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Methane production, consumption and its carbon isotope ratios in the Southern Ocean during the austral summer

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Abstract

The distribution of dissolved CH₄ in the Southern Ocean at 140° E was measured during the austral summer. Surface CH₄ was supersaturated on average, and the calculated mean sea-air flux rate was 0.32 µmol m⁻² d⁻¹. The vertical distributions exhibited ⁵ a CH₄ maximum at approximately 125 m (Δ CH₄, 2.94 nM) below the chlorophyll-rich layer, suggesting a relationship between CH₄ production and plankton dynamics in this area. CH₄ oxidation and ocean movement characteristics in the deep layer led to the enrichment and fluctuation of $\delta^{13}C_{CH_4}$. We estimated the influence of Southern Ocean CH₄, a source of isotopically heavy CH₄ to the atmosphere, on the global CH₄ budget to be approximately 0.19 Gg d⁻¹.

1 Introduction

Considerable attention has recently been focused on biogenic trace gases in ecosystems because they include a significant amount of greenhouse gases. Methane (CH_4) is an effective greenhouse gas that is approximately 20 times more effective in radiative

- ¹⁵ forcing than CO₂ on a per mole basis and contributes significantly to global warming (Schneider, 1989). The atmospheric concentration of CH₄ is currently increasing faster than that of other biogenic greenhouse gases (Pearman and Fraser, 1988; Bouwman, 1990). Each year, 50 million tons of CH₄ are added to the atmosphere, resulting in a relative annual increase of more than 1% (Bouwman, 1990). The primary sources of CH₄ include watlande, nodely fields intesting formentation, and purchasis of argonic methan.
- include wetlands, paddy fields, intestinal fermentation, and pyrolysis of organic matter, i.e., biomass burning (Cicerone and Oremland, 1988). However, methane produced in marine environments also contributes to atmospheric greenhouse gas concentrations and organic carbon cycle pathways. Furthermore, the isotopic signature of CH₄ is recognized as providing constraints on relative source strength and information on reaction dynamics concerning relevant formation, destruction, and biological pathways.



The Southern Ocean, one of the most productive water bodies in the world, has some characteristics unique among the world's oceans, i.e., the near-circular symmetry of most of its physical and chemical characteristics; the immense expanse of cold surface water, which is globally by far the largest; and the most pronounced seasonal variation

⁵ in sea surface temperature of any comparable ocean basin (Lutjeharms, 1990). The temporal and spatial distribution of these physical and chemical variables should also be reflected in the distribution patterns of biological processes. Here we describe the results of isotopic studies of dissolved CH_4 in the Southern Ocean at 140° E to elucidate the origins of CH_4 in the ocean and to estimate its CH_4 contribution to the atmosphere.

10 2 Materials and methods

2.1 Study sites and sampling

Samples were collected during the 43rd Japanese Antarctic Research Expedition (JARE-43), 2002 Marine Science Cruise on the R/V Tangaroa from 6 February to 7 March 2002. The purpose of the expedition was to study the biogeochemical cycles
and biological processes of the Southern Ocean as they relate to global environmental issues. The production and consumption of dissolved CH₄ in Southern Ocean ecosystems were investigated by collecting seawater samples at stations 1 (open water), 5 (marginal ice zone), and 8 (previous ice zone; Fig. 1). Water samples were collected at the indicated depths using a CTD water sampler (SBE 32 24x10-L Carousel Water Sampler). For CH₄ analyses, water samples were put in 125-ml glass vials and sterilized with mercury chloride (1 ml of saturated HgCl₂ solution per vial). The vials were then sealed with a butyl-rubber septum and an aluminum cap, taking care to avoid bubble formation, and stored at 4 °C in the laboratory until analysis.



2.2 Chemical analysis

Salinity and temperature were recorded using a CTD sampler (SBE 911plus). Dissolved oxygen was measured with a dissolved oxygen auto-titrator based on the Scripps Institute of Oceanography design.

5 2.3 Dissolved CH₄ and carbon isotope analysis

In the laboratory, water samples were transferred to a stripping chamber using helium gas replacement in the sample vials. After H_2O and CO_2 were removed in a magnesium perchlorate [Mg(ClO₄)₂] and Ascarite (sodium hydroxide-coated silica) column, CH₄ was collected in a U-shaped tube filled with activated charcoal (AC1) at liquid nitrogen temperature. At the end of the quantitative extraction of CH₄, the U-tube was heated to room temperature (25 °C) by removing a liquid nitrogen trap. The desorbed gas from the AC1 was separated in a molecular sieve column. The purified CH₄ fraction was collected again in an activated charcoal (AC2) tube at liquid nitrogen temperature. The AC2 was then heated to room temperature by removal of the liquid nitrogen. The desorbed CH₄ was cryofocused before being introduced into the system GC and then separated in a PoraPlot Q column (25 m) at 30 °C. The GC was connected to a combustion furnace made of quartz (0.6 mm × 15 cm) filled with CuO at 960 °C. Methane was then combusted into CO₂ and H₂O, and the produced H₂O was removed by diffusion

through a Nafion membrane tube. He-carrier gas was then partially separated using a helium separator, and CO₂ was introduced into the isotope ratio mass spectrometer (Finnigan, MAT 252). The carbon isotopic composition results were expressed as δ^{13} C values, defined as:

 δ^{13} C (‰) = [($R_{\text{SAMPLE}}/R_{\text{STANDARD}}$) - 1] × 1000,

where R_{SAMPLE} and R_{STANDARD} are the isotope ratios (¹³C/¹²C) for samples and standards, respectively. Carbon isotope ratios of dissolved CH₄ were expressed in ‰ deviations from PeeDee belemnite (PDB) carbonate. The δ^{13} C values were reproducible



(1)

to within $\pm 0.3\%$. The atmospheric equilibrium concentration of CH₄ was calculated from in situ water temperatures and the atmospheric mixing ratio (1.7 ppmv; Quay et al., 1991; Holmes et al., 2000) following the methods of Yamamoto et al. (1976).

3 Results and discussion

- ⁵ Methane concentrations and isotope ratio profiles in the Southern Ocean water column during the austral summer (Fig. 2) revealed that methane distribution and production were related to physical and biological properties in the area. CH₄ concentrations and δ^{13} C values of the dissolved CH₄ in surface water were almost in equilibrium with the atmosphere, with mean excess CH₄ (Δ CH₄) and δ^{13} C at 0.06 nM (or 102% saturation)
- ¹⁰ and -46.3‰, respectively. The Δ CH₄ maximum (2.94 nM or about 200% saturation) was observed in the subsurface (at a depth of approximately 125 m) and decreased to a constant value below 1000 m at station 1. The δ^{13} C value at this station was generally enriched below 200 m, in contrast to the CH₄ concentration. However, small enrichments in δ^{13} C were also observed in the CH₄ maximum layer. While CH₄ at sta-
- ¹⁵ tion 5 exhibited no subsurface maximum, the CH₄ concentration gradually decreased with increased δ^{13} C from the surface and reached a constant value below 500 m. At station 8, the CH₄ concentration and δ^{13} C value remained close to atmospheric equilibrium from the surface to the deep region.

As CH₄ is produced and/or oxidized by bacteria and also lost to the atmosphere through gas exchange, the shape of a vertical profile must be determined by the balance between in situ biological production and consumption and physical processes of diffusion, advection, and gas exchange. Thus, dissolved CH₄ and its isotope ratio could be categorized into three parts: surface, subsurface (including the CH₄ maximum), and deeper regions.

²⁵ At the surface where gas exchange occurs, the CH₄ concentration is governed by physical factors, mainly temperature and wind, with gas saturation values up to about



5% above or below saturation (Bieri et al., 1966, 1968). The surface equilibrium of CH_4 in the Southern Ocean could be caused by high wind speeds, given that temperatures in the area are quite stable during the austral summer. The δ^{13} C values of surface dissolved CH₄ at all stations were enriched by 0.2-1.2‰ relative to the atmospheric value (-47 to -47.4‰; Holmes et al., 2000; Stevens, 1993), possibly because of the 5 kinetic fractionation factors during CH_4 invasion and evasion. Fuex (1980) found that the equilibrium fractionation (α_{eq}) for methane was about 1.00033, a value similar to our result and those observed in other areas (e.g., Holmes et al., 2000; Tsunogai et al., 2000; Valentine et al., 2001). The δ^{13} C of dissolved CH₄, however, was enriched by more than 1‰, a value greater than can be attributed to analytical error at station 1 10 where wind speeds were high and were expected to result in a high CH_{4} exchange rate with surface water. This result suggests that the exchange of CH₄ between ocean and atmosphere and its isotopic fractionation should be treated kinetically and considered temporally and spatially variable, as well as related to high in situ δ^{13} C(CH₄), even at the surface. 15

Given that the microbial production of CH₄ cannot occur in an oxic environment (Wolfe, 1971), it is thought that CH₄ forms mostly within the reducing interiors of particles, as supported by incubation experiments (Karl and Tilbrook, 1994; Marty et al., 1997; Owens et al., 1991). In the Southern Ocean waters surrounding Antarctica,
²⁰ phytoplankton blooms fueled by nutrient-rich waters lead to the growth of vast swarms of krill (*Euphausia superba*) each summer. Consequently, settling particles, such as fecal pellets, may be produced during the life cycle of the krill, either directly or indirectly. Chlorophyll-*a* is the most important phytopigment and can be used as a semi-quantitative measure of phytoplankton abundance. Hirawake et al. (2003) reported that
²⁵ chlorophyll-*a* concentrations show clear seasonal variation with a complicated spatial distribution: concentrations ware yory low (< 0.2 mgm⁻³) in October, but rapidly

tial distribution; concentrations were very low (< 0.3 mg m⁻³) in October, but rapidly increased to 1–5 mg m⁻³ through December near the sea-ice edge and in the open ocean. Furthermore, these particles do not consist only of inorganic or dead organic matter; they also host microbial communities, including bacteria, various protozoa, and



algal cells (Fenchel et al., 2000). Therefore, such particles could be expected to include anoxic microsites with active CH_4 production (Alldredge and Cohen, 1987; Kiene, 1991; Sieburth, 1987). Biogenic CH_4 is known to be produced via microbial methanogenesis. Major substrates for methanogenic bacteria include acetate and CO_2/H_2 (Cicerone and

- ⁵ Oremland, 1988; Whiticar et al., 1986). In the former substrate, CH₄ is derived from the methyl group of acetate, and this process depends on the production of acetate at anaerobic sites during decomposition of organic matter. The carbon isotope fractionation factor for reduction of CO₂ to CH₄ has been reported for a pure culture system, and the high fractionation factor of 1.045 was reported for wetlands rich in labile organic
- ¹⁰ matter (Games et al., 1978). The general trend that governs the variation in δ^{13} C of bacterial methane has been examined through paddy soil incubation experiments. The δ^{13} C value of CH₄ from acetate was close to that of methyl carbon in acetate (-43 to -30‰), while that from CO₂/H₂ reduction was -70 to -60‰ (Sugimoto and Wada, 1993). The δ^{13} C(CH₄) value at the Δ CH₄ maximum, i.e., about -43.4‰ at station 1,
- ¹⁵ suggested that the formation of CH₄ in this subsurface was produced via acetate fermentation. Blair and Carter (1992) reported the δ^{13} C value of acetate and estimated the δ^{13} C of CH₄ derived from acetate to be -43‰ in anoxic marine sediment, which agrees well with our results. However, the large δ^{13} C variation in settling organic matter in the Antarctic Ocean (-26.7 to -20.5‰; Wada et al., 1987) may affect the δ^{13} C
- of CH₄ produced via acetate fermentation. The oxidation of the methyl position of acetate to CO₂ may also cause the isotopic fractionation of the produced CH₄ (Whiticar et al., 1986). However, the Δ CH₄ maximum peak was only observed at station 1, suggesting that the magnitude of CH₄ production varied with abundance, distribution, and migration of phytoplankton and zooplankton in the area.
- In the deeper subsurface waters, the ΔCH_4 value became negative in association with ¹³C enrichment, suggesting the oxidation of dissolved CH_4 with less or without new CH_4 production. Thus, the residual, heavier $\delta^{13}C$ CH_4 should be found based on the kinetic isotope effect during oxidation. Several researchers have demonstrated this process with aerobic culture systems and have found that the magnitude of carbon



isotope fractionation varies from 5 to 31% (e.g., Barker and Fritz, 1981; Zyakun et al., 1984). Such water column CH₄ oxidation has also been observed in other areas, such as at the ALOHA station and in the North Atlantic (Holmes et al., 2000), suggesting that the oxidative consumption could occur normally in oxic water column environments.

- Other parameters that could indicate CH₄ oxidation include the preferential loss of CH₄ relative to higher molecular weight hydrocarbons (Whiticar, 1999) and the systematic shift in H isotope ratios (Coleman et al., 1981; Whiticar, 1999). Furthermore, in deep water, at approximately 2500 m, the horizontal and vertical movements of cold water from inshore induced by the geopotential anomaly of the strong steering of the cur-
- ¹⁰ rent by the ridge system around Antarctica (see Lutjeharms, 1990; Orsi et al., 1995) should affect the δ^{13} C level of CH₄. The Δ CH₄ values did not decrease below 500 m and 1000 m at stations 5 and 1, respectively, probably because of the lack of CH₄ consumption in deeper water (Scranton and Brewer, 1978). Also, the isotope ratio varies with depth because of the mixing of different water masses with different histories of CH₄ isput (Holmon et al., 2000). It should be pated that at station 9, leasted in a shollow
- ¹⁵ CH₄ input (Holmes et al., 2000). It should be noted that at station 8, located in a shallow water column close to shore, the strong steering of the summer current may promote vertical homogeneity of the CH₄ concentrations and isotopic compositions.

The degassing of supersaturated surface seawater could release CH_4 and sources of isotopically heavy CH_4 into the earth's atmosphere by simple diffusion and thereby

- ²⁰ contribute to the net flux of CH₄ across the sea-air interface. It is premature to quantitatively calculate the influence of the Southern Ocean on the global CH₄ budget from the present data alone; however, our results do provide some insight into the contribution of the Southern Ocean. The estimated amount of CH₄ that will eventually reach the atmosphere after transport through the unsaturated zone can be determined from
- the empirical relationship between wind speed and gas transfer rate with measured values for wind speed, temperature, and surface concentrations of CH₄, according to the following equation (Liss and Slater, 1974):

 $F = K_{\mathsf{L}} \left(C_{\mathsf{S}} - C_{\mathsf{E}} \right),$



(2)

where $K_{\rm L}$ is the liquid-phase gas-transfer coefficient, $C_{\rm S}$ is the gas concentration in the surface water; and $C_{\rm E}$ is the gas concentration of the solution during equilibrium with the overlying gas phase. The liquid-phase gas-transfer coefficient, $K_{\rm L}$, used in calculating the flux was obtained from Liss and Merlivat (1986):

$$_{5}$$
 $K_{\rm L} = 2.85 V - 9.65 (cm h^{-1}),$

and Wanninkhof (1992):

$$K_{\rm L} = 0.31 V^2 \left(\frac{Sc}{660}\right)^{-1/2} ({\rm cm \ h^{-1}}),$$

where *V* is wind velocity (m s⁻¹), and *Sc* is the Schmidt number. The Schmidt number for CH_4 in seawater is expressed as a decreasing function of temperature (Wanninkhof, 1992):

$$Sc_{CH_4} = 2039.2 - 120.31 T + 3.4209 T^2 - 0.040437 T^3$$

The calculated net sea-air flux of CH₄ in the Southern Ocean is an average of 0.32 μmol m⁻² d⁻¹ (-0.09 to 0.74 μmol m⁻² d⁻¹), using the Liss and Merlivat (1986) and Wanninkhof (1992) transfer coefficients. The ΔCH₄ maximum observed at the base of the mixed layer would result in a diffusive flux of CH₄ into the surface layer. We also obtained δ¹³C of about -41.8‰ for the source of CH₄ formation from the isotopic correlation with the inverse concentration between the surface and the CH₄ maximum and estimated the vertical net flux to be about 0.26 μmol m⁻² d⁻¹ from the one-dimensional vertical mixing coefficient (Li et al., 1984) at station 1. This input accounted for about 80% of the estimated net flux of CH₄ in the Southern Ocean to the atmosphere and suggested that CH₄ was produced by in situ biological processes, diffused through the mixed layer, and then released by sea-air exchange. The consumption loss rate of 0.01 μmol m⁻² d⁻¹, calculated from an average CH₄ concentration in the upper 70 m and an average CH₄ turnover time, was negligible compared to the losses associated



(3)

(4)

(5)

with sea-air exchange because of the long turnover time (an average of 65 yr; Jones, 1991; Ward et al., 1987). The CH₄ flux in this area was much higher than that reported for Drake Passage and the Weddell Sea during the austral summer and autumn, respectively (Heeschen et al., 2004; Tilbrook and Karl, 1994); both locations showed negative flux values (Table 1). However, positive flux values have been found in coastal areas with CH₄ accumulation (Tilbrook and Karl, 1994). This could suggest that sea-air flux of CH₄ varies greatly in time and space depending on physical factors as well as the magnitude of CH₄ diffusion from the CH₄ maximum layer. If this flux value could be applied to the entire Southern Ocean, which has an area of about 37 × 10¹² m² (Peng, 1984), for the duration of the austral summer, the total CH₄ flux to the atmosphere from this region would be 0.19 Gg d⁻¹. The value of δ^{13} C for the CH₄ flux to the atmosphere was calculated using the following equation from Quay et al. (1993) and Hoefs (1987):

$$\delta^{13}C_{CH_4} \text{ flux (\%)} = \left\{ \left[\frac{G\alpha_k \left(\frac{\rho CH_{4[atm]}R_{atm}\alpha_{sol} - \rho CH_{4[ml]}R_{ml}}{G \left(\rho CH_{4[atm]} - \rho CH_{4[ml]}\right)} \right] - 1 \right\} \times 1000, \quad (6)$$

where *R*_{atm} is the ¹³C/¹²C ratio of atmospheric CH₄, *R*_{ml} is the ¹³C/¹²C ratio of CH₄
in the mixed layer, *α_k* is 0.9992 (Knox et al., 1992; Happell et al., 1995), *α*_{sol} is 1.00033 (Fuex, 1980), *p*CH₄ in the methane partial pressure, δ¹³C_{CH_{4[atm]}} is -47.0 to -47.4‰ (Quay et al., 1991; Holmes et al., 2000), and *R*_{PDB}, the isotopic ratio of the PDB standard, is 0.011237 (Craig, 1957). We determined that the average δ¹³C value supplied to the atmosphere in the CH₄ flux from this area was -42.7‰ (Table 1). This
contribution (approx. 0.19 Gg d⁻¹) is a significant part of the global oceanic CH₄ flux of 5–50 Tg yr⁻¹ (2.4–24 µmol m⁻² d⁻¹; Prather, 1995). Thus, the Southern Ocean could be contributing 0.14–1.39% of the total oceanic flux of CH₄. However, if we consider other results from the circum-Antarctic region (Heeschen et al., 2004; Tilbrook and Karl, 1994), the total net sea-air CH₄ flux from the Southern Ocean would be about
0.15 Tg yr⁻¹, equivalent to 0.30–3.0% of the total oceanic CH₄ contribution. Moreover,



the $\delta^{13}C_{CH_4}$ flux could provide information concerning the isotopically heavy source also entering the atmosphere (-54.2%; Whiticar, 1993).

4 Conclusions

The distribution of CH_4 and its isotopic compositions in the Southern Ocean during the austral summer suggest that surface water CH_4 concentrations are controlled by physical factors and ocean water movement from glacial regions. A subsurface CH_4 maximum was associated with the decomposition of sinking organic matter, suggesting a relationship between CH_4 production and plankton dynamics in the area. CH_4 oxidation and physical characteristics of water movements in the deep layer led to the enrichment and fluctuation of $\delta^{13}C_{CH_4}$. We estimated the influence of Southern Ocean CH_4 , a source of isotopically heavy CH_4 to the atmosphere, on the global CH_4 budget to be about 0.19 Gg d⁻¹.

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Table 1. Methane concentrations and $\delta^{13}C_{CH_4}$ and fluxes to the atmosphere from the ocean surface. Numbers in parentheses indicate ranges in value.

Location	Mixed layer [CH ₄]	Mixed layer δ ¹³ C _{CH₄}	Sea-air flux	Sea-air flux $\delta^{13}C_{CH_4}$	Reference
	(nM)	(‰)	(µmol m ⁻² d ⁻¹)	(‰)	
Arabian Sea Caribbean Sea Subtropical Atlantic Atlantic Ocean (50° N–35° S) Open ocean Eastern tropical North Pacific North Atlantic	2.30 (2.26 to 3.96) 2.7 ^a (2.4 to 3.0)	-40.7 (-46.9 to -41.5) -46.1 ^a (-46.6 to -45.5)	$\begin{array}{l} 9.25^{a} \ (4.6 \ to \ 13.9) \\ 0.23 \ (-) \\ 0.08 \ (-) \\ 0.23 \ (0.09 \ to \ 4.65) \\ 2.76^{a} \ (2.05 \ to \ 3.46) \\ 1.88^{a} \ (0.77 \ to \ 3.0) \\ 3.0^{a} \ (1.6 \ to \ 4.4) \end{array}$	-42.6 ^a (-48.2 to -37.0) -44.0 ^a (-45.0 to -43.0)	Owens et al., 1991 Ward et al., 1987 Scranton and Brewer, 1978 Conrad and Seiler, 1988 Ehhalt, 1974 Sansone et al., 2001 Holmes et al., 2000
Southern Ocean					
Drake Passage South Shetland Islands Bransfield Strait Weddell Sea Front at 173~177° E	2.69 (2.22 to 3.09) 3.80 (2.80 to 7.09) 3.18 (2.71 to 3.97) 2.86 ^b 2.72 (2.10 to 3.04)	-46.0 (-)	-0.35 (-0.77 to 0.01) 1.05 (-0.41 to 5.86) 0.15 (-0.54 to 1.30) -0.47 (-)	-54.1 ^b (-55.8 to -52.5)	Tilbrook and Karl, 1994 Tilbrook and Karl, 1994 Tilbrook and Karl, 1994 Heeschen et al., 2004 Swinnerton and Lamontagne, 1974
Front at 140° E	3.16 (3.07 to 3.22)	-46.6 (-46.7 to -46.4)	0.32 (-0.09 to 0.74)	-42.7 (-47.9 to -34.8)	This study

^a average value from the range; ^b calculated value from the raw data









Fig. 2. Depth profiles of ΔCH_4 (diamonds) and $\delta^{13}C_{CH_4}$ (triangles) at **(a)** station 1, **(b)** station 5, and **(c)** station 8 in the Southern Ocean during the austral summer.

