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Controls on methane concentration and stable isotope (δ^2H-CH_4 and δ^{13}C-CH_4) distributions in the water columns of the Black Sea and Cariaco Basin

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[1] Methane (CH_4) concentration and stable isotope (δ^2H-CH_4 and δ^{13}C-CH_4) depth distributions show large differences in the water columns of the Earth's largest CH_4-containing anoxic basins, the Black Sea and Cariaco Basin. In the deep basins, the between-basin stable isotope differences are large, 83‰ for δ^2H-CH_4 and 9‰ for δ^{13}C-CH_4, and the distributions are mirror images of one another. The major sink in both basins, anaerobic oxidation of CH_4, results in such extensive isotope fractionation that little direct information can be obtained regarding sources. Recent measurements of natural ^{14}C-CH_4 show that the CH_4 geochemistry in both basins is dominated (~64 to 98%) by inputs of fossil (radiocarbon-free) CH_4 from seafloor seeps. We derive open-system kinetic isotope effect equations and use a one-dimensional (vertical) stable isotope box model that, along with isotope budgets developed using radiocarbon, permits a quantitative treatment of the stable isotope differences. We show that two main factors control the CH_4 concentration and stable isotope differences: (1) the depth distributions of the input of CH_4 from seafloor seeps and (2) anaerobic oxidation of CH_4 under open-system steady state conditions in the Black Sea and open-system non-steady-state conditions in the Cariaco Basin.

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1. Introduction

[2] The Black Sea and Cariaco Basin are two large permanently anoxic basins that have been sites of numerous studies of methane (CH_4) geochemistry [e.g., *Amouroux et al.*, 2002; *Atkinson and Richards*, 1967; *Ivanov et al.*, 2002; *Reeburgh*, 1976; *Reeburgh et al.*, 1991; *Scranton*, 1988; *Ward et al.*, 1987; *Wiesenburg*, 1975]. The source of CH_4 to the water column in both of these basins was originally considered to be from sediment diagenesis [e.g., *Reeburgh*, 1976; *Reeburgh et al.*, 1991; *Scranton*, 1988]. A sink-based CH_4 budget for the Black Sea was assembled from CH_4 concentration ([CH_4]) and oxidation rate measurements conducted in the water column and sediments at a central and shelf station in July 1988 [*Reeburgh et al.*, 1991]. This budget showed that the diffusive flux of CH_4 from sediments was too small to balance the major CH_4 sink from the water column, anaerobic oxidation of CH_4 (AOM), suggesting an additional CH_4 source. Subsequent reports of seeps, CH_4 clathrate hydrates (clathrates), mud volcanoes, and pockmarks [*Ginsburg et al.*, 1990; *Gulin et al.*, 2003; *Luth et al.*, 1999; *Michaelis et al.*, 2002; *Pape et al.*, 2003; *Vassilev and Dimitrov*, 2002], suggested that fossil (radiocarbon-free) CH_4 may be the dominant source of CH_4 to the Black Sea.

[3] The source of CH_4 to the Cariaco Basin was first investigated with a steady state vertical advection-diffusion model [*Fanning and Pilson*, 1972; *Reeburgh*, 1976]. The steady state assumption used in these Cariaco Basin studies was later challenged and a time-dependent geochemical box model was developed to study CH_4 geochemistry [*Scranton*, 1988; *Scranton et al.*, 1987]. Both steady state and non-steady-state investigations [*Reeburgh*, 1976; *Scranton*, 1988] concluded that AOM occurred, and that diffusion of CH_4, produced by diagenesis in the sediments ($CH_{4[D]}$), provided the source to the water column. Recent natural radiocarbon measurements on Black Sea and Cariaco Basin CH_4 (^{14}C-CH_4) have shown that fossil CH_4 emitted from seeps ($CH_{4[S]}$), not $CH_{4[D]}$, is the dominant source to both water columns [*Kessler et al.*, 2006, 2005].

[4] Here we report [CH_4] and stable isotope (δ^2H-CH_4 and δ^{13}C-CH_4) measurements for the Black Sea and Cariaco Basin (Figures 1 and 2; Figure 3 for Cariaco Basin sediments; and Table 1 for Black Sea seeps). The similarities in CH_4 sources, structure, and marine setting of both basins suggest that the δ^2H-CH_4 and δ^{13}C-CH_4 distributions in the water column might be similar, but the between-basin stable

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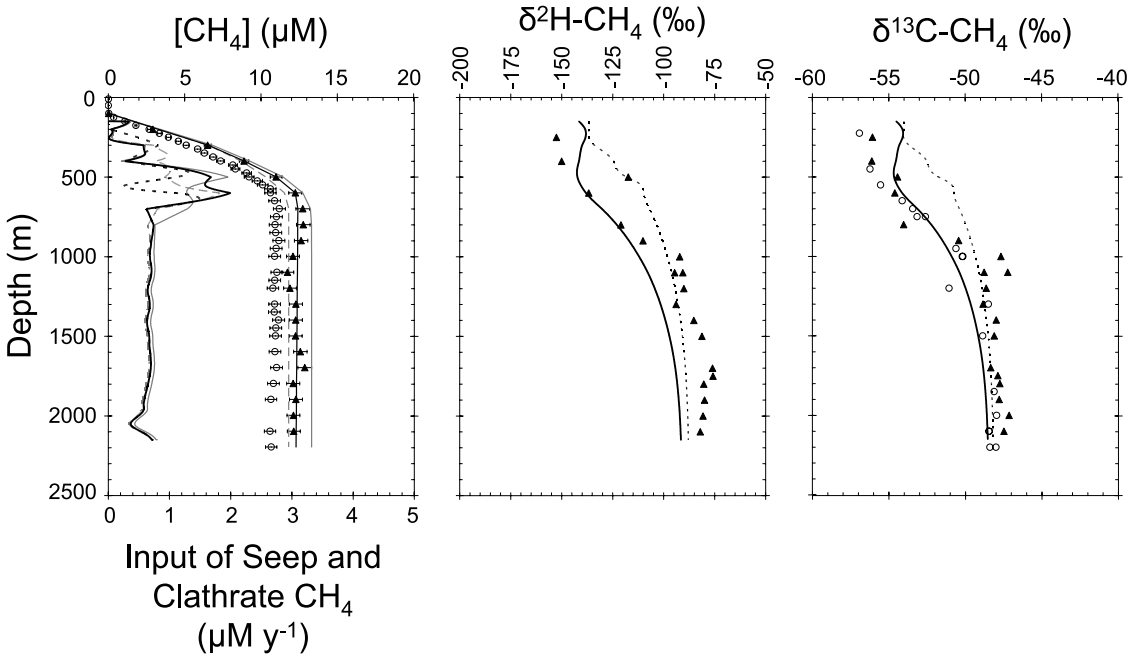

Figure 1. Measured Black Sea CH_4 stable isotope (δ^2H-CH_4 and δ^{13}C-CH_4) and [CH_4] (μM) data collected in the water column in (triangles) May 2001 in the western Black Sea and (circles) July 1988 in the central Black Sea [*Reeburgh et al.*, 2006, 1991]. Precision of the (1) [CH_4] measurements is ±3–4% based on replicate analyses of samples, (2) δ^2H-CH_4 measurements is 2.4‰ based on replicate analyses of standard samples, and (3) δ^{13}C-CH_4 measurements is 0.2‰ based on replicate analyses of standard samples. Error bars for the stable isotope measurements are less than the width of the data points. The black and gray lines (solid, dashed, and dotted) represent the model results in the Black Sea. Two different profiles for the eddy-diffusion coefficients were assigned: (solid black line and gray lines) 150–350 m: 2 $cm^2\ s^{-1}$, 350–650 m: 3 $cm^2\ s^{-1}$, 650–2150 m: 4 $cm^2\ s^{-1}$; (dotted black line) 150–650 m: 1.02 $cm^2\ s^{-1}$, 650–2150 m: 4.07 $cm^2\ s^{-1}$ [*Scranton*, 1988]. The model was initiated with uniform average values of the [CH_4] profile below 700 m depth (black lines) and with uniform upper and lower bounds of the [CH_4] profile (gray lines); the stable isotope models are insensitive to these changes in [CH_4].

isotope differences are large. The CH_4 stable isotope results generally differ by ca. 80‰ for δ^2H-CH_4 and 10‰ for δ^{13}C-CH_4, and the shapes of the distributions are mirror-images of one another (Figures 1 and 2). How can the Black Sea and Cariaco Basin have such strong first-order similarities, yet have such different [CH_4] and CH_4 stable isotope distributions? We compare the bathymetry, geological history and setting, controls on stratification, and circulation in both basins. We also consider previously measured concentrations, oxidation rates, turnover times, and radiocarbon (^{14}C-CH_4) contents of CH_4 to study the geochemistry of $CH_{4[S]}$ in these two large anoxic basins. We derive an open-system stable isotope equation that can be applied to steady state and non-steady-state environments to determine the fractionation factor (α) for AOM that occurs in the water column, stable isotope signature of the CH_4 at the point of release to the water column, or the fraction of the flux of CH_4 to the water column that is oxidized. Finally, we develop one-dimensional (vertical) box models which indicate that the depth distribution of seep inputs to the water column and AOM are the main controls on these stable isotope distributions.

[5] Discoveries of carbonate structures, isotopically light carbonate cements, and seeping CH_4 around coastal-ocean faults indicate that geological CH_4 may be a significant global CH_4 source in oceanic and global CH_4 and carbon cycles [*Bernard et al.*, 1976; *Clark et al.*, 2000; *Gulin et al.*, 2003; *Judd*, 2004; *Kelley et al.*, 2005; *Leifer et al.*, 2004; *Michaelis et al.*, 2002; *Sansone et al.*, 2001; *Sassen et al.*, 2001]. Studying the biogeochemistry of geological CH_4 is complicated in the coastal ocean by advection, mixing, and dilution [*Sansone et al.*, 2001; *Valentine et al.*, 2001]. However, the restricted deep water circulation of semi-enclosed basins allows CH_4 accumulation without ocean-scale dispersion and permits determination of fluxes of CH_4 to the water column averaged over large spatial scales [*Kessler et al.*, 2006, 2005]. The Cariaco Basin, and especially the Black Sea, are globally important CH_4 reservoirs, and the fossil CH_4 geochemistry in both basins may provide analogs to global fossil CH_4 geochemistry in the coastal ocean.

2. Experimental

[6] Water samples were collected from 26 May to 3 June 2001, on board the R/V *Knorr* within a 4.24 km radius of a station in the western section of the Black Sea (42°30.21′N, 30°45.21′E, 2100 m; Figure 4). Black Sea seep gas was

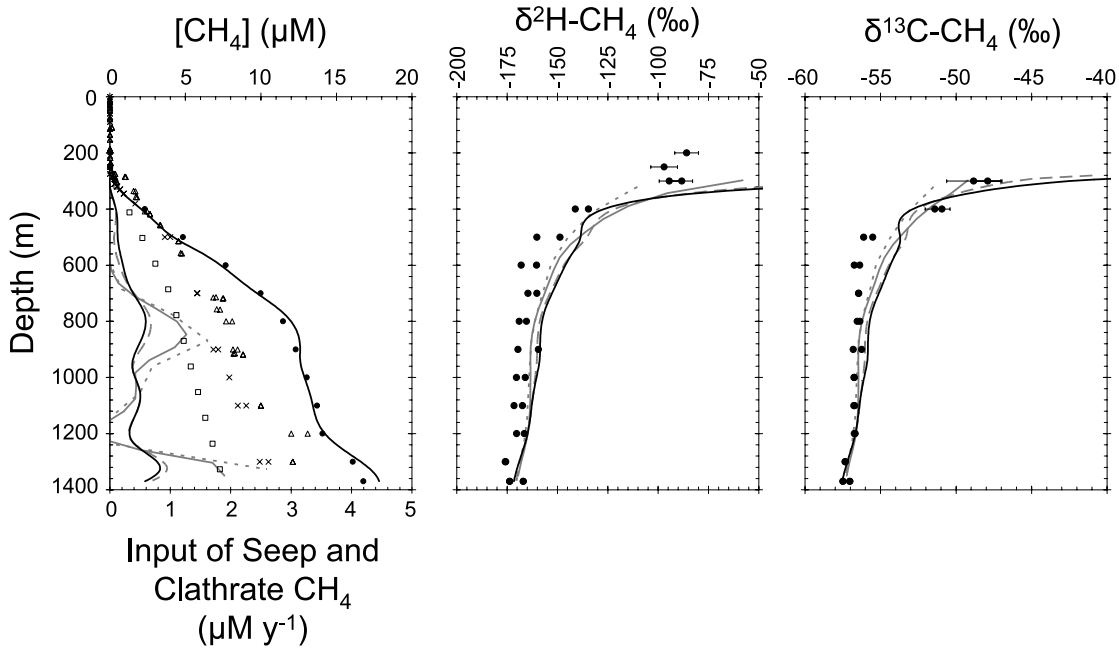

Figure 2. Measured Cariaco Basin CH_4 stable isotope (δ^2H-CH_4 and δ^{13}C-CH_4) and [CH_4] (μM) data collected in the water column in (circles) January 2004 in the eastern basin, (triangles) February to March 1986 in the western basin [*Ward et al.*, 1987], (crosses) November 1982 [*Scranton*, 1988] in the western basin, and (squares) February 1974 in the eastern basin [*Reeburgh*, 1976; *Wiesenburg*, 1975]. The precisions are the same as in Figure 1. The black and gray lines (solid, dashed, and dotted) represent the model results in the Cariaco Basin; (gray dotted line) Δz = 92 m; (solid gray line) Δz = 46 m; (gray dashed line) Δz = 11.5 m; (solid black line) Δz = 5.75 m.

collected from 10–26 September 2004, on board the F/S *Poseidon* with the submersible *JAGO* (Figure 4). Five independent seeps located within a 0.56 km radius around 44°46.48′N, 31°59.42′E (average depth of 222 m) were sampled (Table 1). Water and sediment samples were collected in the Cariaco Basin from 21–24 January 2004, on board the B/O *Hermano Gines*. The station was located in the deepest portion of the eastern basin (10.5°N, 64.66°W, 1370 m) at the time-series station used by the CArbon Retention In A Colored Ocean (CARIACO) program [*Astor et al.*, 2003; *Scranton et al.*, 2001] (Figure 5).

[7] Methane concentrations were measured with a headspace equilibration technique. Samples were prepared for seawater [CH_4] analyses by filling serum vials directly from Niskin bottles. The seawater vials were sealed and an ultrahigh-purity helium headspace was introduced by displacing an equal volume of water. For the Black Sea, 120 cc serum vials were used with a 10 cc helium headspace, while for the Cariaco Basin, 160 cc serum vials were used with a 13 cc helium headspace. Sediment samples for [CH_4] analyses were prepared by making a slurry of 3 cc of sediment (syringe subcores) and 6 cc of helium-purged water in sealed 37.5 cc serum vials. After the samples were allowed to equilibrate for at least 12 hours, [CH_4] analyses were performed by analyzing three 3 cc aliquots of the headspace with gas chromatography (GC) and flame ioni-

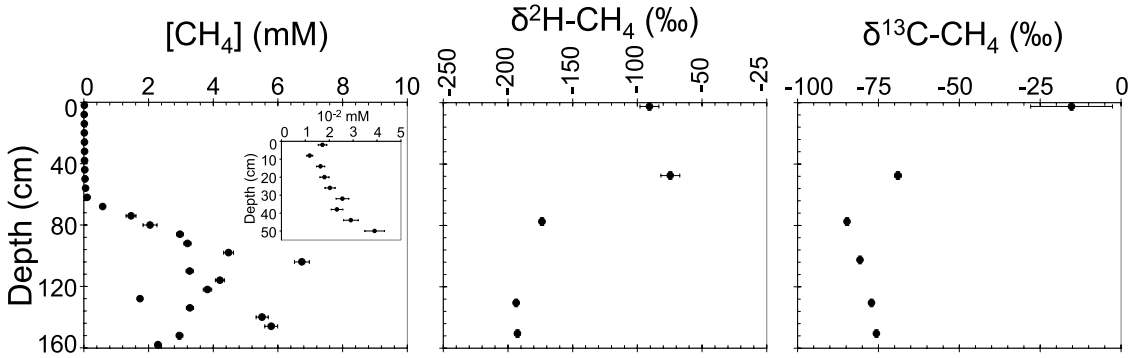

Figure 3. Cariaco Basin CH_4 stable isotope (δ^2H-CH_4 and δ^{13}C-CH_4) and [CH_4] (mM) data collected in the sediment in January 2004 in the eastern basin. The precisions are the same as in Figure 1. The inset shows [CH_4] from the top 55 cm replotted on an expanded concentration scale.

Table 1. Black Sea $CH_{4[S]}$ Isotope Data

Ship Station	Latitude, °N	Longitude, °E	Water Depth ± 4.3 m	δ^{13}C-CH_4 ± 0.2‰	δ^2H-CH_4 ± 2.4‰	^{14}C-CH_4 ± 0.04 pMC
705	44°46.5′	31°59.5′	230	−67.0	−216.9	5.50
708	44°46.5′	31°59.7′	231	−67.6	−251.8	5.05
711	44°46.49′	31°59.55′	222	−67.6	−252.8	5.05
729	44°46.5′	31°59.5′	223	−67.5	−232.5	5.08
752	44°46.4′	31°58.86′	203	−67.8	−244.3	4.44

zation detection (FID) (GC-Mini 2; Shimadzu Corp.; carrier gas (N_2) flow rate = 33 mL/min, column temp = 70°C, 1.5 m column packed with molecular sieve 5A 60/80 mesh). The Black Sea [CH_4] profile was measured at sea. The Cariaco Basin [CH_4] analyses were performed in our UCI laboratory, so all vials were poisoned with a saturated mercuric chloride solution and sealed with blue butyl rubber stoppers and crimp caps. The results have been corrected for the amount of CH_4 still dissolved in solution [*Yamamoto et al.*, 1976].

[8] A previously published procedure was used to collect and prepare CH_4 dissolved in water or sediment for isotopic analyses [*Kessler and Reeburgh*, 2005]. The CH_4 collection, extraction, and analysis procedures are quantitative, there is no isotope fractionation, and the backgrounds are small ($0.52_8 \pm 0.39$ μmoles of CH_4) relative to the average sample size (220 μmoles). (To test the accuracy of the concentration profile measured in the Cariaco Basin by GC-FID in 2004, we calculated the [CH_4] from the quantity of CH_4 collected for isotopic analyses. Both methods agreed within 3% on average below 300 m depth.)

3. Results

[9] Although the general shapes of both δ^2H-CH_4 and δ^{13}C-CH_4 profiles in the water column are similar in their

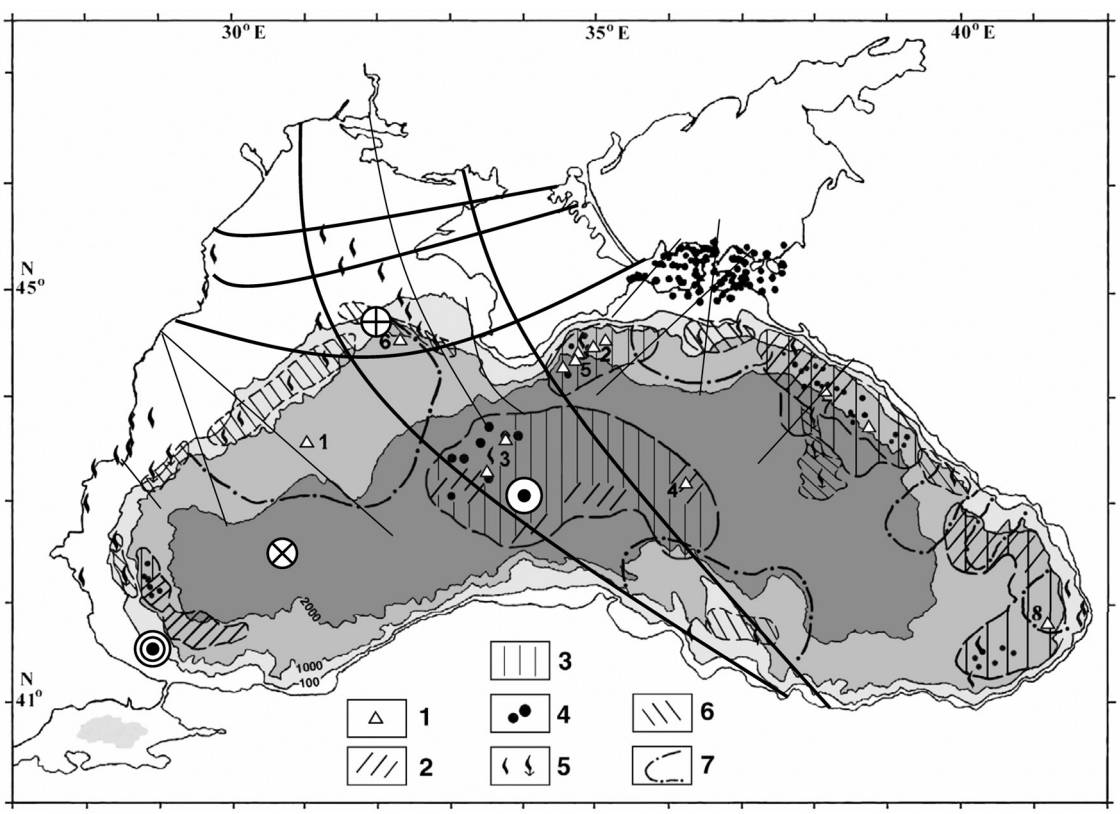

Figure 4. Black Sea sampling locations and deep faults: circle with dot, July 1988 sample site ([CH_4], oxidation rates, and stable isotopes) [*Reeburgh et al.*, 2006, 1991]; double circle with dot, July 1988 shelf sample site ([CH_4] in sediment); circle with cross, May 2001 sample site ([CH_4] and isotopes in the water column); and circle with plus, September 2004 sample site (seep gas collection). The map is from *Vassilev and Dimitrov* [2002] with the following symbols: (1) Clathrate sampling (see Table 1 of *Vassilev and Dimitrov* [2002] for numbering); (2) areas with seismic indications of clathrates; (3) areas of high clathrates prospect; (4) mud volcanoes; (5) areas of intensive fluid discharging; (6) gas seepage and seabed pockmarks; and (7) mine submarine fans. The solid lines are deep faults interpolated after *Kutas et al.* [2004].

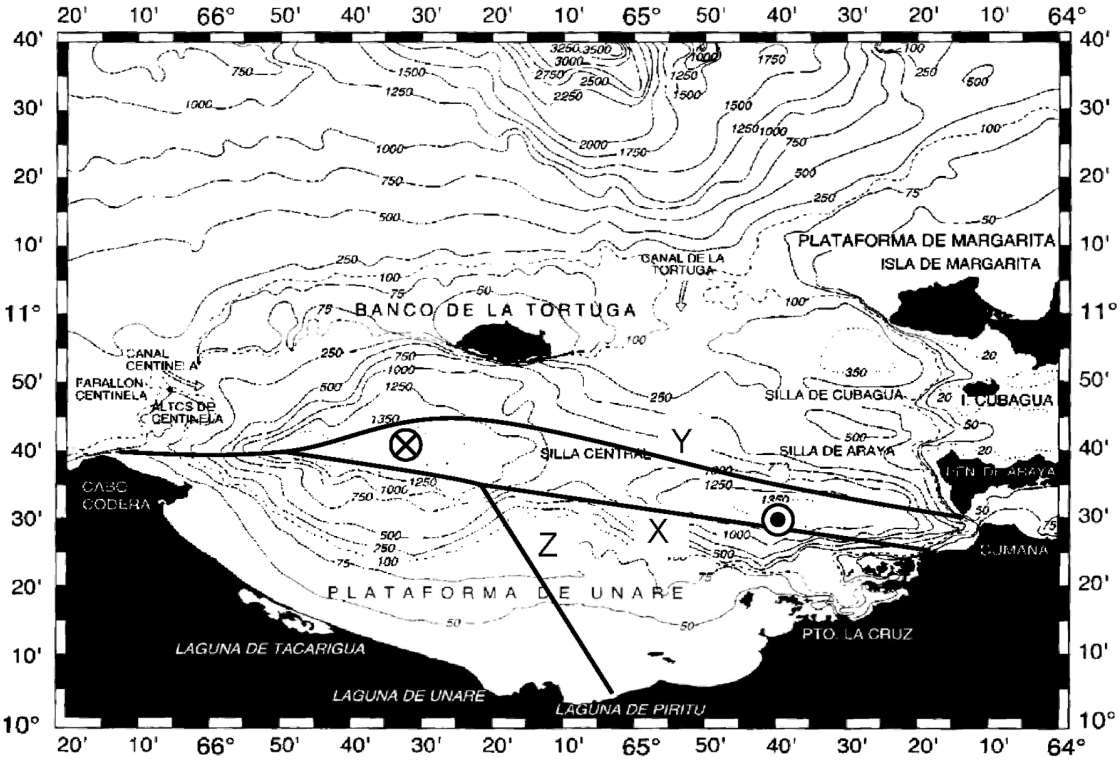

Figure 5. Cariaco Basin sampling locations and faults. The solid lines are faults interpolated after *Audemard et al.* [2005]. (X) El Pilar Fault; (Y) San Sebastián Fault; (Z) San Mateo Fault; circle with dot, eastern basin sampling site; and circle with cross, western basin sample site. The map is from *Scranton et al.* [2001].

respective basins, large differences are evident between the [CH_4] and stable isotopes in the Black Sea and Cariaco Basin (Figures 1 and 2). The isotopically lightest CH_4 in the Black Sea is in the near surface waters (250 m depth; $\delta^2H = -152._6 \pm 2._4$‰; $\delta^{13}C = -56.1 \pm 0.2$‰) and becomes heavier almost linearly until a depth of 1000 m. Below 1000 m, the stable isotope signatures of CH_4 remain nearly uniform at $-84._8 \pm 6._7$‰ and -48.0 ± 0.6‰ for δ^2H and $\delta^{13}C$, respectively. Methane emitted from the sampled Black Sea seeps has a nearly uniform stable isotope signature ($\delta^2H = -240 \pm 15$‰; $\delta^{13}C = -67.5 \pm 0.3$‰; Table 1).

[10] The general shapes of Cariaco Basin δ^2H-CH_4 and $\delta^{13}C$-CH_4 profiles in the water column are mirror-images of the Black Sea profiles (Figures 1 and 2). The isotopically heaviest CH_4 is in the upper water column (200–250 m depth; $\delta^2H = -85.9 \pm 2.4$‰; $\delta^{13}C = -9.8 \pm 0.2$‰ (not shown in Figure 2)) and becomes isotopically lighter until a depth of 600 m. Below 600 m, the isotopes of CH_4 are nearly uniform at -167.8 ± 4.8‰ and -56.7 ± 0.5‰ for δ^2H and $\delta^{13}C$, respectively, which are 83‰ and 9‰ lighter than was measured in the Black Sea.

[11] We have no sediment stable isotope data for the Black Sea. The Cariaco Basin sediment profiles for δ^2H-CH_4 and $\delta^{13}C$-CH_4 (Figure 3) are similar to observations from Skan Bay and Eckernförde Bay [*Alperin et al.*, 1988; *Martens et al.*, 1999]. The depth resolution presented here is coarser than was measured in Skan Bay and Eckernförde Bay, so we may have missed additional features identified at these other sites. The isotopically heaviest CH_4 is in the near-surface sediments ($\delta^2H = -115.9 \pm 2.4$‰; $\delta^{13}C = -15.3 \pm 0.2$‰) most likely owing to isotopic fractionation caused by AOM. For δ^2H-CH_4, the lightest value measured (-193.7 ± 2.4‰) occurs at 130.5 cm depth, while for $\delta^{13}C$-CH_4, the lightest value measured (-84.7 ± 0.2‰) occurs at 77.5 cm depth.

[12] The [CH_4] measured in the water column of the western Black Sea in 2001 is on average 11.5% higher than that measured in the central basin in 1988 at depths below 600 m (Figure 1). This may be an indication of lateral heterogeneity or local sources. The Cariaco Basin [CH_4] in the water column has steadily increased over the measurement history [*Scranton et al.*, 2001]. The bottom water [CH_4] measured in January 2004 has more than doubled since February 1974 [*Kessler et al.*, 2005; *Reeburgh*, 1976; *Wiesenburg*, 1975] (Figure 2).

4. Discussion

[13] To understand and quantify the large between-basin differences in stable isotope results, we review the geological settings, CH_4 budgets, ^{14}C-CH_4 distributions, and evolution of CH_4 in these systems (Table 2). This investi-

Table 2. Basin and Methane Characteristics for the Black Sea and Cariaco Basin

	Black Sea	Cariaco Basin
Width	41°–46°N (560 km)	10°21′–11°02′N (76 km)
Length	28°–42°E (1120 km)	64°12′–66°04′W (205 km)
Area, km^2	423,000[a,b,c]	8220[d,e]
Volume, km^3	534,000[a,b,c]	730 for depths > 275 m[d,e]
Max depth, m	2200[a,b]	E. Basin, 1370; W. Basin, 1400[d]
Sill depth, m	32–34[f]	E. Sill, 135; W. Sill 146[d,g]
Water properties (T, S, σ_θ)		
Surface	25, 17.9, 10	23.4, 36.8, 25.19
Bottom	8.9, 22.3, 17.2	16.7, 36.18, 26.44
Depth of oxic/anoxic interface, m	100–150 m[h]	250–300[i]
Onset of anoxia, years Before Present	7300–7540[b,j]	12600[k]
Freshwater inputs, km^3 yr^{-1}		
Danube	198	
Dnepr	52	
Don	28	
Georgian coast	41	
Turkish coast	25	
Methane concentration, μM	basin center below 600 m: 10.9[h] western basin below 600 m:12.4[m]	1974: Increasing to 7[l] 1998: Increasing to 12.5[i] 2004: Increasing to 16.8[n]
Methane consumption rate, μM yr^{-1}	modeled: 0.015[o] measured: Surface 100 m: 0.36×10^{-3} [h] Below 100 m: 0.6[h]	modeled: 0.0011–0.0153[p] 0.15–0.3[e] measured: year 1987: 0.0129–0.160[q] year 2004: 0.04–0.19[q,n]
Methane Residence Time, years (year 2004)	modeled: 73[o] measured: 3.6–18[h]	modeled: 30–70[e] measured: year 2004: 50–60[q]
Inputs of CH_4 from seeps, mol m^{-2} yr^{-1}	0.53–0.84[m]	0.14–0.17[n]

[a]*Ross et al.* [1974].
[b]*Deuser* [1974].
[c]*Isakov* [1953].
[d]*Maloney* [1966].
[e]*Scranton* [1988].
[f]*Latif et al.* [1991].
[g]*Richards and Vaccaro* [1956].
[h]*Reeburgh et al.* [1991].
[i]*Scranton et al.* [2001].
[j]*Jones and Gagnon* [1994].
[k]*Peterson et al.* [2000].
[l]*Wiesenburg* [1975].
[m]*Kessler et al.* [2006].
[n]*Kessler et al.* [2005].
[o]*Scranton* [1977].
[p]*Reeburgh* [1976].
[q]*Ward et al.* [1987].

gation leads to the derivation of two open-system stable isotope equations and a one-dimensional (vertical) geochemical box model of stable isotopes of CH_4.

4.1. Geological Setting

[14] The Black Sea, the world's largest anoxic basin (area = 4.23×10^5 km^2, max depth = 2200 m; Table 2), was formed as an extensional back-arc basin from the Late Cretaceous to the Eocene, and comprises the West and East Black Sea basins. Current geophysical data suggests that the Black Sea is closing under north-south compressional stress [*Alptekin et al.*, 1986; *Robinson et al.*, 1996; *Zonenshain and Pichon*, 1986]. During the Pleistocene and early Holocene, the Black Sea was an oxygenated fresh- or brackish-water body. The rise of global sea level 9000–9800 years before present (BP) caused an inflow of saline Mediterranean waters through the Bosporus, which accumulated in the bottom of the basin. River runoff capped the saline bottom waters and led to a strong salinity stratification, impeding vertical mixing. Owing to this stratification, the flux of oxygen to the deep basin was restricted to what was transported in by the Mediterranean water. The organic carbon transported to the deep basin far exceeded the input of dissolved oxygen, which led to anoxic conditions being established in the deep basin ca. 7300–7540 years BP [*Deuser*, 1974; *Jones and Gagnon*, 1994] (Table 2).

[15] In contrast, the area of the Cariaco Basin (8.22×10^3 km^2) is significantly smaller than the Black Sea, and contains water whose salinity is close to adjacent open ocean values (Table 2). The continental transform associated with the El Pilar fault system in the Venezuelan borderland is most likely responsible for the formation of the Cariaco Basin; however, the exact tectonic mechanism for this basin's formation is currently unknown. During the Last Glacial Maximum (LGM), lowered sea level caused the Cariaco Basin to be nearly isolated from the Caribbean. The only connection with the open ocean would have been on the western end of the Cariaco Basin at a depth of <30 m. Although the Cariaco Basin was more isolated from the open ocean during the LGM than today, oxic conditions

persisted. This most likely occurred because the upwelling waters were nutrient limited which decreased the surface productivity and transport of organic carbon to the deep basin [*Peterson et al.*, 2000]. Increasing sea level at the end of the LGM allowed for more nutrient rich waters to be upwelled, increasing surface productivity and transport of organic matter to the deep basin. This organic matter flux overwhelmed the oxygen flux to the deep basin establishing the most recent anoxic conditions ca. 12600 year BP [*Peterson et al.*, 2000].

4.2. CH_4 Budgets and Radiocarbon Analyses

[16] The dominant source of CH_4 into both basins has been regarded for the past 30 years as diagenetically-produced, diffusing from sediments. *Reeburgh et al.* [1991] conducted CH_4 concentration and oxidation rate measurements in the central Black Sea, determining that AOM was the dominant sink of CH_4 from the water column (70-fold larger than the next largest sink, evasion at the air:sea interface). The central station was chosen to represent a basin-wide integration of processes affecting the Black Sea CH_4 budget (Figure 4). The Black Sea water column CH_4 distribution was assumed to be in steady state, so the total sink of CH_4 from the water column must be matched with a source of the same magnitude. However, measurements of [CH_4] in the sediments in shelf and deep basin cores indicate that 86.7% or more of the flux of CH_4 to the water column is not accounted for by diffusion from sediments [*Ivanov et al.*, 2002; *Jørgensen et al.*, 2001; *Reeburgh et al.*, 1991]. *Reeburgh et al.* [1991, 2006] concluded that large-scale methanogenesis does not occur in the anoxic Black Sea water column so long as sulfate reduction is occurring [*Hoehler et al.*, 1994, 1998]. Measurements by *Albert et al.* [1995], show that sulfate reduction occurs in the Black Sea water column at nM day^{-1} rates.

[17] The source of CH_4 to the Cariaco Basin was previously investigated with [CH_4] and oxidation rate measurements [*Ward et al.*, 1987] as well as vertical advection-diffusion and time-dependent box models [*Reeburgh*, 1976; *Scranton*, 1988; *Scranton et al.*, 2001]. These studies determined that AOM is the largest sink of CH_4 from the water column in the Cariaco Basin and that the CH_4 geochemistry can be explained with only a source of $CH_{4[D]}$. While recent studies have shown that turbitidy flows, mid-depth (250–350 m) intrusions of oxygenated water, and deep basin intrusions of hypersaline shelf water influence other constituents in the Cariaco Basin water column [*Astor et al.*, 2003; *Holmén and Rooth*, 1990; *Scranton et al.*, 2001], they have been shown to have only minor effects on CH_4 [*Kessler et al.*, 2005; *Scranton et al.*, 2001].

[18] Recent ^{14}C-CH_4 measurements in the Black Sea and Cariaco Basin confirm that the dominant source of CH_4 to these water columns is from fossil CH_4 and not from $CH_{4[D]}$ [*Kessler et al.*, 2006, 2005]. The CH_4 emitted from 5 different seeps in the Black Sea contained small but measurable amounts of radiocarbon (5.02 ± 0.4 pMC; Table 1), contrary to measurements in other oceanic locations [*Grabowski et al.*, 2004; *Kessler*, 2005; *Kessler et al.*, 2005; *Winckler et al.*, 2002a, 2002b] which indicated that $CH_{4[S]}$ is radiocarbon-free. A possible explanation why Black Sea $CH_{4[S]}$ is not radiocarbon-free is that fossil petrogenic CH_4, generated from Late Eocene age source rock [*Robinson et al.*, 1996], acquires modern CH_4 during transit through recently deposited sediments.

[19] Studies of CH_4 dissolved in anoxic sediments indicate that CH_4 can have near-modern ^{14}C-CH_4 contents in shallow (<100 cm depth) sediments [*Kessler*, 2005; *Kessler et al.*, 2005] as well as decadal turnover times, as calculated from measured [CH_4] and rates of AOM [*Iversen and Jørgensen*, 1985; *Reeburgh*, 1980; *Reeburgh et al.*, 1991]. Methane dissolved in the Black Sea water column has similar decadal turnover times to $CH_{4[D]}$ [*Reeburgh et al.*, 1991] (Table 2). The ^{14}C-CH_4 results indicate that the source of CH_4 to the Black Sea water column is a mixture of $CH_{4[S]}$ and $CH_{4[D]}$, because (1) CH_4 produced in shallow sediments has near-modern radiocarbon-contents, (2) $CH_{4[S]}$ is nearly radiocarbon-free, and (3) this oceanic CH_4 has decadal turnover times. The concentration-weighted average of the ^{14}C-CH_4 results in the Black Sea water column (15.72 ± 6.75 percent Modern Carbon [pMC] [*Stuiver and Polach*, 1977]) was used to show that between 64 to 98% of the source flux is from fossil CH_4 [*Kessler et al.*, 2006]. Also, the ^{14}C-CH_4 and [CH_4] results were used to estimate the basin-wide source flux of $CH_{4[S]}$ to the Black Sea water column (3.6 to 5.7 Tg yr^{-1} or 0.53 to 0.84 mol m^{-2} yr^{-1}) [*Kessler et al.*, 2006].

[20] The Cariaco Basin water column radiocarbon results clearly indicate $CH_{4[D]}$ is not the source of CH_4 to the water column. The water column is dominated by fossil CH_4 inputs (^{14}C-CH_4 = 2.5 ± 0.2 pMC) while $CH_{4[D]}$ contained significant radiocarbon contents (86.4 pMC at 45 cm depth) [*Kessler et al.*, 2005]. Since the rates of AOM and [CH_4] in the Cariaco Basin are neither uniform nor in steady state, the CH_4 turnover time in year 2004 was calculated by dividing the total quantity of CH_4 in the basin by the total loss of CH_4 due to AOM; this analysis indicates that the turnover time of CH_4 in the water column is 50–60 years (Table 2). Since the Cariaco Basin is too warm (16.9°C) for clathrates to be stable [*Dickens and Quinby-Hunt*, 1994], the CH_4 dissolved in the water column is almost devoid of radiocarbon, the $CH_{4[D]}$ (CH_4 dissolved in near surface sediments) contains modern quantities of radiocarbon, and the CH_4 has decadal turnover times, then large inputs of fossil $CH_{4[S]}$ must be the source of CH_4 to the water column [*Kessler et al.*, 2005]. In order to quantify the fossil CH_4 input to the water column, *Scranton*'s [1988] time-dependent Cariaco box model was modified to include a source term for $CH_{4[S]}$ [*Kessler et al.*, 2005]. This model was evaluated with and without middepth intrusions of oxygenated water showing that the source of $CH_{4[S]}$ to the Cariaco Basin likely ranges from 0.024–0.028 Tg yr^{-1} (0.14–0.17 mole m^{-2} yr^{-1}). This model predicted that there are large inputs of $CH_{4[S]}$ below 700 m depth.

[21] Both basins are tectonically active, containing major faults [*Alptekin et al.*, 1986; *Audemard et al.*, 2005; *Kutas et al.*, 2004; *Mendoza*, 2000; *Robinson et al.*, 1996; *Suárez and Nábelek*, 1990], which may provide the pathway for geological CH_4 to be emitted. The Black Sea is cross-cut by seven deep interregional and regional fault systems which have been correlated with heat flow and gas release [*Kutas*

et al., 2004] (Figure 4). The Cariaco Basin is bordered and possibly cross-cut by the San Mateo Fault, El Pilar Fault, and San Sebastián Fault [*Audemard et al.*, 2005; *Mendoza*, 2000; *Suárez and Nábelek*, 1990], however, the exact locations of these faults within the basin are unknown (Figure 5). Also, a turbidity flow, correlated with the 9 July 1997 earthquake, has been observed in the Cariaco Basin [*Thunell et al.*, 1999]. More recently, a modeling study suggests a 1967 earthquake might have initiated the release of fossil CH_4 into the Cariaco Basin [*Kessler et al.*, 2005].

4.3. Open-System Stable Isotope Equations

[22] Conventional stable isotope equations describing mixing and kinetic isotope effects are not applicable to the Black Sea and Cariaco Basin. Several studies indicate that seep inputs are heterogeneously distributed across both basins [e.g., *Gulin et al.*, 2003; *Kessler et al.*, 2006, 2005; *Vassilev and Dimitrov*, 2002]. Studies of stable isotope mixing (e.g., Keeling plots [*Keeling*, 1958, 1961; *Pataki et al.*, 2003]) are not applicable to these basins because they do not account for the large isotopic fractionation associated with AOM [*Alperin et al.*, 1988; *Martens et al.*, 1999] and the heterogeneous distribution of inputs. Also, conventional stable isotope equations considering kinetic isotope effects assume a "closed system" (i.e., a fixed amount of reactant is allowed to partially react) [*Bigeleisen and Wolfsberg*, 1958]. The Black Sea and Cariaco Basin are "open systems," where geological CH_4 is continuously added to the water column from seeps, while CH_4 is being removed simultaneously by anaerobic oxidation.

[23] We derive open-system stable isotope equations that account for the continuous input of geological CH_4 to the water column and the isotopic fractionation associated with AOM. These equations can be used to determine the fractionation factor for AOM in the water column, the stable isotope signature of the CH_4 at the point of release to the water column, or the fraction of the input flux of CH_4 to the water column that is oxidized. This derivation assumes: (1) CH_4 is being added to the system at a constant rate with a constant isotope signature, (2) no CH_4 was in the system before the source was turned on, (3) CH_4 is well mixed in the system, and (4) the removal of CH_4, principally by oxidation, is proportional to the amount of CH_4 in the system and is the only cause of isotope fractionation. These equations were derived in a similar manner to equations describing kinetic isotope effects in a "closed system" [*Bigeleisen and Wolfsberg*, 1958]. Consider the two reactions

$$A + B + C + \ldots \xrightarrow{k} X + Y + \ldots$$

$$A' + B + C + \ldots \xrightarrow{k'} X' + Y + \ldots$$

Assuming the reaction is first order in A and A' (or pseudo-first order due to high concentrations of B, C, ...), it follows

$$dA/dt = r_1 - kAB^bC^c \ldots \quad (1)$$

$$dA'/dt = r_2 - k'A'B^bC^c \ldots . \quad (2)$$

Here A is the CH_4 molecule containing the heavy isotope, A' is the CH_4 molecule containing the light isotope, r_1 is the constant rate of addition of A, r_2 is the constant rate of addition of A', and k and k' are the rate constants for the reactions.

[24] Integration of these rate laws leads to the following equations.

$$\ln\left(\frac{r_1 - kAB^bC^c}{r_1}\right) = -kB^bC^ct \quad (3)$$

$$\ln\left(\frac{r_2 - k'A'B^bC^c}{r_2}\right) = -k'B^bC^ct. \quad (4)$$

[25] Dividing equation (3) by equation (4) and simplifying, leads to equation (5),

$$\ln\left[\frac{1}{Rs}\frac{r_1 - kAB^bC^c}{r_2 - k'A'B^bC^c}\right] = \left(\frac{k}{k'} - 1\right)\ln\left(1 - \frac{k'A'B^bC^c}{r_2}\right), \quad (5)$$

where Rs is the isotopic ratio of the source $CH_4 = r_1/r_2$. The following substitutions are used to simplify equation (5): Rt is the isotopic ratio of the CH_4 in the reservoir at time $t = A/A'$, α is the isotopic fractionation factor $= k'/k$, and f is ratio of CH_4 oxidation to CH_4 input rates. Since the natural abundances of ^2H and ^{13}C are about 0.016% and 1% of ^1H and ^{12}C, respectively, and since the kinetic isotope effect is too small to change the concentration of the heavy isotope significantly beyond the 1% level, then the rate of addition and loss of the heavy isotope is much less than that of the light isotope.

$$kAB^bC^c + k'A'B^bC^c \approx k'A'B^bC^c$$

$$r_1 + r_2 \approx r_2$$

These substitutions simplify f,

$$f = \frac{kAB^bC^c + k'A'B^bC^c}{r_1 + r_2} \approx \frac{k'A'B^bC^c}{r_2}$$

and can be used to further simplify equation (5).

$$\ln\left[\frac{1}{Rs}\frac{r_1 - kAB^bC^c}{r_2 - r_2f}\right] = \left(\frac{1}{\alpha} - 1\right)\ln(1 - f).$$

This equation further simplifies to

$$\ln\left[\frac{Rs - \frac{1}{\alpha}Rtf}{Rs(1 - f)}\right] = \ln(1 - f)^{1/\alpha - 1})$$

Taking the exponential of both sides and solving for Rs leads to equation (6)

$$Rs = \frac{fRt}{\alpha - \alpha(1 - f)^{1/\alpha}}, \quad (6)$$

which we convert to delta notation, yielding equation (7).

$$\delta S = \frac{f(\delta W + 1000)}{\alpha - \alpha(1 - f)^{1/\alpha}} - 1000. \quad (7)$$

Here $\delta S = (Rs/Rstd - 1) \times 1000$, $\delta W = (Rt/Rstd - 1) \times 1000$, and $Rstd$ = the isotopic ratio of the standard.

[26] In the steady state case where $f = 1$, equation (7) simplifies to

$$\delta S = \frac{1}{\alpha}(\delta W + 1000) - 1000\cdot \tag{8}$$

[27] Equation (8) can also be derived by equating equations (1) and (2) with 0, dividing the two equations, and simplifying. Step-by-step derivations of equations (7) and (8) are given by *Kessler* [2005].

4.3.1. Black Sea: Testing the Steady State Assumption and Determining the Fractionation Factor for AOM in the Water Column

[28] The δ^{13}C-CH_4 results suggest that the CH_4 dissolved in the waters of the Black Sea is isotopically homogeneous (laterally) and in steady state. The δ^{13}C-CH_4 results collected in 2001 in the western Black Sea are similar to those collected in 1988 at the central station [*Reeburgh et al.*, 2006] (Figure 1). If a reservoir changes to an isotopically different source (e.g., a shift from a $CH_{4[D]}$ source to a $CH_{4[S]}$ source) or if the isotopic ratio of the source remains constant but the flux changes, then an isotopic shift will occur in the reservoir. The timescales for changes in the isotope ratio and the large-scale spatial isotopic gradients of a reservoir are often longer than they are for changes in total CH_4 [*Tans*, 1997]. Thus isotopic steady state is reached after concentration steady state. Since the δ^{13}C-CH_4 results show no spatial or temporal variability, they suggest that the Black Sea is in steady state with respect to CH_4. A similar conclusion can be reached when incorporating these δ^{13}C-CH_4 measurements into equation (7). At depths $\geq$1000 m, δ^{13}C-CH_4 = -48.9 ± 1.1 in year 1988 and -48.0 ± 0.6 in year 2001 (Figure 1). In addition, the previously determined fractionation factors for aerobic and anaerobic oxidation of CH_4 range from approximately 1.01 to 1.02 [*Reeburgh*, 2003]. Since we also measured δ^{13}C-$CH_{4[S]}$, we use equation (7) to calculate the fraction of the CH_4 input that is oxidized (f). This analysis indicates that $f = 1$ when $\alpha = 1.021 \pm 0.001$, indicating that the CH_4 dissolved in the Black Sea water column is in steady state. It should be noted that the previously determined fraction factors for AOM were determined in a sediment environment, while the AOM we are studying occurs in the water column.

[29] If the Black Sea is rigorously determined to be in steady state, the stable isotope results of $CH_{4[S]}$ and CH_4 dissolved in the water column below 1000 m depth (where the basin is well mixed vertically and mixing along an isotopic gradient does not occur) can now be used with Equation 8 to calculate the α for AOM that occurs in the water column. For δ^2H-CH_4 and δ^{13}C-CH_4, α equals $1.20_4 \pm 0.02_5$ and 1.021 ± 0.001, respectively. These fractionation factors for AOM in the water column are larger than was previously determined in sedimentary environments [*Alperin et al.*, 1988; *Martens et al.*, 1999]. If the horizontal transport of CH_4 from the seep site to the western basin sampling site is not fast relative to AOM, horizontal gradients in the stable isotopes will occur. This effect would lower our values for α, making the values we present here upper bounds on the true values. However, such horizontal gradients are not observed between our western and central basin sites (Figure 1).

4.3.2. Cariaco Basin: Determining the Stable Isotope Signature of $CH_{4[S]}$

[30] The open-system non-steady-state stable isotope equation (equation (7)) can be used to predict the stable isotope signature of this $CH_{4[S]}$ at the point of release into the water column since we know the stable isotope signature of CH_4 dissolved in the water column (δW), the ratio of CH_4 input to oxidation rates (f), and α for AOM. (Below 600 m, the water column stable isotope signatures are relatively uniform at -167.8 ± 4.8‰ and -56.7 ± 0.5‰ for δ^2H-CH_4 and δ^{13}C-CH_4, respectively (Figure 2). Modifications of *Scranton*'s [1988] time-dependent model [*Kessler et al.*, 2005], estimate that 0.024–0.028 Tg $CH_{4[S]}$ yr^{-1} are added to the water column, while the specific oxidation rates [*Ward et al.*, 1987] indicate that 0.01 Tg $CH_{4[S]}$ yr^{-1} are being oxidized in 2004.) Thus the stable isotope signatures of the source CH_4 at the point of release into the water column are calculated to be -196.6 ± 5.5 to -202.3 ± 5.8‰ and -60.70 ± 0.53 to -61.50 ± 0.55‰ for δ^2H-CH_4 and δ^{13}C-CH_4, respectively.

4.4. Vertical Time-Dependent Box Model for Stable Isotopes

[31] *Scranton et al.* [1987] developed a time-dependent vertical box model which was later used to describe the Cariaco Basin CH_4 geochemistry in the water column [*Scranton*, 1988]. Following the radiocarbon confirmation that seeps are a dominate source of CH_4 to both basins, Scranton's model was modified to calculate possible depth distributions of inputs of $CH_{4[S]}$ and basin-wide fluxes of $CH_{4[S]}$ to the water column for both the Cariaco Basin and the Black Sea [*Kessler et al.*, 2006, 2005]. Conceptual diagrams of the original model are given by *Scranton et al.* [1987] and *Scranton* [1988].

[32] Here we further modified the basic skeleton of this model to study the depth distributions of the stable isotopes in both basins.

$$\frac{dn_i}{dt} = (F_{Sedi} - F_{Ai})(A_i - A_{i+1}) + F_{Si}V_i - k_iC_iV_i + K_i\frac{(C_{i-1} - C_i)}{\Delta z}A_i + K_{i+1}\frac{(C_{i+1} - C_i)}{\Delta z}A_{i+1}. \tag{9}$$

For box i, dn_i/dt is the rate of change of the number of moles of CH_4, F_{Sedi} is the input of $CH_{4[D]}$ (moles per area per time), F_{Ai} is the oxidation of water column CH_4 by abyssal sediments (moles per area per time), F_{Si} is the input of $CH_{4[S]}$ (moles per volume per time), k_i is the specific rate of AOM (per time), V_i is the volume, A_i and A_{i+1} are the basin areas at the top and bottom of the box, K_i and K_{i+1} are the eddy diffusion coefficients at the top and bottom of the box (area per time), C_i is the [CH_4] in the box, and C_{i-1} and C_{i+1} are the [CH_4] in boxes $i - 1$ and $i + 1$. The area of sediment intersecting each box is calculated by subtracting A_{i+1} from A_i; since the boxes are three-dimensional and the walls are sloped, this leads to a maximum error in the sediment area of <5% [*Scranton et al.*, 1987].

[33] Equation (9) was used to solve for F_S, a vertical profile of the input of $CH_{4[S]}$ [*Kessler et al.*, 2006, 2005]. F_S was then used to predict profiles of δ^2H-CH_4 and δ^{13}C-CH_4 in the water column of the Black Sea and Cariaco Basin using equations (10) and (11). The "L" and "H" subscripts denote the light and heavy isotopes.

$$\frac{dn_{Li}}{dt} = (F_{LSedi} - F_{LAi})(A_i - A_{i+1}) + F_{LSi}V_i - k_{Li}C_{Li}V_i + K_i\frac{(C_{Li-1} - C_{Li})}{\Delta z}A_i + K_{i+1}\frac{(C_{Li+1} - C_{Li})}{\Delta z}A_{i+1} \quad (10)$$

$$\frac{dn_{Hi}}{dt} = (F_{HSedi} - F_{HAi})(A_i - A_{i+1}) + F_{HSi}V_i - k_{Hi}C_{Hi}V_i + K_i\frac{(C_{Hi-1} - C_{Hi})}{\Delta z}A_i + K_{i+1}\frac{(C_{Hi+1} - C_{Hi})}{\Delta z}A_{i+1}. \quad (11)$$

Here

$$MIR_i = (F_{Sedi} - F_{Ai})(A_i - A_{i+1}) + F_{Si}V$$
$$MIR_{Li} = (F_{LSedi} - F_{LAi})(A_i - A_{i+1}) + F_{LSi}V$$
$$MIR_{Li} = \frac{MIR_i}{1 + \left(\partial_{MI}/1000 + 1\right)R_{STD}}$$
$$k_{Li} = \alpha k\frac{C_L + C_H}{\alpha C_L + C_H}$$
$$MIR_{Hi} = (F_{HSedi} - F_{HAi})(A_i - A_{i+1}) + F_{HSi}V$$
$$MIR_{Hi} = \frac{MIR_i\left(\partial_{MI}/1000 + 1\right)R_{STD}}{1 + \left(\partial_{MI}/1000 + 1\right)R_{STD}}$$
$$k_{Hi} = k\frac{C_L + C_H}{\alpha C_L + C_H}$$

Also, δ_{MI} is the isotopic signature of CH_4 input into each box. For both basins, we assume that δ_{MI} is uniform over the entire basin and is the same for both F_{Sedi} and F_{Si}. Also, we assume that the rate of horizontal mixing is fast relative to AOM and that F_{Ai} only causes isotopic fraction of residual CH_4 in the sediment, not the water column. (Tables of the input parameters for these models are found in the auxiliary material[1].)

4.4.1. Black Sea

[34] For the Black Sea, box volume and areas were obtained from *Ross et al.* [1974] and *Deuser* [1974], specific rates of AOM were previously measured by *Reeburgh et al.* [1991] to be uniform at 0.06 yr^{-1}, and box depths (Δz) were set equal to 1.5625 m as decreasing the box depth further did not cause significant changes in the final results. The eddy diffusion coefficients previously reported by *Scranton* [1988] were used here and were varied to assess the models' sensitivities to this parameter. We use piecewise cubic splines to interpolate between the measurements obtaining values for the input parameters at the depth of each box. (See Table S1 in auxiliary material for the Black Sea model input parameters.) Since it is in steady state, equation (9) was set equal to zero and the equation was solved for F_{Si}. The measurements of [CH_4] in the water column conducted in year 2001 were used to predict F_{Si} for each box (Figure 1).

[35] Equations (10) and (11) were used to predict profiles of δ^2H-CH_4 and δ^{13}C-CH_4 in the water column. For the Black Sea, we assume δ_{MI} equals the mean of our seep gas measurements (−240‰ for δ^2H and −67.5‰ for δ^{13}C; Table 1) and use Newton-Raphson's Method to solve this system of non-linear equations for C_L and C_H. This steady state vertical stable isotope model also provides supporting evidence that the Black Sea is in steady state; equations (9)–(11) were evaluated in a steady state manner (i.e., they were set equal to zero and solved) and the modeled and measured isotope results showed close agreement.

[36] In order to test our assumptions that δ_{MI} is uniform over the entire basin, is similar for both F_{Sedi} and F_{Si}, and mixes fast horizontally relative to AOM, we used equations (10) and (11) along with an interpolation to the measured water column profiles of δ^2H-CH_4 and δ^{13}C-CH_4 to model a profile of δ_{MI}. (See Table S1 in auxiliary material for the interpolated profiles of δ^2H-CH_4 and δ^{13}C-CH_4, which are input into this calculation.) This analysis produces a relatively uniform distribution of δ_{MI} below 300 m depth (δ^2H-CH_4 = −241.3 ± 39.5‰ and δ^{13}C-CH_4 = −67.7 ± 4.1‰), similar to our measurements (Table 1) and our model assumptions.

[37] Model sensitivities to variations in the [CH_4] profile in the water column, the eddy-diffusion coefficients (K), and the isotopic fractionation factors were tested. In general, the models are most sensitive to these parameter changes above 800 m depth and the model used to predict a profile of F_S shows a higher sensitivity to these parameters than the stable isotope model. The stable isotope model is more sensitive to changes in K than [CH_4]. Changing the average values of α to the bounds of the standard deviations causes no changes for the δ^{13}C-CH_4 results; however, it does result in average changes of 9 to 17% for δ^2H-CH_4 (see Table S3 in the auxiliary material).

[38] The measured and modeled δ^2H-CH_4 and δ^{13}C-CH_4 results in the water column are most similar to the $CH_{4[S]}$ values in the upper water column (Figure 1 and Table 1). The spatial distribution of model predicted (Figure 1) [*Kessler et al.*, 2006] and experimentally identified Black Sea seeps shows that most seeps are located on the shelf above 1000 m depth (Figure 4), and add CH_4 directly to the upper water column [*Gulin et al.*, 2003; *Lüdmann et al.*, 2004; *Luth et al.*, 1999; *Michaelis et al.*, 2002; *Vassilev and Dimitrov*, 2002] as well as to the atmosphere [*Dimitrov*, 2002]. The short residence time of CH_4 in the upper water column results in less oxidation and greater similarity to the source CH_4.

4.4.2. Cariaco Basin

[39] For the Cariaco Basin, the box volumes, areas, and eddy diffusion coefficients were obtained from *Scranton* [1988] and specific rates of AOM were previously measured by *Ward et al.* [1987]. *Scranton et al.* [1987] originally defined the boxes to have a depth (Δz) of 50 fathoms (92 m) and subsequent adaptations of this model [*Holmén and Rooth*, 1990; *Kessler et al.*, 2005; *Scranton*, 1988] followed this convention. When using this model to solve for a profile of F_S, we find that it is not until the "conventional" box depth is divided by at least a factor

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/gb/2005gb002571.

of 16 (so that Δz = 5.75 m) that this model becomes insensitive to changes in the box depth (Figure 2). (We use piecewise cubic splines to interpolate between the measurements obtaining values for the input parameters at the depth of each box. See Table S2 in the auxiliary material for the Cariaco Basin model input parameters.)

[40] Since the Cariaco Basin is not in steady state, a time-dependent iteration was used to solve equation (9) for F_S. The Cariaco Basin model as initiated with no CH_4 corresponding to year 1967 [*Kessler et al.*, 2005] and an initial guess at the profile of F_S was assigned. The model was run for 37 years (until year 2004 corresponding to when our samples were collected) at a time step of 0.0001 years. (Decreasing the time step further did not change the results significantly.) F_S was modified and the model was reevaluated until the modeled 2004 [CH_4] profile showed close agreement with the measured 2004 [CH_4] profile.

[41] The stable isotope equations (equations (10) and (11)), were similarly evaluated in a time-dependent fashion. For the Cariaco Basin, we assume δ_{MI} equals the results obtained from the open-system non-steady-state stable isotope equation (δ^2H-CH_4 = −199.4‰ and δ^{13}C-CH_4 = −61.1‰).

[42] The model-predicted inputs of $CH_{4[S]}$ show large inputs in the deep basin and none on the shallow shelves, unlike the Black Sea (Figure 2). Once CH_4 is released to the deep basin, it can diffuse toward the shallow water. This CH_4 is partially oxidized as it diffuses upwards, leaving the CH_4 dissolved in the near surface waters most isotopically enriched in the heavy isotopes. In the deep Cariaco Basin, the δ^2H-CH_4 and δ^{13}C-CH_4 values are isotopically much lighter than in the Black Sea. The difference in the extents of CH_4 oxidation between the deep Black Sea and Cariaco Basin is responsible for the differences in deep basin stable isotope values.

5. Conclusions

[43] Fluxes of CH_4 from seafloor seeps are emerging as significant contributors in global and oceanic carbon and CH_4 cycles [e.g., *Judd*, 2004; *Sansone et al.*, 2001]. However, studying their biogeochemistry is difficult in an open ocean environment owing to advection, mixing, and dilution. The restricted circulation of large anoxic basins allows assembling CH_4 budgets, since CH_4 accumulates without open-ocean dispersion. The stable isotope results of CH_4 show large differences between the Black Sea and Cariaco Basin, despite the first-order similarities of the two environments. Radiocarbon results of CH_4 in the Black Sea and Cariaco Basin confirm that the dominant source of CH_4 to both of these basins is fossil and effectively balance both CH_4 budgets. Anaerobic oxidation of CH_4 rates, time series [CH_4] analyses, and the radiocarbon results indicate that both basins are open systems (i.e., CH_4 is being added at the same time it is being oxidized) and that the Cariaco Basin is not in steady state. However, the δ^{13}C-CH_4 results suggest that the Black Sea is in steady state. Application of newly derived open-system stable isotope equations to both basins suggests that the Black Sea is in steady state and permits determination of the α for AOM in a water column environment and the stable isotope signature of $CH_{4[S]}$ released into the Cariaco Basin. Steady state conditions in the Black Sea are responsible for oxidizing CH_4 dissolved in the water column to a different extent than the non-steady-state conditions in the Cariaco Basin; the large differences in δ^2H-CH_4 and δ^{13}C-CH_4 between the deep basins are attributed to this kinetic isotope effect. The distributions of identified seeps provide an explanation why the stable isotope profiles are mirror images between the Black Sea and Cariaco Basin, as highlighted by a vertical box model for the stable isotopes of CH_4.

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