Controls on methane concentration and stable isotope ($\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$) distributions in the water columns of the Black Sea and Cariaco Basin

J. D. Kessler, W. S. Reeburgh, and S. C. Tyler

Received 10 June 2005; revised 6 July 2006; accepted 21 July 2006; published 2 November 2006.

[1] Methane (CH$_4$) concentration and stable isotope ($\delta^2$H-CH$_4$ and $\delta^{13}$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 $\delta^2$H-CH$_4$ and 9% for $\delta^{13}$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 $^{13}$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.

Citation: Kessler, J. D., W. S. Reeburgh, and S. C. Tyler (2006), Controls on methane concentration and stable isotope ($\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$) distributions in the water columns of the Black Sea and Cariaco Basin, Global Biogeochem. Cycles, 20, GB4004, doi:10.1029/2005GB002571.

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., Amouroy 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; Michaels 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$_4$ (14C-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 ($\delta^2$H-CH$_4$ and $\delta^{13}$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 $\delta^2$H-CH$_4$ and $\delta^{13}$C-CH$_4$ distributions in the water column might be similar, but the between-basin stable
isotope differences are large. The CH$_4$ stable isotope results generally differ by ca. 80% for $\delta^2$H-CH$_4$ and 10% for $\delta^{13}$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$_4$ 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 ($\alpha$) 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.

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

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
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).

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 ion-
zation detection (FID) (GC-Mini 2; Shimadzu Corp.; carrier gas (N\textsubscript{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\textsubscript{4}] profile was measured at sea. The Cariaco Basin [CH\textsubscript{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\textsubscript{4} still dissolved in solution [Yamamoto et al., 1976].

A previously published procedure was used to collect and prepare CH\textsubscript{4} dissolved in water or sediment for isotopic analyses [Kessler and Reeburgh, 2005]. The CH\textsubscript{4} collection, extraction, and analysis procedures are quantitative, there is no isotope fractionation, and the backgrounds are small (0.52 ± 0.39 μmoles of CH\textsubscript{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\textsubscript{4}] from the quantity of CH\textsubscript{4} collected for isotopic analyses. Both methods agreed within 3% on average below 300 m depth.)

### 3. Results

Although the general shapes of both δ\textsuperscript{2}H-CH\textsubscript{4} and δ\textsuperscript{13}C-CH\textsubscript{4} profiles in the water column are similar in their

| Ship Station | Latitude, °N | Longitude, °E | Water Depth ± 4.3 m | δ\textsuperscript{13}C-CH\textsubscript{4} ± 0.2‰ | δ\textsuperscript{2}H-CH\textsubscript{4} ± 2.4‰ | δ\textsuperscript{14}C-CH\textsubscript{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                |

**Figure 4.** Black Sea sampling locations and deep faults: circle with dot, July 1988 sample site ([CH\textsubscript{4}], oxidation rates, and stable isotopes) [Reeburgh et al., 2006, 1991]; double circle with dot, July 1988 shelf sample site ([CH\textsubscript{4}] in sediment); circle with cross, May 2001 sample site ([CH\textsubscript{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].
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; $\delta^2$H = $-152.6 \pm 2.4\%$; $\delta^{13}$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 $84.8 \pm 6.5\%$ and $48.0 \pm 0.6\%$ for $\delta^2$H and $\delta^{13}$C, respectively. Methane emitted from the sampled Black Sea seeps has a nearly uniform stable isotope signature ($\delta^2$H = $240 \pm 15\%$; $\delta^{13}$C = $67.5 \pm 0.3\%$; Table 1).

[10] The general shapes of Cariaco Basin $\delta^2$H-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; $\delta^2$H = $-85.9 \pm 2.4\%$; $\delta^{13}$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 $-167.8 \pm 4.8\%$ and $-56.7 \pm 0.5\%$ for $\delta^2$H 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 $\delta^2$H-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 ($\delta^2$H = $-115.9 \pm 2.4\%$; $\delta^{13}$C = $-15.3 \pm 0.2\%$) most likely owing to isotopic fractionation caused by AOM. For $\delta^2$H-CH$_4$, the lightest value measured ($-193.7 \pm 2.4\%$) occurs at 130.5 cm depth, while for $\delta^{13}$C-CH$_4$, the lightest value measured ($-84.7 \pm 0.2\%$) 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, km²            | 423,000ha                     | 8220c                         |
| Volume, km³          | 534,000ha                     | 730 for depths > 275 m        |
| Max depth, m         | 2200h                         | E. Basin, 1370; W. Basin, 1400|
| Sill depth, m        | 32–34f                        | E. Sill, 135; W. Sill 146      |
| Water properties (T, S, σθ) |                       |                                 |
| 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        | 250–300d                      |
| Onset of anoxia, years Before Present | 7300–7540d       | 12600a                        |
| Freshwater inputs, km³ yr⁻¹ |                     |                                 |
| Danube               | 198                           |                                |
| Dnephr               | 52                            |                                |
| Don                  | 28                            |                                |
| Georgian coast       | 41                            |                                |
| Turkish coast        | 25                            |                                |
| Methane concentration, μM | basin center below 600 m: 10.9h | 1974: Increasing to 7i          |
|                      | western basin below 600 m:12.4m | 1998: Increasing to 12.5i       |
|                      | modeled: 0.015q               | 2004: Increasing to 16.8j      |
|                      | measured: Surface 100 m: 0.36 × 10⁻³ h | modeled: 0.0111–0.0153p        |
|                      | Below 100 m: 0.6h             | 0.15–0.3p                     |
|                      | modeled: 73 i                | measured: year 1987: 0.0129–0.160p |
|                      | measured: 3.6–18b            | year 2004: 0.04–0.19i          |
|                      | modeled: 30 – 70              | modeled: 0.14–0.17             |
|Inputs of CH₄ from seeps, mol m⁻² yr⁻¹ | 0.53–0.84q               |                                 |

*Ross et al. [1974].
*Deuser [1974].
*Isakov [1953].
*Maloney [1966].
*Scranton [1988].
*Latif et al. [1991].
*Richards and Faccar [1956].
*Reeburgh et al. [1991].
*Scranton et al. [2001].
*Jones and Gagnon [1994].
*Peterson et al. [2000].
*Wiesenburg [1975].
*Kessler et al. [2006].
*Kessler et al. [2005].
*Scranton [1977].
*Reeburgh [1976].
*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 CH₄.

4.1. Geological Setting

[14] The Black Sea, the world’s largest anoxic basin (area = 4.23 × 10⁵ km², 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 × 10³ km²) 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...
produced in shallow, 1991].

4.2. CH4 Budgets and Radiocarbon Analyses

[16] The dominant source of CH4 into both basins has been regarded for the past 30 years as diagenetically-produced, diffusing from sediments. Reeburgh et al. [1991] conducted CH4 concentration and oxidation rate measurements in the central Black Sea, determining that AOM was the dominant sink of CH4 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 CH4 budget (Figure 4). The Black Sea water column CH4 distribution was assumed to be in steady state, so the total sink of CH4 from the water column must be matched with a source of the same magnitude. However, measurements of [CH4] in the sediments in shelf and deep basin cores indicate that 86.7% or more of the flux of CH4 to the water column is not accounted for by diffusion from sediments [Ivanov et al., 2002; Jorgensen 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 CH4 to the Cariaco Basin was previously investigated with [CH4] and oxidation rate measurements [Ward et al., 1987] as well as vertical advection-diffusion and time-dependent box models [Reeburgh, 1976; Scronant, 1988; Scranton et al., 2001]. These studies determined that AOM is the largest sink of CH4 from the water column in the Cariaco Basin and that the CH4 geochemistry can be explained with only a source of CH4[D]. While recent studies have shown that turbidity 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 CH4 [Kessler et al., 2005; Scranton et al., 2001].

[18] Recent 14C-CH4 measurements in the Black Sea and Cariaco Basin confirm that the dominant source of CH4 to these water columns is from fossil CH4 and not from CH4[D] [Kessler et al., 2006, 2005]. The CH4 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 CH4[D] is radiocarbon-free. A possible explanation why Black Sea CH4[S] is not radiocarbon-free is that fossil petrogenic CH4, generated from Late Eocene age source rock [Robinson et al., 1996], acquires modern CH4 during transit through recently deposited sediments.

[19] Studies of CH4 dissolved in anoxic sediments indicate that CH4 can have near-modern 13C-CH4 contents in shallow (<100 cm depth) sediments [Kessler, 2005; Kessler et al., 2005] as well as decadal turnover times, as calculated from measured [CH4] and rates of AOM [Iversen and Jorgensen, 1985; Reeburgh, 1980; Reeburgh et al., 1991]. Methane dissolved in the Black Sea water column has similar decadal turnover times to CH4[D] [Reeburgh et al., 1991] (Table 2). The 14C-CH4 results indicate that the source of CH4 to the Black Sea water column is a mixture of CH4[S] and CH4[D] because (1) CH4 produced in shallow sediments has near-modern radiocarbon-contents, (2) CH4[S] is nearly radiocarbon-free, and (3) this oceanic CH4 has decadal turnover times. The concentration-weighted average of the 14C-CH4 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 CH4 [Kessler et al., 2006]. Also, the 14C-CH4 and [CH4] results were used to estimate the basin-wide source flux of CH4[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 CH4[D] is not the source of CH4 to the water column. The water column is dominated by fossil CH4 inputs (14C-CH4 = 2.5 ± 0.2 pMC) while CH4[D] contained significant radiocarbon contents (86.4 pMC at 45 cm depth) [Kessler et al., 2005]. Since the rates of AOM and [CH4] in the Cariaco Basin are neither uniform nor in steady state, the CH4 turnover time in year 2004 was calculated by dividing the total quantity of CH4 in the basin by the total loss of CH4 due to AOM; this analysis indicates that the turnover time of CH4 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 CH4 dissolved in the water column is almost devoid of radiocarbon, the CH4[D] (CH4 dissolved in near surface sediments) contains modern quantities of radiocarbon, and the CH4 has decadal turnover times, then large inputs of fossil CH4[S] must be the source of CH4 to the water column [Kessler et al., 2005]. In order to quantify the fossil CH4 input to the water column, Scranton’s [1988] time-dependent Cariaco box model was modified to include a source term for CH4[S] [Kessler et al., 2005]. This model was evaluated with and without middepth intrusions of oxygenated water showing that the source of CH4[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 CH4[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 Náblek, 1990], which may provide the pathway for geological CH4 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. These derivations assume: (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

\begin{align*}
A + B + C + \ldots & \rightarrow X + Y + \ldots \tag{1} \\
A' + B + C + \ldots & \rightarrow X' + Y + \ldots \tag{2}
\end{align*}

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

\begin{align*}
\frac{dA}{dt} & = r_1 - kAB^bC^c \ldots \tag{1} \\
\frac{dA'}{dt} & = r_2 - k'A'B^bC^c \ldots. \tag{2}
\end{align*}

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.

\begin{align*}
\ln\left(\frac{r_1 - kAB^bC^c}{r_1}\right) & = -kB^bC^ct \tag{3} \\
\ln\left(\frac{r_2 - k'A'B^bC^c}{r_2}\right) & = -k'B^bC^ct. \tag{4}
\end{align*}

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

\begin{align*}
\ln\left[\frac{1}{R_s} \frac{r_1 - kAB^bC^c}{r_2 - k'A'B^bC^c}\right] & = \left(\frac{k}{k'} - 1\right)\ln\left(1 - \frac{kAB^bC^c}{k'A'B^bC^c}\right). \tag{5}
\end{align*}

where $R_s$ is the isotopic ratio of the source CH$_4 = r_1/r_2$. The following substitutions are used to simplify equation (5): $R_t$ is the isotopic ratio of the CH$_4$ in the reservoir at time $t = A'[A'']$, $\alpha$ 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 $^3$H and $^{13}$C are about 0.016% and 1% of $^1$H 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.

\begin{align*}
kAB^bC^c + k'A'B^bC^c \approx k'A'B^bC^c \\
r_1 + r_2 \approx r_2
\end{align*}

These substitutions simplify $f$,

\begin{align*}
f & = \frac{kAB^bC^c + k'A'B^bC^c}{r_1 + r_2} \approx \frac{k'A'B^bC^c}{r_2}
\end{align*}

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

\begin{align*}
\ln\left[\frac{1}{R_s} \frac{r_1 - kAB^bC^c}{r_2 - r_2f}\right] & = \left(\frac{1}{\alpha} - 1\right)\ln(1 - f).
\end{align*}

This equation further simplifies to

\begin{align*}
\ln\left[\frac{R_s - 1 - R_sf}{R_s\alpha(1 - f)}\right] & = \ln(1 - f)\frac{\alpha}{\alpha - \alpha(1 - f)^{1/\alpha}}
\end{align*}

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

\begin{align*}
R_s & = f\frac{R_t}{\alpha - \alpha(1 - f)^{1/\alpha}}, \tag{6}
\end{align*}

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

\begin{align*}
\delta S & = f\frac{W + 1000}{\alpha - \alpha(1 - f)^{1/\alpha}} - 1000, \tag{7}
\end{align*}

8 of 13
Here \( \delta S = (R_{d}/R_{std} - 1) \times 1000, \delta W = (R_{t}/R_{std} - 1) \times 1000, \) and \( R_{std} = \) the isotopic ratio of the standard.

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

\[
\delta S = \frac{1}{\alpha} (\delta W + 1000) - 1000. \tag{8}
\]

[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 \( \delta^{13}C-C_{H4} \) results suggest that the CH\(_4\) dissolved in the waters of the Black Sea is isotopically homogeneous (laterally) and in steady state. The \( \delta^{13}C-C_{H4} \) 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\(_4\) source to a CH\(_4\) 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 isotopic 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 \( \delta^{13}C-C_{H4} \) 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 \( \delta^{13}C-C_{H4} \) measurements into equation (7). At depths \( \geq 1000 \) m, \( \delta^{13}C-C_{H4} = -48.9 \pm 1.1 \) in year 1988 and \(-48.0 \pm 0.6 \) 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 \( \delta^{13}C-C_{H4} \), 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 fractionation 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 rigidly determined to be in steady state, the stable isotope results of CH\(_{4(2)}\) 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 \( \alpha \) for AOM that occurs in the water column. For \( \delta^{13}C-C_{H4} \) and \( \delta^{13}C-C_{H4} \), \( \alpha \) equals 1.204 \( \pm 0.025 \) and 1.021 \( \pm 0.001 \), 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 \( \alpha \), 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\(_{4(5)}\)

[30] The open-system non-steady-state stable isotope equation (equation (7)) can be used to predict the stable isotope signature of this CH\(_{4(5)}\) at the point of release into the water column since we know the stable isotope signature of CH\(_4\) dissolved in the water column (\( \delta W \)), the ratio of CH\(_4\) input to oxidation rates (\( f \)), and \( \alpha \) for AOM. (Below 600 m, the water column stable isotope signatures are relatively uniform at \(-167.8 \pm 4.8 \%\) and \(-56.7 \pm 0.5 \%\) for \( \delta^{13}C-C_{H4} \) and \( \delta^{13}C-C_{H4} \), respectively (Figure 2). Modifications of Scraton’s [1988] time-dependent model [Kessler et al., 2005], estimate that 0.024–0.028 Tg CH\(_{4(5)} \) yr\(^{-1}\) are added to the water column, while the specific oxidation rates [Ward et al., 1987] indicate that 0.01 Tg CH\(_{4(5)} \) 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 \(-196.6 \pm 5.5 \) to \(-202.3 \pm 5.8 \%\) and \(-60.70 \pm 0.53 \) to \(-61.50 \pm 0.55 \%\) for \( \delta^{13}C-C_{H4} \) and \( \delta^{13}C-C_{H4} \), respectively.

4.4. Vertical Time-Dependent Box Model for Stable Isotopes

[31] Scraton 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 [Scraton, 1988]. Following the radiocarbon confirmation that seeps are a dominant source of CH\(_4\) to both basins, Scraton’s model was modified to calculate possible depth distributions of inputs of CH\(_{4(5)}\) and basin-wide fluxes of CH\(_{4(5)}\) 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 Scraton et al. [1987] and Scraton [1988].

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

\[
\frac{dn_{i}}{dt} = (F_{Sedi} - F_{d})(A_{i} - A_{i+1}) + F_{Sd}V_{i} - k_{i}C_{i}V_{i} + K_{i} \frac{(C_{i-1} - C_{i})}{\Delta z} A_{i} + K_{i+1} \frac{(C_{i+1} - C_{i})}{\Delta z} A_{i+1}. \tag{9}
\]

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\(_{4(5)}\) (moles per area per time), \( F_{d} \) is the oxidation of water column CH\(_4\) by abyssal sediments (moles per area per time), \( F_{Sd} \) is the input of CH\(_{4(5)}\) (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% [Scraton et al., 1987].
Equation (9) was used to solve for $F_S$, a vertical profile of the input of CH$_4[41]$, [Kessler et al., 2005]. $F_S$ was then used to predict profiles of $\delta^4$H-CH$_4$ and $\delta^{13}$C-CH$_4$ in the water column of the Black Sea and Cariaco Basin by using equations (10) and (11). The “L” and “H” subscripts denote the light and heavy isotopes.

$$\frac{dM^L}{dt} = \left( F_{LSd} - F_{Ld} \right) (A_1 - A_{i+1}) + F_{LSi} V_i - k_L C_L V_i + f \frac{(C_{Li-1} - C_{Li}) A_i + k_{Li+1} (C_{Li+1} - C_{Li}) A_{i+1}}{\Delta z}$$

$$\frac{dM^H}{dt} = \left( F_{HSd} - F_{Hd} \right) (A_1 - A_{i+1}) + F_{HSi} V_i - k_H C_H V_i + f \frac{(C_{Hi-1} - C_{Hi}) A_i + k_{Hi+1} (C_{Hi+1} - C_{Hi}) A_{i+1}}{\Delta z}.$$  \hspace{1cm} (10)

Here

$$MIR_i = \frac{(F_{Sd} - F_{Ai}) (A_1 - A_{i+1}) + F_{Si} V}{MIR_c} \frac{1}{\left( \frac{\partial M}{1000 + 1} \right) R_{STD}}$$

$$k_L = \frac{\alpha}{\alpha L + C_H} C_L / C_H$$

$$MIR_{Hi} = \frac{(F_{Hd} - F_{Hi}) (A_1 - A_{i+1}) + F_{Si} V}{MIR_c} \frac{1}{\left( \frac{\partial M}{1000 + 1} \right) R_{STD}}$$

$$k_H = \frac{1}{\alpha L + C_H} C_L / C_H$$

Also, $\delta_{Mi}$ is the isotopic signature of CH$_4$ input into each box. For both basins, we assume that $\delta_{Mi}$ is uniform over the entire basin and is the same for both $F_{Sd}$ and $F_{Si}$. Also, we assume that the rate of horizontal mixing is fast relative to AOM and that $F_{Hi}$ 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.)

4.4.1. Black Sea

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 [Rhee et al., 1991] to be uniform at 0.06 yr$^{-1}$, and box depths ($\Delta z$) 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 $\delta^4$H-CH$_4$ and $\delta^{13}$C-CH$_4$ in the water column. For the Black Sea, we assume $\delta_{Mi}$ equals the mean of our seep gas measurements ($-240^{\circ}$o for $\delta^4$H and $-67.5^{\circ}$o for $\delta^{13}$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 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 isotopic results showed close agreement.

[36] In order to test our assumptions that $\delta_{Mi}$ is uniform over the entire basin, is similar for both $F_{Sd}$ 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 $\delta^4$H-CH$_4$ and $\delta^{13}$C-CH$_4$ to model a profile of $\delta_{Mi}$. (See Table S1 in auxiliary material for the interpolated profiles of $\delta^4$H-CH$_4$ and $\delta^{13}$C-CH$_4$, which are input into this calculation.) This analysis produces a relatively uniform distribution of $\delta_{Mi}$ below 300 m depth ($\delta^4$H-CH$_4$ = $-241.3 \pm 39.5^{\circ}$o and $\delta^{13}$C-CH$_4$ = $-67.7 \pm 4.1^{\circ}$o), 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 $\alpha$ to the bounds of the standard deviations causes no changes for the $\delta^{13}$C-CH$_4$ results; however, it does result in average changes of 9 to 17% for $\delta^4$H-CH$_4$ (see Table S3 in the auxiliary material).

[38] The measured and modeled $\delta^4$H-CH$_4$ and $\delta^{13}$C-CH$_4$ results in the water column are most similar to the CH$_4[41]$ 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

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 ($\Delta z$) 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 $F_{Si}$, we find that it is not until the “conventional” box depth is divided by at least a factor that...

---

1) Auxiliary materials are available at ftp://ftp.agu.org/apend/gb/2005gb002571.
of 16 (so that $\Delta z = 5.75$ 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 $\delta_{SI}$ equals the results obtained from the open-system non-steady-state stable isotope equation ($\delta^{13}$H-CH$_4 = -199.4\%o$ and $\delta^{13}$C-CH$_4 = -61.1\%o$).

[42] The model-predicted inputs of CH$_4$[SI] 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 $\delta^{13}$H-CH$_4$ and $\delta^{13}$C-CH$_4$ values are isotopically much lighter than in the Black Sea. The difference in the extents of CH$_4$ oxidation between the 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 $\delta^{13}$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 $\alpha$ for AOM in a water column environment and the stable isotope signature of CH$_4[SI]$ 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 $\delta^{13}$H-CH$_4$ and $\delta^{13}$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$_4$.

[44] Acknowledgments. We thank the crews of the RV Knorr and the B/O Hermano Gines for their support at sea, Ramon Varela and David Valentine for scientific support at sea, Richard Seifert for providing the Black Sea seep gas samples, Yrene Astor for her help with Cariaco Basin cruise and equipment coordination, and John Southon, Guaciara dos Santos, and Xiaoai Xu for laboratory support. We thank Max Wolfsberg for beneficial discussions on isotope modeling. This manuscript was improved by unusually thorough, meticulous, and constructive reviews by Marc Alperin, and we are grateful for his efforts. This work was supported by the National Science Foundation (grants OCE-0096280, OCE-0326928) and by instrumentation awards (IRMS and AMS) from the W. M. Keck Foundation.

References

Albert, D. B., C. Taylor, and C. S. Martens (1995), Sulfate reduction rates and low molecular weight fatty acid concentrations in the water column and surficial sediments of the Black Sea, Deep Sea Res., Part I, 42, 1239 – 1260.

Alperin, M. J., W. S. Reeburgh, and J. M. Whiticar (1988), Carbon and hydrogen isotope fractionation resulting from anaerobic methane oxidation, Global Biogeochem. Cycles, 2(3), 279 – 288.

Alptekin, O., J. L. Nåbelek, and M. N. Toksöv (1986), Source mechanism of the Bartin Earthquake of September 3, 1968 in Northwestern Turkey: Evidence for active thrust faulting at the Southern Black Sea margin, Tectonophysics, 122, 73 – 88.

Amouroux, D., G. Roberts, S. Rapsomanikis, and M. O. Andréea (2002), Biogenic Gas (CH$_4$, N$_2$O, DMS) emission to the atmosphere from near-shore and shelf waters of the north-western Black Sea, Estuarine Coastal Shelf Sci., 54, 575 – 587.

Astor, Y., F. Muller-Karger, and M. I. Seranton (2003), Seasonal and inter-annual variation in the hydrography of the Cariaco Basin: implications for basin ventilation, Cont. Shelf Res., 23, 125 – 144.

Atkinson, L. P., and F. A. Richards (1967), The occurrence and distribution of methane in the marine environment, Deep Sea Res., 14, 673 – 684.

Audernard, F. A., G. Romero, H. Rendon, and V. Cano (2005), Quaternary fault kinematics and stress tensors along the southern Caribbean from fault-slip data and focal mechanism solutions, Earth Sci. Rev., 69, 181 – 233.

Bernard, B. B., J. M. Brooks, and W. M. Sackett (1976), Natural gas seepage in the Gulf of Mexico, Earth Planet. Sci. Lett., 31, 48 – 54.

Bigeleisen, J., and M. Wolfsberg (1958), Theoretical and experimental aspects of isotope effects in chemical kinetics, Adv. Chem. Phys., 1, 15 – 76.

Clark, J. F., L. Washburn, J. S. Hornafius, and B. P. Luyendyk (2000), Dissolved hydrocarbon flux from natural marine seeps to the southern California Bight, J. Geophys. Res., 105(C5), 11,509 – 11,522.

Deuser, W. G. (1974), Evolution of anoxic conditions in Black Sea during Holocene, in The Black Sea—Geology, Chemistry, and Biology, edited by E. T. Degens and D. A. Ross, pp. 137 – 136, Am. Assoc. of Petroleum Geol., Tulsa, Okla.

Dickens, G. R., and M. S. Quinby-Hunt (1994), Methane hydrate stability in seawater, Geophys. Res. Lett., 21(19), 2115 – 2118.

Dimitrov, L. (2002), Contribution to atmospheric methane by natural seepages on the Bulgarian continental shelf, Cont. Shelf Res., 22, 2129 – 2442.

Fanning, K. A., and M. E. Q. Pilson (1972), A model for the anoxic zone of the Cariaco Trench, Deep Sea Res., 19, 847 – 863.

Gebour, G. D., A. N. Kreml, M. N. Grigor’ev, G. V. Larkin, A. D. Pavlenkin, and N. A. Satykova (1990), Filtrogenic gas hydrates in the Black Sea, Geol. Geofiz., 31(3), 10 – 19.

Grabowski, K. S., D. L. Knies, S. J. Tuney, J. W. Pohlman, C. S. Mitchell, and R. B. Coffin (2004), Carbon pool analysis of methane hydrate re-

GB4004 KESSLER ET AL.: BLACK SEA AND CARIACO BASIN CH$_4$ ISOTOPES GB4004
gions in the seafloor by accelerator mass spectrometry, *Nacl. Instrum. Methods Phys. Res., Sect. B*, 223 – 224, 435 – 440.

Gulin, S. B., G. G. Polikarpov, and V. N. Egorov (2003), The age of microbial carbonate structures grown at methane seeps in the Black Sea with an implication of dating of the seeping methane, *Mar. Chem.*, 84, 67 – 72.

Hoehler, T. M., M. J. Alperin, D. B. Albert, and C. S. Martens (1994), Field and laboratory studies of methane oxidation in anoxic marine sediments: Evidence for a methanogen-sulfate reducer consortium, *Global Biogeochem. Cycles*, 8(4), 451 – 463.

Hoehler, T. M., M. J. Alperin, D. B. Albert, and C. S. Martens (1998), Thermodynamic control on hydrogen concentrations in anoxic sediments, *Geochim. Cosmochim. Acta*, 62, 1745 – 1756.

Holmén, K. J., and C. G. H. Rooth (1990), Ventilation of the Cariaco Trench, a case of multiple source competition?, *Deep Sea Res.*, 37, 203 – 225.

Isakov, I. S. (Ed.) (1953), *Morskoi Atlas: Izdaniye Morskogo Generałznogo Shitab* (in Russian), vol. 2, 72 pp., Voyennomorskoe Mins. Noyuza SRR, Moscow.

Ivanov, M. V., N. V. Pimenov, I. I. Rusanov, and A. Y. Lein (2002), Microbial processes of the methane cycle at the north-western shelf of the Black Sea, *Estuarine Coastal Shelf Sci.*, 54, 589 – 599.

Iversen, N., and B. B. Jørgensen (1985), Anaerobic methane oxidation rates at depths of methane source transition in marine sediments from Kattegat and Skagerrak (Denmark), *Linnolm. Oceanog.*, 30(5), 944 – 955.

Jones, G. A., and A. R. Gagnon (1994), Radiocarbon chronology of Black Sea sediments, *Deep Sea Res., Part I*, 41, 531 – 557.

Jørgensen, B. B., A. Weber, and J. Zopfi (2001), Sulfate reduction and anaerobic methane oxidation in Black Sea sediments, *Deep Sea Res., Part I*, 48, 2097 – 2120.

Judd, A. G. (2004), Natural seabed gas seeps as sources of atmospheric methane, *Environ. Geol.*, 46, 988 – 996.

Keeling, C. D. (1958), The concentration and isotopic abundances of atmospheric carbon dioxide in rural and marine air, *Science*, 128, 38 – 53.

Kessler, J. D. (2005), Studies on oceanic methane: Concentrations, stable isotopes, and gas leakage in the northern Black Sea, *Deep Sea Res., Part II*, 52, 1593 – 1604.

Kessler, J. D. (2005), Anaerobic methane oxidation, *Science*, 308, 1265 – 1266.

Kessler, J. D., W. S. Reeburgh, J. Southon, and R. Varela (2005), Fossil methane source dominates Cariaco Basin water column methane geochemistry, *Deep Sea Res., Part II*, 52, S1189 – S1210.

Kilpatrick, M. I. (1988), Temporal variations in the methane content of the Cariaco Trench, *Deep Sea Res., Part I*, 35, 157 – 172.

Kilpatrick, and L. J. Kerkhof (1991), Black Sea methane geochemistry, *Deep Sea Res., Part I*, 38, S1189 – S1210.

Kilpatrick, M. I., Y. Astor, R. Bohrer, T.-Y. Ho, and F. Muller-Karger (2001), Stable carbon and hydrogen isotope measurements on Black Sea water column methane, *Deep Sea Res., Part II*, 48, 219 – 232.

Kilpatrick, M. I. (1988), Temporal variations in the methane content of the Cariaco Trench, *Deep Sea Res., Part I*, 35, 157 – 172.

Kilpatrick, M. I. (1988), Temporal variations in the methane content of the Cariaco Trench, *Deep Sea Res., Part I*, 35, 157 – 172.

Kilpatrick, M. I. (1988), Temporal variations in the methane content of the Cariaco Trench, *Deep Sea Res., Part I*, 35, 157 – 172.

Kilpatrick, M. I. (1988), Temporal variations in the methane content of the Cariaco Trench, *Deep Sea Res., Part I*, 35, 157 – 172.
Winckler, G., W. Aeschbach-Hertig, J. Holocher, R. Kipfer, I. Levin, C. Poss, G. Rehder, E. Suess, and P. Schlosser (2002a), Noble gases and radiocarbon in natural gas hydrates, *Geophys. Res. Lett.*, 29(10), 1423, doi:10.1029/2001GL014013.

Winckler, G., W. Aeschbach-Hertig, J. Holocher, R. Kipfer, I. Levin, C. Poss, G. Rehder, E. Suess, and P. Schlosser (2002b), Correction to “Noble gases and radiocarbon in natural gas hydrates”, *Geophys. Res. Lett.*, 29(15), 1735, doi:10.1029/2002GL015735.

Yamamoto, S., J. B. Alcauskas, and T. E. Crozier (1976), Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data*, 21(1), 78–80.

Zonenshain, L. P., and X. L. Pichon (1986), Deep basins of the Black Sea and Caspian Sea as remnants of Mesozoic back-arc basins, *Tectonophysics*, 123, 181–211.

J. D. Kessler, Department of Geosciences, Princeton University, Princeton, NJ 08544-1003, USA. (jdkessle@princeton.edu)

W. S. Reeburgh and S. C. Tyler, Department of Earth System Science, University of California, Irvine, Irvine, CA 92697-3100, USA.