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Late Quaternary Atmospheric CH₄ Isotope Record Suggests Marine Clathrates Are Stable

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One explanation for the abrupt increases in atmospheric CH₄ that occurred repeatedly during the last glacial cycle involves clathrate destabilization events. Because marine clathrates have a distinct deuterium/hydrogen (D/H) isotope ratio, any such destabilization event should cause the D/H ratio of atmospheric CH₄ (δD_{CH_4}) to increase. Analyses of air trapped in the ice from the second Greenland ice sheet project show stable and/or decreasing δD_{CH_4} values during the end of the Younger and Older Dryas periods and one stadial period, suggesting that marine clathrates were stable during these abrupt warming episodes. Elevated glacial δD_{CH_4} values may be the result of a lower ratio of net to gross wetland CH₄ emissions and an increase in petroleum-based emissions.

The ice core record of atmospheric CH₄ changes covering the past 650,000 years exhibits two primary frequencies. Over long time scales (greater than 10,000 years) atmospheric CH₄ changes have a substantial amount of variance concentrated in the precessional bandwidth (19,000 and 23,000 years) (1, 2) that is considered to be an integral part of tropical climate throughout the late Pleistocene. One hypothesis that accounts for this observation involves an energized hydrologic cycle during periods of elevated low-latitude insolation. The invigorated hydrologic cycle promotes an increase in wetland extent driving a concomitant increase in CH₄ emissions that raise atmospheric CH₄ levels during warm periods. Embedded within the precession signal are millennial- and century-scale variations that are tightly coupled to Greenland temperature (3, 4). In general, increasing atmospheric CH₄ levels are synchronous with, or slightly lag (by a few decades), the surface temperature increase over Greenland (5). Assessing the nature of these abrupt CH₄ events is important for understanding how ecosystems and

climate are connected and in estimating the degree to which future CH₄ levels may contribute to changes in Earth's radiation budget.

There are two competing explanations for the abrupt CH₄ increases. One hypothesis holds that the terrestrial biosphere is capable of rapidly increasing CH₄ emissions in response to abrupt changes in the hydrologic cycle that are teleconnected to surface temperatures over Greenland (3, 4). The other explanation involves the sudden release of marine clathrates situated along the continental margin where episodic destabilization events may have been triggered by enhanced ventilation (warming) of upper thermocline waters (6). The majority of the released CH₄ ultimately travels across the air-sea interface leading to atmospheric CH₄ increases.

Model estimates of changes in the primary CH₄ sink (tropospheric hydroxyl radical) during the last glacial termination suggest that the observed CH₄ variations must be due in large part to changes in the sources as opposed to changes in the rate of removal (7). The isotopic composition of atmospheric CH₄ therefore provides additional information on the relative contribution of the various sources. Variations in the D/H ratio of atmospheric CH₄ (δD_{CH_4}) can be used to infer variable clathrate contributions on the basis of their elevated δD

values compared with all terrestrial CH₄ sources (Fig. 1). Methane clathrates within the continental margin sediments are formed almost exclusively by CO₂ reduction or thermal cracking of longer chain hydrocarbons, whereas terrestrial CH₄ emissions are primarily aceticlastic in nature (8, 9). During CO₂ reduction, all the methyl hydrogen atoms come directly from porewater H₂ that is in isotopic equilibrium with the porewater (10). The resulting δD_{CH_4} values are lower than the porewater δD_{H_2O} due to a ~ 180 per mil (‰) biologically induced isotope effect associated with CO₂ reduction (9, 11). Marine clathrate δD_{CH_4} values from 13 near-shore sites scattered throughout the Northern Hemisphere are surprisingly constant ($-189 \pm 27\%$; error is SD) given the diverse nature of the geologic and sedimentologic settings and the varying proportions of microbial and thermogenic CH₄ at each site (12, 13). In contrast, CH₄ production in terrestrial ecosystems is dominated by acetogenesis (acetate fermentation) where three-fourths of the hydrogen atoms in the emitted methane originate from the methyl group associated with the acetate substrate. The remaining hydrogen comes from the local water with the resulting terrestrial δD_{CH_4} values generally ranging from -250 to -380% , with the local δD_{CH_4} value strongly influenced by the δD of precipitation (8, 9).

An atmospheric δD_{CH_4} record (Fig. 2) was generated from the second Greenland ice sheet project (GISP II) ice core using a previously described technique with an external precision of $\pm 4.2\%$ (14). The general picture of δD_{CH_4} variations associated with the deglaciation shows a progressive decrease in δD_{CH_4} as the concentration of CH₄ increases, opposite to that predicted by increasing clathrate contributions due to warming associated with the termination. During the last glacial maximum (LGM), δD_{CH_4} values were generally $\sim 5\%$ higher than the Bolling/Allerod values [15 to 13 thousand years ago (ka)] and $\sim 20\%$ higher than early Holocene values. There are three factors that can be reasonably constrained as contributing to the elevated δD_{CH_4} values during the LGM. All three factors are temperature dependent, so

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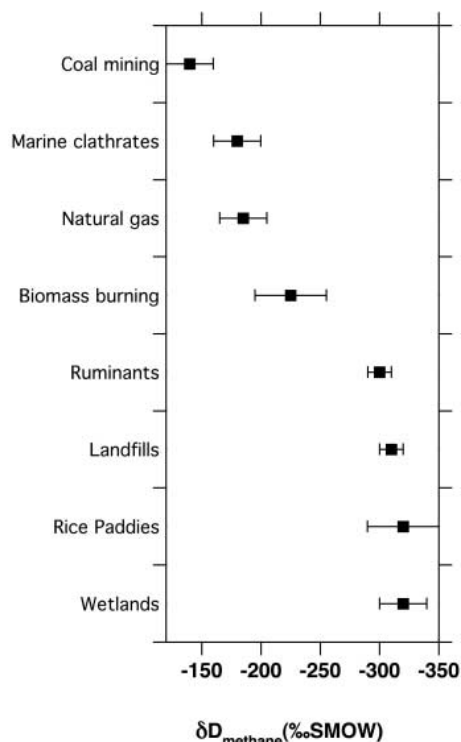


Fig. 1. Characteristic δD_{CH_4} values for various present-day CH_4 sources. All the data except the value for the marine clathrates (13) are from (26–28). Present day atmospheric δD_{CH_4} estimates are $\sim -90 \pm 5\%$ (29). The enriched atmospheric value is the result of a large KIE (+250‰) associated with the primary sink (tropospheric OH) (14). Error bars for each source correspond to the tabulated range of values. SMOW, standard mean ocean water.

estimates have been made on the basis of two different tropical LGM temperature estimates (Table 1). First, colder temperatures during this period would have increased atmospheric δD_{CH_4} through the temperature-dependent kinetic isotope effect (KIE) associated with the primary removal process, OH oxidation in the troposphere. The magnitude of this effect is +3.4‰ on the basis of the laboratory-determined temperature dependence (15), assuming tropospheric temperatures were 5°C colder during the LGM. Secondly, δD changes in mean ocean water arising from changes in continental ice volume impart a direct effect on atmospheric δD_{CH_4} by altering the δD of porewater H_2 that is utilized by CO_2 reducing methanogens (oceanic and terrestrial). A less direct effect occurs as the oceanic δD_{H_2O} change is propagated through the hydrologic cycle and incorporated in terrestrial organic hydrocarbons (16, 17), the primary substrate for the fermentative methanogens. The mean ocean δD_{H_2O} change [7.5‰ (18)] is transferred through the LGM global hydrologic cycle (19, 20), causing changes in δD_{CH_4} values for terrestrial CH_4 that range from -5 to 5‰, depending on the assumed LGM tropical temperatures (8, 9). Finally, a 10% decrease in

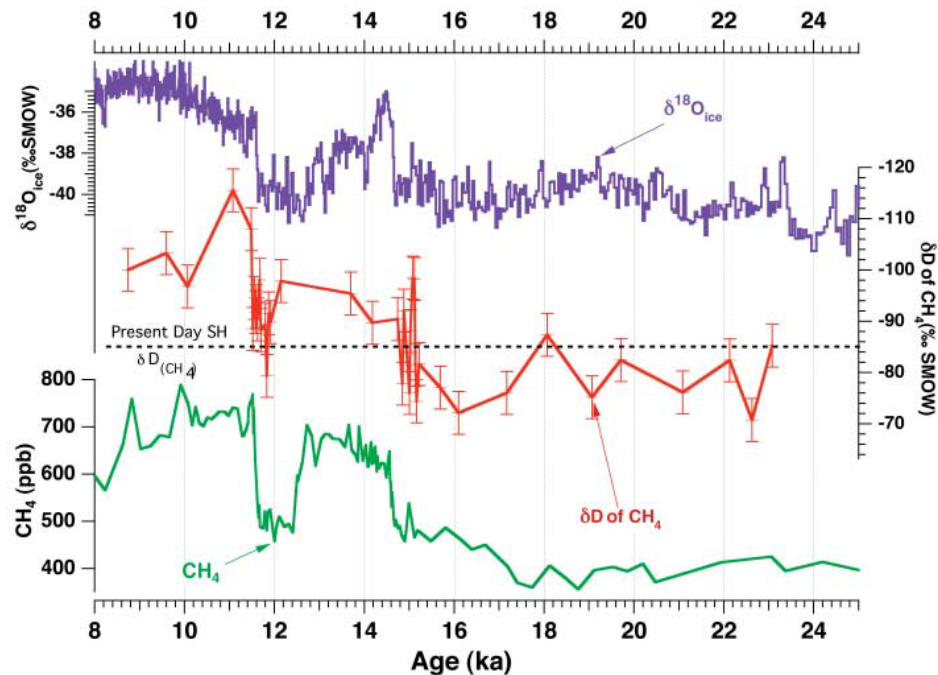


Fig. 2. Results from the last glacial termination as recorded in the GISP II ice core. The upper purple curve is the isotopic temperature (30). The red curve is from the current δD_{CH_4} analyses with 1σ (4.2‰) error bars. The bottom CH_4 concentration curve (green) is from Brook *et al.* (3). ppb, parts per billion. The increased sample resolution associated with the abrupt CH_4 concentration increases associated with the onset of the Bolling/Allerod and the end of the Younger Dryas periods are shown in expanded view in Fig. 3. The present-day δD_{CH_4} value for the Southern Hemisphere (SH) is shown as a horizontal dashed line for reference.

Table 1. Constraining factors influencing δD_{CH_4} during the LGM.

Factor	$\Delta\delta D_{CH_4}$ (LGM to Holocene) (‰)	
	CLIMAP SST*	5°C Tropical cooling
10% decrease in C_3/C_4 ratio during LGM†	-1.9	0
KIE for OH oxidation	0	3.4
Δ Sea level‡	5.1	0 to -5
Total change	+3.2	3.4 to -1.6

*CLIMAP Climate: Long-Range Investigation, Mapping, and Prediction; SST, sea surface temperature. †Assuming the D/H ratio in C_3 and C_4 plants differs by $\sim 15\%$ [C_3 plants have higher δD values (31)], then a 10% reduction in the C_3/C_4 ratio of wetland plants during the LGM (21) would have raised atmospheric δD_{CH_4} values by $\sim 1.9\%$ relative to Holocene values. Assume additional 5°C cooling during LGM yields no change in C_3/C_4 ratio. ‡Seawater δD_{H_2O} during LGM = 7.5‰ standard mean ocean water (18). General circulation model simulations suggest little change in δD_{H_2O} precipitation using CLIMAP SST (19, 20) but a slight decrease in δD_{H_2O} precipitation for 5°C tropical cooling (19). Finally, assume $\delta D_{CH_4}/\delta D_{H_2O} = 0.675$ (8).

the ratio of C_3 - to C_4 -type plants during the LGM (21) would have lowered atmospheric δD_{CH_4} values by 0 to 1.9‰ relative to Holocene values. Together these three factors account for a small portion of the observed 20‰ δD_{CH_4} shift between the LGM and early Holocene, implying that other factors must be considered.

There are at least three additional factors contributing to the atmospheric δD_{CH_4} change associated with the termination that are difficult to quantify. First, elevated δD_{CH_4} values during the LGM may be the result of a decrease in the ratio of net to gross (N/G) CH_4 production. It has been fairly well documented through inhibitor studies that as much as 50% of the CH_4 produced at depth in soils is consumed by

microbially mediated methane oxidation near the soil-atmosphere interface (22). The δD_{CH_4} values for the emitted CH_4 are strongly dependent on the N/G ratio because of the large KIE associated with methane oxidation [-95 to -285‰ (23)]. For example, lowering N/G by 11% during the LGM (with the δD_{CH_4} of gross CH_4 assigned as -300‰ and the KIE for methane oxidation as -95‰) would raise atmospheric δD_{CH_4} by 10‰. The sense of this change is consistent with observations that the methane-producing communities are more sensitive to temperature changes than methane-oxidizing communities (24).

Two additional factors contributing to the elevated δD_{CH_4} values during the LGM involve an increase in the relative proportion

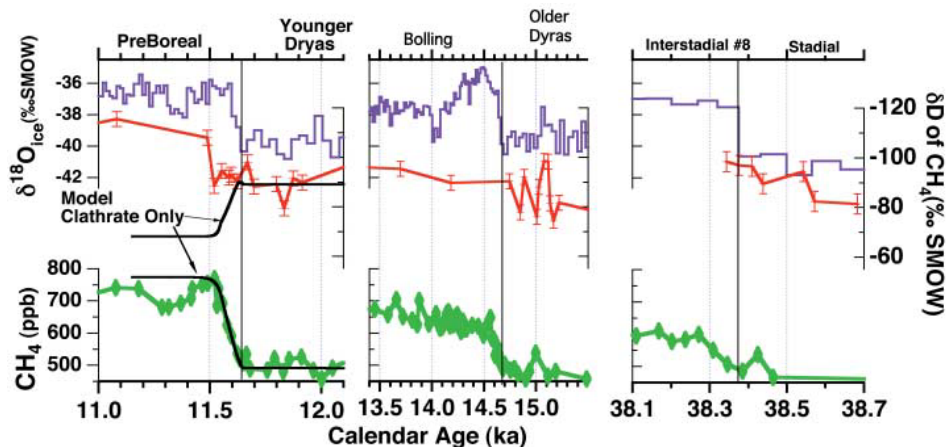


Fig. 3. Expanded views of three abrupt CH_4 concentration events recorded in the GISP II ice core. The isotopic temperature record (30) and atmospheric CH_4 concentration record (3) are plotted for reference. The red curves are from the current $\delta\text{D}_{\text{CH}_4}$ analyses with 1σ errors at each measured depth. The results from the one-box clathrate-only model are shown for the Younger Dryas simulation with black curves. All data in all three panels are plotted on the same y axes for comparison.

of petroleum-based and/or biomass-burning CH_4 emissions, both of which have elevated D/H ratios (Fig. 1). Model simulations of biomass burning, however, suggest lowered CH_4 emissions during the LGM (25). If, as recently suggested (12, 13), CH_4 from petroleum seeps contributed a larger proportion of global sources during the LGM compared with early Holocene periods, then we would expect higher atmospheric $\delta\text{D}_{\text{CH}_4}$ values during the LGM. Assuming global CH_4 emissions during the LGM were 111 Tg/year (3) and the characteristic $\delta\text{D}_{\text{CH}_4}$ value for the terrestrial biosphere was -300‰ , then a 10‰ $\delta\text{D}_{\text{CH}_4}$ signal can be accounted for by increasing the fraction of CH_4 emissions based on petroleum and/or biomass burning by 9% during the LGM (compared with early Holocene emissions).

The high-resolution $\delta\text{D}_{\text{CH}_4}$ records during the end of the Younger and Older Dryas periods (11.5 and 14.7 ka, respectively) and the onset of interstadial 8 (IS8) (38.5 to 38 ka) provide important constraints for assessing clathrate stability during these periods (Fig. 3). With the exception of one short period of increasing $\delta\text{D}_{\text{CH}_4}$ between 15.2 and 15.0 ka, the atmospheric $\delta\text{D}_{\text{CH}_4}$ record from GISP II shows relatively stable or slightly decreasing $\delta\text{D}_{\text{CH}_4}$ values during periods of increasing CH_4 concentration. This trend is not consistent with either a gradual or an episodic release of clathrates, suggesting that marine clathrates were stable throughout the last glacial termination as well as during periods of abrupt warming.

To estimate the magnitude of the atmospheric $\delta\text{D}_{\text{CH}_4}$ shift associated with a hypothetical clathrate destabilization event, a simple one-box model of the atmosphere was developed using the CH_4 concentration history from the end of the Younger Dryas period to constrain total CH_4 emissions (3). The model consists of two sources and a single sink term. Terrestrial

CH_4 emissions, the lifetime of atmospheric CH_4 , the $\delta\text{D}_{\text{CH}_4}$ value for terrestrial CH_4 emissions (-300‰), and the KIE associated with the sink ($+165\text{‰}$) were all held constant throughout the simulation. Then, beginning at model year 11.64 ka, we introduced clathrate-derived CH_4 ($\delta\text{D}_{\text{CH}_4} = -189\text{‰}$) at a rate of 0.8 Tg/year for the next 100 model years, after which clathrate emissions were held constant at 80 Tg/year. The model predicted evolution of CH_4 concentration and $\delta\text{D}_{\text{CH}_4}$ are included in Fig. 3 for comparison with the GISP II data from the Younger Dryas. Assuming clathrate CH_4 was the only new CH_4 source at the end of the Younger Dryas, the predicted $\delta\text{D}_{\text{CH}_4}$ change was $+21\text{‰}$. The relatively constant $\delta\text{D}_{\text{CH}_4}$ values throughout the transition to elevated CH_4 levels suggest little change in the relative proportion of all individual emissions with near-constant characteristic $\delta\text{D}_{\text{CH}_4}$ values.

The transition from the Older Dryas to Bolling period (15 to 14 ka) provides a very different view of the factors influencing $\delta\text{D}_{\text{CH}_4}$ (Fig. 3). During the 300-year period immediately preceding the abrupt increase in atmospheric CH_4 loading, $\delta\text{D}_{\text{CH}_4}$ initially decreases by 15‰ followed by a rapid 10‰ increase, during which time atmospheric CH_4 levels remained effectively constant. Obviously, many more data are needed to document this oscillation but, with the limited data in hand, it appears that a rapid shift in the characteristic $\delta\text{D}_{\text{CH}_4}$ values of various sources is needed in the absence of substantial global emission changes during a period of relative climate stability.

The general trend of decreasing $\delta\text{D}_{\text{CH}_4}$ throughout the termination, combined with relatively stable $\delta\text{D}_{\text{CH}_4}$ values during periods of rapidly increasing CH_4 , suggests that marine clathrates are stable during this period and specifically during abrupt warming events. The

elevated LGM $\delta\text{D}_{\text{CH}_4}$ values are likely to be related to a number of factors, the most important being decreased N/G ratios and an increase in petroleum-based CH_4 emissions during the glacial period. Further insight into these factors will derive from future measurements of $\delta^{13}\text{C}_{\text{CH}_4}$ that are in progress.

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Supporting Online Material

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Materials and Methods

Table S1

References

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