Geophysical Research Letters

RESEARCH LETTER
10.1029/2019GL086756

Key Points:
- Experimental results indicate CH4 clumped isotopes are controlled by rates of microbial CH4 production
- Paired clumped isotopes and 14C measurements imply CH4 formed from older substrates in northern lakes is produced relatively slowly
- Comparison of clumped isotope data and flux estimates suggests that CH4 production rate is not a strong determinant of CH4 ebullition flux

Supporting Information:
- Supporting Information S1
- Table S1

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Citation:

Received 19 Dec 2019
Accepted 5 Mar 2020
Accepted article online 09 Mar 2020

Abstract
The release of long-stored carbon from thawed permafrost could fuel increased methanogenesis in northern lakes, but it remains unclear whether old carbon substrates released from permafrost are metabolized as rapidly by methanogenic microbial communities as recently produced organic carbon. Here, we apply methane (CH4) clumped isotope (Δ18) and 14C measurements to test whether rates of methanogenesis are related to carbon substrate age. Results from culture experiments indicate that Δ18 values are negatively correlated with CH4 production rate. Measurements of ebullition samples from thermokarst lakes in Alaska and glacial lakes in Sweden indicate strong negative correlations between CH4 Δ18 and the fraction modern carbon. These correlations imply that CH4 derived from older carbon substrates is produced relatively slowly. Relative rates of methanogenesis, as inferred from Δ18 values, are not positively correlated with CH4 flux estimates, highlighting the likely importance of environmental variables other than CH4 production rates in controlling ebullition fluxes.

Plain Language Summary
There is concern that carbon from thawed permafrost will be emitted to the atmosphere as methane (CH4). It is currently uncertain whether old organic carbon from thawed permafrost can be converted to CH4 as rapidly as organic carbon recently fixed by primary producers. We address this question by combining radiocarbon and clumped isotope measurements of CH4 from lakes in permafrost landscapes. Radiocarbon (14C) measurements indicate the age of CH4 carbon sources. We present data from culture experiments that support the hypothesis that clumped isotope values are dependent on microbial CH4 production rate. In lake bubble samples, we observe a strong correlation between these two measurements, which implies that CH4 formed from older carbon is produced relatively slowly. We also find that higher rates of CH4 production, as inferred from clumped isotopes, are not linked to higher rates of CH4 emissions, implying that variables other than CH4 production rate strongly influence emission rates.

1. Introduction
Thawing of permafrost provides previously frozen organic carbon to anaerobic microbial communities whose respiration releases CO2 and CH4. The release of these greenhouse gases constitutes a positive feedback to global warming, with a potential contribution of 174 Pg of carbon to the atmosphere by 2100 (Koven et al., 2011; Schuur et al., 2015). Specific attention has been directed to the potential for lakes in permafrost regions to act as CH4 emissions sources (Walter Anthony et al., 2018; Wik et al., 2016). Much of this CH4 could be derived from carbon reservoirs that have been frozen and unavailable for microbial respiration for thousands of years (Walter Anthony et al., 2016), which represents a net input of carbon into the active Earth surface carbon cycle (Archer et al., 2009). 14C measurements of CH4 are an excellent tracer for the age of carbon sources for methanogenesis. However, 18O measurements of CH4 in northern lakes span a large range (modern to >50,000 years old) (Bouchard et al., 2015; Elder et al., 2018; Walter et al., 2008), and our understanding of the mechanisms that control this variability remains limited.
If old organic carbon released from permafrost is less reactive than recently fixed carbon, this may limit microbial metabolisms fueled by older carbon, including methanogenesis. This premise is based on the observation that in sediments and soils, older organic carbon is generally less reactive with respect to microbial degradation (Middelburg, 1989; Trumbore, 2000). Recent studies have found, however, that 14C-depleted organic carbon from permafrost can be highly reactive (Ewing et al., 2015; Heslop et al., 2019; Mann et al., 2015; Vonk et al., 2013).

CH4 stable isotope measurements have the potential to identify differences in CH4 production rates and how they relate to carbon substrate age. In particular, measurements of multiply substituted isotopologues, or clumped isotopes (Ono et al., 2014; Stolper, Sessions, et al., 2014; Young et al., 2017), in microbial CH4 are hypothesized to be controlled by the enzymatic reversibility of CH4 production (Gruen et al., 2018; Stolper et al., 2015; Wang et al., 2015). Enzymatic reversibility of methanogenesis is a function of the forward and reverse reaction rates of methanogenesis (Stolper et al., 2015) and is therefore directly related to the net rate of CH4 production.

In this study, we combined analyses of clumped isotopes (Δ18; see definition in Section 2) and 14C in samples of CH4 emitted in bubbles from eight lakes associated with permafrost in Alaska and Sweden to test whether there is a linkage between relative rates of microbial methanogenesis and the age of carbon substrates. The five lakes from Alaska are thermokarst lakes formed by the thaw of ice-rich permafrost (Douglas et al., 2016; Elder et al., 2019; Walter et al., 2008), while the three Swedish lakes are postglacial lakes surrounded by thawing discontinuous permafrost (Wik et al., 2013). To support this analysis, we also present a compilation of new and published Δ18 and Δ13CH3D measurements from culture experiments to provide empirical evidence that clumped isotope values are related to CH4 production rate. Finally, we compare Δ18 and 14C measurements with CH4 ebullition flux estimates to inform conceptual models of how CH4 production rate relates to lake ebullition fluxes.

2. Methods

2.1. Lake Ebullition Sampling

Ebullition gas samples from the Alaskan lakes (Qalluruq, Cake Eater, Goldstream, Doughnut, and Smith) were collected from submerged, umbrella-style bubble traps, following methods described by Walter et al. (2008), between 2009 and 2013. Bubble traps were fixed in place over identified bubble seeps. Ebullition gas samples from the Stordalen lakes (Inre Harrsjön, Mellersta Harrsjön, and Villasjön) were collected using submerged inverted funnels, as described by Wik et al. (2013), in 2013 and 2014. The Stordalen traps were distributed evenly across the lakes since no coherent bubble seeps were identified. Lake locations and classifications are described in more detail in previous studies (Douglas et al., 2016; Walter et al., 2008; Wik et al., 2013).

2.2. Pure Culture Experiments

Pure cultures of Methanosarcina acetivorans (Sowers et al., 1984) (Strain DSM 2834; DSMZ GmbH) were grown on a carbon substrate of methanol (MeOH) or trimethylamine (TMA). Cultures in Batch 1 and Batch 2 (Table S1 in the supporting information) were grown in 1 L glass vials in 350 mL of sterile media, while cultures for Batch 3 were grown in 40 mL glass vials in 20 mL of sterile media (Text S1). All cultures were grown under a headspace of N2 gas at a pressure of 150 kPa. Batch 1 and 2 cultures included 5 mL of either 99.9% MeOH or TMA as a carbon substrate, while Batch 3 cultures included 0.25 mL of 99.9% MeOH (Table S2). The culture bottles were kept in an incubator at 28°C and shaken at 35 rpm. Headspace CH4 concentrations were either measured prior to sampling for isotopic analysis using an Agilent HP 5890GC-5972MSD (gas chromatograph-mass selective detector; Batch 2) or were measured manometrically during CH4 preparation for isotopic analysis (Batches 1 and 3). Immediately following CH4 concentration measurements, aliquots of headspace gas were sampled using a 5 mL gas tight syringe for isotope measurements (see Section 2.6). Culture incubation times are listed in Table S2.

2.3. Enrichment Culture Experiments

Enrichment cultures were established using sediments from two aquatic environments in Southern California: Baxter Pond, an artificial pond on the Caltech campus (Stolper et al., 2015); and the Ballona
wetlands, a coastal marsh. Cultures were grown in a headspace of 80:20 H2:CO2, in a sterile media (Text S1), with 180 μL of 1 M sodium acetate. The cultures were transferred every 5 days, with an additional 180 μL of 1 M sodium acetate added at each transfer. Twenty days after the fifth transfer, the cultures were analyzed for headspace CH4 concentrations using an Agilent HP 5890GC-5972MSD and sampled for isotopic analysis.

2.4. Estimation of CH4 Production Rates in Culture Experiments

We estimated the net CH4 production rate \( (r_{\text{net}}; \text{mg CH}_4 \text{ hr}^{-1} \text{ ml media}^{-1}) \) using the following equation:

\[
r_{\text{net}} = \frac{f_{\text{CH}_4} V_{\text{HS}} PM_{\text{CH}_4} RT t}{V_m},
\]

where \( f_{\text{CH}_4} \) is the fractional concentration of CH4 in the culture headspace, \( V_{\text{HS}} \) is the volume of the headspace (in L), \( P \) is the headspace pressure (kPa), \( M_{\text{CH}_4} \) is the molar mass of CH4 (mg mol\(^{-1}\)), \( R \) is the ideal gas constant, \( T \) is temperature (K), \( t \) is the time from culture inoculation to sampling (hours), and \( V_m \) is the volume of the culture media (ml). CH4 production rates for experiments performed at MIT were calculated from data reported by Gruen et al. (2018).

2.5. CH4 Radiocarbon Measurements

CH4 \(^{14}\text{C}/^{12}\text{C}\) ratios for the Alaskan lake samples were measured at the National Ocean Sciences Accelerator Mass Spectrometry facility, as described by Brosius et al. (2012) and Walter Anthony et al. (2012). \(^{14}\text{C}/^{12}\text{C}\) analysis for the samples from Stordalen mire was analyzed at the A.E. Lalonde Accelerator Mass Spectrometry Laboratory (University of Ottawa), using a preparation procedure based on that of Pack et al. (2015). Radiocarbon data are expressed in fraction modern (Fm) as defined by Stuiver and Polach (1977). Blank tests were conducted alongside all sample \(^{14}\text{C}\) analyses, and no evidence for significant blank carbon was found.

2.6. Clumped Isotope and Other Stable Isotope Measurements

CH4 was purified from mixed gas samples using a vacuum line cryotrapping method described previously (Douglas et al., 2016; Stolper, Lawson, et al., 2014; Stolper, Sessions, et al., 2014), resulting in CH4 purity of ~99.9%.

CH4 \(^5\text{D}, ^{13}\text{C}, \) and \( \Delta_{18} \) for all samples, except the Batch 3 pure culture experiments, were measured using a prototype Thermo 253 Ultra (Eiler et al., 2013) at Caltech, as described in detail previously (Stolper, Sessions, et al., 2014). The Batch 3 pure culture experiments were analyzed for \( \text{CH}_4 \) \(^5\text{D}, ^{13}\text{C}, \) and \( \Delta^{13}\text{CH}_3\text{D} \) and for three samples \( \Delta^{13}\text{CH}_2\text{D}_2 \), using a production model Thermo 253 Ultra at the University of California, Berkeley, as described by Eldridge et al. (2019). \(^5\text{D} \) and \(^{13}\text{C} \) values are expressed using delta notation relative to Vienna Standard Mean Ocean Water and Vienna Pee Dee Belemnite, respectively.

Most (90%) of the clumped isotope compositions presented here are expressed using \( \Delta_{18} \) notation as described by Stolper, Sessions, et al. (2014), where

\[
\Delta_{18} = \left( \frac{18R}{18R^*} \right) - 1,
\]

and

\[
18R = \left( \frac{[^{13}\text{CH}_3\text{D}]}{[^{12}\text{CH}_2\text{D}_2]} + \frac{[^{13}\text{CH}_2\text{D}_2]}{[^{12}\text{CH}_4]} \right).
\]

\( 18R^* \) is the \(^{18}\text{R} \) value expected for a random internal distribution of isotopologues, given the \(^{13}\text{C} \) and \(^5\text{D} \) values of the sample (Stolper, Sessions, et al., 2014) and is expressed as

\[
18R^* = \left( 6 \times \left[ 2R \right]^2 \right) + \left( 4 \times 2R \times 13R \right).
\]

\( \Delta_{18} \) data are reported as per mil (‰), where 0‰ refers to a random distribution of CH4 isotopologues (i.e., \( 18R = 18R^* \)). All samples are referenced against a laboratory standard with a \( \Delta_{18} \) value of 2.981 ± 0.015‰ (Stolper, Sessions, et al., 2014). External reproducibility for \( \Delta_{18} \), \(^5\text{D} \), and \(^{13}\text{C} \) values (1σ) was 0.38 ‰, 0.22 ‰, and 0.06 ‰ respectively.
CH$_4$ samples from the Batch 3 culture experiments were measured for $\delta^D$, $\delta^{13}C$, and $\Delta^{13}$CH$_3$D and for three samples $\Delta^{12}$CH$_2$D$_2$. A complete description of the analytical methods used for this measurement is found in Eldridge et al. (2019). The equations for these measurements (corresponding to Equations 2–4), and details on standards and reproducibility are listed in the Text S1. Where both $\Delta^{13}$CH$_3$D and $\Delta_{18}$ measurements are discussed together we use the term $\Delta_{18}$, as this is the more general term (Stolper, Sessions, et al., 2014).

$\delta^{13}C$ of CO$_2$ from the Alaskan gas samples were measured at Florida State University, as described by Walter Anthony et al. (2012).

2.7. Gas Concentration and Flux Measurements

The concentrations of CH$_4$ and other gases in the Alaskan lake samples were measured at the University of Alaska-Fairbanks, as described in Walter Anthony et al. (2012). For most Alaskan samples, bubble gas fluxes are estimated using the average flux measurements of seeps from a given seep classification (Lindgren et al., 2016; Walter Anthony & Anthony, 2013) (Table S1). In the Alaskan data set, all samples were collected from identified point source seeps, and flux estimates were not dependent on the area of the traps.

CH$_4$ concentrations in the Stordalen lake samples were measured at the Abisko Scientific Research Station as described by Wik et al. (2013). Gas fluxes were estimated by measuring gas volume accumulations in bubble traps manually. To account for scaling effects related to the area of the traps, for these samples, we report flux in terms of L CH$_4$ day$^{-1}$ m$^{-2}$ (Table S1). In one case where a sample-specific flux was not available, we adopted the 6-year average flux for that trap. In all samples, CH$_4$ flux was calculated by multiplying the estimated gas flux by the measured CH$_4$ concentration.

2.8. Model of CH$_4$ Kinetic Isotope Effects

Predicted CH$_4$ kinetic isotope effects are based on the model of Stolper et al. (2015), with modifications of two model parameters. First, we reduced $\kappa_f^{13}$CH$_3$D (the ratio of rate constants that describe the relative rate of formation of two isotopologues from a methyl precursor for $^{13}$CH$_3$D/$^{12}$CH$_4$) from 1.935 to 1.934 to account for low $\Delta_{18}$ and $\Delta_{13}$CH$_3$D values (~$-5$‰) observed in some culture experiments. Second, we reduced $\kappa_f^{12}$CH$_2$D$_2$ (as above but for $^{12}$CH$_2$D$_2$/$^{12}$CH$_4$) from 1.89 to 1.63 to account for measurements of $\Delta^{13}$CH$_3$D and $\Delta^{12}$CH$_2$D$_2$ in CH$_4$ from pure culture experiments (Young et al., 2017) that indicate negative $\Delta^{12}$CH$_2$D$_2$ corresponding to negative $\Delta^{13}$CH$_3$D values.

The kinetic isotope effect model relates CH$_4$ isotopologue ratios to the degree of reversibility of CH$_4$ generation ($\rho$). In order to relate modeled $\Delta_{18}$ and $\Delta_{13}$CH$_3$D values to net CH$_4$ production rates ($r_{net}$), we used the following equation from Stolper et al. (2015):

$$\rho = \frac{12^{12}CH_4}{12^{12}CH_4 k_{rev} + 12^{12}CH_4 k_{net}}$$

where $k_{rev}$ and $k_{net}$ are the first-order rate constants of reverse methanogenesis and net extracellular $^{12}$CH$_4$ production, respectively. These reaction constants are related to the net ($r_{net}$) and reverse ($r_{rev}$) reaction rates of methanogenesis by the following relationships:

$$r_{net} = k_{net}[CH_4]$$

$$r_{rev} = k_{rev}[CH_4]$$

where $[CH_4]$ is the intracellular concentration of CH$_4$.

Combining Equations 5–7, it follows that

$$r_{net} = \frac{r_{rev}}{\rho} - r_{rev}$$

To compare the modeled relationship between $\Delta_{18}/\Delta^{13}$CH$_3$D values and $r_{net}$ with empirical estimates of CH$_4$ production rates from culture experiments, we made three assumptions. First, we assumed a constant value for $r_{rev}$ (Timmers et al., 2017; Vavilin, 2013; Vavilin & Rytov, 2013), specifically $4 \times 10^{-4}$ mg CH$_4$ hr$^{-1}$ ml$^{-1}$. This value was chosen because it produces the best fit, as defined by the lowest root mean square error.
Figure 1. Plot of the natural log of CH4 production rate (rnet) vs. \( \Delta_{18} \) or \( \Delta^{13} \text{CH}_3 \text{D} \) in pure and enrichment culture experiments. Data are from Douglas et al. (2016), Gruen et al. (2018), and this study (new data indicated by black dots). Solid and dashed lines indicate predicted values based on a model of methanogenesis kinetic isotope effects (Stolper et al., 2015) (Section 2.8). The gray rectangle indicates the empirical ranges of these two variables observed in northern lake gas samples. Data are from wetland sediments indicate higher \( \Delta_{18} \) values for a given CH4 production rate than the pure culture experiments, possibly as a result of higher values of rrev or the occurrence of anaerobic CH4 oxidation (Figure S1). The modeled relationship between rnet and \( \Delta_{18} \) from the pure cultures spans a plausible range of values for northern lakes, based on CH4 production rates from incubation experiments of thermokarst lake sediments (Heslop et al., 2015) (Figure 1). Although there is uncertainty in quantitatively relating \( \Delta_{18} \) to CH4 production rates in environmental samples, we propose that \( \Delta_{18} \) values can be used as an indicator of relative differences in CH4 production rates between samples.

3.2. Linkages Between Carbon Substrate Age and Rates of Methanogenesis

There is a significant positive correlation (p < 0.05) between \( \Delta_{18} \) and Fm for both the Alaskan and Stordalen lakes (Figure 2), although the relationship is offset to higher Fm values in the Stordalen lakes. Based on our working hypothesis described above, the observed correlations imply that the rate of methanogenesis within these environments is lower when CH4-producing microbial communities metabolize older carbon substrates.

Other biogeochemical variables, including variation in methanogenic pathways, methane oxidation, and substrate depletion could also potentially influence \( \Delta_{18} \) values in these environments, although the effects of these variables on \( \Delta_{18} \) are not well defined (Ash et al., 2019; Giunta et al., 2019; Gruen et al., 2018; Wang et al., 2016; Young et al., 2017). However, the relationship between \( \Delta_{18} \) and CH4 production rate in pure culture experiments appears to be consistent across different methanogenic pathways (Figure 1). Furthermore, the absence of a significant correlation between CH4 Fm and \( \delta^{13} \text{C} \) values in these samples (Figure S4) implies that variation in methane oxidation or substrate depletion is probably not controlling the observed relationship between \( \Delta_{18} \) and Fm (Hayes, 2001; Whiticar, 1999). Lake Qalluruq on the north
slope of Alaska may be anomalous because isotopic and gas composition data imply its CH₄ emissions are derived from microbial methanogenesis in subpermafrost coal deposits that underlie the lake (Douglas et al., 2016; Walter Anthony et al., 2012). If this lake is excluded, we still observe a significant relationship between Δ₁₈ and Fm for the Alaskan samples (Figure 2).

A plausible mechanism linking Δ₁₈ values and Fm is that older carbon reservoirs have undergone a greater degree of microbial decomposition (Middelburg, 1989; Trumbore, 2000) and therefore contain a greater proportion of recalcitrant organic molecules that limit microbial metabolisms. The range of Δ₁₈ values in the Alaskan and Stordalen samples overlaps, implying a similar range of CH₄ production rates in these ecosystems despite the large difference in carbon substrate ages. The mean age of organic carbon in the Stordalen lake catchments is significantly younger than that in the Alaskan lakes, largely due to the Stordalen lakes catchments history of Holocene deglaciation (Walter Anthony et al., 2016). Differences in organic matter reactivity could explain the different Δ₁₈-Fm relationships between the Alaskan and Stordalen sample sets. In the Alaskan thermokarst lakes, old organic matter has largely been stored frozen and was therefore subject to limited decomposition and could remain relatively reactive (Ewing et al., 2015). In contrast, the organic matter in the Stordalen lake sediments is not predominantly derived from thawed permafrost (Kokfelt et al., 2010) and therefore is more likely to become increasingly refractory with time. The reactivity of organic carbon is also likely influenced by active layer dynamics prior to freezing. For example, yedoma is composed of eolian deposits (Schuur et al., 2015) and undergoes different soil formation processes than other terrestrial permafrost.

It is noteworthy that organic matter in thawed permafrost has been shown to be highly available for microbial degradation regardless of its ¹⁴C age (Ewing et al., 2015; Mann et al., 2015; Vonk et al., 2013). In addition, deep yedoma permafrost (>12 m depth) from Central Alaska contains a high proportion of labile organic compounds (reduced and saturated OC compounds), and in laboratory incubations produces CH₄ more rapidly than shallower permafrost or active layer soils (Heslop et al., 2019). We consider reduced reactivity of organic carbon to be the simplest mechanism linking older carbon substrates to slower rates of methanogenesis, but other environmental variables such as the concentration of alternate electron acceptors or temperature could also explain this linkage. Both thawing and intact permafrost often contain relatively high concentrations of iron oxides, nitrate, or sulfate that can be reduced to respire organic carbon, thereby inhibiting methanogenesis. (Herndon et al., 2017; Heslop et al., 2019; Keuper et al., 2012; Winkel et al., 2019). Additionally, rates of methanogenesis have been shown to increase at higher temperatures (Yvon-Durocher et al., 2014). Deep thawed permafrost does not warm substantially in the summer as compared to shallower sediments or soils, and warm summer temperatures could cause higher rates of methanogenesis in shallow lake sediments relative to deeper environments (Wik et al., 2014).

### 3.3. Relative Rates of Methanogenesis Are Not Positively Related to CH₄ Eubllition Flux

In the Alaskan thermokarst lakes, we also observe that Δ₁₈ is positively correlated with the logarithm of CH₄ flux (Figure 3b). This relationship is counterintuitive, as it implies that CH₄ produced more slowly, from older carbon substrates, is released with a higher flux. Our proposed explanation for this result relies on a conceptual model for thermokarst lake ebullition seeps proposed by Walter et al. (2007) (Figure 3a). In this model, small “point-source” seeps release CH₄ from relatively young lake sediments. In contrast, large “hot-spot” seeps release CH₄ from old thawed permafrost that is concentrated along preferential flow pathways at depth before being emitted near the active thermokarst erosion zone. The Δ₁₈ data set implies that point-source seeps are fed by relatively rapid production of CH₄ but are limited in the volume of sediment across which they integrate gas, resulting in relatively low CH₄ fluxes. Conversely, hotspot seeps are...
fueled by relatively slow production of CH₄ and as such must integrate gas across a much larger volume of thawed permafrost to result in the observed higher CH₄ fluxes. While hotspot seeps occur less frequently than point-source seeps, their large fluxes mean they can emit a large proportion of the total lake ebullition CH₄ fluxes. At Goldstream Lake, which has been intensively studied in terms of seep densities, hotspot seeps emit 50–70% of total lake ebullition CH₄ fluxes (Walter Anthony & Anthony, 2013).

In contrast, in the Stordalen lakes, we do not observe a significant correlation (p < 0.05) between CH₄ ebullition flux and either Δ₁⁸ for the Stordalen lakes; (f) plot of CH₄ flux vs. Fm for the Stordalen lakes. Horizontal error bars in (b) and (e) indicate analytical error (2σ) for Δ₁⁸. Panels (b), (c), (e), and (f) include data that do not have paired ¹⁴C and Δ₁⁸ measurements (Table S1).

Figure 3. (a) Conceptual model of CH₄ ebullition fluxes in the Alaskan thermokarst lakes; (b) plot of CH₄ flux vs. Δ₁⁸ for the Alaskan lakes. Dashed black line: regression fit excluding Lake Qalluruq (y = 0.39x – 0.95; R² = 0.66; p < 0.01). (c) Plot of CH₄ flux vs. Fm for the Alaskan lakes. Dashed black line: regression fit excluding Lake Qalluruq (y = –3x + 1.07; R² = 0.47; p = 0.09). Dotted lines in (b) and (c) indicate 95% confidence intervals for regression fits. Error bars in (b) and (c) indicate standard deviations for average fluxes for different seep types (Walter Anthony & Anthony, 2013). (d) Conceptual model of CH₄ ebullition fluxes in Stordalen glacial lakes; (e) plot of CH₄ flux vs. Δ₁⁸ for the Stordalen lakes; (f) plot of CH₄ flux vs. Fm for the Stordalen lakes. Horizontal error bars in (b) and (e) indicate analytical error (2σ) for Δ₁⁸. Panels (b), (c), (e), and (f) include data that do not have paired ¹⁴C and Δ₁⁸ measurements (Table S1).
The two different models of CH$_4$ ebullition fluxes discussed above reflect the different sedimentary and geomorphological environments in the Alaskan and Stordalen lakes. The Alaskan thermokarst lakes form in ice-rich permafrost. It is possible that voids produced by melting ice wedges and heterogeneities in thawed permafrost soils enhance the formation of preferential gas flow pathways (Heslop et al., 2015; Rowland et al., 2011; Walter et al., 2008). In contrast, the Stordalen lake basins contain relatively homogenous organic-rich mud overlying bedrock (Kokfelt et al., 2010; Wik et al., 2013), which likely minimizes preferential gas flow pathways. These differences are consistent with studies suggesting that the flux and age of CH$_4$ emitted from permafrost-associated lakes is influenced by their geological and geomorphological setting (Elder et al., 2018).

This study only considered ebullition fluxes of CH$_4$, and there are no studies comparing $\Delta_{18}$ with $^{14}$C or flux for dissolved CH$_4$. Where comparison is possible, dissolved CH$_4$ tends to contain younger carbon than ebullition CH$_4$ (Elder et al., 2019) and is more likely to have its stable isotope composition influenced by methane oxidation (Elder et al., 2019; Jansen et al., 2019). Further study will be needed to assess whether the patterns observed here for ebullition CH$_4$ also apply to diffusive CH$_4$ fluxes. However, for the studied lakes, ebullition fluxes are estimated to be the dominant source of CH$_4$ emissions in the ice-free season (Jansen et al., 2019; Sepulveda-Jauregui et al., 2015).

4. Conclusions

As permafrost thaws, increasing quantities of long-stored carbon will be made available to anaerobic, CH$_4$-producing microbial communities in lakes. Our data from two different types of northern lakes, supported by results from culture experiments, suggest that methanogenesis using these old carbon substrates will proceed at slower rates than methanogenesis fueled by modern carbon in similar environments. When combined with flux estimates, these results also imply that the inferred relative rates of methanogenesis are not a strong determinant of observed CH$_4$ ebullition fluxes. More research is needed to constrain the mechanism behind this apparent limitation on the rate of CH$_4$ production from older carbon, to determine whether these results are representative of other northern lakes and other emissions pathways, and to better understand the relationship between rates of methanogenesis and CH$_4$ fluxes. If found to be a widespread phenomenon, relatively slow rates of CH$_4$ production from old carbon substrates could prove to be important in modeling and predicting the emission of CH$_4$ produced from thawed permafrost.

Acknowledgments

We thank Nami Kitchen for help with $\Delta_{18}$ analyses, Sarah Murseli for help with $^{14}$C analyses, and Nathan Dallaska for help with CH$_4$ concentration measurements. Victoria Orphan and Jared Leadbetter provided laboratory facilities for culture experiments. This research was partially supported by funds from the Trottier Institute for Science and Public Policy to PMJD, from Royal Dutch Shell to JME and ALS, from the Agouron Institute to MKL, from the Heising-Simons Foundation to DA Stolper, and from Vetenskapsrådet 2013-5562 to PC. Data supporting this article are available at https://doi.org/10.6084/m9.figshare.11831340.v1.

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