.com/nggeo/journal/v6/n8/full/ngeo1856.html> plants being favoured under glacial, low- CO_2 conditions^{35–37}. The effect of this C3/C4 plant shift on $\delta^{13}\text{CH}_4$ has been estimated to be about 0.7‰ (ref. 33). This estimate, however, is a lower limit as it was based on the direct competition of C3 and C4 grasses for prescribed grassland areas derived from a modern vegetation map³⁸. Taking an extension of grasslands under glacial conditions into account^{36,37,39}, we expect a significantly stronger effect. The weight of CO_2 variability for the isotopic signature of plant precursor material is also indicated by the striking correlation between CO_2 and $\delta^{13}\text{CH}_4$ over the entire 160 kyr period. Pronounced deviations in this correlation occur immediately after some abrupt increase in CH_4 (that is, Dansgaard–Oeschger events 17, 21, 24 and the onsets of both interglacials, Fig. 1). Note that each of these intervals is preceded by a significant increase in sea level^{3,4}, which would have flooded low-lying coastal regions. This implies that changes in the source signature do not follow a simple one-to-one relationship with CO_2 , but that $\delta^{13}\text{CH}_4$ is most likely a convoluted signal of wetland area and ecosystem response.

Second, a further effect on $\delta^{13}\text{CH}_4$ is caused by the change of the isotopic signature of C3 vegetation, linked to a change in isotopic fractionation during CO_2 uptake³⁹. Differences in the range of 3–4‰ are reported in C3 plant materials in equatorial Africa between rainforest habitats on the one extreme and open savanna-type habitats on the other⁴⁰. Accordingly, a shift from forest- and rainforest-type ecosystems during interglacial conditions to seasonally inundated savanna-type ecosystems during the glacial would also lead to CH_4 emissions increasingly enriched in ^{13}C during the MIS 5–4 transition.

Indicative evidence for such ecosystem changes may be found in coastal marine sediment records. For example, $\delta^{13}\text{C}$ of plant biomarkers in sediment cores off the East Atlantic coast close to the river mouths of the Congo and Angola basins indicate 3–4‰ higher values during glacial times⁴¹, similar to evidence from the Guinea Plateau margin recording Sahara/Sahel vegetation⁴². A comparable marine geological study from the Cariaco Basin in the tropical West Atlantic reported a 4–5‰ $\delta^{13}\text{C}$ decrease in leaf waxes from the Last Glacial Maximum (LGM) to the preboreal Holocene⁴³. We acknowledge that such signature changes may reflect vegetation shifts only in river catchment areas. Furthermore, it remains unclear whether changes in atmospheric CO_2 exert a similar influence on $\delta^{13}\text{C}$ of plant material in permanent wetlands. However, we assume that during generally drier glacial conditions an even larger part of tropical CH_4 emissions are caused by seasonally inundated flood plains⁴⁴ whose vegetation is controlled by the postulated influence of climate and CO_2 on the carbon isotope composition of the plant precursor material. Moreover, shifts in the isotopic signature of such seasonal wetland ecosystems would also be documented in coastal marine sediment records through riverine transport.

Considering the still insufficient understanding of the factors controlling ecosystem composition and CH_4 emissions, a definitive quantification of the combined effects of shifts in the C3/C4 plant ratio and changes in the C3 plant isotopic signature on low-latitude $\delta^{13}\text{CH}_4$ seems to be premature. Our estimates show that none of the proposed processes discussed above is likely to explain the full range of observed $\delta^{13}\text{CH}_4$ changes over the MIS 5–4 transition (~4‰) or even over the full glacial sequence (~8‰). However, the sum of the individual processes together with changes in the ratio of net to gross production of CH_4 in wetlands²⁸ lie well within the range of the observed $\delta^{13}\text{CH}_4$ changes. We stress that, except for a change in net to gross production of CH_4 , all these effects are neutral with respect to $\delta\text{D}(\text{CH}_4)$, in line with our results. In essence, a change in the carbon isotopic signature of CH_4 from tropical, seasonally inundated floodplains controlled by changing climate and CO_2 conditions, seems to be an essential ingredient to explain the large changes in $\delta^{13}\text{CH}_4$ at times when CH_4 concentrations remained rather constant.

Implications for glacial–interglacial CH_4 changes

The conclusions above encourage a reinterpretation of the changes over the past glacial–interglacial transition. In previous work¹¹, we proposed changes in the source mix to explain CH_4 changes over termination I, where we kept the isotopic signatures of individual sources essentially constant. A close look at the evolution of CH_4 and $\delta^{13}\text{CH}_4$ during the transition indicates that only the 1.1‰ depletion of $\delta^{13}\text{CH}_4$ into the Bølling–Allerød is synchronous with a concurrent steep CH_4 rise of about 150 ppb (Fig. 2), whereas the rapid Younger Dryas—Preboreal Holocene transition exhibits a more gradual change in $\delta^{13}\text{CH}_4$. A decoupling of $\delta^{13}\text{CH}_4$ and CH_4 thus also applies for the rapid CH_4 changes during termination I. Similar to the strong increase in $\delta^{13}\text{CH}_4$ during the MIS 5–4 transition, at least part of the deglacial $\delta^{13}\text{CH}_4$ decrease during termination I could alternatively be attributed to a progressive depletion of the isotopic signature of CH_4 sources. Such a depletion in $\delta^{13}\text{CH}_4$ source signatures from the LGM to the Holocene would also have a pronounced effect on the change in the source mix required to explain the CH_4 changes. For example, our previous box model approach assumed temporally constant wetland isotopic signatures over the past 25 kyr leading to comparable wildfire CH_4 emissions for the LGM and the Holocene. However, if we increase the glacial $\delta^{13}\text{CH}_4$ signature of tropical floodplains and biomass burning emissions owing to isotopic changes in the plant precursor material, much smaller wildfire emissions are required for the LGM to close the methane isotope budget. Accordingly, such a tropical source signature change would bring reconstructions of wildfire activity from charcoal records^{22,45} and $\delta^{13}\text{CH}_4$ into closer agreement.

The expanded database of $\delta^{13}\text{CH}_4$ variations over the past glacial cycle presented here provides unique information on unexpected changes in the CH_4 source regions. Fast methane concentration rises at Dansgaard–Oeschger warmings and during the deglaciations do not seem to be driven by large relative source or sink mix changes, or by activation of northern high-latitude sources alone. Rather, the new isotopic data constraints suggest that glacial changes in atmospheric CH_4 and $\delta^{13}\text{CH}_4$ are related to a predominant tropical wetland source, which responded quickly to Dansgaard–Oeschger climate variability and associated changes in the hydrological cycles. Scaling of other non-geological sources, as well as emission feedbacks on atmospheric CH_4 lifetimes, probably contributed to major CH_4 changes, but were in most cases either neutral with regard to $\delta^{13}\text{CH}_4$ or of lesser importance.

Our new data provide strong evidence that shifts in the isotopic signature of tropical floodplain emissions could be the main driver of $\delta^{13}\text{CH}_4$ variability, especially in glacial periods. $\delta^{13}\text{CH}_4$ changes are probably modulated by feedbacks of climate and atmospheric

CO₂ on the composition of wetland ecosystems in the low latitudes. Quantifying individual source and sink contributions to the glacial δ¹³CH₄ changes will remain elusive until the uncertainties in source and sink variability are reduced. Further high-resolution studies of δD(CH₄) could complement the data presented here, but a deeper understanding of wetland dynamics and vegetation shifts is also required and should be implemented in CH₄ emission schemes in dynamic vegetation models.

Methods

We reconstructed atmospheric δ¹³CH₄ records using wet extraction techniques and continuous flow gas chromatography combustion isotope ratio mass spectrometry (GC/C/IRMS) measurements carried out on ice-core material from both the European Project for Ice Coring in Antarctica (EPICA) core from Dronning Maud Land (EDML) and the Vostok cores. At the Alfred Wegener Institute we analysed 151 samples from the EDML core (including 32 replicates, reproducibility of 0.2‰, 1σ) to construct a high-resolution record between 20 and 75 kyr BP with an average temporal resolution of better than one sample every 500 years. The period covering the two most pronounced climatic excursions in the Greenland temperature record during MIS 3 (Dansgaard–Oeschger events 7 and 8) were sampled with a resolution of ~200 years. A complementary record of 79 samples of Vostok ice-core material covering a time period from 50 to 160 kyr BP was measured at the Pennsylvania State University with an analytical uncertainty of 0.3‰ (1σ), equivalent to an average temporal resolution of 1,660 years. Both data sets overlap well between 50 and 75 kyr BP, suggesting the spliced record is likely to be a good representation of the true atmospheric record between 20 and 160 kyr BP. The two records were corrected for instrumental interference from atmospheric krypton, for gravitational settling in the firn and for a minor interlaboratory offset of 0.14‰. Owing to the uncertainties concerning firn transport characteristics at the core sites under glacial conditions and the exact timings of the onsets of relevant rapid CH₄ increases, we did not apply a general correction for diffusive fractionation. The largest CH₄ rises are estimated to cause δ¹³C shifts in the range of 0.6–1.0‰. We marked those seven δ¹³CH₄ samples that are potentially affected by diffusive fractionation in the respective figures to illustrate their limited reliability. All δ¹³C values are reported versus Vienna PeeDee Belemnite.

We further analysed 20 samples of EDML ice for δD(CH₄) with an external precision of about 2.5‰ (1σ). The measurements were carried out at the University of Bern using a purge and trap extraction coupled to a gas chromatography pyrolysis isotope ratio mass spectrometer (GC/P/IRMS) and cover the MIS 5–4 transition with an average resolution of 1.5 kyr in between 54 and 85 kyr BP. The δD(CH₄) values are reported with respect to the international Vienna Standard Mean Ocean Water scale.

The δ¹³CH₄ and δD(CH₄) records are dated according to the unified Antarctic ice-core chronology⁴⁶. For additional details on the chronology, analytical methods, correction procedures and corresponding references, please refer to the Supplementary Information.

Data. All data are available at www.pangaea.de (<http://doi.pangaea.de/10.1594/PANGAEA.812116>) and in the NOAA/World Data Center for Paleoclimatology archive (http://hurrucane.ncdc.noaa.gov/pls/paleox/f?p=519:1:::1_P1_STUDY_ID:14651)

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Author contributions

L.M., T.S., M. Bock and M. Behrens carried out the measurements. R.S. modelled the diffusion fractionation in the firn column. L.M. and H.F. wrote the manuscript. All authors worked on the scientific interpretation, contributed to the discussion with ideas and comments or helped to review the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.