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## A survey of methane isotope abundance ( $^{14}\text{C}$ , $^{13}\text{C}$ , $^2\text{H}$ ) from five nearshore marine basins that reveals unusual radiocarbon levels in subsurface waters

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[1] Methane ( $\text{CH}_4$ ) in the subsurface ocean is often supersaturated compared to equilibrium with the modern atmosphere. In order to investigate sources of  $\text{CH}_4$  to the subsurface ocean, isotope surveys ( $^{14}\text{C}\text{-CH}_4$ ,  $\delta^{13}\text{C}\text{-CH}_4$ ,  $\delta^2\text{H}\text{-CH}_4$ ) were conducted at five locations: Skan Bay (SB), Santa Barbara Basin (SBB), Santa Monica Basin (SMB), Cariaco Basin (CB), and the Guaymas Basin (GB). Depth distributions of  $\text{CH}_4$  concentration and isotopic abundance were determined for both the sediment and water column at the SB, SBB, SMB, and CB sites;  $\text{CH}_4$  emitted from seeps on the continental shelf adjacent to the SBB as well as seeps and decomposing clathrate hydrates in the GB was also collected, purified, and analyzed. Methane isotope distributions in the sediments were consistent with known methanogenic and methanotrophic activity; seep- and clathrate-hydrate-derived  $\text{CH}_4$  was found to be depleted in radiocarbon. However, surprising results were obtained in the water column at all sites investigated. In SB the radiocarbon content of the subsurface  $\text{CH}_4$  concentration maximum was on average 41% less than its suspected sediment  $\text{CH}_4$  source, suggesting  $\text{CH}_4$  seepage in the bay. In the SBB, SMB, and CB, the  $^{14}\text{C}\text{-CH}_4$  contents in the subsurface ocean were 1.2 to 3.6 times greater than modern carbon quantities suggesting a source of  $^{14}\text{C}$  from atmospheric nuclear weapons testing, nuclear power plant effluents, or cosmogenic isotope production.

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### 1. Introduction

[2] Inputs of radiocarbon-free (fossil) methane released from seeps and decomposing methane clathrate hydrates (clathrates) have been shown to be the dominant methane ( $\text{CH}_4$ ) source to both the Cariaco Basin and Black Sea with input fluxes of  $0.14\text{--}0.17\text{ mol m}^{-2}\text{ a}^{-1}$  ( $0.024\text{--}0.028\text{ Tg a}^{-1}$ ) and  $0.53\text{--}0.84\text{ mol m}^{-2}\text{ a}^{-1}$  ( $3.60\text{--}5.65\text{ Tg a}^{-1}$ ), respectively [Kessler *et al.*, 2006a, 2005]. Natural radiocarbon measurements of  $\text{CH}_4$  ( $^{14}\text{C}\text{-CH}_4$ ) confirmed that the principal  $\text{CH}_4$  source into both basins is fossil. Measurements of the stable isotopic content of  $\text{CH}_4$  ( $\delta^2\text{H}\text{-CH}_4$  and  $\delta^{13}\text{C}\text{-CH}_4$ )

dissolved in the water column do not uniquely identify if that  $\text{CH}_4$  was released to the water column, (1) from seeps and decomposing clathrates or (2) after recent methanogenesis. The  $^{14}\text{C}\text{-CH}_4$  analyses provide that unique distinction. Even though the Cariaco Basin and Black Sea are large marine anoxic basins, with areas of 8220 and 423,000  $\text{km}^2$ , respectively, and exhibit relatively similar  $\text{CH}_4$  fluxes from fossil sources, extrapolating these fluxes to a global estimate remains a challenge. Additional measurements must be made of the fluxes of  $\text{CH}_4$  from seeps and decomposing clathrates to coastal ocean waters outside of anoxic basins which is where the majority of seeps and clathrates are found. A few analytical studies have estimated  $\text{CH}_4$  fluxes from seeps and vents to the coastal ocean however they are challenged by open ocean dispersion and  $\text{CH}_4$  oxidation processes [Clark *et al.*, 2000; Heeschen *et al.*, 2005; Hovland *et al.*, 1993; Rosenberg *et al.*, 1988]; these complicate the  $\text{CH}_4$  systems and cause the methane concentration ( $[\text{CH}_4]$ ) to be typically 3 orders of magnitude less than in these enclosed basins. Only one procedure has been published to quantify the radiocarbon content of  $\text{CH}_4$  dissolved in seawater or sediment and that procedure does not produce quantitative results when the  $[\text{CH}_4]$  is very low

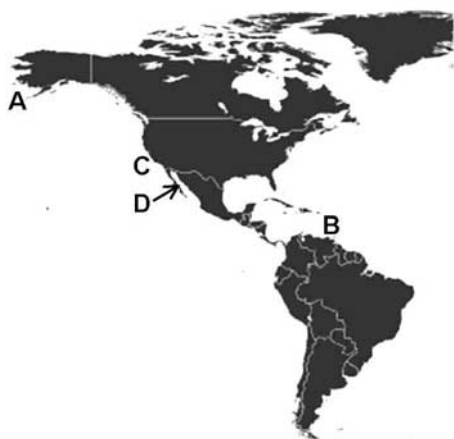
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**Figure 1.** Map of sample collection sites. Site A, Skan Bay, Unalaska Island, Alaska; site B, Cariaco Basin, Venezuela; site C, Santa Barbara and Santa Monica basins, California; site D, Guaymas Basin, Gulf of California.

in seawater (<15 nM) or sediments (<5  $\mu\text{M}$ ) [Kessler and Reeburgh, 2005].

[3] Maxima in  $[\text{CH}_4]$  have been investigated in the subsurface and middepth ocean water column with  $[\text{CH}_4]$ , oxidation rate, and stable isotope measurements [e.g., Burke et al., 1983; Cynar and Yayanos, 1992; Cynar and Yayanos, 1993; de Angelis and Lee, 1994; Sansone et al., 2001; Sasakawa et al., 2008; Ward, 1992; Ward and Kilpatrick, 1993]. The close proximity of these  $[\text{CH}_4]$  maxima to the ocean surface enables them to be significant  $\text{CH}_4$  sources to the atmosphere [Cynar and Yayanos, 1993; Sansone et al., 2001], while the elevated  $[\text{CH}_4]$  allows the use of the procedures established by Kessler and Reeburgh [2005] to conduct quantitative measurements of  $^{14}\text{C}\text{-CH}_4$ . Fossil radiocarbon-free  $\text{CH}_4$  may be the source as  $\text{CH}_4$  released by seeps is transported to these maxima horizontally along isopycnal surfaces [Sansone et al., 2001] or vertically when bubbles released from depth dissolve in subsurface waters [Rehder et al., 2002]. However, subsurface  $[\text{CH}_4]$  maxima have also been suggested to have a biological origin, being produced in situ in zooplankton guts, fecal pellet micro-environments, decomposing detritus, during phytoplankton blooms, and/or from bubbles expelled by the anal duct of fish [Brooks and Sackett, 1973; Burke et al., 1983; Cynar and Yayanos, 1991; Damm et al., 2008; de Angelis and Lee, 1994; Reeburgh, 2007; Sasakawa et al., 2008; Ward, 1992; Wilson et al., 2004]. A recent study has also suggested that  $\text{CH}_4$  is produced aerobically in subsurface waters via methylphosphonate decomposition in phosphate-stressed waters [Karl et al., 2008]. The strengths of these maxima are variable, possibly related to internal tides and waves, wind events, and variability of in situ production [Burke et al., 1983; Cynar and Yayanos, 1992; Cynar and Yayanos, 1993; Damm et al., 2008; de Angelis and Lee, 1994; Heeschen et al., 2005; Ward, 1992; Ward and Kilpatrick, 1993]. We conducted concentration and natural isotopic measurements on  $\text{CH}_4$  ( $^{14}\text{C}\text{-CH}_4$ ,  $\delta^2\text{H}\text{-CH}_4$ ,  $\delta^{13}\text{C}\text{-CH}_4$ ) to determine the source of  $\text{CH}_4$  to subsurface and middepth  $[\text{CH}_4]$  maxima. Subsurface and middepth  $[\text{CH}_4]$  maxima were identified and analyzed in the water columns of Skan Bay (SB), Santa

Barbara Basin (SBB), Santa Monica Basin (SMB), and Cariaco Basin (CB). Methane dissolved in the sediments of SB, SBB, SMB, and CB as well as released from seeps on the continental shelf adjacent to the SBB and seeps and clathrates in the Guaymas Basin (GB) were analyzed to investigate cycling of  $\text{CH}_4$  among various marine environments to study the potential contributions to the water column  $[\text{CH}_4]$  maxima. Using the established procedures of Kessler and Reeburgh [2005], the radiocarbon quantification limits due to low  $\text{CH}_4$  yields from low  $\text{CH}_4$  concentration environments is discussed.

## 2. Experimental Procedures

[4] Seawater and sediment samples were collected from 28 August to 10 September 2003 in Skan Bay, Alaska on board the R/V *Alpha Helix*, from 21 to 24 January 2004 in the Cariaco Basin on board the B/O *Hermano Gines*, and from 21 to 30 June 2004 in the Santa Monica and Santa Barbara basins on board the R/V *New Horizon*. Seep gas was collected by scuba from the continental shelf adjacent to the Santa Barbara Basin [Kinnaman et al., 2007] on 25 March (Brian Seep) and 16 April 2004 (Shane Seep). Seep and  $\text{CH}_4$  clathrate hydrate gases were collected in the Guaymas Basin, Gulf of California with the remotely operated vehicle (ROV) *DORISS* from 26 April to 10 May 2003 (Figure 1).

[5] Methane concentration was measured with a headspace equilibration technique based on Henry's Law. For water column  $[\text{CH}_4]$  analyses, serum vials were filled directly from Niskin bottles. At least 3 vial volumes were allowed to overflow before the vials were sealed with stoppers and crimp caps. A headspace of ultrahigh purity helium was introduced by displacement and the vials were vigorously shaken. Samples for sediment  $[\text{CH}_4]$  analyses were prepared by making a slurry of sediment (syringe subcores) and helium purged water in 37.5 mL serum vials. The details of the sample preparation for  $[\text{CH}_4]$  analyses are found in Table 1. After the samples were allowed to equilibrate for at least 12 h, two to three aliquots of the headspace were removed for concentration analysis with gas chromatography (GC) and flame ionization detection (GC-Mini 2; Shimadzu Corp.; carrier gas ( $\text{N}_2$ ) flow rate = 33 mL/min, column temperature = 70°C, 1.5 m column packed with molecular sieve 5A 60/80 mesh). Depending on the logistics of the research cruise, the GC measurements were either conducted at sea or on shore. For ship-based analyses, the vials were sealed with gray camel-toe stoppers, while for shore-based measurements the vials were sealed with blue butyl rubber stoppers and poisoned with a saturated solution of mercuric chloride. The results have been corrected for the amount of  $\text{CH}_4$  still dissolved in solution using Bunsen solubility coefficients [Yamamoto et al., 1976].

[6] We used the procedures described by Kessler and Reeburgh [2005] to quantitatively collect, prepare, and measure the natural isotopic content of  $\text{CH}_4$  ( $^{14}\text{C}\text{-CH}_4$ ,  $\delta^2\text{H}\text{-CH}_4$ ,  $\delta^{13}\text{C}\text{-CH}_4$ ) in low concentration seawater and sediment. These procedures demonstrated that to achieve a precision of  $\pm 5$  percent modern carbon (pMC) in a radiocarbon measurement that at least 1.81  $\mu\text{mol}$  of  $\text{CH}_4$  must be collected. This "detection limit" of 1.81  $\mu\text{mol}$  of  $\text{CH}_4$  is controlled by the size and precision of the background or

**Table 1.** Sample Preparation for Methane Concentration Analyses

	Description	Measurement Location	Serum Vial Volume (mL)	Headspace Volume (mL)	Sediment Volume (mL)	Helium-Purged Water Volume (mL)
Skan Bay	Water	Ship	120	10	NA	NA
Santa Barbara Basin	Water	Ship & Shore	160	10	NA	NA
Santa Monica Basin	Water	Ship & Shore	160	10	NA	NA
Cariaco Basin	Water	Shore	160	13	NA	NA
Skan Bay	Sediment	Ship	37.5	29.5	3	5
Santa Barbara Basin	Sediment	Ship & Shore	37.5	21.5	6	10
Santa Monica Basin	Sediment	Ship & Shore	37.5	21.5	6	10
Cariaco Basin	Sediment	Shore	37.5	28.5	3	6

blank (i.e., the CH<sub>4</sub> collected when an ocean sample containing no CH<sub>4</sub> is analyzed). The majority of sites investigated here contain relatively low CH<sub>4</sub> concentrations and even though these procedures have been shown to quantitatively collect CH<sub>4</sub>, the quantity collected approaches the quantity of the background (or blank). Methane samples were extracted at sea from 114 L of seawater and 0.07 to 0.35 L of sediment. Thus, to achieve a precision of  $\pm 5$  pMC or greater, CH<sub>4</sub> must be extracted from seawater with a concentration of at least 15.9 nM or sediment with a concentration of at least 5.2  $\mu$ M. Methane samples were collected that were above and below these thresholds. Collecting less than 1.81  $\mu$ mol required dilution with radiocarbon-free carbon (so that the sample + diluent equaled 1.81  $\mu$ mol) to conduct a successful <sup>14</sup>C accelerator mass spectrometry (AMS) measurement [Currie *et al.*, 2000].

[7] We calculated how the precision is affected if we collect less than 1.81  $\mu$ mol of CH<sub>4</sub> and must dilute the sample. Equations were derived by Kessler and Reeburgh [2005] to calculate the error in the final results determining that the final error is mainly attributable to the imprecision of the blank. The <sup>14</sup>C AMS measurement of the diluted samples took into account errors associated with counting statistics, the total blank, and the isotopic signature of the blank, so we calculated how the error in our undiluted sample is affected by dilution. In order to calculate how the final error of our sample analysis was associated with dilution error, we solved the isotope mass balance equation (equations (1) and (2)) for <sup>14</sup>C<sub>sample</sub> and took the quadratic sum of the partial differentials with respect to each variable. Following simplification, this process led to equation (3):

$$^{14}\text{C}_{\text{measured}} = ^{14}\text{C}_{\text{sample}}F + ^{14}\text{C}_{\text{diluent}}(1 - F), \quad (1)$$

$$F = \frac{\text{mol CH}_4\text{sample}}{\text{mol CH}_4\text{sample} + \text{mol CH}_4\text{diluent}}, \quad (2)$$

$$\sigma_{^{14}\text{C}_{\text{sample}}} = \sqrt{\frac{(^{14}\text{C}_{\text{diluent}} - ^{14}\text{C}_{\text{measured}})^2 \sigma_F^2 + F^2 \left( (F - 1)^2 \sigma_{\text{diluent}}^2 + \sigma_{\text{measured}}^2 \right)}{F^4}}. \quad (3)$$

The radiocarbon content of the diluent does not vary between diluted samples and was measured by conventional <sup>14</sup>C AMS (1 mg C; <sup>14</sup>C<sub>diluent</sub> = 0.08 pMC;  $\sigma_{\text{diluent}}$  = 12.5%

percent standard deviation (psd)). The quantities mol CH<sub>4</sub>sample and mol CH<sub>4</sub>diluent in equation (2) are measured manometrically (MKS Baratron) and  $\sigma_F$  is relatively small (0.56% psd). Thus, the terms mol CH<sub>4</sub>sample and  $\sigma_{\text{measured}}$  are the main controls on the final error of the undiluted sample. To determine which environments contain enough CH<sub>4</sub> to result in a quantitative measurement, the quantity (mol) of sample collected can be translated into the [CH<sub>4</sub>] in seawater and sediment (Figure 2); this is possible because the sample collection procedures have been shown to quantitatively extract and collect CH<sub>4</sub> from ocean samples [Kessler and Reeburgh, 2005]. Figure 2 displays results for values of <sup>14</sup>C<sub>measured</sub>,  $\sigma_{\text{measured}}$ , <sup>14</sup>C<sub>diluent</sub>,  $\sigma_{\text{diluent}}$ , and [CH<sub>4</sub>] encountered in SBB, SMB, and CB and how they affect the final error. This analysis shows that  $\sigma_{\text{measured}}$  is the main control on the final error of the undiluted sample.

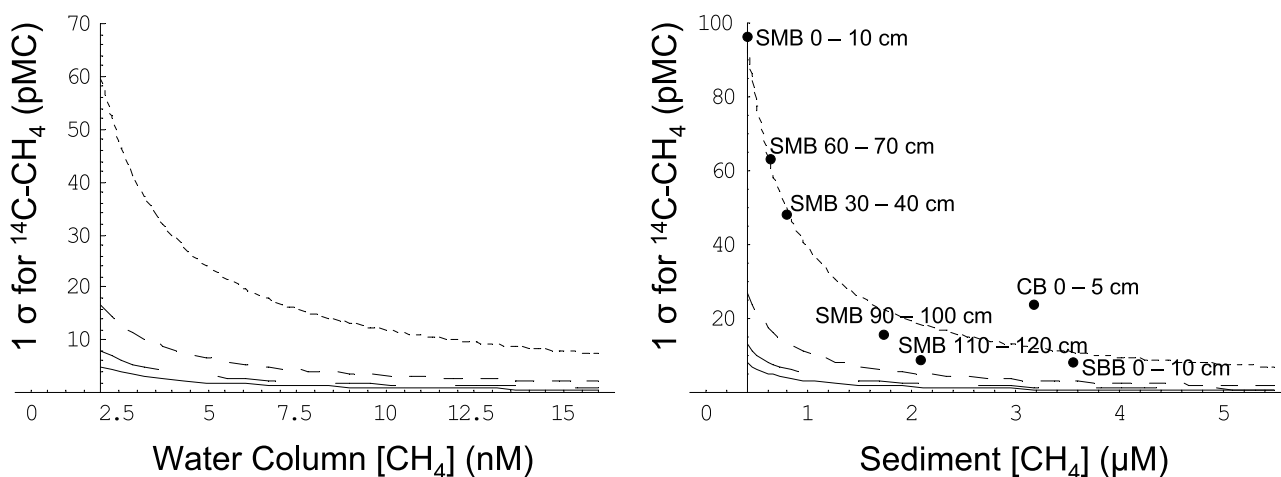
[8] The precision was especially low for  $\delta^2\text{H-CH}_4$  analyses (Figures 3–9). When measuring  $\delta^2\text{H-CH}_4$ , we used standard procedures to reduce the H<sub>2</sub>O produced from CH<sub>4</sub> combustion to H<sub>2</sub> with activated zinc [Coleman *et al.*, 1982; Kessler and Reeburgh, 2005]. In standard H<sub>2</sub>O reductions, it is important to keep the ratio of zinc to H<sub>2</sub>O constant at 50 mg zinc to 1 mg H<sub>2</sub>O to standardize the effect of isotopic fractionation caused by H<sub>2</sub> absorption by the zinc [Demény, 1995]. However, because of the small sample sizes, one zinc particle often exceeded this prescribed ratio, causing an extra factor of uncertainty in the measurements.

### 3. Results and Discussion

#### 3.1. Skan Bay

[9] The water column [CH<sub>4</sub>] profile displayed a subsurface maximum at 15 m depth (Figure 3). This [CH<sub>4</sub>] maximum is correlated with a decrease in beam transmission caused by an increase in particulate matter in the near surface waters (Figure 3) and initially led us to suspect the CH<sub>4</sub> was produced by methanogenesis in particulate matter. The source of this subsurface [CH<sub>4</sub>] maximum was investigated with [CH<sub>4</sub>] and isotope measurements in the water column and sediments.

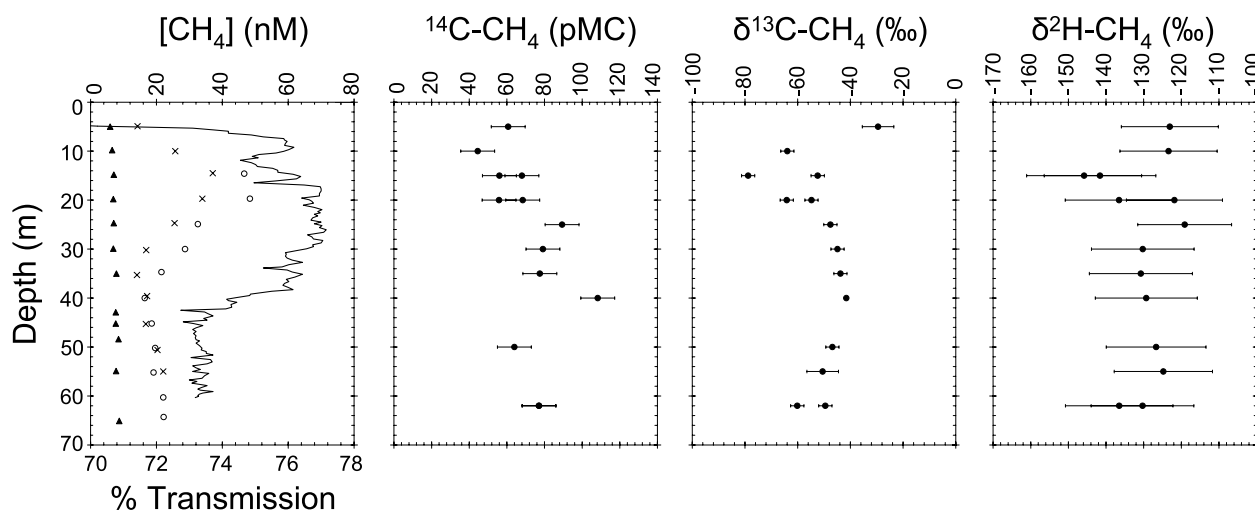
[10] The sediment [CH<sub>4</sub>] showed low surface values but increased rapidly from 20 to 50 cm depth (Figure 4). This concentration profile is similar to previous measurements



**Figure 2.** The  $^{14}\text{C}\text{-CH}_4$  errors as a function of methane concentration (equation (3)) in seawater and sediment caused by diluting small samples ( $<1.81 \mu\text{mol}$ ) with radiocarbon-free  $\text{CO}_2$  to conduct a successful  $^{14}\text{C}$  AMS measurement:  $^{14}\text{C}_{\text{diluent}} = 0.08$ ,  $\sigma_{\text{diluent}} = 0.01$ ,  $F_{\text{seawater}} = ((\text{nM} \times 114\text{L})/1000)/1.81$ ,  $F_{\text{sediment}} = (\mu\text{M} \times 0.35\text{L})/1.81$ , and  $\sigma_F = 0.0056 \times F$ . Solid line,  $^{14}\text{C}_{\text{measured}} = 100$  and  $\sigma_{\text{measured}} = 0.3$ ; long dashed line,  $^{14}\text{C}_{\text{measured}} = 1$  and  $\sigma_{\text{measured}} = 1$ ; short dashed line,  $^{14}\text{C}_{\text{measured}} = 100$  and  $\sigma_{\text{measured}} = 2$ ; dotted line,  $^{14}\text{C}_{\text{measured}} = 1$  and  $\sigma_{\text{measured}} = 7.5$ . The points labeled SMB are from Santa Monica Basin sediment methane (depth = 0–120 cm); the point labeled SBB is from Santa Barbara Basin surface sediment (depth = 0–10 cm); the point labeled CB is from Cariaco Basin surface sediment (depth = 0–5 cm). The principal factor controlling the  $^{14}\text{C}\text{-CH}_4$  error is  $\sigma_{\text{measured}}$ .

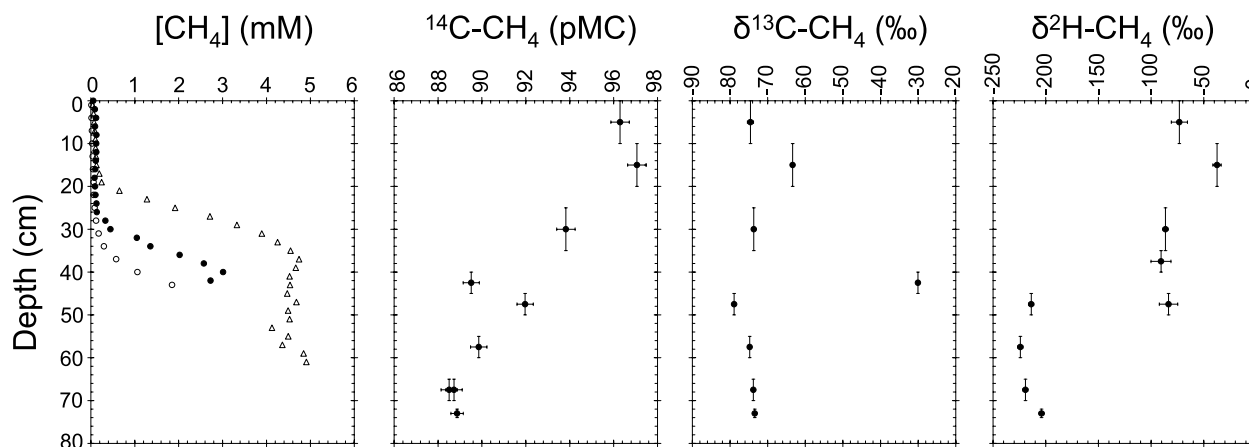
which were shown to be controlled by methanogenesis, anaerobic oxidation of methane, and molecular diffusion [Alperin and Reeburgh, 1984; Alperin et al., 1988; Reeburgh, 1980; Valentine and Reeburgh, 2000]. The natural radiocarbon content of  $\text{CH}_4$  dissolved in SB sediments decreased nearly linearly with depth. Near modern values were displayed in surface sediments (96–98 pMC, 0–20 cm

depth) and within the total measurement depths, the values did not decrease below 88 pMC (Figure 4). The linear increase in  $^{14}\text{C}\text{-CH}_4$  toward surface sediments indicates that  $\text{CH}_4$  is produced locally in the surface sediments and is not dominated by  $\text{CH}_4$  diffusing up from depth. This result is consistent with depth distributions in the  $\delta^{13}\text{C}\text{-CH}_4$  observed previously [Valentine and Reeburgh, 2000] and



**Figure 3.** Skan Bay water column methane concentration, natural isotope results, and transmission data. The methane concentration samples were collected on 30 August 2003, 1500 LT (open circle); 31 August 2003, 1800 LT (cross); and 7 September 2003, 2200 LT (solid triangle) (outside Skan Bay in the open Bering Sea). The transmission data displayed was collected on 31 August 2003 although similar results were obtained during the entire cruise. Samples for natural isotope analyses were collected from 3 to 6 September 2003. The precision of the concentration measurements ( $\pm 1\sigma$ ) is 3–4% and is approximately the width of the data points. Beam transmission is represented by the solid line. The  $^{14}\text{C}\text{-CH}_4$  results are expressed as percent modern carbon (pMC). Isotope measurement errors of  $\pm 1\sigma$  are displayed.



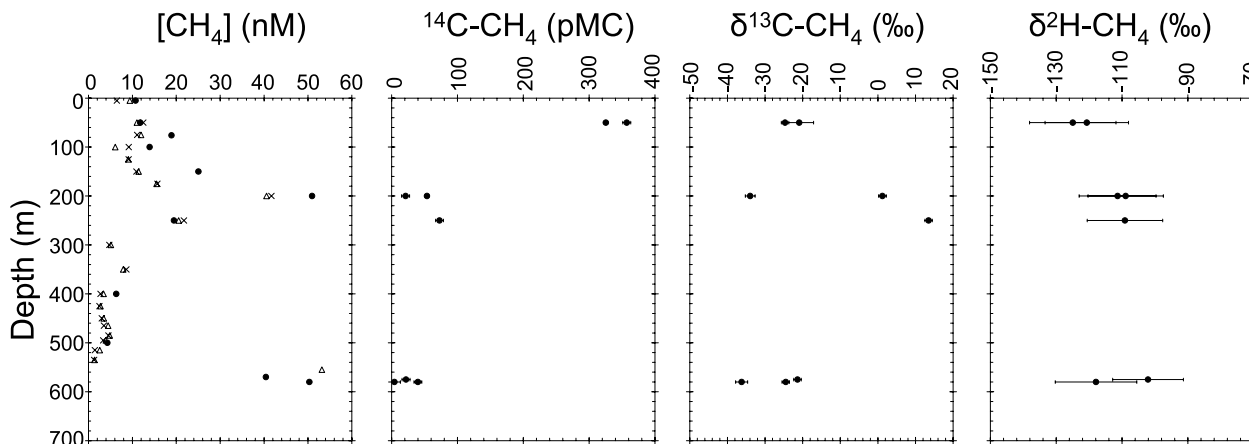


**Figure 4.** Skan Bay sediment methane concentration and natural isotope results. The methane concentration samples were collected on 30 August 2003, box core (open circle); 31 August 2003, box core (solid circle); and 7 September 2003, gravity core (open triangle). Samples for natural isotope analyses were collected from 3 September 2003 (depths from 0 to 50 cm), 5 September 2003 (depths from 55 to 70 cm), and 6 September 2003 (depth 73 cm). Precision of the concentration measurements ( $\pm 1\sigma$ ) is 3–4%. The  $^{14}\text{C}-\text{CH}_4$  results are expressed as percent modern carbon (pMC). Isotope measurement errors of  $\pm 1\sigma$  are displayed.

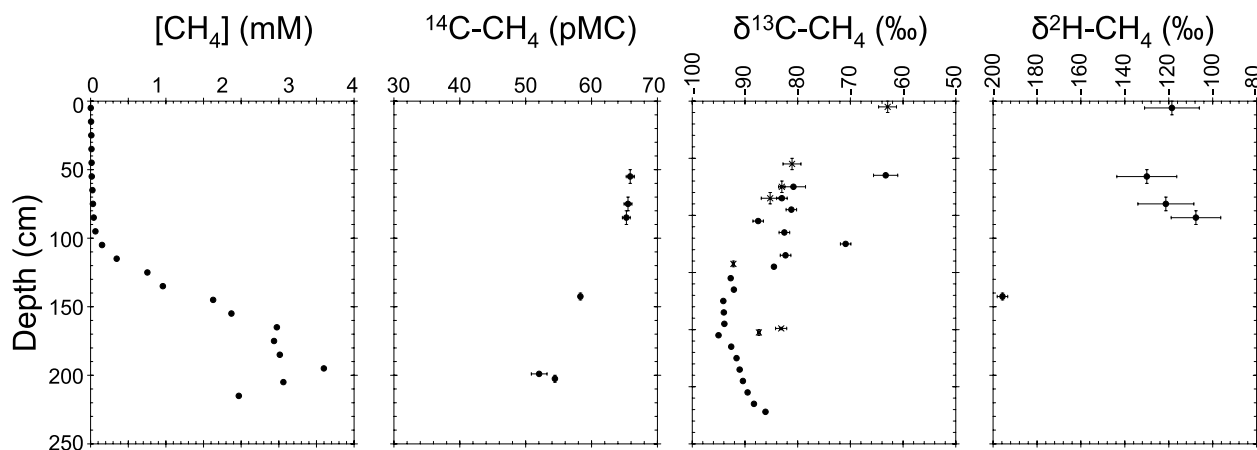
with the cultivation of methanogens from this depth interval [Kendall *et al.*, 2007], and strongly suggests active methanogenesis in this zone. Our stable isotope results are similar to previous analyses [Alperin and Reeburgh, 1984; Alperin *et al.*, 1988; Valentine and Reeburgh, 2000] which demonstrated the effects of diffusion and anaerobic oxidation of methane. A single point in the depth range 40–45 cm has a  $\delta^{13}\text{C}-\text{CH}_4$  value equal to  $-30.1\text{‰}$ , which is heavier than reported in previous studies [Alperin and Reeburgh, 1984; Alperin *et al.*, 1988; Valentine and

Reeburgh, 2000] and may result from local heterogeneities in the bay.

[11] Even though the precision is low owing to low  $\text{CH}_4$  yields, the  $\delta^2\text{H}-\text{CH}_4$  and  $\delta^{13}\text{C}-\text{CH}_4$  results in the subsurface [ $\text{CH}_4$ ] maximum in Skan Bay's water column (15 m depth) suggest a biogenic origin, following the conventions presented by Whiticar [1999]. This  $\text{CH}_4$  could be produced in situ or transported to this zone. As  $\text{CH}_4$  diffuses away from this subsurface [ $\text{CH}_4$ ] maximum, the stable isotopes suggest that it is subjected to water column oxidation. (Oxidizing



**Figure 5.** Santa Barbara Basin water column methane concentration and natural isotope results. The methane concentration samples were collected on 24 June 2004 (solid circle), measured on shore, 22 June 2004 (open triangle), measured at sea, and 22 June 2004 (cross), measured at sea. Samples for natural isotope analyses were collected from 22 June 2004 (depth 250 m), 23 June 2004 (depth 50, 200, 575, 580 m), and 24 June 2004 (depth 50, 200, 580 m). The  $^{14}\text{C}-\text{CH}_4$  results are expressed as percent modern carbon (pMC). The precision is the same as in Figure 4. The possibility exists that the  $\delta^{13}\text{C}-\text{CH}_4$  results at 200 m and 250 m that are  $>0\text{‰}$  display the results of isotopic fractionation during sample preparation; however, this does not influence the  $^{14}\text{C}-\text{CH}_4$  results since they are normalized to such effects [Stuiver and Polach, 1977].

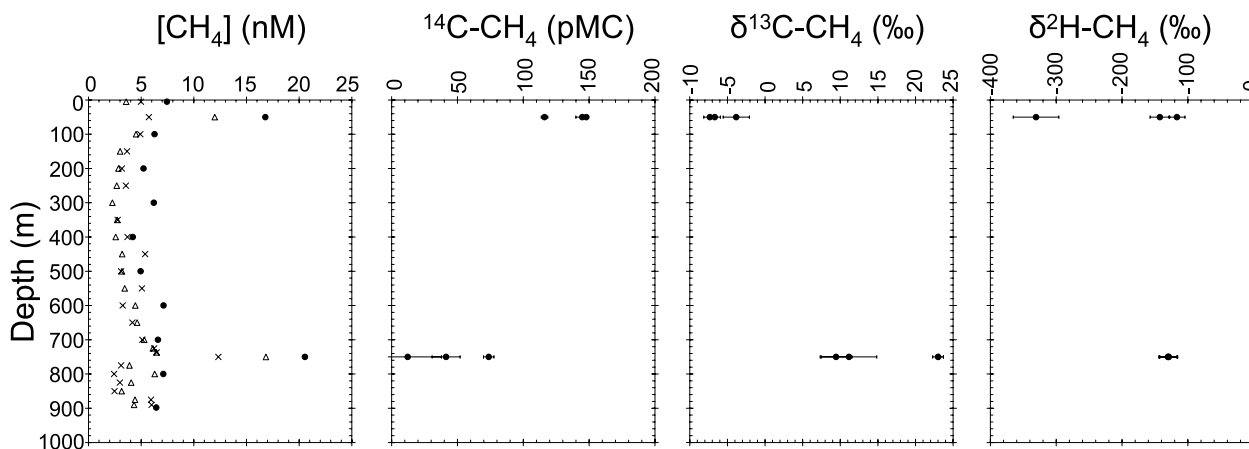


**Figure 6.** Santa Barbara Basin sediment methane concentration and natural isotope results. The methane concentration samples were collected on 24 June 2004. The  $\delta^{13}\text{C-CH}_4$  analyses were conducted at different laboratories using different procedures: University of California Santa Barbara using the procedures of *Kinnaman et al.* [2007] (solid circle) and University of California Irvine using the procedures of *Kessler and Reeburgh* [2005] (cross). All other analyses were conducted using the procedures described in section 2. Samples for natural isotope analyses were collected from 23 June 2004 (depth 199 cm) and 24 June 2004 (all other depths). The  $^{14}\text{C-CH}_4$  results are expressed as percent modern carbon (pMC). The precision is the same as in Figure 4.

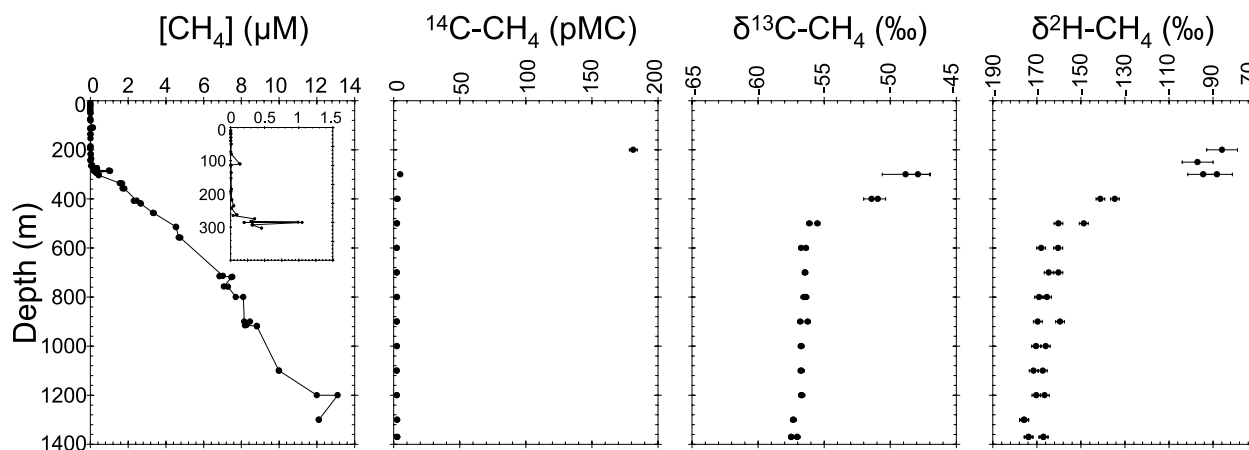
CH<sub>4</sub> causes the residual CH<sub>4</sub> to become enriched in the heavy isotope relative to the source CH<sub>4</sub> [*Kinnaman et al.*, 2007; *Valentine et al.*, 2001].) This potentially biogenic CH<sub>4</sub> in the subsurface maximum did not emanate from the sediments as evidenced from the  $^{14}\text{C-CH}_4$  results.  $^{14}\text{C-CH}_4$  results are not modern between 0 and 20 m depth as would be necessary for a shallow sediment source to the subsurface [CH<sub>4</sub>] maximum (Figure 3), but instead have an average value of 58.9 pMC. The relatively low water column  $^{14}\text{C-CH}_4$  results cannot be attributed to a turnover time of several millennia because (1) this depth interval (0–20 m) is not significantly below the sill depth of 10 m

and exchange with the open Bering Sea is likely rapid and (2) annual winter storms cause the water of Skan Bay to be flushed [*Alperin*, 1989].

[12] The source of this subsurface [CH<sub>4</sub>] maximum has two possible explanations. The CH<sub>4</sub> could be formed in zooplankton guts or fecal pellet microenvironments where the principal substrate is not modern, possibly terrestrial, carbonaceous material [*de Angelis and Lee*, 1994]. This nonmodern carbon substrate theory is supported by the decrease in beam transmission caused by an increase in particulate matter in the near surface waters. Studies at other sites (e.g., southern California) have measured terrestrial



**Figure 7.** Santa Monica Basin water column methane concentration and natural isotope results. The methane concentration samples were collected on 25 June 2004 (solid circle), measured on shore, 21 June 2004 (cross), measured at sea, and 25 June 2004 (open triangle), measured at sea. Samples for natural isotope analyses were collected from 25 June 2004 (one sample at 750 m) and 26 June 2004 (all other samples). The  $^{14}\text{C-CH}_4$  results are expressed as percent modern carbon (pMC). The precision is the same as in Figure 4.



**Figure 8.** Cariaco Basin water column methane concentration and natural isotope results. The methane concentration samples were collected on February to March 1986 [Ward *et al.*, 1987], and the isotope samples were collected on 21–22 January 2004 [Kessler *et al.*, 2005; Kessler and Reeburgh, 2005; Kessler *et al.*, 2006b]. The precision is the same as in Figure 4.

sources of particulate organic carbon (POC) to the ocean via rivers that contain below modern quantities of radiocarbon [Komada *et al.*, 2005, 2004]. However, this scenario would require that the bulk carbon pool be transferred intact during anaerobic fermentation. The <sup>14</sup>C-CH<sub>4</sub> results could also be explained as a combination of seep (fossil) and sediment CH<sub>4</sub> inputs. While no seeps have been discovered in SB we did observe ebullition at the margins and at the sandy beach at the head of the bay. Also, vents and clathrates are present along the Aleutian Islands and in the Bering Sea [Satyavani *et al.*, 2003; Taran *et al.*, 1992] and the Aleutian Islands are a tectonically active region [e.g., Johnson and Satake, 1993]. Several additional studies are needed to confirm the source of this subsurface CH<sub>4</sub>: (1) radiocarbon analyses of POC in the SB water column and riverine POC input to SB and (2) investigating the possibility of seep CH<sub>4</sub> inputs. Presently, we favor the hypothesis that biogenic methane generated deep in the sediments is transported laterally to the sediment-bedrock interface and migrates along this

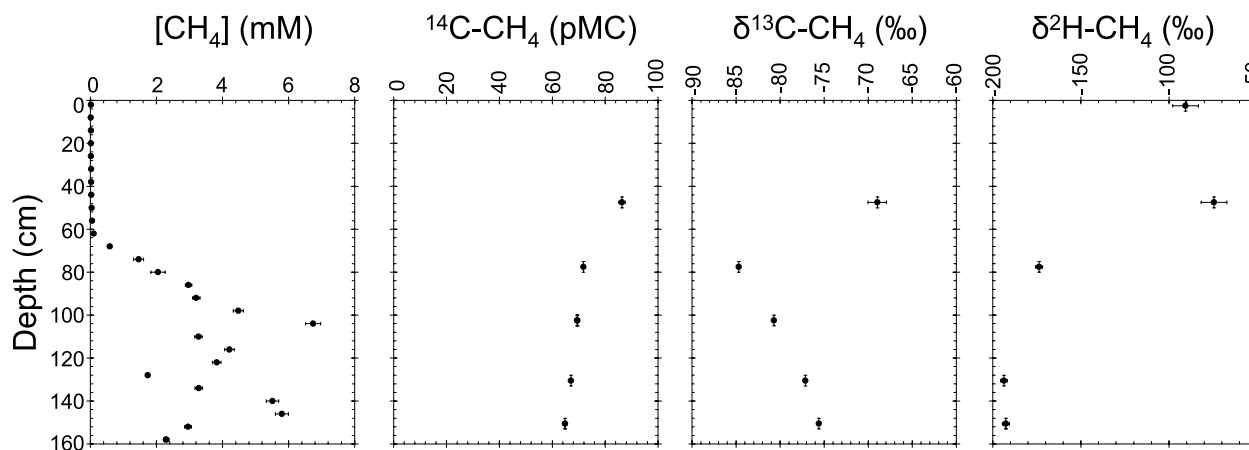
discontinuity until being released into the water column at approximately 20 m water depth.

### 3.2. Santa Barbara, Santa Monica, Cariaco, and Guaymas Basins

#### 3.2.1. Seep and Hydrate Methane

[13] Both SBB and SMB display subsurface and mid-depth [CH<sub>4</sub>] maxima in the water column (Figures 5 and 7). In the SBB, [CH<sub>4</sub>] maxima occurred at 75 m, 200 m, and 580 m depth, while in the SMB, [CH<sub>4</sub>] maxima occurred at 50 m and 750 m depth. In the CB, previous studies have identified [CH<sub>4</sub>] maxima between 100 and 300 m depth [Ward *et al.*, 1987]. The source(s) of these [CH<sub>4</sub>] maxima were investigated by measuring the natural isotopic content of CH<sub>4</sub> dissolved in the water column and sediment of SBB, SMB, and CB as well as emitted from seeps along the SBB and seeps and decomposing clathrates in GB.

[14] Conventional knowledge is that CH<sub>4</sub> emitted from seeps and decomposing clathrates is devoid of natural



**Figure 9.** Cariaco Basin sediment methane concentration and natural isotope results. All methane samples were collected on 23 January 2004 [Kessler *et al.*, 2005, 2006b]. The precision is the same as in Figure 4.



**Table 2.** Seep Gas Samples on the Shelf Adjacent to the Santa Barbara Basin: Isotopic Measurements on Pure Methane Component

Sample	pMC	$\pm 1\sigma$	$\delta^{13}\text{C}$	$\pm 1\sigma$	$\delta^2\text{H}$	$\pm 1\sigma$
Brian Seep Vial1	0.21	0.02	-41.66	0.20	-187.5	2.4
Brian Seep Vial3	0.10	0.02	-42.00	0.20	-188.7	2.4
Brian Seep Vial5	0.08	0.02	-42.04	0.20	-191.9	2.4
Shane Seep Vial2	0.11	0.02	-50.49	0.20	-206.6	2.4
Shane Seep Vial4	0.08	0.02	-50.48	0.20	-209.9	2.4
Shane Seep Vial6	0.01	0.02	-50.53	0.20	-207.2	2.4
Shane Seep VialGas3	0.00	0.02	-50.57	0.20	-210.7	2.4
Shane Seep VialGas6	-0.02	0.02	-50.53	0.20	-209.1	2.4

radiocarbon, however, the number of measurements testing this is extremely small. In the Gulf of Mexico (Bush Hill) and Cascadia Margin (Hydrate Ridge and Bullseye Vent), clathrate and vent CH<sub>4</sub> was shown to be devoid of natural radiocarbon [Grabowski *et al.*, 2004; Winckler *et al.*, 2002]. However, in the Black Sea, CH<sub>4</sub> emitted from seeps on the northwestern Black Sea shelf contained small, but measurable, amounts of radiocarbon ( $5.0 \pm 0.4$  pMC) [Kessler *et al.*, 2006a]. We measured the natural isotopic content of CH<sub>4</sub> emitted from seeps along the margin of the SBB and seeps and decomposing clathrates in GB, to further classify this CH<sub>4</sub> reservoir and ultimately aid in determining the source of [CH<sub>4</sub>] maxima in the water column. Along the SBB, 8 seep samples were collected in the vicinity of Brian Seep and Shane Seep (Table 2). In GB, 11 seep samples from natural seeps, 3 seep samples from a seep formed when excavating the surface sediments, 1 sediment and methane clathrate hydrate sample, and 1 sediment gas sample were collected (Table 3). The radiocarbon analyses all displayed similar values; the CH<sub>4</sub> is almost devoid of radiocarbon ( $^{14}\text{C-CH}_4 = 0.2 \pm 0.1$  pMC) although Shane Seep displayed the most  $^{14}\text{C}$  depleted values ( $^{14}\text{C-CH}_4 = 0.04 \pm 0.06$  pMC) and GB displayed the most  $^{14}\text{C}$  enriched values ( $^{14}\text{C-CH}_4 = 0.26 \pm 0.06$  pMC). The stable isotopes suggest a thermogenic source according to the conventions presented by Whiticar [1999] (Brian Seep  $\delta^{13}\text{C-CH}_4 = -41.90 \pm 0.21\%$ ,  $\delta^2\text{H-CH}_4 = -189.4 \pm 2.3\%$ ; Shane Seep  $\delta^{13}\text{C-CH}_4 = -50.52 \pm 0.04\%$ ,  $\delta^2\text{H-CH}_4 = -208.7 \pm 1.8\%$ ;

GB  $\delta^{13}\text{C-CH}_4 = -53.55 \pm 0.94\%$ ,  $\delta^2\text{H-CH}_4 = -189.2 \pm 3.4\%$ ).

### 3.2.2. Sediment Methane

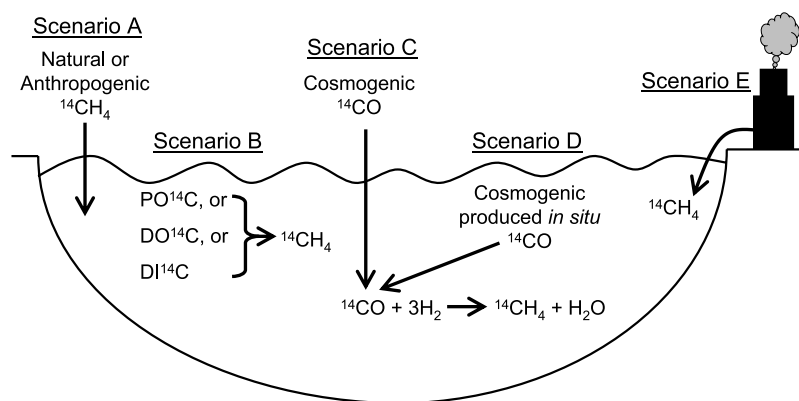
[15] The radiocarbon content of SBB sediment CH<sub>4</sub> decreased with depth (Figure 6). The results are similar to SB in that the  $^{14}\text{C-CH}_4$  content is greater above the zone of anaerobic oxidation of methane (~100 cm depth in SBB) than below, indicating that anaerobic oxidation is a near-quantitative sink of CH<sub>4</sub> diffusing upward and the dominant source of CH<sub>4</sub> to near surface sediments is local methanogenesis. The youngest value measured (67 pMC) occurred at 50 cm depth. The only sample measured above 50 cm contained a [CH<sub>4</sub>] below the quantification limit, leading to qualitative results (Figure 2). In the SMB, our sediment coring did not penetrate deep enough to reach regions of high [CH<sub>4</sub>], so the  $^{14}\text{C-CH}_4$  results were unquantifiable (Figure 2). The CH<sub>4</sub> dissolved in CB sediments contained modern quantities of radiocarbon (Figure 9). The highest value measured occurred at a depth interval of 45–50 cm and contained a value of 86.4 pMC. One sample was collected in the depth interval of 0–5 cm, but low [CH<sub>4</sub>] led to a qualitative result (Figure 2).

### 3.2.3. Water Column [CH<sub>4</sub>] Maxima

[16] In the water columns of both the SBB and SMB, the results varied depending on the time of sampling (Figures 5 and 7). The middepth and subsurface [CH<sub>4</sub>] maxima in the southern California Bight have been observed to vary on times scales of hours as well as seasons [Ward, 1992; Ward and Kilpatrick, 1993]. The variation in the concentration maxima, which may be correlated with some variation in our natural isotope results, has been suspected to be caused by internal tides and waves, wind events, and variability of in situ production [Burke *et al.*, 1983; Cynar and Yayanos, 1992; Cynar and Yayanos, 1993; de Angelis and Lee, 1994; Ward, 1992; Ward and Kilpatrick, 1993]. Our water column stable isotope results indicate a CH<sub>4</sub> source that has undergone significant microbial oxidation because the isotopically lighter CH<sub>4</sub> reacts faster than the heavier CH<sub>4</sub> leaving the residual CH<sub>4</sub> isotopically enriched in the heavy isotope. The middepth and deep basin [CH<sub>4</sub>] maxima in both the SBB and SMB displayed highly variable results; the  $^{14}\text{C-CH}_4$  content varied from 4 to 74 pMC over a sampling period of

**Table 3.** Guaymas Basin, Gulf of California: Isotopic Measurements on Pure Methane Component

Sample	Description	pMC	$\pm 1\sigma$	$\delta^{13}\text{C}$	$\pm 1\sigma$	$\delta^2\text{H}$	$\pm 1\sigma$
T0563-BLACK	Vent Gas	0.30	0.02	-54.03	0.20	-191.2	2.4
T0563-BLUE	Vent Gas	0.28	0.02	-54.19	0.20	-192.2	2.4
T0563-RED	Vent Gas	0.31	0.02	-53.93	0.20	-191.6	2.4
T0566-BLACK	Vent Gas	0.20	0.02	-53.95	0.20	-189.5	2.4
T0566-BLUE	Vent Gas	0.31	0.02	-53.82	0.20	-193.8	2.4
T0566-RED	Vent Gas	0.33	0.02	-54.20	0.20	-190.3	2.4
T0573-BLACK	Vent Gas	0.21	0.02	-53.41	0.20	-187.4	2.4
T0573-BLUE	Vent Gas	0.17	0.02	-53.07	0.20	-189.8	2.4
T0573-RED	Vent Gas	0.19	0.02	-53.01	0.20	-190.4	2.4
T0578-BLACK	Vent Gas	0.31	0.02	-53.44	0.20	-185.5	2.4
T0578-BLUE	Vent Gas	0.15	0.02	-53.46	0.20	-188.2	2.4
T0576-BLACK	Excavation Vent	0.21	0.02	-53.08	0.20	-183.8	2.4
T0576-BLUE	Excavation Vent	0.28	0.02	-53.37	0.20	-185.5	2.4
T0578-RED	Excavation Vent	0.24	0.02	-49.64	0.20	-184.7	2.4
T0576-RED	Sediment Gas	0.23	0.02	-53.44	0.20	-185.8	2.4
T0582-RED	Sediment Gas + Clathrate	0.29	0.02	-53.77	0.20	-187.5	2.4



**Figure 10.** Schematic diagram of possible sources of  $^{14}\text{CH}_4$  to the subsurface ocean. scenario A:  $^{14}\text{CH}_4$  that forms naturally (cosmogenically) or anthropogenically in the atmosphere and diffuses into the subsurface ocean; scenario B: POC, DOC, or DIC that has elevated quantities of radiocarbon that is a substrate for  $\text{CH}_4$  formation; scenario C:  $^{14}\text{CO}$  that is formed cosmogenically in the atmosphere, diffuses into the subsurface ocean, and is reduced to  $^{14}\text{CH}_4$ ; scenario D:  $^{14}\text{CO}$  that is formed cosmogenically in the subsurface ocean and is reduced to  $^{14}\text{CH}_4$ ; scenario E:  $\text{CH}_4$  emitted from nuclear power plants that has elevated quantities of radiocarbon.

10 days. Clearly multiple sources of  $\text{CH}_4$  exist to these middepth and deep basin  $[\text{CH}_4]$  maxima with  $\text{CH}_4$  endmembers containing a  $^{14}\text{C}$ - $\text{CH}_4$  content that is either approximately radiocarbon-free or approximately modern. A larger, time-dependent data set related to physical and biological parameters is necessary to more completely characterize this system.

[17] The subsurface  $[\text{CH}_4]$  maxima in SBB, SMB and CB contained greater than modern radiocarbon contents (Figures 5, 7, and 8). In the SMB at 50 m depth, the  $^{14}\text{C}$ - $\text{CH}_4$  results vary between 116 and 148 pMC. In the CB, the  $^{14}\text{C}$ - $\text{CH}_4$  content of the subsurface  $[\text{CH}_4]$  maximum (200 m depth) is  $180 \pm 3$  pMC (Figure 8). Finally, in the SBB water column, highly elevated  $^{14}\text{C}$ - $\text{CH}_4$  values of 325 to 357 pMC were measured in the near surface waters at 50 m depth (Figure 5). These elevated  $^{14}\text{C}$ - $\text{CH}_4$  values do not appear to be the results of sample contamination.

[18] These highly elevated subsurface  $^{14}\text{C}$ - $\text{CH}_4$  results may display the influence of three different processes: (1) atmospheric nuclear weapons testing, (2) cosmogenic isotope production, or (3) nuclear power plant effluents (Figure 10). These three processes are considered in the following sections.

### 3.2.3.1. Atmospheric Nuclear Weapons Testing as a Possible Source of $^{14}\text{CH}_4$ to the Subsurface Ocean

[19] Elevated quantities of radiocarbon were injected into the atmosphere and ocean as a result of the testing of nuclear weapons. This “bomb” carbon reached a peak in the atmosphere in year 1964 with a value of 190 pMC [Levin and Kromer, 2004]. If this bomb carbon selectively took the form of  $\text{CH}_4$  and entered the near surface waters, it could account for our observations in the SMB and CB (Figure 10, scenario A). Beginning in 1987, measurements began to be conducted showing that the atmospheric content of  $^{14}\text{C}$ - $\text{CH}_4$  ranges from 92 to 135 pMC [Lassey et al., 2007b; Lowe et al., 1988]. Also, particulate organic carbon (POC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) containing bomb  $^{14}\text{C}$  may serve

as substrates for  $\text{CH}_4$  formation in the subsurface ocean (Figure 10, scenario B). Radiocarbon measurements on POC, DOC, and DIC indicate that the  $^{14}\text{C}$  content does not exceed 120 pMC [Druffel et al., 1996; Druffel et al., 1992; Druffel et al., 1989; Williams et al., 1992] in the SMB, central North Pacific Ocean, or the Sargasso Sea. The  $^{14}\text{C}$ - $\text{CH}_4$  results observed in the SMB and CB are so elevated that the carbon source for  $\text{CH}_4$  formation would have to be almost entirely from bomb carbon and exclude mixing with other sources. Thus, it seems unlikely that bomb carbon is the source of the elevated  $^{14}\text{C}$ - $\text{CH}_4$  signal in the SMB and CB, however, we cannot rule out this possibility. Clearly, bomb carbon is not the source of  $\text{CH}_4$  to the subsurface SBB.

### 3.2.3.2. Cosmogenic Isotope Production as a Possible Source of $^{14}\text{CH}_4$ to the Subsurface Ocean

[20] Radiocarbon produced by nuclear spallation of oxygen by cosmic ray neutrons may also explain the elevated  $^{14}\text{C}$ - $\text{CH}_4$  values measured in the near surface waters of the CB, SMB, and SBB. The production of  $^{14}\text{C}$  atoms can occur in the lower atmosphere as well as in near surface waters and ice [Lal and Jull, 1990; Lal et al., 1990, 1987; MacKay et al., 1963]. The  $^{14}\text{C}$  atom first reacts with  $\text{O}_2$  forming  $^{14}\text{CO}$  [Lal and Jull, 1990; Lal et al., 1987; MacKay et al., 1963]. Away from anthropogenic contamination, the lower troposphere  $\text{CO}$  radiocarbon content is elevated beyond what is attributable to atmospheric nuclear weapons testing [Jöckel et al., 1999; Mak et al., 1994; Quay et al., 2000]. This  $^{14}\text{CO}$  may diffuse into surface waters (Figure 10, scenario C) or be produced in situ (Figure 10, scenario D) [Lal and Jull, 1990]. This cosmogenic  $^{14}\text{CO}$  could then be reduced in the subsurface ocean to  $^{14}\text{CH}_4$  and contribute to the observed elevated  $^{14}\text{C}$ - $\text{CH}_4$  signal. However, several lines of evidence show that this is an unlikely explanation.

[21] First, we calculate the percent of the elevated  $^{14}\text{CH}_4$  pool that is from  $^{14}\text{CO}$  formed in the atmosphere which diffuses into the subsurface ocean (Figure 10, scenario C).

We convert the measured values of <sup>14</sup>C-CH<sub>4</sub> from pMC to [<sup>14</sup>CH<sub>4</sub>] [Karlen *et al.*, 1968; Stuiver and Polach, 1977]:

$$\text{pMC} = \frac{R_{\text{sample}}}{R_{\text{Std}}} 100, \quad (4)$$

$$\text{pMC} = \frac{\left(\frac{[^{14}\text{CH}_4]}{[^{12}\text{CH}_4]}\right)_{\text{sample}} \left(1 - \frac{2(25+\delta^{13}\text{C})}{1000}\right)_{\text{sample}}}{0.95 \times 1.176 \times 10^{-12}} 100, \quad (5)$$

$$\frac{[^{14}\text{CH}_4]}{[^{12}\text{CH}_4]_{\text{sample}}} = \frac{\text{pMC} \cdot 0.95 \times 1.176 \times 10^{-12}}{100 \left(1 - \frac{2(25+\delta^{13}\text{C})}{1000}\right)}. \quad (6)$$

Given the measured values of <sup>14</sup>C-CH<sub>4</sub> (150 to 350 pMC), [<sup>12</sup>CH<sub>4</sub>] (20 to 50 nM), and δ<sup>13</sup>C (~−40‰), [<sup>14</sup>CH<sub>4</sub>]<sub>sample</sub> = 3.3 × 10<sup>−11</sup> to 1.9 × 10<sup>−10</sup> nM. Next, by taking the radiocarbon content of atmospheric CO that was observed in the remote atmosphere away from fossil fuel influences (10 to 30 molecules of <sup>14</sup>CO per cm<sup>3</sup> of air [Jöckel *et al.*, 1999]) and combining it with the solubility of CO in seawater (0.02 L of CO per liter of H<sub>2</sub>O [Schmidt, 1979]), this possible source only supplies a [<sup>14</sup>CO] in seawater ranging from 3 to 9 × 10<sup>−13</sup> nM. Even if this <sup>14</sup>CO is quantitatively reduced to <sup>14</sup>CH<sub>4</sub>, cosmogenic <sup>14</sup>CO that is formed in the atmosphere and diffuses into the subsurface ocean only accounts for 0.2 to 2.8% of the observed [<sup>14</sup>CH<sub>4</sub>] in the SMB, SBB, and CB.

[22] Second, cosmogenic <sup>14</sup>C could be formed directly in subsurface seawater (Figure 10, scenario D), however, the estimated production rate (9 × 10<sup>−3</sup> at. cm<sup>−2</sup> min<sup>−1</sup> [Lal *et al.*, 1988]) is too low to support the observed signals. We assume that the cosmogenic <sup>14</sup>C produced primarily in the uppermost 1–2 m is homogenized over a depth of 200 m, to the depth of our observed signals; this assumption converts the in situ production rate from Lal *et al.* [1988] to 1.1 × 10<sup>−15</sup> nmol of <sup>14</sup>CH<sub>4</sub> L<sup>−1</sup> d<sup>−1</sup>. As a first-order estimate, we assume that the oxidation of <sup>14</sup>CH<sub>4</sub> in the subsurface [CH<sub>4</sub>] maxima balances the production of <sup>14</sup>CH<sub>4</sub>. Several studies have measured the CH<sub>4</sub> oxidation rate in subsurface [CH<sub>4</sub>] maxima with values ranging from 0.01 to 0.08 nmol L<sup>−1</sup> d<sup>−1</sup> [Ward and Kilpatrick, 1993; Ward *et al.*, 1987]; we translate these total CH<sub>4</sub> oxidation rates to the oxidation rate of <sup>14</sup>CH<sub>4</sub> by multiplying by the ratio of [<sup>14</sup>CH<sub>4</sub>]/[<sup>12</sup>CH<sub>4</sub>], calculated with equations (4)–(6), resulting in <sup>14</sup>CH<sub>4</sub> oxidation rates ranging from 1.6 × 10<sup>−14</sup> to 3.0 × 10<sup>−13</sup> nmol of <sup>14</sup>CH<sub>4</sub> L<sup>−1</sup> d<sup>−1</sup>. Thus, in situ cosmogenic <sup>14</sup>C production only accounts for 0.4 to 6.9% of the necessary source of <sup>14</sup>C needed to balance the oxidation of <sup>14</sup>CH<sub>4</sub>.

[23] Third, even if these calculations underestimate the contribution of <sup>14</sup>CO from the atmosphere or produced cosmogenically in situ, abiotic or biotic reactions between <sup>14</sup>CO and H<sub>2</sub> needed to produce <sup>14</sup>CH<sub>4</sub>, require 3 molecules of H<sub>2</sub> per <sup>14</sup>CO molecule and may be prohibited owing to low H<sub>2</sub> concentrations [Bullister *et al.*, 1982; Herr and Barger, 1978; Herr *et al.*, 1981; Scranton *et al.*, 1984]. Unfortunately, no radiocarbon measurements on CO dissolved in ocean waters have been reported. Given an oceanic CO concentration of 4 nM [Bullister *et al.*, 1982; Jones, 1991; Wilkniss *et al.*, 1979], this would require the

quantitative extraction of CO from 525 L of seawater to collect 2.1 μmol of carbon for a <sup>14</sup>C AMS measurement.

[24] Fourth, cosmogenic <sup>14</sup>C produced in the atmosphere can diffuse into the surface waters of the ocean, and Lal *et al.* [1988] estimate this flux to be 120 at. cm<sup>−2</sup> min<sup>−1</sup>. As above, we assume that this cosmogenic <sup>14</sup>C is homogenized over a depth of 200 m to the depth of our observed signals and that the oxidation of <sup>14</sup>CH<sub>4</sub> is balanced by the source of <sup>14</sup>C from the atmosphere to 1.4 × 10<sup>−11</sup> nmol of <sup>14</sup>CH<sub>4</sub> L<sup>−1</sup> d<sup>−1</sup>, while the second assumption is used with equations (4)–(6) to convert total CH<sub>4</sub> oxidation rates measured in subsurface maxima [Ward and Kilpatrick, 1993; Ward *et al.*, 1987] to <sup>14</sup>CH<sub>4</sub> oxidation rates ranging from 1.6 × 10<sup>−14</sup> to 3.0 × 10<sup>−13</sup> nmol of <sup>14</sup>CH<sub>4</sub> L<sup>−1</sup> d<sup>−1</sup>. Only 0.1 to 2.1% of this atmospheric cosmogenic <sup>14</sup>C source is necessary to account for the observed <sup>14</sup>C and balance <sup>14</sup>CH<sub>4</sub> oxidation [Ward and Kilpatrick, 1993; Ward *et al.*, 1987]. While cosmogenic <sup>14</sup>C that is formed in the atmosphere and diffuses into surface seawater easily provides enough atoms of <sup>14</sup>C to account for the observed signals in the SMB, SBB, and CB, this most likely is not the source of <sup>14</sup>CH<sub>4</sub>. If this <sup>14</sup>C enters the ocean as <sup>14</sup>CO<sub>2</sub>, it is immediately diluted with DIC (Figure 10, scenario B). No oceanic measurements of <sup>14</sup>C DIC have been shown to be greater than what is attributable to the atmospheric testing of nuclear weapons. And as we showed above, the injection of atmospheric <sup>14</sup>CO and <sup>14</sup>CH<sub>4</sub> (Figure 10, scenarios A and C), is not strong enough to account for the observed subsurface results, especially in SBB. If cosmogenic <sup>14</sup>C that is formed in the atmosphere is truly the source of the elevated quantities of <sup>14</sup>CH<sub>4</sub> to subsurface [CH<sub>4</sub>] maxima, it is currently unknown what molecular form of <sup>14</sup>C enters the ocean.

### 3.2.3.3. Nuclear Power Plant Effluents as a Possible Source of <sup>14</sup>CH<sub>4</sub> to the Subsurface Ocean

[25] Southern California has several nuclear power plants which use ocean water for cooling: Diablo Canyon (near San Luis Obispo) and San Onofre (halfway between Los Angeles and San Diego). The possibility exists that the elevated values in the SMB and SBB are the results of contaminated effluents (Figure 10, scenario E). Measurements have confirmed that pressurized light water reactors and boiling water reactors are sources of <sup>14</sup>CH<sub>4</sub> to the atmosphere with emissions (proportional to the electrical power generated) of 219 and 24 GBq GWe<sup>−1</sup> a<sup>−1</sup>, respectively [Eisma *et al.*, 1995; Hertelendi *et al.*, 1989; Kunz, 1985; Wahlen *et al.*, 1989]. Recently, these estimates have been extrapolated to a global estimate of <sup>14</sup>CH<sub>4</sub> emitted from nuclear power production of 286 ± 26 GBq GWe<sup>−1</sup> a<sup>−1</sup> [Lassey *et al.*, 2007a, 2007b]. Eisma *et al.* [1995] reported the pMC of CH<sub>4</sub> emitted from nuclear power plants in northwestern Europe with values ranging from 124.3 to 467.1 pMC. If similar radiocarbon contents of CH<sub>4</sub> are released by the nuclear power plants along the Southern California coast, this could provide the most plausible explanation of the observed SBB and SMB results. Unfortunately, the number of measurements of this elevated <sup>14</sup>C-CH<sub>4</sub> maximum in the SBB and SMB is small with no time series or transects data. Until a larger sampling effort is undertaken, nuclear power byproducts should be viewed as



the most plausible explanation rather than the definitive source.

#### 4. Conclusions

[26] Natural isotopic measurements (<sup>14</sup>C-CH<sub>4</sub>, δ<sup>2</sup>H-CH<sub>4</sub>, δ<sup>13</sup>C-CH<sub>4</sub>) were used to study CH<sub>4</sub> cycling among seeps, sediments, and the water column to gain insight into the sources of subsurface and middepth [CH<sub>4</sub>] maxima in the ocean water column. These experiments highlight the quantification limitations of the current procedures. While we measured the natural isotopic content of subsurface [CH<sub>4</sub>] maxima with concentrations ranging from 15 to 50 nM, the background seawater [CH<sub>4</sub>] is approximately 2 nM. Using the established procedures [Kessler and Reeburgh, 2005], radiocarbon measurements are currently unquantifiable at these background concentrations. Two main factors control the sensitivity of these procedures: (1) the variability of the size of the blank and (2) the size of the sample recovered. If a new procedure is developed or the current procedures are modified to recover more CH<sub>4</sub> by quantitatively extracting CH<sub>4</sub> from a larger volume of water, then the sensitivity may increase.

[27] In SB, the subsurface [CH<sub>4</sub>] maximum is not solely from modern anoxic sediments. A source of older carbon clearly contributes to the maximum, however, it is currently unknown if that older CH<sub>4</sub> source is from previously unknown seeps or a substrate of older carbon used for CH<sub>4</sub> formation in the water column. The subsurface [CH<sub>4</sub>] maxima in the SBB, SMB, and CB contains quantities of radiocarbon greater than modern and is clearly not emitted from seeps or decomposing clathrates. In the SMB and CB, this elevated <sup>14</sup>C-CH<sub>4</sub> content could be from the atmospheric testing of nuclear weapons; while this is a plausible explanation, it is not probable as it excludes mixing with any other sources of CH<sub>4</sub> and other carbon sources used for CH<sub>4</sub> formation. In the SBB, the <sup>14</sup>C-CH<sub>4</sub> content ranges from 325 to 357 pMC which is definitely too high to be attributed to the atmospheric testing of nuclear weapons. The source of this “hot” <sup>14</sup>C-CH<sub>4</sub> in the SBB, and possibly also in the SMB, is most likely not from cosmogenic production and the most plausible explanation may be from nuclear power plant effluents. The fact that SB does not contain elevated <sup>14</sup>C-CH<sub>4</sub> quantities similar to what is found in SBB, SMB, and CB is an exciting observation. Cosmogenic isotope production and the atmospheric testing of nuclear weapons are globally distributed sources of <sup>14</sup>C. In fact, high-latitude sites have less geomagnetic shielding, so SB should have more cosmogenic contributions to subsurface <sup>14</sup>C-CH<sub>4</sub>. However, SB is significantly smaller and has a much shallower depth than SBB, SMB, and CB and upwelling, mixing, and ventilation as well as dilution with methane from sediment and coastal sources are more rapid and likely to occur processes.

[28] This data set provides surprising results of the isotopic content of CH<sub>4</sub> in subsurface [CH<sub>4</sub>] maxima. Particularly surprising results occurred in the SBB, SMB, and CB, which show for the first time that the subsurface ocean contains elevated <sup>14</sup>C-CH<sub>4</sub> values ranging from 1.2 to 3.6 times modern. These elevated results point to a source of <sup>14</sup>C from atmospheric nuclear weapons testing, nuclear power plant effluents, or cosmogenic isotope production. Unfortunately, the number of samples analyzed globally in

the elevated <sup>14</sup>C-CH<sub>4</sub> subsurface maxima is small ( $n = 6$ ), so larger data sets involving time series measurements and transects are clearly necessary for more definitive explanations. The existing techniques are very labor intensive, thus limiting the number of samples we can analyze per cruise, and are not sensitive down to the background [CH<sub>4</sub>] in seawater. This scale of a sampling effort is contingent upon the development of new isotopic sampling, preparation, and analysis methods so that the natural isotopes of oceanic CH<sub>4</sub> can be studied without the existing limitations.

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