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Methane production and bubble emissions from arctic lakes: Isotopic implications for source pathways and ages

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[1] This study reports an atmospheric methane (CH_4) source term previously uncharacterized regarding strength and isotopic composition. Methane emissions from 14 Siberian lakes and 9 Alaskan lakes were characterized using stable isotopes (^{13}C and D) and radiocarbon (14C) analyses. We classified ebullition (bubbling) into three categories (background, point sources, and hot spots) on the basis of fluxes, major gas concentrations, and isotopic composition. Point sources and hot spots had a strong association with thermokarst (thaw) erosion because permafrost degradation along lake margins releases ancient organic matter into anaerobic lake bottoms, fueling methanogenesis. With increasing ebullition rate, we observed increasing CH_4 concentration of greater radiocarbon age, depletion of $^{13}C_{CH4}$, and decreasing bubble N_2 content. Microbial oxidation of methane was observed in bubbles that became trapped below and later within winter lake ice; however, oxidation appeared insignificant in bubbles sampled immediately after release from sediments. Methanogenic pathways differed among the bubble sources: CO_2 reduction supported point source and hot spot ebullition to a large degree, while acetate fermentation appeared to contribute to background bubbling. To provide annual whole-lake and regional CH_4 isofluxes for the Siberian lakes, we combined maps of bubble source distributions with long-term, continuous flux measurements and isotopic composition. In contrast to ty~ical values used in inverse models of atmospheric CH_4 for northern wetland sources ($^{13}C_{CH4}$ = -58‰, ^{14}C age modern), which have not included northern lake ebullition as a source, we show that this large, new source of high-latitude CH_4 from lakes is isotopically distinct ($^{13}C_{CH4}$ = -70‰ ^{14}C age 16,500 years, for North Siberian lakes).

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1. Introduction

[2] Atmospheric methane (CH_4) is a potent greenhouse gas responsible for ~20% of the direct radiative forcing from all long-lived greenhouse gases *[intergovernmental Panel on Climate Change (IPCC),* 2007). Its concentration in the atmosphere results from a balance between sources and sinks. While potential new, large sources are still being identified *[Keppler et al.,* 2006], some known sources are poorly quantified because of difficulties in assessing high variability in emission rates *[Fung et al.,* 1991; *Intergovernmental Panel on Climate Change (lPCC),* 2001, *Mikaloff Fletcher et al.,* 2004a]. Wetlands playa major role in global atmospheric CH_4 dynamics, representing ~ 10-30% (50-150 Tg CH_4 a^{-1}) of known sources *[Matthews and Fung, 1987; Fung et al.,* 1991], with northern wetlands contributing substantially to the total (<6 to 40 Tg CH_4 $^{a-1}$) *[Roulet et al.,* 1994; *Reeburgh et al.,* 1998; *Worthy et al.,* 2000; *IPCC,* 2001; *Zhuang et al.,* 2006]. This wide range in wetland emission estimates results primarily from uncertainties in the areal extent of wetlands and from the large spatial and temporal variability of short-term local CH_4 emission measurements *[Reeburgh et al.,* 1998; *Mikaloff Fletcher et al.,* 2004a, 2004b].

[3] Local CH_4 emissions from most lakes and wetlands can vary by several orders of magnitude on the scale of a few meters or over several hours. Heterogeneity in ebullition (bubbling) is a major contributor to this variability, and the spatial and temporal patchiness of ebullition challenges efforts to quantity this mode of emission. As a result, many studies of CH_4 emissions from lakes and wetlands report only emissions *via* molecular diffusion and aquatic plant transport *[Kling et al.,* 1992; K. M. Walter et al., A new method to evaluate methane emissions from northern lakes:

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Surveying bubbles in lake ice, submitted to *Bio Science,* 2008, hereinafter referred to as K. M. Walter et a\., submitted manuscript, 2008]. Studies that aimed to assess ebullition with greater accuracy showed that ebullition .in lakes is a dominant, yet inadequately quantified mode of CH_4 emission leading to a systematic underestimation from lakes globally *[Casper et al.,* 2000; *Bastviken et al.,* 2004; *Walter et al.,* 2006; K. M. Walter et al., submitted manuscript, 2008].

[4] Model estimates of northern wetland emissions have yet to include ebullition from lakes *[Zhaung et al., 2004; Mikaloff Fletcher et al.,* 2004a, 2004b; *Bousquet et al., 2006; Chen and Prinn,* 2006]. Recent studies that quantified the patchiness of ebullition showed that adding emission estimates of CH_4 from North Siberian thermokarst lakes increased current estimates of total northern wetland emission by 10-63% *[Walter et al.,* 2006]. Thermokarst (thaw) erosion resulting from permafrost degradation along lake margins drives CH_4 emissions from North Siberian lakes by depositing thawed Pleistocene-aged organic matter into anaerobic lake bottoms, fueling methanogenesis. Expansion of thermokarst lakes in continuous permafrost regions of Siberia during recent decades constitutes a positive feedback to climate warming *[Smith et al.,* 2005; *Walter et al.,* 2006]. Global circulation models predict that greatest warming will occur at high latitudes *[IPCC,* 2001, 2007] with significant permafrost degradation during the 21st century *[Sazonova et al.,* 2004; *Lawrence and Slater,* 2005], raising concerns about the increase of CH_4 emissions from northern lakes and wetlands to future climate change.

[5] Isotopic signatures of atmospheric CH_4 and its sources can be used in isotope mass balance models to define the magnitudes of different sources and sinks *[Hein et al., 1997; Houweling et al.,* 1999; *Mikaloff Fletcher et al.,* 2004a, 2004b; *Bousquet et al.,* 2006]. For instance, inverse modeling of high-resolution spatiotemporal atmospheric CH_4 concentrations and its ^{13}C isotope ratio was used to determine the relative contributions of northern wetland emissions and biomass burning in the tropics *[Lowe et al., 1994; Mikaloff Fletcher et al.,* 2004a, 2004b; *Bousquet et al.,* 2006]. Similarly, the ^{14}C isotope ratio of CH_4 has been used to estimate the contribution of fossil carbon ($^{14}C_{free}$) attributed to natural gas seepage and coal mining *[Lowe et al.,* 1994; *Wahlen et al.,* 1989]. Stable hydrogen isotopes can be combined with stable carbon isotopes and used to distinguish sources of CH_4 including bacterial formation, thermogenic formation and biomass burning *[Whiticar et al.,* 1986], as well as to detennine the effect of microbial oxidation in lake and wetland environments *[Coleman et al.,* 1981; *Happell et al.,* 1994]. In aquatic environments, variations in the $?^{13}C$ of CH_4 and carbon dioxide (CO_2) can reveal the importance of different biochemical pathways of methanogenesis including CO_2 reduction and acetate fermentation *[Whiticar et al.,* 1986; *Chasar et al.,* 2000a, 2000b; *Chanton et al.,* 2005], particularly as these pathways vary spatially in thennokarst-influenced ecosystems *[Prater et al.,* 2007]. Differences in $?D_{CH4}$ are also useful for determining CH_4 sources, but are primarily linked to ?D of the source water *[Sugimoto and Wada,* 1995; *Waldron et al.,* 1999a; *Chanton et al.,* 2006]. Careful bottom-up studies of processes driving CH_4 emissions and isotope signatures are necessary to help define source estimates in models.

[6] The purpose of this study is to characterize CH_4 production and emission from a variety of arctic and boreal lakes in Siberia and Alaska using ^{13}C, D and ^{14}C isotopic ratios to help elucidate the role of lake ebullition, particularly that associated with thermokarst erosion (ground subsidence resulting from the thawing of ground ice), in global atmospheric CH_4 dynamics. Specific objectives include (1) characterizing the isotopic composition of different types of CH_4 bubble sources including background bubbling, point sources and hot spots; (2) identifying factors that influence these signatures such as CH_4 production pathways and environmental water- sources, (3) exploring the potential for CH_4 oxidation in lake bubbles; and (4) combining careful measurements of ebullition patchiness with isotopic signatures of bubbles and measured fluxes to determine whether whole-lake and regional CH_4 isofluxes (flux-weighted average isotopic signatures) differ from previous estimates based on methods that ignored point source and hot spot ebullition.

2. Methods

2.1. Location of Study Lakes

[7] Most isotopic studies in northern lakes have been conducted in North America and Europe *[Wahlen et al., 1989, Quay et al.,* 1988, *Martens et al.,* 1986], with little attention to Russian lakes *[Nakagawa et al.,* 2002], which comprise ~ 70% of arctic lakes *[Holmes and Lammers,* 2006]. We studied a variety of lakes in the boreal forest and tundra of the Kolyma River Basin in Siberia and in Alaska situated on permafrost substrates of various types including: (l) Pleistocene-aged, organic-rich, silty ice-complex "yedoma" near Cherskii in northeast Siberia (68°45'N, 161°20'E) *[Zimov et al.,* 1997, 2006]; (2) Holocene organic soil on top of organic-rich, Pleistocene-aged retransported silt near Fairbanks in Interior Alaska (64°49'N, 147°52'W), and (3) organic-poor glacial deposits near Toolik Lake in northern Alaska (68°28'N, 149°34'W) (Table 1 and Figure 1). Siberian and Interior Alaskan lakes that we studied were formed by thermo karst activity. Study lakes in northern Alaska arc kettle lakes that formed upon thaw of ice blocks deposited in glacial drift and outwash plains of late Pleistocene glaciation *[Hamilton,* 2003]. These types of lakes are occasionally influenced by thermokarst along margins today.

2.2. Sample Collection and CH_4 Flux Measurements

[8] We collected gas from several different types of lake bubbling events in Siberia and Alaska from 2001 to 2004. In 2001 we stirred surface sediments in a variety of tundra and boreal thermokarst lakes in Siberia and collected bubbles through a handheld funnel into glass serum vials that we sealed with butyl rubber stoppers. Samples were stored in a refrigerator at 4°C in the dark. We did not measure flux in conjunction with bubble samples collected by stirring lake sediments. In 2003-2004 in Siberia all bubble samples werc collected from natural ebullition events into floating traps without disturbing sediments. Bubble traps (~1-m diameter), placed permanently under the surface of lakes and beneath winter ice, were either freely floating to capture the average "background" ebullition, or they were fixed in place over discrete points of

Table 1. Lake Location and Size, Gas Collection Technique, and Sampling Dates of Bubbles From Study Sites

Region	Location	Site	Classification[a]	Thermokarst	Bubble Collection Date	Area (m^2)	Max Depth (m)	Collection Technique[b]
Northeast Siberia	1	Shuchi Lake	boreal, yedoma	moderate	Jul 2001, May 2003–Jun 2004	58,051	11.0	S, N, IK
Northeast Siberia	1	Tube Dispenser Lake	boreal, yedoma	active	May 2003–Jun 2004	110,175	16.5	N
Northeast Siberia	1	Grass Lake	boreal, yedoma	inactive	May 2003–Jun 2004	5363	12.5	N
Northeast Siberia	1	Station Road Yedoma Pond 1	boreal, yedoma	active	Jul 2001	~225	1.8	S
Northeast Siberia	1	Tower Road Yedoma Pond 2	boreal, yedoma	active	Jul 2001	~226	2.3	S
Northeast Siberia	1	Tower Road Yedoma Pond 3	boreal, yedoma	active	Jul 2001	~227	2.3	S
Northeast Siberia	1	Kitchen Sand Pond 1	boreal, sand	none	Jul 2001	~228	1.3	S
Northeast Siberia	1	Volodya Sand Pond 2	boreal, sand	none	Jul 2001	~100	1.6	S
Northeast Siberia	1	Airport Sand Pond 3	boreal, sand	none	Jul 2001	~900	1.3	S
Northeast Siberia	1	Meadow Lake	boreal, HA-FD	moderate	Jul 2001		2.3	S
Northeast Siberia	2	Young Tundra Thaw Pond	tundra, yedoma	active	Jul 2001			
Northeast Siberia	2	No Fish Ambarchik Lake	tundra, yedoma	moderate	Jul 2001			
Northeast Siberia	2	Ambarchik Fish Lake	tundra, yedoma	moderate	Jul 2001			
Northeast Siberia	2	Tundra Floodplain Lake	tundra, HA-FD	moderate	Jul 2001			
Interior Alaska	3	Rosie Creek Beaver Pond	boreal, HA-RPL	active	Nov 2004	6324	1.5	N
Interior Alaska	3	Goldstream Valley Lake	boreal, RPL	active	Nov 2004	9797		N
North Slope, Alaska	4	Toolik Lake	tundra, GD	none	Oct 2004	1,470,000	24.0	IK
North Slope, Alaska	4	E1	tundra, GD	none	Oct 2004	30,099	12.4	IK
North Slope, Alaska	4	E5	tundra, GD	none	Oct 2004	113,172	11.9	IK
North Slope, Alaska	4	E6	tundra, GD	none	Oct 2004	19,967	3.2	IK
North Slope, Alaska	4	NE2	tundra, GD	none	Oct 2004			IK
North Slope, Alaska	4	N2	tundra, GD	none	Oct 2004	13,663	10.7	IK
North Slope, Alaska	4	N3	tundra, GD	none	Oct 2004	9349		IK

[a]Yedoma is icy, organic-rich Pleistocene loess, and sand is man-made sand. HA-FD, olocene alluvium and flooplain deposits; HA-RPL, Holocene alluvium and reworked Pleistocene loess from Stage 3; RPL reworked Pleistocene loess from Stage 3; GD, glacial deposits.

[b]S, stirred surface sediments; N, natural bubbling into traps; IK, ice koshka.

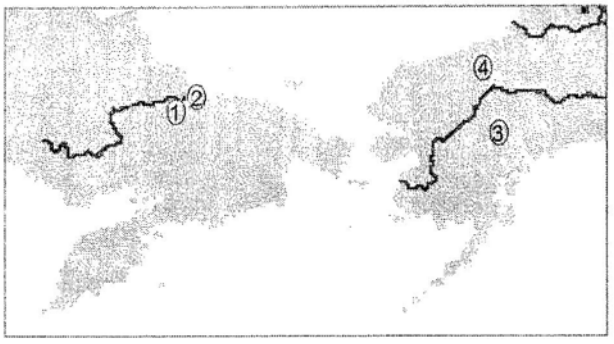

Figure 1. Location of boreal (locations 1 and 3) and tundra (locations 2 and 4) study sites in Siberia and Alaska.

bubbling, called "point sources" and "hot spots." Units of flux differ for the discrete types of bubbling. Background ebullition, captured by randomly placed traps, is a function of trap area and expressed as mg CH_4 m^{-2} d^{-1}, whereas units for point source and hot spot bubbling are mg CH_4 $spot^{-1}$ d^{-1} because emissions from discrete, small holes in lake sediments (<2 cm diameter) were independent of bubble trap area. *Walter et al.* [2006] showed that point source and hot spot bubbling, which had a probability of ~,0.001% of being captured by randomly placed bubble traps and which accounted for ~70% of emissions from lakes, were distinctly different from background ebullition with regards to ebullition rates. Bubble samples collected into serum vials within ~2 h of release from the lake bottom are labeled as "fresh" hereafter. Samples collected from background traps accumulated slowly and therefore sat up to a few days in the traps before collection; these are labeled "not fresh."

[9] In the spring of 2003, we collected bubbles trapped in lake ice by carefully tapping into frozen gas pockets from the ice surface and capturing trapped gases into serum vials as the bubbles streamed up from inside the ice. These samples, which represented wintertime point source bubbling (described by *Walter et al.* [2006]), are here referred to as "ice koshkas" (i.e., the Russian term for pockets of CH_4-rich gas bubbles trapped in lake ice). In autumn 2005, ice-koshka samples were collected from tundra lakes in northern Alaska, and fresh bubbling from hot spots was captured from two boreal thermokarst lakes near Fairbanks.

[10] Year-round flux dynamics for background, point source, and hot spot bubbling from Siberian lakes were presented in detail by *Walter et al.* [2006; K. M. Walter et al., submitted manuscript, 2008]. To show the relationship between CH_4 isotope values and bubbling rates in this study, we used the 10-day average ebullition flux surrounding each sample date for the bubbles collected for isotopic analyses in our regressions. To calculate the whole-lake and regional isofluxes, we applied seasonal rates of ebullition to the range of isotope values determined for CH_4 bubbling from these arctic lakes.

[11] Lake water samples in Siberian lakes were collected with a Van Dorn bottle from 14 June 2003 through 11 August 2003 just above the sediment surface for determination of $?D_{H2O}$. Water was poured into glass vials avoiding air bubbles. Vials were capped and stored at 4°C in the dark until analysis in August 2005.

2.3. Gas Concentration and Isotope Procedures

[12] Concentrations of CO_2, O_2, N_2 and CH_4 in lake bubble samples were measured by gas chromatography using a thermal conductivity detector (TCD Shimadzu 8A). O_2 values presented in this paper were corrected for argon (Ar) on the basis of atmospheric molar ratios of N_2/Ar. Argon coeluted with O_2 and comprised 0.01 to 1% of peak area. We measured $^{13}C/^{12}C$ of CH_4 by direct syringe injection using gas chromatography/mass spectrometry (Hewlett-Packard 5890 Series II GC coupled to a Finnigan MAT Delta S). Subsamples of gas were combusted to CO_2, purified, and catalytically reduced to graphite *[Stuhler and Polach,* 1977], and the $^{14}C/^{12}C$ isotopic ratios were measured by accelerator mass spectrometry at the Keck Carbon Cycle AMS Facility at the University of California, Irvine. We determined *D/H* of CH_4 on a Finnigan MAT delta +XP using a Trace GC with a poroplot column and the reduction column set at 1450°C. Lake water samples were analyzed for $?D_{H2O}$ by the zinc reduction method *[Coleman et al.,* 1982].

[13] Stable isotope compositions are expressed in ? (‰)= 10^3 ((Rsample/Rstnndard)-I)where R is $^{13}C/^{12}C$ or *D/H* and standards refer to the Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW), respectively. The analytical errors of the stable isotopic analyses are ±0.l‰ $?^{13}C$ and ±l.0‰ *?D.* We express radiocarbon data as percent modem carbon, pmC (%) = $(C^{14}C/^{12}C)$sample/$(^{14}C/^{12}C)$standard) × 100, which is the percentage of $^{14}C/^{12}C$ ratio normalized to $?^{13}C$ = -25‰ and decay corrected relative to that of an oxalic standard in 1950 *[Stuiver and Polach, 1977].*

2.4. Methane Production Pathway

[14] Methanogenesis is an ancient process that relies on relatively simple substrates, for example carbon monoxide, carbon dioxide, acetate, formate, methylamine, methanol, and dimethylsufide, that are produced by other metabolic processes *[Conrad,* 1989]. The two main pathways of bacterial methane production in anaerobic sediments are CO_2 reduction and acetate fermentation:

$$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad \text{(fermentation/syntrophic oxidation)} \tag{1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (CO_2 \text{ reduction}) \tag{2}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad \text{(acetate fermentation)} \tag{3}$$

[15] We used two approaches to estimate the relative proportion of these two major pathways of methanogenesis [*Whiticar et al.*, 1986; *Hornibrook et al.*, 2000]: (1) the apparent C fractionation factor (α_C) between CH_4 and CO_2 and (2) a simple isotopic mixing model based on the relative proportion of the pathways. The α_C is defined:

$$\alpha_c = \frac{\left(\delta^{13}C_{CO2} + 10^3\right)}{\left(\delta^{13}C_{CH4} + 10^3\right)} \tag{4}$$

Table 2. Concentrations of Major Constituents (CH_4, N_2, CO_2, and O_2) and Isotopes' Compositions ($\delta^{13}C_{CO2}$[a], $\delta^{13}C_{CH4}$, δD_{CH4}, and δD_{H2O}) of Gas Bubbles and Lake Water From Siberia and Alaska[a]

Lake	Bubble Source	CH_4%	N_2%	CO_2%	O_2%	$\delta^{13}C_{CO2}$	$\delta^{13}C_{CH4}$	δD_{CH4}	δD_{H2O} (Depth)
				Siberia					
Shuchi Lake									−154 ± 2.6, 3 (1 m)
	SS	39.7 ± 32.7, 5	48.8 ± 36.9, 5	4.0 ± 3.0, 5	8.5 ± 10.7, 5		−62.0 ± 5.1, 5	−354 ± 17, 4	−159 ± 2.9, 3 (10 m)
	B	63.8 ± 16.1, 6	30.3 ± 14.6, 6	0.3 ± 0.3, 6	5.7 ± 2.0, 6	−17.8 ± 4.9, 10	−66.8 ± 5.6, 10	−380 ± 13, 3	
	PS	78.9 ± 4.6, 14	16.6 ± 3.4, 14	0.9 ± 0.6, 15	3.7 ± 1.3, 15	−11.1 ± 6.9, 11	−79.7 ± 3.1, 13	−384 ± 6, 10	
	HOT	84.3 ± 6.9, 38	12.7 ± 5.4, 38	0.7 ± 0.3, 38	2.7 ± 1.5, 38	−14.8 ± 2.6, 24	−79.6 ± 0.5, 35	−394 ± 4, 32	
	IK	53.0 ± 2.7, 3	43.7 ± 4.3, 3	0.3 ± 0.1, 3	3.9 ± 1.1, 3	−26.2 ± 2.6, 4	69.3 ± 4.3, 4	−346 ± 13, 4	
Tube Dispenser Lake									−161 ± 8.1, 3 (15 m)
	B	55.0 ± 7.1, 5	39.8 ± 8.4, 5	0.2 ± 0.1, 5	5.6 ± 1.6, 5	−19.6 ± 3.2, 11	−62.4 ± 2.6, 14	−377 ± 28, 9	
	HOT	79.0 ± 11.6, 2	16.5 ± 9.9, 2	1.0 ± 0.7, 2	3.7 ± 2.5, 2	−9.6 ± 10.3, 3	−77.1 ± 4.7, 3	−416 ± 4, 2	
Grass Lake									−172 ± 2.9, 3 (10 m)
	B	2.7, 1	68.9 ± 1.7, 2	0.2 ± 0, 2	29.3 ± 1.4, 2		−58.6 ± 24.3, 4	−339 ± 1, 2	
Station Road Yedoma Pond 1	SS						−56.1 ± 2.5, 3		
Tower Road Yedoma Pond 2	SS	29.8, 1	65.5, 1	4.5, 1	1.1, 1		−58.3 ± 3.0, 3	−388 ± 0, 2	
Tower Road Yedoma Pond 3	SS						−62.0 ± 6.3, 3	−402, 1	
Kitchen Sand Pond 1	SS	11.8 ± 1.1, 2	86.9 ± 1.7, 2	1.3 ± 0.1, 2	0.9 ± 0.6, 2		−58.2 ± 1.1, 2	−360, 1	
Volodya Sand Pond 2	SS	10.7 ± 8.2, 3	87.6 ± 8.2, 3	1.9 ± 1.3, 3	0.7 ± 0.3, 3		−53.7 ± 7.1, 3	−373 ± 8, 2	
Airport Sand Pond 3	SS	2.7 ± 2.7, 2	94.1 ± 2.5, 2	4.3 ± 2.7, 3	0.4 ± 0.05, 3		−57.7, 1		
Meadow Lake	SS	37.1 ± 7.5, 4	62.3 ± 6.6, 4	1.8 ± 0.3, 4	0.6 ± 0.6, 4		−57.2 ± 5.2, 4	−389 ± 14, 2	
No Fish Ambarchik Lake	SS	24.1 ± 14.6, 3	72.0 ± 13.5, 3	3.5 ± 1.2, 3	0.8 ± 0.3, 3		−63.3 ± 2.1, 3		
Ambarchik Fish Lake	SS	21.7 ± 7.9, 2	75.8 ± 7.9, 2	2.1 ± 0, 2	0.7 ± 0.1, 2		−60.2 ± 0.4, 2		
Young Tundra Thaw Pond	SS	70.2 ± 0.6, 2	22.5 ± 1.7, 2	6.6 ± 1.2, 2	1.1 ± 0, 2		−56.1 ± 3.2, 2		
Tundra Floodplain Lake	SS	49.7 ± 7.7, 3	45.6 ± 5.9, 3	4.2 ± 1.2, 3	1.3 ± 0.7, 3		−61.0 ± 2.0, 3	−372 ± 8, 2	
				Alaska					
Rosie Creek Beaver Pond	HOT	69.3 ± 12.3, 7	27.3 ± 10.2, 7	1.6 ± 0.3, 7	2.0 ± 2.6, 7		−75.5 ± 0.4, 5	−353 ± 2, 5	
Goldstream Lake	HOT	88.7 ± 1.4, 3	9.5 ± 1.1, 3	0.8 ± 0.1, 3	1.1 ± 0.1, 3		−70.7 ± 1.2, 2	−346 ± 6, 2	
Lake E1	IK	34.2 ± 2.8, 4	53.5 ± 1.4, 3	0 ± 0.1, 4	11.1 ± 2.0, 3		−73.5 ± 1.1, 4	−329 ± 10, 4	
Lake E6	IK	59.7 ± 5.8, 7	28.7 ± 4.3, 7	0.2 ± 0.1, 7	10.8 ± 1.5, 7		−67.6 ± 0.6, 7	−330 ± 4, 7	
Lake N2	IK	39.7 ± 1.1, 2	49.1 ± 1.0, 2	0.1 ± 0, 2	10.6 ± 0.4, 2		−75.2 ± 0.2, 2	−328 ± 2, 2	
Lake N3	IK	49.5 ± 3.0, 4	37.2 ± 2.3, 4	0.1 ± 0, 4	12.3 ± 0.7, 4		−72.2 ± 0.7, 4	−323 ± 2, 4	
Lake NE2	IK	38.4 ± 2.9, 5	53 ± 3.1, 5	0.1 ± 0, 5	8.0 ± 0.5, 5		−73.8 ± 2.4, 5	−327 ± 1, 5	

[a]Estimates are presented as mean ± standard deviation, n. For sample sizes of $n = 2$, error estimates are half of the absolute difference between two measurements. It should be noted that much of the data presented in Table 2 are used in Figures 2, 3, 5, and 7 and represent multiple sampling events at the same sites. For instance, at Shuchi Lake, seven different background traps, six point sources, and three hot spots were sampled repeatedly across time. Bubble types are stirred surface sediments (SS), background (B), point sources (PS), hot spots (HS), and ice koshkas (IK). We have not presented the $\delta^{13}C_{CO2}$ of samples collected in 2001 because we cannot trust that CH_4 oxidation did not occur in the refrigerated sample bottles during storage. Data on $\delta^{13}C_{CO2}$ of Alaskan gases were not collected.

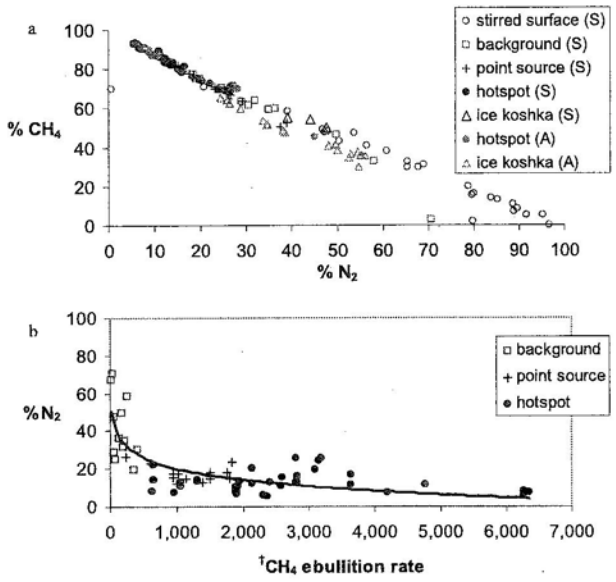

Figure 2. (a) The concentrations of CH_4 and N_2 in bubbles collected from lakes in Alaska (A) and Siberia (S). The negative linear relationship is described by $[CH_4] = -1.03[N_2] + 95.5$, $R^2 = 0.97$. It should be noted that much of the data presented in Figure 2a represent multiple sampling events at the same site, as indicated in Table 2. (b) Methane ebullition rate versus N_2 composition of background, point source, and hot spot bubbles from Siberian lakes, expressed as $[N_2] = -8.5*\ln(CH_4 \text{ flux}) + 79$, $r^2 = 0.63$. The data indicate that the N_2 content of bubbles is influenced by the rate of ebullition, whereby high bubbling rates strip N_2 from lake sediments. Although background, point sources and hot spots are presented together as a continuum of bubble types, it should be noted that the units of ebullition measured with bubble traps for the discrete types differ: background ebullition (mg CH_4 m^{-2} d^{-1}) and point source and hot spot ebullition (mg CH_4 $spot^{-1}$ d^{-1}).

Where $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ represent the $\delta^{13}C$ of CO_2 and CH_4 in bubbles respectively. This estimation of a_c is approximate because CH_4 and CO_2 are not related in the same way for the CO_2 reduction and acetate fermentation pathways (equations (2) and (3)); however, a_c values have been utilized to differentiate between dominant pathways of methanogenesis in natural and artificial systems *[Sugimoto and Walda,* 1995 *Waldron et al.,* 1999b; *Chasar et al.,* 2000a; *Chanton et al.,* 2006; *Prater et al., 2007].*

[16] Second, we also used a simple mixing model to estimate the relative proportion of the acetate fermentation and CO_2 reduction pathways:

$$(f_{CO2} + f_{ace})(\delta^{13}C_{CH4}) = f_{CO2}(\delta^{13}CH_{4(CO2)}) + f_{ace}(\delta^{13}CH_{4(ace)}) \quad (5)$$

where f_{CO2} is the proportion of CH_4 produced by CO_2 reduction; f_{ace} is the proportion of CH_4 produced by acetate fermentation; $?C^{13}_{CH4}$ is the isotope ratio of measured CH_4, the mixture of both pathways; and $b^{13}CH_{4(CO2)}$ is the isotope ratio of CH_4 produced by the CO_2 reduction pathway, and calculated using the isotope fractionation factor α_{CO2} of 1.079, which was determined in a study where CO_2 reduction was the sole pathway of CH_4 in natural wetlands [*Lansdown et al.*, 1992] and used in other studies to determine the pathway of CH_4 production in lake sediments [*Nakagawa et al.*, 2002]. $\delta^{13}CH_{4(CO2)}$ is calculated:

$$\delta^{13}CH_{4(CO2)} = \frac{\delta^{13}CO_2 + 10^3}{\alpha_{CO2}} - 10^3 \quad (6)$$

$?^{13}CH_{4(ace)}$ is the isotope ratio of CH_4 produced by the acetate fermentation pathway, and assumed to be -43‰ when acetate fermentation occurs in sediments with a sufficient supply of fresh organic material (Case 1), and -27‰ when sediments are extremely depleted in fresh organic material (Case 2) *[Nakagawa et al., 2002].*

3. Results

3.1. Concentrations of Gases in Bubbles

[17] Concentrations of the major gas constituents of bubbles varied by lake and bubble sourec (Table 2). Methane was the predominant constituent of point source and hot spot bubbling (range 67-94%; mean ± std. dev. 82 ± 7%, $n = 55$). Methane was less concentrated and more variable in bubbles collected by stirring surface sediments and in background bubble traps (range 0-77%, mean ± std. dev. 39 ± 25%, $n = 39$). We found a negative linear relationship between the concentration of CH_4 and N_2 in bubbles and a negative curvilinear relationship between ebullition rate and %N (Figure 2). Oxygcn (O_2) concentration in gas bubbles ranged from 0.4% to 29%, depended on the source of bubbling (Table 2), and was negatively related to CH_4 concentration ($[O_2] = -0.08[CH_4] + 10.0$, $F = 29.05_{(1146)}$ $P < 0.0001$). The concentration of CO_2 was low (0-2%) in samples collected from fresh bubbling in Siberia and Alaska in 2003-2004 (Table 2).

3.2. Stable Isotopes in Bubbles and Lake Water

[18] The stable isotope signatures $?^{13}C_{CO2}$, $h^{13}C_{CH4}$, $?D_{cH4)}$ of bubbles and ?D of Siberian and Alaskan lake water varied by lake and bubble source (Table 2). Siberian point sources and hot spot bubbles had less enriched $?^{13}C_{CH4}$ values (-79.5 ± 2.3‰, n = 34) than bubbles collected from background traps or by stirring surface sediments (-61.6 ± 5.7‰, $n = 60$) (t-value = 21.4_{85} $P < 0.0001$) (Figure 3), the latter being similar to typical values reported in the literature for northern lakes and wetlands *(-64‰ [Quay et al.,* 1988]; -61‰ *[Martens et al., 1986]; -58‰ [Lansdown et al.,* 1992]), including Siberian alasses (typical round landforms in permafrost terrain, consisting of a shallow lakes surrounded by wetlands; -61.1 ± 4.4‰, *[Nakagawa et al.,* 2002]). Point source CH_4 trapped in lake ice as ice koshkas (-69.3 ± 4.3‰, $_{11} = 4$) during the entire winter was more enriched in $?^{13}_{CH4}$ than fresh point source bubbles (-79.7 ± 3.0‰, $n = 13$) (t-value = 5.43_{15}, $P < 0.0001$).

[19] The ?D of lake water was -154 ± 2.6 at 1-m depth in Shuchi Lake, and was more depleted at depth in three lakes (-158.7±2.1%0 at 10-m Shuchi Lake; -161 ±8.1 at 15-m, Tube Dispenser Lake; and -172 ± 2.9 at 10-m Grass Lake)

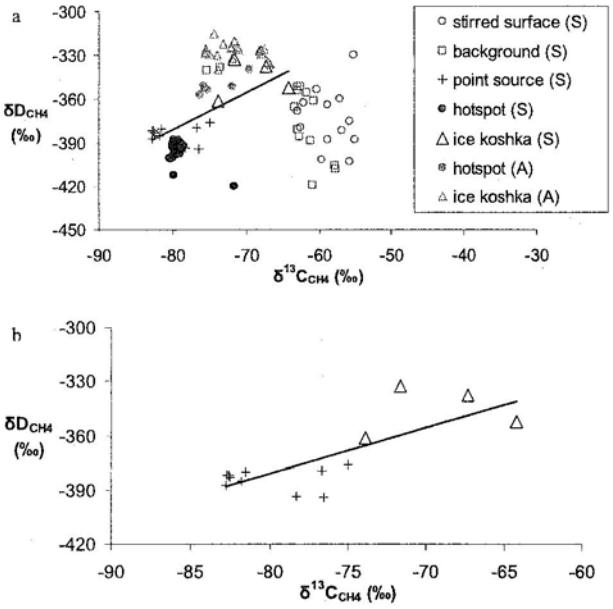

Figure 3. The $\delta^{13}C$ and δD of CH_4 in bubbles from Siberian (S) and Alaskan (A) lakes for (a) all samples and for (b) Siberian point sources and ice koshkas alone. The regression line for point sources (plus signs) collected fresh from ebullition events with ice koshkas (triangles, point sources that are trapped all winter as bubble stacks in ice) is expressed as $\delta D_{CH4} = 2.5*\delta^{13}C_{CH4} - 180$, $r^2 = 0.60$. The enrichment of both $\delta^{13}C$ and δD of CH_4 relative to point sources suggests CH_4 diffusion out of bubbles trapped in ice.

(Table 2). The *?D* of CH_4, which ranged widely in this study (- 315‰ to -420‰), differed by study region and bubble type (Figure 3). The ?D of Siberian CH_4 of point sources and hot spots (-392 ± 8‰, $n = 40$) was *?D* depleted compared to Alaskan hot spots (- 351 ± 5‰, $n = 7$) (t-value = 12.745, $P < 0.0001$). $?D_{CH4}$ was more depleted in thermokarst ponds situated on yedoma (-388‰ to -402‰) compared to manmade sandy ponds sitting on bedrock (-360‰ to - 381 ‰). $?D_{CH4}$ of interior Alaska thermokarstlakes (-340‰ to -355‰) was more depleted than that of the more northern tundra lakes that lacked intensive thermokarst (-321‰ to -339‰) (Table 2). Ice koshkas were enriched by 46‰) in Siberia and 24‰ in Alaska relative to the fresh point source counterparts in both regions (Siberia -346 ± 13‰, $n = 4$; Alaska -328 ± 5‰, $n = 22$).

[20] The $?^{13}C_{C02}$ of point sources (-12.2 ± 7.5‰, $n = 12$) and hot spots (- 14.2 ± 4.1 ‰, $n = 27$) was enriched relative to background bubbles (-18.7 ± 4.1 ‰, $n = 27$).

3.3. Radiocarbon of Bubble CH_4

[21] Lake bubble samples exhibited a wide range of 14C ages, with a substantial number of samples containing ^{14}C–depleted CH_4 (Table 3). CH_4 from high-emission point sources and hot spots of CH_4 bubbling were older (11,355 to 42,900 years), while the low-emission background bubbling (1345 to 8845 years) and stirred bubbles from surface sediments (>modern to 3695 years) contained CH_4 of younger ages (Figure 4).

3.4. Methane Production Pathways

[22] The apparent C fractionation factor *(eve)* between CH_4 and CO_2 was higher in hot spot ($a_C = 1.071 \pm 0.006$, $n = 21$) and point source bubbling ($a_c = 1.073 \pm 0.0$ 11, $n = 12$) in Siberian lakes and ponds compared to the (a_C of background bubbling ($a_c = 1.048 \pm 0.005$, $n = 20$) (Figure 5). Ebullition rate was positively related to the fraction of CH_4 produced via the CO_2 reduction pathway as determined through the mixing model (equations (4) and (5) and Table 4) based on $?^{13}C_{CH4}$, indicating that the CO_2 reduction pathway dominated CH_4 emitted from high-emission point sources and hot spots, while acetate fermentation appeared to play a more important role in lower-emission background bubbling (Figure 6).

4. Discussion

4.1. Major Gas Constituents **in** Bubbles

[23] A negative linear relationship between the concentration of CH_4 and N_2 in bubbles (Figure 2a) indicates that CH_4 is the gas predominately produced in sediments *[Nakagawa et al.,* 2002]. Bubble N_2 content may also be a sensitive indicator of ebullition rates because there is a strong inverse relationship between the N_2 concentrations in bubbles and the rate of ebullition *[Chanton et al.,* 1989) (Figure 2b). Nitrogen is present in pore waters when sediments are deposited and, when depleted, it is resupplied by diffusion from overlying waters. High rates of bubbling strip N_2 from the pore waters, depleting the dissolved N_2 pool in pore waters *[Kipphut and Martens,* 1982; *Chanton et al.,* 1989]. Bubbles collected from hot spots and point sources had the highest CH^4/N_2 ratios, while bubbles released from shallow surface sediments (background, stirred), where lower ebullition rates were observed, had lower CH_4/N_2 ratios. Lower CH_4/N_2 ratio in gas collected from ice koshkas compared to gas collected from fresh point source and hot spot bubbling streams is likely the result of N_2 diffusion from lake water into bubbles that sit under the ice at the top of the water column prior to entrapment in ice that grows slowly around the bubbles.

[24] Bubbles produced in the anaerobic lake sediments should be free of O_2; however, bubbles rise through the water column absorbing O_2, and sit in bubble traps at the surface for several hours to days prior to collection. Holding time in the trap likely accounts for the variability observed in O_2 content, particularly between winter and summer samples (Figure 7). In summer, photosynthesizing periphyton was observed growing in bubble traps, producing O_2 that could diffuse into trapped CH_4-rich bubbles. We suspect that trace amounts of O_2 present in stirred surface sediments are from benthic photosynthesis on the surface of lake sediments. Bubbles from small, stagnant Siberian ponds had the lowest O_2 concentrations, possibly because these ponds lack the wind-driven currents that supply O_2 to lake bottoms in larger lakes. Higher O_2 (8.5% and 29%) corresponding to very low CH_4 (5.2% and 2.7%) in two individual outlier bubble samples (individual data points not shown) collected from the nonthermokarst margin of Shu chi

Table 3. Radiocarbon Content of CH_4 (and CO_2) in Lake Bubbles From Siberia and Alaska Presented as Percent Modern Carbon (pmC) and ^{14}C Age[a]

Lake Name	Margin Type	Bubble Trap Number	Depth (m)	Bubble Source	Fresh	Field Date	$^{14}C_{CH4}$, pmC (%)	± (%)	$^{14}C_{CH4}$ Age (Years)	± (%)	$^{14}C_{CO2}$, pmC (%)	± (%)	$^{14}C_{CO2}$ Age (Years)	± (%)
						Siberia								
Shuchi Lake	NT	-	0.75	SS	F	12 Jul 2001	97.8	0.2	175	20	95.7	0.2	355	25
	NT	21	1.4	B	NF	7 Aug 2003	84.6	0.3	1345	30				
	T	20	1.8	B	NF	23 Jul 2003	51.4	0.1	5350	25				
	T	4	2.25	HOT	F	12 May 2003	0.5	0.1	42,800	1400				
	T	4		HOT	F	16 Jun 2003	0.8	0.1	38,670	860				
	T	4		HOT	F	23 Jul 2003	0.9	0.1	37,920	780				
	T	4		HOT	F	6 Sep 2003	1.2	0.1	35,570	590				
	T	4		HOT	F	15 Oct 2003	0.8	0.1	39,120	920				
	T	4		HOT	F	27 Dec 2003			42,900	2200				
	T	4		HOT	F	21 Feb 2004			41,200	1800				
	T	4		HOT	F	27 Apr 2004			39,500	1400				
	T	23	1.75	PS	NF	23 Jul 2003	49.9	0.1	5590	20				
	T	23	1.75	PS	F	29 Jul 2003	24.3	0.1	11,355	40				
	T	5	4.75	PS	F	10 May 2003	6.4	0.1	22,050	120				
	T	8	0.8	PS	F	23 Jul 2003	21.7	0.1	12,285	40				
	T	33	1.5	B	NF	23 Jul 2003	66.3	0.2	3305	20				
Tube Dispenser Lake	T	33		B	NF	29 Jul 2003	74.5	0.3	2360	30				
	T	44	3.1	B	NF	23 Jul 2003	41.1	0.1	7145	30				
	T	11	5	HOT	F	10 May 2003	1.2	0.1	35,260	570				
Grass Lake		16	12	B	NF	17 Jun 2003	36.1	0.2	8185	40				
		16		B	NF	10 Sep 2003	76.0	0.2	2210	20				
Tower Road Yedoma Pond 2		-	0.75	SS	F	28 Jul 2001	105.2	0.3	>modern	20				
Tower Road Yedoma Pond 3		-	0.75	SS	F	28 Jul 2001	109.4	0.2	>modern	20				
Tundra Floodplain Lake		-	0.35	SS	F	20 Jul 2001	63.1	0.2	3695	20	60.9	0.1	3980	20
		-		SS	F	20 Jul 2001	79.0	0.2	1890	25	77.9	0.3	2010	30
						Alaska								
Rosie Creek Beaver Pond		-	1.5	HOT	F	1 Nov 2004	15.9	0.1	14,760	35				
		-	1.5		F	1 Nov 2004	11.2	0.1	17,585	40				
Goldstream Valley Lake		-	1.3	HOT	F	1 Nov 2004	3.9	0.1	26,020	100				

[a]Error symbols represent standard deviation of accelerator mass spectrometer analyses for each sample. The symbol "±" indicates the standard deviation of accelerator mass spectrometer analyses for each sample. NT, nonthermokarst; T, thermokarst; F, fresh (gas was transferred to sample bottles from traps within ~2 hours of collection in traps); NF, not fresh (gas sat in traps underwater up to several days prior to collection into sample bottles); HOT, hot spot.

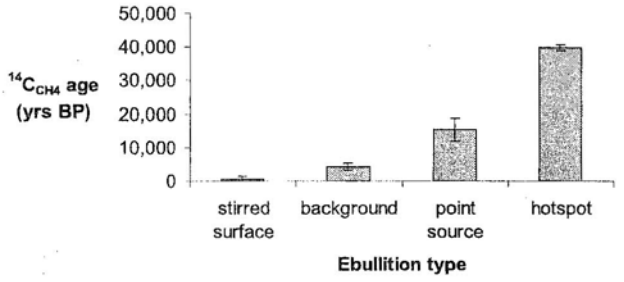

Figure 4. The radiocarbon age (years) of CH_4 in gas samples collected from stirred sediments (n = 6), background bubble traps (n = 7), and specific point sources (n = 3) and hot spots (n = 8) of bubbling in Siberian lakes. The radiocarbon age of methane appeared to increase in positive relation to bubbling rate: low ebullition background bubbling had younger radiocarbon ages of methane than the higher ebullition point sources and hot spots. Error bars show standard error of radiocarbon age data for each ebullition type.

Lake and from Grass Lake are explained by the presence of photosynthetic benthic algae and moss which produce O_2 rich bubblles that mix with tbe CH_4-rich bubbles upon their ascent and during entrapment in submerged bubble traps, Like N_2, higher O_2 concentrations in ice koshkas (4.4-12.8%,) relative to fresh point source bubbling (3.9± 1.4%) suggests O_2 diffusion into bubbles that sit under ice exposed to the O_2-rich lake water prior to entrapment in winter lake ice. Given that N_2 concentrations increased by 160%, in ice koshkas relative to fresh point sources, while O_2 concentrations increased by only 13%, suggests that an O_2- consuming process, such as methane oxidation, also occurs prior to ice entrapment or within the ice.

4.2. Stable Isotopes in Bubbles

[25] The stable isotope signature of CH4 bubbles can be influenced by multiple factors, including CH_4 oxidation, the isotopic composition of CH_4 precursors, degree of substrate utilization, temperature, and biochemical pathways of methanogcncsis *[Whiticar et al.,* 1986; *Alperin et al., 1992; Sugimoto and Wada,* 1995; *Valentine et al.*, 2004; *Templeton et al.,* 2006; *Kinnaman et al., 2007].*

4.3. Methane Oxidation

[26] Biological CH_4 oxidation results in the enrichment of the remaining $?D_{CH4}$ and $?^{13}C_{CH4}$ with no additional fractionation to the reported $^{14}C_{CH4}$ values because they are corrected by any potential fractionation with the ^{13}C values. In the literature, a positive correlation between $?D_{CH4}$ and C^{13} C_{CH4} with a slope of 5-13.5 suggests the occurrence of aerobic oxidation *[Coleman et al.,* 1981; *Happell et al., 1994; Powelson and Abichou,* 2007], while some evidence suggests that the slope may be somewhat greater in anaerobic oxidation *[Alperin et al.,* 1988]. While we cannot entirely rule out CH_4 oxidation in these study lakes since our sample sizes were small for some types of bubbling, we concluded that biological oxidation did not cause the variation observed in the stable isotope signature of fresh CH_4 bubbles because no correlation was observed between $?D_{CH4}$ and $?^{13}C_{CH4}$ when looking at all bubbles collected freshly from lake sediments (Figure 3 point sources, hot spots and background). Considering a high number of individual samples within a single thermokarst lake, Shuchi Lake, the lack of relationship between O_2 concentration and $?^{13}C_{CH4}$ within the three ebullition types validates the conclusion that CH_4 oxidation is not a primary factor influencing the isotope signature in these samples (Figure 7), However, when comparing the $?D_{CH4}$ and $?^{13}C_{CH4}$ of fresh Siberian point sources with that of ice koshkas, a slope of 2.5 (R^2 = 0.6) (Figure 3b) suggests that some isotopic enrichment due to CH_4 oxidation occurred in CH_4, likely when the point source bubbles sit in the O_2-rich lake water under the ice prior to entrapment in the thickening ice.

4.4. Methane Production Pathways

[27] The CO_2 reduction pathway has a larger apparent C fractionation factor (equation (3), ac = 1.055-1.090) than acetate fermentation ac = 1.040-1.055) *[Whiticar et al.,* 1986]. However, without further information, the ac has limited diagnostic power given that a host of factors such as environmental variability, temperature, substrate concentrations, and available Gibbs free energies lead to variability in ac for each pathway *[Valentine et al.,* 2004, *Conrad,* 2005; *Penning et al.,* 2005]. *Using* the ac as a general guide in Siberian lakes and ponds, the CO_2 reduction pathway appeared to be more prevalent in hot spot (ac = 1.071 ± *0,006, n* = 21) and point source bubbling (ac = 1.073 ± 0.0 11, *n* = 12), whereas the lower ac of background bubbling ac = 1.048 ± 0.005, *n* = 20) suggests the influence of acetate fermentation in the sediments where these bubbles were produced (Figure 5). This conjecture is supported by the results of the mixing model (equations (4) and (5)), which yielded a range oflikely proportions of CO_2

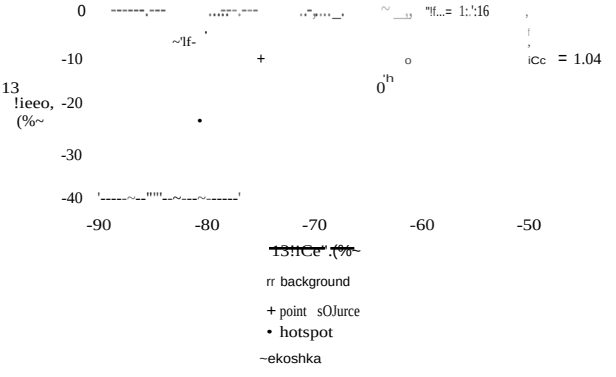

Figure 5. The ($?^{13}C_{C02}$ and $?^{13}C_{CH4}$ of different bubble sources collected from Shuchi Lake and Tube Dispenser Lake in Siberia. Solid lines are constant carbon isotopic fractionation *(ac)* values of 1.04 and 1.06. The ac values of bubbles indicate the pathway of CH_4 production, in which ac > *1.06* suggests CH_4 is produced mainly by CO_2 reduction, and ac < 1,055 suggests CH_4 produced increasingly by acetate fermentation, A shift towards lighter $?^{13}C_{C02}$ values of the ice koshkas (open triangles) relative to point sources may represent alteration from the original point source signatures because of CH_4 oxidation prior to ice enclosure or within the ice.

Table 4. Estimation of CO_2 Reduction and Acetate Fermentation Contributions to CH_4 Production of Different Bubble Sources in Two Siberian Lakes[a]

Lake	Bubble Source	α_C	$\delta^{13}C_{CH4}$	$^{13}CH_{4,CO2}$	Case 1		Case 2	
					CO^2%	Ace%	CO^2%	Ace%
Shuchi Lake	background	1.051 ± 0.005, 9	−66.8 ± 5.6, 10	−85.0 ± 4.6, 9	57	43	69	31
	point source	1.072 ± 0.011, 13	−79.7 ± 3.1, 13	−78.4 ± 6.4, 11	100	0	100	0
	hot spot	1.070 ± 0.003, 18	−79.6 ± 0.5, 35	−81.8 ± 2.4, 24	94	6	96	4
Tube Dispenser Lake	background	1.046 ± 0.005, 11	−62.4 ± 2.6, 14	−86.3 ± 3.0, 11	45	55	60	40
	hot spot	1.073 ± 0.017, 3	−77.1 ± 4.7, 3	−76.9 ± 9.6, 3	100	0	100	0

[a]Carbon α_C values exceeding 1.060 indicate greater CH_4 production by CO_2 reduction, while α_C values less than 1.055 suggest increasing acetate fermentation (Table 3). Cases 1 and 2 assume $\delta^{13}C$ of acetate derived from labile and recalcitrant sediment organic matter, respectively. Mean values are reported with standard deviation and n number of samples.

reduction and acetate fermentation pathways with different sediment organic matter reactivity (Table 4). The results of this analysis suggested the dominance of the CO_2 reduction pathway for point source and hot spot bubbling, while acetate fermentation contributed to background ebullition (Figure 6).

[28] A host of factors can influence methanogenic pathways including substrate quality, pH, temperature, diversity of archea, H_2 partial pressure, and iron (Fe) content in northern aquatic sediments *[Nozhevnikova et al.,*]994, *Valentine et al.,* 2004, *Conrad,* 2005; *Penning et al., 2005; Blodau et al.,* 2008). High availability of labile organic substrates in lake and wetland sediments, particularly in sediments containing live plants, can support acetate production *[Duddleston et al.,* 2002], leading to methanogenesis by acetate fermentation; whereas environments with less labile organic substrates, or the absence of particular compounds exuded by living plants, can be dominated by the CO_2 reduction pathway *[Nakagawa et al., 2002].* Temperature decreases with depth in the North Siberian thermokarst lakes, and the CO_2 reduction pathway is favored at low temperatures *[Nozhevnlkova et al., 1994).* While low pH may lead to the build up of acetate in some acidic bogs with a dominance of CO_2 reduction pathway, relatively high pH in Siberian lake sediments ranging from 7.1 to 9.1 (K. Walter, unpublished data, 2002-2004) suggests this is not the case in these lakes. Oligotrophic conditions in wetlands have also been shown to favor the CO_2 reduction pathway, but this seems unlikely in the thawed yedoma horizons of Siberian lakes, where soil nitrogen and phosphorus concentrations are high *[Dutta et al., 2006).*

4.5. Radiocarbon Ages of CH_4 Ebullition

[29] Despite the wide range in ^{14}Cage dates of CH_4 from Siberia and Alaska (Table 3), the large number of samples depleted in ^{14}C indicate the influence of substrates derived from ancient organic matter in supporting methanogenesis and ebullition. These results differ from other lakes and wetlands with modem $^{14}C_{CH4}$ ages indicating the production of CH_4 from recently produced organic matter *[Wahlen et al.,* 1989; *Chanton et al.,* 1995; *Chasar et al.,* 2000b; *Nakagawa et al.,* 2002]. Only *Zimov et al.* [1997] have reported ^{14}C ages of CH_4 as old as 27,000 years, and these were measured from two of the same lakes used in this study. Rather than reflecting the absolute age of any particular substrate, radiocarbon ages of CH_4 in this study may ref1ect a mixture of CH_4 produced from substrates of different ages, from both modern lake sediments and thawed permafrost C which fixed over the span of up to tens of thousands of years. Given that CO_2 reduction is a key pathway for CH_4 production in thermokarst lakes, the ^{14}C-depleted pool of dissolved inorganic carbon (DIC) contributes directly to ^{14}C-depleted values of CH_4 in bubbles (equation (2)). The ^{14}C age of CH_4 was related positively to the magnitude of CH_4 ebullition according to different ebullition categories (Figure 4). High-emission point sources and hot spots of CH_4 bubbling were older (11,355 to 42,900 years), while the younger ages of low-emission background bubbling (1345 to 8845 years) and stirred bubbles from surface sediments (>modern to 3695 years) indicated that a larger proportion of more modern substrates fueled methanogenesis. Similar ancient radiocarbon ages of CH_4 bubbles (14,760 to 26,020 years) (Table 3) from thermokarst lakes in interior Alaska suggest that this pattern is not unique to Siberia and may occur across northern high latitudes.

4.6. Organic Substrates for Methanogenesis in Thermokarst Lakes

[30] Nakagawa et al. [2002] suggested that the oldest $^{14}CH_4$ ages that they measured (up to 93.1 pmC, or 500 years B.P.), which came from deeper lakes, indicated the contribution of older CH_4 that was produced from

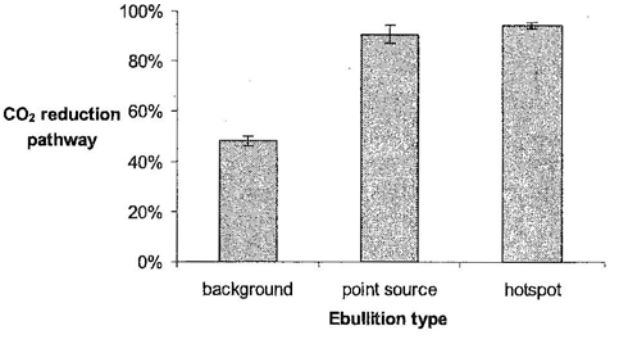

Figure 6. The proportion of CO_2 reduction pathway contributing to background (n = 19), point source (n = 12), and hot spot (n = 18) ebullition in Siberian lakes. The CO_2 reduction pathway contributed more to methane production for the high ebullition point sources and hot spots as compared to the lower ebullition background bubbling areas. Error bars show standard error of the percent CO_2 reduction pathway contribution towards bubble gas for each ebullition type.

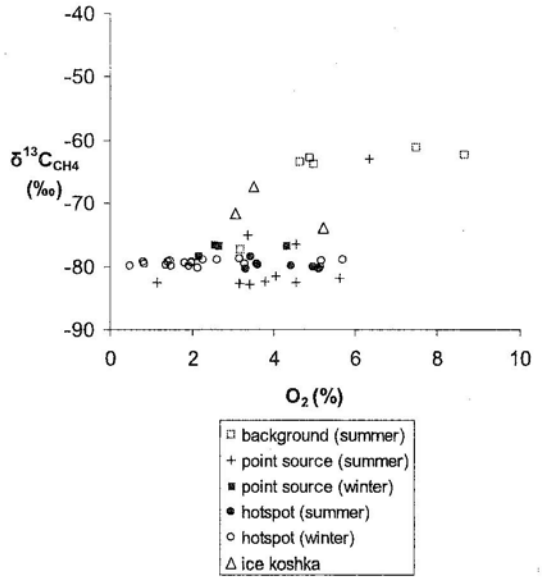

Figure 7. Oxygen concentration versus $\delta^{13}C_{CH4}$ for individual samples from Shuchi Lake. Relatively tight constraint of $\delta^{13}C_{CH4}$ despite wide variability in percent O_2 suggests that CH_4 oxidation was not a dominant process controlling $\delta^{13}C_{CH4}$ signatures of lake bubbles. Likely the two groupings of $\delta^{13}C_{CH4}$ values (~−80‰ for point sources and hot spots versus ~−60‰ for background bubbling) reflect differences in methane source pathways with CO_2 reduction dominating methanogenesis for point sources and hot spots, while acetate fermentation contributes to background bubbling. Variation in O_2 concentration is best explained by seasonal differences in photosynthesis and heterotrophic respiration in lake water. During summer, bubbles collecting in traps over the period of several hours to days absorb O_2 from lake water, particularly when photosynthesizing periphyton cover the traps.

recalcitrant material. In this study the exceedingly high rates of hot spot ebullition (up to >30 L CH_4 $spot^{-1}$ d^{-1} *[Walter et al.,* 2006]) with exceptionally old radiocarbon ages ($^{14}CH4$ 0.5 to 1.2 Pille, or 39,000 to 43,000 years B.P.) suggests that a considerable amount of CH_4 is produced at depth in Siberian thermokarst lakes, and that the organic matter source in Pleistocene loess is relatively labile. Laboratory incubations of Pleistocene organic matter extracted from undisturbed yedoma permafrost confirmed thc high quality of organic substrates contained in the deep lake horizons of North Siberia *[Zimov et al.,* 1997; *Walter et al.,* 2007a].

[31] Radiocarbon-depleted peat accumulates over long time periods in anaerobic lake and wetland environments because of slow decomposition of poor quality organic matter, particularly under cold conditions *[Smith et al.,* 2005]. Because of the recalcitrant nature of peat, CH_4 emitted from peatlands is dominated by the decomposition of fresh, labile terrestrial substrates such as root exudates that were fixed during recent photosynthesis *[King et al., 2002; Chasar et al.,* 2000b; *Chanton et al.,* 1995]. In shallow thermokarst features such as collapse scar bogs, the predominant role of thermokarst erosion may be to create anaerobic environments that facilitate productivity of fen vegetation and associated CH_4 production via the fermentation pathway *[Prater et al.,* 2007]. Deep, open-water thermokarst lakes represent a different situation because the labile properties of ^{14}C-depleted Pleistocene organic matter can, under the right circumstances, be preserved for centuries to millennia because organic matter is frozen in permafrost. Upon thaw in deep, anaerobic lake bottoms, this Pleistocene-age organic matter is readily converted to ^{14}C-depleted DIC, leading to production of CH_4 at greater depths and emitted through hot spots. These hot spots appear to represent conduits that funnel or integrate methane production over large volumes at depth (Figure 8). Using the mean CH_4 production potential observed in laboratory incubations of thawed yedoma (145 g CH_4 m^{-3} soil a^{-1} we estimate that at least 2.5 m^3 to 8.5 m^3 of thawed yedoma would be required to sustain observed hot spot ebullition emissions of 2175 ± 1195 mg CH_4 d^{-1}. Relatively younger radiocarbon ages of CH_4 emitted through point sources and particularly from background bubbling indicate that Holocene-age organic matter also contributes in part to methanogenesis (Table 3 and Figure 4).

[32] The relationships between CH_4 emission rate and $^{14}C_{CH4}$ age (Figure 4) and CO_2 reduction pathway (Figure 6) demonstrate that CH_4 production at depth differs from CH_4 production in shallow lake sediments (Figure 8). At depth, despite the lower concentration of organic matter in Pleistocene-aged yedoma as compared to the overlying younger organic-rich lake sediments, the large volume of the thaw bulb beneath lakes contains a large, labile pool of ^{14}C-depleted organic matter deposited in lakes by permafrost thaw. This pool enhances CH_4 produced in microsites primarily through CO_2 reduction, resulting in high emission rates as bubbles from microsites are channeled out of sediments through bubble pathways. In shallower surface sediments, Holocene-aged organic matter, which represents terrestrial and aquatic detritus that accumulated on lake bottoms, may produce CH_4 under a combination of CH_4 production pathways. and may be subject to methane oxidation in surface sediments when O_2 is present. We did not observe evidence for CH_4 oxidation in the few background bubble samples in this study. Similarly to other nonthermokarst lake and wetland environments, fresh organic substrates associated with modern aquatic plant and algae production in thermokarst lakes appears to fuel methanogenesis at least in part in surface sediments *via* the acetate fermentation pathway.

4.7. Variation of ?D-CH_4 in Lake Bubbles

[33] Using the mean precipitation ?^{18}O inputs of -21‰ to the Kolyma River Basin *[Welp et al.,* 2005] with the Local Meteorological Water Line (?D = 7.0 * ?^{18}O - 11.7, $R^2 = 0.99$), we estimated the mean ?D of precipitation in our Siberian study sites to be -158‰. This value is similar to the weighted average of monthly data of ?D in rainwater (-156‰) from 1997 to 1999 in Yakutsk *[Nakagawa et al.,* 2002], to the southeast of our Siberian study region, and to the mean annual <?D of all precipitation for interior Yukon Territory, Canada (-160‰ *[Anderson et al.,* 2005]), which is again similar to the region of our boreal study lakes (B. Finney, personal communication, 2005). The semiarid

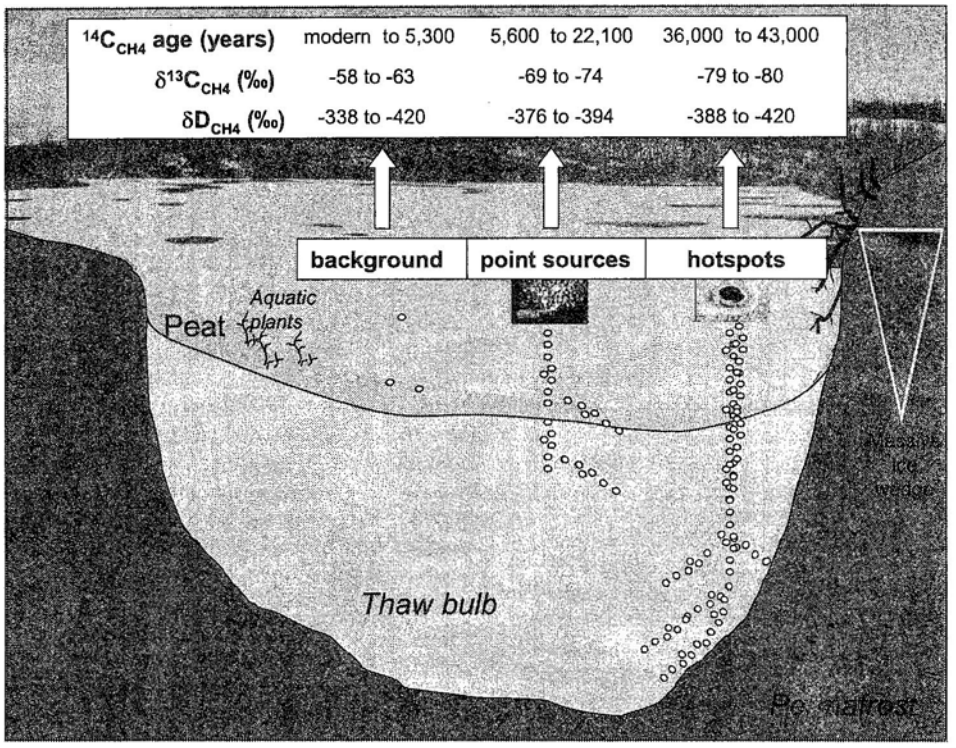

Figure 8. Schematic of CH_4 production and emission in North Siberian thermokarst lakes, summarizing isotopic information for background, point source, and hot spot bubbling and hypothesizing sediment depth at which each bubbling source originates. Thermokarst erosion is depicted on the right-side shoreline. Figure 8 modified from work by *Walter et al.* [2007a].

climates of the interior boreal regions of Alaska and Siberia promote lake water evaporation, resulting in a slight deuterium enrichment of water in some lakes (-154.0 ± 2.6‰ at 1 m, -158.7 ± 2.1‰ at 10 m, Shuchi Lake) (Table 2). The ?D of lake water in other boreal lakes was -128.8 ± 0.7‰ (Smith Lake, interior Alaska *[Chanton et al.,* 2006]), -159 ± 2‰ (interior Yukon Lake Jellybean *[Anderson et al., 2005]),* and -136 to -117‰ (East Siberian alasses *[Nakagawa et al.,2002]).*

[34] Isotopic separations between the ?D of environmental water and CH_4 in high-latitude wetlands was described by *Chanton et al.* [2006] on the basis of the fractionation of deuterium during methanogenesis ($?D_{CH4} = 1.55\ ?_{H2O}$ - 145.4, $r^2 = 0.69$ in Alaskan samples). Assuming a similar evaporative enrichment between $?D_{H2O}$ of precipitation and $?D_{H2O}$ of lake water in interior Alaska to that of Siberia (~2‰), and using the equation of *Chanton et al.* [2006], we would expect $?D_{CH4}$ of -397‰ in Siberian lakes. This expected value was indeed close to the observed mean $?D_{CH4}$ values for background (-380 ± 13‰, $n = 3$), point source (-384 ± 6‰, $n = 10$) and hot spot (-394 ± 4‰, $n = 32$) ebullition. Particularly low $?D_{CH4}$ values in hot spot bubbles from Tube Dispenser Lake, a deep lake undergoing active thermokarst erosion, were on the order of -416 ± 4‰, $n = 2$, suggesting possibly that hot spot CH_4 emitted from these thermokarst lakes was produced in an environment with a different water source than modem lake water.

[35] Thennokarst lakes expand by thawing permafrost along their margins. In the yedoma region of North Siberia, Pleistocene-age, massive ice wedges are up to 80-m deep and occupy 50-90% of the permafrost by volume *[Zimov et al.,* 1997, 2006]. Here the isotopic signature of water released from thawing ice wedges should contribute to the signature of environmental water where CH_4 is produced. Cross sections of yedoma ice wedges measured near our boreal lake study sites in Siberia had hydrogen isotopes ranging from 50 -260 to -235‰ *[Vasilchuk et al.,* 2001]. The highly depleted $?D_{H2O}$ reflects precipitation under cold Pleistocene climate conditions. Another possible explanation for the variation in the observed $?D_{CH4}$ values is variation in in situ H_2 concentrations *[Burke, 1993].*

4.8. Using Ebullition Patchiness to Estimate Whole-Lake and Regional Isofluxes for Methane

[36] We determined an isotope signature of annual CH_4 emissions (isoflux) from two Siberian lakes by weighting the seasonal isotope signature of each component of the flux by the relative contribution of each component to whole-lake annual emissions (Table 5). We used 95% of whole-lake emissions in our calculations because the isotope signature of CH_4 emitted by molecular diffusion, which accounted for 5 ± 1% of the annual flux *[Walter et al.,* 2006], was not determined in this study. This new method of weighting different bubble sources improves emission estimates for lakes because it accounts for the patchiness of

Table 5. Ebullition Flux-Weighted Estimates of CH_4 Isotope Emissions From Two Intensively Studied Siberian Lakes[a]

Season 2003–2004	Flux Component	Whole Lake (g CH_4 m^{-2} of Lake a^{-1})	Percent of Annual Flux	Mean				Isoflux[a]			
				δD_{CH4} (‰)	$\delta^{13}C_{CH4}$ (‰)	$\Delta^{14}C_{CH4}$ (‰)	$^{14}C_{CH4}$ Age (Years)	δD_{CH4} (‰)	$\delta^{13}C_{CH4}$ (‰)	$\Delta^{14}C_{CH4}$ (‰)	$^{14}C_{CH4}$ Age (Years)
Summer	background	5.7 ± 2	22 ± 6	−372.0 ± 26.3, 14	−63.4 ± 9.4, 28	−390 ± 186, 7	4,271 ± 2,650, 7	−2120.5	−361.5	−2221.9	24,347
	point source	6.2 ± 0.7	25 ± 5	−382.8 ± 3.8. 9	−74.2 ± 8.8. 15	−683 ± 155. 3	9,743 ± 3,627. 3	−2373.4	−460.0	−4231.9	60,409
	hotspots	1 ± 0.7	4 ± 2	−397.5 ± 3.3, 6	−79.9 ± 0.5. 12	−991 ± 2. 4	37,820 ± 1,580. 4	−397.5	−79.9	−990.9	37,820
	molecular diffusion	1.3 ± 0.1	5 ± 1								
Winter	background[b]	0.5 ± 0	2 ± 0	−333.6	−58.2	−390 ± 186, 7	4,271 ± 2,650, 7	−166.8	−29.1	−194.9	2,136
	point source[c]	8.3 ± 0.9	34 ± 7	−346.1 ± 13.2. 4	−69.3 ± 4.3, 4	−936	22,050. 1	−2872.3	−574.8	−7770.5	183,015
	hotspots	2 ± 1.3	8 ± 5	−394.5 ± 7.1. 28	−79.2 ± 1.6, 26	−993 ± 3, 5	40,332 ± 3,157. 5	−789.0	−158.4	−1986.0	80,664
Whole lake total		25	100	−367.7	−70.3	−738.5	16,524	−8.720	−1.664	−17.396	388,391
Regional total								−0.096	−0.183	−1.914	4.3×10^{16}

[a]Methane fluxes reflect the mean and standard deviation of year-long continuous measurements of ebullition and diffusion at two Siberian lakes [*Walter et al.*, 2006]. Mean isotope values are reported with standard deviation and *n* number of samples. The regional total (Gt CH_4 ‰ $region^{-1}$ a^{-1}) was determined by multiplying the lake total isoflux by 11% lake cover of 10^6 km^2 for yedoma territory. The isoflux is calculated as the sum of each isotope signature (‰) multiplied by the CH_4 flux (g CH_4 m^{-2} of lake a^{-1}).

[b]Isotopes of background bubble samples were not measured for winter. Summer values were used in the calculations. We assume the error is insignificant given that background bubbling accounts for only 2% of annual emissions. Enrichment factors of 10% were applied to background bubbles trapped in lake ice on the basis of the isotopic enrichment observed between fresh point sources and ice koshkas.

[c]We used stable isotope values measured from ice koshka gas collected in spring to incorporate any oxidation or diffusion effects on emission signals from point sources that are trapped during long periods of time in ice. Radiocarbon age and calculated CH_4 production pathways for point sources of all seasons reflect isotope signatures of bubbles collected freshly in traps.

ebullition flux, a parameter of natural lake and wetland emissions that is typically not addressed. If we had neglected the diversity in ebullition dynamics, excluding the point source and hot spot emissions, our isotope results for North Siberian lakes would have been biased towards isotope signatures reflecting background bubbling and stirring of surface sediments, which are the only components that most studies consider.

[37] Similarly, taking into account the distribution of point source and hot spot bubbling yielded a more accurate estimate of whole lake CH_4 isotope fluxes (Table 5). The point source-weighted distribution of CH_4 isotopes resulted in average whole-lake emission isotope signatures of $?D_{CH4}$ - 368‰, $?^{13}C_{CH4}$ -70.3‰, and $^{14}C_{CH4}$ age 16,524 years (Table 5). The $?^{13}C_{CH4}$ was lighter in the whole-lake flux-weighted estimate than values derived by stirring surface sediments (-62.0‰) or trapping background bubbling (-63.4‰). The radiocarbon age of CH_4 emissions was the parameter influenced most by the different measurement techniques. The more ancient flux-weighted estimate of 16,524 years reflects the importance of Pleistocene-aged organic matter released from permafrost upon thaw of in deeper lake sediments *[Zimov et al.,* 1997], while the much younger age of CH_4 in bubbles stirred from surface sediments (175 years for one sample from intensive study lakes, 998 ± 1659 years, $n = 6$ for all Siberian lakes) and background bubbling (4271 ± 2650 years, n = 7) indicates contributions of younger organic matter sources in methanogenesis closer to the sediment surface. Radiocarbon age dating of lake sediment cores for 17 lakes in North Siberia supports this interpretation with modern ages of organic matter at the surface and Pleistocene-age (up to 48,500 to 55,900 ± 6170 years (^{14}C-dead)) organic matter in deeper sublake strata where yedoma thawed (data not shown).

[38] The ability to improve lake CH_4 emission estimates by accounting for the patchiness of different bubble sources that have distinct isotopic compositions enables researchers to estimate more accurately whole lake and regional isofluxes. Assigning CH_4 isotope values to measured emissions yields isofluxes that can be used by inverse modelers to better constrain sources and sinks of atmospheric CH_4. In this study, extrapolating the whole-lake isoflux that includes point source and hot spot emissions from Siberian thermokarst lakes to the areal extent of yedoma territory (10^6 km^2), yielded isofluxes of $?D_{CH4}$ - 0.096 Gt ‰ a^{-1}, $?^{13}C_{CH4}$ -0.0183 Gt ‰ a^{-1}, and $^{14}C_{CH4}$ age 4.3 x 10^{16} years (Table 4) for a large region of Siberia that has been underrepresented in global estimates of CH_4 emissions from wetlands and from which lake ebullition emissions have been altogether excluded *[Matthews and Fung,* 1987; *Aselmann and Crutzen,* 1989; *Botch et al., 1995].*

[39] Results from two inverse modeling studies using CH_4 isotopes suggested that, compared with bottom-up estimates of current atmospheric CH_4 sources, the inverse estimates required larger tropical CH_4 fluxes from both bacterial and biomass burning sources with a simultaneous reduction of northern sources *[Mikaloff Fletcher et al.,* 2004a, 2004b]. The source-process inversion *[Mikaloff Fletcher et al.,* 2004a] attributed the decrease in northern hemisphere sources to a reduction in fossil fuel and landfill emissions; while the regional inversion approach *[Mikaloff Fletcher et al.,* 2004b] assigned the largest CH_4 source

decrease to boreal Eurasian wetlands (comparing bottom-up estimates of fluxes versus prediction of the inverse model). Output from the inversion scenarios predicted emissions of 9-24 Tg CH_4 a^{-1} from boreal Eurasia as a sum of all sources, which were grouped into three categories: bacterial CH_4, biomass burning, and fossil fuels. Our results from Siberia are not consistent with the findings of *Mikaloff Fletcher et al.* [2004b] because instead of a reduction of northern CH_4 sources, which is required by the inversions, we observed increased CH_4 emissions from Siberian thermokarst lakes *[Walter et al.,* 2006] and isofluxes from Siberian lakes that are more ^{13}C-depleted than values assumed by *Mikaloff Fletcher et al.* [2004b]. Inverse modeling must reconcile this additional source of high-latitude atmospheric CH_4 (lake bubbles), in particular from northern Eurasian yedoma lakes, which has now been characterized and whose $?^{13}C_{CH4}$ is depleted (-70.3‰) relative to the typical value used for northern wetland emissions (-58‰) and the annual mean value of atmospheric CH_4 (-47.3‰). A recent first-order estimate of pan-arctic lake emissions suggests that arctic lakes contribute 24 ± 10 Tg CH_4 a^{-1} by the mode of point source and hot spot bubbling *[Walter et al.,* 2007b]. If significantly?^{13}C-depleted CH_4 is characteristic of point source and hot spot bubbling from the wider range of arctic and subarctic lakes, which seems to be the case on the basis of the $?^{13}C_{CH4}$ of Alaskan lakes in Table 2, then this ~6% contribution towards the global atmospheric annual CH_4 budget from lake ebullition, a previously unaccounted for source, should play a role in inverse modeling.

[40] Our documentation of a large, ^{14}C-depleted CH_4 source from lake ebullition must also be considered in models, which until now have attributed high-latitude ^{14}C-free CH_4 and recent changes to high-latitude CH_4 concentrations to leaky gas pipelines, coal mining and natural seepage from gas reservoirs in Siberia *[Wahlen et al., 1989; Dlugokencky et al.,* 2003], not to aquatic sediments. Estimates of ^{14}C-CH_4 derived from fossil fuel energy range from 95 to 110 Tg CH_4 a^{-1} *[IPCC,* 2001; *Mikaloff Fletcher et al.,* 2004b]. Annual emissions from Siberian lakes, 3.8 Tg CH_4 a^{-1} with an average radiocarbon content of ~12 pMC *[Walter et al.,* 2006], are less than 3.5% of fossil fuel CH_4 sources. However, radiocarbon ages up to 26,000 years (3.9 pMC) from Alaskan thermokarst lakes suggest that ^{14}C-depleted CH_4 ebullition is not unique to Siberia, and should be more thoroughly quantified for lakes and reservoirs globally. Given the large pool of organic matter locked up in boreal and arctic permafrost (~950 Gt C *[Zimov et al.,* 2006]), continued warming of permafrost in the future *[Sazonova et al.,* 2004; *Lawrence and Slater,* 2005] could lead to accelerated release of ^{14}C-depleted CH_4 from expanding thermokarst lakes.

5. Conclusions

[41] On the basis of the concentrations and isotopic compositions of gases in bubbles from North Siberian lakes we have distinguished two major types of bubbles that represent two zones of CH_4 production in lakes (Figure 8):

[42] 1. Bubbles stirred from surface sediments in lakes or captured in randomly placed traps that represent background bubbling, had young radiocarbon ages, lower concentrations of CH_4, higher concentrations of N_2, and were formed by nearly equal contributions of CO_2 reduction and acetate fermentation. Their relatively young radiocarbon ages suggest that Holocene-age organic matter sources, at least in part, fueled methanogenesis.

[43] 2. We characterized a second bubble source, with ^{14}C-depleted CH_4, high CH_4 concentrations, lower concentrations of N_2, and extremely high CH_4 emission rates.

[44] We hypothesize that the extremely high emission rates may be explained by bubble focusing. As CH_4 production exceeds its solubility limits, CH_4 bubbles come out of solution forcing their way through lake sediments to lower pressure states. Small bubble streams merge into larger byways, like the tributaries of rivers joining into the main flow channel. The deeper the site of CH_4 production, the stronger the stream of bubbles that coalesces from a large volume of sediments into a point source or hot spot of emission that exits through a small hole (< cm diameter) at the sediment water interface. It is possible that point sources evolve into hot spots as thaw bulbs deepen during thermokarst lake development; however long-term observation of individual point sources and hot spots would be required to test this hypothesis. Presumably the radiocarbon ages would get older with time. Continuous flux measurements and lake bottom benchmarkers showed that hot spot vents in the Siberian thermokarst lakes remained in the same location for at least 4 years (K. M. Walter et al., personal observation, 2006). In contrast, background bubbling represents nonchanneled or weakly channeled bubbling. Methane bubbles released as background flux likely form in small microsites closer to the sediment-water interface, and can more easily escape the sediments as individual bubbles.

[45] The alternative hypothesis to the tributary hypothesis is that point sources and hot spots are from the decay of particulate organic matter (e.g., tree trunk, dead mammoth), which is testable by coring or excavating the hot spot. Nondestructive geophysical methods that have been used in peatlands *[Comas et al.,* 2005] such as ground penetrating radar and electrical resistivity could also be used to examine the sediment structure and gas contents of lake sediments and thaw bulbs.

[46] The particular characteristics of hot spot bubbling are not unique to North Siberian yedoma lakes. Given that we found hot spots with CH_4 of high concentration and ^{14}C depletion in Alaskan thermokarst lakes as well, we propose that these two distinct zones of CH_4 bubble production (deep point sources versus shallow background) occur across geographical regions in all lakes in which thermokarst erosion delivers a large, labile source of organic substrate to deep anaerobic lake sediments.

[47] In this study we characterized the distinct $?^{13}C_{CH4}$ and ^{14}C-depeted CH_4 signatures of arctic lake ebullition, combining them with improved bottom-up flux estimates *[Walter et al.,* 2006; K. M. Walter etl., submitted manuscript, 2008], to reveal a large new source of high-latitude atmospheric CH_4. Qualitative assessment of this new isotope CH_4 source contradicts patterns presented by recent inverse modeling, which predicted a reduction in boreal wetland sources relative to other latitudes in contrast to bottom-up source estimates. Instead of providing a Eurasian source reduction scenario, we suggest an increase in boreal wetland sources with ^{14}C signatures that overlap with

estimates of fossil fuel emissions. Since thermokarst erosion is a driving factor of CH_4 emissions in arctic lakes, and thermokarst lake area appears to be increasing in zones of continuous permafrost since 1970 *[Smith et al., 2005; Walter et al.*, 2006]. understanding the isotopic implications of further thermokarst lake expansion as permafrost in arctic regions continues to warm and thaw will help atmospheric modelers define CH_4 sources and predict changes.

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