Methane production, consumption, and air-sea exchange in the open ocean: An evaluation based on carbon isotopic ratios

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Abstract. The concentration of methane and its isotopic composition did not appear to vary significantly in the subtropical North Pacific during 1996-1997. Methane enters the atmosphere via the upper mixed layer at a rate of 1.6 μmol m⁻² d⁻¹ (± 0.1) with a δ¹³C value of approximately -42% (±1.5), with no apparent seasonal variation. In comparison, the sea-air flux of methane in the Sargasso Sea was between 1.6 and 4.4 μmol m⁻² d⁻¹ with an isotopic composition between -43 and -45%. Excess methane in surface waters appears to be generated throughout the upper 300 m of the water column by bacterial methanogenesis. The methane concentration maxima occur at the pycnocline, suggesting that the maxima are supported by methanogenesis in suspended particles that accumulate at these depths. Particle incubation experiments show that methane production may occur in these microenvironments. The lack of a diurnal signal implies that methane production and consumption in the ocean is independent of day-night cycles such as photosynthesis, grazing and vertical migration of zooplankton. The flux to the atmosphere appears to be the main sink for methane in the upper ocean; microbial oxidation and downward eddy diffusion account for only 3 and 6%, respectively, of the total methane loss from the upper 300 m. Below that depth, concentrations decrease and isotopic ratios vary with depth due to bacterial oxidation and mixing of water masses of different ages and different histories of methane input.

1. Introduction

Concern about rising levels of greenhouse gases, such as methane, in the atmosphere has prompted reevaluation of the sources of these gases. The oligotrophic gyres of the North Pacific and the North Atlantic comprise vast areas which, by virtue of their size, may play an important role as sources of reduced gases to the atmosphere [e.g., Dore et al., 1998]. Supersaturation of methane in surface water is a persistent feature of most ocean waters [Lamontagne et al., 1973; Cicerone and Oremland, 1988]. The global oceanic source of methane to the atmosphere has been estimated at 5-50 Tg yr⁻¹, which is 3-30% of all natural sources of methane [Prather, 1995]. The large uncertainty in the estimates of the magnitude of the marine source of this gas, which is 3.7 times more effective per mole at trapping radiated heat than CO₂ [Lashof and Ahuja, 1990], emphasizes the need for better understanding of the temporal and spatial variations in the marine methane cycle.

However, the source of the methane excess in surface water remains poorly understood. River runoff and outgassing from sediments provide methane to the coastal and nearshore ocean [Lamontagne et al., 1973; Sackett and Brooks, 1975; Sansone and Martens, 1981; Bugna et al., 1996; Sansone et al., 1999], but these sources cannot account for the presence of above atmospheric-equilibrium levels of methane observed in the open ocean far from land. Tracking of hydrothermal methane released from sources at the seafloor show that this methane is consumed near the source areas and does not generally reach the sea surface [e.g., Faber et al., 1994; Motl et al., 1995]. In order to advance our understanding of the upper ocean methane cycle, this paper provides estimates of the amount and isotopic composition of methane entering the atmosphere from oligotrophic ocean regions.

2. Methods

Methane concentrations and isotopic ratios were measured in water column samples from Station ALOHA (A Long-term Oligotrophic Habitat Assessment) [Karl and Lukas, 1996], 100 km north of Oahu, Hawaii, in the North Pacific subtropical gyre (Figure 1a) and from the Sargasso Sea and Gulf Stream (Figure 1b). Water samples for methane analyses were collected at Station ALOHA during Hawaii Ocean Time-series (HOT) cruises in October 1996 (HOT 76) and January (HOT 76), April (HOT 82) and July (HOT 85) 1997. Sargasso Sea and Gulf Stream samples were collected in April 1997 on the Duke University/University of North Carolina Oceanographic Consortium cruise CH0497. Subsamples were transferred from 12-L Niskin bottles to 230-mL serum bottles and preserved with 1 mL of supersaturated HgCl₂ solution, as described by Popp et al. [1995]. Atmospheric methane concentrations and isotopic compositions were also measured at Station ALOHA in April and July, 1997. Atmospheric samples from 5 m above the sea surface at the bow of the ship, with the bow headed into the wind, were collected in 250-mL glass
bulbs through which several volumes of air were pumped before the stopcocks were closed.

A free-floating MULTITRAP array [Knauer et al., 1979], consisting of individual collectors (.0039 m²) affixed to a PVC cross, was deployed at Station ALOHA to collect sinking particles at 250 m water depth for 3 days. The three traps in the array were filled with 0.22-µm filtered seawater which was slightly more saline than ambient seawater and fitted with baffles at the tops of the traps to minimize trap flushing during recovery. The traps were retrieved after 3 days, and the water in the traps was partially siphoned off, leaving approximately 500 mL in each trap. The traps were gently mixed, and the particles were allowed to settle for a few seconds. The remaining water was siphoned into 230-mL glass serum bottles (leaving no headspace); 1 mL of supersaturated HgCl₂ solution was added, and the bottles were sealed with rubber septa and aluminum crimp-seals. These bottles represented the time-zero methane concentrations. The remaining water with particles was transferred to 230-mL serum bottles in the same way. Two samples were sealed with no addition of HgCl₂ and one was sealed with 1 mL of HgCl₂ to function as a killed control. All samples were stored in the dark for 15 days.

Samples were analyzed by isotope-ratio-monitoring gas-chromatography/ mass-spectrometry (irm gc/ms) using the methods described by Popp et al. [1995] and Sansone et al. [1997]. Analysis of triplicate water samples gave concentration analytical precisions of ±0.2 nM; isotopic ratio analytical precisions were ± 0.3% for samples > 2.5 nM and ± 0.7% for samples < 2.5 nM. Comparison of duplicate samples measured for CH₄ concentration using the irm gc/ms method and conventional gas-stripping gas chromatography using a Varian 3300 gas chromatograph equipped with a Porapak Q packed analytical column and flame ionization detector showed that both methods yielded the same concentrations (± < 0.1 nM, n=5).

Equilibrium methane concentrations (Ceq, the methane concentrations that would be expected if the water was in equilibrium with atmospheric methane) were calculated from the solubility data of Yamamoto et al. [1976]. In situ temperatures and salinities (Station ALOHA; Hawaii Ocean Time-series data set [http://hahana.soest.hawaii.edu/hot/hot_gofs.html] Atlantic Ocean Stations: C. Terry, personal communication, 1997) were used, and an atmospheric methane concentration of 1.7 ppm [Quay et al., 1991; this work] was assumed.

Fluxes of methane from the sea surface to the atmosphere (shown in Table 1) were calculated using the following equation:

\[ F = K_L(C_{meas} - C_{eq}) \]

where \( F \) is flux, \( K_L \) is the gas transfer coefficient, \( C_{meas} \) is the methane concentration in the surface mixed layer, and \( C_{eq} \) is the air-equilibrated gas concentration [Liss and Slater, 1974; Barber et al. 1988]. The gas transfer coefficient, \( K_L \), used in calculating the flux was obtained from

\[ K_L = U^* - 12.1 \text{ cm h}^{-1}, \]

where \( U^* \) is the friction velocity calculated from the wind speed 10 m above the sea surface [Barber et al., 1988] \((K_L = 7.1-16.0 \text{ cm h}^{-1} \text{ at wind speeds of } 5.3 \text{ to } 8.2 \text{ m s}^{-1})\). Average monthly wind speeds were obtained from the National Data Buoy Center (Buoy 51001, located 400 km northwest of Station ALOHA; Buoy 41002, located 100 km west of Stations 5 and 6 in the North Atlantic).

3. Results

The mean atmospheric methane concentration and isotopic composition at Station ALOHA were 1.4 ± 0.01 ppm and -47.35% ± 0.01%, respectively, in April 1997 (n = 2) and 1.7 ppm and -47.37% (n = 1) in July 1997. Methane concentration and isotopic-ratio profiles from the water column reveal that intra-annual variations were generally small at Station ALOHA (Figure 2). Methane exceeded atmospheric equilibrium concentrations in the upper 300 m, with subsurface maxima of 2.9-3.5 nM between 100 and 300 m (37-67% supersaturated relative to atmospheric equilibrium). Tilbrook and Karl [1995] reported similar concentrations at a site to the north of Station ALOHA (~2-3 nM in the upper 400 m). The
Figure 2. Methane concentrations (filled squares) and isotopic composition (open squares) at station ALOHA in October 1996, January 1997, April 1997, and July 1997. More than one symbol at a given water depth indicates duplicate or triplicate samples. The October and January profiles include samples from both day (1400 UT) and night (0100 UT) casts. The dashed lines indicate the concentrations expected at equilibrium with the atmosphere (1.7 ppm), the dotted lines denote the isotopic composition of atmospheric methane (-47.4‰), and the solid lines represent seawater density (sigma-T).
Figure 3. Methane concentrations (filled squares) and isotopic composition (open squares) at the Gulf Stream and in the Sargasso Sea. More than one symbol at a given water depth indicates duplicate or triplicate samples. The dashed lines indicate the concentrations expected at equilibrium with the atmosphere (1.7 ppm), the dotted lines denote the isotopic composition of atmospheric methane (-47.4%), and the solid lines represent seawater density (sigma-t).

$\delta^{13}C$ values were constant throughout 1996-1997 and ranged from -44 to -47% in the upper 300 m. Between 300 and 600 m, methane concentrations decreased rapidly to 0.9-1.6 nM and then more slowly to between 0.7 and 1.1 nM at 1000 m, or between 24 and 35% of atmospheric equilibrium values. Isotopic ratios increased below 300 m, with maxima at 600 m, decreasing again below that depth. During July 1997, the only data set that extends deeper than 1000 m, methane continued its slow decline in concentration and isotopic ratio to 3800 m (0.6 nM, -41.10%).

The Sargasso Sea and Gulf Stream profiles were similar to those from Station ALOHA (Figure 3). Methane was supersaturated with respect to atmospheric concentrations by 25-90% in the upper 250 m (with a maximum concentration of 3.6 nM) and was isotopically heavier than atmospheric methane (-44.9 to -47%). Below 250 m, concentrations decreased in the Sargasso Sea to a minimum at 1000 m of 1.4 nM (50% of the atmospheric equilibrium concentration) then increased at 2000 m to 2.2 nM. At the Gulf Stream, the concentration minimum (1.4 nM) occurred at a shallower depth of 500 m. Isotopic compositions mirrored concentrations, with a maximum of -31.9% at 1000 m in the Sargasso Sea and of -32.0% at 800 m at the Gulf Stream (the deepest sample). The $\delta^{13}C$ decreased below 1000 m in the Sargasso Sea to -41.9% at 2000 m. The concentrations measured in this work are slightly higher than the values of 0.5-2.7 nM reported by Jones [1991] for the Sargasso Sea.

To compare nighttime and daytime methane concentrations and isotopic values, water samples were taken at 0100 and 1400 UT during the October and January Station ALOHA cruises (Figure 4). The data shown in Figure 4 is the same as in Figure 2 (HOT 76 and HOT 79), except the data shown in Figure 2 represent the average values of the night and day samples.

In the incubation experiments of water from Station ALOHA, methane concentrations in the bottles with particles increased over the 15-day incubation period by 0.23 and 0.24 nM (Figure 5). This increase is slightly greater than the error associated with these analyses. However, the $\delta^{13}C$ values of the samples increased by 1.1 and 1.8%, a much larger change than the analytical margin of error (± 0.3%). The control showed no significant change in either concentration or isotopic composition.

4. Discussion

4.1. Ocean-Atmosphere Methane Exchange

The overall methane surplus in the upper water column relative to atmospheric levels indicates that the North Pacific and Sargasso Sea/Gulf Stream regions supply this gas to the
atmosphere. During the 1996-1997 samplings at Station ALOHA, we calculate that between 1.4 and 1.7 μmol CH₄ m⁻² d⁻¹ was degassed to the atmosphere (Table 1). These estimates for the flux to the atmosphere are similar to those of Tilbrook and Karl [1995], who calculated methane fluxes of 0.9-3.5 μmol m⁻² d⁻¹ at the ADIOS station a few hundred kilometers northwest of Station ALOHA. In the Sargasso Sea and Gulf Stream, the air-sea flux was 4.4 and 1.6 μmol CH₄ m⁻² d⁻¹, respectively. The larger flux in the Sargasso Sea was due mainly to the higher wind speed and surface methane concentration, both of which were likely induced by a storm that occurred prior to and during the cruise. The storm probably deepened the surface mixed layer, bringing methane up from the subsurface maximum.

The eddy diffusive flux of methane from the subsurface maximum into the surface mixed layer was much smaller than the flux from the sea to the air (Table 1). In the North Pacific, the diffusive flux was calculated to be 0.09-0.13 μmol m⁻² d⁻¹, based on an eddy diffusion coefficient of 1.7 cm² s⁻¹ [Li et al., 1984] and concentration gradients of 0.006-0.009 μmol m⁻³.

Figure 4. Daytime (circle) and nighttime (crosses) methane concentrations and isotopic composition at Station ALOHA during October 1996 and January 1997.
In the North Atlantic, the calculated eddy diffusive flux was 0.26 μmol m⁻² d⁻¹ in the Sargasso Sea and 0.19 μmol m⁻² d⁻¹ in the Gulf Stream. These fluxes account for only 7-8% of the flux to the atmosphere from surface waters we calculated for the North Pacific and 6-12% of the flux for the North Atlantic, similar to the 5% estimates for the western subtropical North Atlantic [Scranton and Brewer, 1977] and 8% for the ADIOS site [Tilbrook and Karl, 1995]. However, the oceanic depletion cannot be due to isotopic fractionation associated with oceanic methane equilibration with the atmosphere. This is because dissolved methane concentrations in the upper 300 m in 1996 and 1997 at Station ALOHA were on average 40% above equilibrium concentrations; in the North Atlantic the degree of supersaturation was 56%.

Alternatively, microbial consumption of methane in the upper ocean would lead to ¹³C enrichment of the residual methane [Coleman et al., 1981; Whiticar, 1996; Reeburgh et al., 1997] and may explain the heavier than expected isotopic values of methane in surface waters. However, the long turnover time (5 to > 100 years) associated with microbial methane oxidation in the open ocean [Ward et al., 1987; Jones, 1991] indicates that this process is relatively unimportant in the removal of methane from surface waters. Approximately 0.03 μmol CH₄ m⁻² d⁻¹ is consumed by microbes, assuming an average turnover time for methane in the upper ocean of 65 years [Ward et al., 1987; Jones, 1991]. This was estimated by dividing the average methane concentration in the upper 300 m (2.87 nM) by the turnover time and integrating this over 300 m. Thus microbial oxidation and downward eddy diffusion account for only 2 and 6%, respectively, of the total methane loss from the upper 300 m. Instead, flux to the atmosphere appears to be the main sink for methane in the upper ocean (Table 2). A downward flux out of the upper 300 m of 0.10 μmol m⁻² d⁻¹ is estimated based on the individual water column profiles in Table 1.

4.2. Upper Ocean Isotopic Budget

The isotopic composition of methane removed from the upper 300 m by in situ oxidation was calculated using published fractionation factors (αₖ) and the following equation [Hoeft, 1987]

\[ R_{\text{oxid}} = R_{\text{water}} / \alpha_k, \]

where \( R_{\text{oxid}} \) is the \(^{13}\text{C}/^{12}\text{C} \) ratio in the methane oxidized in the upper 300 m and \( R_{\text{water}} \) is the \(^{13}\text{C}/^{12}\text{C} \) ratio in the water column. The values of \(^{13}\text{C}_{\text{oxid}} \) were then calculated [Hoeft, 1987]:

\[ ^{13}\text{C}_{\text{CH}_4\text{oxid}} \% = \{(R_{\text{oxid}}/R_{\text{PD}}) - 1\} \times 10^3, \]

where \( R_{\text{PD}} \) is the isotopic ratio of the PDB standard, is 0.011237 [Craig, 1957]. Averaging the air-sea flux rates in Table 1 yields a mean flux rate of 1.6 μmol m⁻² d⁻¹ for the North Pacific. If this flux is typical for the entire North Pacific oligotrophic gyre, whose area is ~26.3 x 10⁶ km² [Winn et al., 1994], 0.25 Tg y⁻¹ of methane with an isotopic composition of between -42.5 and -43.0‰ is being supplied to the atmosphere from this oceanic region.

The isotopic ratios of methane in the upper ocean at Station ALOHA are less depleted in \(^{13}\text{C} \) than previously published measurements of biologically produced methane (-50 to -110‰) [Whiticar et al., 1986; Krzycki et al., 1987; Alperin et al., 1992]. However, the oceanic depletion cannot be due to isotopic fractionation associated with oceanic methane equilibration with the atmosphere. This is because dissolved methane concentrations in the upper 300 m in 1996 and 1997 at Station ALOHA were on average 40% above equilibrium concentrations; in the North Atlantic the degree of supersaturation was 56%.

The isotopic signatures in the upper ocean indicate that all three sampling sites are sources of isotopically heavy methane to the atmosphere. The ratio of the net gas fluxes of \(^{13}\text{C}_{\text{CH}_4} \) to \(^{12}\text{C}_{\text{CH}_4} \) to the atmosphere from the sea surface was calculated from [Quay et al., 1993]

\[ \text{Flux}^{13}\text{C}_{\text{CH}_4}/^{12}\text{C}_{\text{CH}_4} = G_{\text{flux}} \alpha_k \frac{p_{\text{CH}_4(\text{atm})} R_{\text{em}}}{p_{\text{CH}_4(\text{atm})} / G [p_{\text{CH}_4(\text{atm})}],} \]

where \( R_{\text{em}} \) is the \(^{13}\text{C}/^{12}\text{C} \) ratio in the atmosphere, \( R_{\text{em}} \) is the \(^{13}\text{C}/^{12}\text{C} \) ratio in the mixed layer, \( \alpha_k \) is 0.9992 [Knox, et al., 1992, Happell et al., 1995]. \( \alpha_k \) is 1.00033 [Fuex, 1980], \( p_{\text{CH}_4} \) is the methane partial pressure, and \(^{13}\text{C}_{\text{CH}_4(\text{atm})} \) is -47.0 to -47.4‰ [Quay et al., 1991, this work]. The gas transfer rate values (G) cancel. The value assumed for \( \alpha_k \) is based on n = -2/3 [Knox, et al., 1992]. The isotopic ratio of the net flux is relatively insensitive to the value of \( \alpha_k \) or \( \alpha_{\text{atm}} \).
Table 1. Calculated Methane Sea-to-Air Fluxes in the North Pacific (Station ALOHA) and North Atlantic.

<table>
<thead>
<tr>
<th>Station ALOHA</th>
<th>North Atlantic(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average mixed layer conc., nM</td>
<td>2.9</td>
</tr>
<tr>
<td>Wind speed(^c), m s(^{-1})</td>
<td>5.3</td>
</tr>
<tr>
<td>Sea-air flux, (\mu)mol m(^{-2}) d(^{-1})</td>
<td>1.6</td>
</tr>
<tr>
<td>Upward diffusive flux from subsurface maximum, (\mu)mol m(^{-2}) d(^{-1})</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Positive fluxes are upward.
\(^a\)Samples taken in April 1997.
\(^b\)Surface concentration.
\(^c\)From National Data Buoy Center (buoy 51001 for Station ALOHA and buoy 41002 for North Atlantic Stations) (http://seaboard.ndbc.noaa.gov).

The $\delta^{13}$C value of methane consumed by bacteria is thus calculated to be between -50.3\%o ($\alpha_c = 1.005$) and -73.4\%o ($\alpha_c = 1.03$). The $\alpha_c$ values were taken from Barker and Fritz [1981] and Coleman et al. [1981].

The isotopic composition for the methane leaving the surface layer by eddy diffusion is taken to be the average isotopic composition (-45.6\%) of the methane in the upper 300 m (assuming no fractionation during eddy diffusion in water).

If 1.7 \(\mu\)mol m\(^{-2}\) d\(^{-1}\) methane is exiting the upper 300 m (upward and downward flux + removal by oxidation), the same amount must be produced to compensate for the diffusive and oxidative losses if the system is to maintain the relatively constant concentrations observed during 1996-1997. Similarly, the isotopic composition of methane produced in the upper 300 m should be equal to that exiting the upper 300 m by oxidation and eddy diffusion. The $\delta^{13}$C of methane leaving the upper water column by flux to the atmosphere, eddy diffusion, and oxidation was estimated as follows:

$$
\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-total}} = (\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-flux} L_{\text{flux}}} + (\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-diff} L_{\text{diff}}} + (\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-oxid} L_{\text{oxid}}}) / \text{total loss},
$$

where $L_{\text{flux}}$ is the fraction of the overall methane loss due to sea-air flux, $L_{\text{diff}}$ is the fraction of the overall methane loss due to eddy diffusion, and $L_{\text{oxid}}$ is the fraction of the overall methane loss due to oxidation. Here $\delta^{13}$C$_{\text{CH}_4 \text{ exit-oxid}}$ was set equal to -50.3\% for the upper estimate of $\delta^{13}$C exiting the upper 300 m via oxidation and to -73.4\% for the lower estimate. According to these mass balance calculations, the isotopic composition of newly produced methane at Station ALOHA should be around -43\%. These calculations show that the heavier than expected isotopic signature of methane in the surface layer does not reflect the residual effect of microbial oxidation but suggest instead that some process associated with methanogenesis controls the isotopic ratio. Tilbrook and Karl [1995] found that although methane may be produced photochemically in water exposed to direct sunlight, abiotic methane production was unimportant in water exposed to lower light levels. Therefore we conclude that most of the methane is produced biogenically.

Table 2. Methane Fluxes in the Upper 300 m at Station ALOHA.

<table>
<thead>
<tr>
<th>Flux, (\mu)mol m(^{-2}) d(^{-1})</th>
<th>$\delta^{13}$C-CH(_4), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4) Loss From Upper 300 m</td>
<td></td>
</tr>
<tr>
<td>Upward</td>
<td>1.57 ± 0.1</td>
</tr>
<tr>
<td>Downward</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>Oxidation</td>
<td>0.03 ± 0.003</td>
</tr>
<tr>
<td>Input to Upper 300 m</td>
<td></td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Average concentrations were 3.0 nM for the upper 300 m and 2.57 nM for the mixed layer. Average isotopic compositions were -45.6\% for the upper 300 m and -46.2\% for the mixed layer.

4.3. Methane Production and Oxidation in the Upper Ocean

Although it is evident that methane is produced in the upper ocean, it is not clear by what mechanism methanogenesis occurs. Previous studies have reported a correlation between methane and zooplankton-ATP (adenosine triphosphate), chlorophyll, and/or density [Traganza et al., 1979; Brooks et al., 1981; Conrad and Seiler, 1988]. However, methane concentrations and isotopic compositions at Station ALOHA did not correlate with either ATP or chlorophyll a (Hawaii Ocean Time-series data set). One exception is the April 1997 profile, in which the chlorophyll a maximum at 100 m coincided with a shallow methane concentration maximum and a slight elevation in $\delta^{13}$C at this depth. Instead, methane dynamics appear to be related to density, since concentration maxima occurred at the pycnocline ($\sigma_t = 25.5 - 25.9$) during all four cruises in the North Pacific (Figure 2). In the Sargasso Sea the maximum concentration coincided with $\sigma_t = 25.2$ and at the Gulf Stream with $\sigma_t = 24.3$ (Figure 3). Similarly, methane maxima occur primarily in a range of $\sigma_t$ from 24 to 26 in the Gulf of Mexico [Brooks et al., 1981]. This suggests that the observed methane maxima were supported by methanogenesis in sus-
toward heavier values. Potential microniches for strictly an-
gelis and Lee [1994]. Further, Cynar and Yayanos [1991] and
pleted in methanogenic substrates, as suggested by Marty
ane is produced in microniches in which methanogenic sub-
particles that accumulate at the pycnocline [e.g., Sie-
burch et al., 1987].

It has been suggested that diurnal variations in dissolved
gases in the pycnocline of the ocean might occur in tandem
with other biologically mediated parameters such as bacterial
activity. We compared methane profiles (0-1000 m) from
samples taken at 0100 and 1400 UT during the October and
January ALOHA cruises and found no significant diurnal
differences in either methane concentration or isotopic com-
position (Figure 4). The lack of a diurnal signal implies that
methane production and consumption in the ocean is inde-
pendent of day-night cycles such as photosynthesis, grazing,
and vertical migration of zooplankton.

One explanation for the high $\delta^{13}$C values is that the meth-
an is produced in microniches in which methanogenic sub-
substrates may become limiting, driving the $\delta^{13}$C of the methane
toward heavier values. Potential microniches for strictly an-

bacterial methanogens in an oxygenated water column in the
open ocean include fish guts, fecal pellets, and detrital parti-
cles [Oremland, 1979; Marty, 1993; de Angelis and Lee,
1994; Karl and Tilbrook, 1994], which could become de-
pleted in methanogenic substrates, as suggested by Marty
[1993].

Alternatively, the nature of the methanogenic pathway may
contribute to the higher than expected $\delta^{13}$C values. Carbonate
reduction is believed to be the primary means of methane for-
mation in marine sediments [Whiticar, 1996]. However, high
fractionation factors (e.g., 1.05 - 1.1) are associated with this
pathway, which has been found to result in methane with $\delta^{13}$C
values of -60 to -110‰ [Whiticar et al., 1986]. Laboratory es-
timates of $\alpha$ for fermentation of methylated compounds such
as acetate and methylamines, however, are lower (1.025 -
1.055) [Blair and Carter, 1992; Whiticar, 1996]. If these methanogenic substrates have initial isotopic compositions
that are not too different from that of bulk marine organic
matter (approximately-20‰), this mechanism for methane
formation could yield $\delta^{13}$C-CH$_4$ as heavy as -44‰. Be-
cause sulfate-reducing bacteria outcompete methanogens for
acetate where there is abundant sulfate, it is likely that meth-
an production in the upper ocean occurs via fermentation of
methylamines, as suggested by Sieburth [1987] and de An-
gelis and Lee [1994]. Further, Cymar and Tavanos [1991] and
Sieburth [1993a, b] have isolated methylamine-utilizing
methanogens from the upper ocean. Thus bacterial consortia
in the water column producing methane via different pathways
(e.g., methylophytes) than those in sediments could lead to the
relatively heavy methane isotopic signature measured in the
upper ocean.

Preliminary experiments to determine methane production
potential in particulate matter, and its isotopic composition,
were carried out in July 1997 (Figure 5). The $\delta^{13}$C enrichment
of 1.1 and 1.8‰ observed in the methane after incubation
supports the production by mass balance calculations that the
$\delta^{13}$C values of methane produced in the upper water column
are higher than expected for biogenic methane not because of
oxidation but because of substrate limitation and/or the methanogenic pathway used. Although sample size was
small, the results suggest that methane may be produced in
sinking particles and encourage future research into particle-
associated methanogenesis. Karl and Tilbrook [1994], how-
ever, found that methane was not produced in particles col-
lected in sediment traps and concluded that methane forma-
tion was associated with the sinking particles and perhaps
originated in larger particles which could break up during set-
ting through the water column and in the traps. Their traps
had 335-μm screens near the tops of the traps which prevented
large particles from entering the traps. Screens were not used
in our traps, and the particles which we collected were per-
haps large enough for the maintenance of the anaerobic con-
ditions believed necessary for methanogenesis.

4.4. Intermediate and Deep Water
The progressive enrichment of methane in $\delta^{13}$C with depth,
in tandem with decreasing concentration, is most likely related
to the oxidation of the methane with little or no new produc-
tion of the gas. Below the euphotic zone, variations in meth-
an concentration and isotopic composition at Station
ALOHA correspond to the depths of different water masses.
The core of North Pacific Intermediate Water (NPIW) is lo-
cated at 500 m [Hasumuma, 1978; Bingham and Lukas,
1996]. Below this, Antarctic Intermediate Water (AAIW) ex-
tends to around 1500 m, with its core at 800 m [Bearman,
1989; Bingham and Lukas, 1996]. Part of the NPIW interacts
with the North Pacific gyre system and circulates around the
western boundary of the Pacific [Reid and Mantyla, 1978]. By
the time this water mass, known as modified NPIW, reaches
the central North Pacific, it has interacted with other water
masses and currents and is older than the water above or
below it [Wyrski, 1977]. This is evident in the high $\delta^{13}$C values
at 600 m which likely reflect isotopic fractionation associated
with in situ methane oxidation. Below this depth, $\delta^{13}$C-CH$_4$
decreases, probably reflecting mixing between the modified
NPIW and the AAIW below it. The deepest water mass in our
profiles (July 1997) is North Pacific Deep Water (NPDW), lo-
cated between 3000 and 4000 m [Mantyla, 1975]. The con-
tinuing decrease in $\delta^{13}$C-CH$_4$ to 4000 m may reflect mixing
between NPDW and the water masses above.

Methane concentrations do not decrease noticeably below
around 800 m, probably because consumption of methane all
but stops in older, deeper waters [Scranton and Brewer,
1978]. However, isotopic ratios will vary with depth due to
mixing of water masses of different ages and different histo-
ries of methane input. For example, a water mass that has had
a significant input of methane, such as from mid-ocean hy-
drothermal venting [e.g., Mottil et al., 1995], should have a
relatively heavy isotopic ratio due to fractionation during oxida-
tion of this added methane. This history of methane input
and oxidation, however, may not be evident from the methane
concentrations alone because older waters have fairly uniform
low concentrations.

5. Conclusion
Methane concentrations were supersaturated (up to 90%) with
respect to the atmosphere in the upper 300 m in both the
Although it has been well known for some time that the upper
part of the oceans are supersaturated with methane, the con-
estancy of the elevated concentrations and upper ocean $\delta^{13}$C
values (approximately -45‰) over a 1 year annual cycle has
been shown here.
On the basis of the concentrations and isotopic ratios, we conclude that methane production and consumption processes in the North Pacific gyre region varied little on a seasonal basis in 1996-1997. Methane with a consistently heavier isotopic value than atmospheric methane was transferred from the sea surface to the atmosphere at Station ALOHA at an apparently uniform rate throughout the year. The excess methane in the surface waters appears to be generated throughout the upper 300 m of the water column by bacterial methanogenesis and is not supplied solely from the depth of the methane maximum. The methane concentration maxima occur at the pycnocline, suggesting that the maxima are supported by methanogenesis in suspended particles that accumulate at these depths. In support of this, experiments showed that methane concentrations increased in water in which particles collected at 250 m water depth were incubated. The lack of a diurnal signal implies that methane production and consumption in the ocean is independent of day-night cycles such as photosynthesis, grazing, and vertical migration of zooplankton. The flux to the atmosphere appears to be the main sink for methane in the upper ocean; microbial oxidation and downward eddy diffusion account for only 2 and 6%, respectively, of the total methane loss from the upper 300 m. Below the upper 300 m, methane concentrations and isotopic compositions reflect methane oxidation and mixing of different water masses.

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